

Aerosol source apportionment in southern Africa

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Thesis accepted for the degree **Doctor of Philosophy in Environmental Science** at the North-West University

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Graduation August 2021
24078298

PREFACE

Aerosols play a significant role in the climate system through their effect on the radiative balance of the earth and their influence on atmospheric chemistry. While the sources and formation mechanisms of atmospheric aerosols have been studied extensively in the northern Hemisphere, such studies have been limited in the southern Hemisphere. Although a number of large-scale regional initiatives such as SAFARI-92, SAFARI-2000, and EUCAARI from 2009 – 2011 have contributed to a greater understanding of aerosols (and trace gases) in the region, much remains much to be understood about the physical, chemical and optical properties of aerosols.

South Africa, and especially the industrial Highveld, is a major source of anthropogenic and natural aerosols in the southern Hemisphere. South Africa has one of the three largest industrialised economies on the African continent and boasts significant mining and metallurgical industries. It is the largest regional energy producer on the continent generating the majority of the electricity in coal-fired power stations.

Previous aerosol source apportionment studies in South Africa have identified mineral dust, residential fuel burning, sea salt, and biomass burning to be the major contributing aerosol sources. Further understanding of the sources and quantification of the aerosol loading in regions across South Africa is needed to ensure air pollution is effectively managed and controlled, and the impacts on human health are minimised.

South Africa has recognised the importance of air quality and its impact on human health with the declaration of the Vaal Triangle, Highveld and Waterberg-Bojanala regions as Air Quality Priority Areas. These Air Quality Priority Areas are recognised to be areas that either have or will have the potential for poor air quality, and as such, require specific intervention measures to address air pollution.

The aim of this research was to evaluate the composition and characteristics of the atmospheric aerosol loading at four selected sites in each Air Quality Priority Area by undertaking aerosol source apportionment. Four areas were selected, namely, Lephalale (in the Waterberg-Bojanala), Kwazamokhule and Embalenhle (in the Highveld) and Zamdela (in the Vaal Triangle). Domestic fuel burning, a significant contributor to air pollution in townships, is widely practised within the township sampling sites with other key sources of air pollution such as coal-fired power stations and petrochemical facilities also influencing the aerosol loading at the sampling sites.

The specific objectives of the project were to:

- (a) Evaluate the atmospheric aerosol loading in each site;
- (b) Characterise the chemical composition of the aerosol loading in each site;
- (c) Determine the sources contributing to the aerosol loading in each site using receptor modelling; and
- (d) Apportion the aerosol loading in each site to the contributing sources of emissions using receptor modelling.

This thesis is divided into seven chapters. **Chapter 1** provides an overview of atmospheric aerosols, their sources, characteristics and impacts on climate. Source apportionment studies undertaken regionally across southern Africa and locally, in South Africa are discussed. The research goals are also provided. **Chapter 2** outlines the data and methodology, including a discussion of the statistical methods and receptor models applied to the datasets. **Chapter 3** describes the air pollution sources contributing to the aerosol loading in each region while **Chapter 4** presents the atmospheric transport patterns over the southern African sub-continent. An overview of the climate and local meteorological conditions in each region is also given. The existing ambient air quality situation in each region and during each sampling campaign is discussed in **Chapter 5**. The elemental and chemical composition of the fine and coarse fraction aerosols in each region are provided in **Chapter 6**. **Chapter 7** presents the findings from the aerosol source apportionment in each region with the summary and conclusions of the study discussed in **Chapter 8**.

Sections of this thesis have been presented at the combined National Association for Clean Air (NACA) and 16th International Union of Air Pollution Prevention and Environmental Protection Associations (IUAPPA) World Clean Air Congress held from 29 September – 4 October 2013 in Cape Town, South Africa. A poster entitled 'Aerosol Source Apportionment in Lephalale, South Africa' has also been presented at the NACA conference held from 9 – 10 October 2014 in Umhlanga, Kwazulu-Natal.

ACKNOWLEDGEMENTS

I hereby acknowledge the North West University and the Climatology Research Group for the financial assistance given to me during the completion of my PhD. Eskom is acknowledged for the funding of the sampling campaigns in Lephalale and Kwazamokhule while Sasol is acknowledged for the funding of the Embalenhle and Zamdela sampling campaigns. Local meteorological data was provided from the South African Weather Services (SAWS) with ambient air quality and meteorological monitoring data obtained via the South African Air

Quality Information System (SAAQIS) for ambient air quality monitoring stations operated by the Department of Environmental Affairs, Eskom and Sasol. Census data and household fuel burning statistics were obtained from Statistics SA. NOAA Air Resources Laboratory (ARL) is acknowledged for the provision of the HYSPLIT transport and dispersion model and/or READY website (<https://www.ready.noaa.gov>).

Collection of aerosol data from the sampling sites was made possible through the loan of the 'Gent' Stacked Filter Unit from Professor Willy Maenhaut at Ghent University. Joe Malahlela is thanked for the weighing of the filters and preparation of the sampling equipment. Filter samples were analysed at the Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) in Créteil, France and at the North-West University, Potchefstroom campus, South Africa for more recent campaigns. Professor Paola Formenti, Sylvain Triquet and Servanne Chevaillier are thanked for the XRF and IC analyses undertaken in France. At the North-West University, Potchefstroom campus, Johan Hendriks, Yvonne Visagie, Professor Paul Beukes and Jan-Stefan Swartz are thanked for performing the XRF and ICP analyses. Andrew Venter is acknowledged for his assistance in the chemical preparation procedures. Dr Brigitte Language is thanked for her assistance with the datasets for each sampling site.

This research has been conducted under the guidance of my supervisor, Professor Stuart Piketh who is thanked for his support and guidance and for continuing to encourage me to finish my PhD. I am most appreciative of my trips to Belgium and France during my studies. All of 20 years later, I remain grateful to have completed my studies under his supervision.

My family is thanked for their support during my research, especially during the final months of completion. To my husband, Freddy, for your love and patience and our two beautiful little boys, Joshua and Ryan. You are all so precious to me.

And finally, without my Lord, Jesus Christ, this would not have all been possible. To new beginnings.

'Forget the former things; do not dwell on the past. See, I am doing a new thing! Now it springs up; do you not perceive it? I am making a way in the wilderness and streams in the wasteland.' Isaiah 43: 18-19.

ABSTRACT

South Africa, and especially the Highveld region, contributes significantly to the atmospheric aerosol loading over southern Africa. South Africa has recognised the importance of localised air quality and its impact on human health with the declaration of the Vaal Triangle, Highveld and Waterberg-Bojanala regions as Air Quality Priority Areas. In this thesis, the composition and sources of the aerosol loading at identified sites in each of these regions, namely, Lephalale (in the Waterberg-Bojanala), Kwazamokhule and Embalenhle (in the Highveld) and Zamdela (in the Vaal Triangle) have been examined. Fine and coarse aerosol samples were collected at each selected site during summer and winter spanning the period 2012 to 2017. The chemical and elemental composition of aerosol samples collected at each site has been evaluated and apportioned to contributing sources using three source apportionment methods, namely, Principal Component Analysis (PCA), Positive Matrix Factorisation (PMF) and Chemical Mass Balance (CMB) receptor modelling. Using these methods, it has been shown that soil dust (natural and anthropogenic), secondary aerosols, domestic combustion (coal combustion and waste burning) and wood and biomass burning contribute to the fine and coarse aerosol loading in each region. Motor vehicles and industrial activities were also identified in the Highveld and Vaal Triangle regions. Overall, soil dust and secondary aerosols are the main contributing sources in both aerosol size fractions and as such, measures to mitigate particulate air pollution in South Africa should consider these key sources. Given the ease of application and limitations associated with each of the three source apportionment methods, the use of PCA as an initial screening tool, followed by the application of PMF, is the recommended approach for aerosol source apportionment studies in South Africa.

Key terms: Aerosols, Source Apportionment, Principal Component Analysis, Positive Matrix Factorisation, Chemical Mass Balance Modelling.

OPSOMMING

Suid-Afrika en veral die Hoëveldstreek, dra aansienlik by tot die atmosferiese aërosol lading oor Suider-Afrika. Suid-Afrika het die belangrikheid van plaaslike luggehalte en die impak daarvan op menslike gesondheid erken met die verklaring van die Vaaldriehoek-, Hoëveld- en Waterberg-Bojanala-streke as luggehalteprioriteitsgebiede. In hierdie proefskrif is die samestelling en bronne van die aërosollading by geïdentifiseerde terreine in elk van hierdie streke, naamlik Lephalale (in die Waterberg-Bojanala), Kwazamokhule en Embalenhle (in die Hoëveld) en Zamdela (in die Vaaldriehoek) ondersoek. Fyn en growwe aerosol monsters is versamel by elke geselekteerde terrein gedurende die somer en winter wat strek van die tydperk 2012 tot 2017. Die chemiese en element samestelling van aërosolmonsters wat op elke terrein ingesamel is, is geëvalueer en toegeken aan bydraende bronne met behulp van drie brontoedieningsmetodes, naamlik Hoofkomponentanalise (PCA), Positiewe Matriksfaktorisasie (PMF) en Chemiese Massabalans reseptor modellering (CMB). Met behulp van hierdie metodes is getoon dat grondstof (natuurlike en antropogeniese), sekondêre aërosols, huishoudelike verbranding (steenkoolverbranding en afvalverbranding), hout- en biomassa-brand bydra tot die fyn en growwe aërosollading in elke streek. Motorvoertuie en industriële aktiwiteite is ook in die Hoëveld- en Vaaldriehoekstreke geïdentifiseer. Algehele, grondstof en sekondêre aërosols is die belangrikste bydraende bronne in beide aërosolgroottes en as sodanig moet maatreëls om lugbesoedeling deur stofdeeltjies in Suid-Afrika te verminder, hierdie sleutelbronne oorweeg. Gegewe die gemak van toepassing en beperkings wat verband hou met elk van die drie bronbeoordelingsmetodes, is die gebruik van PCA as 'n aanvanklike siftingsinstrument, gevolg deur die toepassing van PMF, die aanbevole benadering vir aërosolbrontoeskrywingstudies in Suid-Afrika.

Sleutelterme: Aërosols, Bronbeoordeling, Hoofkomponentanalise, Positiewe Matriksfaktorisasie, Chemiese Massabalansmodellering.

**To my mom,
Maria Helen Walton
1959 - 2019**

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ABBREVIATIONS

AD	Aerodynamic diameter
Al₂O₃	Aluminium oxide
As	Arsenic
B	Boron
Ba	Barium
Be	Beryllium
Br⁻	Bromine ion
BS	Bootstrap
BS-DISP	Bootstrap-Displacement
BTEX	Benzene, Toluene, Ethyl-Benzene and Xylene
C	Carbon
Ca	Calcium
Ca⁺	Calcium ion
CaO	Calcium oxide
Cd	Cadmium
Cl	Chlorine
Cl⁻	Chloride ion
CMB	Chemical Mass Balance
CO	Carbon monoxide
Cr	Chromium
Cr (VI)	Hexavalent Chromium
CRG	Climatology Research Group
CuO	Copper(II) oxide
DEA	Department of Environmental Affairs
DISP	Displacement
EC	Elemental Carbon
EAD	Equivalent Aerodynamic Diameter
EF	Enrichment Factor
EOF	Empirical Orthogonal Functions
ESP	Electrostatic Precipitator
F⁻	Fluoride ion
Fe	Iron
FeO	Iron(II) oxide
Fe₂O₃	Iron(III) oxide
FGC	Flue Gas Conditioning

FGD	Flue Gas Desulphurisation
H₂S	Hydrogen sulphide
H₂SO₄	Sulphuric acid
Hg	Mercury
HPA	Highveld Priority Area
IC	Ion Chromatography
IPP	Independent Power Producer
K	Potassium
K⁺	Potassium ion
K₂O	Potassium oxide
KNO₃	Potassium nitrate
K₂SO₄	Potassium sulphate
KCl	Potassium chloride
MDL	Method Detection Limit
ME-2	Multilinear Engine version 2
MEC	Member of the Executive Council
Mg²⁺	Magnesium ion
Mn	Manganese
Na	Sodium
Na⁺	Sodium ion
NH₄⁺	Ammonium ion
NH₄NO₃	Ammonium nitrate
NH₄SO₄	Ammonium sulphate
NO	Nitrogen oxide
NO₃⁻	Nitrate ion
NO₂	Nitrogen dioxide
NO_x	Nitrogen oxides
OC	Organic Carbon
OM	Organic Matter
P	Phosphorus
PAH	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PbO	Lead(II) oxide
PCA	Principal Component Analysis
PM	Particulate matter
PM_{2.5}	Particulate matter with an aerodynamic diameter of less than 2.5 µm
PM₁₀	Particulate matter with an aerodynamic diameter of less than 10 µm

PMF	Positive Matrix Factorisation
PO₄³⁻	Phosphate ion
PVC	Polyvinyl chloride
RM	Reconstructed Mass
S	Sulphur
SAWS	South African Weather Services
Se	Selenium
SFU	Stacked Filter Unit
Si	Silicon
SiO₂	Silicon dioxide
S/N	Signal-to-noise ratio
SO₄²⁻	Sulphate ion
SO₂	Sulphur dioxide
Sr	Strontium
Ti	Titanium
TiO₂	Titanium dioxide
TSP	Total Suspended Particulates
TSV	Total Spatial Variance
USEPA	United States Environmental Protection Agency
V	Vanadium
VOC	Volatile Organic Compounds
VTAPA	Vaal Triangle Airshed Priority Area
WBPA	Waterberg-Bojanala Priority Area
WD-XRF	Wavelength-Dispersive X-Ray Fluorescence
Zn	Zinc
ZnO	Zinc oxide
Zr	Zirconium

CHAPTER 1 OVERVIEW

Chapter 1 provides an overview of the state of knowledge of atmospheric aerosols in a global and local context. The impacts of aerosols on climate are highlighted and their sources and characteristics are described. Source apportionment studies undertaken in southern Africa are discussed. An outline of the research goals is also given.

1.1 Introduction

Atmospheric aerosols play an important role in the Earth's climate and atmospheric chemistry (Andreae and Crutzen, 1997; IPCC, 2013). Aerosols impact climate through their effect on the radiative balance of the Earth. Aerosol particles have a direct effect by scattering and absorbing solar radiation and an indirect effect by increasing cloud condensation nuclei concentrations, which in turn increase cloud droplet concentrations and thus backscattering of solar radiation (Hand and Malm, 2007; IPCC, 2013). Aerosol-cloud interactions constitute the largest uncertainty in current estimates of aerosol radiative forcing (IPCC, 2013). To reduce the uncertainties associated with aerosols and climate, a greater understanding of aerosols is required together with their optical, physical, and chemical properties and their spatial and temporal variability.

While atmospheric aerosols, their sources and formation mechanisms have been studied extensively in the northern Hemisphere, such studies are limited in the southern Hemisphere. Two major studies were undertaken in southern Africa in 1992 and 2000 which contributed to significant insights into aerosols and trace gases in the region. The Southern African Fire Atmosphere Research Initiative in 1992 (SAFARI-92) (Lindesay *et al.*, 1996) focused on the factors influencing the process and distribution of biomass burning in southern Africa, as well as the chemistry, transportation and source strength of the burn products (Andreae *et al.*, 1994; Lindesay *et al.*, 1996; van Wilgen *et al.*, 1997). Significant findings of the campaign showed that the distinct biogeophysical systems of southern Africa are linked by the regional atmospheric circulation system and that, in addition to biomass burning, there are other contributing sources to aerosols and trace gases in the region. These other sources include plant and soil microbial action, industrial, marine and mineral emissions. While much was learnt from this campaign around biomass burning, detailed information on these other aerosol and trace gases sources, and the processes generating them, was not determined. The impacts of the deposition of these emissions on biogeochemical cycling and other ecosystem functioning aspects were also not thoroughly assessed. As such, a more comprehensive study, the Southern African Regional

Science Initiative (SAFARI-2000), was undertaken in 2000 to investigate emissions, transportation, transformation, and deposition of trace gases and aerosols over southern Africa (Swap *et al.*, 2002). Despite new information obtained on biogenic emissions, biomass burning was as the main contributing source to aerosols and trace gases in southern Africa. Industrial emissions such as metal smelting and coal-fired power stations were important on sub-regional scales but were identified to be small contributors in terms of the overall aerosol mass (Swap *et al.*, 2003).

A more recent study, the European Integrated project on Aerosol, Cloud, Climate and Air Quality Interactions (EUCAARI) was undertaken from 2009 to 2011 with the South African Highveld selected for inclusion in the study due to its global impact (Swap *et al.*, 2003). The main emphasis of the study was to further understand aerosol optical properties, indirect aerosol effects, aerosol chemistry, new particle formation and to validate satellite and modelling results (Laakso *et al.*, 2012; 2013). Measurements undertaken at Elandsfontein (Laakso *et al.*, 2010) found that aerosol optical properties were correlated with particulate mass and number concentration during polluted conditions and that under such conditions, aerosol optical properties were influenced predominantly by submicron primary particles. During clean conditions, various smaller sources contributed to the atmospheric aerosol loading with submicron particles also potentially contributing. New particle formation was found to substantially enhance particle number concentrations in both clean and polluted air masses but had no influence on aerosol mass concentration or the optical properties of polluted air masses.

A greater level of understanding of the optical properties of aerosols and their spatial and temporal variability remains of continued importance for the southern African region where aerosol particles play a significant role in the climate system (Nyanganyura *et al.*, 2005; Queface *et al.*, 2011). South Africa, and especially the industrial Highveld, is a major source of anthropogenic and natural aerosols in the southern sub-continent (Held, 1996). South Africa has one of the three largest industrialised economies on the African continent and accounts for a significant portion of significant mining and metallurgical industries (Venter *et al.*, 2012). As the largest regional energy producer on the continent, South African generates most of the electricity in coal-fired power stations (Tiitta *et al.*, 2014; Josipovic *et al.*, 2019). Coal is also used in the petrochemical sector to produce liquid fuel and petrochemicals. Domestic fuel combustion continues to be used for space heating and cooking purposes in many townships while emissions from biomass burning also have a large seasonal impact (Vakkari *et al.*, 2013; 2014).

Particulate matter is the most significant pollutant of concern in many areas in South Africa (Alteri and Keen, 2019). The adverse health effects associated with exposure to elevated levels

of particulate matter are well documented. They include a range of acute and chronic respiratory and cardiovascular effects, irreversible changes in physiological function (e.g. lung function) and premature mortality (WHO, 2006). The South African Comparative Risk Assessment (Norman *et al.*, 2007) estimated air pollution to account for 4 637 (or 0.9%) of all deaths in South Africa in 2000. Of this, 3.7% of mortality was from cardiopulmonary disease and 5.1% of mortality was associated with cancers of the trachea, bronchus and lungs in adults 30 years and older. Acute respiratory infections were estimated to account for 1.1% of mortality in children under 5 years old. In recent years, toxic metals have been receiving increasing global interest due to their carcinogenic (either 'known' or 'probable') and non-degradable nature (Zhang *et al.*, 2004). Due to their high toxicity, heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb) and mercury (Hg) have been classified amongst the priority metals for human health impacts (Tchounwou *et al.*, 2012). These metals are classified as human carcinogens and are known to impact human health even at low concentrations (Morais *et al.*, 2012; Tagliani *et al.*, 2017). Exposure to As affects all of the organ systems (cardiovascular, dermatologic, nervous, hepatobiliary, renal, gastro-intestinal and respiratory) as well as increasing mortality rates associated with cancers of the bladder, kidney, skin and liver. Breathing high levels of Cr (VI) can irritate and damage the nose, stomach and intestines as well as causing renal damage, asthma and cancer of the respiratory tract (Tchounwou *et al.*, 2003). Cd accumulates in the human body, damaging the liver, kidneys, lungs, bones, placenta and the central nervous system (Castro-González & MéndezArmenta, 2008) as well causing various reproductive, developmental, hepatic, hematological and immunological effects (Apostoli and Catalani, 2011). Exposure to Hg and Pb during childhood has been associated with irreversible neurodevelopmental effects, leading to reduced cognitive performance, decrease in intelligence, attention deficit disorder, mental retardation and Autism Spectrum Disorder (Debes *et al.*, 2016; Jeong *et al.*, 2017; Geier *et al.*, 2018). Coal-fired power stations are the most significant contributors to Hg emissions in South Africa (Garnham and Langerman, 2016) and have been estimated to account for 77% of the total Hg emitted (Pirrone *et al.*, 2009).

Within South Africa, several aerosol source apportionment studies have been undertaken to further understand aerosol characteristics and their contributing sources. These studies (Maenhaut *et al.*, 1996; Annegarn *et al.*, 1998; Piketh *et al.*, 1999; Engelbrecht *et al.*, 2000; 2001; 2002) identified mineral dust, industry, residential fuel burning, sea salt and biomass burning to be the major contributing aerosol sources. South Africa has recognised the importance of air pollution and its impacts on human health with the declaration of three Priority Areas, namely the Vaal Triangle Airshed Priority Area (VTAPA) in 2006, the Highveld Priority Area (HPA) in 2007 and the Waterberg-Bojanala Priority Area (WBPA) in 2012. The existing air quality situation in the VTAPA and the HPA is considered to be poor and intervention is required

in these areas to resolve the situation. Declaration of the WBPA as a Priority Area is in anticipation of the area becoming a pollution ‘hotspot’ in the future.

This study assesses the origin (sources) and composition of the aerosol loading at four selected sites within each of the Priority Areas through aerosol source apportionment. Sampling campaigns were undertaken at Lephalale (in the Waterberg-Bojanala), Kwazamokhule and Embalenhle (on the Highveld) and Zamdela (in the Vaal Triangle) in South Africa over the period 2012 – 2017. Sampling was undertaken using the ‘Gent’ Stacked Filter Unit (SFU) sampler which collects particles that have an equivalent aerodynamic diameter (EAD) of less than 10 μm in separate coarse and fine fractions. The chemical composition of the aerosol loading was analysed using Wavelength-Dispersive X-Ray Fluorescence (WD-XRF) and Ion Chromatography (IC) analysis. Source apportionment of the aerosol loading was then undertaken using Principal Component Analysis (PCA), Positive Matrix Factorisation (PMF) and Chemical Mass Balance (CMB) receptor modelling.

1.2 Literature Review

1.2.1 Aerosol Classification and Properties

An aerosol is defined in its most basic form as a collection of solid or liquid particles suspended in a gas (Colbeck and Lazaridis, 2014). All aerosol particles in the atmosphere are defined as either primary or secondary particles that originate from either anthropogenic or natural sources (Pöschl, 2005). Anthropogenic sources include, amongst others, domestic combustion, transportation, industrial emissions, agriculture and biomass burning whereas natural sources, amongst others, include fires, volcanoes, sea salt and wind erosion. Primary particles are directly emitted as particles while secondary particles are formed in the atmosphere through gas-to-particle conversions (Pöschl, 2005; Colbeck and Lazaridis, 2014). Primary particles include dust, soot and fly ash whereas secondary particles include sulphate (SO_4^{2-}) and nitrate (NO_3^-). All aerosol particles are formed either by the condensation of gases or vapours, or by mechanical or communitive processes. Aerosols may then be transformed by coagulation and condensation processes while being transported and diluted in the atmosphere (Papastefanou, 2008).

Atmospheric aerosol size distributions can be divided into three separate modes, namely, Aitken nuclei mode ($< 0.1 \mu\text{m}$), accumulation mode (< 2.0 but $> 0.1 \mu\text{m}$) and coarse particle mode ($> 2.0 \mu\text{m}$) (Mönkkönen *et al.*, 2005). The origin of each of the three aerosol modes is associated with various aerosol sources and formation (such as coagulation) and removal mechanisms (such as rainout, washout and sedimentation) (Figure 1.1). Usually the nuclei mode does not significantly increase the aerosol mass concentration as it rarely accounts for more than a few

percent of the total aerosol mass. Particles in this mode originate predominantly by the condensation of hot vapours during combustion and gas-to-particle conversion in the atmosphere (Colbeck and Lazaridis, 2014). Brownian motion of particles smaller than $0.1\ \mu\text{m}$ in diameter can cause particles to diffuse and, if the concentration is high enough, result in collisions to coagulate into larger particles. The presence of substantial nuclei mode particles in the aerosol size distribution is indicative of the presence of fresh combustion aerosol (Papastefanou, 2008). Due to the coagulation of particles in the nuclei mode and heterogeneous nucleation of secondary aerosols, the accumulation mode tends to account for the majority of the aerosol surface area and a substantial part of the aerosol mass (Whitby and Cantrell, 1976; Willeke and Whitby, 1975). Due to a sharp decrease in the number of particles larger than $0.3\ \mu\text{m}$ in diameter, the mass transfer from the accumulation mode to the coarse particle mode is limited. At relative humidity below 100%, almost all aerosol particles in the coarse particle mode are formed by mechanical processes such as grinding, wind-blown dust, sea spray and volcanoes (Papastefanou, 2008; Eleftheriadis and Loannidou, 2020).

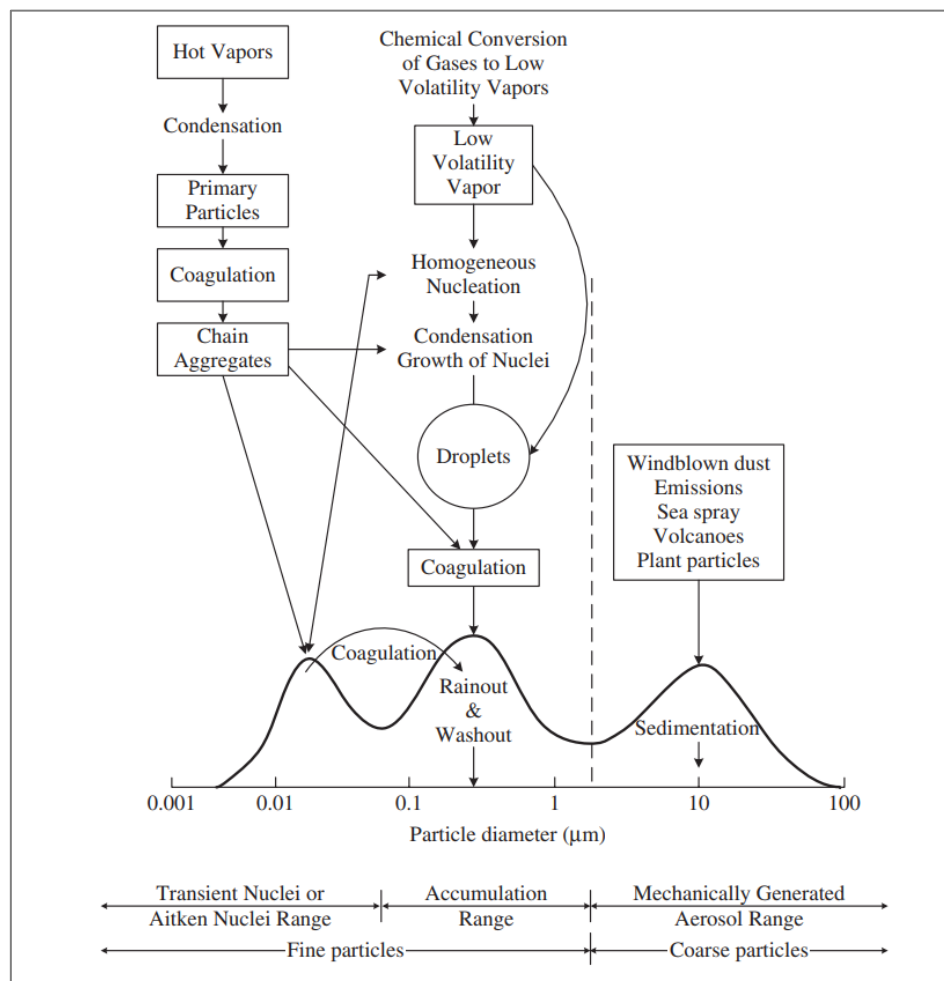


Figure 1.1: Distribution of particle surface area of an atmospheric aerosol (Colbeck and Lazaridis, 2014)

1.2.1.1 Aerosol Source Characteristics

The chemical species often found in different source emissions according to their chemical abundances are summarised in Table 1.1. The relative abundance of the fine and coarse mode aerosol varies in terms of chemical composition, physical properties and mass depending on the nature of the contributing sources. In general, the predominant chemical components of aerosols are SO_4^{2-} , NO_3^- , ammonium (NH_4^+), sea salt, mineral dust, organic compounds and black or elemental carbon, each of which contributes approximately 10 - 30% of the total aerosol mass (Pöschl, 2005). The fine particle fraction is generally composed of aerosols originating from anthropogenic sources and includes elements such as Pb, bromine (Br), carbon (C), SO_4^{2-} , NO_3^- and NH_4^+ . Coarse particles have different sources of origin and chemical composition and are dominated by crustal elements such as magnesium (Mg), aluminium (Al), silicon (Si), potassium (K), calcium (Ca), titanium (Ti), manganese (Mn), iron (Fe) and strontium (Sr). Coarse particles originate from fugitive dust sources from wind-blown dust, vehicle dust entrainment and fugitive industrial emissions (e.g. materials handling activities) although emissions from incomplete combustion (fly ash), plant tissues and grinding operations may also contribute (Cooper, 2011).

1.2.1.1.1 Biomass Burning

Large-scale burning of savannas and forested areas as well as domestic burning of fuelwood, charcoal, agricultural waste and other forms of biomass is a significant source of particulate emissions (Maenhaut *et al.*, 1996). Emissions of particulates from biomass burning are generated predominantly as submicron particles in the accumulation mode (Crutzen and Andreae, 1990). Smoke aerosols of savannah and grassland fires are comprised mainly of organic carbon (OC) and black carbon (BC), with the latter ranging between 10 – 30% of the aerosol mass (Andreae *et al.*, 1998). In the water-soluble component, potassium (K^+), NH_4^+ , chloride (Cl^-) and SO_4^{2-} are the most abundant species. Savanna fires are also a substantial source of elements such as phosphorus (P), K, Ca, Mn, zinc (Zn), Sr and iodine (I) in the coarse fraction and chlorine (Cl), K, copper (Cu), Zn, Br, rubidium (Rb), antimony (Sb), I, Cs and Pb in the fine fraction (Maenhaut *et al.*, 1996). Other biomass burning species include organic acids such as formate, acetate and oxalate (Jaffrezo *et al.*, 1998).

Potassium in fine particulate matter has frequently been used as a conventional biomass-burning tracer (Cachier *et al.*, 1991). Various studies (Gao *et al.*, 2003; Li *et al.*, 2003) have shown that particles from fresh smoke of savannah fires contain potassium chloride (KCl) whereas aged smoke particles contain potassium sulphate (K_2SO_4) and potassium nitrate (KNO_3). This was supported by Aurela *et al.* (2016) who confirmed that K^+ in the fresh smoke of

savannah fires was likely to be in the form of KCl instead of K_2SO_4 and KNO_3 . In the same study, the chemical composition of fresh biomass burning plumes was seen to be comprised mainly of SO_4^{2-} , OC, EC, NH_4^+ and K^+ in the fine fraction (in the PM_{10} range), while Na^+ , Cl^- , NO_3^- and oxalate were divided between the fine and coarse fractions.

In the domestic burning of wood, emissions are variable and are dependent on the burn conditions, nature of the wood and the burning devices (McDonald *et al.*, 2000). Domestic wood burning profiles comprise significant quantities of carbonaceous material with carbon accounting for 63 – 96% of the fine fraction mass (Watson *et al.*, 2001). Other residential wood combustion studies (McDonald *et al.*, 2000; Hedberg *et al.*, 2002; Fine *et al.*, 2004; Schmidl *et al.*, 2008) have shown that EC carbon accounts for more than 50% of the aerosol mass, followed by EC, while inorganic species each contribute to less than 5% of the total aerosol mass. Of the inorganic species, the most abundant species were K^+ followed by Cl^- , SO_4^{2-} and NO_3^- with most of the inorganic fine particles in the form of KCl and K_2SO_4 (Nyström *et al.*, 2017).

1.2.1.1.2 Coal Combustion

Coal-fired power stations can emit significant quantities of particulate matter, trace gases such as nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and carbon monoxide (CO) as well as trace amounts of heavy metals. The physical and chemical properties of particulate matter emitted from coal-fired power stations are dependent on the coal used as fuel (Lee, 2001), the combustion conditions in the boiler (Gladney *et al.*, 1976; Wu *et al.*, 2011) and the emission control technologies that are utilised (Liu *et al.*, 2009). Particulate matter from coal-fired power stations is comprised primarily of sulphur (S), Si, Al and Fe in both the fine and coarse fractions (Bray *et al.*, 2017). Heavy metals such as Sb, As, beryllium (Be), Cd, Cr, cobalt (Co), Pb, Mn, Hg, nickel (Ni) and selenium (Se) are also present. Local studies undertaken in South Africa have also confirmed the presence of As, Sb, Cd, Cr and Pb in the fly ash of a coal-fired power station (Ayanda *et al.*, 2012). Elevated levels of Cd, Sb, Hg, As and Pb have also been measured in soil samples surrounding coal-fired power stations on the Mpumalanga Highveld (Clark *et al.*, 2015; Dalton *et al.*, 2018).

In coal-fired power station profiles, SO_4^{2-} has very high abundances in the particle phase (Watson *et al.*, 1996). Crustal elements such as Si, Ca and Fe are present at 30 – 50% of the corresponding levels seen in geological material. However, Al is present at similar or higher levels in the power generation profile as compared to the geological profiles. Other elements such as P, K, Ti, Cr, Mn, Sr, zirconium (Zr) and Ba have less than 1% abundances. Selenium has also been detected at abundances of 0.2 – 0.4% in coal-fired power station emissions which do not have scrubbers installed (Watson *et al.*, 1996).

Profiles for coal-fired power stations differ substantially from domestic coal combustion, despite utilising similar fuels, due to the different emission control technologies used (Watson *et al.*, 1996) as well as the combustion conditions, which play a significant role in the formation of particulates (Zhaung and Biswas, 2001). Coal used in domestic coal combustion usually contains a lower amount of volatile organic compounds that influences conditions for complete combustion. As such, a catalyst such as paper and wood kindling is often used for ignition (Makonese *et al.*, 2017). The combustion temperature is also much lower in domestic coal combustion, leading to incomplete combustion of devolatilised particulate matter (Zhou *et al.*, 2016). Domestic coal combustion profiles are predominantly comprised of carbonaceous material, with carbon accounting for 63 – 96% of the fine fraction mass (Watson *et al.*, 2001). Other species released from domestic coal combustion include Si, K, Al, Fe, Ca, Zn, Na, Mg and Ti which are generated in variable quantities during each of the combustion phases (ignition, flaming and char burning) of the burn cycle (Masekameni *et al.*, 2019). During the ignition phase, Ca, Si, Fe and K are released in substantial quantities. High emissions of Si and K are seen during this phase due to the use of wood as kindling for ignition. During the flaming phase, K increases due to the pyrolysis of the wood kindling while, during the char burning phase, a decline in K is seen. All other species (with the exception of Ca) show an increase as combustion progresses (Masekameni *et al.*, 2019).

1.2.1.1.3 Geological Material

Geological material contains large abundances of Al, Si, K, Ca and Fe (Watson *et al.*, 2004). The total abundance of K is approximately 15 – 30 times the abundance of K⁺. The abundances of Al, K, Ca and Fe are similar amongst the geological source profiles although Si abundances range from 14 – 20% in unpaved and paved road dust, respectively. While geological material tends to have considerable highly variable abundances of EC, natural soils contain insignificant amounts of EC. Organic carbon ranges from 5 – 15% in geological material, being most abundant in paved road dust and agricultural dust. Higher abundances of OC, EC and Pb are seen in paved road dust due to emissions from motor vehicles (Watson *et al.*, 2004). Emissions from motor vehicles include brake and tyre wear, exhaust emissions and fly ash from road asphalt (Gunawardana *et al.*, 2012). A sandpaper-like effect on asphalt and bitumen can also cause additional contamination due to the abrasion of paints used on the road and guardrails (Adamiec *et al.*, 2016). Such abrasion is a significant source of Ni and As (Ozaki *et al.*, 2004). Studies (Fukuzaki *et al.*, 1986; Fauser *et al.*, 1999; Adachia and Tainoshob, 2004; Schauer *et al.*, 2006 and Hjortenkrans *et al.*, 2007) have determined that significant amounts of Zn, Cd, Co, Cr, Cu, Hg, molybdenum (Mo), Ni and Pb are associated with dust from tyre wear with Zn being the most abundant metal from tyre wear. The greatest wear occurs during acceleration, braking

and cornering. Another source of road dust is the wear that occurs from braking systems. During braking, brakes are exposed to excessive heat from friction, which is transmitted to the brake discs, thereby releasing particulates. Studies undertaken by Adachia and Tainoshob (2004) and Hjortenkrans *et al.* (2007) reported that brake dust contained Fe as well as significant quantities of Cu, Sb, barium (Ba), Al, Si, S, Ti, Zn, Ni, Cr, Pb and a small amount of Cd.

1.2.1.1.4 Motor Vehicles

Fine particulate released from motor vehicle tailpipes is primarily composed of EC and OC, (Maricq, 2007) contributing to over 95% of the total particulate mass (Watson *et al.*, 2004). The relative abundance of EC is influenced by engine type, engine operating conditions and the use of emission control equipment. Generally, diesel engines have higher EC emission rates relative to OC, while the opposite is true for petrol engines (Maricq, 2007). Organic carbon from motor vehicle exhausts consists mainly of low volatility organic compounds derived from fuel and lubricating oil. Factors influencing OC emissions include the fuel and lubricating oil properties, temperature, engine operating speed, engine load, engine age and condition (Kweon *et al.*, 2003; Lapuerta *et al.*, 2003; Sakurai *et al.*, 2003; Brandenberger *et al.*, 2005; Maricq, 2007).

Other species such as Pb and Br are also present in low abundances in motor vehicle tailpipe emissions (Watson *et al.*, 1996). Zn is seen in most motor vehicle exhaust profiles, although also generally present in low abundances (Watson *et al.*, 2004). Particulate matter released from motor vehicle exhausts also includes, although to a much lesser degree, inorganic species such as SO_4^{2-} and other trace elements (Kittelson *et al.*, 2006; Maricq, 2007). Sulphur is present as an impurity in fuel and is also used in additives in lubricating oil, as well as trace elements such as Zn, P, Ca and Mg (Cadle, 1997; Spikes, 2004; Maricq, 2007).

1.2.1.1.5 Secondary Aerosols

Abundances of SO_4^{2-} , NO_3^- and NH_4^+ in directly emitted particles cannot account for the concentrations of the species measured in the atmosphere since ambient concentrations contain both primary and secondary particles (Watson *et al.*, 2004). Pollutants such as SO_2 , NH_3 and nitrogen oxides (NO_x) are the precursors for secondary particles such as sulphuric acid (H_2SO_4), ammonium bisulphate (NH_4HSO_4), ammonium sulphate (NH_4SO_4) and ammonium nitrate (NH_4NO_3) (Seinfeld, 1986; Watson *et al.*, 1994). Sulphuric acid combines with NH_3 to form ammonium bisulphate and/or ammonium sulphate. These compounds are water-soluble and are found in the fine aerosol fraction (Watson *et al.*, 2004). NH_3 can also react with nitric acid to form NH_4NO_3 (Lefer and Talbot, 2001). Ammonium nitrate can account for up to 10 –

30% of the fine aerosol mass (Wexler and Seinfeld, 1990). However, this reaction is reversible, and as such NH_4NO_3 particles can easily evaporate with an increase in temperature and decrease in relative humidity (Stelson and Seinfeld, 1982a, 1982b; Allen *et al.*, 1989). Several of these particles, especially those containing NH_4NO_3 , are volatile and readily transfer mass between the gas and particle phase to maintain a chemical equilibrium (Stelson and Seinfeld, 1982a-c).

1.2.1.1.6 Marine Aerosol

Marine aerosols originate from a variety of production and transformation processes. Sea spray aerosol originates directly from the sea surface due to wind-driven bursting of bubbles or sea spray processes (O'Dowd *et al.*, 2004) while secondary aerosols are formed from subsequent oxidation of biogenic gases released from marine biota (Meskhidze and Nenes, 2006; O'Dowd *et al.*, 2004). Marine aerosols are mostly dominated by sea salt (O'Dowd *et al.*, 2004) which is concentrated in the coarse aerosol mode. Sea salt aerosols are comprised mainly of sodium chloride (NaCl) although other species such as K^+ , Mg^{2+} and Ca^{2+} can also be found in sea salt. Secondary SO_4^{2-} is also produced through the photo-oxidation of dimethyl sulphide, a product of phytoplankton decomposition (Seinfeld and Pandis, 2006; Fu *et al.*, 2011). Marine aerosols also contain large quantities of organic matter especially during periods of high biological activity (O'Dowd *et al.*, 2004; Sciare *et al.*, 2009; Miyazaki *et al.*, 2010).

Table 1.1: Chemical species in various emission sources (after Watson et al., 2004)

Source	Particle Size	Chemical Abundances in % Mass			
		< 0.1%	0.1 to 1%	1 to 10%	> 10%
Paved Road Dust	Coarse	Cr, Sr, Pb, Zr	SO ₄ ²⁻ , Na ⁺ , K ⁺ , P, S, Cl, Mn, Zn, Ba, Ti	EC, Al, K, Ca, Fe	OC, Si
Unpaved Road Dust	Coarse	NO ₃ ⁻ , NH ₄ ⁺ , P, Zn, Sr, Ba	SO ₄ ²⁻ , Na ⁺ , K ⁺ , P, S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Construction	Coarse	Cr, Mn, Zn, Sr, Ba	SO ₄ ²⁻ , K ⁺ , S, Ti	OC, Al, K, Ca, Fe	Si
Agricultural Soil	Coarse	NO ₃ ⁻ , NH ₄ ⁺ , Cr, Zn, Sr	SO ₄ ²⁻ , Na ⁺ , K ⁺ , S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Natural Soil	Coarse	Cr, Mn, Sr, Zn, Ba	Cl ⁻ , Na ⁺ , EC, P, S, Cl, Ti	OC, Al, Mg, K, Ca, Fe	Si
Motor vehicle	Fine	Cr, Ni, Y	NH ₄ ⁺ , Si, Cl, Al, Si, P, Ca, Mn, Fe, Zn, Br, Pb	Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , S	OC, EC
Biomass / Vegetative Burning	Fine	Ca, Mn, Fe, Zn, Br, Rb, Pb	NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , Na ⁺ , S	Cl ⁻ , K ⁺ , Cl, K	OC, EC
Residual Oil Combustion	Fine	K ⁺ , OC, Cl, Ti, Cr, Co, Ga, Se	NH ₄ ⁺ , Na ⁺ , Zn, Fe, Si	V, OC, EC, Ni	S, SO ₄ ²⁻
Incinerator	Fine	V, Mn, Cu, Ag, Sn	K ⁺ , Al, Ti, Zn, Hg	NO ₃ ⁻ , Na ⁺ , EC, Si, S, Ca, Fe, Br, La, Pb	SO ₄ ²⁻ , NH ₄ ⁺ , OC, Cl
Coal-fired boiler	Fine	Cl, Cr, Mn, Ga, As, Se, Br, Rb, Zr	NH ₄ ⁺ , P, K, Ti, V, Ni, Zn, Sr, Ba, Pb	SO ₄ ²⁻ , OC, EC, Al, S, Ca, Fe	Si
Marine	Fine and Coarse	Ti, V, Ni, Sr, Zr, Pd, Ag, Sn, Sb, Pb	Al, Si, K, Ca, Fe, Cu, Zn, Ba, La	NO ₃ ⁻ , SO ₄ ²⁻ , S, OC, EC	Cl ⁻ , Na ⁺ , Na, Cl

1.2.2 Source Apportionment Methods

Source apportionment is used to identify air pollution sources and to quantify their contribution to ambient pollution levels in an airshed (Belis *et al.*, 2014). Greater understanding and quantification of the contributing air pollution sources is important for the formulation and implementation of effective air pollution mitigation measures and control strategies in a given airshed. Emissions of particulate matter from sources often have unique chemical profiles which can be used to determine the contribution of sources to the total aerosol loading at a receptor (Watson, 1984).

There are three main approaches to aerosol source apportionment (Viana *et al.*, 2008a). The first apportionment method is based on the assessment of monitoring data using basic

numerical data treatment to identify air pollution sources. The advantage of this method lies in its relative simplicity and the resultant low impact of mathematical artefacts due to the treatment of data. The second apportionment method is based on the compilation of emission inventories and dispersion modelling simulations. This method requires detailed emission inventories for input into a dispersion model which are not always readily available and diffuse emission sources, such as wind-blown dust, are also not easily quantifiable. The third method, receptor modelling, is based on the statistical assessment of particulate chemical data collected at receptor sites (Viana *et al.*, 2008a). The fundamental principle of receptor modelling is that mass and species conservation can be assumed and as such, a mass balance analysis can be used to identify and quantify sources of particulate matter in the atmosphere (Viana *et al.*, 2008a; Li *et al.*, 2013). Receptor models range from multivariate models such as PCA and PMF, which require little knowledge about emission sources prior to receptor modelling, to more complex models such as CMB, which requires more detailed information about the emission sources (Figure 1.2) (Viana *et al.*, 2008a).

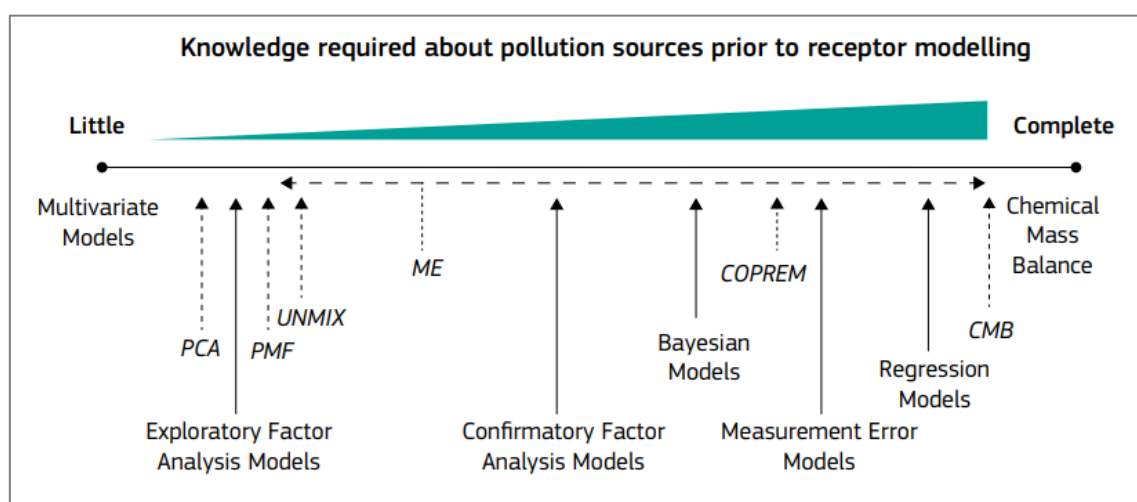


Figure 1.2: Summary of receptor modelling methods (Viana *et al.*, 2008a; Belis *et al.*, 2014)

Receptor modelling is more widely used in source apportionment compared with the other two apportionment methods. Multivariate models such as PCA and PMF are commonly used due to the wide availability of the software and the fact that detailed prior knowledge about the emission sources and source profiles is not needed. These models attempt to apportion the sources based on observations or internal correlations at the receptor sites. A significant limitation of these models is that the resulting components or factors may represent mixtures of emission sources rather than separate source profiles as determined by the models. The CMB modelling approach conversely assumes detailed knowledge of the composition of the emission sources and is the preferable choice when there are minimal changes in the source profiles

between the emission source and the receptors. However, as this is often not the case, pure CMB approaches can be problematic for aerosol source apportionment (Viana *et al.*, 2008a).

1.2.2.1 Factor Analysis

Spearman (1927) established the first mathematical foundation for receptor model variability analysis. Spearman was the first to use factor analysis to try and determine whether intelligence consisted of one or many abilities. Thurstone (1935, 1947) generalised this through his work on multiple-factor analysis and the formulation of a model of intelligence. In 1956, Lorenz (1956) undertook the first environmental application by applying empirical orthogonal function (EOF) analysis to statistical weather predictions (Cooper, 2011). Blifford and Meeker (1967) were the first to apply receptor modelling for aerosol source apportionment purposes. Blifford and Meeker used a PCA with several types of axis rotations to evaluate particle composition data collected by the National Air Sampling Network over the period 1957 to 1961 in 30 cities in the United States. Given the variability in particulate sources in these different cities and the few elements measured (a total of 13), an insufficient amount of interpretable information could be extracted from the dataset. Following from this, Prinz and Stratmann (1968) used factor analysis to evaluate the aromatic hydrocarbon content of the air in 12 West German cities as well as data on the air quality of Detroit in Michigan. Both studies found three factor solutions and used an orthogonal varimax rotation to easily interpret the results. Hopke *et al.* (1976) and Gaarenstroom *et al.* (1977) used factor analysis to analyse the particle composition of samples from Boston in Massachusetts and Tucson in Arizona, respectively. In the Boston samples, six common factors were identified and interpreted to be soil, sea salt, oil-fired power plants, motor vehicles, refuse incineration and an unknown manganese-selenium source. In the Tucson samples, soil, automotive, several secondary aerosol materials and several unknown factors were identified (Hopke and Cohen, 2011).

However, a problem with multivariate methods such as factor analysis is that these methods are unable to provide quantitative information on source contributions to particle mass or of specific elemental concentrations. To solve this, an alternative method was developed, known as the Unmix receptor model (Henry and Kim, 1989; Kim and Henry, 1999; Kim and Henry, 2000; Henry, 2003), to provide information on source contributions when only ambient particulate analytical results are available. However, this method had several problems (Paatero and Tapper, 1993) and as such, Paatero (1997, 1999) developed a new approach for factor analysis called PMF which uses a weighted least-squares fit to obtain the source profiles and mass contributions (Hopke and Cohen, 2011). The advantages of PMF relative to traditional factor analysis methods (such as PCA) is that data below the detection limit or missing values can be included in the analysis by assigning them high uncertainties to minimise their influence

(Paatero and Tapper, 1994). Extreme values can also be downweighted to reduce their influence in the model (Huang and Conte, 2009). The major difference between PCA and PMF is that non-negativity of factors is included in the PMF model. A significant advantage of PMF over PCA is that PMF uses a point-by-point minimisation scheme rather than relying on information from the correlation matrix. This allows the profiles to be directly compared to the input matrix without any transformation (Lee *et al.*, 1999; Pongkiatkul and Oanh, 2012).

PMF has been widely used in numerous air quality studies for aerosol source apportionment (Paatero and Tapper, 1994; Paatero, 1997). PMF has also been used in research of molecular line spectra (Juvela *et al.*, 1996), wet deposition (Anttila *et al.*, 1995) and harbour bottom sediments (Poulton *et al.*, 1995).

1.2.2.2 Chemical Mass Balance

The concept of a CMB model was first proposed by Winchester and Nifong (1971), Hidy and Friedlander (1972), Kneip *et al.* (1972) and Miller *et al.* (1972). These applications used unique 'tracer' chemical species associated with each source type to identify contributing sources. In 1973, Friedlander (1973), proposed the ordinary weighted least-squares solution which did not have the same stringent constraints of a unique 'tracer' chemical species in each source type and also provided uncertainty estimates associated with source contributions. This method was applied by Gordon (1980, 1988) and Kowalczyk *et al.* (1978). However, this method was limited as only the uncertainties of the receptor concentrations were included (Watson *et al.*, 2004). In 1979, Watson (1979) and Dunker (1979) independently suggested a mathematical solution known as effective variance weighting which included the uncertainty in both the measurement of the source composition profiles and the ambient concentrations (Hopke and Cohen, 2011). This solution, termed the effective-variance least squares, was adopted by Watson *et al.* (1984) and was incorporated into the United States Environmental Protection Agency (USEPA) CMB receptor model (Hopke and Cohen, 2011). The main strength of the CMB model, unlike other receptor models (such as PMF) is that large datasets are not required for input into the model. Also, outputs from the CMB model do not require further source interpretation unlike factor analysis. However, a significant limitation of the CMB model is the availability and selection of source profiles that are best representative of the emission sources at a receptor site (Belis *et al.*, 2014). While a large number of profiles and composite profiles are available for significant primary sources, there is much variability in emissions depending on fuel type, combustion conditions and other factors. As such, these readily available profiles are not always indicative of the properties of a specific source at a receptor site (Subramanian *et al.*, 2007)

Since its development, the CMB receptor model has been extensively used for the source apportionment of PM₁₀ and PM_{2.5} (and VOCs) and has also been used in combination with extinction efficiency receptor models (Lowenthal *et al.*, 1994; Watson and Chow, 1994) and with aerosol equilibrium models (Watson *et al.*, 1994). Since 2001, the CMB model has not been used as widely for source apportionment (Hopke, 2016). Viana *et al.* (2008a) and Belis *et al.* (2013) reviewed the use of receptor models for source apportionment in Europe, with the latter reporting a shift away from the traditional use of PCA, enrichment factors and classical factor analysis towards receptor models such as PMF. The use of the CMB model was ambiguous, with its application limited by the availability of source profiles and long-term speciated particulate matter data. In more recent years, the CMB model has been used to apportion sources of primary organic aerosol using specific organic tracers known as molecular markers (Schauer *et al.*, 2002; Simoneit, 2002; Subramanian *et al.*, 2007; Zhang *et al.*, 2009).

1.2.3 Aerosol Source Apportionment Studies

Numerous source apportionment studies have been undertaken in various locations in the United States and Europe since the 1960s (Viana *et al.*, 2018a; Belis *et al.*, 2013; Hopke, 2016). Source apportionment has also been widely utilised in China since 1987 (Lee *et al.*, 1999). More recently, aerosol source apportionment have been undertaken (amongst others) in the United States (Chow and Watson, 2002; Hwang and Hopke, 2007; Lee *et al.*, 2008; Karnae and John, 2011; Hadley, 2017), Europe (Andriani *et al.*, 2011; AQUELLA, 2007; Belis *et al.*, 2013; El Haddad *et al.*, 2011; Junninen *et al.*, 2009; Larsen *et al.*, 2008; Maenhaut *et al.*, 2016; Maenhaut, 2018; Mossetti *et al.*, 2005; Pandolfi *et al.*, 2008; Perrone *et al.*, 2012; Viana *et al.*, 2008b; Yin *et al.*, 2010), Australia (Chan *et al.*, 2008; Cohen *et al.*, 2012; Friend and Ayoko, 2009; Friend *et al.*, 2011a, 2011b; Friend *et al.*, 2012) and Asia (Begum *et al.*, 2007; Bisht *et al.*, 2015; Chowdhury *et al.*, 2007; Dumka *et al.*, 2017; Gadi *et al.*, 2019; Gupta *et al.*, 2007; Jain *et al.*, 2017a, 2017b; Lin *et al.*, 2010; Li *et al.*, 2016; Ryou *et al.*, 2018; Sharma *et al.*, 2016; Sharma and Mandal, 2017; Shivani *et al.*, 2019; Singh *et al.*, 2011). Source apportionment, particularly using receptor models, has been used to a lesser extent on the African continent with most studies focused on southern Africa.

Within southern Africa, aerosol source apportionment studies have been undertaken in Namibia (Annegarn *et al.*, 1983; Kloppe *et al.*, 2020), Botswana (Chimidza and Moloi, 2000; Jayaratne and Verma, 2001; Selin Lindgren *et al.*, 1998), Zimbabwe (Nyanganyura *et al.*, 2007), Zambia (Queface *et al.*, 2011) and South Africa (Annegarn *et al.*, 1998; Engelbrecht *et al.*, 2000; 2001; 2002; Formenti *et al.*, 1998; Kgabi, 2010; Maenhaut *et al.*, 1996; Piketh *et al.*, 1999; Queface *et al.*, 2011; Salma *et al.*, 1994; Shikwambana and Sivakumar, 2019; Tiitta *et al.*, 2014; Tshela and Djolov, 2018). In Namibia, Annegarn *et al.* (1983) identified sea salt and mineral dust as the

dominant aerosol sources in the Namib Desert. This was also seen by Klopper *et al.* (2020) who identified sea salt and mineral dust as the main sources as well as an ammonium neutralised source, fugitive dust and industry on the Namibian coast. In Botswana, soil dust, coal combustion (Chimidza and Moloi, 2000) and biomass burning (Jayaratne and Verma, 2001) were identified as the dominant aerosol sources. Source apportionment of aerosol data collected at Rukomechi Research Station in northern Zimbabwe (Nyanganyura *et al.*, 2007) determined the main contributing sources to be mineral dust, biomass burning and sea salt. Other sources included biogenic emissions and an anthropogenic copper component. Biomass burning was determined to be the main contributor to the total aerosol loading followed by mineral dust sources in both aerosol fractions. Queface *et al.* (2011) investigated the aerosol optical properties at Mongu in Zambia and Skukuza in South Africa and observed that the atmospheric aerosol loading at both sites was dominated by fine fraction aerosols throughout most of the year. A significant increase in fine mode aerosols was observed at Skukuza throughout the period August to November as a result of the biomass burning season. However, the fine fraction aerosol loading was also observed to be high during the non-biomass burning season which suggests that fine fraction aerosol sources at this site are not limited to biomass burning, but likely include combustion emissions from the South African Highveld.

Within South Africa, aerosol source apportionment studies are fairly limited (Mathuthu *et al.*, 2019), with few studies using the PMF and CMB receptor modelling methods. Source apportionment studies have previously been undertaken at various remote sites (Maenhaut *et al.*, 1996; Piketh *et al.*, 1999; Salma *et al.*, 1994), industrialised rural areas (Kgabi, 2010; Tshehla and Djolov, 2018), as well as within low-income, high-density urban areas where domestic fuels are still used for heating and cooking purposes (Annegarn *et al.*, 1998; Engelbrecht *et al.*, 2000; 2001; 2002; Formenti *et al.*, 1998). Source apportionment of aerosols at Kruger National Park and on the Highveld during SAFARI-92 (Maenhaut *et al.*, 1996) showed that mineral dust and sea salt were the dominant sources in the coarse fraction aerosols, with mineral dust, sea salt, biomass burning and SO_4^{2-} dominating the fine fraction aerosols. Approximately 40% of the fine aerosol was attributed to biomass burning and one third of it to a SO_4^{2-} component. At the remote Ben Macdhui site, Piketh *et al.* (1999) determined the dominant sources of fine and coarse aerosols to be biomass burning, aeolian dust, industrial sulphur aerosols and marine aerosols in the southern African haze layer. Interestingly, biomass burning did not contribute significantly to the total aerosol loading over South Africa. A recent study (Tshehla and Djolov, 2018) used PMF to apportion sources of particulate matter from an industrialised rural area (Steelpoort and surrounding areas) in the Limpopo Province. The dominating sources were found to be crustal/road dust, ferrochrome smelters and domestic wood burning with coal combustion, agricultural activities and vehicle emissions also identified

as contributing sources. In townships, residential fuel burning is a significant source of air pollution (Engelbrecht *et al.*, 2000; 2001; 2002), particularly during the winter months when increased fuel burning together with very stable atmospheric conditions, promotes the increase in concentrations. Using CMB receptor modelling, Annegarn *et al.* (1998) determined residential burning to contribute to 36.5% of the annual average fine fraction aerosol loading in Soweto, increasing to 64.6% during the winter months. This was also confirmed by Engelbrecht *et al.* (2000) who found that residential fuel burning in Qalabotjha accounted for 62.1% of the fine fraction aerosol and 42.6% of the coarse mode aerosol during the winter months. Biomass burning was also determined to be a major source in this township, accounting for 13.8% and 19.9% of the fine and coarse mode fractions, respectively.

A number of aerosol studies have recently been undertaken in South Africa to further understand the composition, origin and formation of aerosols as well as their spatial and temporal variability. Studies, amongst others, have been undertaken in Elandsfontein on the Highveld (Laakso *et al.*, 2010; 2012) as part of the EUCARRI campaign, and at three sites in the North-West Province, namely, Botsalano (Aurela *et al.*, 2016; Hirsikko *et al.*, 2013; Laakso *et al.*, 2008; Vakkari *et al.*, 2011; 2013); Marikana (Hirsikko *et al.*, 2012; 2013; Vakkari *et al.*, 2013; Van Zyl *et al.*, 2014; Venter *et al.*, 2012) and Welgegund (Beukes *et al.*, 2013; Jaars *et al.*, 2014; Tiitta *et al.*, 2014; Vakkari *et al.*, 2014; Venter *et al.*, 2016; 2017; 2018; 2020).

At Botsalano, a semi-clean savannah site (Laakso *et al.*, 2008; Vakkari *et al.*, 2011; 2013) and Marikana, a polluted industrial site (Hirsikko *et al.*, 2012; Hirsikko *et al.*, 2013), diurnal and seasonal particle sources and formation in South Africa have been characterised. These studies found that regional new particle formation was responsible for a large fraction of fine particle number concentration in both sites. Local sources such as domestic fuel burning in the informal settlements, was also found to be a significant contributing source to the diurnal variation of aerosols, particularly in polluted areas. Seasonally, domestic fuel burning and regional biomass burning were identified as the main aerosol sources in the polluted and semi-clean sites, respectively. Aurela *et al.* (2016) further studied the chemical composition of ambient and fresh biomass burning aerosols at Botsalano which showed that the site was frequently impacted by air masses that have passed over significant point sources in the Waterberg region (such as Matimba Power Station) and the western Bushveld Igneous Complex (the platinum group smelters). The air masses were comprised predominantly of Particulate Organic Matter (POM) during spring and SO_4^{2-} during summer (due to higher relative humidity during this season).

At Welgegund, a regional background site, organic aerosols were identified to be the main constituent of aerosols in the PM_1 fraction during the dry season at Welgegund. SO_4^{2-} and NH_4^+ were also seen to be high in the PM_1 fraction, especially when aged air masses passed over the

industrial Highveld region. The composition of the organic aerosol was determined to be oxidised organic aerosols and biomass burning organic aerosols in the dry season and low-volatile and semi-volatile organic aerosols in the wet season. The highly oxidised organic aerosols were associated with plumes from the Vaal Triangle and Highveld regions (Tiitta *et al.*, 2014). An assessment of inorganic aerosols at the same site (Venter *et al.*, 2018), also showed SO_4^{2-} and NH_4^+ to be the dominant species in the PM_1 fraction while SO_4^{2-} and NO_3^- were seen to be dominant in the $\text{PM}_{1-2.5}$ and $\text{PM}_{2.5-10}$ fractions. Sources of SO_4^{2-} and NO_3^- were determined to be aged air masses passing over source regions with elevated SO_2 and NO_2 emissions as well as marine aerosol contributions to NO_3^- . Similarly, at Marikana, SO_4^{2-} and NH_4^+ were the most abundant species in the smaller ($\text{PM}_{2.5}$) size fraction. NO_3^- also had the highest concentration in the $\text{PM}_{2.5-10}$ size fraction while Ca^{2+} was the next most abundant species in the $\text{PM}_{2.5-10}$ size fraction (Venter *et al.*, 2018). SO_4^{2-} has also been reported as the dominant inorganic ion in rain samples collected near anthropogenic source regions as well as background sites in South Africa (Conradie *et al.*, 2016), demonstrating the regional impacts of SO_4^{2-} . Venter *et al.* (2017) studied trace metal concentrations at Welgegund in the same three size fractions and determined Fe to be the most abundant species in all size fractions followed by Ca as the next most abundant species. Cr and Na were the third and fourth most abundant species, respectively. Most of the trace metals were found in the PM_1 and $\text{PM}_{1-2.5}$ size fractions, indicating an industrial influence while wind-blown dust was also shown to contribute in the $\text{PM}_{2.5-10}$ fraction. Fe was also seen to be the most abundant species at Marikana with Mg the next most abundant species. Relatively higher concentrations of Na, boron (B) and Al were also recorded. As also seen at Welgegund, anthropogenic and crustal sources were determined to be the main contributors to the trace metal concentrations (Van Zyl *et al.*, 2014).

Conradie *et al.* (2016) studied the chemical composition (and fluxes) of atmospheric wet deposition at four sites in South Africa, namely, Amersfoort, Vaal Triangle, Louis Trichardt and Skukuza. Based on the ionic composition of the aerosols, the key sources were determined to be marine, crustal, fossil fuel combustion, agriculture and biomass burning at all four sites. However, fossil fuel burning was found to be more significant at Amersfoort and the Vaal Triangle given their proximity to anthropogenic source regions while marine and biomass burning was more significant at the remote sites of Louis Trichardt and Skukuza.

Shikwambana and Sivakumar (2019) investigated BC, SO_4^{2-} , dust and marine aerosols in South Africa using satellite data and model simulations. Black carbon aerosols were shown to be dominant in the north-eastern parts of South Africa whereas SO_4^{2-} dominated the aerosol loading in the eastern parts of the country. Dust aerosols dominated the north-western parts of the country. Seasonally, BC aerosols were dominant in the eastern parts during spring

(attributed to biomass burning from the north and north-eastern parts of the subcontinent) while SO_4^{2-} was more dominant in the eastern parts during summer (due to an increase in relative humidity). Dust aerosols were more dominant in the north-western parts during summer. Marine aerosols dominated the coastal areas, the Indian Ocean as well as the north-eastern parts of the country, particularly during summer.

1.3 Research Goals

As pollution from particulate matter is a significant concern in many regions in South Africa, there is a need to formulate and implement effective air pollution control strategies in these regions. For this, a thorough understanding of the composition and sources of aerosol particles is required. While a number of attempts have been made to determine and apportion sources of particulate matter in South Africa, there remains a need for additional research.

The aim of this research is to evaluate the composition and characteristics of the atmospheric aerosol loading at selected sampling sites in South Africa by undertaking aerosol source apportionment. These sampling sites fall within each of the three declared Priority Areas which have been recognised to be areas that either have or will have the potential for poor air quality, and as such, require specific intervention measures to address air pollution. Domestic fuel burning, a significant contributor to air pollution in townships, is widely practised within each of the selected sampling sites with other key sources of air pollution also located close to the sampling sites.

The specific objectives of the project are to:

- (e) Evaluate the atmospheric aerosol loading in each site;
- (f) Characterise the chemical composition of the aerosol loading in each site;
- (g) Determine the sources contributing to the aerosol loading in each site using receptor modelling; and
- (h) Apportion the aerosol loading in each site to the contributing sources of emissions using receptor modelling.

This chapter has provided an overview of atmospheric aerosols in terms of their role in climate change and their sources and classification. A discussion of aerosol source apportionment studies undertaken in southern Africa and locally, in South Africa, has also been given. The research methodology employed in this study will be discussed in Chapter 2.

CHAPTER 2 DATA AND METHODOLOGY

Chapter 2 provides an overview of the sampling sites, sampling methodology and analytical techniques used for the chemical analysis of the particulate samples. The statistical methods used in this research, as well as the receptor models, are described.

2.1 Sampling Site Selection

Ambient aerosol sampling was undertaken at four sites in South Africa, namely, Lephalale in the Limpopo Province, Kwazamokhule and Embalenhle in the Mpumalanga Province and Zamdela in the Free State Province (Figure 2.1).

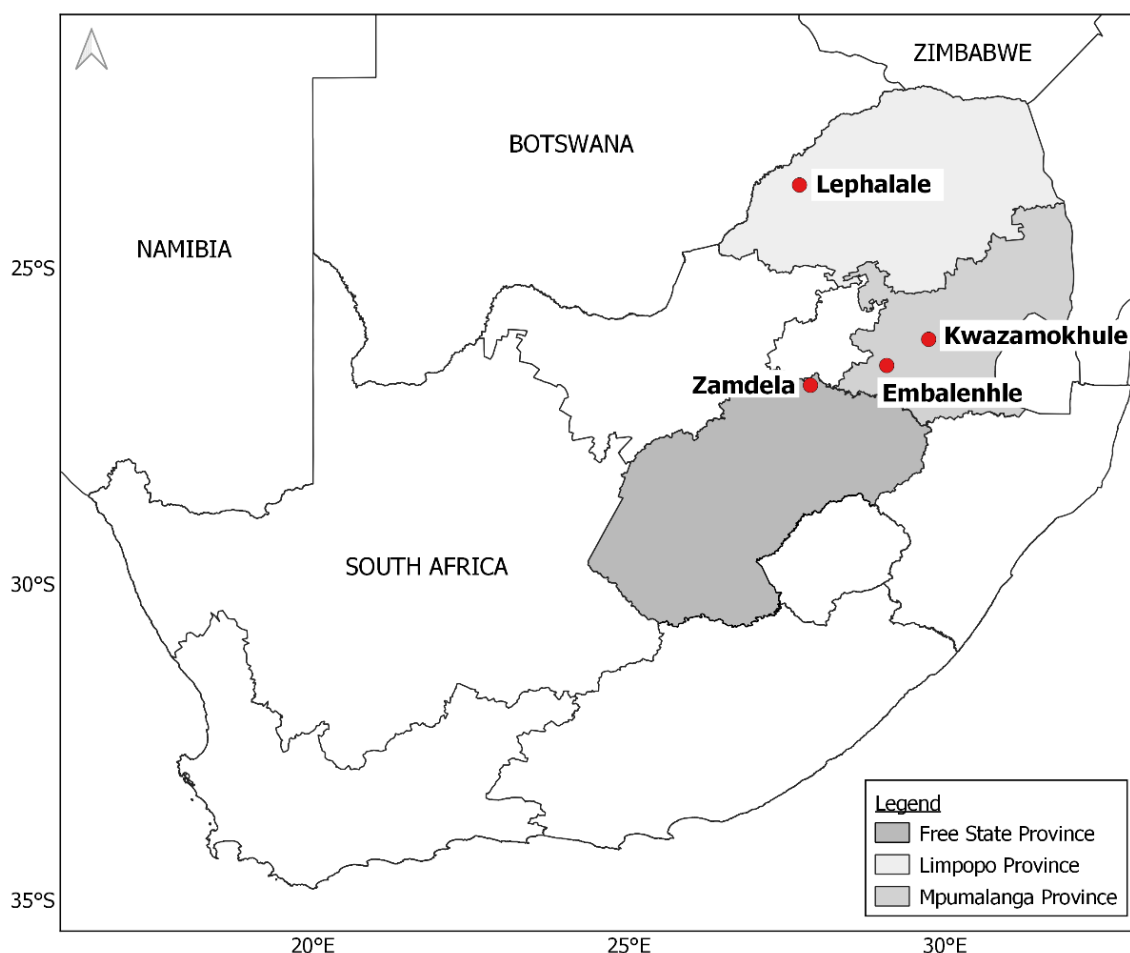


Figure 2.1: Location of the four aerosol sampling sites (red dots) in South Africa

All four sites fall within declared Priority Areas in South Africa. As per Section 18 (1) of the National Environmental Management: Air Quality Act, 2004 (Act No. 39 of 2004), the Minister or Member of the Executive Council (MEC) may declare an area as a priority area if the Minister or

MEC reasonably believes that ambient air quality standards are being, or may be, exceeded in the area, or any other situation exists which is causing, or may cause, a significant negative impact on air quality in the area, and the area requires specific air quality management to rectify the situation. To date, three Priority Areas have been declared in South Africa (Figure 2.2), namely, the VTAPA which was declared a Priority Area on 21 April 2006, the HPA which was declared on 23 November 2007 and the WBPA on 15 June 2012. While both the Vaal Triangle Airshed and the Highveld are existing air pollution 'hotspots', the Waterberg region is not considered to be an air pollution 'hotspot' and has been declared a priority area anticipating future developments in the area which could result in the area experiencing severe air pollution problems. Lephalale falls within the WBPA, Kwazdela, Kwazamokhule and Embalenhle are located within the HPA and Zamdela is located within the VTAPA.

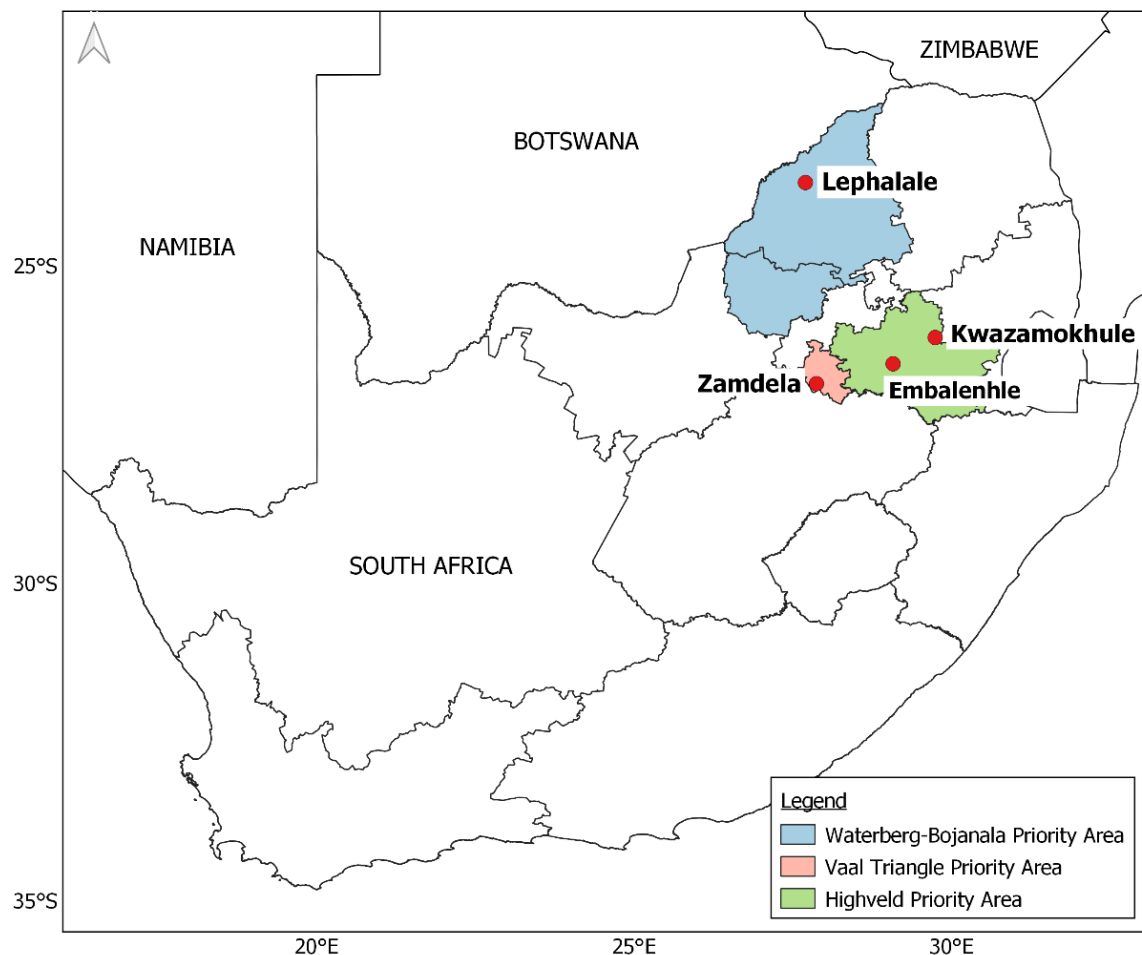


Figure 2.2: Location of the aerosol sampling sites (red dots) in each of the declared Priority Areas in South Africa

2.1.1 Waterberg District

2.1.1.1 Lephalale

Aerosol sampling was undertaken at three sites in Lephalale, namely Lephalale town (23°41'47.87" S, 27°41'42.40" E), Marapong township (23°39'21.38" S, 27°37'40.76" E) and Steenbokpan (23°41'13.42" S, 27°19'19.60" E) from 15 August to 01 September 2012 (winter campaign) and from 11 to 24 February 2013 (summer campaign) (Figure 2.3). The third site, Steenbokpan, is a background site located approximately 40 km west of Lephalale town and is located downwind of Medupi Power Station. Medupi Power Station was still in the process of being constructed during the 2012 and 2013 sampling campaigns with the first unit commissioned onto the National Grid in 2015. During the summer 2013 sampling campaign, construction at Medupi was suspended due to labour unrest.

Lephalale's local economy is built on the coal supply agreement between Exxaro Grootgeluk Coal Mine and Eskom's Matimba and Medupi Power Stations. Lephalale town is a rapidly growing middle to high-income residential area with approximately 17,639 inhabitants (Census 2011). Marapong township is a low-income, high-density residential area with approximately 26,227 inhabitants. In the township, approximately 63.5% of households are formal dwellings (i.e. those built from brick) while the remaining 36.5% of households are informal (i.e. those built with corrugated iron and other materials) dwellings. Access to basic services such as sanitation (74.7%) and refuse removal (76.3%) is relatively high, although the burning of household waste continues to occur in the township. Based on the Census 2011 findings, approximately 70% of households in Marapong township are electrified, although domestic fuels such as paraffin and wood are still used for cooking and space heating purposes.

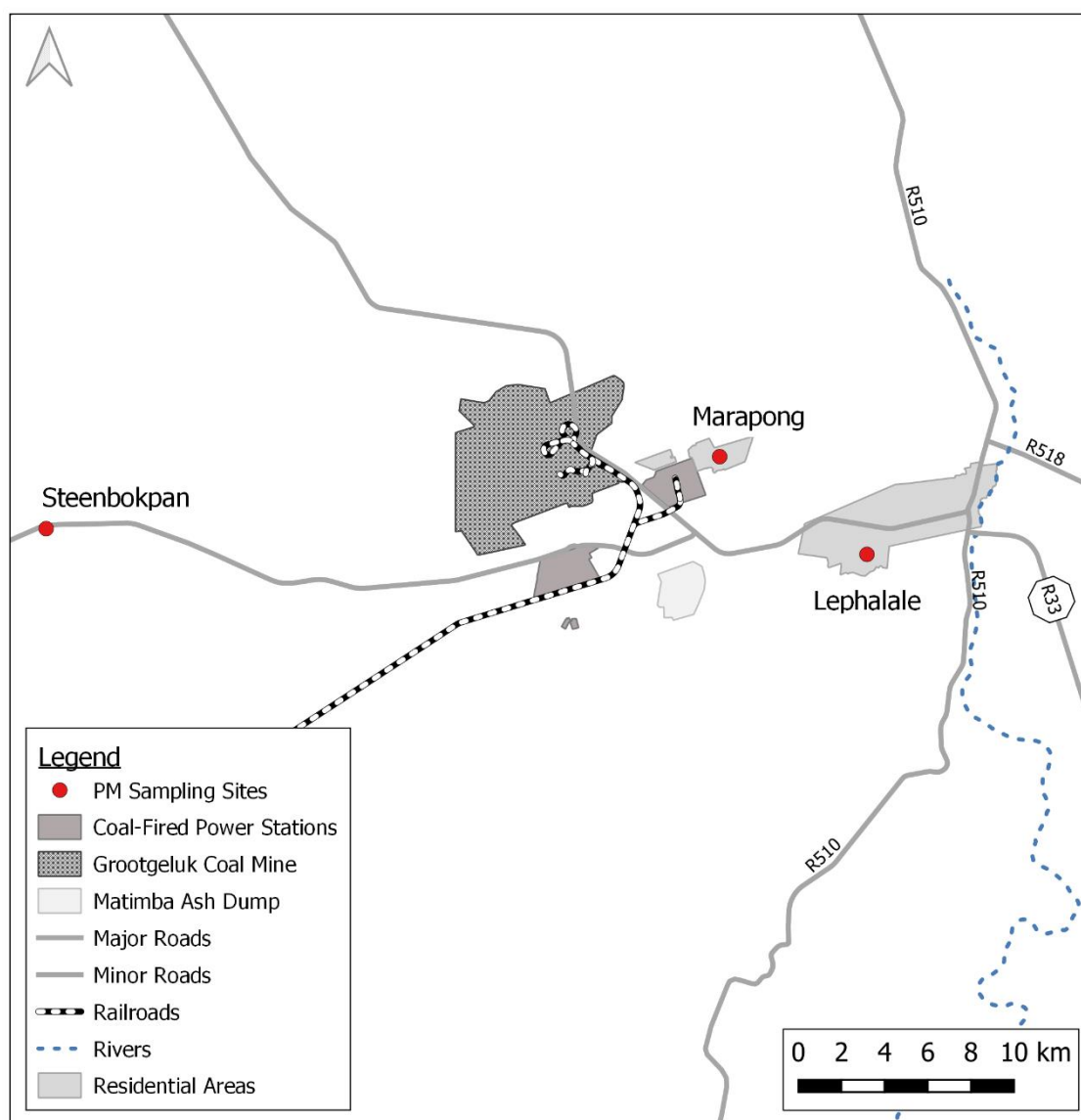


Figure 2.3: Location of the aerosol sampling sites (red dots) in Lephalale, Marapong and Steenbokpan for the winter 2012 and summer 2013 sampling campaigns

2.1.2 Highveld Region

2.1.2.1 Kwazamokhule

Sampling was undertaken in Kwazamokhule ($26^{\circ}08'17.27''$ S, $29^{\circ}44'20.98''$ E) from 6 – 22 July 2015 (winter campaign) and 22 February – 7 March 2016 (summer campaign). The sampling site was located next to Eskom's ambient air quality monitoring station at Hendrina ($26^{\circ}08'17.71''$ S, $29^{\circ}44'20.23''$ E) (Figure 2.4). A General Household Survey (GHS), including a Community Health Survey, was also conducted in Kwazamokhule from March – June 2015 to evaluate health, socio-demographics, living conditions and energy use patterns in the township.

Kwazamokhule is a low-income, high density residential area with approximately 20,427 inhabitants (Census 2011). Kwazamokhule has a complex mixture of formal and informal housing. Based on the findings of the Kwazamokhule GHS, most of the housing is comprised of formal structures (79.3%) while 18.1% is considered to be informal dwellings. Approximately 85.8%, 93.3% and 83% of households in Kwazamokhule have access to basic services such as water, sanitation and waste collection. However, despite access to waste collection, a number of households continue to burn their waste (Eskom, 2016). Based on the Census 2011 findings, only 65% of households in the township are electrified. As such, domestic fuels such as coal and wood continue to be widely used in the township for cooking and heating purposes.

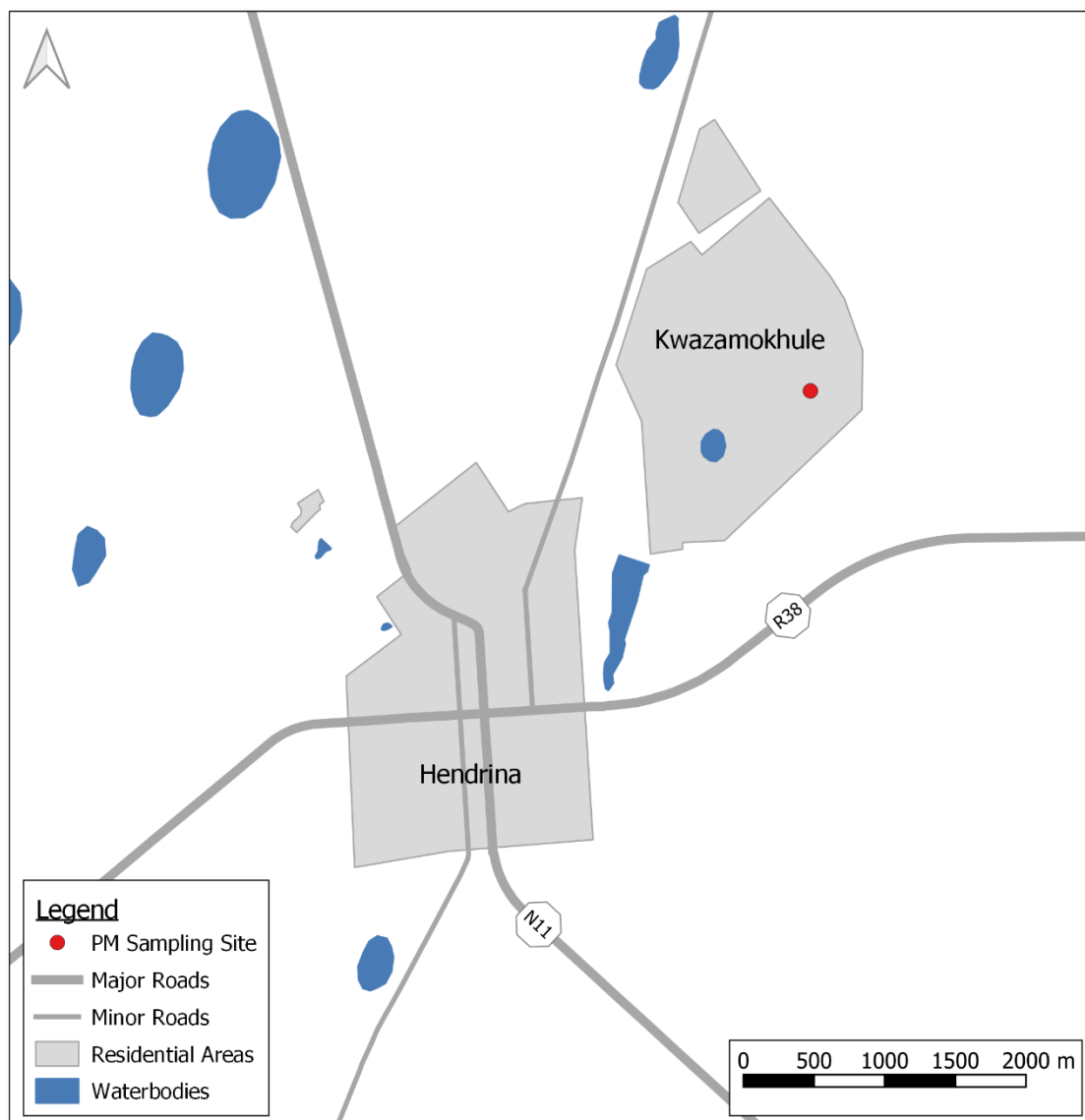


Figure 2.4: Location of the aerosol sampling site (red dot) in Kwazamokhule for the winter 2015 and summer 2016 sampling campaigns

2.1.2.2 Embalenhle

Aerosol sampling was undertaken from 15 – 31 July 2016 and 5 – 17 August 2016 (winter campaigns) and 14 – 28 February 2017 (summer campaign) at two sites; Embalenhle school (26°32'4.53"S, 29° 4'21.04"E) and upwind of Embalenhle at Kinross (26°26'5.71"S, 29° 3'25.42"E in summer and 26°24'52.60"S, 29° 4'11.64"E in winter) (Figure 2.5). Kinross, located approximately 12 km north of Embalenhle, was selected as an upwind sampling site to determine any other additional significant contributing sources in the area (other than emissions from the township). A GHS was conducted in October 2013 to assess health, socio-demographics, living conditions and energy use patterns in the township.

Embalenhle is a low-income residential area, neighbouring the Sasol Synfuels Complex in Secunda. Embalenhle has approximately 125213 inhabitants (Sasol, 2017). Based on the findings of the Embalenhle GHS, approximately 53.8% of households are informal dwellings, which is considerably higher than the 41.7% of informal housing reported in the Census 2011 findings. Almost all households have access to water, sanitation and waste collection services. However, a high service delivery failure rate is reported for waste collection and as a result, there is widespread and frequent burning of waste in the township. Based on Census 2011, approximately 83% of households are electrified in the township although domestic fuels such as coal, wood and paraffin are still utilised.

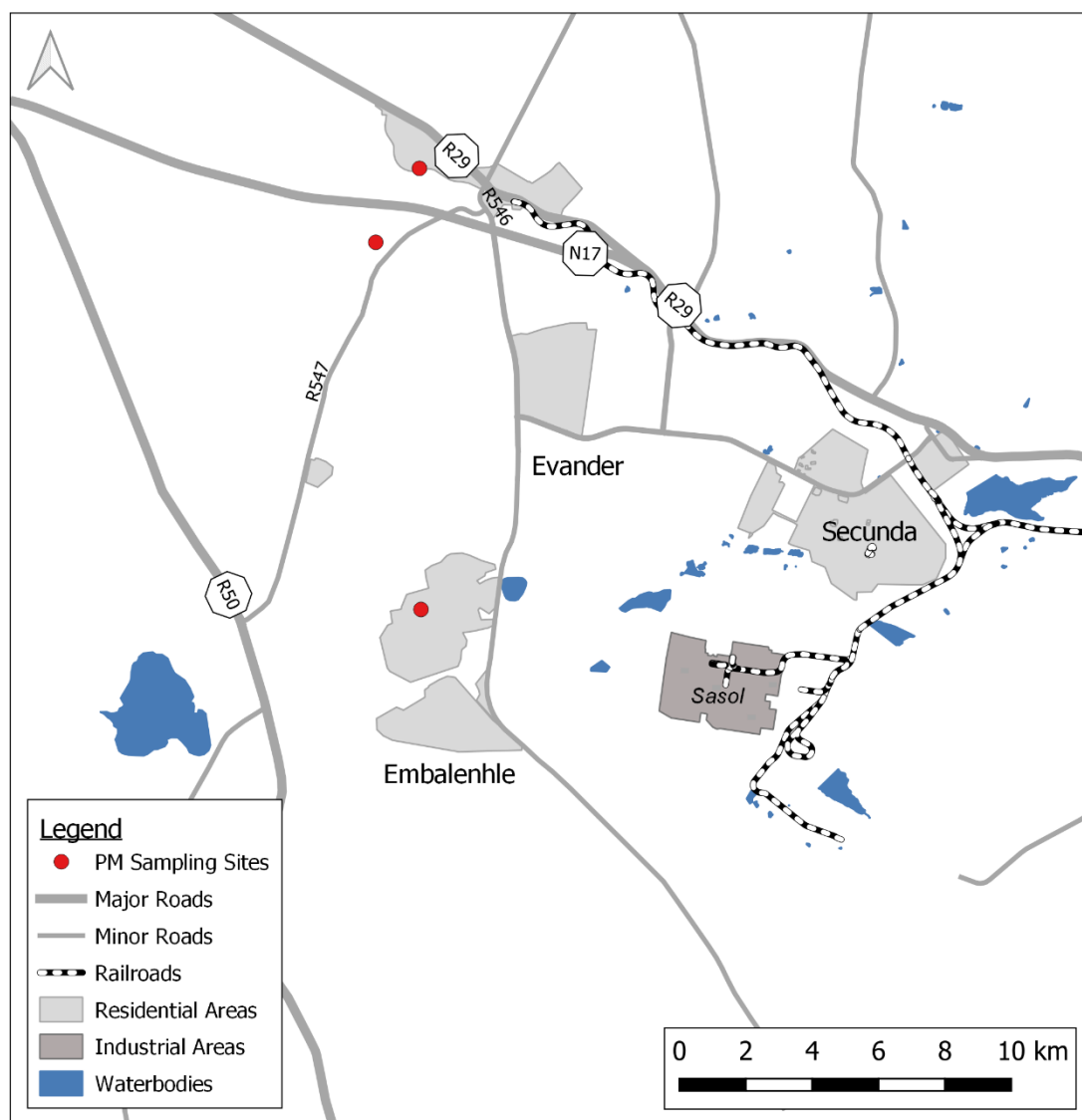


Figure 2.5: Location of the aerosol sampling sites (red dots) in Embalenhle and Kinross for the winter 2016 and summer 2017 sampling campaigns

2.1.3 Vaal Triangle

2.1.3.1 Zamdela

Aerosol sampling was undertaken from 15 – 30 July 2016 (winter campaign), 12 – 24 September 2016 (spring campaign) and 15 February – 2 March 2017 (summer campaign) at two sites; Zamdela school (26°51'9.80"S, 27°51'23.31"E) and upwind of Zamdela at Bongani Mabaso Eco Park (26°46'39.53"S, 27°50'14.14"E) (Figure 2.6). A GHS was conducted in October 2016 to assess health, socio-demographics, living conditions and energy use patterns in the township.

Zamdela is located south of Sasol in Sasolburg with a population of approximately 902 inhabitants (Sasol, 2017). Based on the findings of the Zamdela GHS, 37.6% of households are informal dwellings which is significantly higher than the figure of 19.5% reported in the Census 2011 findings. A high percentage (93.3%) of households have access to water yet only 50.5% of households have suitable sanitation on their property. Waste collection is low with only 59.7% of households indicating they have access to a weekly waste removal service. Coupled with a high service delivery failure of waste collection, waste disposal and burning is a significant issue in the township. Based on the Census 2011 findings, approximately 80% of households are electrified with coal, wood and paraffin also utilised in the township.

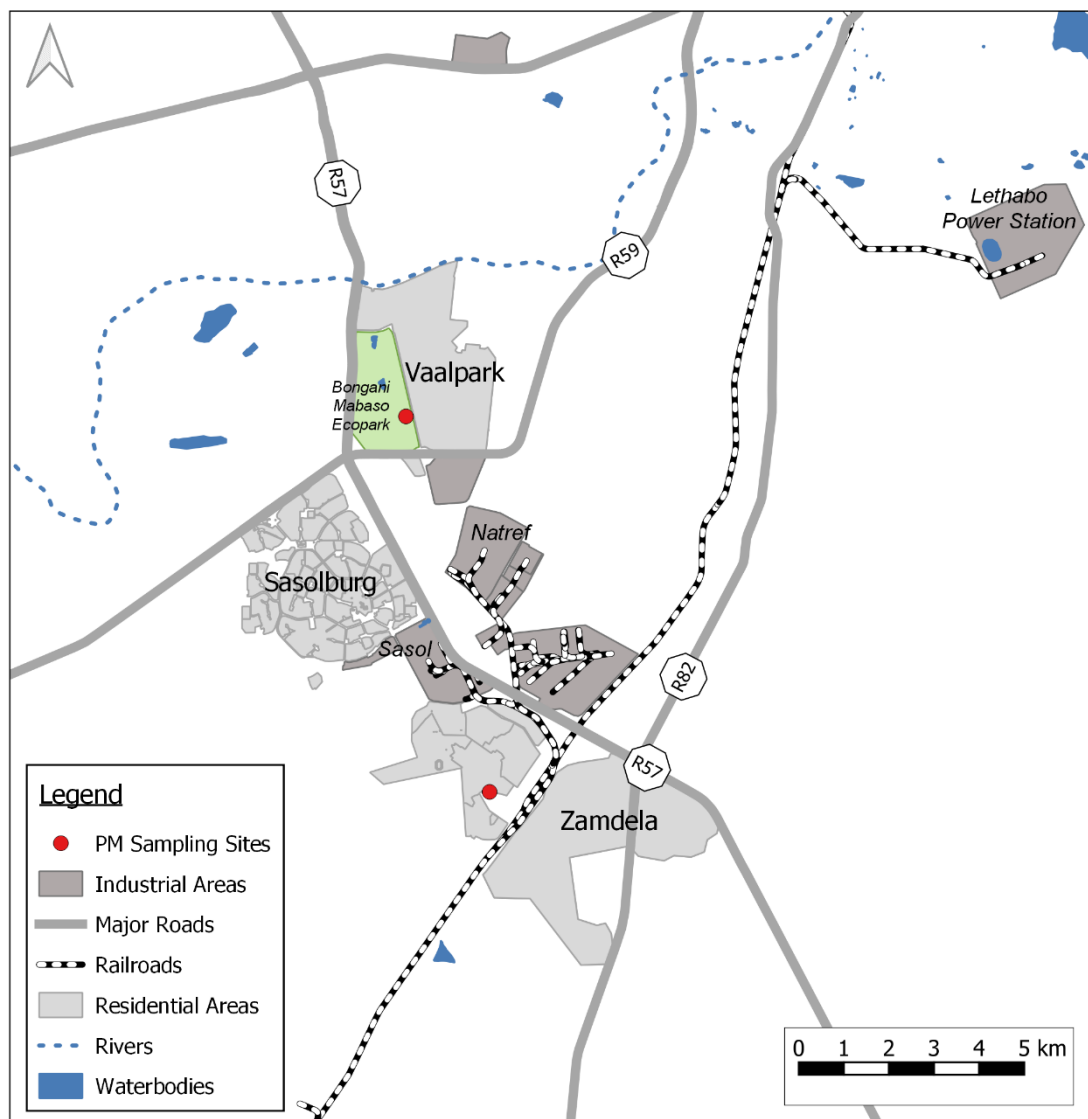


Figure 2.6: Location of the aerosol sampling sites (red dots) in Zamdela and Ecopark for the winter 2016, spring 2016 and summer 2017 sampling campaigns

2.2 Sample Collection

Sampling was undertaken using the 'Gent' SFU sampler (Maenhaut *et al.*, 1994; Hopke *et al.*, 1997) (Figure 2.7). The sampler collects particles that have an aerodynamic diameter (AD) of less than 10 μm in separate coarse and fine fractions. The coarse fraction corresponds to aerosols collected with an AD between 10 and 2.5 μm while the fine fraction corresponds to aerosols collected with an AD lower than 2.5 μm . Two 47-mm Nuclepore® polycarbonate filters with pore diameters of 8.0 μm and 0.4 μm were sequentially used during sampling. The flow rate was set to 16 litres per minute. The filters were weighed prior to and after sampling, using an XP26 DeltaRange Microbalance (Mettler-Toledo AG, Greifensee, and CH) with a sensitivity of 1 μg , to determine the gravimetric mass that was deposited after 12 hours of exposure. Sampling of both particle sizes was undertaken twice a day, in the morning and at night, from approximately 06:00 – 18:00 and 18:00 – 06:00 in Lephalale and Kwazamokhule (winter campaign). For the summer sampling campaign in Kwazamokhule, the sampling times were moved to 10:00 – 22:00 and 22:00 – 10:00 to split the bimodal ambient concentration peaks recorded at the sampling site into different samples. Sampling at Embalenhle and Zamdela was also undertaken from 10:00 – 22:00 and 22:00 – 10:00. A direct comparison of the samples from the Lephalale and Kwazamokhule (winter) sampling campaigns could not be undertaken with the Kwazamokhule (summer), Embalenhle and Zamdela sampling campaigns as the morning and evening peak in concentrations in the earlier sampling campaigns are distributed across both sampling periods. A summary of the samples collected for each sampling campaign is provided in Table 2.1.

Table 2.1: Summary of samples collected during each of the sampling campaigns. The number of samples selected for chemical analysis is shown in brackets

Region	Location	Site	Season	Period	Samples Collected / Analysed
Waterberg District	Lephalale	Lephalale Town	Winter	15 Aug – 1 Sep 2012 ⁽¹⁾	36 (27)
			Summer	11 – 24 Feb 2013 ⁽¹⁾	29 (25)
		Marapong Township	Winter	15 Aug – 1 Sep 2012 ⁽¹⁾	36 (27)
			Summer	11 – 24 Feb 2013 ⁽¹⁾	29 (25)
		Steenbokpan	Winter	15 Aug – 1 Sep 2012 ⁽¹⁾	36 (27)
			Summer	11 – 24 Feb 2013 ⁽¹⁾	29 (25)
Highveld Region	Kwazamokhule	Eskom Kwazamokhule Air Quality Monitoring Station	Winter	6 – 22 Jul 2015 ⁽¹⁾	33 (33)
			Summer	23 Feb – 7 Mar 2016 ⁽²⁾	26 (26)
	Embalenhle	Embalenhle School	Winter	15 Jul – 1 Aug 2016 ⁽²⁾	50 (50)
				5 – 11 Aug 2016 ⁽²⁾	
		Upwind (Kinross)	Summer	14 – 28 Feb 2017 ⁽²⁾	33 (33)
			Winter	5 – 18 Aug 2016 ⁽²⁾	25 (25)
Vaal Triangle	Zamdela	Zamdela School	Winter	15 – 31 Jul 2016 ⁽²⁾	57 (57)
				12 – 24 Sep 2016 ⁽²⁾	
			Summer	13 Feb – 2 Mar 2017 ⁽²⁾	27 (27)
		Upwind (Bongani Mabaso Eco Park)	Winter	12 – 24 Sep 2016 ⁽²⁾	24 (24)
			Summer	15 Feb – 2 Mar 2017 ⁽²⁾	33 (33)

Notes:

Sampling undertaken from 06:00 – 18:00 and 18:00 – 06:00

Sampling undertaken from 10:00 – 22:00 and 22:00 – 10:00

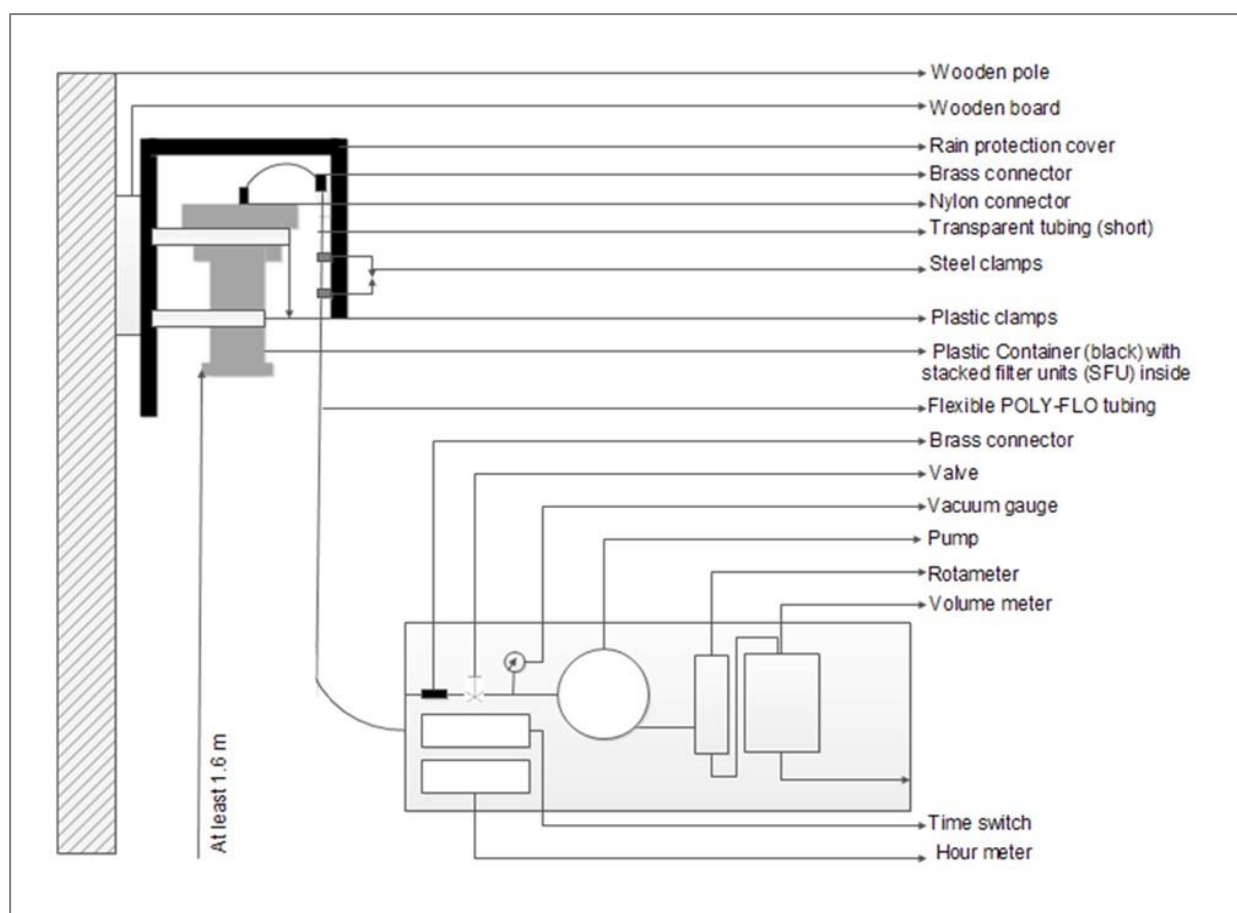


Figure 2.7: Schematic diagram of the Stacked Filter Unit sampling line (adapted from Maenhaut, 1994; van den Berg, 2015)

2.3 Particulate Sample Analysis

After sampling, the Nuclepore® filters were stabilised for 24 hours prior to weighing and then placed in a stabilised environment prior to analysis. Several analytical techniques were employed for the analysis of the samples, namely Wavelength-Dispersive X-Ray Fluorescence (WD-XRF) and ion chromatography (IC). WD-XRF and IC analysis were performed at the Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) in Créteil, France for the Lephalale and Kwazamokhule samples and at the North-West University, Potchefstroom Campus, South Africa for the Embalenhle and Zamdela samples.

2.3.1 Wavelength-Dispersive X-Ray Fluorescence

WD-XRF spectrometry analysis in France was performed using a PW-2404 spectrometer by PANalytical. Excitation X-rays are produced by a Coolidge tube ($I_{\text{max}} = 125 \text{ mA}$, $V_{\text{max}} = 60 \text{ kV}$) with a Rh anode. The primary X-ray spectrum can be controlled by inserting filters (Al, at different thickness) between the anode and the sample. Each element was analysed three

times according to specific conditions (voltage, tube filter, collimator, analysing crystal and detector), lasting 8 to 10 s.

Data was collected for the following 18 elements: Na, Mg, Al, Si, P, sulphur (S), Cl, K, Ca, Ti, vanadium (V), Cr, Mn, Fe, Zn, As, Cd and Pb using SuperQ software. The elemental mass thickness ($\mu\text{g.cm}^{-2}$), that is, the analyzed elemental mass per unit surface, was obtained by comparing the filter yields with a sensitivity curve measured in the same geometry on a set of certified XRF calibration standards (Micromatter™). These standards are prepared by vacuum deposition resulting in a highly uniform deposit on a polycarbonate membrane. In most cases, the standards present an element free of interferences and are thin enough to ignore thickness effects. Materials used are 99.9% pure or better and each standard thickness is certified to $\pm 5\%$. Finally, for these samples, the quantification limit of the technique ranged between 7.4×10^{-3} and $341 \times 10^{-3} \mu\text{g.cm}^{-2}$ depending on the element.

In South Africa, WD-XRF spectrometry analysis was undertaken using a Panalytical Axios^{max} spectrometer. This instrument implemented sequential sampling of the selected element and has a rhodium x-ray tube with a 4 kW generator. The system uses helium gas as a medium within the analysis chamber. An area with a 20 mm diameter was analysed on the surface of each sampled filter. Micromatter™ calibration standards were used for calibration purposes which are National Institute of Standards and Technology (NIST) traceable reference materials. These standards have a Nuclepore® polycarbonate aerosol membrane backing mounted in a 25 mm ring mount. Each element had two calibration points, i.e. a very light standard ranging between 3 - 8 $\mu\text{g.cm}^{-2}$ and a heavier standard ranging between 40 - 60 $\mu\text{g.cm}^{-2}$.

2.3.2 Ion Chromatography

For the IC analysis undertaken in France, analysis of the aerosol water-soluble ionic fraction was undertaken with a Metrohm IC 850 device equipped with an injection loop of 100 μl . For anionic species, IC was equipped with MetrosepA supp 16 (250/4.0mm) column associated with a metrosepA supp 16 guard pre-column heated at 65 °C. For simultaneous separation of inorganic and short-chain organic anions, elution was realized with eluant composed at 20% by ultrapure water and at 80% by a solution 7.5 mM Na_2CO_3 and 0.75mM NaOH. The elution flow rate was 0.8 mL/min. For cationic species, IC was equipped with Metrosep C4 (250/4.0 mm) column associated to a metrosep C4 guard column heated at 30 °C. Elution has been realized with an eluant of 0.7 mM of dipicolinic acid and with 1.7 mM of nitric acid. The elution flow rate was 1 mL/min. The IC analysis was performed for the following anions and cations; fluoride (F^-), chloride (Cl^-), bromide (Br^-), NO_3^- , SO_4^{2-} , phosphate (PO_4^{3-}), sodium (Na^+), NH_4^+ , potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), acetate and oxalate.

In South Africa, IC analysis of the water-soluble ionic fraction was undertaken with a Dionex ICS-3000 system consisting of two flow lines (Conradie *et al.*, 2016). One flow line was used to detect anion species and the other flow line for cation species. Before chemical analysis was commenced, the filters were leached in 10 mL de-ionised water in an ultrasonic bath for 30 minutes. A five-point calibration from 20 ppb to 500 ppb was conducted using certified stock solutions obtained from Industrial Analytical (Muyemeki *et al.*, 2021). The IC analysis was performed for F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , formic acid, acetic acid and oxalate.

2.4 Ambient Air Quality and Meteorological Monitoring

Ambient air quality and meteorological monitoring data were obtained from various government and private agencies operating ambient air quality and meteorological monitoring stations in each region. Surface meteorological data was also obtained from the South African Weather Services (SAWS) which has a network of Automatic Weather Stations (AWS) distributed across South Africa. The location of the ambient air quality and meteorological monitoring stations in each region is shown in Figure 2.8 to Figure 2.11 with a detailed description of each station provided in Table 2.2.

2.4.1 Waterberg District

2.4.1.1 Lephalale

Ambient air quality and meteorological monitoring data was obtained from Eskom's ambient air quality monitoring station in Marapong from January 2011 to December 2013. This station was sited to measure emissions from the neighbouring Matimba Power Station. Monitoring data from January to December 2013 was also obtained from the DEA's ambient air quality and meteorological monitoring station in Onverwacht. This station forms part of the Waterberg Priority Area Air Quality Monitoring Network and has been operational since October 2012. The SAWS also operate a weather station in the residential area of Onverwacht. Meteorological data was obtained from this station from January 2011 – December 2013.

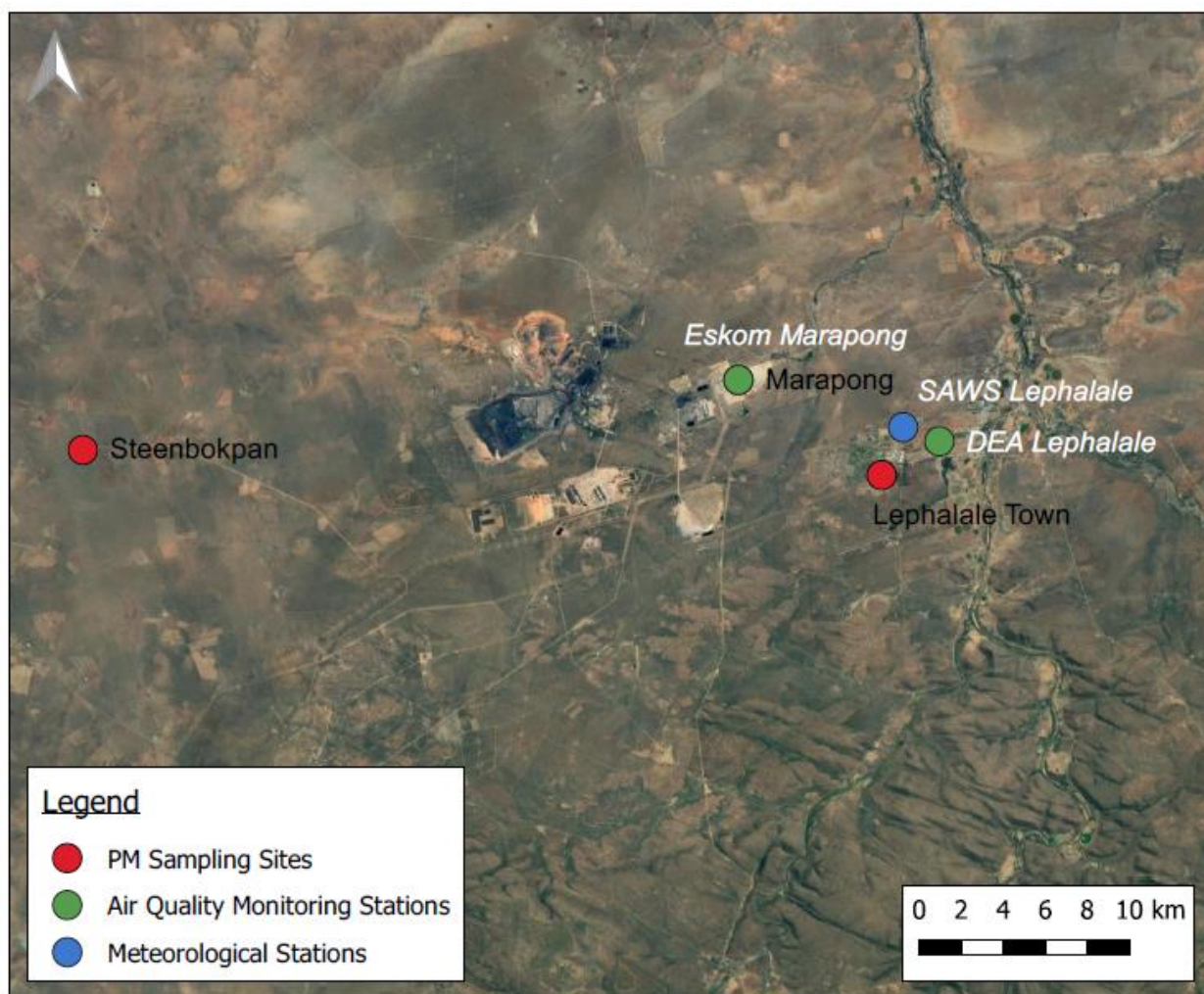


Figure 2.8: Location of ambient air quality and meteorological monitoring stations in the Waterberg District

2.4.2 Highveld Region

2.4.2.1 Kwazamokhule

Eskom in conjunction with the Climatology Research Group (CRG) installed a permanent continuous monitoring station on the eastern side of Kwazamokhule in January 2015. The DEA also operates an ambient air quality monitoring and meteorological station in Hendrina which forms part of the Highveld Priority Area Air Quality Monitoring Network. Pollutant and meteorological data was also obtained from these stations from January 2014 to December 2017 (where available).



Figure 2.9: Location of ambient air quality and meteorological monitoring stations in Kwazamokhule on the Highveld

2.4.2.2 Embalenhle

A continuous monitoring station owned by the Climatology Research Group was installed at Embalenhle School during both sampling campaigns. Sasol has a network of continuous ambient air quality and meteorological monitoring stations in the area including Bossjesspruit, Sasol Club, Embalenhle and more recently, Embalenhle North and South. Monitoring data was obtained from Sasol's Embalenhle monitoring station which is located approximately 4 km to the east of Embalenhle. The DEA also operates a continuous monitoring station in Secunda which forms part of the Highveld Priority Area Air Quality Monitoring Network. This station was sited to measure domestic fuel burning emissions in Embalenhle as well as emissions from Sasol Synfuels Complex located to the east. Pollutant and meteorological monitoring data was obtained from these stations from January 2014 to December 2017. Meteorological data was also obtained from the SAWS weather stations in Secunda and Carolina.

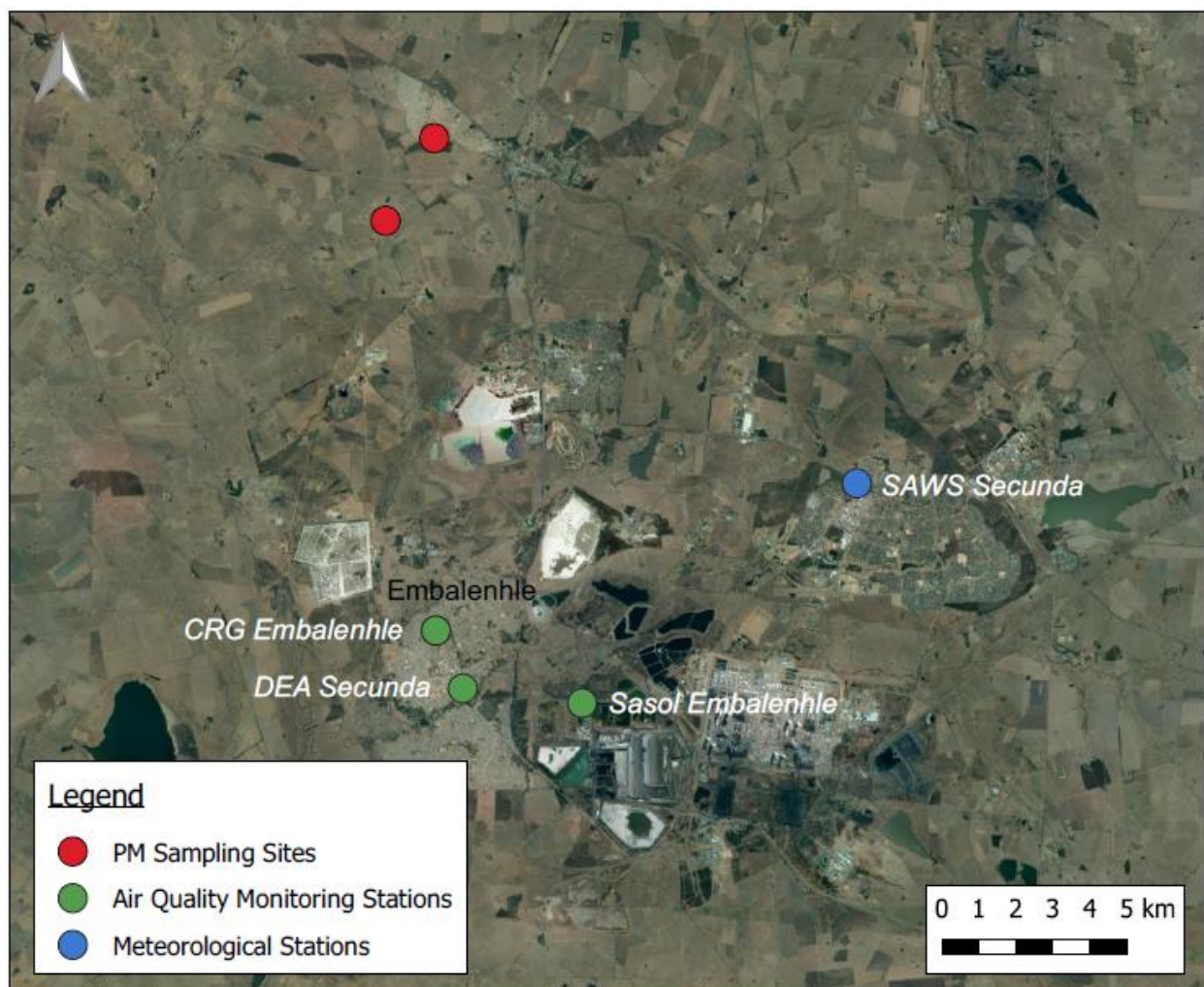


Figure 2.10: Location of ambient air quality and meteorological monitoring stations in Embalenhle on the Highveld

2.4.3 Vaal Triangle Region

2.4.3.1 Zamdela

A continuous monitoring station owned by the Climatology Research Group was installed at Zamdela School during both sampling campaigns. The DEA also operates a continuous monitoring station in Zamdela as part of the Vaal Triangle Airshed Priority Area Monitoring Network. This station is located to the south of Sasol and measures emissions from industries in Sasolburg as well as domestic fuel burning in Zamdela. Pollutant and meteorological monitoring data was obtained from this station from January 2015 to December 2016. The closest SAWS weather station to the sampling sites is located to the north in Vereeniging. Meteorological data was obtained from this station from January 2016 to December 2017.

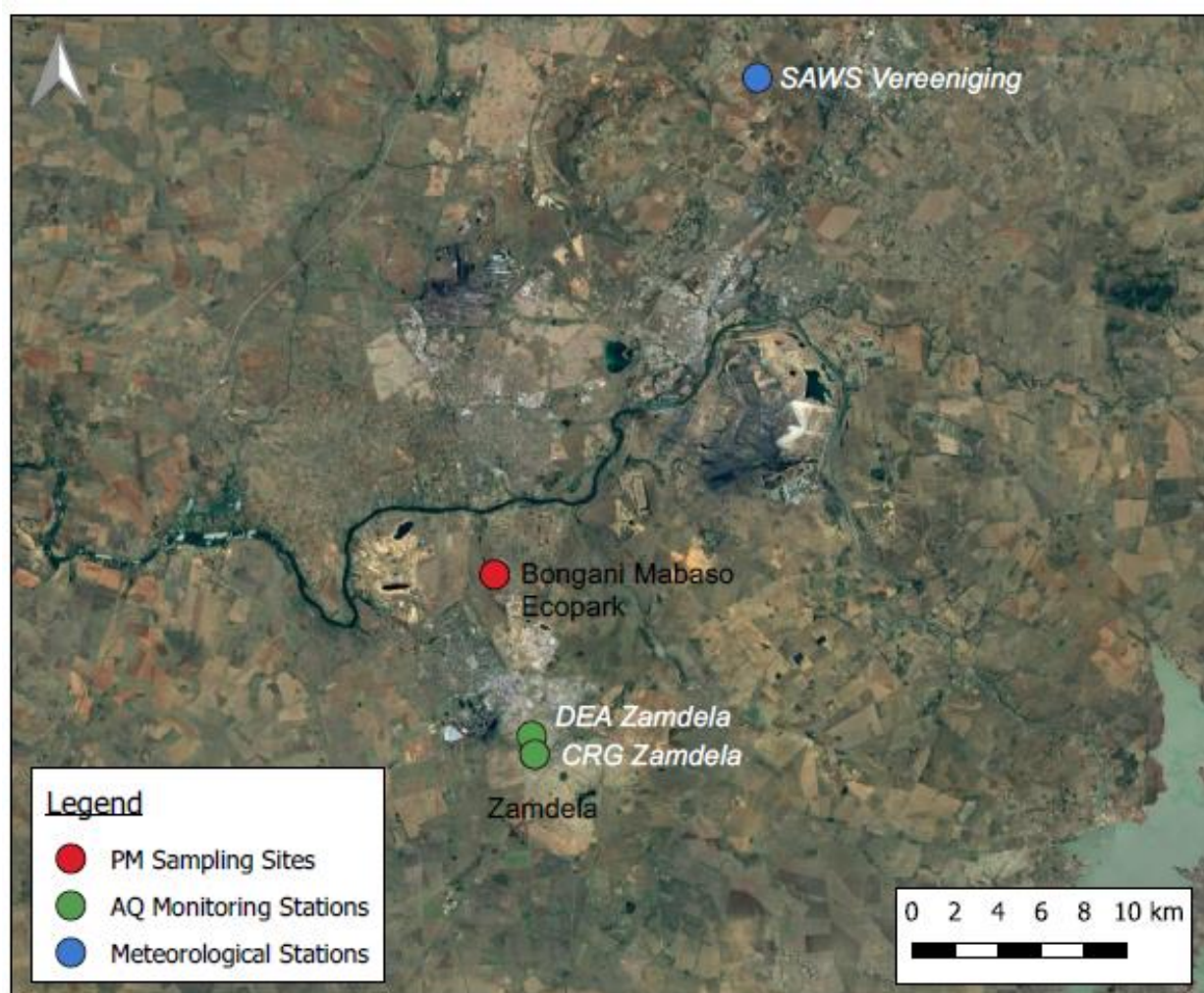


Figure 2.11: Location of ambient air quality and meteorological monitoring stations in the Vaal Triangle

Table 2.2: Ambient air quality and meteorological monitoring undertaken in each region

Region	Sampling Site	Station Owner	Station Location	Latitude (S)	Longitude (E)	Parameters Recorded	Data Period
Waterberg District	Lephalale	DEA	Lephalale	23°40'55.20"	27°43'19.20"	PM ₁₀ , PM _{2.5} , SO ₂ , NO, NO ₂ , NO _x , O ₃ , CO, BTEX and meteorological	Jan 2013 – Dec 2013
		Eskom	Marapong	23°39'21.60"	27°37'40.80"	PM ₁₀ , PM _{2.5} , SO ₂ , NO, NO ₂ , NO _x , O ₃ and meteorological	Jan 2011 – Dec 2013 ⁽¹⁾
		SAWS	Onverwacht	23°40'33.60"	27°42'18.00"	Meteorological	Jan 2011 – Dec 2013
Highveld Region	Embalenhle	CRG	Embalenhle	26°32'04.53"	29° 04'21.04"	PM ₁₀ , PM _{2.5} , SO ₂ , NO, NO ₂ , NO _x , O ₃ , CO and H ₂ S	Jun 2016 – Jul 2017
		DEA	Secunda	26°33'02.34"	29°04'44.82"	PM ₁₀ , PM _{2.5} , SO ₂ , NO ₂ , O ₃ , CO, BTEX, Hg and meteorological	Jan 2014 – Nov 2016 ⁽²⁾
		Sasol	Embalenhle	26°33'06.00"	29°06'45.00"	PM ₁₀ , PM _{2.5} , SO ₂ , NO, NO ₂ , NO _x , O ₃ , CO, H ₂ S, NH ₃ and meteorological	Jan 2014 – Dec 2017
		SAWS	Secunda	26°29'49.20"	29°11'09.60"	Meteorological	Jan 2014 – Dec 2017
	Kwazamokhule	Eskom	Kwazamokhule	26°08'17.71"	29°44'20.23"	PM ₁₀ , PM _{2.5} , SO ₂ , NO, NO ₂ , O ₃ , CO, CO ₂ , CH ₄ , H ₂ O and meteorological	Jan 2015 – Mar 2016
		DEA	Hendrina	26°07'55.20"	29°44'02.40"	PM ₁₀ , PM _{2.5} , SO ₂ , NO, NO ₂ , O ₃ and meteorological	Jan 2014 – Dec 2017
	Carolina	SAWS	Carolina	26°40'04.80"	30°07'04.80"	Meteorological	Jan 2014 – Apr 2015 ⁽³⁾
Vaal Triangle Regio	Zamdela	DEA	Zamdela	26°50'41.60"	27°51'18.40"	PM ₁₀ , PM _{2.5} , SO ₂ , NO, NO ₂ , NO _x , O ₃ , CO, BTEX and BC	Jan 2016 – Dec 2017
		CRG	Zamdela	26°51'09.80"	27°51'23.31"	PM ₁₀ , PM _{2.5} , SO ₂ , NO, NO ₂ , NO _x , O ₃ , CO and H ₂ S.	Jun 2016 – Jun 2018
	Vereeniging	SAWS	Vereeniging	26°34'08.40"	27°57'28.80"	Meteorological	Jan 2016 – Dec 2017 ⁽⁴⁾

Notes:

- (1) Ambient data from Jan 2012 – Dec 2013
(2) No data available from Dec 2016 – Aug 2017
(3) Carolina meteorological station was decommissioned from May 2015
(4) Wind speed and wind direction data only available from Jan – Jun 2016

2.5 Reconstructed Mass

The fine and coarse aerosol mass for the sampling sites was reconstructed from the ionic and elemental mass measured on the selected filters due to concerns with the gravimetric data. Reconstructed mass (RM) is expressed as the sum of its seven chemical components, namely, (1) organic ions; (2) organic matter (OM) or OC; (3) EC; (4) geological minerals; (5) salt; (6) trace elements and (7) 'others' or 'remaining mass' representing components that are unaccounted or unidentified (Chow *et al.*, 2015). Reconstructed mass equations have the general form:

$$\text{RM} = \text{Inorganic ions} + \text{OM} + \text{EC} + \text{Geological minerals} + \text{Salts} + \text{Trace Elements} + \text{Others}$$

Various approaches have been used for PM mass reconstruction and are detailed in Chow *et al.* (2015). The methodology used to reconstruct the sample mass was as follows: SO_4^{2-} , NO_3^- and NH_4^+ was summed without weighting factors to determine the mass contribution from inorganic ions (Andrews *et al.*, 2000; Chow *et al.*, 1994; Chow *et al.*, 1996; Maenhaut *et al.*, 2002; Solomon *et al.*, 1989). The geological mineral contribution was determined using the IMPROVE 'soil' formula (Malm *et al.*, 1994) which expresses minerals as the sum of the oxides of Al, Si, Ca, K and Fe assuming the common oxide forms of Al_2O_3 , SiO_2 , CaO , K_2O and Fe_2O_3 , respectively (Macias *et al.*, 1981). The IMPROVE 'soil' formula includes the following modifications, namely, (1) Fe_2O_3 and FeO occur in equal proportions; (2) K has a soil (K_2O) and non-soil component therefore K in soil was estimated as 0.6 Fe, and (3) titanium dioxide (TiO_2) was included (Malm *et al.*, 1994). All of the initial element coefficients were then multiplied by 1.16 to compensate for the exclusion of minor soil constituents such as MgO , Na_2O and H_2O from the crustal mass formula (Chan *et al.*, 1997). The resulting formula was applied:

$$\text{Geological minerals} = 2.20 \text{ Al} + 2.49 \text{ Si} + 1.63 \text{ Ca} + 1.94 \text{ Ti} + 2.42 \text{ Fe}$$

The sea salt contribution was determined using the formula $\text{Cl} + 1.4486 \text{ Na}$, where 1.4486 is the ratio of the concentration of all elements except Cl in sea water to the Na concentration in sea water (Maenhaut *et al.*, 2002). Trace elements, excluding S and geological species, were added to the RM by summing the trace elements in the form of CuO , ZnO and PbO (Macias *et al.*, 1981) as well as summing the remaining trace elements in their elemental form (Andrews *et al.*, 2000; Chow *et al.*, 1994; Chow *et al.*, 1996; Maenhaut *et al.*, 2002). The remaining mass or 'others' was assumed to be non-crustal K based on the formula $\text{K} - 0.6 \text{ Fe}$ (Maenhaut *et al.*, 2002), the sum of organic acids (Putaud *et al.*, 2000) and other species unaccounted for.

OC and EC were not measured in the sampling datasets and as such, were estimated from a review of available literature. Of the studies undertaken locally in domestic fuel burning

townships, OC and EC accounted for more than half of the PM₁₀ and PM_{2.5} mass in Qalabotjha (Engelbrecht *et al.*; 2001), while contributions to PM_{2.5} ranged between 28% - 60% in Soweto depending on the season (Annegarn *et al.*, 1998). In Zamdela, Feig *et al.* (2015) reported that BC accounted for between 6 – 12% of the PM_{2.5} mass concentrations similar to the findings of Maritz *et al.* (2015), which determined that BC and OC contributed to 12% and 24% of the total PM_{2.5} mass concentrations, respectively at five sites, namely, Amersfoort, Louis Trichardt, Skukuza, Vaal Triangle and Botsalano. For the sampling sites, it was conservatively assumed that OC and EC combined comprised 30% of the particulate mass.

2.6 Source Apportionment Models

For the purposes of this study, the three receptor modelling approaches of PCA, PMF and CMB modelling were selected for source apportionment of the aerosol data collected from each sampling site. While the Highveld and Vaal Triangle regions are recognised to have complex airsheds, the emission sources in Lephalale in the Waterberg are less complex and better understood. As a first step in determining the possible emission sources in each region, the multivariate methods of PCA and PMF were initially applied to the datasets. Subsequently, CMB receptor modelling was undertaken for the Highveld and Vaal Triangle regions based on the identified emission sources in a further attempt to apportion particulate matter. Given the variability of emission sources in each region and the limitations associated with each receptor modelling approach, the selection of three different models allows for inter-comparison between the different methods to determine their suitability for use in the South African context.

2.6.1 Principal Component Analysis

2.6.1.1 Model Overview

PCA is a statistical factor analysis method which extracts a series of principal components that explain the majority of the variance in the dataset (Paatero *et al.*, 2005). The principal components are then rotated so that they can be quantitatively interpreted as 'known' sources with the contribution from each source determined from the factor scores.

PCA analyses the correlation between measured concentrations of chemical species in a number of samples on the assumption that highly correlated compounds come from the same source. While this method can be used to determine the contributing sources, a thorough understanding of the possible source characteristics is required for an accurate interpretation of the results.

Since PCA does not require source composition data, it can therefore be used to identify sources, and estimate their contributions, where detailed information on source characteristics is not available, but where a significant amount of measured concentration data is present.

PCA assumes that a) the composition of the emission sources is constant over the sampling period at the receptors; b) chemical species do not interact with each other and their concentrations are linearly additive; c) source profiles are linearly independent of each other; measurement errors are random and uncorrelated; d) the number of species is greater than or equal to the number of sources; e) the number of samples is significantly larger than the number of source types and f) variability of the ambient concentrations is mainly due to differences in source contribution and not as a result of measurement uncertainty or changes in source composition.

However, this method is recognised to have several limitations, including a) it requires large ambient datasets ($n > 100$); b) the number of factors to retain must be determined and the emission sources interpreted from the selected factors; c) vectors and components are usually related to broad contributing source types rather than specific emission sources; d) the analysis is sensitive to extreme values in the datasets; e) many solutions can be obtained without clarity on whether an optimum solution has been found; f) uncertainties in the measured data cannot be accounted for accurately, and g) missing data and values below the detection limit cannot be properly managed (Paatero *et al.*, 2005). Due to the limitations associated with this method, and the development of new quantitative techniques, it is recommended that PCA should be used as a preliminary screening and exploratory tool instead of a receptor model (Hopke, 2015; Hopke and Jaffe, 2020).

2.6.1.2 Input Files

PCA was undertaken for the coarse and fine aerosol fractions at each sampling site using the SPSS Statistics software. This was performed by using the orthogonal transformation method with varimax rotation and retention of principal components whose eigenvalues were greater than 1. Factor loadings indicate the correlation of each species with each component and are related to the emission sources. Four to eight factors were modelled with each size fraction, with the most suitable number of factors retained. The number of factors retained in the final analysis was based on the ability to interpret the resulting source profiles. For the purpose of this study, only the chemical species with factor loadings of 0.60 and above were retained for source apportionment purposes. The preliminary findings from the PCA were used to inform the PMF and CMB receptor modelling.

2.6.2 Positive Matrix Factorisation

2.6.2.1 Model Overview

PMF is a multivariate factor analysis technique that decomposes a matrix of speciated sample data into two matrices: factor contributions (G) and factor profiles (F) (Norris *et al.*, 2014). Factor contributions and profiles are determined by the following equation:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2$$

where:

g and f are the matrices to be determined;

x_{ij} is the measured data matrix;

u_{ij} are the known uncertainties for each data value x_{ij} .

The PMF solution minimises the object function, Q , via a conjugate gradient algorithm based upon the calculated data uncertainties. Q is a critical parameter for PMF with two versions output from the model runs, Q_{true} and Q_{robust} . Q_{true} is the goodness-of-fit parameter calculated including all points while Q_{robust} is the goodness-of-fit parameter calculated excluding points not fit by the model (i.e. samples for which the uncertainty-scaled residual is greater than 4). The difference between the two is a measure of the impact of data points with high scaled residuals, indicative of sources that are not always present during the sampling campaign. In addition, similar Q_{true} and Q_{robust} values result if the uncertainties are too high (Norris *et al.*, 2014).

The two most common PMF programs are PMF2 and Multilinear Engine (ME-2), as well as the EPA PMF developed by the USEPA which uses the ME-2 program. EPA PMF requires multiple iterations of the underlying ME-2 to determine the optimum factor contributions and profiles. ME-2 performs the iterations via the conjugate gradient algorithm until convergence to a minimum Q value (i.e. the lowest Q_{robust} value) is obtained. Outputs from ME-2 are then fed back through EPA PMF and formatted into a readable and interpretable format (Brown *et al.*, 2015). EPA PMF also has three error estimate methods to determine variability in the PMF solution, namely (Norris *et al.*, 2014):

- (1) Bootstrap (BS) intervals which is used to identify whether there are a small number of observations that can significantly impact the solution. Bootstrap error intervals include effects from random errors and partially include effects of rotational ambiguity. Rotational ambiguity arises due to the presence of infinite solutions that are similar to the solution

generated by the PMF. Bootstrap errors are robust and are not influenced by the sample uncertainties.

- (2) Displacement (DISP) intervals include the effects of rotational ambiguity but exclude the effects of random data errors. The DISP error estimate is directly affected by data uncertainties.
- (3) BS-DISP (a hybrid method) error intervals include effects of random errors and rotational ambiguity. BS-DISP results are more robust than DISP results.

BS is performed by randomly selecting blocks of observations from the original dataset and creating a new input data file of the selected samples with the same number of samples and species as the original dataset (Brown *et al.*, 2015). For each BS run, the BS factors are compared with the base run factors. The BS factor is mapped to the base factor with which the BS factor has the highest correlation above a user-specified threshold (default of 0.6). If no base factors have a correlation above the threshold for a given BS factor, that factor is considered to be 'unmapped'. Mapping of over 80% of factors indicates that the BS uncertainties can be interpreted and that the number of selected factors is suitable (Norris *et al.*, 2014). With DISP, each variable in the factor profile in the selected (base) PMF solution is 'displaced' from its fitted value far enough so that Q increases by a predetermined amount, $dQ^{\max}$. Each such extended displacement is interpreted as the upper or lower interval estimate of the 'displaced' variable, providing an uncertainty estimate for each species in each factor profile (Brown *et al.*, 2015). For DISP, the key diagnostics include the number of swaps at the lowest $dQ^{\max}$ level and the percent change in Q ($\%dQ$). Factor swaps occurring at the lowest $dQ^{\max}$ level is indicative of significant rotational ambiguity and that the solution is unstable. A decrease in Q of less than 1% is considered to be acceptable (Norris *et al.*, 2014). BS-DISP is a combination of the BS and DISP error methods in which each resampled dataset is decomposed into profile and contribution matrices whereafter fitted elements in the factor profile matrix are displaced. Only the key species in each factor are selected for displacement in BS-DISP (Brown *et al.*, 2015). BS-DISP provides the change in Q associated with the displacement where a change in Q is greater than 1% considered to be significant (Norris *et al.*, 2014). A key diagnostic output from BS-DISP is the extent of factor swapping. If factor swaps are seen at the lowest $dQ^{\max}$ level, further evaluation of the base solution and DISP and BS results is required (Norris *et al.*, 2014).

PMF is based on the assumption that a) the composition of the emission sources is constant over the sampling period at the receptors; b) species do not interact with each other than their concentrations are linearly additive; c) source profiles are linearly independent of each other; d) the number of species is greater than or equal to the number of sources; e) unique tracer

components are included and f) there are more samples than source types (Norris *et al.*, 2014). To achieve a valid solution with PMF, it is recommended that the sample size should consist of at least 100 samples (Takami *et al.*, 2016), as smaller sample sizes may result in some instability in the solution (Brown *et al.*, 2015).

2.6.2.2 Input Files

Calculations for source apportionment were undertaken using the EPA PMF 5.0 software. Model input included receptor (ambient) concentrations and realistic uncertainties. Data screening was conducted during the preparation of the ambient data input files. Separate ambient data and uncertainty input files were generated for the coarse and fine aerosol fractions for each sampling site. Particulate mass can also be included in the PMF runs. For this research, the reconstructed particulate mass for each site was used instead of the gravimetric data as this produced a more stable solution. Receptor (ambient) concentrations were obtained from the chemical analysis. Species with all samples falling Below Detection Limit (BDL) were excluded from further analysis. Negative values in the dataset were recognised as BDL values and were replaced by half of the detection limit. The corresponding uncertainties were calculated as $(5/6) \times \text{MDL}$ (Polissar *et al.*, 1998). The Method Detection Limit (MDL) for each element was defined as three times the standard deviation of the average of the blank filters (Barbaro *et al.*, 2019). Missing values were flagged as -99 (Coulter, 2004). For concentrations greater than the MDL, uncertainties were calculated using the formula (Norris *et al.*, 2014):

$$\text{Uncertainty} = \sqrt{(\text{Error Fraction} \times \text{Concentration})^2 + (0.5 \times \text{MDL})^2}$$

The first step categorised species as ‘strong’, ‘weak’ or ‘bad’ in each of the datasets. Species can either be categorised according to their signal-to-noise ratio (S/N), which is automatically calculated within the software or can be specified by the user. Since all species were given a set uncertainty in the input files, species categorisations were determined based on the residuals and observed/predicted statistics after the initial base runs. Species with all samples BDL were automatically categorised as ‘bad’. All other species were categorised as ‘strong’ for the initial runs. After the initial runs, where required, species categories were changed to ‘weak’ after the residuals and plots were assessed. Species categorised as ‘weak’ have their uncertainties tripled while a species categorised as ‘bad’ excludes the species from the rest of the analysis. Residuals between +3 and -3 indicate a species is well modelled, whereas if a species has many large scaled residuals, it may be an indication of a poor fit or that the species is present in an infrequent source (Norris *et al.*, 2014).

For the error estimation of the identified stable solution, the model error estimation methods were utilised. The DISP calculation was first performed to confirm that there were no significant decreases in Q (greater than 1%) and that there were no factor swaps at the lowest $dQ^{\max}$. BS was then performed to determine if all factors were mapped above 80%. For the final BS-DISP run, the key species in each factor were displaced in BS-DISP to determine, amongst others, the overall fraction of BS-DISP runs that met all BS-DISP criteria, the decrease in Q and the factor swaps at the lowest $dQ^{\max}$. Solutions with interpretable factors that met the DISP and BS diagnostic criteria but not all the BS-DISP criteria were not necessarily considered to be fatal although it indicated that the solution had some uncertainty (Brown *et al.*, 2015). Four to eight factors were tested in the model with the final solution selected on the basis of the interpretability of the factors and the results of the error estimation methods.

2.6.3 Chemical Mass Balance Modelling

2.6.3.1 Model Overview

CMB receptor models are used to apportion measured pollutant concentrations to their sources and to determine the proportional contribution of each source. CMB models use the chemical and physical characteristics of particles (and gases) measured at the sources and receptors to identify the presence of sources and quantify their contributions to receptor concentrations (Schauer *et al.*, 2005).

The CMB receptor model consists of a least-squares solution to a set of mass balance equations that express the ambient (receptor) chemical concentrations as a linear sum of the products of source profile abundances and source contributions. Input data into the CMB model includes the ambient concentrations, with uncertainty estimates and the source profiles. Model outputs provide the contribution by each source type and their associated uncertainties (Watson *et al.*, 2004).

The chemical mass balance can be expressed in the following way:

$$C_i = \sum_{j=1}^p a_{ij} S_j, i = 1, n$$

where:

C_i is the ambient concentration of species i ;

a_{ij} is the fractional concentration of species i in the emissions from source j ;

S_j is the total mass concentration contributed by source j ;

p is the number of sources;

n is the number of species, with $n \geq p$.

Based on a selection of source profiles, the CMB model provides information on which profile combinations are likely to provide contributions using various statistical performance measures (Watson *et al.*, 1991). For every sample, the significant measures that are evaluated are: 1) the source contributions estimates and their uncertainties; 2) 'chi-square', which is the weighted sum of the squares of the differences between calculated and measured species concentrations. Chi-square values between one and two indicate acceptable fits while values less than one indicate good fits to the data; 3) 'r-square', which is the fraction of the variance in the measured concentrations accounted for by the variance in the calculated species concentrations. R-square values greater than 0.9 indicate a good fit to the measured data, and 4) 'percent mass' or the percent of the total mass accounted for by the source contribution estimates. Percent mass values of between 80 – 120% are considered to be good (Kuhns *et al.*, 2002).

Additional outputs from the CMB model include ratios of calculated to measured concentration (C/M) and the ratio of the difference between calculated and measured concentration divided by the uncertainty of this difference (R/U) for each chemical species. Both these ratios provide information on the fits of the individual species in the CMB model (Kuhns *et al.*, 2002).

The 'Eligible Space Dimension and Maximum Uncertainty' clusters identify collinearity of similarity between source profiles. Two parameters are used, namely the, maximum source uncertainty (default value of 1.0 in the CMB model) and the minimum source projection on the eligible space (default value of 0.95 in the CMB model) (Henry, 1992). The first parameter, the maximum source uncertainty determines the eligible space to be spanned by the eigenvectors whose inverse singular values are less than or equal to the maximum source uncertainty. The 'Number of Estimable Sources' are the estimable source contributions based on their source contributions and calculated uncertainties (Kuhns *et al.*, 2002).

Collinearity, or similarity between source profiles, may be observed when small source contribution estimates are associated with large uncertainties. Source contribution estimates are not invalidated due to the presence of profiles in the eligible space clusters. These clusters provide suggestions to improve the relative uncertainties of the source contribution estimates by either eliminating one or more of the source profiles, or by linearly combining the profiles into a new profile representing the combined contribution from both source types (Kuhns *et al.*, 2002).

The CMB model is based on the assumptions that a) source profiles are constant over the receptor and source sampling period; b) chemical species do not react with each other; c) all significant sources contributing to the measured receptor concentrations are identified and characterised; d) the number of sources or source categories is less than or equal to the number of chemical species; e) the source profiles are linearly independent of each other, and f) measurement uncertainties are random, uncorrelated and normally distributed (Watson *et al.*, 2004).

However, these assumptions are a limitation of the CMB model as a) source compositions are not constant; b) components do react with each other and systems are not linear; c) it is generally not known as to how many sources contribute to a receptor; d) there are more sources than components which can be practically measured; e) many sources have very similar compositions; f) measurement errors are not necessarily random, uncorrelated or normally distributed, and g) few sources have their own unique tracer components (Watson, 1984).

2.6.3.2 Input Files

Calculations for source apportionment were performed using the CMB8.2 software developed by the USEPA. Model input included receptor (ambient) concentrations, source profiles and realistic uncertainties for both receptor and source profile species. Receptor concentrations were obtained from the chemical analysis. The same data screening and verification approach followed during PMF were applied to the CMB receptor input files.

The S/N was applied to screen out species that have poor measurement results using the formula:

$$S/N \text{ Ratio} = \frac{\text{Sum of Species Concentration}}{\text{Average of Detection Limit} \times \text{Number of Below Detection Limit}}$$

A small S/N ratio (less than 0.2) indicates that the species has a high noise level (either due to poor detection or a large number of BDL values) and should be omitted from the dataset, while species with a large S/N ratio are well measured (Pongkiatkul and Kim Oanh, 2012).

Measurement uncertainties are representative of the measurement errors and give the models the necessary confidence level in the validity of a data point. Measurement errors from both sampling and laboratory analyses should be included in the uncertainty values (Kim Oanh *et al.*, 2009). The uncertainty assigned to a specific data point should therefore be based on both the

sampling and analytical errors. The sampling uncertainty is rarely available and only laboratory analytical uncertainty can be included in the ambient data files. In general, laboratory analytical uncertainties are inversely proportional to the species concentrations in the samples (i.e. the higher the species concentration is, the lower analytical uncertainty will be). For the CMB model input, uncertainty values ranging from 5% to 30% were applied to the measured values, with larger uncertainties applied to values near or below the detection limit (Maenhaut, *pers.comm*).

2.6.3.3 Source Profiles

Source profiles were determined from the USEPA's SPECIATE database of volatile organic gas and particulate matter speciation profiles of air pollution sources (USEPA, 1999). Where possible, use was made of local speciation profiles, otherwise the most representative speciation profile was selected. Local speciation profiles have been developed for various sources in Qalabotjha in the Free State Province (Engelbrecht *et al.*, 2000; 2001; 2002) and Soweto in the Gauteng Province (Annegarn *et al.*, 1998). Species unavailable in the speciation profiles contained within the SPECIATE database could not be used in the CMB analysis. It should also be noted that the methods (e.g XRF, PIXE) used to analyse certain species are not consistent across the SPECIATE database, which could result in discrepancies since each method has a unique precision, accuracy and detection limit (Kuhns *et al.*, 2002).

Various source profiles were tested in the CMB model to determine their suitability, with a total of 28 retained for use in the CMB runs. Individual source profile data were tested in the CMB model for collinearity which occurs when two or more source profiles are very similar in their composition and the CMB model cannot distinguish between profiles. When collinear profiles are found, composite profiles may be created which are weighted averages of profiles from each of the sub-categories. The profiles were tested with ambient data from several samples until acceptable values for the CMB statistical performance measures were achieved.

Source profiles included in the CMB modelling are provided in Table 2.3. A local biomass burning profile was obtained from the Qalabotjha region which was observed to be high in Cl⁻ and K, the elements typically associated with vegetative burning (Figure 2.12). Two composite coal-fired power station profiles with an ESP were included as well as a local emission profile from Lethabo Power Station in the Gauteng Province (Figure 2.12). Four local residential coal combustion profiles were tested. The residential coal combustion profile is representative of low-cost, bituminous coal with high ash, S and volatiles content. Cl⁻ and K are present in domestic coal burning emissions, while the elements also observed in soil sources (Al and Si) are also represented in the coal burning profile (Figure 2.12). Additional low-smoke, de-volatilised D-grade residential coal burning profiles were also tested for their suitability. Vehicle exhaust

emissions for different fuels (leaded petrol, unleaded petrol and diesel) were also tested for their suitability, with a leaded petrol and diesel profile retained (Figure 2.12). The refuse tip burning profile generated during a source sampling campaign in Soweto (Annegarn *et al.*, 1998) was only generated for the fine fraction aerosol. However, this profile was retained for use in the CMB model runs since it was the only profile of waste burning emissions available. The profile shows the presence of Cl, the product of the burning of plastic-containing waste in the refuse tips. The local soil dust profile from the Qalabotjha region shows the elements typically associated with soil (Al, Si and Fe) to be present (Figure 2.12). This profile is believed to be representative of wind-blown soil dust from open areas in the vicinity of the site and is not contaminated by vehicle debris typical of road dust collected at busy intersections (Annegarn *et al.*, 1998). A paved and unpaved road dust profile was also included. Secondary aerosols were accounted for using an NH_4SO_4 and NH_4NO_3 profile to account for secondary aerosol conversions between source and receptor. The inclusion of secondary aerosols as individual chemical compounds instead of mixtures with other emission source profiles is recognised as a limitation of the CMB model and can lead to misinterpretation of results (Viana *et al.*, 2008a). Industrial source profiles for a petrochemical plant were included for the Zamdela and Embalenhle CMB runs with an iron and steel plant also included for Zamdela. These included four local emission profiles from Iscor (now Arcelormittal South Africa) and Samancor in the Gauteng Province.

Table 2.3: Source profiles used in the Chemical Mass Balance Modeling

Source Type	Source Name	Source Profile Reference	Description
Biomass / Vegetative Burning	Biomass Burning	SPECIATE Profile 4012 and 4013	Grass burning profile representing veld fires in the Qalabotjha region during winter months. The sample is from grass collected at the Grootvlei railway station, approximately 25 km north-west of Qalabotjha. Sample from smoke of a kindled grass fire, collected in a sampling hood (Engelbrecht <i>et al.</i> , 2000; 2001; 2002)
Coal-Fired Power Plant	Coal-Fired Power Plant Composite (with ESP)	SPECIATE Profile 11215	Profile represents a composite of Profiles 11204, 11205, 11206, 11207, 11208, 11210, and 11212.
	Coal-Fired Power Plant (with ESP)	SPECIATE Profile 11201	Dilution train samples. Representative sample from set of nine in the Philadelphia area (Howes <i>et al.</i> , 1983)
	Industrial Fly Ash	SPECIATE Profile 3987 and 3986	Emission profile from Lethabo coal-fired power plant near Vereeniging in Gauteng; iso-kinetically sampled from stack, 200m up from ground level using a dilution stack sampler (Engelbrecht <i>et al.</i> , 2000; 2001; 2002)
Geological Material	Paved Road Dust	SPECIATE Profile 4348 and 4349	Composite of five paved road dust profiles from San Antonio, TX, and Laredo, TX (Chow <i>et al.</i> , 2004)
	Unpaved Road Dust	SPECIATE Profile 4348 and 4349	Composite of two unpaved road dust profiles from Guadalupe, TX, and Eagle Pass, TX (Chow <i>et al.</i> , 2004)
	Soil Dust	SPECIATE Profile 3994 and 3995	Soil sample collected 10 km south-east of Sasolburg in the Free State. Representative of soil from the Qalabotjha region. Sample collected in a re-suspension chamber (Engelbrecht <i>et al.</i> , 2000; 2001; 2002)
	Soil Dust	-	Vereeniging soil profile obtained from the Mintex source profile library (Annegarn <i>et al.</i> , 1998)
Industrial	Iron and Steel Plant, Electric Arc Dust	SPECIATE Profile 3988 and 3989	Iron electric arc furnace dust collected from Iscor, Vanderbijlpark iron and steel plant; Iso-kinetically sampled from duct leading to bag filter plant (Engelbrecht <i>et al.</i> , 2000; 2001; 2002)
	Iron and Steel Plant, Electric Arc Furnace Dust	SPECIATE Profile 3996 and 3997	Iron electric arc furnace dust collected from USCO, Vereeniging iron and steel plant. Re-suspended bag filter dust (Engelbrecht <i>et al.</i> , 2000; 2001; 2002)
	Iron and Steel Plant, Sinter Plant Dust	SPECIATE Profile 3990 and 3991	Sinter plant dust collected from Iscor, Vanderbijlpark iron and steel. Re-suspended bag filter dust (Engelbrecht <i>et al.</i> , 2000; 2001; 2002)
	Iron and Steel Plant, Ferromanganese Furnace Dust	SPECIATE Profile 3992 and 3993	Ferromanganese furnace dust collected from Samancor, Meyerton iron and steel plant. Re-suspended bag filter dust (Engelbrecht <i>et al.</i> , 2000; 2001; 2002)
	Oil Refinery	SPECIATE Profile 4398	Composite of HEAT_D1 and HEAT_D2 (Chang <i>et al.</i> , 2004)
	Oil Catalytic Cracker	SPECIATE Profile 4375	Composite of five profiles of stack emissions from a Texas petroleum refinery's catalytic cracker (BVCAT01, BVCAT02, BVCAT03, BVCAT04, and BVCAT05) (Chow <i>et al.</i> , 2004)
Marine Aerosol	Marine Aerosol	SPECIATE Profile 43101C, 431012.5 and 4310110	Estimate - Assumes a Cl:Na ratio of 1 and all constituents (except Cl) retain bulk sea water ratios (Watson, 1979)
Motor Vehicles	Gasoline Exhaust (Leaded)	SPECIATE Profile 4000 and 4001	Leaded gasoline motor vehicle combustion emissions. Sample collected from the exhaust of idling pick-up truck in South Africa (Engelbrecht <i>et al.</i> , 2000; 2001; 2002)

	Heavy Duty Vehicles (Diesel)	SPECIATE Profile 3461, 3462, 3463 and 3465	Diesel exhaust sample from the Wheeler Ridge Weigh Station located south of Bakersfield, CA. Emissions from a total of 174 trucks were sampled over the course of six replicate runs
	Light Duty Vehicles (Unleaded)	SPECIATE Profile 31203	Vehicle exhaust gases sampled with a dilution sampler and constant volume sampling system (Cooper <i>et al.</i> , 1987)
Other	Landfill Material	SPECIATE Profile 4081 and 4080	Landfill material. Sample collected from a sanitary filling location, Aragón (Vega <i>et al.</i> , 2004; Chow <i>et al.</i> , 2002; Vega <i>et al.</i> , 2000)
	Cement Dust	-	Cement dust profile (Annegarn <i>et al.</i> , 1998)
Refuse Burning	Burning Refuse Tip	-	Composite of three refuse tip source profiles generated during a source sampling campaign (Annegarn <i>et al.</i> , 1998)
Residential Fuel Burning	Residential Coal Combustion	SPECIATE Profile 4010 and 4011	Sample from a coal stove chimney burning regular D-grade domestic coal presently being used in stoves and braziers by Qalabotjha residents. Product is a low-cost, bituminous coal containing high ash, sulphur and volatiles contents (Engelbrecht <i>et al.</i> , 2002)
		SPECIATE Profile 4008 and 4009	Sample of brazier fire smoke burning regular D-grade domestic coal presently being used in stoves and braziers by township residents; collected by hood connected to a dilution stack sampler (Engelbrecht <i>et al.</i> , 2002)
		SPECIATE Profile 4006 and 4007	Low-smoke, de-volatilized D-Grade coal, township area (Engelbrecht <i>et al.</i> , 2002)
		SPECIATE Profile 4004 and 4005	Sample from a coal stove chimney burning low-smoke fuel, de-volatilized D-grade coal. This product produces less smoke than D-grade coal on being ignited. Similar to CHARTECH (Engelbrecht <i>et al.</i> , 2002)
	Residential Wood Combustion	SPECIATE Profile 42303C, 423032.5 and 4230310	Average of 16 samples from 8 sources: 45% fireplaces and 55% wood stoves (DeCesar and Cooper, 1980)
Secondary Aerosols	Ammonium Nitrate – Prill Tower	SPECIATE Profile 2540910, 25409C and 254092.5	Profile to account for possible conversion of nitrogen to nitrate between source and receptor (Cooper <i>et al.</i> , 1987)
	Ammonium Sulphate Production	SPECIATE Profile 2541010, 254102.5 and 25410C	Profile to account for possible conversion of sulphur to sulphate between source and receptor (Cooper <i>et al.</i> , 1987)



Figure 2.12: Selected SPECIATE source profiles

2.7 Air Mass Trajectory Analysis

The air mass history during the sampling campaigns in each study region was examined using back trajectories calculated with the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) version 4.8 modelling software. This software was developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler and Hess, 1997; 1998; Draxler, 1999; Stein *et al.*, 2015; Rolph *et al.*, 2017). The model was run with the GDAS meteorological archive (spatial resolution of $1^{\circ} \times 1^{\circ}$) produced by the US National Weather Service's National Centre for Environmental Prediction (NCEP) and archived by ARL (Air Resources Laboratory, 2017). For each sampling campaign, individual 72-hour back trajectories for air masses at an arrival height of 100 m above ground level were calculated. As the geomorphology in HYSPLIT is not well defined, an arrival height of 100 m above ground level was selected as lower arrival heights could result in increased error margins on single trajectory calculations (Tiitta *et al.*, 2014). Errors for individual trajectories range from 15 – 30% of the back trajectory distance travelled (Stohl, 1998; Riddle *et al.*, 2006). The individual trajectories were then grouped into clusters of similar air mass origins using the trajectory cluster analysis tool in the HYSPLIT model. The number of clusters retained was determined by the percent change in the total spatial variance (TSV) whereby a large increase in the change of TSV indicates that 'different' rather than 'similar' clusters are being paired (Draxler *et al.*, 2020).

An overview of the particulate sampling sites, methodologies and analytical techniques has been provided and the statistical methods and receptor models were described. Chapter 3 provides a discussion of air pollution sources.

CHAPTER 3 SOURCES OF ATMOSPHERIC AEROSOL LOADING

A discussion of the sources of air pollution contributing to the atmospheric aerosol loading in each of the study areas is provided in the section below.

3.1 Sources of Emission

South Africa has one of the most industrialised economies in Africa. The most heavily industrialised area is located in the Mpumalanga Highveld, accounting for approximately 90% of South Africa's industrial emissions of particulate matter, SO₂ and NO₂ (Freiman and Piketh, 2003; Wenig *et al.*, 2003). Power generation activities are centred on the Highveld due to the presence of extensive coalfields. Other significant sources of emission include household fuel burning, motor vehicles, heavy and light industry and mining activities. The Vaal Triangle is also considered a significantly polluted area with numerous industries, a coal-fired power station and various mining activities. Other sources of concern include domestic fuel burning, vehicle tailpipe emissions, biomass burning, landfills and agricultural activities (DEA, 2009).

While both the Highveld and Vaal Triangle are considered to have 'poor' air quality, the Waterberg region is classified as having 'potentially poor' air quality in the National Framework for Air Quality Management in the Republic of South Africa (DEA, 2013). Within the Lephalale area, sources of emission include two coal-fired power stations, South Africa's largest opencast coal mine, domestic fuel burning, waste disposal and refuse burning and agricultural activities. Proposed future developments in the area include new open-pit coal mines and associated Independent Power Producer (IPP) plants. These proposed industrial developments will establish the Lephalale region an important role player in air quality in future years to come

The spatial distribution of air pollution sources surrounding each of the study areas is shown in Figure 3.1 to Figure 3.3 with further discussion of each of the air pollution sources contributing to ambient particulate concentrations provided in the section below.

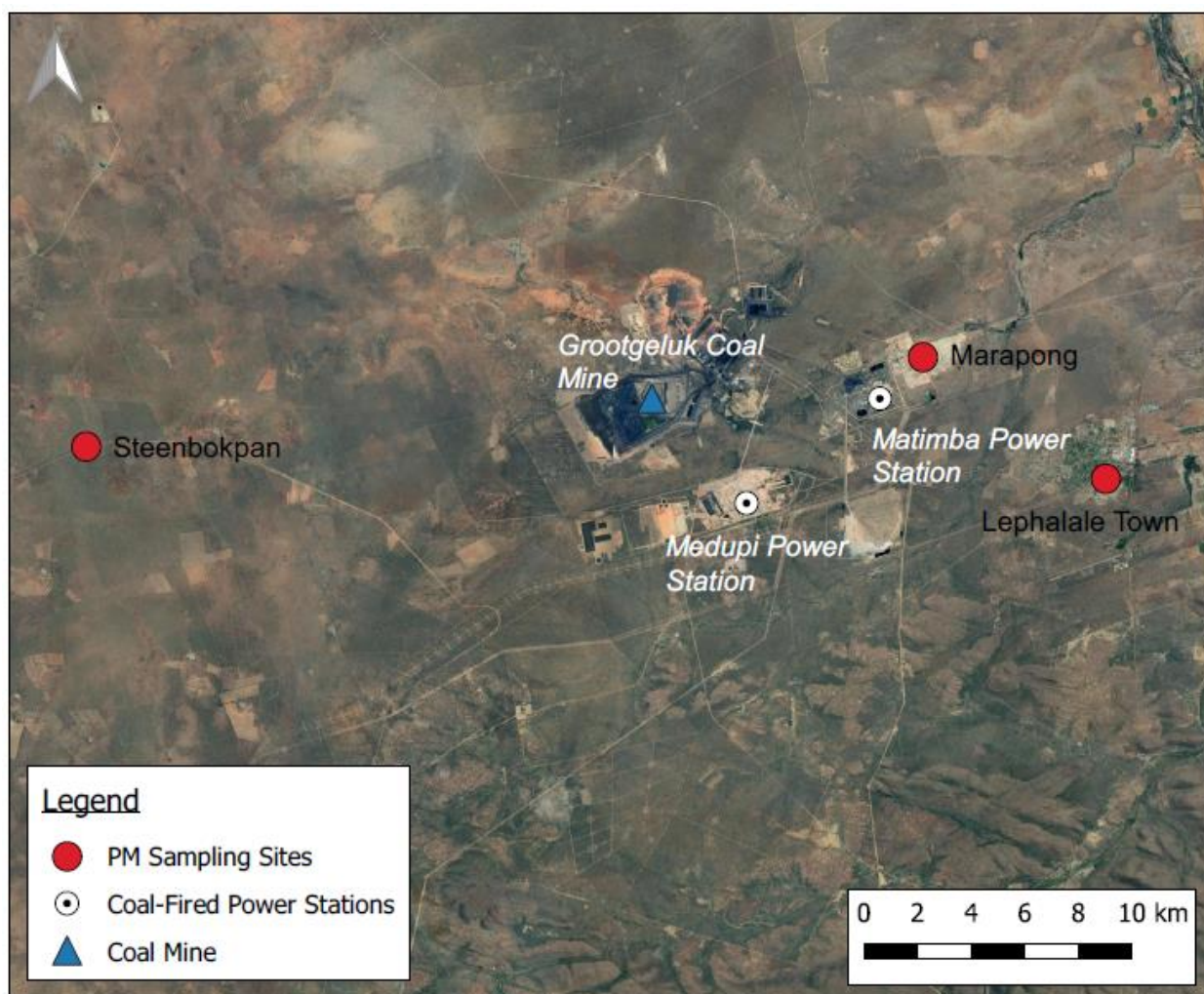


Figure 3.1: Sources of emission surrounding the Waterberg sampling sites

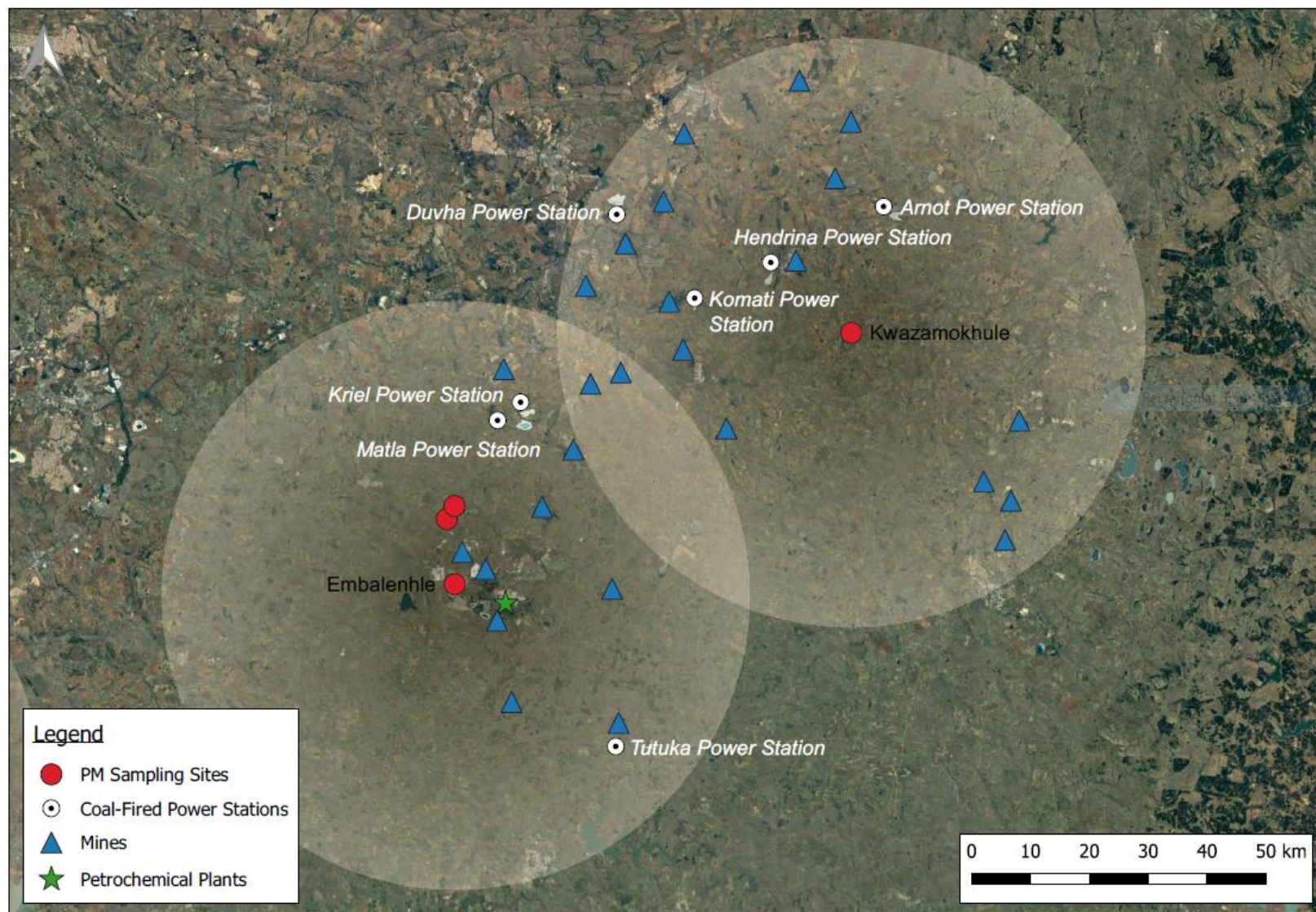


Figure 3.2: Sources of emission surrounding the Highveld sampling sites

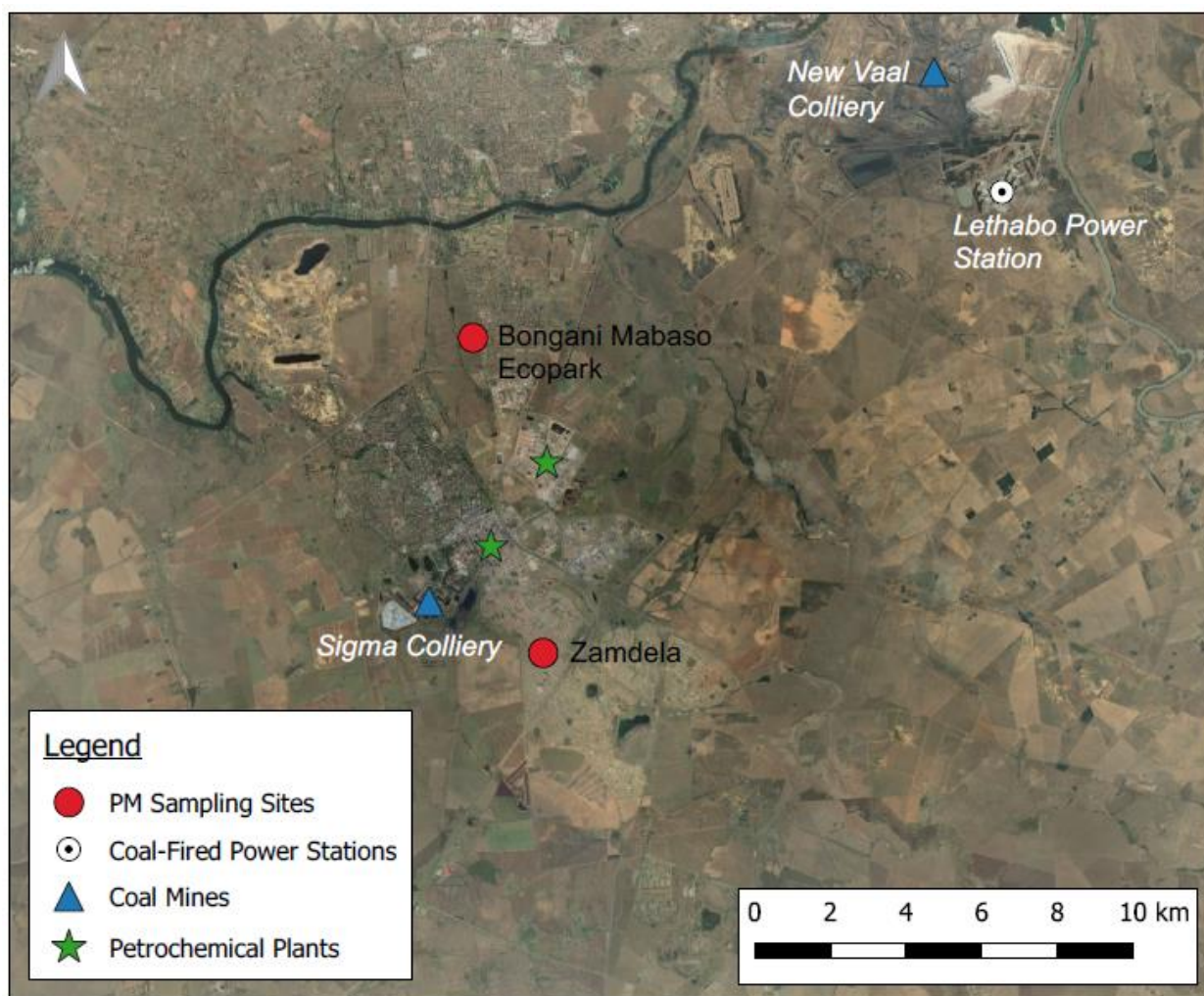


Figure 3.3: Sources of emission surrounding the Vaal Triangle sampling sites

3.1.1 Biomass Burning

Emissions from biomass burning have been determined to be a significant source of aerosols and trace gases (Crutzen and Andreae, 1990; Akagi *et al.*, 2011; Mao *et al.*, 2013; Yokelson *et al.*, 2012; Andreae, 2019). Biomass burning includes burning of forested areas for land clearing, widespread burning of grasslands and savannas to sustain grazing lands, burning of harvest debris and the use of biomass fuel for heating purposes (Andreae *et al.*, 1994). Burning of agricultural fields is another type of biomass burning that may be a regionally significant source of aerosols, particularly during the dry season (Lacaux *et al.*, 1993; Duan *et al.*, 2004; Yang *et al.*, 2020).

On a global scale, biomass burning is the most significant global source of BC and primary organic aerosol (POA), accounting for 59% and 85% of global BC and POA emissions, respectively (Bond *et al.*, 2013). Biomass burning also contributes up to one-half of global CO emissions and 20% of NO_x emissions (Olivier *et al.*, 2005; Wiedinmyer *et al.*, 2011). Other

pollutants released from biomass burning include greenhouse gases such as CO₂, CH₄ and nitrous oxide (N₂O) (Ciais *et al.*, 2013; Tian *et al.*, 2016; Le Quéré *et al.*, 2018) as well as VOCs, of which biomass burning is the second largest global contributor (Yokelson *et al.*, 2008; Akagi *et al.*, 2011).

Emissions from fires are related to the vegetation types burnt and the burn intensities (flaming or smouldering) (Li *et al.*, 2003). The amount of fuel consumed by flaming and smouldering combustion depends on the vegetation type and the burning conditions (Andreae, 2019). Dry grassland fires are dominated by flaming combustion and a rapid passage of the fire front, resulting in little residual smouldering. Such flaming fires have more complete combustion and release more CO₂ (Andreae, 2019) and also produce large amounts of soot aggregates (Li *et al.*, 2003). During flaming combustion, the oxygen supply is limited, and parts of the flame are quenched before the oxidation of carbon radicals is complete, resulting in the formation of soot (Andreae *et al.*, 1998). Forest fires, particularly those with high moisture contents and widespread fuels, have a long residual smouldering combustion phase. These smouldering fires have less complete combustion and release large quantities of CO, up to 30% of carbon burned (Andreae, 2019).

Savanna burning is the single largest source of biomass burning globally (Andreae, 1991), with Africa comprising more than 60% of the savanna on Earth. Biomass burning is a seasonal source, starting in June close to the equator and slowly moving southward, reaching maximum intensity in South Africa and neighbouring countries in September (Scholes *et al.*, 1996a and b).

Biomass burning is an important source in the long-range transport of aerosols and trace gases across the subcontinent. During SAFARI 2000, biomass burning products were shown to be effectively transported towards the south and influence the air quality throughout the region, including South Africa. An analysis of transport patterns from Zambia has indicated that pollutants emitted from north of South Africa frequently impact the Highveld region, particularly during the spring season (Figure 3.4) (Dlamini, 2005). Biomass burning emissions that most significantly impact South Africa originate from neighbouring countries such as Zambia, Zimbabwe and Mozambique (Adesina *et al.*, 2015; Kumar *et al.*, 2013; Magi *et al.*, 2009; Queface *et al.*, 2011; Venter *et al.*, 2020). Biomass burning aerosols from central and southern Africa have also been shown to be transported to the Indian Ocean and Australia (Annegarn *et al.*, 2002; Pak *et al.*, 2003; Sinha *et al.*, 2004) as well as the Amazon Basin, Atlantic Ocean and Southern Ocean (Barkley *et al.*, 2019).

Since SAFARI 2000, a number of recent studies (Lourens *et al.*, 2011; Queface *et al.*, 2011; Venter *et al.*, 2012; Hersey *et al.*, 2015; Tiitta *et al.*, 2014; Vakkari *et al.*, 2013; Maritz *et al.*,

2015; Aurela *et al.*, 2016; Adesina *et al.*, 2015; Venter *et al.*, 2020) have demonstrated the regional influence of biomass burning on ambient aerosol and trace gas concentrations at various sites in South Africa.

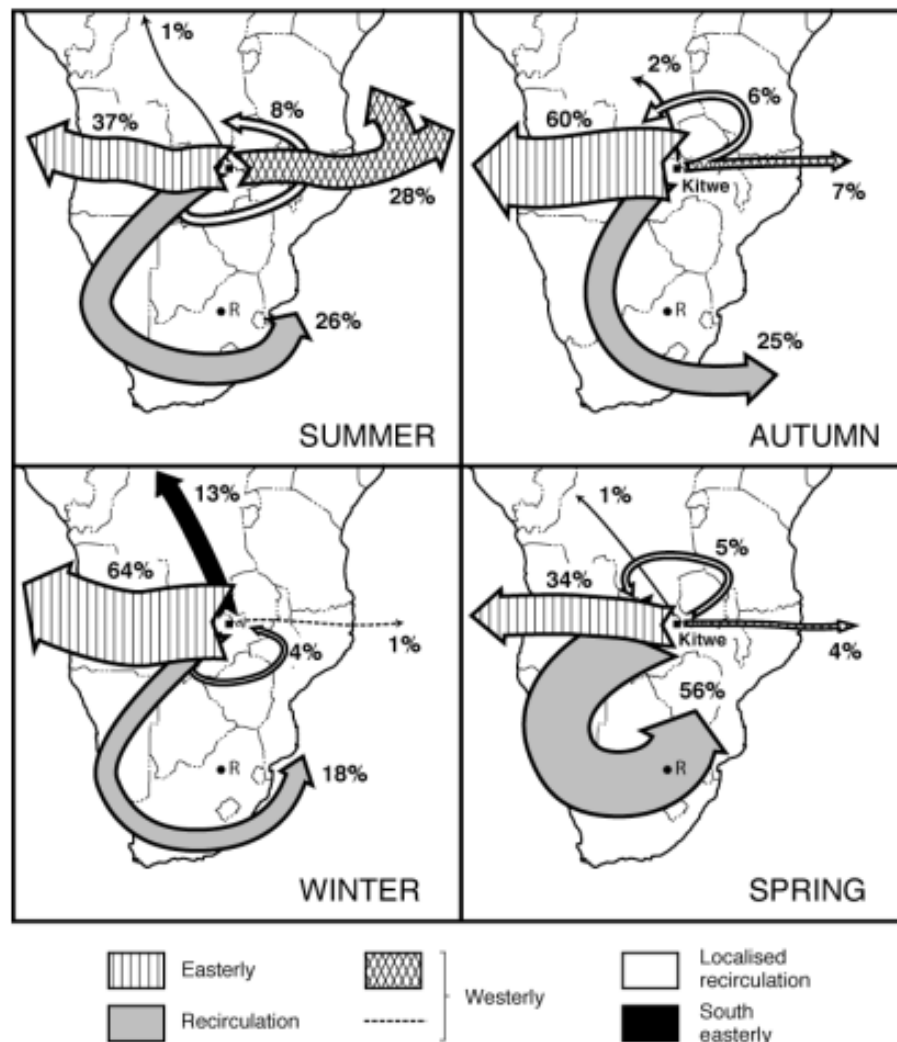


Figure 3.4: Major recirculation patterns and transport seasonality for the period 1990 – 1994 (Dlamini, 2005)

Biomass burning is a persistent air quality concern within South Africa. Almost 90% of all biomass burning emissions are believed to be anthropogenic in nature (Koppman *et al.*, 2005). Fires are usually anthropogenically induced for land management purposes such as crop land management, bush encroachment prevention and firebreaks. Prescribed and natural fires are used as a management tool for the maintenance of wildlife forage in many national parks and game reserves in southern Africa (Scholes *et al.*, 1996b).

A marked trend in fire incidence is observed from the northeastern and eastern parts to the western parts of South Africa (Forsyth *et al.*, 2010; Strydom and Savage, 2016) (Figure 3.5). These fires are concentrated in the savannah, grassland and fynbos biomes which have high to extreme risk of veld fires (Kruger *et al.*, 2006). The highest number of fires occur in the dry winter months of August and September (Strydom and Savage, 2016).

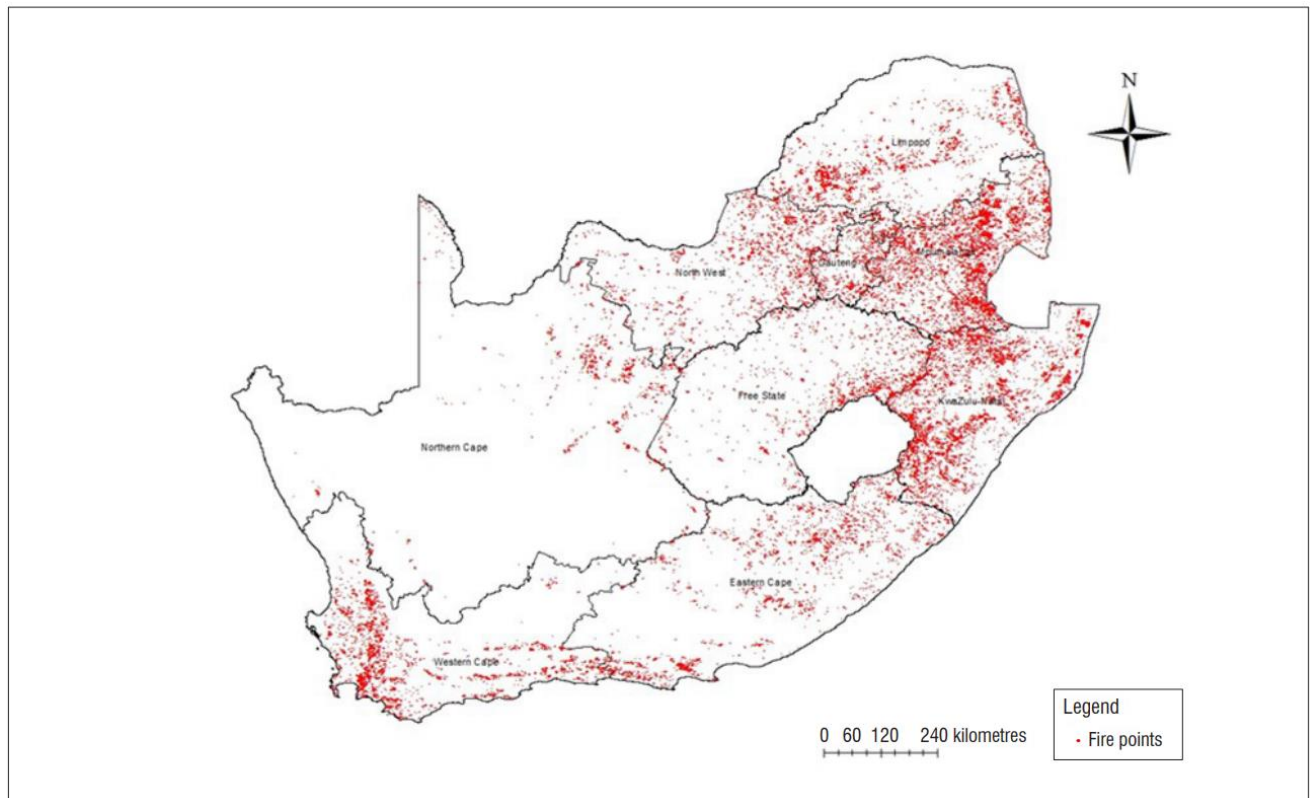


Figure 3.5: Distribution of fires in South Africa between 2003 - 2013 (after Strydom and Savage, 2016)

3.1.2 Domestic Fuel Burning

Domestic fuels continue to be used for cooking and space heating purposes within informal, low-income and densely populated areas in South Africa. These fuels are a significant source of air pollution, particularly during the stable winter months. Domestic fuel burning has been determined to have the greatest negative impact on human health of all air pollution sources in South Africa (Scorgie *et al.*, 2004; Friedl *et al.*, 2008). This is due to emissions being released at low levels (i.e within the human breathing zone), the co-occurrence of peak emissions with periods of poor atmospheric dispersion and the release of these emissions within densely populated areas (Scorgie *et al.*, 2004). Domestic fuel burning also results in high levels of indoor air pollution to which the household inhabitants are exposed. Adesina *et al.* (2020) determined that indoor particulate concentrations can increase by between a factor of two to

five in a domestic fuel burning household compared to a non-domestic fuel burning household in Kwazamokhule.

Despite electrification, many households continue to use domestic fuels with approximately 80% of residents that have access to electricity in low-income residential areas still choosing to continue to use solid fuels (Mduli and Vogel, 2010). A wide variety of domestic fuel types are available, although their use within a specific community or settlement is dependent on several factors including availability, accessibility and affordability of the different fuels (Wagner *et al.*, 2005). Coal and wood are the main fuels consumed in low-income communities during winter due to their multi-functional nature as these fuels can be used for cooking, heating and lighting purposes (Nkosi *et al.*, 2017). Coal is predominantly used on the Highveld due to the concentration of the coal mines, as well as in Gauteng and in the North-Eastern Free State (Pauw *et al.*, 2008; Mduli and Vogel, 2010; Makonese *et al.*, 2015; Langerman *et al.*, 2018). Wood is predominantly used in rural areas in South Africa (Pauw *et al.*, 2008; Langerman *et al.*, 2018). Other substances such as paraffin, liquid petroleum gas (LPG) and animal dung are also used in low-income communities (Ludwig *et al.*, 2003). During summer, fuels utilized include paraffin, candles and gas. While gas is a popular choice for cooking, it is often too expensive compared to paraffin. Paraffin is the most commonly used fuel in completely unelectrified communities since this can also be used for cooking and lighting (Muller *et al.*, 2003).

Pollutants released from burning these fuels include CO, NO₂, SO₂, inhalable particulates and polycyclic aromatic hydrocarbons (PAHs). Particulates are the dominant pollutant emitted from the burning of wood. Smoke from wood burning contains respirable particles that are small enough in diameter to enter and deposit in the lungs. These particles comprise a mixture of inorganic and organic substances including aromatic hydrocarbon compounds, trace metals, nitrates and sulphates. PAHs are produced as a result of incomplete combustion and are potentially carcinogenic in wood smoke (Maroni *et al.*, 1995). The main pollutants emitted from the combustion of paraffin are NO₂, particulates, CO and PAHs.

Domestic fuel burning shows a characteristic diurnal and seasonal signature. Periods of elevated domestic fuel burning, and hence emissions, occur in the early morning and evening for space heating and cooking purposes (Annegarn *et al.*, 1998; Feig *et al.*, 2016). Seasonally, an increase in domestic fuel burning is recorded during the winter months of April to October due to increased atmospheric stability and an increased demand for space heating and cooking as temperatures decrease (Annegarn *et al.*, 1998; Lourens *et al.*, 2011; Feig *et al.*, 2016).

Household fuel burning statistics in residential areas in South Africa are reported as part of the census surveys, with the most recent survey completed in 2011. Data on household fuel usage

was also obtained during the GHS undertaken in Kwazamokhule in 2015 and in Embalenhle and Zamdela in 2016.

In Kwazamokhule, access to electricity is limited, with Census 2011 reporting that approximately 65% of households have access to electricity in the township (Table 3.1). However, the Kwazamokhule GHS conducted in 2015 found that less than 50% of households used electricity for cooking and heating purposes with domestic fuels such as coal and wood still used mainly for these purposes (Eskom, 2016). Census 2011 also reports that approximately 40% of households use coal with only 1% of households using wood as a domestic fuel. However, these figures were found to be much higher during the GHS in 2015 with more than 50% of households in Kwazamokhule SP, Manfred and Maphela found to be using either coal or wood for cooking and more than 60% of households in the same areas using these fuels for heating purposes (Eskom, 2016). This suggests that the usage of coal and especially, wood, is more prevalent in the township than was shown in the Census 2011 findings. The difference between Census 2011 and the GHS findings is likely attributed to the fact that the census only obtained information on the primary energy carrier rather than the entire range of energy carriers utilised for heating and cooking purposes (Sasol, 2017).

The other Highveld site, Embalenhle, has a higher number of households that are electrified with approximately 83% of electrified households in the township (Table 3.1). The Census 2011 findings showed coal to be the main domestic fuel used in the township although according to the Embalenhle GHS in 2013, 45.3% of households in Embalenhle used either coal, wood or paraffin for cooking purposes (compared to 13.7% in the Census 2011 data). A distinct seasonal pattern is also seen in the use of coal and wood in this township with over double the consumption of these fuels during the winter months (Sasol, 2017).

In Zamdela in the Vaal Triangle, approximately 80% of households are electrified based on Census 2011 (Table 3.1). According to the Census 2011 findings, paraffin and coal are the main domestic fuels used in the township. The Zamdela GHS in 2016 reported that 34.6% of households in Zamdela use either coal, wood or paraffin for cooking purposes (Sasol, 2017), which is considerably higher than the 12.5% reported in Census 2011.

A GHS was not conducted in Marapong township during the Lephalale sampling campaigns in 2012 and 2013. Census 2011 reports that over 70% of households are electrified in Marapong township with paraffin and then wood being the main domestic fuels used in the township (Table 3.1). However, given the discrepancies seen between Census 2011 and the GHS results in other townships, it is likely that these fuels are being used in more households than is reported in the Census 2011 data.

Table 3.1: Household fuel usage (%) in Marapong, Kwazamokhule, Embalenhle and Zamdela (Census 2011)

Site	Fuel	Lighting (%)	Cooking (%)	Heating (%)
Marapong	Electricity	72.90	72.11	76.12
	Gas	0.11	1.24	1.22
	Paraffin	1.09	24.23	19.85
	Wood	-	2.15	2.57
	Coal	-	0.11	0.05
	Animal dung	-	0.08	0.05
	Candles	25.72	0.00	0.00
	Solar	0.18	0.06	0.13
	Other	0.00	0.03	0.00
Kwazamokhule	Electricity	83.73	56.88	53.88
	Gas	0.75	1.22	1.24
	Paraffin	0.63	3.63	0.79
	Wood	-	1.19	1.02
	Coal	-	36.87	42.88
	Animal dung	-	0.03	0.03
	Candles	14.57	0.00	0.00
	Solar	0.33	0.15	0.16
	Other	0.00	0.03	0.00
Embalenhle	Electricity	90.20	85.13	72.14
	Gas	0.15	0.70	2.06
	Paraffin	1.72	9.13	4.04
	Wood	0.00	0.25	0.81
	Coal	0.00	4.36	20.59
	Animal dung	0.00	0.06	0.14
	Candles	7.65	0.28	0.00
	Solar	0.28	0.09	0.22
	Other	0.00	0.00	0.00
Zamdela	Electricity	82.35	80.83	76.00
	Gas	0.21	6.47	4.76
	Paraffin	4.96	11.94	9.92
	Wood	0.00	0.23	2.20
	Coal	0.00	0.31	6.82
	Animal dung	0.00	0.04	0.13
	Candles	12.32	0.14	0.00
	Solar	0.16	0.06	0.16
	Other	0.00	0.00	0.00

3.1.3 Industrial Emissions

3.1.3.1 Petrochemical Industry

South Africa's petroleum industry is made up of numerous activities including extracting and importing crude oil, coal and gas. The petrochemicals sector is built on coal gasification due to the abundance of coal reserves which has led to the establishment of a well-developed synthetic fuels industry in South Africa (DoE., 2018).

Sasol Synfuels Operations operates the world's only coal-based synthetic fuels manufacturing facility in Secunda which produces synthesis gas (syngas) through coal gasification and natural gas reforming. Syngas is converted into synthetic fuel (synfuel) components, pipeline gas and chemical feedstock for the downstream production of solvents, polymers, comonomers and other chemicals. The fuel components are used to manufacture petrol and diesel fuels, aviation jet fuel, paraffin and LPG (DoE, 2018).

In Sasolburg, Sasol's Sasolburg Operations supplies utilities as well as reformed and syngas to the other Sasol Business Units operating on the site. Steam and electricity are generated in coal-fired steam stations while natural gas is reformed to produce syngas which is distributed to Sasol Wax to produce a range of waxes and paraffins, and to Sasol Solvents to produce products such as methanol, butanol and acrylates. Off-gases from various processes are used by Sasol Nitro to manufacture ammonia, nitric acid, ammonium nitrate and ammonium nitrate-based products including commercial explosives and fertilisers (von Gruenewaldt *et al.*, 2018). Also located in Sasolburg, Natref, a joint venture between Sasol Oil (Pty) Ltd and Total South Africa (Pty) Ltd, is South Africa's only inland crude oil refinery. Products produced at the refinery include refined oil, petrol, diesel, jet fuel and LPG (DoE, 2018).

The main emissions released from petrochemical processes include SO_x, NO_x and particulates as well as CO, NH₃, hydrocarbons, aldehydes and cyanides (USEPA, 2015). The Highveld Priority Area AQMP (DEA, 2012b) determined the petrochemical industry to be the second largest source of NO_x and SO₂ emissions in the Highveld, accounting for 15% and 12% of total NO_x and SO₂ emissions. However, the petrochemical industry was only responsible for 3% of total PM₁₀ emissions compared to substantial PM₁₀ contributions from the power generation, metallurgical and mining sectors. Within the Highveld region, key petrochemical facilities include Sasol Synfuels located to the immediate west of the Embalenhle sampling site in Secunda.

Within the Vaal Triangle, the VTAPA AQMP (DEA, 2009) identified the petrochemical industry to be the second largest contributor to SO₂ emissions in the region, accounting for 14% of total SO₂ emissions. The petrochemical industry was also the third most significant contributor to NO_x

and PM₁₀ emissions, accounting for 12% and 13% of total NO_x and PM₁₀ emissions, respectively. Key petrochemical industries in the Vaal Triangle include Sasol and Natref, which are located to the north of the Zamdela sampling site.

3.1.3.2 Power Generation

Emissions from coal-fired power stations in South Africa are significant on both a regional and global scale (Pretorius *et al.*, 2015). Coal-fired power stations release significant quantities of SO₂, NO_x, PM, Hg and greenhouse gases. The energy sector in South Africa is the biggest contributor to SO₂ and NO_x emissions (70% and 55% respectively) and the second highest contributor to PM emissions (36%) of all air pollution sources in South Africa (DEA, 2012a; Scorgie *et al.*, 2004; Masekoameng *et al.*, 2010; Pretorius, 2015). Coal-fired power stations are also the main contributor to Hg emissions in South Africa, estimated to contribute to 65% of total emissions (Masekoameng *et al.*, 2010). Elevated levels of Hg (and other metals such as Cd, Sb and As) have been measured in soils in Bloemfontein, with the Bloemfontein Power Station (decommissioned in 2006) being one of the potential sources of contamination while it was in operation (Clark *et al.*, 2015).

Eskom is responsible for the generation of 95% of South Africa's electricity (Eskom, 2010), the remainder generated by coal-fired power plants owned by the private sector, municipalities and Sasol (Ziramba, 2009; Menyah and Wolde-Rufael, 2010). Eskom-owned coal-fired power stations include Arnot, Duvha, Camden, Grootvlei, Hendrina, Kendal, Komati, Kriel, Kusile, Lethabo, Majuba, Matla, Matimba, Medupi and Tutuka (Eskom, 2012), most of which are centred on the Highveld where South Africa's coal reserves are located. These power stations burn bituminous coal and employ a range of particulate control technologies including either Fabric Filter Plants (FFP) and cold-sided Electrostatic Precipitators (ESPs) with SO₃ Flue Gas Conditioning (FGC) (Garnham and Langerman, 2016; Pretorius, 2015).

Power stations are considered to be one of the largest contributors to poor air quality in the Highveld region. Power stations within a 50 km radius of the Highveld sampling sites (Kwazamokhule and Embalenhle) include Arnot, Camden, Duvha, Hendrina, Kendal, Komati, Kriel, Matla and Tutuka power stations. Currently, Arnot, Camden, Hendrina and Duvha all have FFPs with an ESP and FGC also installed at Duvha. Control measures at Kriel and Matla include an ESP and FGC, while Tutuka has an ESP (Garnham and Langerman, 2016). Generally, particulate removal efficiencies of FFP's are higher than those of ESP's due to challenges associated with the low sulphur content of the coal and other operational and maintenance issues associated with ESPs (Pretorius, 2015). In the Highveld, power generation

is the main source of NO_x and SO₂ emissions (73% and 82%, respectively) and the third most significant source of PM₁₀ emissions (12%) (DEA, 2012b).

In the Vaal Triangle, power generation is the main source of SO₂ emissions, contributing to 78% of SO₂ emissions in the region (DEA, 2009). Power generation is the second most significant source for both NO_x and PM₁₀ emissions (39% and 53% respectively). Lethabo Power Station is the only power station situated within the Vaal Triangle and is located approximately 17 km to the north-east of the Zamdela sampling site. Lethabo is one of Eskom's largest coal-fired power stations and is unique in that it burns very low-grade coal with a calorific value of 16 MJ/kg, with an ash content of up to 42%. Measures to reduce particulate emissions from Lethabo Power Station include an ESP and an FGC Plant (Garnham and Langerman, 2016).

Located to the west of Lephalale, Matimba Power Station is the largest direct dry-cooled power station in the world. The power station obtains its coal from the adjacent Grooteegeluk Coal Mine. Control equipment installed on Matimba Power Station includes an ESP and an FGC Plant to reduce particulate emissions. Construction of the neighbouring Medupi Power Station began in 2007 with the first unit commissioned onto the National Grid in 2015. All units are expected to come online by 2021. Medupi is the fourth largest coal plant in the southern hemisphere and the largest dry-cooled, coal-fired power station in the world. Control measures at Medupi Power Station include fabric filters to reduce particulate emissions and low NO_x burners and overfire air for lower NO_x emissions. Flue Gas Desulphurisation (FGD) will be employed six years after commissioning to reduce SO₂ emissions (Garnham and Langerman, 2016).

Other potential developments in the area include Exxaro who has proposed the development of a 1200 MW coal-fired power station known as Thabametsi approximately 17 km north-west of Lephalale. Resgen has also proposed the development of a 45 MW coal-fired power station known as Boikarabelo Power Station in Steenbokpan.

3.1.4 Mining

Fugitive dust emissions are the main pollutant associated with opencast mining activities. Fugitive dust emissions are generated from drilling and blasting, bulldozing, materials handling activities, vehicle entrainment on unpaved roads and wind erosion from open exposed areas such as rock dumps and tailings dams.

Coal mining in South Africa is centred on the Highveld, with approximately 60% of the country's deposits located in eMalahleni and surrounding areas. The Highveld Priority Area AQMP (DEA, 2012b) identified industrial sources (inclusive of coal mining) to be the largest contributor to PM₁₀ emissions (89%) in the Highveld Priority Area. In the Medium-Term Review of the 2011

HPA AQMP (DEA, 2015), mining activities alone were the largest contributor to particulate emissions (49%). In Embalenhle, localised mining activities include Sasol's underground mining operations in the area, namely Bosjesspruit, Brandspruit, Middelbult, Syferfontein and Twistdraai which supply Sasol Synfuels in Secunda with coal. Sasol has also recently opened the Impumelelo coal mine in 2019 which replaces the Brandspruit mine. Evander Gold Mine (now renamed Evander 7 Shaft) and its tailings dams are located to the northwest, north and northeast of Embalenhle. Mining activities near Kwazamokhule are located to the north of the township. Neighbouring mines include Optimum coal mine, located approximately 13 km to the northwest and Anglo American Coal SA's Goedehoop coal mine, approximately 12 km to the east.

In the Vaal Triangle, mining activities were identified to contribute to 12% of total PM₁₀ emissions, the fourth most significant source after industries (53%), power generation (16%) and vehicle activity (14%) (DEA, 2009). In the Zamdela area, mining activities include Sigma Colliery to the northwest of the township. Sigma Colliery is owned by Sasol Mining (Pty) Ltd and supplies coal to Sasol's petrochemical plant in Sasolburg.

In the Waterberg region, mining activities are not a significant source of emissions. However, the Waterberg Coalfield contains about 40% of South Africa's remaining coal resources, and as such, mining is anticipated to increase in the future. Exxaro's Grootgeluk Coal Mine, located to the west of Lephalale, is the largest opencast coal mine in South Africa. A number of mining developments have also been proposed in the future in the Lephalale area, which has the third biggest coal reserves in South Africa.

3.1.5 Waste Burning

Waste burning is a significant source of local emissions in many townships. Poor service delivery has resulted in the uncontrolled and illegal burning of waste in many of South Africa's townships. The GHS surveys conducted in Kwazamokhule, Embalenhle and Zamdela (Eskom, 2016; Sasol, 2017) found that waste burning occurs on a widespread and frequent basis, particularly in Embalenhle and Zamdela. Lack of access to waste collection services as well as high waste collection service delivery failure rates results in the burning of the uncollected waste. This burning can occur just outside the home or in places where waste is illegally dumped alongside roads or other open public spaces. Such burning occurs to reduce waste quantities, eliminate odours, or for aesthetic reasons (Cogut, 2016).

Open burning of waste also occurs at landfill sites to reduce the quantity of waste in landfills that are filled beyond their capacity or have insufficient capacity due to poor planning. Open burning

in landfills usually involves burning large quantities of unselective waste which can include hazardous medical and industrial waste (Cogut, 2016).

Emissions from waste burning are dependent upon the burning conditions and the composition of the waste that is being burned (Cogut, 2016). The major composition of waste generated in most parts of Africa is biodegradable organic waste (Bello *et al.*, 2016). Plastics make up an estimated 10% of household waste (Bello *et al.*, 2016; Verma *et al.*, 2016). The burning of plastics such as polyvinyl chloride (PVC) releases large quantities of chlorine in the form of HCl (Christian *et al.*, 2010). Chloride-containing plastic waste also releases high quantities of dioxins and furans (Hedman *et al.*, 2006). Open waste burning also releases significant quantities of particulates and a wide variety of chemical compounds including BC, air toxics and greenhouse gases (Li *et al.*, 2012). Heavy metals such as Cd, Cr, Mn, Sb, As, Pb and Hg are emitted from open burning of waste although the quantity and type of metals emitted vary significantly based upon the content of the waste being burned (Cogut, 2016).

Emissions from air pollution sources influencing the atmospheric aerosol loading in each of the study areas have been discussed. An overview of atmospheric transport patterns and the local meteorological conditions in each region is described in Chapter 4.

CHAPTER 4 CLIMATE AND METEOROLOGICAL CONDITIONS

Atmospheric transport patterns over southern Africa and their influence on the horizontal and vertical distribution of aerosols is discussed. An overview of the climate and local meteorological conditions influencing air pollution dispersion and dilution in each region is also provided.

4.1 Atmospheric Transport Patterns over southern Africa

4.1.1 Synoptic Circulation Patterns

Southern Africa is situated in the region of large-scale subsidence occurring between the Hadley and Ferrel cells of the southern hemisphere's general circulation (Newell *et al.*, 1972). Five major synoptic scale circulation patterns dominate over southern Africa (Figure 4.1), of which the most important is the semi-permanent subtropical continental anticyclone (Tyson and Preston-Whyte, 2000). Anticyclonic conditions are most prevalent during the winter months, occurring with a frequency of 70 – 80% during June and July (Tyson *et al.*, 1996b). Other important synoptic scale circulation types over southern Africa include barotropic quasi-stationary easterly waves, transient ridging anticyclones originating in the midlatitude westerlies and baroclinic disturbances in the westerlies. Easterly waves occur during summer while ridging anticyclones occur frequently throughout the year. Westerly disturbances have a semi-annual cycle, peaking in the spring and autumn months while continental anticyclones are the single most frequently occurring systems from March to September (Tyson *et al.*, 1996a).

Based on the major circulation patterns dominating over southern Africa, Garstang *et al.* (1996) identified five aerosol and trace gas transport modes, namely, direct easterly or westerly transport, easterly or westerly advection out of an initially anticyclonic circulation and anticyclonic recirculation (Figure 4.2). Of all these, anticyclonic transport to the east coast of South Africa and the Indian Ocean is the dominant transport mode (Tyson *et al.*, 1996b).

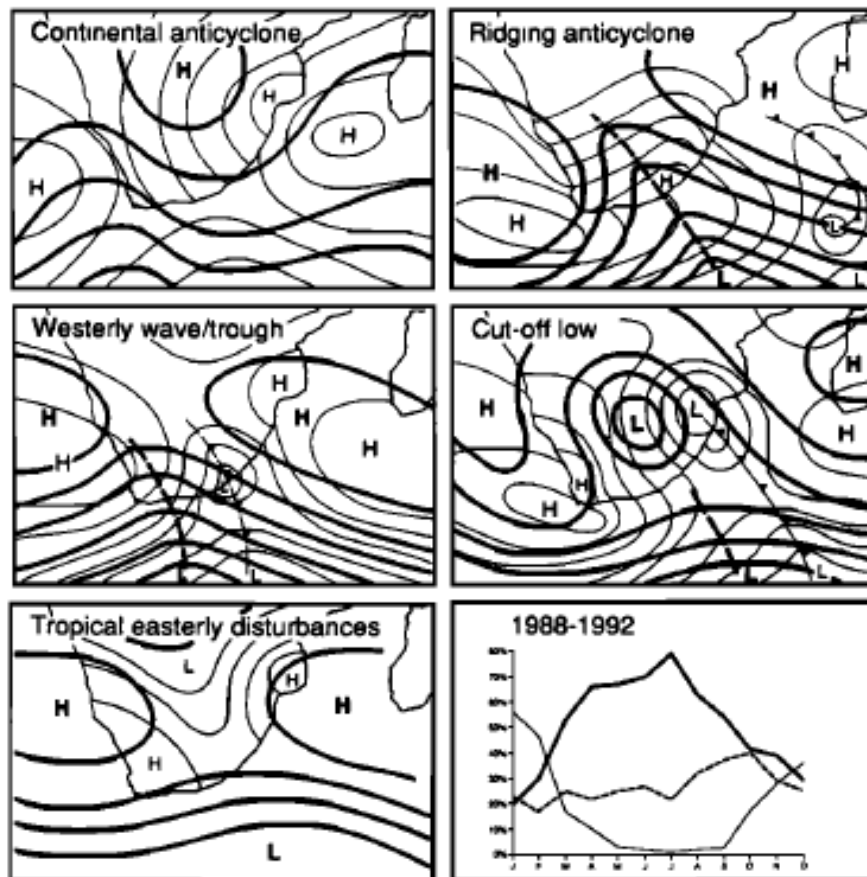


Figure 4.1: Major synoptic-scale circulation patterns over southern Africa (Tyson *et al.*, 1996b)

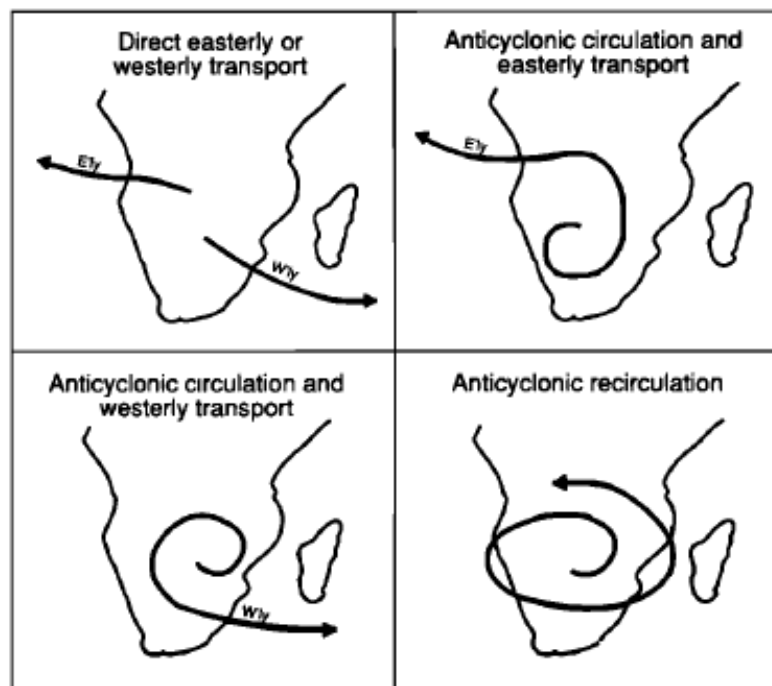


Figure 4.2: Schematic representation of the major aerosol and trace gas transport modes

4.1.1.1 Vertical Structure of the Atmosphere

The vertical component of dispersion in the atmosphere is a function of the buoyancy present, which is greatest under unstable conditions and least under stable conditions (Diab, 1975; Mohan and Siddiqui, 1998). Southern Africa is dominated by a downward mean vertical motion due to large-scale subsidence associated with the prevailing semi-permanent, subtropical anticyclones. This subsidence results in adiabatic warming and drying of the atmosphere, thereby preventing convective mixing and producing very stable conditions. Under these conditions, surface radiative inversions, elevated inversions and absolutely stable layers are formed.

These inversions, and the presence of absolutely stable layers, are of significance since they control the vertical and horizontal transport of aerosols and trace gases in the atmosphere. Surface radiative inversions occur most frequently at night during the winter months, reaching a depth of 500 metres over plateau regions in winter (Tyson *et al.*, 1976) and a strength of 5 – 7 °C (Tyson and Preston-Whyte, 2000). In contrast, elevated subsidence inversions occur throughout the day and during all seasons of the year, with a mean annual height ranging from 1000 to 2500 metres over coastal and plateau areas, respectively (Cosijn and Tyson, 1996). Strengths of elevated inversions seldom exceed 2 °C (Tyson and Preston-Whyte, 2000). Absolutely stable layers, which are considered to be a less stringent measure of stability, occur at ~700, ~500 and ~300 hPa levels over the plateau with an additional stable layer at ~850 hPa over coastal areas. Of these, the ~700 and ~500 hPa stable layers have the greatest control on the vertical and horizontal transport of aerosols, with the ~500 hPa associated with the haze layer that is present over most of southern Africa, particularly during the winter months (Cosijn and Tyson, 1996).

4.2 Local Meteorological Conditions

4.2.1 Temperature

Temperature affects the amount of pollutants emitted into the atmosphere through its influence on the degree of space heating required. In townships where access to and affordability of electricity is limited, an increase in domestic fuel combustion is observed during the winter months as the demand for space heating and cooking increases. In addition, extremely stable atmospheric conditions as a result of strong continental anticyclones result in an increase in low-level pollution during these months. The seasonal influence of other regional air pollution sources such as biomass burning is also observed during the cooler winter and spring months.

Lephalale is situated in the northern region of the Waterberg District and experiences a hot, dry climate. For the period January 2011 to December 2013, mean temperatures ranged from 26.3 °C in February to 15.2 °C in June and July (Table 4.1 and Figure 4.3). A highest mean maximum temperature of 38.0 °C was recorded during summer in January. Mean minimum temperatures remained above freezing in winter with a minimum temperature of 1.2 °C recorded in June.

Temperatures recorded on the Highveld are generally lower than the northern parts of the country, with mean temperatures ranging from 19.9 °C in January to 8.9 °C in June in Secunda. Mean temperatures in Carolina ranged from 18.9 °C in February to 8.3 °C in July (Table 4.1 and Figure 4.3). A highest mean maximum temperature of 33.5 °C was recorded in Secunda in January where a mean minimum temperature of -5.6 °C was recorded in Carolina in August. Mean minimum temperatures on the Highveld fall below freezing during the cooler winter months.

Zamdela in the Vaal Triangle is situated at a high altitude, resulting in a dry climate and ranging seasonal temperatures. Throughout January 2016 to December 2017, mean temperatures in Vereeniging ranged from 21.5 °C in December to 10.2 °C in July (Table 4.1 and Figure 4.3). The highest mean maximum temperature of 34.4 °C was recorded in January with a mean minimum temperature of -3.9 °C recorded in June.

In general, the Waterberg region experiences higher temperatures during all seasons compared to the other two regions with temperatures remaining above freezing during winter. On the Highveld and in the Vaal Triangle, temperatures are lower and fall below freezing during the winter months. The demand for space heating and cooking in the townships in each of these regions increases during the winter months when temperatures start to decline. Space heating requirements in the cooler Highveld and Vaal Triangle regions are likely to commence earlier in autumn as temperatures begin to decrease and extend into the spring months as temperatures start to warm up. The increased demand for space heating during winter results in an increase in emissions which become trapped in the lower atmosphere due to stable atmospheric conditions.

Table 4.1: Mean, mean minimum and mean maximum temperatures (°C) in each region

Month	Waterberg District			Highveld Region						Vaal Triangle		
	SAWS Lephalale (2011 – 2013)			SAWS Secunda (2014 – 2017)			SAWS Carolina (2014 – 2015) ⁽¹⁾			SAWS Vereeniging (2016 – 2017)		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Jan	25.8	18.0	37.3	19.9	10.0	33.5	18.8	9.8	29.8	21.3	11.6	34.4
Feb	26.3	17.6	37.5	19.8	10.3	31.8	18.9	10.1	30.9	21.2	12.4	31.5
Mar	25.5	15.8	38.0	18.0	6.7	30.5	16.8	6.8	28.0	19.4	5.9	30.1
Apr	21.4	11.6	34.9	15.3	3.5	28.8	14.0	3.3	25.7	16.8	4.5	29.8
May	18.5	4.5	32.8	12.2	-0.3	26.5	11.9	0.3	26.6	12.2	1.0	25.3
Jun	15.2	1.2	29.5	8.9	-4.6	23.7	9.7	-4.7	23.8	10.4	-3.9	23.3
Jul	15.2	2.5	29.1	9.1	-4.0	23.2	8.3	-5.3	21.9	10.2	-2.6	24.6
Aug	17.9	3.0	33.9	12.1	-3.6	27.3	11.1	-5.6	25.8	12.8	-2.0	27.3
Sep	22.8	7.5	36.7	16.2	0.9	32.1	15.4	-2.4	31.3	18.3	2.8	31.4
Oct	24.3	11.1	39.6	17.6	2.7	32.7	15.0	1.2	30.3	19.2	3.9	33.0
Nov	26.2	14.5	39.6	18.1	5.5	32.6	15.7	5.4	27.9	21.0	10.8	34.0
Dec	25.2	17.0	36.8	19.7	10.3	33.0	17.7	6.6	30.2	21.5	13.2	33.7

Notes:

(1) Data not available from May – December 2015

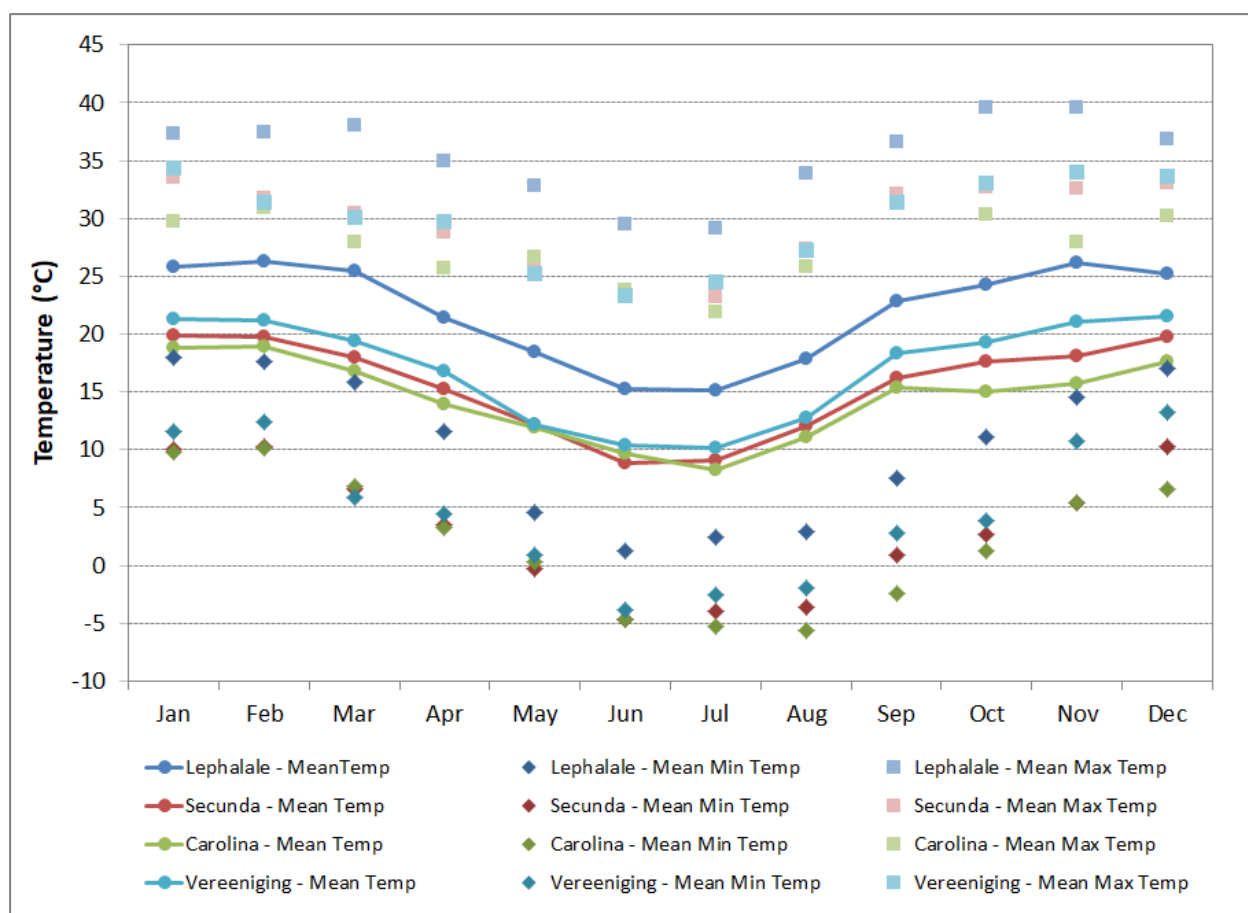


Figure 4.3: Mean, mean minimum and mean maximum temperatures (°C) in each region

4.2.2 Precipitation and Relative Humidity

Precipitation is one of the major mechanisms for removing aerosol particles in the atmosphere (Zheng *et al.*, 2019). Aerosol particles are removed by precipitation as a result of two main processes, namely, in-cloud and below-cloud removals. In-cloud removal processes involve the activation of hygroscopic aerosols which act as cloud condensation nuclei. These aerosol particles attach to the cloud droplets and are removed by falling raindrops from within the cloud (Chate *et al.*, 2003). Below-cloud removals is the process through which raindrops capture aerosol particles as they fall, thereby removing them from the atmosphere (Chate and Devara, 2005). Aerosol wet removal mechanisms are complicated and depend upon many factors including, amongst others, the aerosol size distribution, raindrop size distribution, water content, precipitation intensity and temperature (Zhao and Zheng, 2006). Mechanical collision during precipitation is the most important way of removing aerosol particles (Chate and Pranesh, 2004). While drizzle has a limited effect on the removal of fine particulate matter, light to heavy precipitation is effective in removing both fine and coarse particulate matter. A longer duration of

precipitation also results in a higher removal efficiency for coarse particulate matter (Zheng *et al.*, 2019).

Relative humidity is a significant factor affecting the chemical composition, size distributions and optical properties of aerosol particles (Day *et al.*, 2000; Hallquist *et al.*, 2009). Relative humidity plays an important role in visibility degradation (Qu *et al.*, 2015). At higher relative humidity, hygroscopic growth of aerosol particles modifies the scattering and absorption properties, which has significant impacts on radiative forcing and atmospheric visibility (Rastak *et al.*, 2014; Wang *et al.*, 2017). Higher relative humidity also encourages the gas-to-particle conversion process of precursor gases which results in the formation and accumulation of secondary species, thereby contributing to visibility impairment (Ma *et al.*, 2017).

All three regions experience a marked seasonality of precipitation with cool, dry winters and warm, wet summers. In general, Lephalale experiences less rainfall than the Highveld and Vaal Triangle regions with an average annual rainfall of 402 mm from January 2011 to December 2013. On the Highveld, both Secunda and Carolina experienced higher rainfall with an average annual rainfall of 613 mm and 487 mm from January 2014 to December 2017 (where available). The Vaal Triangle also had high rainfall throughout January 2016 to December 2017 with an annual average of 645 mm. All three regions experience the highest rainfall during the summer months (November – January) and the lowest rainfall during the winter months (June – August) (Figure 4.4 and Table 4.2). Relative humidity is generally low to moderate in Lephalale, with a minimum of 34.2% in spring (September) and a maximum of 61.8% in summer (January). Relative humidity in the Highveld region, on the other hand, generally ranges from moderate to high, reaching a maximum of 68.8% in Secunda in late summer/early autumn (February and March) and 76.5% in Carolina in autumn (March). In the Vaal Triangle, relative humidity ranged from a minimum of 40.3% in spring (September) and a maximum of 62.9% in autumn (May).

In general, pollution levels during summer in the Waterberg, Highveld and Vaal Triangle regions will be lower due to the higher rainfall experienced during these months. Rainfall events will wash out aerosol particles (and other pollutants) from the atmosphere. During the cooler winter months, less rainfall, combined with increased atmospheric stability, results in the accumulation of pollutants in the lower atmosphere.

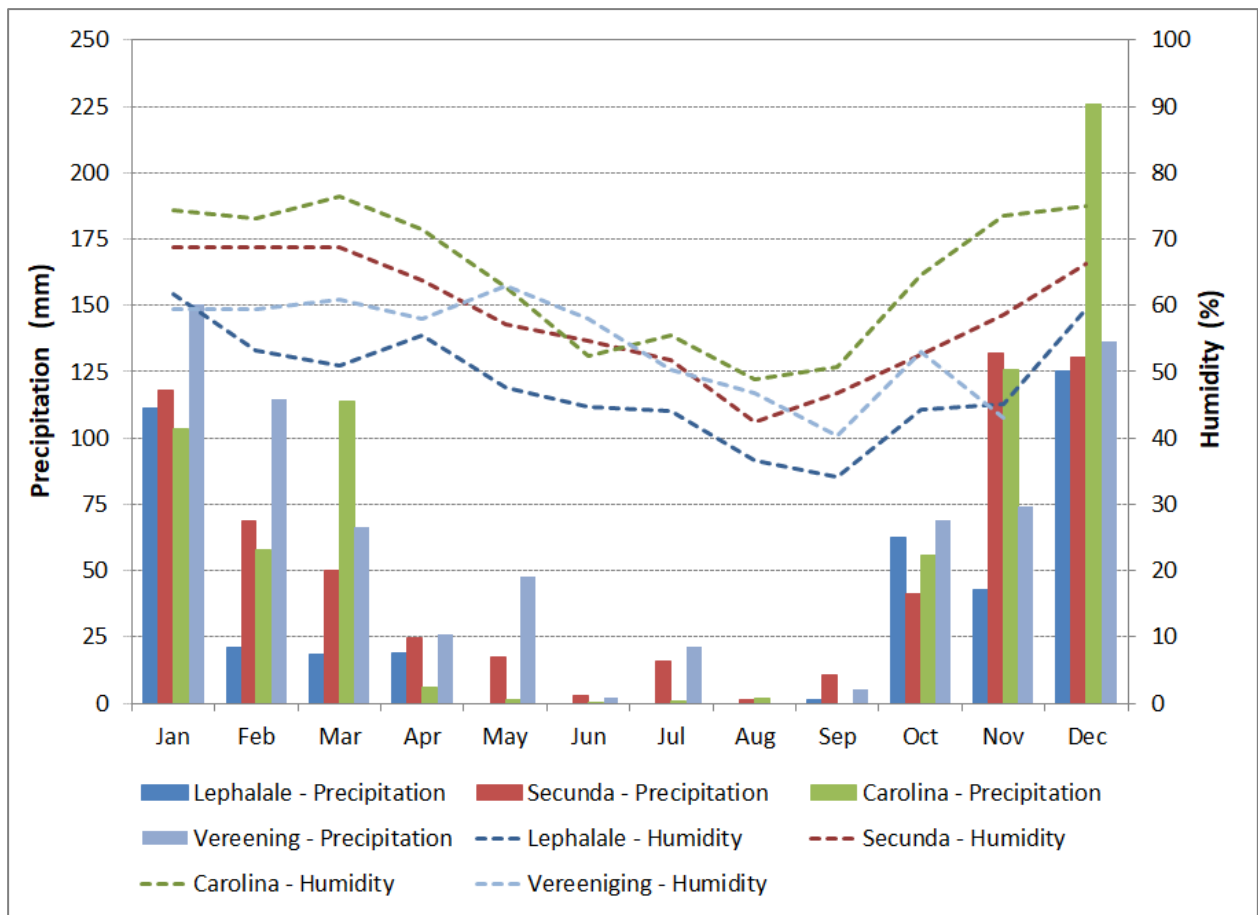


Figure 4.4: Average monthly precipitation (mm) and relative humidity (%) in each region

Table 4.2: Average monthly precipitation (mm) and relative humidity (%) in each region

Month	Waterberg Region		Highveld Region				Vaal Triangle Region	
	SAWS Lephalale (2011 – 2013)		SAWS Secunda (2014 – 2017)		SAWS Carolina (2014 – 2015) ⁽¹⁾		SAWS Vereeniging (2016 – 2017) ⁽²⁾	
	Rainfall	Humidity	Rainfall	Humidity	Rainfall	Humidity	Rainfall	Humidity
Jan	111	61.8	118	68.7	103	74.3	150	59.5
Feb	21	53.2	69	68.8	58	73.0	115	59.4
Mar	18	51.0	50	68.8	114	76.5	66	60.8
Apr	19	55.6	24	63.7	6	71.5	26	57.9
May	0	47.5	18	57.2	1	62.7	48	62.9
Jun	0	44.7	3	54.7	0	52.3	2	58.0
Jul	0	44.1	16	51.8	1	55.5	21	50.2
Aug	0	36.7	1	42.4	2	48.9	0	46.9
Sep	1	34.2	11	46.8	0	50.8	5	40.3
Oct	63	44.3	41	52.5	56	64.6	69	53.0
Nov	43	45.2	132	58.5	126	73.5	74	43.0
Dec	125	59.5	131	66.2	226	75.1	136	-
Annual Average	402	48.1	613	58.3	487	69.0	645	51.6

Notes:

(1) Data not available from May – December 2015

(2) Humidity data not available for the period September 2016 – June 2017; Rainfall and humidity data not available for December 2017

4.2.3 Wind Field

Wind direction and wind speed have a significant influence on the dispersion and dilution of air pollution in the atmosphere. Winds have a direct influence on transport, atmospheric stability and mixing of air pollution (Tyson and Preston-Whyte, 2000).

4.2.3.1 Waterberg

The surface wind field in Lephalale is dominated by winds from the east-northeast and easterly directions, shifting to the east-southeast, south-east and south-southeast in Marapong (Figure 4.5). Calm conditions have a low frequency of occurrence in the region with the exception of the SAWS Lephalale weather station which recorded a high frequency of calm conditions (29% of the time). Wind speeds are generally slow to moderate in the region with average wind speeds ranging between 2 – 4 m/s.

A distinct variation is not observed in the seasonal wind field in the Lephalale region (Figure 4.6). Seasonal winds remain predominantly from the east and east-northeast (Lephalale) and southeast (Marapong) during all seasons. An increase in wind speeds is noted during the spring months (September – November).

Localised emission sources in the Lephalale area include Grootgeluk Coal Mine and Matimba and Medupi Power Stations. The prevailing wind field in the Lephalale area suggests emissions from these sources will be transported away from the residential areas of Marapong and Lephalale although the contribution of these sources (especially low-level emitting sources such as coal mining) to the aerosol loading in the area cannot be discounted. Marapong is situated close to Grootgeluk Coal Mine with Matimba's ash dump to the south.

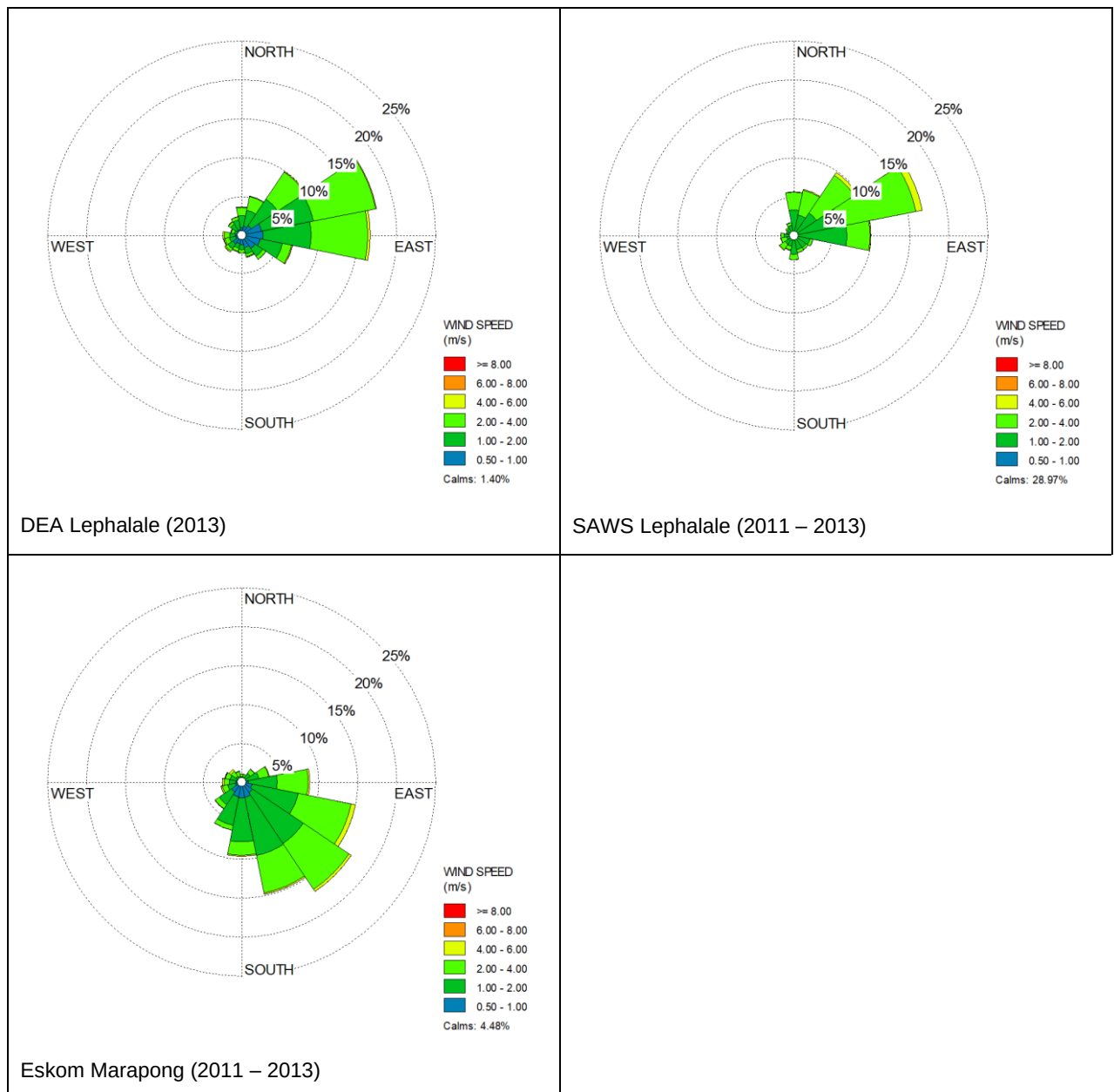


Figure 4.5: Wind field of the Lephalale region for 2011 - 2013

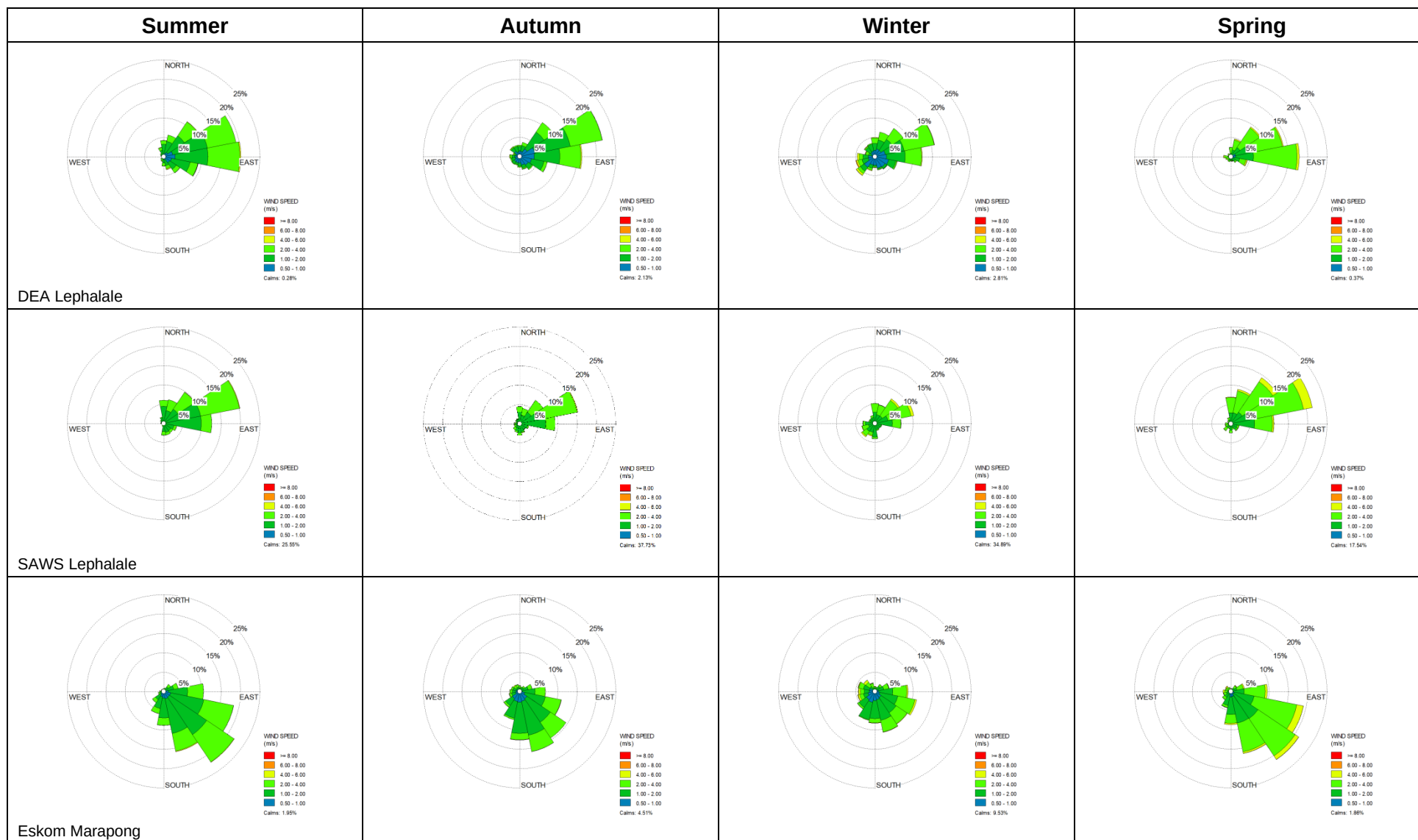


Figure 4.6: Seasonal wind field of the Lephale region for 2011 - 2013

4.2.3.2 Highveld Region

The western Highveld region is characterised by winds from the north-east and east-northeast in Embalenhle with a slight shift to the north and north-northeast observed in Secunda (Figure 4.7). In Kwazamokhule further to the east, the wind field shows a similar signature to Embalenhle with an additional component observed from the south-southeast. The DEA Hendrina station shows a predominant easterly and westerly wind field. Winds are generally moderate to fast in the region with calm conditions occurring infrequently (less than 14% of the time).

The seasonal wind field in the region is dominated by winds from the easterly sector during summer with more prevalent westerly components observed during winter (Figure 4.8). This is consistent with the seasonal changes that occur in the circulation over southern Africa with easterly waves prevalent during summer and westerly waves intensifying during winter and shifting northwards (Tyson and Preston-Whyte, 2000).

The prevailing wind field in Embalenhle shows that surrounding sources such as Sasol Synfuels to the immediate west and mining to the north may contribute to the aerosol loading in the township. In Kwazamokhule, the frequent northwesterly and easterly winds suggest that emissions from Hendrina Power Station and the surrounding coal mines will influence the aerosol loading in the township during these periods.

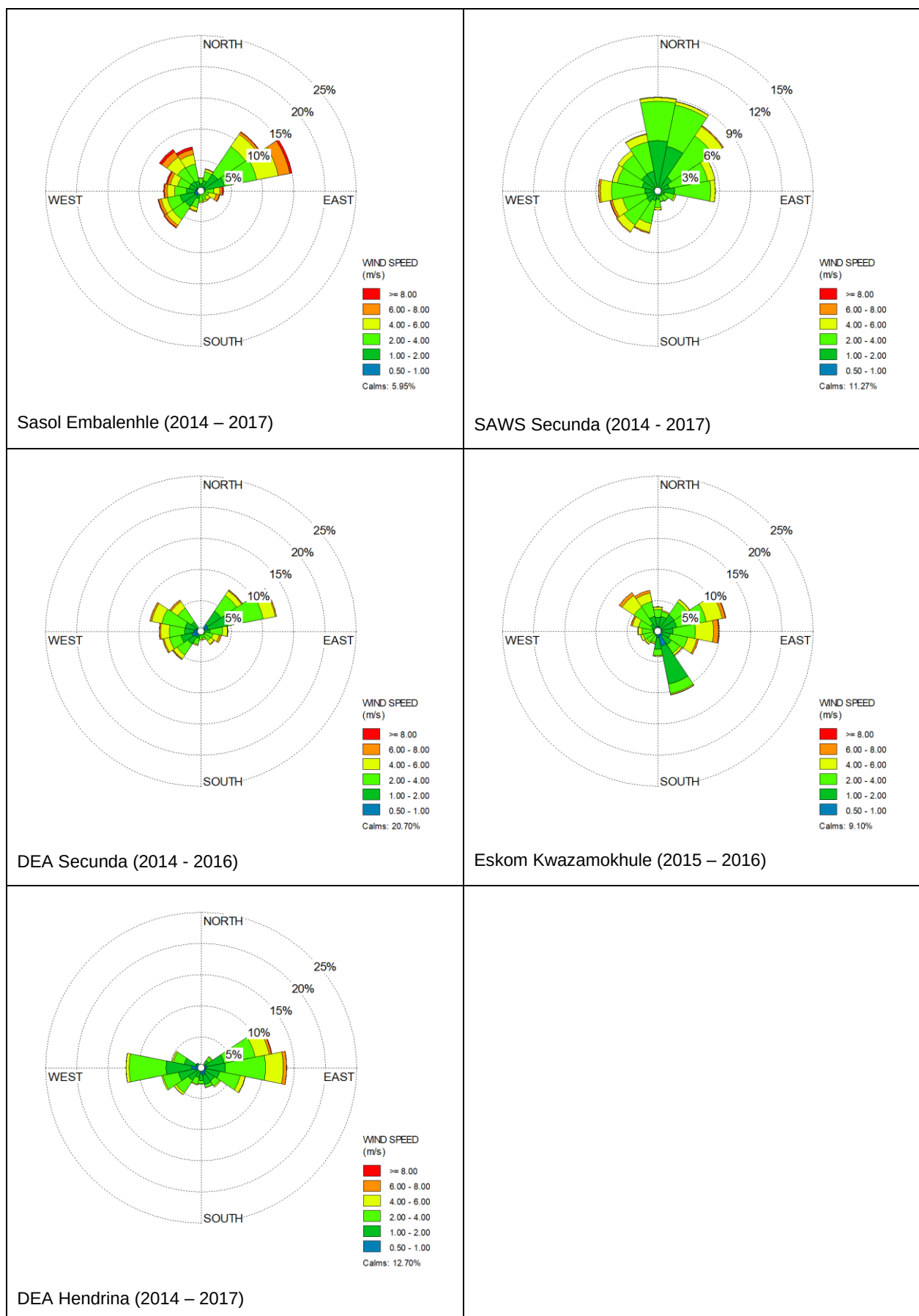
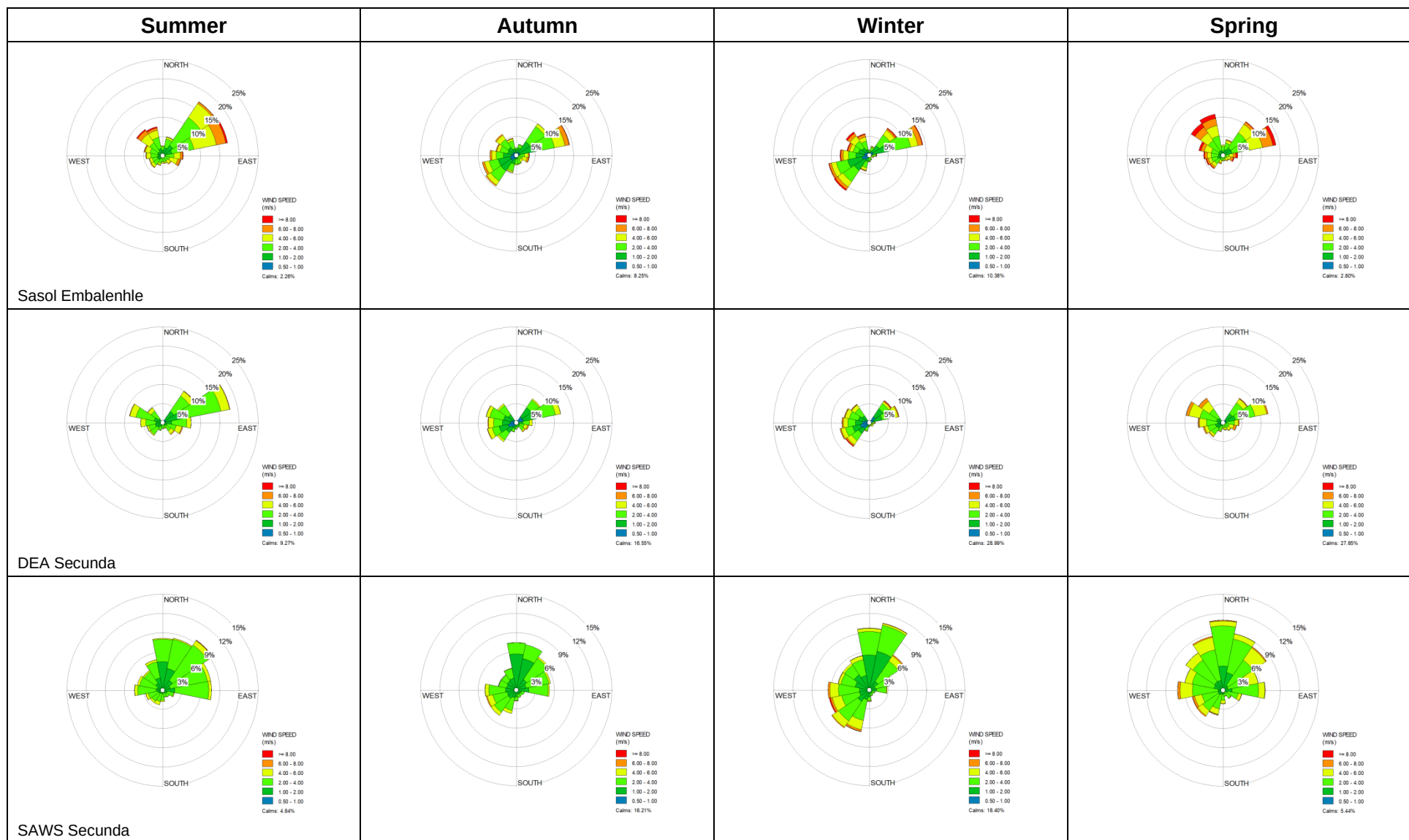


Figure 4.7: Wind field of the Highveld region for 2014 – 2017



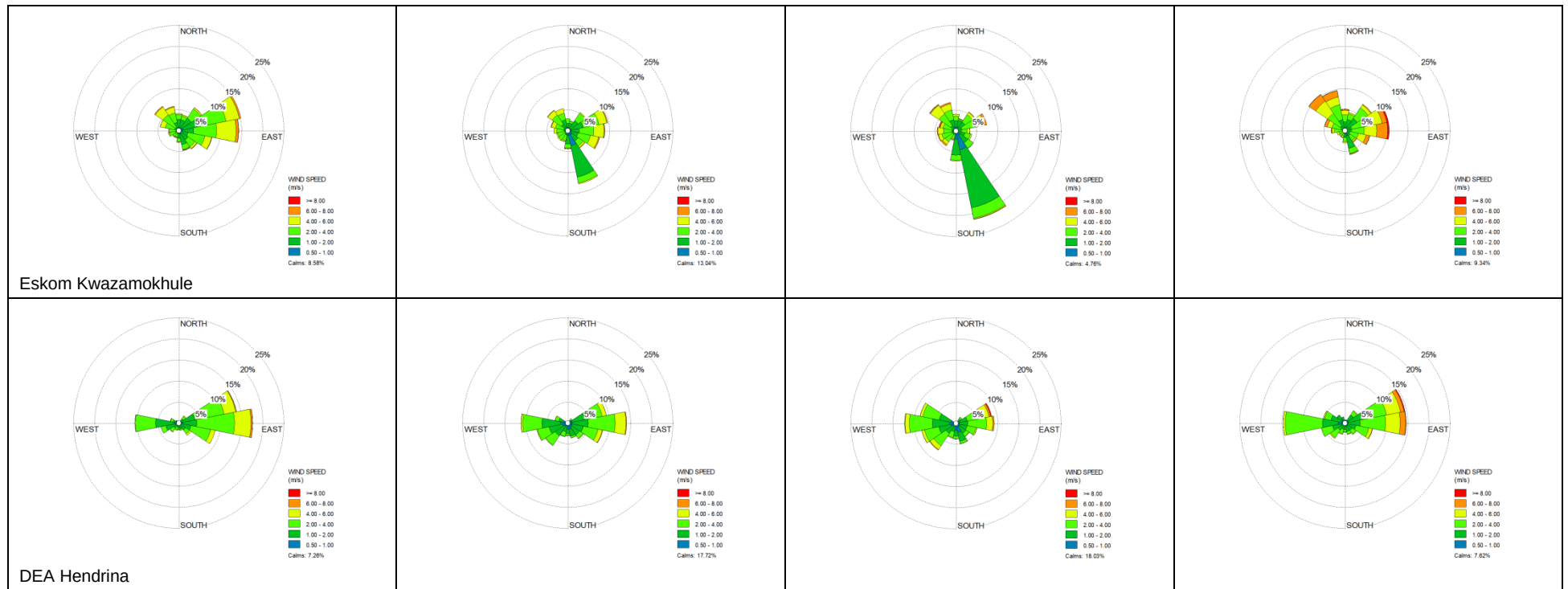


Figure 4.8: Seasonal wind field of the Highveld region for 2014 - 2017

4.2.3.3 Vaal Triangle

The surface wind field at Zamdela is dominated by winds from the easterly and westerly sectors at both stations (Figure 4.9). Wind speeds were moderate to fast with calm conditions occurring less than 5% of the time. The seasonal wind field at Zamdela is dominated by winds from the easterly sector during summer and autumn and from the westerly sector during winter and spring based on the seasonal circulation changes over southern Africa (Figure 4.10).

Zamdela is located to the immediate south of the petrochemical facilities of Sasol and Natref with Sigma Colliery located to the northwest of the township. Emissions from these local sources will influence the township when winds originate from the northerly and northwesterly sectors. Wind-blown dust from surrounding agricultural activities is also a likely source of dust emissions in the township.

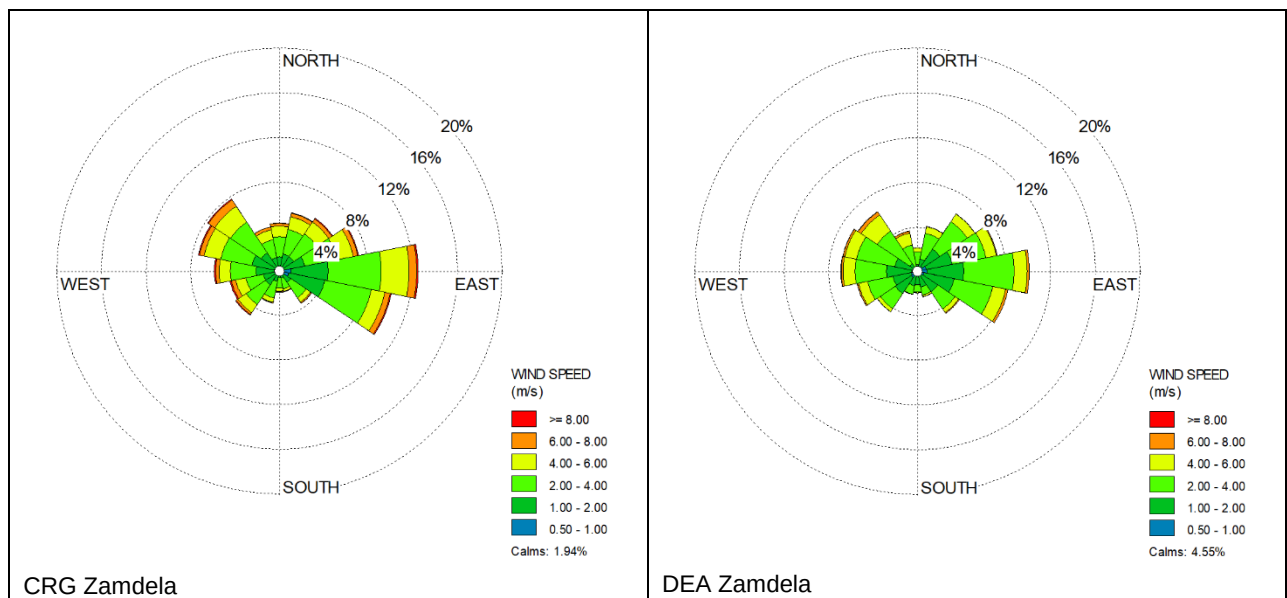


Figure 4.9: Wind field of the Vaal Triangle region for 2016 – 2017

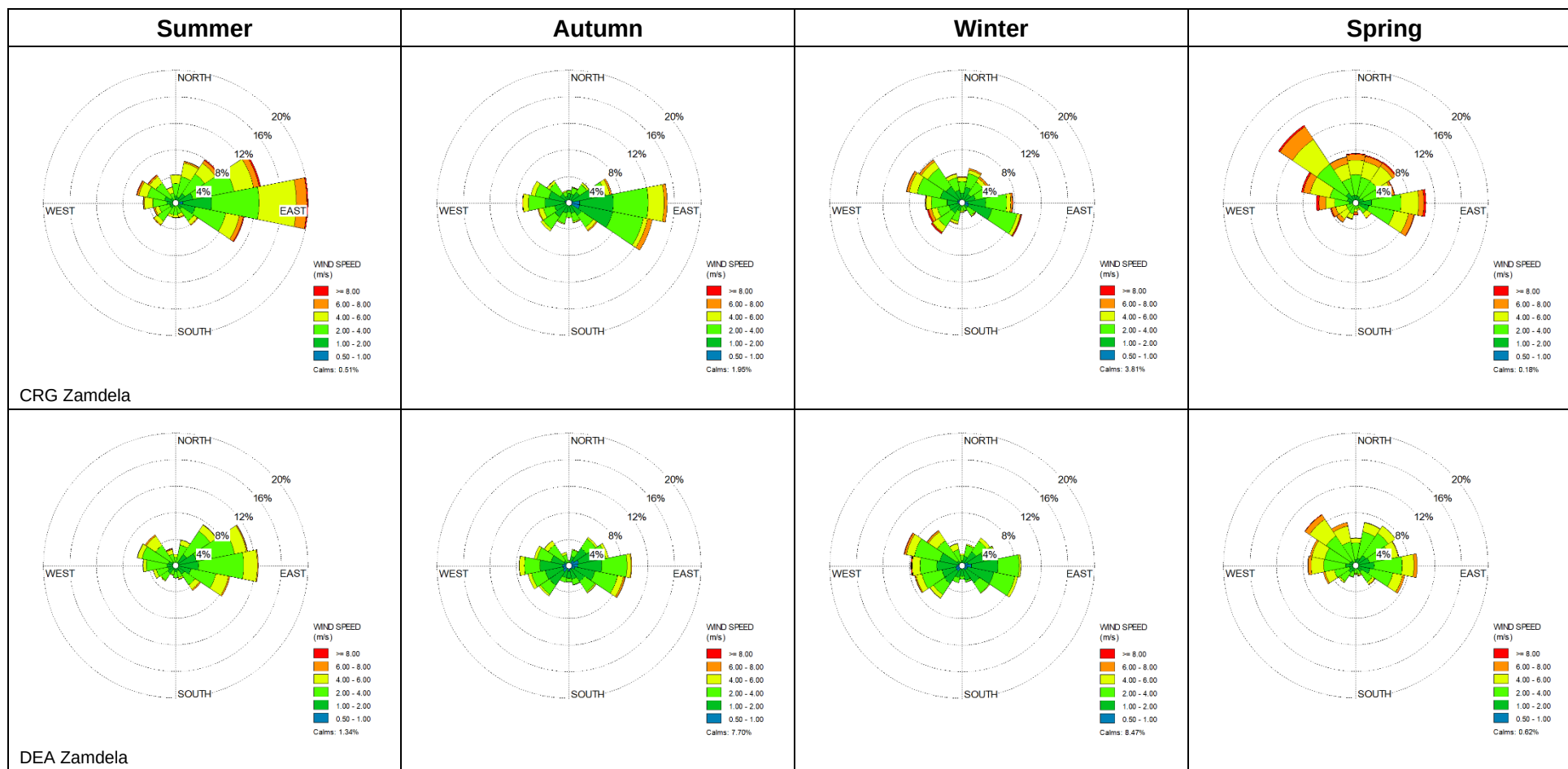


Figure 4.10: Seasonal wind field of the Vaal Triangle region for 2016 – 2017

The prevailing atmospheric transport patterns influencing the distribution of aerosols over the southern African sub-continent has been considered. The climate and local meteorological conditions in each of the study regions have also been described. The existing ambient air quality situation in each region and during each sampling campaign is presented in Chapter 5.

CHAPTER 5 EXISTING AIR QUALITY SITUATION

The existing ambient air quality situation in each region and during each sampling campaign is evaluated using available ambient air quality monitoring data. The spatial and temporal variability of particulate concentrations is also discussed.

5.1 National Ambient Air Quality Standards

National ambient air quality standards for SO₂, NO₂, PM₁₀, O₃, C₆H₆, Pb and CO were published on 24 December 2009 (Government Notice 1210 of 2009, Government Gazette 32816) in terms of section (9)1 of the NEM:AQA, 2004 (Act No. 39 of 2004). On 29 June 2012, National ambient air quality standards for PM_{2.5} were also established (Government Notice 486 of 2012; Government Gazette 35463). The National ambient air quality standards for PM₁₀ and PM_{2.5} as applicable to this study, are presented in Table 5.1.

Table 5.1: National ambient air quality standards

Pollutant	Averaging Period	Concentration (µg/m ³)	Frequency of Exceedance	Compliance Date
Particulate Matter (PM ₁₀)	24-hour	75	4	01 Jan 2015
	Annual	40	0	01 Jan 2015
Particulate Matter (PM _{2.5})	24-hour	40	4	01 Jan 2016 – 31 Dec 2029
		25	4	01 Jan 2030
	Annual	25	0	01 Jan 2016 – 31 Dec 2029
		20	0	01 Jan 2030

5.2 Ambient Air Quality Situation

5.2.1 Waterberg Region

5.2.1.1 Lephalale

Ambient PM₁₀ concentrations in Marapong are elevated with a 99th percentile 24-hour average PM₁₀ concentration of 266.27 µg/m³ recorded over the period January 2012 to December 2013 (Table 5.2). However, in Lephalale, ambient PM₁₀ concentrations are lower with a 99th percentile 24-hour average PM₁₀ concentration of 73.5 µg/m³ recorded in 2013. Measured PM₁₀ concentrations in Marapong are over three times the 24-hour average PM₁₀ standard of 75

$\mu\text{g}/\text{m}^3$ with a total of 281 exceedances of the standard recorded over the monitoring period. The standard was exceeded on three occasions in Lephalale, within the allowable four exceedances per annum. Annual average PM_{10} concentrations exceeded the annual average PM_{10} standard of $40 \mu\text{g}/\text{m}^3$ in Marapong with an annual average concentration of $85.5 \mu\text{g}/\text{m}^3$ and $71.1 \mu\text{g}/\text{m}^3$ recorded in 2012 and 2013, respectively. Annual average PM_{10} concentrations were compliant in Lephalale for 2013 with an annual average concentration of $31.4 \mu\text{g}/\text{m}^3$.

Ambient 24-hour average $\text{PM}_{2.5}$ concentrations in Marapong are also elevated with a 99th percentile 24-hour average $\text{PM}_{2.5}$ concentration of $102.5 \mu\text{g}/\text{m}^3$ recorded during 2012 – 2013 (Table 5.2). However, ambient $\text{PM}_{2.5}$ concentrations in Lephalale fell below the 24-hour average $\text{PM}_{2.5}$ standard with a 99th percentile concentration of $35.8 \mu\text{g}/\text{m}^3$ recorded in 2013. Measured $\text{PM}_{2.5}$ concentrations in Marapong are almost three times the 24-hour average $\text{PM}_{2.5}$ standard of $40 \mu\text{g}/\text{m}^3$. The $\text{PM}_{2.5}$ standard was exceeded on 190 occasions in Marapong, well over the allowable four exceedances per annum. Annual average $\text{PM}_{2.5}$ concentrations also exceeded the annual average $\text{PM}_{2.5}$ standard of $25 \mu\text{g}/\text{m}^3$ in Marapong in 2012 with an annual average concentration of $43.3 \mu\text{g}/\text{m}^3$ although annual average concentrations were compliant in 2013 ($12.1 \mu\text{g}/\text{m}^3$). Annual average $\text{PM}_{2.5}$ concentrations in Lephalale fell below the annual average standard in 2013 with an annual average concentration of $13.7 \mu\text{g}/\text{m}^3$.

A distinct seasonal variation is observed in the dataset with elevated PM_{10} and $\text{PM}_{2.5}$ concentrations during the winter and early spring months for the period 2012 - 2013 (Figure 5.1 - Figure 5.2). The strong seasonal variation is also seen in the PM_{10} and $\text{PM}_{2.5}$ concentrations recorded during the aerosol sampling campaigns, with elevated concentrations during the winter 2012 sampling campaign and significantly lower concentrations during the summer 2013 sampling campaign. The elevated concentrations during the winter months are likely associated with increased domestic fuel burning combined with strong atmospheric stability which traps pollutants in the lower atmosphere. In summer, the demand for space heating is lower and as such, emissions from domestic fuel burning are reduced. Good atmospheric dispersion also promotes the effective transport and dilution of pollutants during the warmer, summer months.

During the winter 2012 sampling campaign, 99th percentile 24-hour average PM_{10} concentrations exceeded the 24-hour average PM_{10} standard with a concentration of $120.7 \mu\text{g}/\text{m}^3$ recorded in Marapong (Table 5.2). The PM_{10} standard was exceeded on 12 occasions (out of a total of 18 days) in Marapong. 99th percentile 24-hour average $\text{PM}_{2.5}$ concentrations exceeded the 24-hour average $\text{PM}_{2.5}$ standard with a concentration of $74.8 \mu\text{g}/\text{m}^3$ recorded in Marapong. The $\text{PM}_{2.5}$ standard was exceeded on nine occasions (out of a total of 18 days) in Marapong. During the summer 2013 campaign, a decrease in concentrations is noted with a 99th percentile 24-hour average PM_{10} concentration of $59.1 \mu\text{g}/\text{m}^3$ and $58.8 \mu\text{g}/\text{m}^3$ recorded in

Marapong and Lephalale, respectively. Ambient $PM_{2.5}$ concentrations also fell below the standard with a 99th percentile 24-hour average concentration of $23.3 \mu\text{g}/\text{m}^3$ and $20.0 \mu\text{g}/\text{m}^3$ recorded in Marapong and Lephalale, respectively. A similar trend is observed in PM_{10} and $PM_{2.5}$ concentrations at both Marapong and Lephalale during the summer sampling campaign which is indicative of a common contributing source to the atmospheric aerosol loading at both sites.

The diurnal profile of ambient PM_{10} and $PM_{2.5}$ concentrations in Marapong and Lephalale is shown in Figure 5.3. A characteristic bi-modal distribution is seen in the diurnal profile with elevated concentrations during the early morning (05:00 – 09:00) and in the evening (17:00 – 22:00) in Marapong. These times correspond with increased periods of domestic fuel burning for space heating and cooking in Marapong as well as increased vehicular traffic emissions as people leave and return from work. The diurnal profile in Lephalale is less pronounced suggesting the contribution of a local source to the aerosol loading in Marapong, especially during the winter months.

A high degree of variability in PM_{10} and $PM_{2.5}$ concentrations is evident between Lephalale and Marapong which is indicative of the complex nature of air quality over small spatial scales. Localised sources have a greater impact in Marapong, particularly during the winter months, despite the township's proximity to Lephalale.

Table 5.2: Summary of air quality statistics for Lephalale and Marapong

DEA Lephalale (Jan 2013 – Dec 2013)

Pollutant	Averaging Period	National Standard	Allowable Exceedances	Period Average (Mean)	99% Confidence Interval	Number of data points	Number of Exceedances	Standard Deviation	Median	Percentiles		
										P25	P75	P99
PM ₁₀	24 Hour	75	4	31.4	29 - 34	303	3	18.0	28.5	16.2	43.6	73.5
	Annual	40	0	31.4	-	1	0	-	-	-	-	-
PM _{2.5}	24 Hour	40	4	13.7	13 - 15	304	0	8.0	12.3	7.5	19.2	35.8
	Annual	20	0	13.7	-	1	0	-	-	-	-	-

Eskom Marapong (Jan 2012 – Dec 2013)

Pollutant	Averaging Period	National Standard	Allowable Exceedances	Period Average (Mean)	99% Confidence Interval	Number of data points	Number of Exceedances	Standard Deviation	Median	Percentiles		
										P25	P75	P99
PM ₁₀	24 Hour	75	4	78.5	73 - 84	713	281	55.2	65.2	43.6	98.7	266.3
	Annual	40	0	78.5	-	2	2	-	-	-	-	-
PM _{2.5}	24 Hour	40	4	28.3	26 – 31	705	190	25.3	17.8	9.4	41.7	102.5
	Annual	20	0	28.3	-	2	1	-	-	-	-	-

Table 5.3: Statistics for 24-hour average PM₁₀ and PM_{2.5} concentrations during the aerosol sampling campaigns in Lephalale and Marapong

DEA Lephalale

Statistics	15 Aug – 1 Sep 2012		11 Feb – 24 Feb 2013	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Period Average (µg/m ³)	N/A	N/A	23.5	9.9
Number of Exceedances	N/A	N/A	0	0
Standard Deviation	N/A	N/A	14.1	5.3
Median (µg/m ³)	N/A	N/A	20.6	8.8
99 th Percentile (µg/m ³)	N/A	N/A	58.8	20.0
% Data Capture	N/A	N/A	100	100

Notes:

N/A = Not Available

Eskom Marapong

Statistics	15 Aug – 1 Sep 2012		11 Feb – 24 Feb 2013	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Period Average (µg/m ³)	87.7	43.6	37.0	14.8
Number of Exceedances	12	9	0	0
Standard Deviation	20.8	14.0	12.7	5.0
Median (µg/m ³)	92.0	40.4	33.7	12.6
99 th Percentile (µg/m ³)	120.7	74.8	59.1	23.3
% Data Capture	100	94	100	100

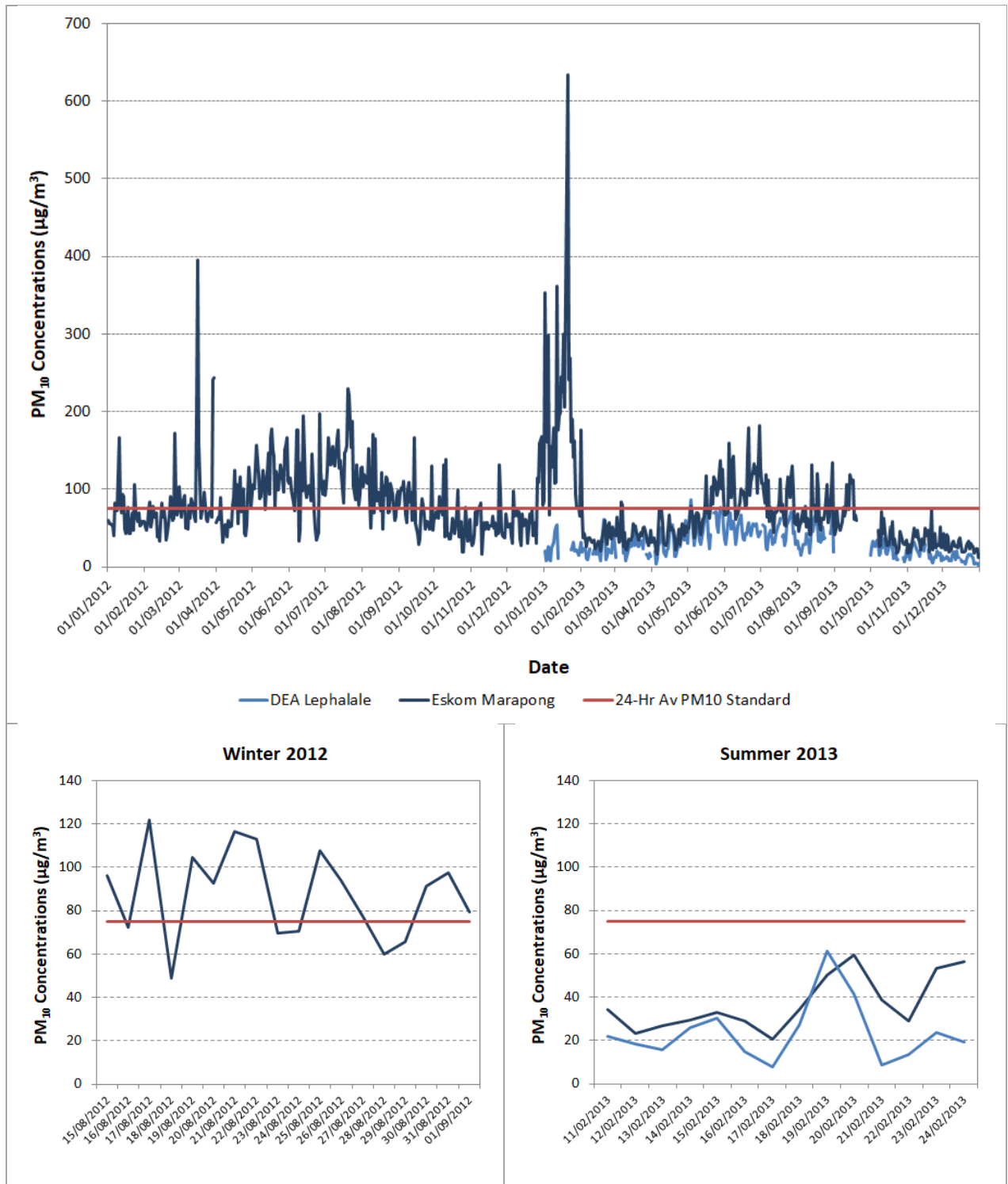


Figure 5.1: Ambient 24-hour average PM₁₀ concentrations for the period (top), winter 2012 (bottom left) and summer 2013 (bottom right) sampling campaigns in Lephale and Marapong.

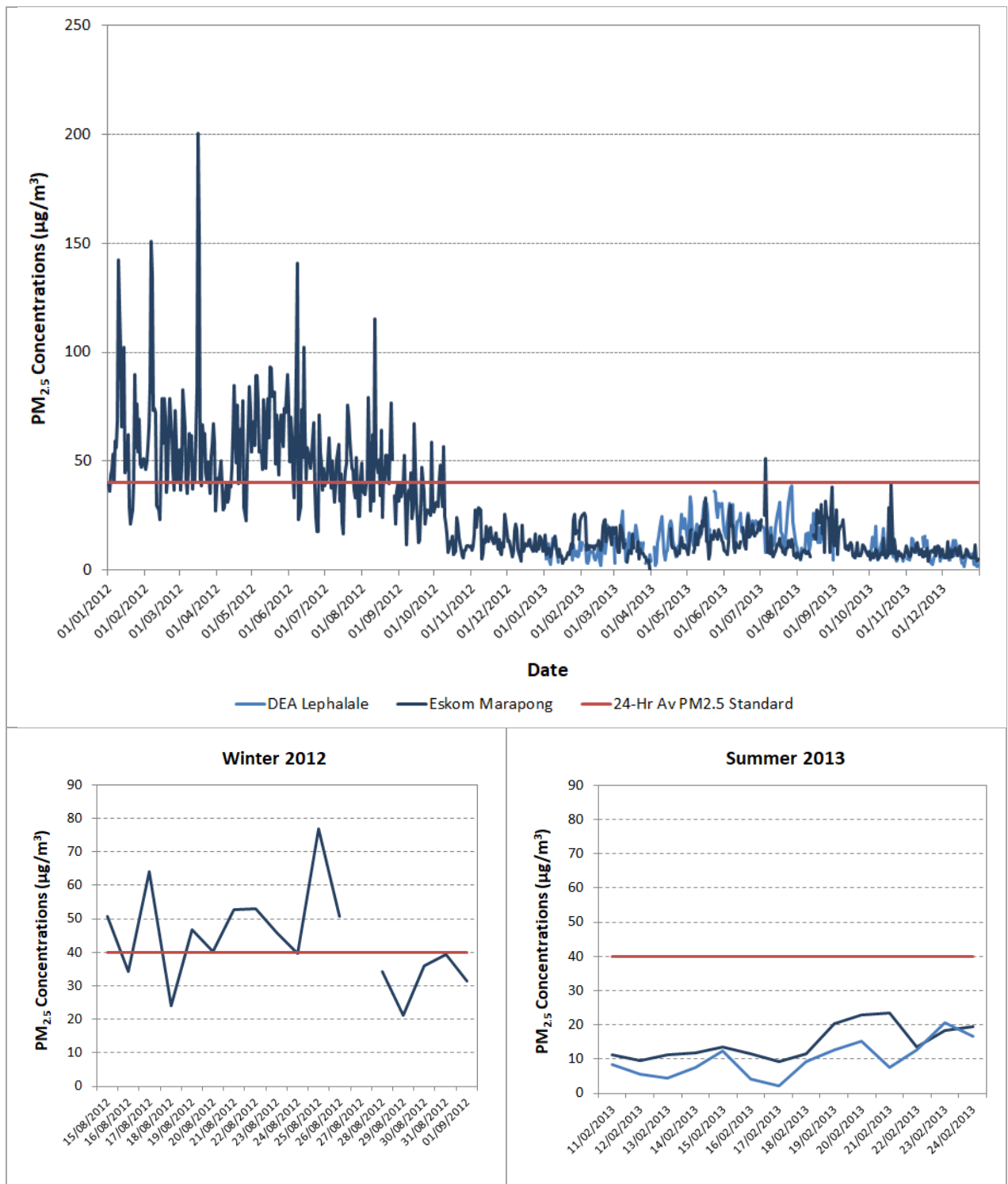


Figure 5.2: Ambient 24-hour average PM_{2.5} concentrations for the period (top), winter 2012 (bottom left) and summer 2013 (bottom right) sampling campaigns in Lephalale and Marapong.

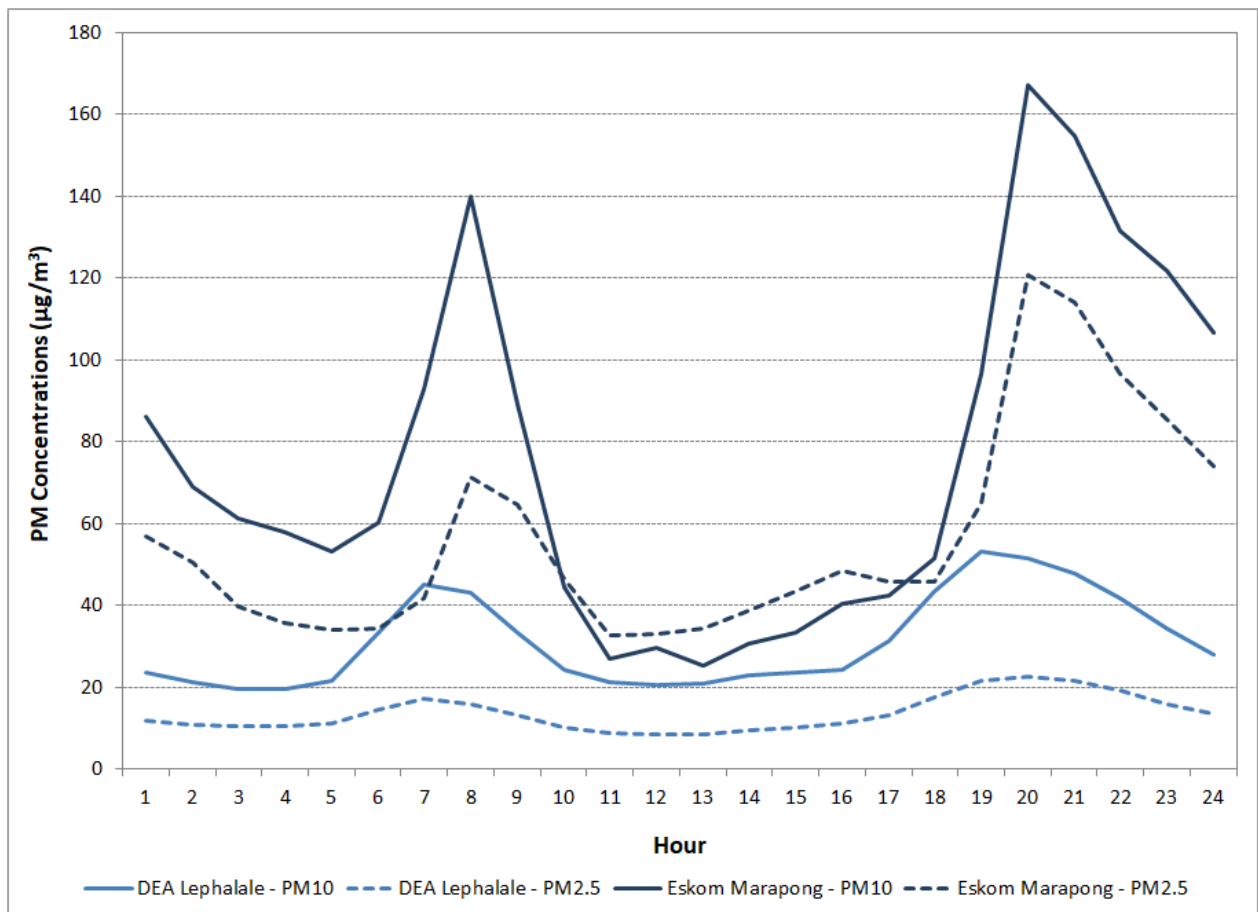


Figure 5.3: Diurnal PM₁₀ and PM_{2.5} concentrations in Lephalale and Marapong

5.2.2 Highveld Region

5.2.2.1 Kwazamokhule

Over the respective monitoring periods, elevated 99th percentile 24-hour average PM₁₀ concentrations of 99.4 µg/m³ and 183.7 µg/m³ were recorded in Hendrina and Kwazamokhule, respectively (Table 5.4). A total of 55 and 140 exceedances were recorded in Hendrina and Kwazamokhule over the respective three year and one year monitoring periods. It is interesting to note that a significantly higher number of exceedances were recorded in Kwazamokhule over a shorter space of time. This would suggest that the DEA Hendrina station is not capturing the impact of domestic fuel burning emissions, although it was primarily sited to measure the impacts from the Hendrina Power Station. Annual average PM₁₀ concentrations exceeded the annual average PM₁₀ standard on one occasion in 2014 (45.1 µg/m³) in Hendrina and in 2015 (75.6 µg/m³) in Kwazamokhule. However, it should be noted that data capture at the DEA Hendrina station was below 60% for 2014 and 50% for 2017 and as such, an annual average PM₁₀ concentration cannot be accurately determined.

Ambient 24-hour average PM_{2.5} concentrations in Kwazamokhule and surrounding areas are also elevated with a 99th percentile 24-hour average PM_{2.5} concentration of 52.1 µg/m³ and 102.8 µg/m³ recorded respectively in Hendrina and Kwazamokhule (Table 5.4). A total of 49 (Hendrina) and 124 (Kwazamokhule) exceedances were recorded over the respective monitoring periods. As seen with ambient PM₁₀ concentrations, higher PM_{2.5} concentrations are recorded in Kwazamokhule. Annual average PM_{2.5} concentrations exceeded the annual average PM₁₀ standard in 2014 (25.8 µg/m³) in Hendrina and in 2015 (38.5 µg/m³) in Kwazamokhule. However, as mentioned above, data capture was low at the DEA Hendrina station in 2014 and 2017.

A distinct seasonal variation in PM₁₀ and PM_{2.5} concentrations is also seen in Hendrina and Kwazamokhule, with elevated PM₁₀ and PM_{2.5} concentrations during the winter 2015 sampling campaign and significantly lower concentrations during the summer 2016 sampling campaign (Figure 5.4 - Figure 5.5). The strong seasonality of emissions from domestic fuel burning combined with the prevailing atmospheric conditions during the seasons is likely to contribute to the variability seen in the PM₁₀ and PM_{2.5} concentrations at these sites.

During the winter 2015 sampling campaign, 99th percentile 24-hour average PM₁₀ concentrations exceeded the 24-hour average PM₁₀ standard with a concentration of 81.3 µg/m³ and 149.9 µg/m³ recorded in Hendrina and Kwazamokhule, respectively (Table 5.5) The 24-hour average PM₁₀ standard was exceeded 16 times (out of a total of 17 days) in Kwazamokhule. Ambient 99th percentile 24-hour average PM_{2.5} concentrations exceeded the 24-hour average PM_{2.5} standard with a concentration of 83.6 µg/m³ (and 15 exceedances) recorded in Kwazamokhule during the winter sampling campaign. The standard was approached in Hendrina with a 99th percentile 24-hour average concentration of 39.3 µg/m³. During the summer 2016 campaign, 99th percentile 24-hour average PM₁₀ concentrations of 65.6 µg/m³ and 84.4 µg/m³ were recorded in Hendrina and Kwazamokhule, respectively (Table 5.5). Ambient 99th percentile 24-hour average PM_{2.5} concentrations of 37.1 µg/m³ and 56.6 µg/m³ were also recorded in Hendrina and Kwazamokhule, respectively. The PM₁₀ and PM_{2.5} standards were exceeded on one and three occasions (out of a total of 14 days), respectively. In general, ambient PM₁₀ and PM_{2.5} concentrations show different signatures in both Hendrina and Kwazamokhule, suggesting the contribution of different sources to these sites. In summer, the difference is less pronounced.

The diurnal profile of ambient PM₁₀ and PM_{2.5} concentrations in Hendrina and Kwamokhule is shown in Figure 5.6. The diurnal profile shows elevated concentrations during the early morning (05:00 – 09:00) and in the evening (16:00 – 21:00). The morning and evening peaks are not as

pronounced at Hendrina which shows the significant influence of domestic fuel burning on ambient particulate concentrations in Kwazamokhule.

A high degree of variability in particulate concentrations is also seen in Kwazamokule and Hendrina which again demonstrates the complex nature of air quality over small spatial scales. Significantly higher particulate concentrations are recorded in Kwazamokhule compared to Hendrina, which is located to the southwest of Kwazamokhule. During the cooler winter months, increased emissions from domestic fuel burning are likely to be a significant contributor to the air quality in Kwazamokhule.

Table 5.4: Summary of air quality statistics for Hendrina and Kwazakmohule

DEA Hendrina (Jan 2014 – Dec 2017)

Pollutant	Averaging Period	National Standard	Allowable Exceedances	Period Average (Mean)	99% Confidence Interval	Number of data points	Number of Exceedances	Standard Deviation	Median	Percentiles		
										P25	P75	P99
PM ₁₀	24 Hour	75	4	31.8	30 - 34	1070	55	21.6	26.7	16.6	41.9	99.4
	Annual	40	0	31.8	-	4	1	-	-	-	-	-
PM _{2.5}	24 Hour	40	4	17.7	17 - 18	1070	49	11.1	15.5	9.9	23.1	52.1
	Annual	20	0	17.7	-	4	1	-	-	-	-	-

Eskom Kwazamokhule (Jan 2015 – Mar 2016)

Pollutant	Averaging Period	National Standard	Allowable Exceedances	Period Average (Mean)	99% Confidence Interval	Number of data points	Number of Exceedances	Standard Deviation	Median	Percentiles		
										P25	P75	P99
PM ₁₀	24 Hour	75	4	68.6	63 – 74	398	140	41.8	57.4	37.7	96.4	183.7
	Annual	40	0	75.6 ⁽¹⁾	-	1	1	-	-	-	-	-
PM _{2.5}	24 Hour	40	4	35.6	33 - 38	404	124	22.4	28.1	20.4	47.2	102.8
	Annual	20	0	38.5 ⁽¹⁾	-	1	1	-	-	-	-	-

Notes:

(1) For the period Jan – Dec 2015

Table 5.5: Statistics for 24-hour average PM₁₀ and PM_{2.5} concentrations during the aerosol sampling campaigns in Hendrina and Kwazamokhule

DEA Hendrina

Statistics	6 – 22 Jul 2015		23 Feb – 7 Mar 2016	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Period Average (µg/m ³)	56.5	27.6	26.2	15.2
Number of Exceedances	1	0	0	0
Standard Deviation	13.9	8.1	15.9	10.0
Median (µg/m ³)	51.8	26.2	20.8	9.9
99 th Percentile (µg/m ³)	81.3	39.3	65.6	37.1
% Data Capture	100	100	81.3	81.3

Eskom Kwazamokhule

Statistics	6 – 22 Jul 2015		23 Feb – 7 Mar 2016	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Period Average (µg/m ³)	113.6	59.0	43.6	27.1
Number of Exceedances	16	15	1	3
Standard Deviation	27.2	14.4	23.0	13.1
Median (µg/m ³)	109.9	58.4	49.1	21.8
99 th Percentile (µg/m ³)	149.9	83.6	84.4	56.6
% Data Capture	100	100	100	100

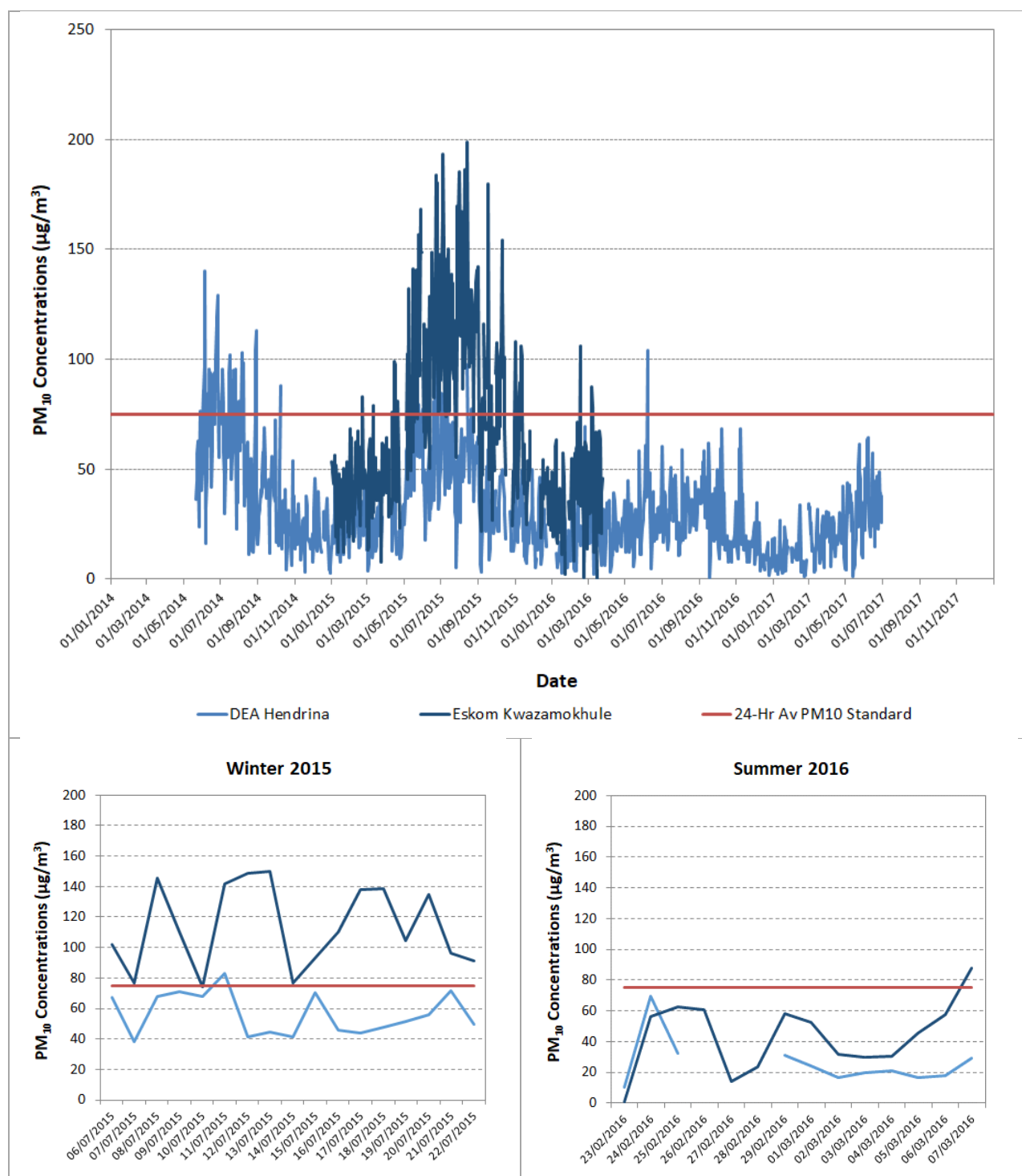


Figure 5.4: Ambient 24-hour average PM₁₀ concentrations for the period (top), winter 2015 (bottom left) and summer 2016 (bottom right) sampling campaigns in Hendrina and Kwazamokhule.

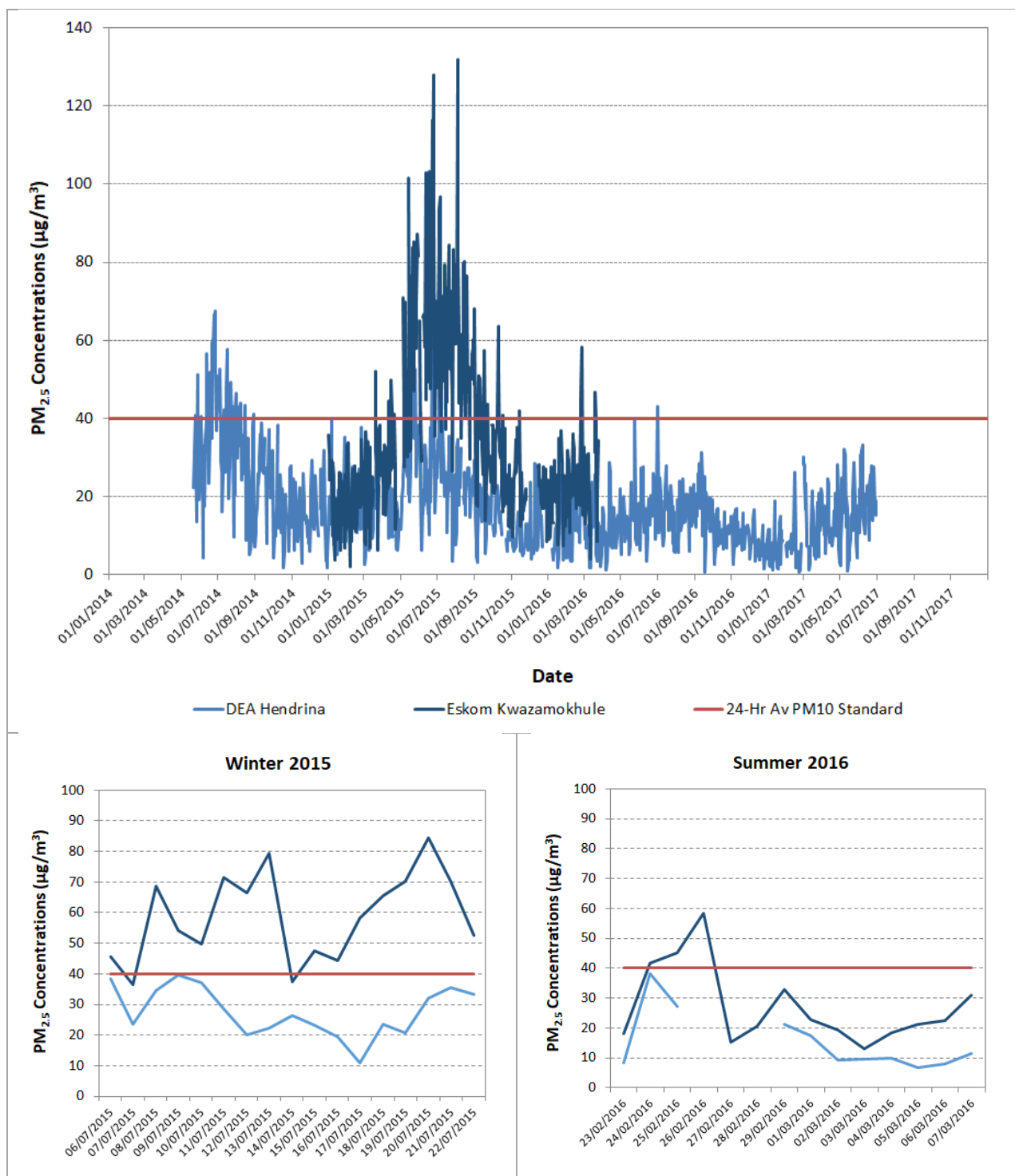


Figure 5.5: Ambient 24-hour average PM_{2.5} concentrations for the period (top), winter 2015 (bottom left) and summer 2016 (bottom right) sampling in Hendrina and Kwazamokhule.

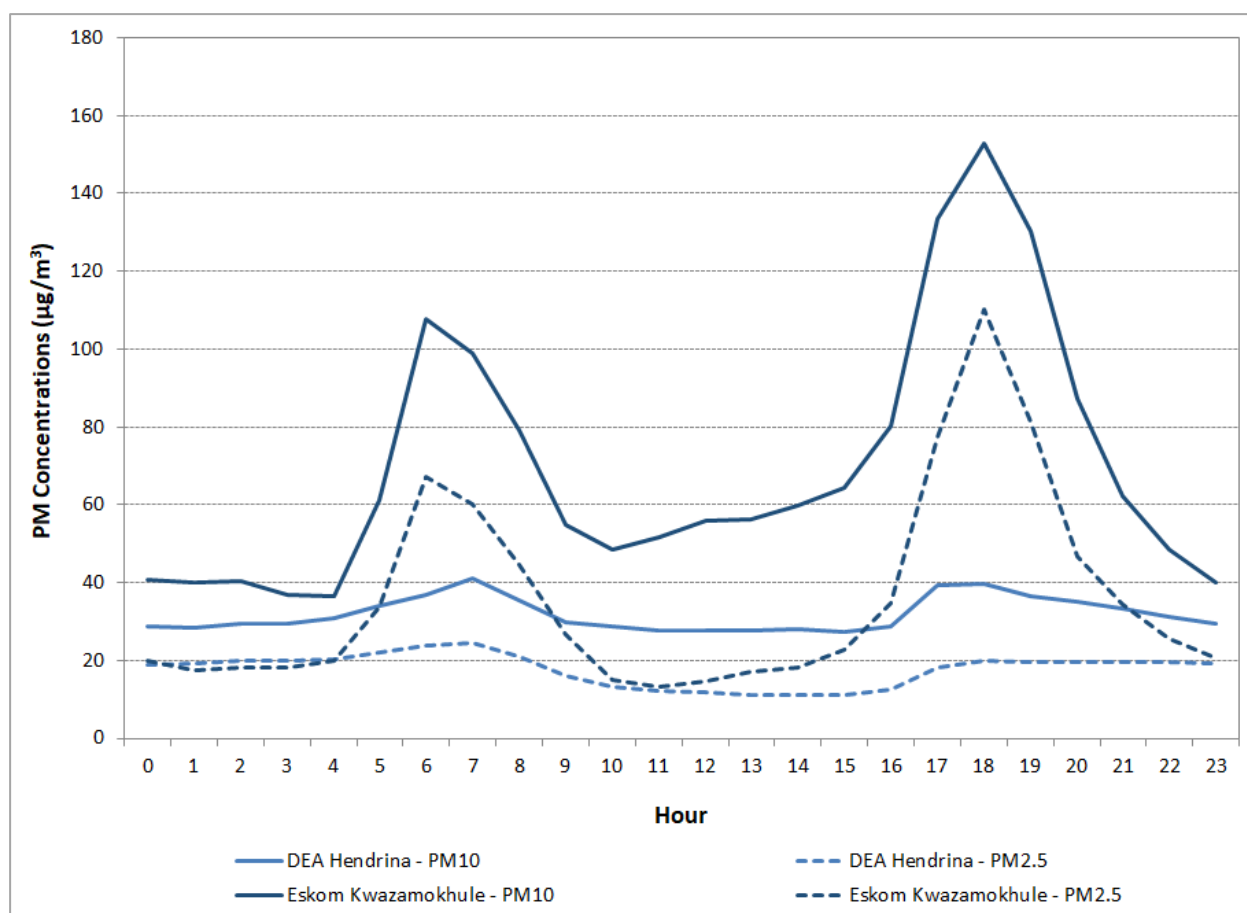


Figure 5.6: Diurnal PM₁₀ and PM_{2.5} concentrations in Hendrina and Kwazamokhule

5.2.2.2 Embalenhle

A similar trend to the other townships is also seen in Embalenhle with elevated ambient particulate concentrations recorded, particularly during the winter months. Over the respective monitoring periods, 99th percentile 24-hour average PM₁₀ concentrations ranged from 153.6 µg/m³ – 219.7 µg/m³ in Embalenhle (Table 5.6). Measured PM₁₀ concentrations were well over the 24-hour average PM₁₀ standard with a total of 48, 189 and 267 exceedances recorded at the CRG, DEA and Sasol monitoring stations, respectively. Annual average PM₁₀ concentrations were also in non-compliance at the DEA monitoring station for 2014 (54.1 µg/m³) and 2016 (85.2 µg/m³) and at the Sasol monitoring station for 2014 (66.6 µg/m³), 2016 (49.4 µg/m³) and 2017 (52.4 µg/m³). However, it should be noted that data capture at both the DEA and Sasol monitoring stations was below 50% for PM₁₀ concentrations during 2015 and as such, an annual average PM₁₀ concentration cannot be accurately determined. A full calendar year of PM₁₀ (and PM_{2.5}) monitoring data is also not available at the CRG monitoring station to determine compliance.

Ambient 99th percentile 24-hour average PM_{2.5} concentrations in Embalenhle ranged from 59.2 – 116.8 µg/m³ over the respective monitoring periods (Table 5.6). A total of 40, 163 and 66 exceedances were recorded at the CRG, DEA and Sasol monitoring stations, respectively. Annual average PM_{2.5} concentrations were also in non-compliance at the DEA monitoring station for 2014 (25.8 µg/m³) and 2016 (47.7 µg/m³) with the annual average standard approached (but not exceeded) at the Sasol monitoring station in 2014 (19.3 µg/m³), 2016 (21.9 µg/m³) and 2017 (21.4 µg/m³). As noted with PM₁₀ concentrations, data capture for PM_{2.5} concentrations was also below 50% at both stations in 2015.

The seasonal variation seen in the other townships datasets is also noted in Embalenhle with elevated concentrations recorded during the winter 2016 sampling campaign compared to the summer 2017 sampling campaign (Figure 5.7- Figure 5.8). The highest 99th percentile PM₁₀ and PM_{2.5} concentrations were recorded at the DEA monitoring station during the winter 2016 sampling campaign although the respective standards were also exceeded on several occasions at the Sasol monitoring station during these periods (Table 5.7). No data was available at the CRG monitoring station for the winter sampling campaigns due to technical problems with the instruments. The summer 2017 sampling campaign showed a reduction in the measured 99th percentile concentrations with no exceedances recorded at either the CRG or Sasol monitoring stations (no data available at the DEA monitoring station for this period). In general, a higher degree of variability is seen in PM₁₀ and PM_{2.5} concentrations during the winter sampling campaign at the DEA and Sasol monitoring stations, which is indicative of a dominant local source contribution, such as domestic fuel burning, to the air quality in Embalenhle township. During the summer sampling campaign, a similar trend is seen at the Sasol and CRG monitoring stations supporting a regional contributing source.

The diurnal profile of ambient PM₁₀ and PM_{2.5} concentrations in Embalenhle is shown in Figure 5.9. Elevated concentrations are recorded in the early morning (05:00 – 09:00) and evening (17:00 – 22:00). The evening peak in PM₁₀ and PM_{2.5} concentrations is not as pronounced at the Sasol Embalenhle monitoring station which could be due to its location slightly east of Embalenhle township.

Table 5.6: Summary of air quality statistics for Embalenhle

CRG Embalenhle (Jun 2016 – Jul 2017)

Pollutant	Averaging Period	National Standard	Allowable Exceedances	Period Average (Mean)	99% Confidence Interval	Number of data points	Number of Exceedances	Standard Deviation	Median	Percentiles		
										P25	P75	P99
PM ₁₀	24 Hour	75	4	48.3	42 - 54	240	48	37.0	36.3	21.4	64.5	154.1
	Annual ⁽¹⁾	40	0	ND	-	0	ND	-	-	-	-	-
PM _{2.5}	24 Hour	40	4	23.9	21 - 27	240	40	19.6	17.1	11.4	30.1	84.8
	Annual ⁽¹⁾	20	0	ND	-	0	ND	-	-	-	-	-

Notes:

ND = Not Determined

(1) Complete calendar year of data not available for 2016 and 2017

DEA Secunda (Jan 2014 – Nov 2016)

Pollutant	Averaging Period	National Standard	Allowable Exceedances	Period Average (Mean)	99% Confidence Interval	Number of data points	Number of Exceedances	Standard Deviation	Median	Percentiles		
										P25	P75	P99
PM ₁₀	24 Hour	75	4	52.3	47 – 58	708	189	56.2	31.3	9.1	78.5	219.7
	Annual	40	0	52.3	-	3	2	-	-	-	-	-
PM _{2.5}	24 Hour	40	4	27.5	25 - 30	708	163	29.5	16.0	6.1	37.8	116.8
	Annual	20	0	27.5	-	3	2	-	-	-	-	-

Sasol Embalenhle (Jan 2014 – Dec 2017)

Pollutant	Averaging Period	National Standard	Allowable Exceedances	Period Average (Mean)	99% Confidence Interval	Number of data points	Number of Exceedances	Standard Deviation	Median	Percentiles		
										P25	P75	P99
PM ₁₀	24 Hour	75	4	51.8	49 - 54	1203	267	35.4	42.0	26.5	69.5	153.6
	Annual	40	0	51.8	-	4	3	-	-	-	-	-
PM _{2.5}	24 Hour	40	4	19.3	18 - 21	1202	66	19.7	15.7	10.6	23.9	59.2
	Annual	20	0	19.3	-	4	0	-	-	-	-	-

Table 5.7: Statistics for 24-hour average PM₁₀ and PM_{2.5} concentrations during the aerosol sampling campaigns in Embalenhle

CRG Embalenhle

Statistics	15 Jul – 1 Aug 2016 ⁽¹⁾		5 – 18 Aug 2016 ⁽¹⁾		14 Feb – 1 Mar 2017	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Period Average (µg/m ³)	N/A	N/A	N/A	N/A	18.4	11.8
Number of Exceedances	N/A	N/A	N/A	N/A	0	0
Standard Deviation	N/A	N/A	N/A	N/A	12.6	8.4
Median (µg/m ³)	N/A	N/A	N/A	N/A	20.4	11.1
99 th Percentile (µg/m ³)	N/A	N/A	N/A	N/A	46.3	29.2
% Data Capture	0	0	0	0	100	100

Notes:

N/A = Not available

(1) No data due to technical problems with the instruments

DEA Secunda

Statistics	15 Jul – 1 Aug 2016		5 – 18 Aug 2016		14 Feb – 1 Mar 2017 ⁽¹⁾	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Period Average (µg/m ³)	126.6	74.6	140.4	69.8	N/A	N/A
Number of Exceedances	12	14	12	11	N/A	N/A
Standard Deviation	73.5	39.2	80.1	27.8	N/A	N/A
Median (µg/m ³)	114.9	78.5	127.6	72.7	N/A	N/A
99 th Percentile (µg/m ³)	249.5	141.2	339.6	105.4	N/A	N/A
% Data Capture	100	100	100	100	0	0

Notes:

N/A = Not available

(1) No data available from Dec 2016 – Aug 2017

Sasol Embalenhle

Statistics	15 Jul – 1 Aug 2016		5 – 18 Aug 2016		14 Feb – 1 Mar 2017	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Period Average (µg/m ³)	70.0	25.7	71.1	22.7	21.5	12.7
Number of Exceedances	8	2	5	0	0	0
Standard Deviation	41.1	12.5	23.8	8.6	13.8	9.8
Median (µg/m ³)	58.1	22.7	73.2	21.0	22.0	11.7
99 th Percentile (µg/m ³)	159.5	52.4	115.8	39.2	47.7	31.2
% Data Capture	100	100	100	100	100	100

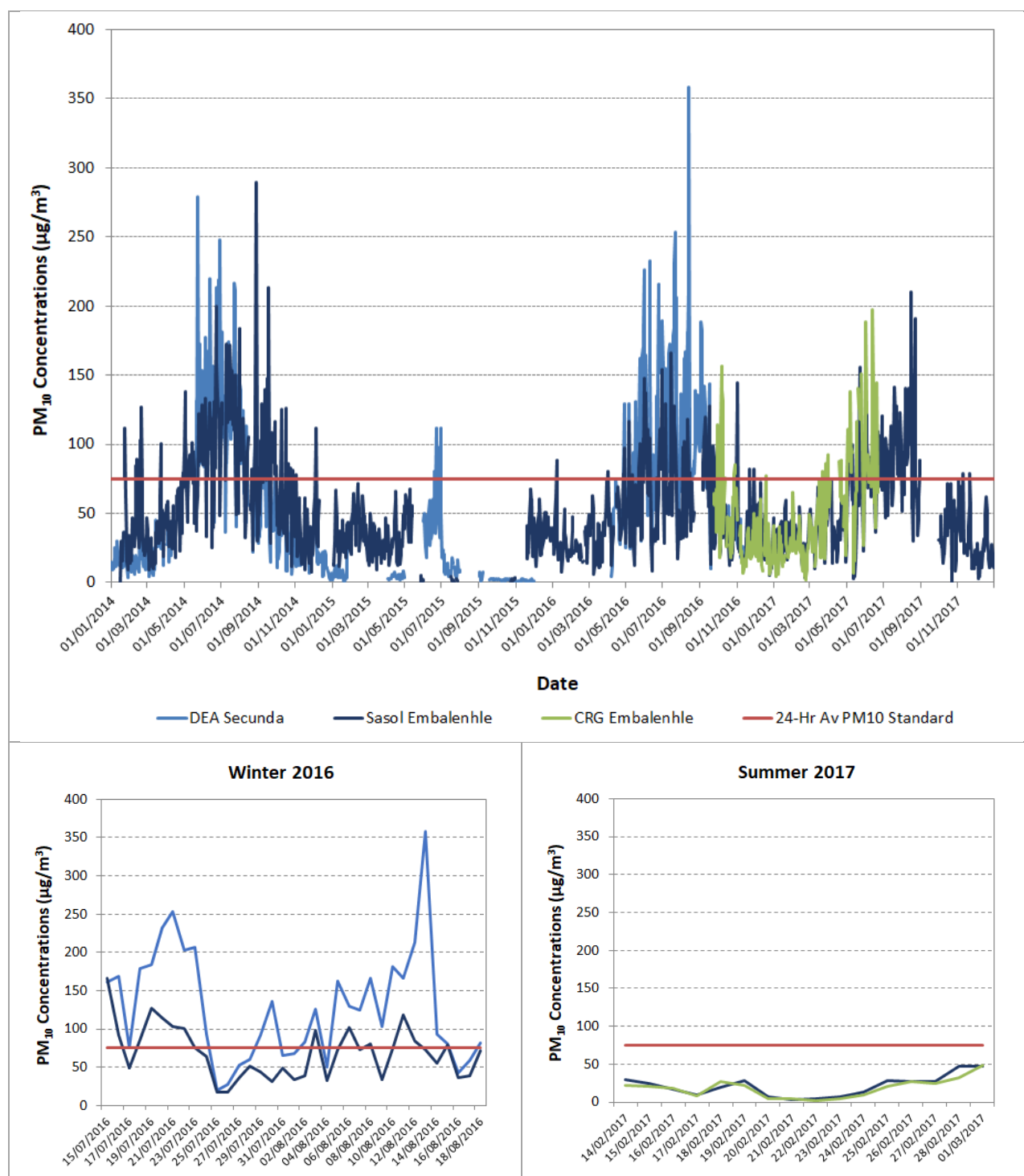


Figure 5.7: Ambient 24-hour average PM₁₀ concentrations for the period (top), winter 2016 (bottom left) and summer 2017 (bottom right) sampling campaigns in Embalenhle.

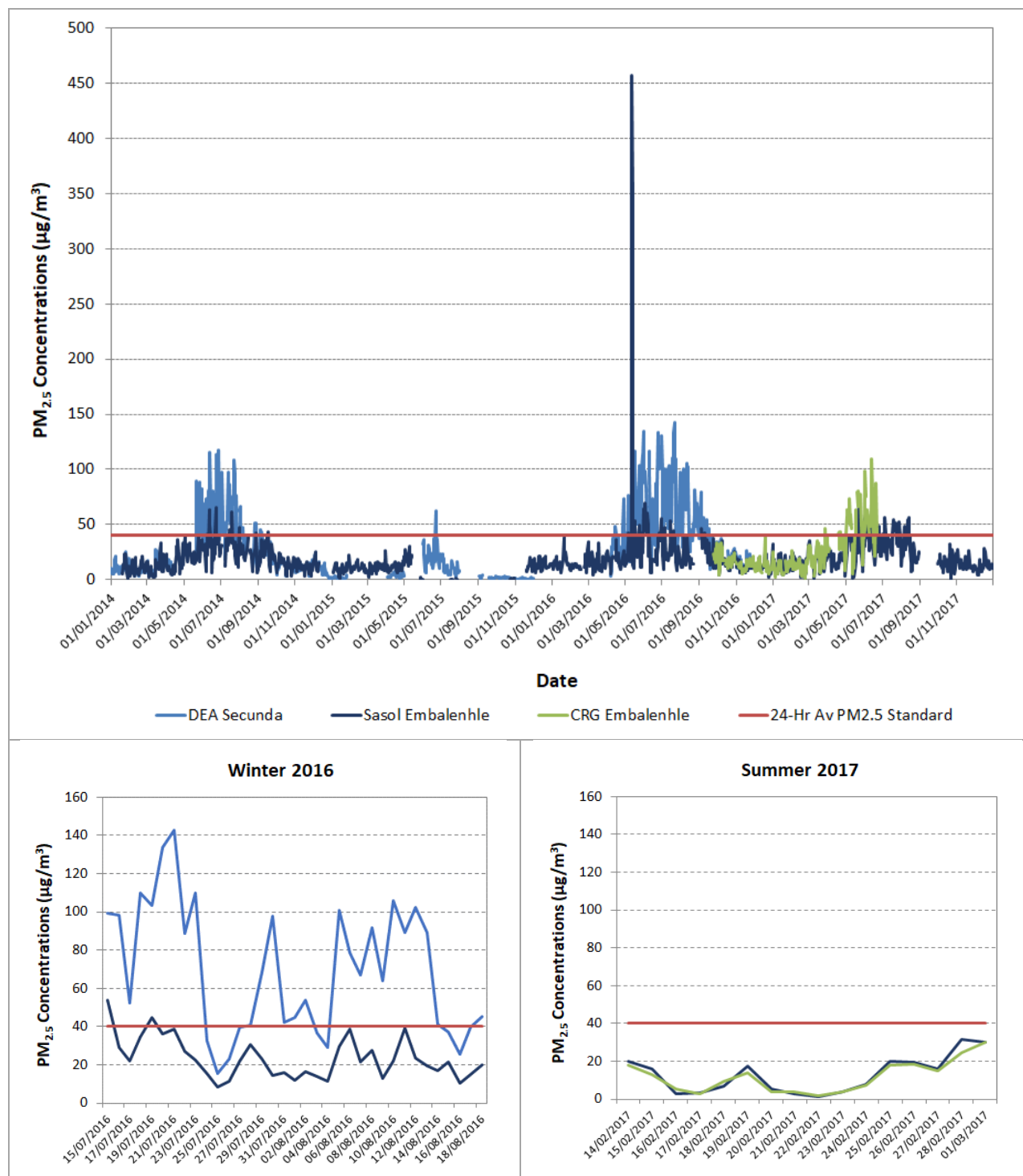


Figure 5.8: Ambient 24-hour average PM_{2.5} concentrations for the period (top), winter 2016 (bottom left) and summer 2017 (bottom right) and sampling campaigns in Embalenhle.

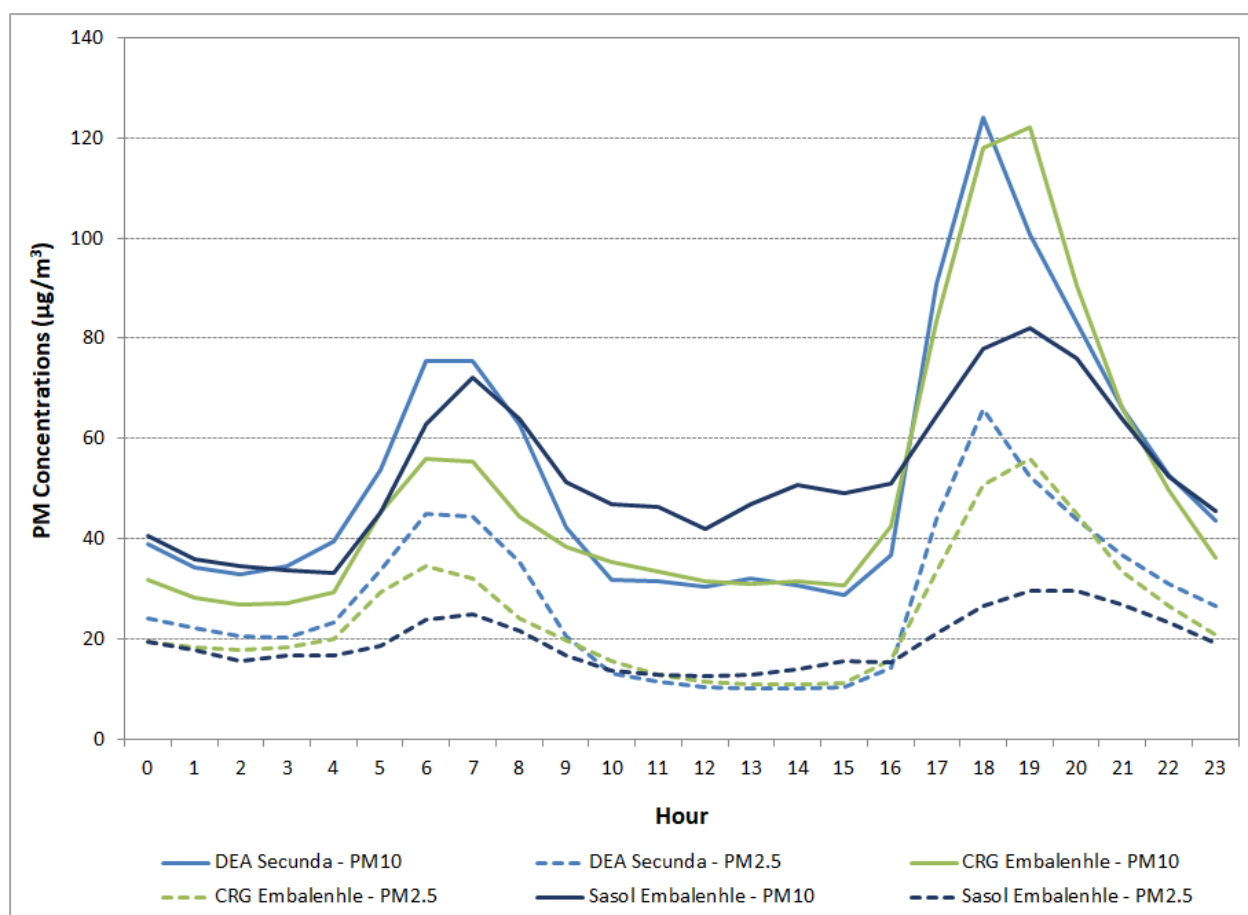


Figure 5.9: Diurnal PM₁₀ and PM_{2.5} concentrations in Embalenhle

5.2.3 Vaal Triangle Region

5.2.3.1 Zamdela

A similar situation as seen in the other townships is observed in Zamdela with elevated PM concentrations recorded in the township. Over the respective monitoring periods, 99th percentile 24-hour average PM₁₀ concentrations ranged from 151.7 µg/m³ – 282.0 µg/m³. Measured PM₁₀ concentrations were well over the 24-hour average PM₁₀ standard with a total of 132 and 230 exceedances recorded at the DEA and CRG monitoring stations, respectively (Table 5.8). Annual average PM₁₀ concentrations were also in non-compliance at the DEA station for both 2016 (64.7 µg/m³) and 2017 (49.5 µg/m³). Although a full calendar year of PM₁₀ monitoring data is not available to determine compliance at the CRG station, it can be inferred that annual average PM₁₀ concentrations are also in non-compliance.

Ambient 99th percentile 24-hour average PM_{2.5} concentrations in Zamdela ranged from 92.3 – 95.7 µg/m³ over the respective monitoring periods (Table 5.8).. A total of 103 and 154

exceedances were recorded at the CRG and DEA monitoring stations, respectively. Annual average PM_{2.5} concentrations were also in non-compliance at the DEA station for both 2016 (35.3 µg/m³) and 2017 (29.6 µg/m³) (and also likely at the CRG station).

A distinct seasonal variability is seen in the dataset with elevated PM₁₀ and PM_{2.5} concentrations during the winter and early spring months (Figure 5.10 - Figure 5.11). This seasonal variability is evident in the PM₁₀ and PM_{2.5} concentrations recorded during the summer and winter sampling campaigns. Ambient PM₁₀ concentrations are elevated during the winter sampling campaign with a 99th percentile 24-hour average PM₁₀ concentration of 326.1 µg/m and 167.4 µg/m recorded at the CRG and DEA Zamdela monitoring stations, respectively. Ambient PM_{2.5} concentrations were also elevated with a 99th percentile 24-hour average PM_{2.5} concentration of 107.7 µg/m and 84.8 µg/m recorded at the CRG and DEA Zamdela monitoring stations, respectively. Both the 24-hour average PM₁₀ and PM_{2.5} standards were exceeded on numerous occasions during the winter sampling campaign. During the summer sampling campaign, particulate concentrations remain elevated although a reduction is seen in the measured concentrations and the frequency of exceedance (Table 5.9). It is interesting to note that particulate concentrations recorded at the CRG monitoring station are higher than the DEA Zamdela monitoring station, despite the proximity of both of these stations within the Zamdela township. A similar trend in particulate concentrations appears to be evident both monitoring stations during both sampling campaigns (where data is available) which does suggest that these stations have a common contributing source(s).

The diurnal profile of ambient PM₁₀ and PM_{2.5} concentrations in Zamdela is shown in Figure 5.12. Elevated concentrations are recorded in the early morning (06:00 – 09:00) and evening (17:00 – 21:00). The morning peak in PM₁₀ and PM_{2.5} concentrations is not as pronounced as observed in other townships.

Table 5.8: Summary of air quality statistics for Zamdela

CRG Zamdela (Jun 2016 – Jun 2017)

Pollutant	Averaging Period	National Standard	Allowable Exceedances	Period Average (Mean)	99% Confidence Interval	Number of data points	Number of Exceedances	Standard Deviation	Median	Percentiles		
										P25	P75	P99
PM ₁₀	24 Hour	75	4	110.9	102 - 120	364	230	65.2	98.4	60.8	150.6	282.0
	Annual ⁽¹⁾	40	0	ND	-	0	ND	-	-	-	-	-
PM _{2.5}	24 Hour	40	4	37.5	35 - 40	287	103	19.1	33.0	23.8	47.2	92.3
	Annual ⁽¹⁾	20	0	ND	-	0	ND	-	-	-	-	-

Notes:

ND = Not Determined

(1) Complete calendar year of data not available for 2016 and 2017

DEA Zamdela (Jan 2016 – Dec 2017)

Pollutant	Averaging Period	National Standard	Allowable Exceedances	Period Average (Mean)	99% Confidence Interval	Number of data points	Number of Exceedances	Standard Deviation	Median	Percentiles		
										P25	P75	P99
PM ₁₀	24 Hour	75	4	57.8	55 - 61	615	132	30.3	53.0	36.6	71.4	151.7
	Annual	40	0	57.9	-	2	2	-	-	-	-	-
PM _{2.5}	24 Hour	40	4	32.4	31 - 34	602	154	18.0	28.8	20.6	40.2	95.7
	Annual	20	0	32.4	-	2	2	-	-	-	-	-

Table 5.9: Statistics for 24-hour average PM₁₀ and PM_{2.5} concentrations during the aerosol sampling campaigns in Zamdela

CRG Zamdela

Statistics	15 – 31 Jul 2016		12 – 24 Sep 2016		13 Feb – 2 Mar 2017	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Period Average (µg/m ³)	168.0	49.5	129.1	25.9	50.1	37.7
Number of Exceedances	14	8	12	1	2	4
Standard Deviation	85.1	26.7	50.5	10.2	19.3	27.0
Median (µg/m ³)	175.0	39.5	120.9	25.3	51.3	27.9
99 th Percentile (µg/m ³)	326.1	107.7	208.8	42.7	83.8	101.9
% Data Capture	100	93.8	100	100	94.1	94.1

DEA Zamdela

Statistics	15 – 31 Jul 2016		12 – 24 Sep 2016		13 Feb – 2 Mar 2017	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Period Average (µg/m ³)	79.7	44.0	80.6	31.7	47.7	N/A
Number of Exceedances	6	6	6	5	1	N/A
Standard Deviation	48.4	24.7	40.4	16.8	15.5	N/A
Median (µg/m ³)	63.8	39.4	68.1	33.6	42.9	N/A
99 th Percentile (µg/m ³)	167.4	84.8	164.2	61.5	86.0	N/A
% Data Capture	82.4	82.4	100	92.3	61.1	N/A

Notes:

N/A = Not Available

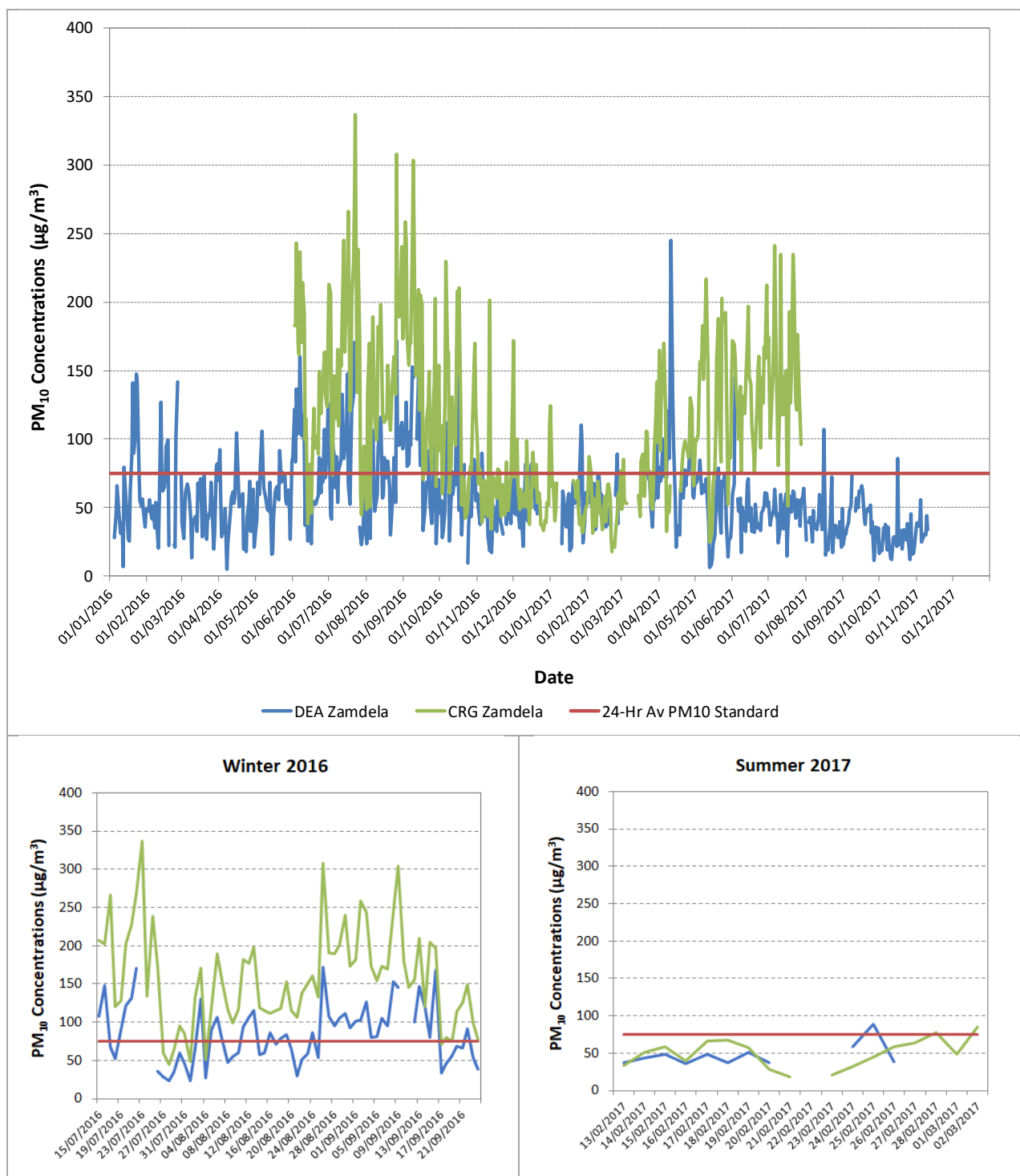


Figure 5.10: Ambient 24-hour average PM₁₀ concentrations for the period (top), winter 2016 (bottom left) and summer 2017 (bottom right) sampling campaigns in Zamdela.

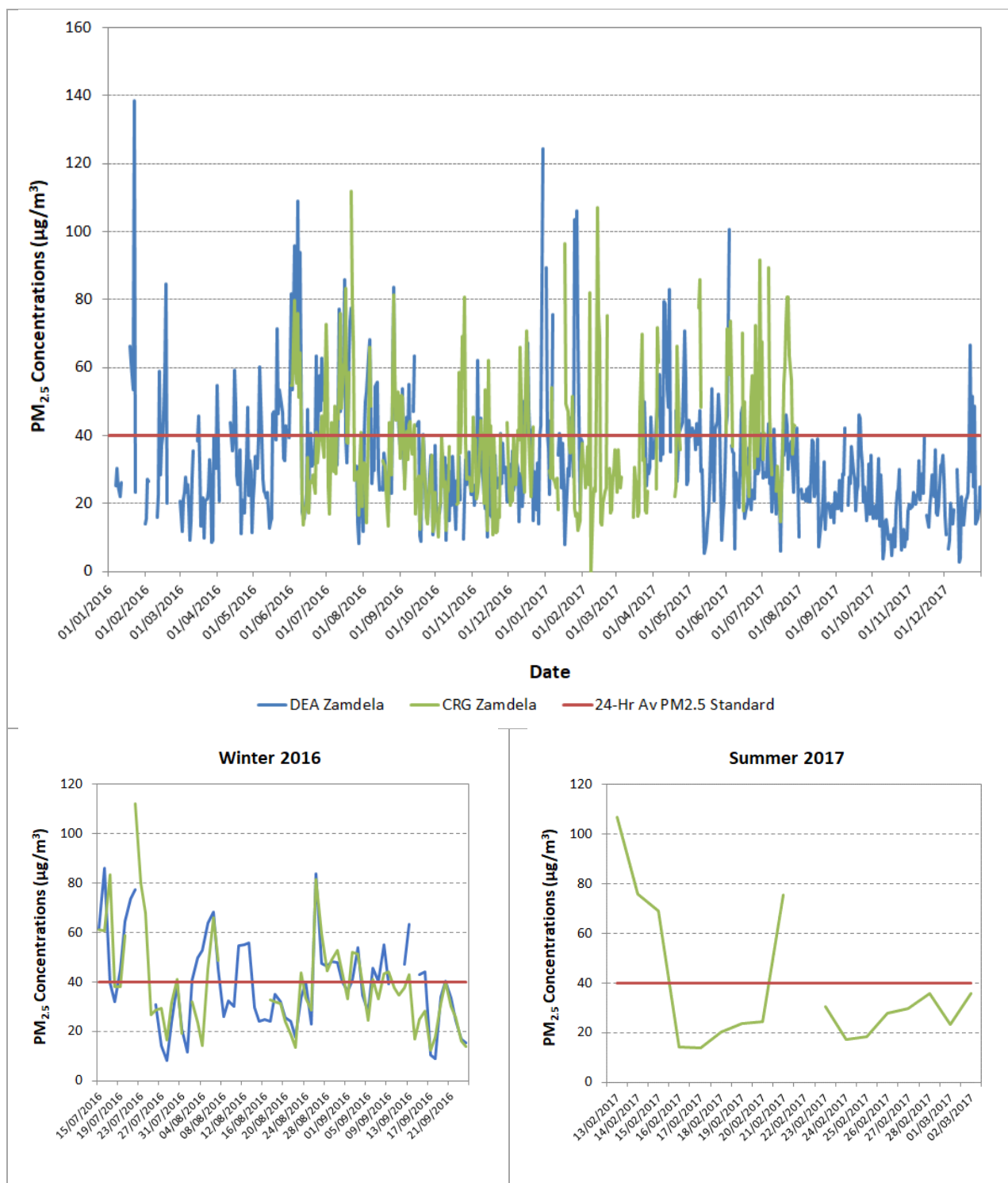


Figure 5.11: Ambient 24-hour average PM_{2.5} concentrations for the period (top), winter 2016 (bottom left) and summer 2017 (bottom right) sampling campaigns in Zamdela.

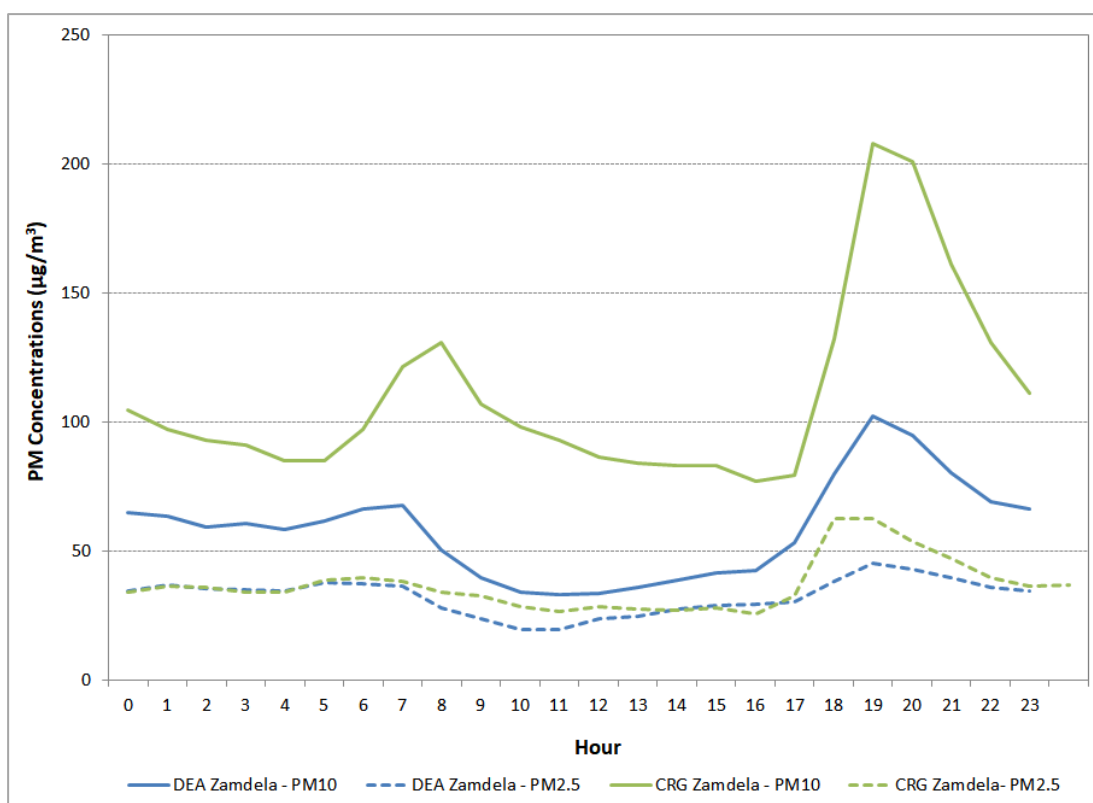


Figure 5.12: Diurnal PM₁₀ and PM_{2.5} concentrations in Zamdela

5.2.4 Discussion

In all three regions, ambient PM₁₀ and PM_{2.5} concentrations are elevated and frequently exceed their applicable ambient air quality standards, especially in the short-term. Despite the complex nature of the airshed of the Highveld and Vaal Triangle compared to the Lephalale area, PM₁₀ and PM_{2.5} concentrations in all three regions are similar, thereby indicating a local source of emissions in each of the townships during the winter months. This is also seen in the higher particulate concentrations recorded at the ambient air quality monitoring stations sited within townships compared to monitoring stations located outside townships. During summer, this variability between monitoring stations, even in the same areas, is not as pronounced and shows a similar trend in particulate concentrations observed during the warmer summer months which is indicative of a common regional source. This demonstrates the dominance of domestic fuel burning as a significant local source of emissions in the townships during the winter months.

The existing air quality situation in each region and during each aerosol sampling campaign has been characterised. The elemental and chemical composition of the aerosol loading at each site is discussed in Chapter 6.

CHAPTER 6 AEROSOL CHEMICAL COMPOSITION

The gravimetric mass of the fine and coarse aerosol fraction within each of the three regions is presented in the section below. The chemical composition of the fine and coarse aerosol fraction within each region is also discussed.

6.1 Waterberg Region

6.1.1 Lephale

6.1.1.1 Gravimetric Analysis

The fine and coarse aerosol mass for the Lephale sampling sites was reconstructed from the ionic and elemental mass. As the reconstructed mass concentrations are likely to be lower than those that were measured, the reconstructed mass is used to show trends in the datasets rather than to determine compliance with the relevant ambient air quality standards.

During the winter 2012 sampling campaign, higher aerosol concentrations were recorded in Marapong compared to Lephale and Steenbokpan (Table 6.1 and Figure 6.1). Coarse fraction aerosol concentrations are significantly higher than the fine fraction in Marapong, while this difference is not observed to be as substantial at the Lephale and Steenbokpan sampling sites. Of the three sites, the highest coarse aerosol concentrations were measured in Marapong while in the fine fraction, similar aerosol concentrations were measured in Marapong and Lephale.

A decrease in fine and coarse aerosol concentrations is seen during the summer 2013 sampling campaign at all three sites (Table 6.1 and Figure 6.2). Coarse fraction aerosol concentrations are higher than the fine fraction in Marapong and similar in both Lephale and Steenbokpan. The highest fine and coarse aerosol concentrations are seen in Marapong while similar aerosol concentrations are observed in Lephale and Steenbokpan.

In general, a similar trend in aerosol concentrations is seen in Lephale and Steenbokpan, thereby indicating that both sites are impacted by a regional source(s) of air pollution. A different signature is evident in Marapong, particularly during the winter-months, which is indicative of the influence of localised air pollution sources.

Table 6.1: Mean aerosol concentrations ($\mu\text{g}/\text{m}^3$) and standard deviations at Lephalale Town, Marapong and Steenbokpan for the winter 2012 and summer 2013 sampling campaigns

Sampling Site	Winter 2012		Summer 2013	
	Fine	Coarse	Fine	Coarse
Lephalale Town	20.8 ± 6.4	28.8 ± 8.2	8.7 ± 4.5	10.3 ± 3.5
Marapong	23.3 ± 9.0	87.3 ± 41.0	17.9 ± 9.6	34.6 ± 17.8
Steenbokpan	9.6 ± 4.6	10.7 ± 5.8	8.7 ± 4.5	9.0 ± 5.1

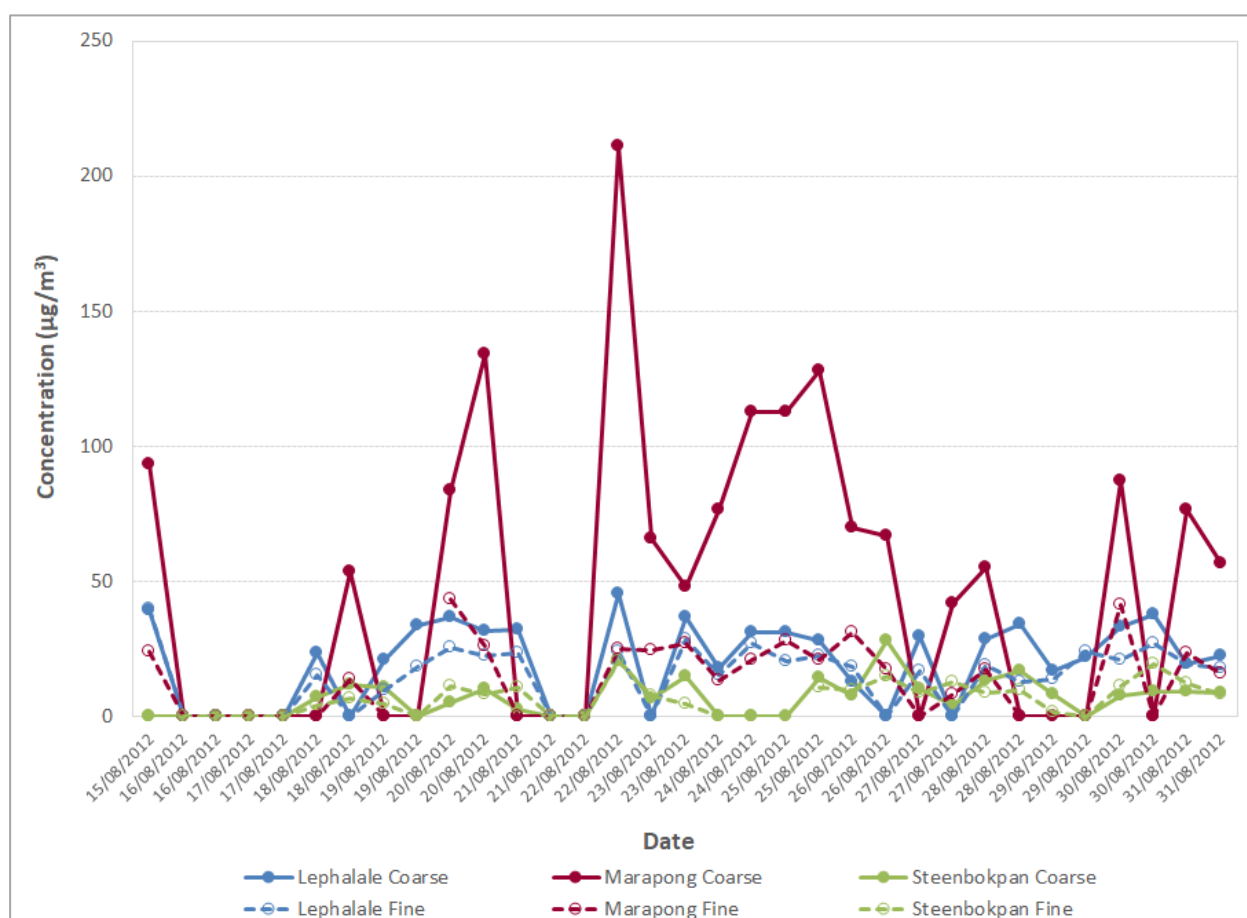


Figure 6.1: Fine and coarse aerosol concentrations at Lephalale Town, Marapong and Steenbokpan for the period 15 August – 1 September 2012

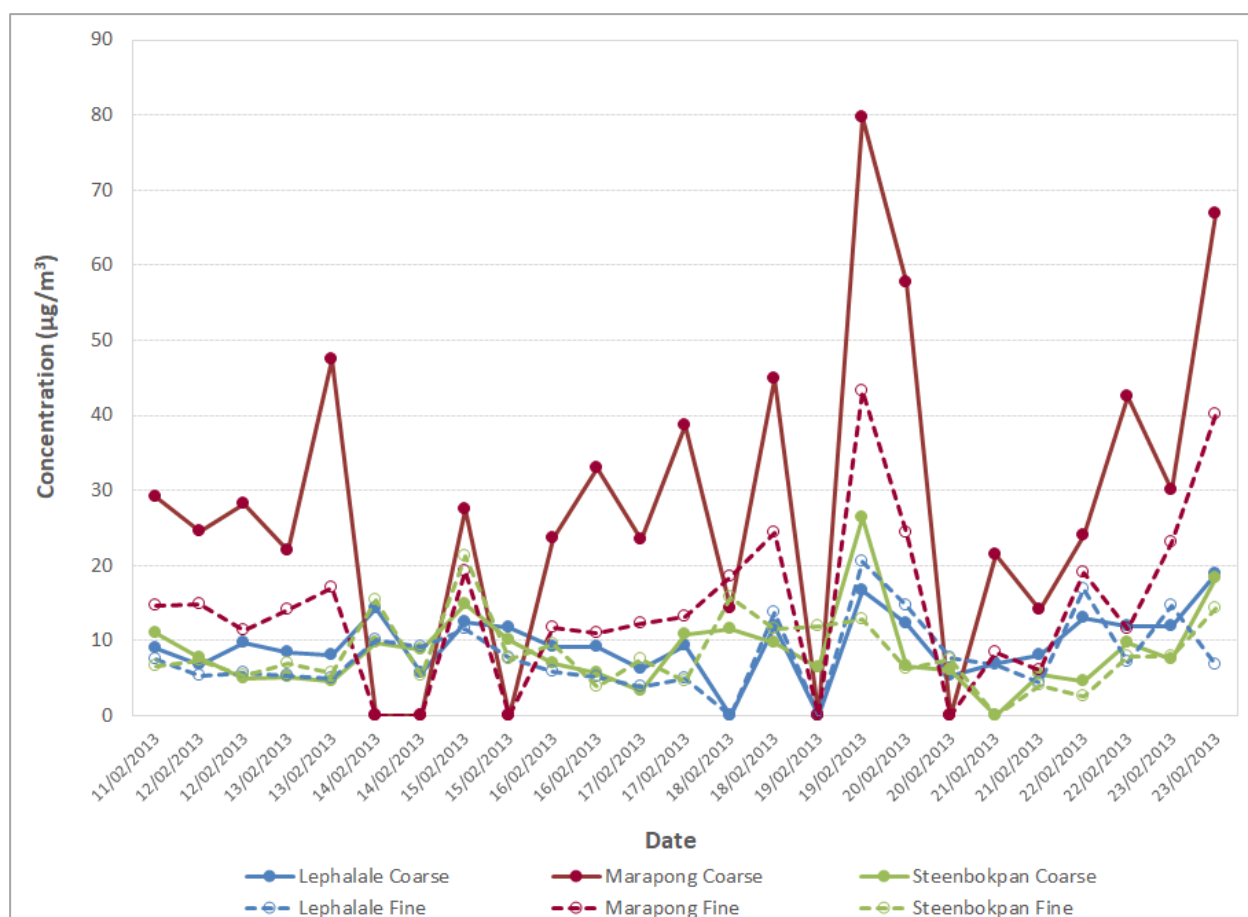


Figure 6.2: Fine and coarse aerosol concentrations at Lephalale Town, Marapong and Steenbokpan for the period 11 – 24 February 2013

6.1.1.2 Chemical Analysis

6.1.1.2.1 Winter Sampling Campaign

Fine Fraction

The results of the winter 2012 sampling campaign show Al, Si and S as the dominant elements at all three sites in the elemental fine aerosol fraction (Table 6.2). Al ranged from 11 – 21% and Si ranged from 21 – 38%, with the lowest abundances measured at the Steenbokpan site. Correlation coefficients (r) calculated between Al and Si show a high degree of correlation in the fine fraction ($r \geq 0.99$ at all three sites) as well as between other species such as Fe, Mg and K. Calculated enrichment factors (EF) of these elements relative to the Earth's crust composition (Mason, 1966) and using Al as the reference element, indicates that Si and Fe were mainly from a crustal source while K and Ti were from both anthropogenic and crustal sources (Table 6.3). EF values < 1 are indicative of a natural origin while $EF > 5$ are attributed to elements of a significant anthropogenic origin (Li *et al.*, 2020). These elements are likely the fine fraction

counterpart of the soil dust component that is seen in the coarse fraction (Maenhaut *et al.*, 1996).

Concentrations of S are also relatively high in the fine fraction at all three sites, contributing to 21%, 13% and 34% of the detected fine elemental fraction in Lephalale town, Marapong and Steenbokpan, respectively. The highest S abundances seen in the 'remote' Steenbokpan site indicate that emissions from Matimba Power Station are transported 25 km downwind before reaching ground level. The secondary aerosol, SO_4^{2-} , is produced in the atmosphere by oxidation of SO_2 which is primarily produced from fossil fuel combustion (Wolf and Hidy, 1997) and occurs predominantly in the fine aerosol size fraction. At all three sites, SO_4^{2-} is the most abundant species, contributing to 49%, 41% and 47% of the detected ionic fine fraction mass in Lephalale town, Marapong and Steenbokpan. NO_3^- and NH_4^+ are the next most abundant species in the detected ionic fraction at all three sites, with NO_3^- accounting for 12 – 13% and NH_4^+ accounting for 10 – 12%. A strong correlation is observed between SO_4^{2-} and NH_4^+ ($r = 0.89$ at Lephalale town, $r = 0.92$ at Marapong and $r = 0.92$ at Steenbokpan) in the fine fraction, thereby indicating that these species have a secondary origin from atmospheric gas to particle conversion processes. NH_4^+ generally combines with SO_4^{2-} and NO_3^- in the atmosphere to form NH_4SO_4 and NH_4NO_3 (Appel *et al.*, 1981). The strong correlation shown between SO_4^{2-} and NH_4^+ as well as between S and SO_4^{2-} in the fine fraction ($r = 0.96$ at Lephalale town, $r = 0.96$ at Marapong and $r = 0.91$ at Steenbokpan) supports a coal combustion source. The extremely high EF for S indicates the dominance of anthropogenic sources of S in the region (Table 6.3).

The biomass burning species, K^+ and oxalate were also detected although K^+ and oxalate occur in relatively low abundances. K^+ contributes to 7 - 8% of the detected ionic fine aerosol mass at all three sites and oxalate ranges from 3 – 6% thereof (Table 6.2). Wood is used as a domestic fuel in Marapong which could account for the origin of these species.

Coarse Fraction

In the elemental coarse fraction, Al and Si remain the dominating elements at all three sites with Al ranging between 14 – 20% and Si ranging between 31 – 42% of the detected elemental coarse aerosol mass (Table 6.2). Fe abundances are also relatively high in the coarse fraction, ranging between 9 – 17% of the detected elemental coarse aerosol mass. A strong correlation is observed between Al and Si in the coarse fraction ($r = 0.98$, 1.00 and 0.99 at Lephalale town, Marapong and Steenbokpan, respectively) as well as between other crustal elements such as Ca, Fe, Mg and K. This is also confirmed with the calculated EF values for Ca, Si and K which suggests that crustal dust sources are likely to be the primary source of these elements in the coarse fraction. In the ionic coarse component, the secondary aerosols, SO_4^{2-} and NO_3^- are the

most abundant species, ranging from 14 – 28% and 22 – 24%, respectively, of the detected ionic coarse fraction (Table 6.2). A strong relationship is seen between S and SO_4^{2-} with $r = 0.87, 0.98$ and 0.94 at Lephalale town, Marapong and Steenbokpan, respectively. Moderate correlations are seen between SO_4^{2-} and NO_3^- ($r = 0.52, 0.40$ and 0.66 at Lephalale Town, Marapong and Steenbokpan, respectively). The coarse fraction also contains SO_4^{2-} (and NO_3^-) since acidic gases such as sulphuric (and nitric) acid vapours may react with coarse particles to form secondary coarse acidic aerosols (Schlesinger and Cassee, 2003). Ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ can be used to evaluate the sources of these two ionic species (Gao *et al.*, 1996). $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios > 1 indicate a greater contribution of NO_3^- from vehicle emissions while $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios < 1 indicate a significant contribution of SO_4^{2-} from industrial activities. For the three sites, average $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios were $1.47 \pm 0.57, 0.99 \pm 0.41$ and 1.69 ± 0.64 at Lephalale Town, Marapong and Steenbokpan, respectively, indicating a mixed mobile and industrial emission source at these sites. However, average fine fraction ratios (0.29 ± 0.16 at Lephalale Town, 0.36 ± 0.16 at Marapong and 0.34 ± 0.17 at Steenbokpan). show an industrial contribution of these species at all three sites.

Table 6.2: Mean concentrations and standard deviations of the measured species at Lephalale Town, Marapong and Steenbokpan for the period 15 August – 1 September 2012

Species		Lephalale Town		Marapong		Steenbokpan	
		Fine	Coarse	Fine	Coarse	Fine	Coarse
Elemental Composition ($\mu\text{g}/\text{m}^3$)	Cl	BDL	0.2 ± 0.3	BDL	0.5 ± 0.4	BDL	0.3 ± 0.4
	S	0.9 ± 0.4	0.2 ± 0.2	0.6 ± 0.3	0.4 ± 0.2	0.7 ± 0.4	0.1 ± 0.0
	Ca	BDL	0.3 ± 0.1	BDL	1.6 ± 0.8	BDL	BDL
	Fe	0.5 ± 0.2	0.9 ± 0.3	0.5 ± 0.2	2.1 ± 1.1	0.1 ± 0.1	0.2 ± 0.2
	Na	0.3 ± 0.1	0.2 ± 0.2	0.1 ± 0.1	0.4 ± 0.2	0.1 ± 0.1	0.3 ± 0.3
	Mg	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.1	0.0 ± 0.0	0.1 ± 0.0
	Al	0.7 ± 0.3	1.1 ± 0.3	0.9 ± 0.4	3.3 ± 1.6	0.2 ± 0.1	0.3 ± 0.2
	Si	1.3 ± 0.5	2.1 ± 0.6	1.7 ± 0.7	7.0 ± 3.4	0.4 ± 0.3	0.7 ± 0.4
	P	0.0 ± 0.0	BDL	0.0 ± 0.0	BDL	BDL	0.2 ± 0.9
	K	0.6 ± 0.2	0.3 ± 0.2	0.5 ± 0.2	0.8 ± 0.5	0.3 ± 0.2	0.1 ± 0.1
	Ti	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.1	0.4 ± 0.3	0.1 ± 0.1	0.0 ± 0.0
Water-Soluble Ionic Composition ($\mu\text{g}/\text{m}^3$)	F ⁻	0.0 ± 0.0	0.2 ± 0.1	0.1 ± 0.1	0.4 ± 0.1	0.0 ± 0.0	0.1 ± 0.1
	Cl ⁻	0.2 ± 0.1	0.3 ± 0.3	0.2 ± 0.1	0.5 ± 0.6	0.2 ± 0.0	0.4 ± 0.5
	NO ₃ ⁻	0.5 ± 0.2	0.6 ± 0.2	0.4 ± 0.2	1.0 ± 0.4	0.5 ± 0.2	0.5 ± 0.3
	SO ₄ ²⁻	2.0 ± 0.9	0.5 ± 0.2	1.2 ± 0.8	1.1 ± 0.5	1.7 ± 1.0	0.3 ± 0.1
	Na ⁺	0.2 ± 0.1	BDL	0.2 ± 0.1	BDL	0.3 ± 0.2	BDL
	NH ₄ ⁺	0.5 ± 0.4	0.1 ± 0.4	0.3 ± 0.3	0.1 ± 0.1	0.4 ± 0.4	0.1 ± 0.1
	K ⁺	0.3 ± 0.2	0.3 ± 0.9	0.2 ± 0.1	0.1 ± 0.3	0.3 ± 0.1	0.1 ± 0.1
	Ca ²⁺	0.1 ± 0.0	0.5 ± 0.6	0.2 ± 0.2	0.5 ± 0.7	0.1 ± 0.0	0.6 ± 0.5
	Mg ²⁺	0.0 ± 0.0	0.1 ± 0.2	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.0
	Formate	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Oxalate	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.2	0.1 ± 0.1	0.0 ± 0.0

Notes:

BDL = Below Detection Limit

BDL species not shown include Acetate, Mn, Zn, Cr, V, Pb, Cd and As

Table 6.3: Enrichment factors for selected species at Lephalale Town, Marapong and Steenbokpan for the period 15 August – 1 September 2012

Species	Lephalale Town		Marapong		Steenbokpan	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
S	208.9	24.0	99.6	18.5	484.7	49.4
Ca	BDL	0.9	BDL	1.1	BDL	BDL
Fe	1.2	1.4	1.0	1.1	1.2	1.4
Si	0.5	0.6	0.5	0.6	0.6	0.6
K	2.7	1.0	1.8	0.8	5.2	1.1
Ti	1.5	2.1	2.7	2.5	12.8	2.1

6.1.1.2.2 Summer Sampling Campaign

Fine Fraction

The results of the summer 2013 sampling campaign show Si and S as the dominant elements at all three sites in the elemental fine aerosol fraction (Table 6.4). Al is abundant in the elemental profile at Marapong, contributing to 13% of the detected elemental fine aerosol mass at this site. Si contributes between 14 – 34% at all three sites while S contributes between 24 – 58% of the detected elemental fine aerosol mass. A slight decrease in Si concentrations is seen during summer compared to winter, whereas S concentrations show a significant increase during the summer months, especially at Steenbokpan. In the ionic fine aerosol fraction, SO_4^{2-} and NH_4^+ are the most significant species with SO_4^{2-} contributing to over half of the detected soluble fine aerosol mass at all three sites. A significant increase in SO_4^{2-} concentrations is also seen in summer due to an increase in relative humidity which favours SO_4^{2-} production (Aurela *et al.*, 2016; Shikwambana and Sivakumar, 2019). NH_4^+ ranged between 18 – 22% of the detected ionic fine aerosol mass. The strong correlations observed between SO_4^{2-} and NH_4^+ ($r = 0.99$ at all three sites) and SO_4^{2-} and S ($r = 0.99$, $r = 1.00$ and $r = 0.99$ at Lephalale town, Marapong and Steenbokpan, respectively) again support the origin of these species from a coal combustion source. The anthropogenic origin of these species is also confirmed in the extremely high EF calculated for S at all three sites (Table 6.5). Emissions from Matimba Power Station are likely to be the most significant source during this season. As also seen in the winter profile, emissions from Matimba Power Station have the greatest impact downwind at Steenbokpan.

Coarse Fraction

In the elemental coarse aerosol fraction, Si and Al are the most significant elements with Si contributing between 32 – 45% and Al contributing between 12 – 16% of the detected elemental coarse aerosol mass at all three sites (Table 6.4). The relative summer contributions of these elements are similar to that observed in the winter profile. The strong correlations shown between Si, Al and other crustal species in this size fraction support a crustal origin of these species, as is also shown in the calculated EF for these species (Table 6.5). It is noted that during this sampling campaign, construction at Medupi Power Station was suspended and as such, the relative concentrations and abundances of the crustal species recorded in the summer profile are likely to be representative of background conditions. In the ionic coarse aerosol fraction, a high degree of variability is seen in the chemical profiles. F^- is the most abundant species at Marapong (21%) while Na^+ is the most abundant at Lephalale (24%) and Steenbokpan (22%). SO_4^{2-} is the next most abundant species at all three sites, contributing to 15%, 20% and 16% of the detected ionic coarse aerosol mass at Lephalale Town, Marapong and Steenbokpan, respectively. An increase in the abundance of F^- is seen at Marapong during summer. Potential sources of this species include, amongst others, coal combustion, soil dust and biomass burning (Feng *et al.*, 2003; Saxena *et al.*, 2017). NO_3^- is also significant in this fraction, accounting for 17%, 10% and 15% of the detected ionic coarse aerosol mass at Lephalale Town, Marapong and Steenbokpan, respectively. Compared to winter, NO_3^- contributions are lower in summer as low temperatures are favourable for particulate NO_3^- formation (Querol *et al.*, 2008). For the three sites, average NO_3^-/SO_4^{2-} ratios for the coarse fraction were 1.15 ± 0.63 , 0.71 ± 0.51 and 1.24 ± 0.62 at Lephalale Town, Marapong and Steenbokpan, respectively, indicating a mixed mobile and industrial emission source at two of the sites. Average fine fraction ratios (0.07 ± 0.05 at Lephalale Town, 0.07 ± 0.05 at Marapong and 0.06 ± 0.07 at Steenbokpan) show that industrial activities are the significant source of these species at all three sites.

Table 6.4: Mean concentrations and standard deviations of the measured species at Lephalale Town, Marapong and Steenbokpan for the period 11 – 24 February 2013

Species		Lephalale Town		Marapong		Steenbokpan	
		Fine	Coarse	Fine	Coarse	Fine	Coarse
Elemental Composition ($\mu\text{g}/\text{m}^3$)	Cl	0.1 ± 0.1	0.3 ± 0.3	0.1 ± 0.1	0.3 ± 0.2	0.0 ± 0.0	0.2 ± 0.0
	S	0.9 ± 0.7	0.1 ± 0.0	0.8 ± 0.6	0.2 ± 0.1	1.0 ± 0.7	0.1 ± 0.0
	Ca	0.0 ± 0.0	0.2 ± 0.0	0.2 ± 0.1	0.6 ± 0.3	BDL	0.1 ± 0.0
	Fe	0.1 ± 0.1	0.3 ± 0.1	0.3 ± 0.2	0.8 ± 0.4	0.1 ± 0.0	0.2 ± 0.1
	Na	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.2 ± 0.1
	Mg	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Al	0.1 ± 0.1	0.3 ± 0.1	0.5 ± 0.3	1.0 ± 0.5	0.1 ± 0.1	0.3 ± 0.2
	Si	0.3 ± 0.2	0.7 ± 0.3	1.2 ± 0.7	2.9 ± 1.6	0.3 ± 0.1	0.6 ± 0.5
	P	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	K	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.1	0.2 ± 0.1	0.0 ± 0.0	0.1 ± 0.1
	Ti	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
	Mn	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
	Zn	0.1 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.1
	Cr	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	V	BDL	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	BDL	0.0 ± 0.0
	Pb	BDL	0.2 ± 0.1	0.0 ± 0.0	0.2 ± 0.1	0.0 ± 0.0	0.2 ± 0.1
	As	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.1
Water-Soluble Ionic Composition ($\mu\text{g}/\text{m}^3$)	F ⁻	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.2	0.5 ± 0.2	0.1 ± 0.1	0.1 ± 0.1
	Cl ⁻	0.1 ± 0.1	0.3 ± 0.3	0.1 ± 0.0	0.3 ± 0.2	0.0 ± 0.0	0.2 ± 0.2
	NO ₃ ⁻	0.1 ± 0.0	0.2 ± 0.2	0.1 ± 0.0	0.2 ± 0.1	0.1 ± 0.0	0.2 ± 0.2
	SO ₄ ²⁻	2.3 ± 1.7	0.2 ± 0.1	2.1 ± 1.4	0.5 ± 0.4	2.7 ± 2.0	0.2 ± 0.3
	Na ⁺	0.2 ± 0.1	0.3 ± 0.2	0.2 ± 0.1	0.4 ± 0.2	0.2 ± 0.1	0.3 ± 0.2
	NH ₄ ⁺	0.8 ± 0.6	0.0 ± 0.0	0.7 ± 0.5	0.1 ± 0.1	0.9 ± 0.6	0.0 ± 0.0
	K ⁺	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.1	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.1
	Ca ²⁺	0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.1	0.4 ± 0.2	0.0 ± 0.0	0.1 ± 0.0
	Mg ²⁺	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Formate	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	BDL
	Acetate	0.0 ± 0.0	BDL	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	BDL
	Oxalate	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.2 ± 0.1	0.2 ± 0.9

Notes:

BDL = Below Detection Limit

BDL species not shown include Ni, Sr and Cd

Table 6.5: Enrichment factors for selected species at Lephalale Town, Marapong and Steenbokpan for the period 11 – 24 February 2013

Species	Lephalale Town		Marapong		Steenbokpan	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
S	1133.3	58.2	281.5	22.4	1440.6	76.5
Ca	0.9	1.2	0.9	1.2	BDL	0.8
Fe	1.4	1.7	1.1	1.2	1.0	1.2
Si	0.7	0.8	0.8	0.8	0.7	0.7
K	1.5	1.2	1.2	0.7	1.0	1.2
Ti	1.5	1.9	2.0	2.4	1.7	1.9
Mn	3.7	3.3	1.9	1.4	4.9	3.8
V	BDL	4.4	2.2	3.4	BDL	5.5

As the Lephalale region is not considered to be industrialised as a whole, the sources of emission impacting the airshed are well known and characterised. While this is reflected in the similar chemical profiles seen for each of the sampling areas, there is distinct variability in the relative contributions of each of the species measured at the three sampling sites as well as a strong seasonal influence. The greatest impacts from Matimba Power Station are observed further downwind at Steenbokpan, with a significant increase in S and SO_4^{2-} during the summer months. Marapong is located upwind of Matimba Power Station which could account for the reduced impacts seen at this site. The increase in SO_4^{2-} concentrations is also evident at all three sites during summer due to an increase in relative humidity which favours SO_4^{2-} production. During the winter months, emissions from Matimba Power Station are likely emitted above the stable layer and, as such, have less ground-level impact during this season. During summer, increased atmospheric turbulence promotes an increase in ground-level S concentrations. As coal is not predominantly used as a domestic fuel in Marapong, emissions from Matimba Power station are likely to be the main contributor to S at all three sites.

6.2 Highveld Region

6.2.1 Kwazamokhule

6.2.1.1 Gravimetric Analysis

During the winter 2015 sampling campaign, coarse fraction aerosol concentrations were generally higher than the fine fraction at Kwazamokhule (Table 6.8 and Figure 6.3). Coarse fraction aerosol concentrations were elevated over the sampling period, with a maximum 24-hour average PM_{10} concentration of $110.2 \mu\text{g}/\text{m}^3$ recorded on 19 July 2015. The 24-hour average PM_{10} standard was exceeded on five occasions during the sampling campaign. Fine

fraction aerosol concentrations also exceeded the 24-hour average PM_{2.5} standard on 1 occasion with a maximum 24-hour average PM_{2.5} concentration of 86.7 µg/m³ recorded on 10 July.

As would be expected, a decrease in the fine and coarse fraction aerosol concentrations was observed during the summer 2016 sampling campaign (Table 6.8 and Figure 6.4). However, various power outages were experienced at the Kwazamokhule sampling site during this campaign which resulted in data loss and as such, trends in the summer dataset could not be accurately determined. For the available data, both coarse and fine aerosol concentrations fell below their respective 24-hour average standards with a maximum 24-hour average PM₁₀ and PM_{2.5} concentration of 37.7 µg/m³ and 36.6 µg/m³ recorded, respectively.

Table 6.6: Mean aerosol concentrations (µg/m³) and standard deviations at Kwazamokhule for the winter 2015 and summer 2016 sampling campaigns

Sampling Site	Winter 2015		Summer 2016	
	Fine	Coarse	Fine	Coarse
Kwazamokhule	35.1 ± 23.3	68.9 ± 35.8	23.9 ± 12.7	15.8 ± 15.3

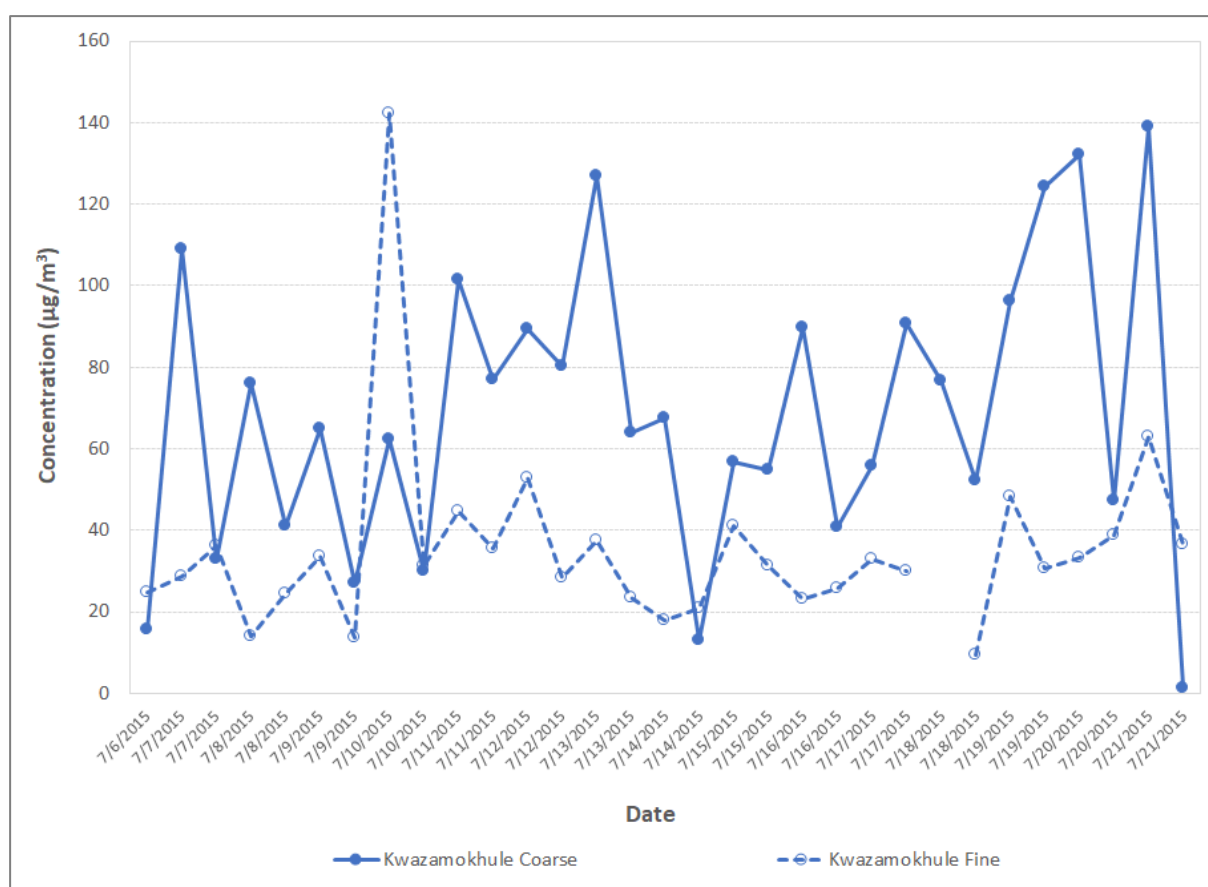


Figure 6.3: Fine and coarse aerosol concentrations at Kwazamokhule for the period 6 – 22 July 2015

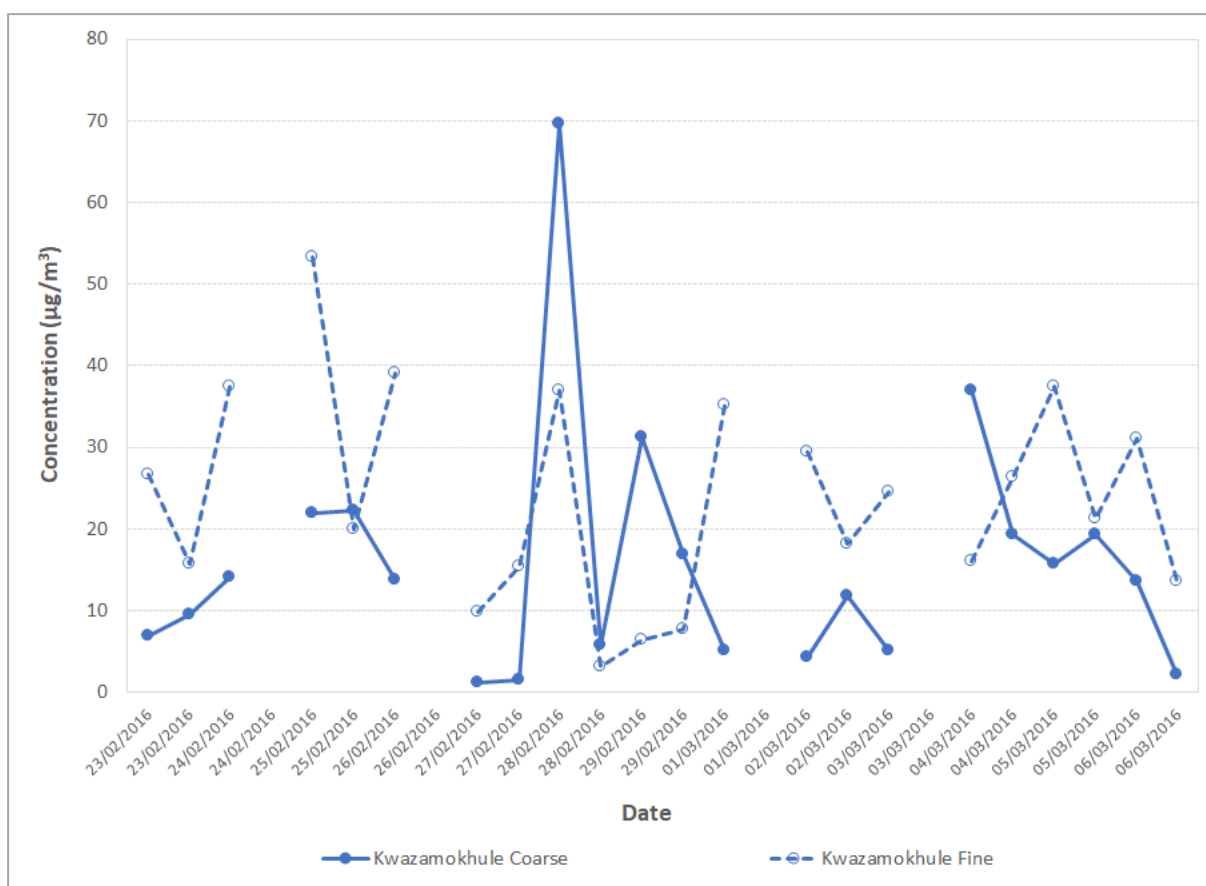


Figure 6.4: Fine and coarse aerosol concentrations at Kwazamokhule for the period 22 February – 7 March 2016

6.2.1.2 Chemical Analysis

Fine Fraction

The results of both sampling campaigns indicate Si, Al and S as the dominant elements at Kwazamokhule in the detected elemental fine fraction (Table 6.7). Si contributed to 28% and 24% of the detected elemental fine fraction aerosol during the winter and summer sampling campaigns, respectively. Al contributed to 14% in winter and 12% in summer. S accounted for 23% of the detected elemental fine fraction in winter, increasing to 42% in summer. The low EF calculated for Si and Ca at all three sites is indicative of a crustal origin of these species, while the extremely high EF calculated for S at all three sites supports an anthropogenic origin of this species (Table 6.8). In the ionic fine fraction, SO_4^{2-} is the most significant species, contributing to 48% (winter) and 61% (summer) of the detected fine ionic fraction. NH_4^+ is the next most abundant species during both campaigns, accounting for 18% and 24% during winter and summer, respectively. A good correlation is seen between S and SO_4^{2-} ($r = 0.70$ during winter and $r = 0.99$ during summer) and SO_4^{2-} and NH_4^+ in the fine fraction ($r = 0.69$ during winter and $r = 0.87$ during summer), which is indicative of a common origin such as a coal combustion

source. The biomass burning elements, K^+ and oxalate, contributed to 7% and 1% of the detected ionic fine fraction aerosol. These species showed good correlations ($r = 0.68$ during winter and $r = 0.59$ during summer), thereby indicating a possible biomass burning and/or residential wood burning source.

Coarse Fraction

In the detected elemental coarse fraction, Si, Al and Fe had the highest abundances during both sampling campaigns (Table 6.7). Si abundances were similar during both campaigns, contributing to 40% (winter) and 39% (summer) of the detected elemental coarse fraction aerosol. Strong correlations are seen between these species and other elements such as Ca, Mg and K, which is indicative of a distinctive soil component in this fraction. This is also supported by the low EF calculated for these species (Table 6.8). In the ionic component, SO_4^{2-} and F^- were the dominant ions in this fraction. As also seen in the Lephalale region, the abundance of F^- was highest during the summer sampling campaign, accounting for 45% of the detected ionic coarse fraction. SO_4^{2-} accounts for 39% and 27% of the detected ionic coarse fraction during the winter and summer sampling campaigns, respectively. NO_3^- , NH_4^+ and Ca^{2+} each contributed to 9 - 10% of the detected ionic coarse fraction during winter and 2%, 8% and 6%, respectively, during summer. Average NO_3^-/SO_4^{2-} ratios for the coarse fraction were 0.27 ± 0.12 (winter) and 0.13 ± 0.11 (summer) at Kwazamokhule which indicates a strong industrial origin of these species.

Table 6.7: Mean concentrations and standard deviations of the measured species at Kwazamokhule for the period 6 – 22 July 2015 and 22 February – 7 March 2016

Species		Kwazamokhule (Winter)		Kwazamokhule (Summer)	
		Fine	Coarse	Fine	Coarse
Elemental Composition ($\mu\text{g}/\text{m}^3$)	Cl	0.1 ± 0.1	0.2 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
	S	0.9 ± 0.6	0.6 ± 0.3	1.1 ± 1.3	0.3 ± 0.3
	Ca	0.1 ± 0.2	0.7 ± 0.3	0.1 ± 0.1	0.3 ± 0.1
	Fe	0.5 ± 1.0	3.3 ± 1.6	0.3 ± 0.2	1.1 ± 0.6
	Na	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
	Mg	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.0
	Al	0.5 ± 0.9	2.8 ± 1.3	0.3 ± 0.3	1.0 ± 0.5
	Si	1.1 ± 1.9	6.0 ± 2.8	0.6 ± 0.6	2.1 ± 1.1
	P	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	K	0.3 ± 0.2	0.7 ± 0.3	0.1 ± 0.1	0.2 ± 0.1
	Ti	0.1 ± 0.1	0.3 ± 0.2	0.0 ± 0.0	0.1 ± 0.1
	Mn	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Zn	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0
	Cr	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	V	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Pb	0.1 ± 0.0	0.0 ± 0.0	BDL	BDL
	As	0.0 ± 0.0	0.0 ± 0.0	BDL	BDL
	Ni	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Sr	0.0 ± 0.0	0.0 ± 0.0	BDL	BDL
Water-Soluble Ionic Composition ($\mu\text{g}/\text{m}^3$)	F ⁻	0.3 ± 0.6	0.7 ± 0.3	0.5 ± 0.4	1.6 ± 0.8
	Cl ⁻	0.1 ± 0.2	0.2 ± 0.1	BDL	0.0 ± 0.0
	NO ₃ ⁻	0.2 ± 0.2	0.5 ± 0.2	0.0 ± 0.0	0.1 ± 0.0
	SO ₄ ²⁻	1.9 ± 1.3	2.0 ± 1.0	3.1 ± 3.7	1.0 ± 1.0
	Na ⁺	0.2 ± 0.6	0.3 ± 0.1	0.0 ± 0.0	0.1 ± 0.1
	NH ₄ ⁺	0.7 ± 0.5	0.5 ± 0.3	1.2 ± 2.0	0.3 ± 0.3
	K ⁺	0.3 ± 0.2	0.2 ± 0.1	0.1 ± 0.0	0.1 ± 0.1
	Ca ²⁺	0.1 ± 0.1	0.5 ± 0.3	0.1 ± 0.1	0.2 ± 0.1
	Mg ²⁺	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Formate	0.1 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	BDL
	Acetate	0.0 ± 0.1	0.0 ± 0.0	BDL	BDL
	Oxalate	0.0 ± 0.0	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.0

Notes:

BDL = Below Detection Limit

BDL species not shown include Cd

Table 6.8: Enrichment factors for selected species at Kwazamokhule for the period 6 – 22 July 2015 and 23 February – 7 March 2016

Species	Kwazamokhule 2015		Kwazamokhule 2016	
	Fine	Coarse	Fine	Coarse
S	408.5	36.1	968.0	62.2
Ca	0.4	0.5	0.5	1.4
Fe	1.8	1.9	1.6	3.4
Si	0.6	0.6	0.7	0.7
K	2.9	0.8	2.1	1.3
Ti	2.1	2.3	1.7	4.0
Mn	2.9	2.2	16.6	3.9
V	6.7	4.7	3.1	11.3

Kwazamokhule is situated in the industrialised Highveld region which is characterised by a diverse emission source profile. A similar chemical profile was observed at Kwazamokhule during both seasons indicating similar contributing sources at this site. As seen in the other regions, the summer season shows higher S and SO₄²⁻ abundances (with the exception of the coarse fraction during summer). While domestic coal combustion is likely to be an important localised source during the winter months, regional sources, such as the surrounding coal-fired power stations, are also likely to be significant contributors during both the summer and winter seasons.

6.2.2 Embalenhle

6.2.2.1 Gravimetric Analysis

During the winter 2016 sampling campaign, higher aerosol concentrations were generally recorded at Embalenhle compared to the upwind Kinross site (Table 6.9 and Figure 6.5). Coarse fraction aerosol concentrations are also significantly higher than fine fraction at Embalenhle, while the opposite is seen at Kinross which shows higher fine fraction aerosol concentrations during the sampling campaign. During July 2016, elevated coarse fraction concentrations were measured at Embalenhle between 15 to 23 July, with a decrease observed from 24 to 31 July. Rainfall was experienced during the latter part of July, resulting in the reduction in aerosol concentrations. The 24-hour average PM₁₀ standard was exceeded 8 times at Embalenhle, with a maximum 24-hour average PM₁₀ concentration of 289.0 µg/m³ recorded on 20 July. Fine fraction concentrations exceeded the 24-hour average PM_{2.5} standard on 1 occasion at Embalenhle with a maximum 24-hour average PM_{2.5} concentration of 51.6 µg/m³ recorded on 18 July. During August, coarse fraction aerosol concentrations at Embalenhle

remained high with a maximum 24-hour average PM₁₀ concentration of 179.6 µg/m³ recorded on 6 August. Five exceedances of the standard were recorded during the August sampling campaign. At Kinross, no exceedances of the standard were recorded with a maximum 24-hour average PM₁₀ concentration of 35.5 µg/m³ recorded on 7 August. Fine fraction aerosol concentrations are similar at both sites, with a maximum 24-hour average PM_{2.5} concentration of 29.5 µg/m³ and 22.4 µg/m³ recorded on 10 August at Embalenhle and Kinross, respectively.

During the summer 2017 sampling campaign, aerosol concentrations remained higher in Embalenhle compared to Kinross (Table 6.9 and Figure 6.5), although a significant decrease in coarse fraction aerosol concentrations was observed at Embalenhle with a maximum 24-hour average PM₁₀ concentration of 48.0 µg/m³ recorded on 19 February. Coarse fraction concentrations at Kinross were also low with a maximum 24-hour average PM₁₀ concentration of 24.1 µg/m³ recorded on 28 February. Fine fraction concentrations remained similar to those observed during the winter sampling period, with a maximum 24-hour average PM_{2.5} concentration of 37.0 µg/m³ and 19.8 µg/m³ recorded at Embalenhle and Kinross, respectively. Rainfall was experienced from 19 to 25 February which is evident in the reduced aerosol concentrations recorded during this period.

During summer, a similar signature was observed in the coarse and fine fraction aerosol concentrations at both sites while this is not as evident during winter. Localised sources of pollution, such as domestic fuel burning in Embalenhle are likely to contribute to an increase in aerosol concentrations during this season while during summer, a regional source(s) is likely to have a greater contribution to the aerosol loading at these sites.

Table 6.9: Mean aerosol concentrations (µg/m³) and standard deviations at Embalenhle and Kinross for the winter 2016 and summer 2017 sampling campaigns

Sampling Site	Winter 2016		Summer 2017	
	Fine	Coarse	Fine	Coarse
Embalenhle	34.1 ± 12.9	114.2 ± 86.2	19.0 ± 10.8	11.2 ± 17.1
Kinross	16.3 ± 6.7	10.3 ± 14.5	7.4 ± 7.7	5.9 ± 7.3

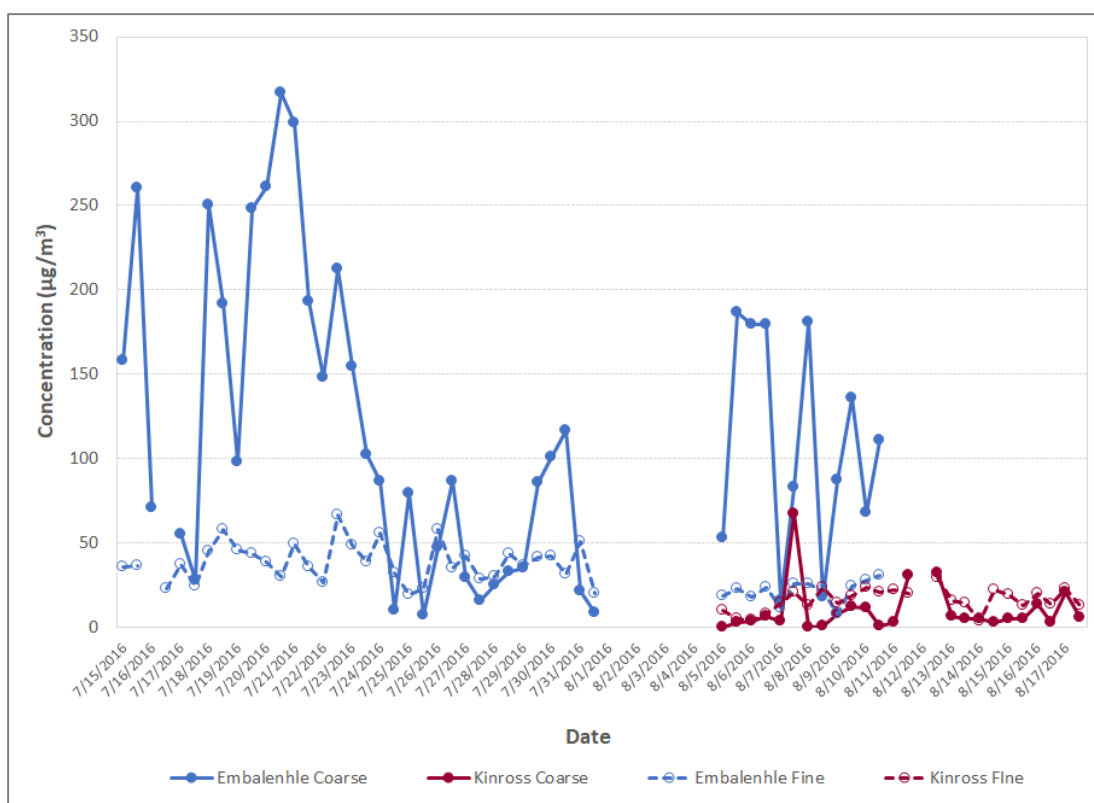


Figure 6.5: Fine and coarse aerosol concentrations at Embalenhle and Kinross for the period 15 – 31 July and 5 – 17 August 2016

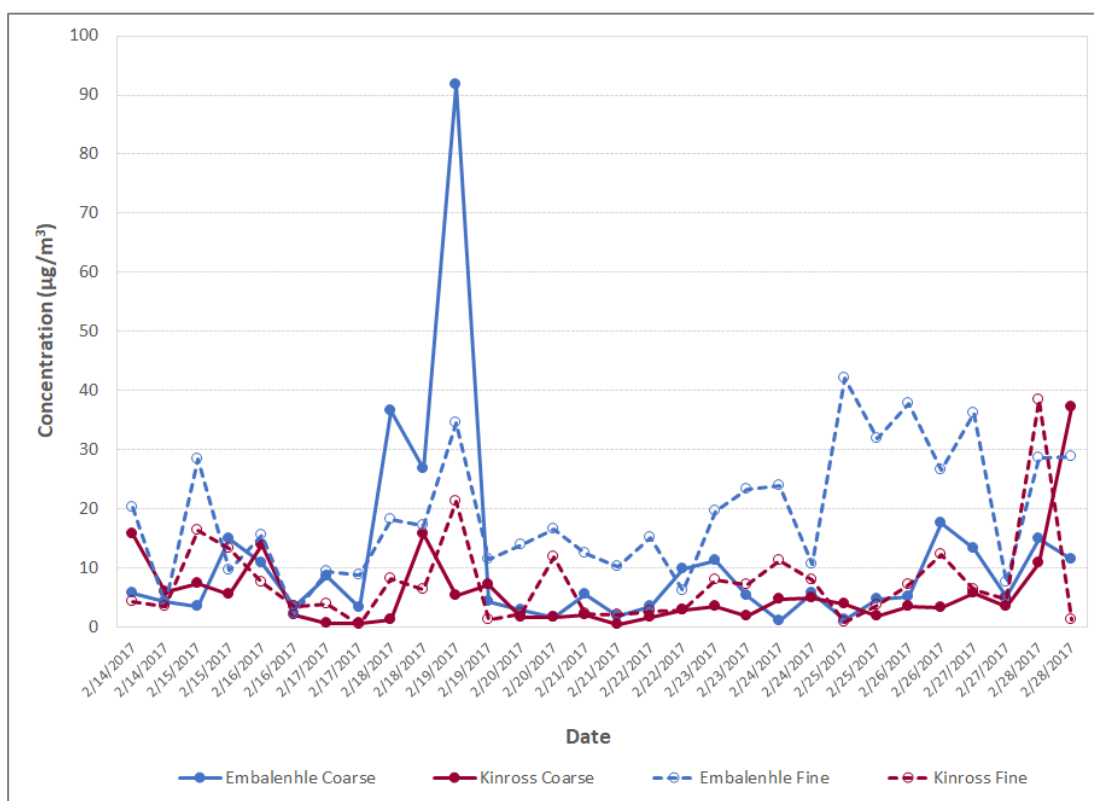


Figure 6.6: Fine and coarse aerosol concentrations at Embalenhle and Kinross for the period 14 – 28 February 2017

6.2.2.2 Chemical Analysis

6.2.2.2.1 Winter Sampling Campaign

Fine Fraction

During the winter 2016 sampling campaign, Si and Na were identified as dominant elements at both sampling sites in the detected elemental fine aerosol fraction (Table 6.10). Si ranges from 23 – 35% while Na ranged from 22 – 42% of the detected fine elemental fraction. Si is strongly correlated with Ca, Fe, Mg, Al and Ti (and the ionic species, Ca^{2+} , Mg^{2+}) at Embalenhle ($r > 0.90$) and with Mg and Al at Kinross ($r > 0.80$), thereby suggesting a crustal origin of these elements in the fine fraction as is also supported in the low EF calculated for these species (Table 6.11). The next most abundant elements are S and Al, each contributing to 8 – 10% of the detected elemental fine fraction aerosol. S and SO_4^{2-} are strongly correlated ($r = 0.92$ at Embalenhle and $r = 0.93$ at Kinross), which is indicative of a coal combustion source. Coal is used as domestic fuel in Embalenhle and Sasol is located to the immediate right of Embalenhle. A number of coal-fired power stations are also present in the region with Kriel Power Station and Matla Power Station the closest to Kinross. As is also seen in the other regions, S is strongly enriched in the fine fraction (Table 6.11). In the ionic fine fraction, SO_4^{2-} contributes to over half of the detected ionic fine fraction aerosol at both sampling sites followed by NH_4^+ which contributes to 19% of the detected ionic fine fraction aerosol at both sites. SO_4^{2-} and NH_4^+ are strongly correlated ($r = 0.99$) at both sites, indicating a common secondary origin, such as coal combustion, of these species. F^- is the third most dominant ionic species, contributing to 14% and 8% of the detected ionic fine fraction at Embalenhle and Kinross, respectively. K^+ contributed to 3 - 4% of the detected ionic fine fraction aerosol at both sites while oxalic had a low contribution (less than 2%) at both sites. These species show a good correlation at Kinross ($r = 0.72$) although this is not as strong at Embalenhle ($r = 0.47$).

Coarse Fraction

Si and Na remain the dominant elements in the detected elemental coarse aerosol fraction, with Si ranging from 31 – 42% and Na ranging from 14 – 40% of the detected coarse elemental fraction at both sites (Table 6.10). Al is the next most abundant species contributing to 11% of the detected coarse elemental fraction at both sites. Al and Si are both strongly correlated ($r = 1.00$ and $r = 0.91$ at Embalenhle and Kinross, respectively) with these elements also showing strong correlations ($r > 0.80$) with Ca, Na and Mg at Embalenhle and Ca, Fe and Mg at Kinross, thereby indicating a crustal origin of these sources in the coarse fraction. In the ionic component, F^- , SO_4^{2-} and Ca^{2+} are the dominant ionic species at both sites. F^- contributes to

27 – 44%, SO_4^{2-} contributes to 17 – 32% and Ca^{2+} accounts for 12 – 13% of the detected ionic coarse fraction aerosol. SO_4^{2-} is strongly correlated with NH_4^+ in this size fraction ($r = 0.67$ at Embalenhle and 0.96 at Kinross) and shows a moderate correlation with NO_3^- ($r = 0.60$ at Embalenhle and 0.74 at Kinross). For both sites, average coarse fraction $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios were 0.14 ± 0.20 (Embalenhle) and 0.44 ± 0.31 (Kinross) indicative of industrial activities being the dominant source of these species. Average fine fraction $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios were 0.06 ± 0.04 (Embalenhle) and 0.06 ± 0.04 (Kinross), again supporting an industrial origin.

Table 6.10: Mean concentrations and standard deviations of the measured species at Embalenhle and Kinross for the period 15 July – 17 August 2016

Species		Embalenhle		Kinross	
		Fine	Coarse	Fine	Coarse
Elemental Composition ($\mu\text{g}/\text{m}^3$)	Cl	0.2 ± 0.4	2.9 ± 3.8	0.1 ± 0.0	0.1 ± 0.1
	S	0.6 ± 0.4	0.6 ± 0.4	0.5 ± 0.3	0.2 ± 0.2
	Ca	0.4 ± 0.4	4.8 ± 3.8	0.2 ± 0.1	0.4 ± 0.2
	Fe	0.1 ± 0.1	1.5 ± 2.0	0.1 ± 0.1	0.1 ± 0.1
	Na	1.6 ± 1.1	6.6 ± 3.8	2.2 ± 1.1	3.0 ± 2.9
	Mg	0.4 ± 0.3	3.9 ± 3.0	0.1 ± 0.1	0.4 ± 0.2
	Al	0.7 ± 0.5	5.3 ± 4.1	0.4 ± 0.2	1.1 ± 0.6
	Si	2.4 ± 0.3	20.2 ± 15.8	1.2 ± 0.5	3.0 ± 1.5
	P	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
	K	0.4 ± 0.2	1.8 ± 1.3	0.4 ± 0.2	0.4 ± 0.3
	Ti	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.1
	Mn	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Zn	0.1 ± 0.3	0.3 ± 0.6	0.0 ± 0.0	0.1 ± 0.0
	Cr	0.0 ± 0.0	0.1 ± 0.4	0.0 ± 0.0	0.0 ± 0.0
	V	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Pb	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	As	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Ni	0.0 ± 0.0	0.0 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
	Sr	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Water-Soluble Ionic Composition ($\mu\text{g}/\text{m}^3$)	F ⁻	0.5 ± 0.4	5.3 ± 4.1	0.3 ± 0.1	1.1 ± 1.4
	Cl ⁻	0.1 ± 0.1	0.7 ± 1.3	0.0 ± 0.0	0.1 ± 0.2
	NO ₃ ⁻	0.1 ± 0.0	0.2 ± 0.2	0.1 ± 0.1	0.3 ± 0.3
	SO ₄ ²⁻	1.9 ± 1.6	2.0 ± 1.6	2.2 ± 1.5	1.3 ± 1.5
	Na ⁺	0.1 ± 0.0	0.3 ± 0.2	0.1 ± 0.0	0.2 ± 0.2
	NH ₄ ⁺	0.7 ± 0.5	1.0 ± 0.8	0.7 ± 0.4	0.3 ± 0.4
	K ⁺	0.1 ± 0.1	0.3 ± 0.2	0.1 ± 0.1	0.1 ± 0.1
	Ca ²⁺	0.2 ± 0.2	1.5 ± 1.2	0.1 ± 0.0	0.5 ± 0.7
	Mg ²⁺	0.0 ± 0.0	0.5 ± 0.5	0.0 ± 0.0	0.1 ± 0.2
	Formic	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Acetic	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Oxalic	0.1 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0

Table 6.11: Enrichment factors for selected species at Embalenhle and Kinross for the period 15 July – 11 August 2016 (Embalenhle) and 5 – 18 August 2016 (Kinross)

Species	Embalenhle		Kinross	
	Fine	Coarse	Fine	Coarse
S	229.3	26.7	247.0	23.1
Ca	1.4	2.5	0.7	0.3
Fe	0.3	0.6	0.3	0.2
Si	1.1	1.1	0.8	0.8
K	2.8	1.5	3.7	1.2
Ti	0.4	0.6	0.4	0.4
Mn	0.2	0.2	0.5	0.1
V	0.1	0.1	0.2	0.1

6.2.2.2.2 Summer Sampling Campaign

Fine Fraction

During the summer 2017 sampling campaign, Si, Ca and S were identified as the dominant elements at both sampling sites in the detected fine elemental fraction (Table 6.13). Si ranged from 14 – 26% and Ca ranged from 18 – 28% with the highest abundances of both elements measured at Embalenhle. Strong correlations are observed between Si, Fe, Mg, Al (and K at Embalenhle) at both sites. Calculated EFs for Fe, Si, K, Ti and Mn suggest a mixed crustal and anthropogenic origin of these species while V shows a strong anthropogenic origin. Ca is also enriched in the fine fraction at both sites, indicative of an anthropogenic origin of this species (Table 6.12). S ranged from 14 – 44% with the highest abundances (and enrichment) of S again seen at Kinross. In the fine ionic fraction, SO_4^{2-} and NH_4^+ are the dominant species at both sites. SO_4^{2-} abundances contribute to 65% of the detected fine ionic fraction at both sites followed by NH_4^+ as the next most significant species (22 – 25%). Strong correlations are seen between SO_4^{2-} and NH_4^+ ($r = 0.99$ at both sampling sites) and between SO_4^{2-} and S ($r = 1.00$ at Kinross), supporting a coal combustion source. K^+ and oxalic each contributed to 1% or less of the detected ionic fine fraction aerosol at both sites with a moderate correlation seen at Embalenhle ($r = 0.55$) and Kinross ($r = 0.64$).

Coarse Fraction

In the detected coarse elemental fraction, Si remains the main contributing species at both sites (24 – 31%) with S identified as the next most significant at Embalenhle (15%) and Ca at Kinross (29%) (Table 6.13). Strong correlations are seen between Si, Mg, Al and K at both sites. Calculated EF for these species indicates a crustal origin of Si and both a crustal and anthropogenic origin of Ca, Fe, K, Ti, Mn and V. In the coarse ionic fraction, SO_4^{2-} contributes to at least 40% of the detected coarse ionic aerosol component, followed by F^- which ranged from 21 – 23% of the detected coarse ionic fraction. NH_4^+ abundances are also high, contributing to 14% of the detected coarse ionic fraction at both sites. As seen in the other sites, SO_4^{2-} and NH_4^+ abundances are significantly higher during the summer compared to winter. Strong correlations between SO_4^{2-} and NH_4^+ ($r = 0.98$ at Embalenhle and $r = 0.97$ at Kinross) support a common origin of these species. SO_4^{2-} also shows a moderate correlation with NO_3^- ($r > 0.50$). Average coarse fraction $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios were 0.14 ± 0.17 (Embalenhle) and 0.10 ± 0.09 (Kinross) indicative of a strong industrial origin of these species at both these sites. This is also seen in the fine fraction with average $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios of 0.03 ± 0.04 (Embalenhle) and 0.01 ± 0.01 (Kinross).

Table 6.12: Enrichment factors for selected species at Embalenhle and Kinross for the period 14 – 28 February 2017

Species	Embalenhle		Kinross	
	Fine	Coarse	Fine	Coarse
S	1425.1	569.1	3254.3	133.6
Ca	30.7	3.1	29.4	7.1
Fe	1.2	0.8	24.8	2.1
Si	1.6	1.0	2.6	1.0
K	1.9	2.6	2.4	3.3
Ti	4.2	6.6	2.5	8.2
Mn	4.7	4.9	13.2	5.8
V	43.1	46.3	352.6	38.5

Table 6.13: Mean concentrations and standard deviations of the measured species at Embalenhle and Kinross for the period 14 – 28 February 2017

Species		Embalenhle		Kinross	
		Fine	Coarse	Fine	Coarse
Elemental Composition ($\mu\text{g}/\text{m}^3$)	Cl	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	S	1.0 ± 1.2	0.8 ± 1.5	0.9 ± 1.4	0.2 ± 0.2
	Ca	2.1 ± 4.7	0.4 ± 0.5	0.4 ± 0.2	1.6 ± 3.9
	Fe	0.4 ± 0.8	0.3 ± 0.3	0.0 ± 0.1	0.3 ± 0.3
	Na	0.3 ± 0.4	0.4 ± 0.4	0.1 ± 0.1	0.3 ± 0.3
	Mg	0.4 ± 0.9	0.4 ± 0.4	0.0 ± 0.1	0.2 ± 0.2
	Al	0.5 ± 1.0	0.5 ± 0.6	0.1 ± 0.1	0.5 ± 0.8
	Si	1.0 ± 3.7	1.6 ± 1.8	0.3 ± 0.4	1.3 ± 1.6
	P	0.0 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	K	0.2 ± 0.3	0.1 ± 0.1	0.0 ± 0.0	0.2 ± 0.1
	Ti	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.1
	Mn	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Zn	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.2 ± 0.1
	Cr	0.0 ± 0.0	BDL	0.0 ± 0.0	BDL
	V	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Pb	BDL	0.1 ± 0.0	BDL	0.1 ± 0.0
	Cd	BDL	0.4 ± 0.2	BDL	0.4 ± 0.2
	As	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Ni	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Sr	0.4 ± 1.0	0.1 ± 0.0	0.1 ± 0.0	0.4 ± 1.0
Water-Soluble Ionic Composition ($\mu\text{g}/\text{m}^3$)	F ⁻	0.4 ± 0.7	0.8 ± 1.2	0.3 ± 0.4	0.5 ± 0.5
	Cl ⁻	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	NO ₃ ⁻	0.2 ± 0.6	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.1
	SO ₄ ²⁻	6.0 ± 6.6	1.4 ± 1.8	3.6 ± 5.5	1.0 ± 1.1
	Na ⁺	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.1
	NH ₄ ⁺	2.3 ± 2.4	0.5 ± 0.6	1.2 ± 1.5	0.3 ± 0.4
	K ⁺	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Ca ²⁺	0.1 ± 0.1	0.3 ± 0.5	0.2 ± 0.2	0.2 ± 0.3
	Mg ²⁺	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
	Formic	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Acetic	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Oxalic	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.0	0.0 ± 0.0

Notes:

BDL = Below Detection Limit

The diverse emission source profile of the industrialised Highveld region is reflected in the different chemical profiles seen at the Embalenhle and Kinross sampling sites during both seasons. In general, the upwind site of Kinross shows higher abundances of S and SO_4^{2-} compared to Embalenhle. While the prevailing east-northeasterly wind field at Embalenhle shows that emissions from neighbouring sources such as Sasol would likely be transported towards the township, the measured S and SO_4^{2-} abundances suggest that these high-level emissions are not significantly impacting the township. Kinross, which shows higher S and SO_4^{2-} abundances, is likely to rather be impacted by emissions from Kriel and Matla Power stations to the north than Sasol as the wind field is dominated by winds from the north and north-northeast. This is supported by the high contributions of SO_4^{2-} evident in the ionic coarse fraction which is indicative of aged air masses. Higher abundances of S and SO_4^{2-} are also observed at both sampling sites during summer, as is also seen in the other study regions.

6.3 Vaal Triangle Region

6.3.1 Zamdela

6.3.1.1 Gravimetric Analysis

During the winter 2016 sampling campaign, higher aerosol concentrations were generally recorded at Zamdela compared to the upwind Ecopark site (Table 6.14 and Figure 6.7). Coarse fraction aerosols were also generally higher than the fine fraction during both winter sampling campaigns. During July 2016, elevated aerosol concentrations were recorded from 15 to 23 July with a decrease in concentrations observed from 24 to 30 July as a result of rainfall. This decrease is particularly evident in the coarse fraction and less so in the fine fraction aerosol. Coarse fraction aerosol concentrations at Zamdela exceeded the 24-hour average PM_{10} standard on six occasions with a maximum 24-hour average PM_{10} concentration of $120.5 \mu\text{g}/\text{m}^3$ recorded on 22 July. In the fine fraction, aerosol concentrations were also elevated and exceeded the 24-hour average $\text{PM}_{2.5}$ standard on three occasions. A maximum 24-hour average $\text{PM}_{2.5}$ concentration of $86.8 \mu\text{g}/\text{m}^3$ was recorded on 29 July. During September 2016, simultaneous measurements were undertaken at Zamdela and Ecopark. Coarse fraction aerosol concentrations were also elevated during this sampling period, with lower concentrations observed on 17 and 18 September 2016 as a result of rainfall. Five exceedances of the standard were recorded at Zamdela during the September sampling campaign with a maximum 24-hour average PM_{10} concentration of $109.3 \mu\text{g}/\text{m}^3$ recorded on 15 September. No exceedances were recorded at Ecopark with a maximum 24-hour average PM_{10} concentration of $46.9 \mu\text{g}/\text{m}^3$ recorded on 13 September. Fine fraction aerosol concentrations were low with no exceedances of the standard recorded. A maximum 24-hour average $\text{PM}_{2.5}$

concentration of 44.5 $\mu\text{g}/\text{m}^3$ and 34.3 $\mu\text{g}/\text{m}^3$ were recorded on 12 September at Zamdela and Ecopark, respectively.

During the summer 2017 sampling campaign, a significant decrease in coarse fraction aerosol concentrations is evident with no exceedances of the 24-hour average PM_{10} standard recorded at either sampling site (Table 6.14 and Figure 6.8). A maximum 24-hour average PM_{10} concentration of 14.8 $\mu\text{g}/\text{m}^3$ and 29.8 $\mu\text{g}/\text{m}^3$ was recorded at Zamdela and Ecopark, respectively. However, the fine fraction aerosol concentration is higher at both sites, with a maximum 24-hour average $\text{PM}_{2.5}$ concentration of 31.8 $\mu\text{g}/\text{m}^3$ and 19.0 $\mu\text{g}/\text{m}^3$ recorded at Zamdela and Ecopark, respectively. During the sampling campaign, higher aerosol concentrations were recorded from 13 to 19 February, with a decrease observed from 20 to 24 February. Heavy rain was experienced in the region on 20 and 21 February, resulting in a decrease in aerosol concentrations. Light rain was experienced for the remainder of the sampling campaign.

Coarse and fine fraction aerosol concentrations at both sites show a similar signature over the summer sampling period, indicating that both sites are impacted by a regional source(s) of air pollution during summer. The impact of localised emissions from the Zamdela township is more pronounced during winter when increased periods of domestic fuel burning together with prevailing meteorological conditions, result in an increase in ambient aerosol concentrations in the township.

Table 6.14: Mean aerosol concentrations ($\mu\text{g}/\text{m}^3$) and standard deviations at Zamdela and Ecopark for the winter 2016 and summer 2017 sampling campaigns

Sampling Site	Winter 2016		Summer 2017	
	Fine	Coarse	Fine	Coarse
Zamdela	35.7 $\pm$ 19.6	58.4 $\pm$ 49.3	17.2 $\pm$ 12.1	6.3 $\pm$ 6.1
Ecopark	17.1 $\pm$ 11.9	21.1 $\pm$ 17.6	7.9 $\pm$ 8.6	8.7 $\pm$ 12.0

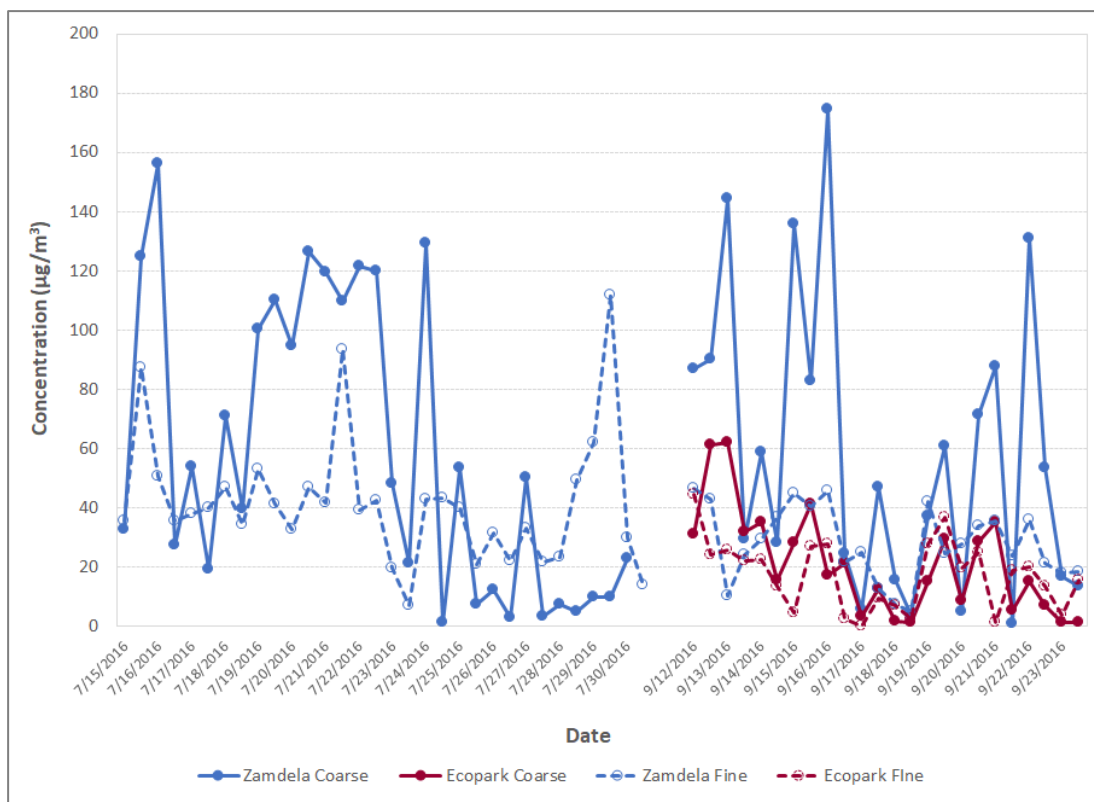


Figure 6.7: Fine and coarse aerosol concentrations at Zamdela and Ecopark for the period 15 – 31 July 2016 and 12 – 23 September 2016

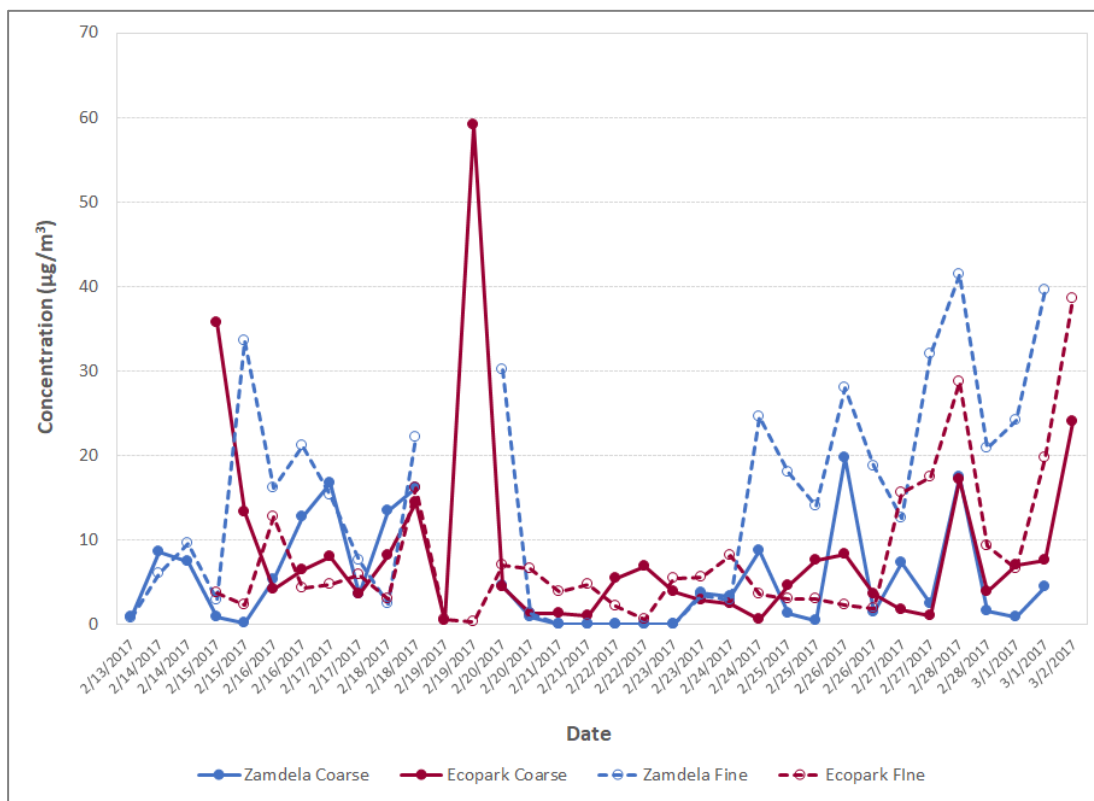


Figure 6.8: Fine and coarse aerosol concentrations at Zamdela and Ecopark for the period 13 February- 2 March 2017

6.3.1.2 Elemental Analysis

6.3.1.2.1 Winter Sampling Campaign

Fine Fraction

During the winter 2016 sampling campaign, Si and Na were identified as the dominant elements at both sampling sites in the detected elemental fine aerosol fraction (Table 6.15). For both sites, Si abundances ranged between 24 – 33% and Na abundances ranged between 26 – 35% of the detected elemental fine fraction. S, Al and K are the next most abundant species with S ranging from 9 – 12% and both Al and K ranging from 9 – 11%. Calculated EFs for Fe, Si, Ti, Mn and V are indicative of a crustal origin of these species (Table 6.16), as also supported in the strong correlations seen between Al and Si ($r = 0.99$ at both sites) in this size fraction. Strong correlations are observed between S and SO_4^{2-} ($r = 0.98$ at Zamdela and 0.99 at Ecopark) and NH_4^+ and SO_4^{2-} ($r = 0.97$ at Zamdela and $r = 0.96$ at Ecopark) in the fine fraction, supporting a coal combustion source.

In the ionic component, SO_4^{2-} contributes to 46% and 49% of the fine ionic fraction at Zamdela and Ecopark, respectively. Likely sources of SO_4^{2-} and S include domestic coal combustion in Zamdela and the Lethabo Coal-Fired Power Station which is located approximately 17 km to the northeast of Zamdela. The neighbouring petrochemical facilities of Sasol and Natref are also a likely source of these species. The next most abundant species were F^- and NH_4^+ with F^- ranging from 15 – 20% and NH_4^+ ranging from 17 – 18% of the detected ionic fine aerosol fraction. Sources of F^- in the Vaal Triangle region include coal combustion, soil dust and biomass burning as well as industrial sources such as phosphate fertilizer production, brick manufacturing and iron and steel plants. The biomass burning elements, K^+ and oxalic, showed a high degree of correlation ($r = 0.87$ at Zamdela and $r = 0.92$ at Ecopark) indicating a possible biomass burning or residential wood burning source. Abundances of K^+ and oxalic ranged from 4 – 5% and 2 – 3 %, respectively, in the fine fraction.

Coarse Fraction

In the detected coarse elemental fraction, Si, Na, Al are once again the dominant elements at both sites with Si abundances ranging between 34 – 42%, Na abundances ranging between 18 – 29% and Al abundances ranging between 12 – 14% (Table 6.15). A strong correlation is seen between Al and Si ($r = 0.99$ at both sites) in the coarse aerosol fraction. Other crustal species such as Mg, Mn, Fe, Ti and Ca also show good correlations, supporting crustal dust sources as the primary origin of these elements in this size fraction. This is also confirmed in the low EF calculated for these species (Table 6.16). In the ionic component, F^- and SO_4^{2-} have the highest

abundances, contributing between 37 – 39% and 24 – 25%, respectively, of the detected ionic coarse fraction. Good correlations are seen between F^- and a number of species including SO_4^{2-} , NO_3^- , oxalic, S, Ca, Mg, Al, Si and K which could indicate various contributing sources to this species in the coarse fraction. Strong correlations are seen between SO_4^{2-} and NH_4^+ ($r = 0.98$ at Zamdela and $r = 0.94$ at Ecopark) and between SO_4^{2-} and S ($r = 0.99$ at Zamdela and $r = 0.97$ at Ecopark), which is indicative of a coal combustion source. NO_3^- accounts for 2 – 3% of the coarse fraction aerosol at both sites with moderate correlations seen between SO_4^{2-} and NO_3^- ($r = 0.60$ at both sites). Average NO_3^-/SO_4^{2-} ratios were 0.16 ± 0.11 (Zamdela) and 0.11 ± 0.07 (Ecopark) indicative of a strong industrial origin of these species in the coarse fraction. This is also seen in the fine fraction with average NO_3^-/SO_4^{2-} ratios of 0.08 ± 0.08 (Zamdela) and 0.05 ± 0.05 (Ecopark). The elevated contribution of SO_4^{2-} in this size fraction, as well as the presence of other secondary species, is indicative of aged air masses, as is also observed at the Highveld sampling sites.

Table 6.15: Mean concentrations and standard deviations of the measured species at Zamdela and Ecopark for the period 15 - 30 July and 12 - 23 September 2016

Species		Zamdela		Ecopark	
		Fine	Coarse	Fine	Coarse
Elemental Composition ($\mu\text{g}/\text{m}^3$)	Cl	0.2 ± 0.4	0.4 ± 0.5	0.0 ± 0.0	0.1 ± 0.0
	S	0.8 ± 0.7	0.4 ± 0.4	0.7 ± 0.8	0.2 ± 0.2
	Ca	0.5 ± 0.4	2.2 ± 1.7	0.2 ± 0.2	0.9 ± 0.6
	Fe	0.1 ± 0.1	0.7 ± 1.5	0.1 ± 0.1	0.6 ± 1.7
	Na	2.3 ± 2.0	4.5 ± 3.3	2.2 ± 2.1	3.4 ± 3.0
	Mg	0.3 ± 0.2	0.9 ± 0.7	0.2 ± 0.1	0.4 ± 0.3
	Al	1.0 ± 0.8	3.5 ± 2.5	0.5 ± 0.4	1.3 ± 0.9
	Si	3.0 ± 2.2	10.5 ± 7.6	1.5 ± 1.2	4.0 ± 2.8
	P	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
	K	0.8 ± 0.5	1.3 ± 1.0	0.7 ± 0.6	0.6 ± 0.4
	Ti	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Mn	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Zn	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
	Cr	0.0 ± 0.0	0.0 ± 0.3	0.0 ± 0.0	0.1 ± 0.4
	V	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Pb	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	As	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Ni	0.0 ± 0.0	0.0 ± 0.1	0.0 ± 0.0	0.0 ± 0.1
	Sr	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Water-Soluble Ionic Composition ($\mu\text{g}/\text{m}^3$)	F ⁻	1.3 ± 0.9	3.1 ± 2.4	0.8 ± 0.5	1.8 ± 1.1
	Cl ⁻	0.0 ± 0.1	0.2 ± 0.3	0.1 ± 0.1	0.1 ± 0.2
	NO ₃ ⁻	0.2 ± 0.5	0.3 ± 0.3	0.1 ± 0.3	0.1 ± 0.1
	SO ₄ ²⁻	3.1 ± 2.8	2.1 ± 2.3	2.7 ± 2.9	1.1 ± 1.1
	Na ⁺	0.1 ± 0.1	0.3 ± 0.2	0.1 ± 0.1	0.3 ± 0.2
	NH ₄ ⁺	1.2 ± 1.2	0.7 ± 1.0	1.0 ± 1.1	0.2 ± 0.2
	K ⁺	0.3 ± 0.2	0.3 ± 0.3	0.3 ± 0.3	0.1 ± 0.1
	Ca ²⁺	0.3 ± 0.2	1.2 ± 1.0	0.2 ± 0.2	0.6 ± 0.4
	Mg ²⁺	0.0 ± 0.0	0.2 ± 0.2	0.1 ± 0.1	0.2 ± 0.2
	Formic	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.1	0.0 ± 0.1
	Acetic	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.1
	Oxalic	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1

Table 6.16: Enrichment factors for selected species at Zamdela and Ecopark for the period 15 – 31 July (Zamdela) and 12 - 24 September (Zamdela and Ecopark)

Species	Zamdela		Ecopark	
	Fine	Coarse	Fine	Coarse
S	203.7	23.9	256.1	29.5
Ca	1.1	1.9	0.9	0.6
Fe	0.3	0.4	0.3	1.0
Si	0.9	0.9	0.8	1.0
K	3.5	1.5	3.6	2.4
Ti	0.2	0.3	0.4	0.7
Mn	0.2	0.2	0.2	0.9
V	0.1	0.1	0.1	0.3

6.3.1.2.2 Summer Sampling Campaign

Fine Fraction

During the summer 2017 sampling campaign, S, Ca and Si were identified as the dominant elements at both sites in the fine fraction (Table 6.18). Ca abundances range between 10% - 13% while Si contributes to 14% of the detected elemental fine aerosol mass at both sites. Si shows a strong correlation with Mg ($r = 0.93$ and 0.89 at Zamdela and Ecopark, respectively) and Al ($r = 0.95$ and 0.98 at Zamdela and Ecopark, respectively). Calculated EF for Ca show this species has both a crustal and anthropogenic origin in this size fraction (Table 6.17). It is interesting to note the significant increase in S contributions during summer with S contributing to 45 – 47% of the detected elemental fine aerosol mass at both sites (compared to 9% and 12% at Zamdela and Ecopark, respectively, during winter). With the demands of space heating and cooking decreasing during the summer months and the corresponding decrease in domestic fuel burning, a decrease in S abundances is expected to have been observed during the summer months. As such, during the summer months, S is likely to originate from Lethabo Coal-Fired Power Station and the neighbouring petrochemical facilities instead of a local domestic coal burning source. The extremely high EF calculated for S confirms the anthropogenic origin of this species (Table 6.17) while the strong correlation observed between SO_4^{2-} and NH_4^+ ($r = 1.00$ at both sites) as well as between S and SO_4^{2-} in the fine fraction ($r = 1.00$ at Zamdela and $r = 0.99$ at Ecopark) supports this. In the ionic component, SO_4^{2-} and NH_4^+ are the most significant contributing ions with SO_4^{2-} abundances ranging from 67 – 68% and NH_4^+ abundances ranging from 24 – 27%. The biomass burning elements, K^+ and oxalic, showed good correlations ($r = 0.67$ at Zamdela and $r = 0.81$ at Ecopark), thereby indicating a

possible biomass burning and/or residential wood burning source although these species had low abundances (less than 2% at both sites) and as such, is not a significant source at both sites (as would be expected during the summer months).

Coarse Fraction

In the coarse fraction, Si, Al and Ca are the dominating elements with Si abundances ranging between 24 – 26%, Ca ranging between 27 – 28% and Al contributing to 10% of the detected elemental fine fraction aerosol mass at both sites (Table 6.18). The origin of these species from a crustal dust source in this fraction is supported based on the strong correlations seen between Al and Si ($r = 0.97$ at Zamdela and $r = 0.99$ at Ecopark), Al and Mg ($r = 0.95$ at Zamdela and $r = 0.78$ at Ecopark) as well as other crustal species such as Fe, Ti and K. The calculated EF for Si indicates a crustal origin of this species while Fe, K and Ti have both crustal and anthropogenic sources (Table 6.17). The species, Ca, Mn and V, have a strong anthropogenic origin at both sites. In the ionic component, SO_4^{2-} , NH_4^+ and F^- are the dominant ions at both sites, with SO_4^{2-} contributing to almost half of the detected ionic coarse aerosol mass (44 – 46%) and NH_4^+ ranging between 16 – 18%. Both SO_4^{2-} and NH_4^+ show an increase in summer compared to winter whereas F^- decreases significantly to between 19 – 21% (compared to 37 – 39% during winter). NO_3^- accounts for 1 – 3% of the coarse fraction aerosol at both sites with a moderate correlation only seen between NO_3^- and SO_4^{2-} ($r = 0.63$) at Ecopark. Average $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios were 0.15 ± 0.13 (Zamdela) and 0.04 ± 0.5 (Ecopark) in the coarse fraction and 0.04 ± 0.05 (Zamdela) and 0.15 ± 0.21 (Ecopark) in the fine fraction, indicative of a strong industrial origin of these species at both these sites.

Table 6.17: Enrichment factors for selected species at Zamdela and Ecopark for the period 13 February – 2 March 2017

Species	Zamdela		Ecopark	
	Fine	Coarse	Fine	Coarse
S	2002.2	236.1	2106.2	135.1
Ca	3.6	12.4	7.5	5.8
Fe	0.3	1.5	0.5	1.7
Si	0.9	0.8	1.3	0.8
K	2.5	1.8	3.7	1.8
Ti	0.8	4.0	1.6	4.5
Mn	9.2	6.0	9.7	6.7
V	31.4	83.8	23.3	24.7

Table 6.18: Mean concentrations and standard deviations of the measured species at Zamdela and Ecopark for the period 15 February – 3 March 2017

Species		Zamdela		Ecopark	
		Fine	Coarse	Fine	Coarse
Elemental Composition ($\mu\text{g}/\text{m}^3$)	Cl	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.0 ± 0.0
	S	1.8 ± 1.6	0.3 ± 0.2	1.4 ± 1.5	0.3 ± 0.2
	Ca	0.4 ± 0.3	2.0 ± 4.1	0.4 ± 0.2	1.6 ± 3.7
	Fe	BDL	0.4 ± 0.3	BDL	0.3 ± 0.3
	Na	0.2 ± 0.1	0.4 ± 0.3	0.1 ± 0.1	0.3 ± 0.3
	Mg	0.1 ± 0.1	0.3 ± 0.2	0.1 ± 0.1	0.2 ± 0.1
	Al	0.2 ± 0.2	0.7 ± 0.6	0.2 ± 0.2	0.5 ± 0.6
	Si	0.5 ± 0.5	2.0 ± 1.6	0.4 ± 0.4	1.3 ± 1.4
	P	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	K	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
	Ti	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.1
	Mn	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Zn	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0
	Cr	BDL	0.0 ± 0.0	BDL	0.0 ± 0.0
	V	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Pb	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Cd	0.3 ± 0.1	0.4 ± 0.3	0.2 ± 0.1	0.4 ± 0.2
	As	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Ni	BDL	0.0 ± 0.0	BDL	0.0 ± 0.0
	Sr	0.0 ± 0.0	0.4 ± 1.1	0.0 ± 0.0	0.4 ± 0.9
Water-Soluble Ionic Composition ($\mu\text{g}/\text{m}^3$)	F ⁻	0.2 ± 0.2	0.7 ± 0.5	0.2 ± 0.2	0.5 ± 0.4
	Cl ⁻	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	NO ₃ ⁻	0.2 ± 0.2	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	SO ₄ ²⁻	7.0 ± 6.4	1.5 ± 1.2	5.3 ± 5.7	1.2 ± 1.0
	Na ⁺	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.1
	NH ₄ ⁺	2.8 ± 2.3	0.6 ± 0.5	1.9 ± 1.9	0.4 ± 0.3
	K ⁺	0.1 ± 0.1	0.1 ± 0.0	0.0 ± 0.1	0.0 ± 0.0
	Ca ²⁺	0.1 ± 0.1	0.3 ± 0.3	0.1 ± 0.1	0.2 ± 0.3
	Mg ²⁺	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Formic	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Acetic	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Oxalic	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.0

Notes:

BDL = Below Detection Limit

Zamdela is situated in the Vaal Triangle which is characterised by a complex emission source profile including industrial, petrochemical, power generation and mining activities. In general, similar chemical profiles are observed at Zamdela and Ecopark which indicates that both sites are impacted by the same air pollution sources during each season. During winter, greater variation is seen in the chemical profiles. This suggests that the contribution from localised emissions in Zamdela (and immediate surrounds) compared to the upwind site is more pronounced during winter (as would be expected given the prevailing stable meteorological conditions during these months). During summer, a similar chemical profile is observed at both sites in both the ionic and elemental component, which supports a regional source(s) of air pollution.

6.4 Discussion

Fine Fraction

Overall, in all three regions, the most abundant species include Al, Si and S in the detected elemental fine fraction and SO_4^{2-} and NH_4^+ in the detected ionic fine fraction. Al and Si abundances in the fine fraction are variable in the township sites with Al ranging from 5 – 21% and Si ranging from 14 – 38% of the detected fine elemental fraction. The highest Al and Si contributions are observed in Marapong township. While a marked seasonality is not seen in Al and Si abundances, a slight reduction in their contributions is observed in the summer months compared to the winter months. Similar abundances of S are seen in Marapong, Embalenhle and Zamdela townships with S ranging from 8 – 13% of the detected fine elemental fraction across these sites during winter. However, this contribution is higher at Kwazamokhule where S accounts for 23% of the detected fine elemental fraction. In summer, a marked difference is seen with S ranging from 14 – 47% of the detected fine elemental fraction across all the sites. In the detected fine ionic fraction, SO_4^{2-} abundances range from 42 – 52% during winter and 58 – 67% during summer. Strong correlations are seen between S and SO_4^{2-} at all the township sites during both seasons, which is indicative of a coal combustion source of these species. NH_4^+ abundances are lower, ranging from 10 – 19% and 18 – 27% during winter and summer, respectively. Abundances of S, SO_4^{2-} and NH_4^+ show a pronounced seasonal signature with higher contributions at all the sites during the summer months. During this season, an increase in the relative humidity enhances the production of SO_4^{2-} and NH_4^+ while increased atmospheric turbulence promotes an increase in ground-level S concentrations. During winter, the impacts from tall emitting sources such as power stations are reduced as emissions are released above the stable layer and as such, have less ground-level impact. As such, low-level, localised sources such as domestic coal combustion are more likely to have a significant contribution to the fine aerosol loading in the township sites during the winter months. These low-level

emissions become trapped below the stable layer resulting in dense air pollution in the townships.

Coarse Fraction

In the coarse aerosol, the most abundant species include Al and Si in the detected elemental coarse fraction and SO_4^{2-} and F^- in the detected ionic coarse fraction at almost all the sites. Al abundances ranged from 8 – 21% and Si abundances ranged from 26 – 45% of the detected coarse elemental fraction at the township sites. Similar Si abundances were measured at the township sites during both seasons with the exception of Embalenhle and Zamdela which had reduced Si contributions during summer. Strong correlations are seen between Al and Si (and other crustal elements) at all the township sites during both seasons supporting a crustal origin of these elements. SO_4^{2-} abundances in the detected coarse ionic fraction are elevated, ranging from 17 – 39% during winter and 20 – 44% during summer at the township sites. Although observed in the fine fraction, a marked seasonal signature in SO_4^{2-} contributions is not seen in the coarse fraction. The elevated contribution of SO_4^{2-} in this size fraction is indicative of the influence of aged air masses from surrounding industrialised regions. Emissions from coal-fired power stations in the Highveld region are likely to impact SO_4^{2-} abundances over the Highveld and Vaal Triangle sites while local sources such as Matimba Power Station are likely contributors in the Lephalale region. The next most abundant species in the ionic fraction, F^- , ranges from 10 – 44% of the detected coarse ionic fraction with higher contributions measured in Marapong and Kwazamokhule townships during the summer, and the opposite observed in Embalenhle and Zamdela townships.

The chemical composition of the fine and coarse aerosol fraction within each region has been discussed in this section. Aerosol source apportionment using three different source apportionment techniques is undertaken in Chapter 7.

CHAPTER 7 AEROSOL SOURCE APPORTIONMENT

The meteorological conditions influencing the aerosol loading at each site during the summer and winter sampling campaigns is discussed. Source apportionment using three different receptor modelling techniques are applied to each of the datasets. Key sources contributing to the aerosol loading in each of the regions are identified and their contribution determined.

7.1 Meteorological Influences on Aerosol Loading during the Sampling Campaigns

7.1.1 Waterberg

7.1.1.1 Lephalale

During the winter 2012 sampling campaign, the meteorological conditions in Lephalale were dominated by fine weather, warm and clear conditions associated with a high-pressure system which prevailed for the duration of the campaign. Daily average temperatures ranged from 8.8 °C to 35.5 °C during the campaign (Table 7.1). No rainfall events were experienced during the sampling campaign, which would impact aerosol concentrations (Table 7.1). The surface wind field was dominated by winds from the northeast and north-northeast at Lephalale town and from the east and east-southeast at Marapong (Figure 7.1).

During the summer 2013 sampling campaign, a surface trough extended over the Lephalale region for the first part of the campaign, with light rain experienced on 14 and 15 February 2013. A passing cold front also brought light rain to the region on 20 February 2013 with a subsequent decrease in aerosol concentrations. No other rainfall events occurred during the remainder of the sampling campaign. Daily average temperatures were warm to hot and ranged from 18.5 °C to 37.5 °C during the sampling campaign (Table 7.1). A similar wind field was observed at both the DEA and SAWS monitoring stations with winds originating predominantly from the east-northeast with a shift to the east-southeast and south-east seen at Marapong (Figure 7.1).

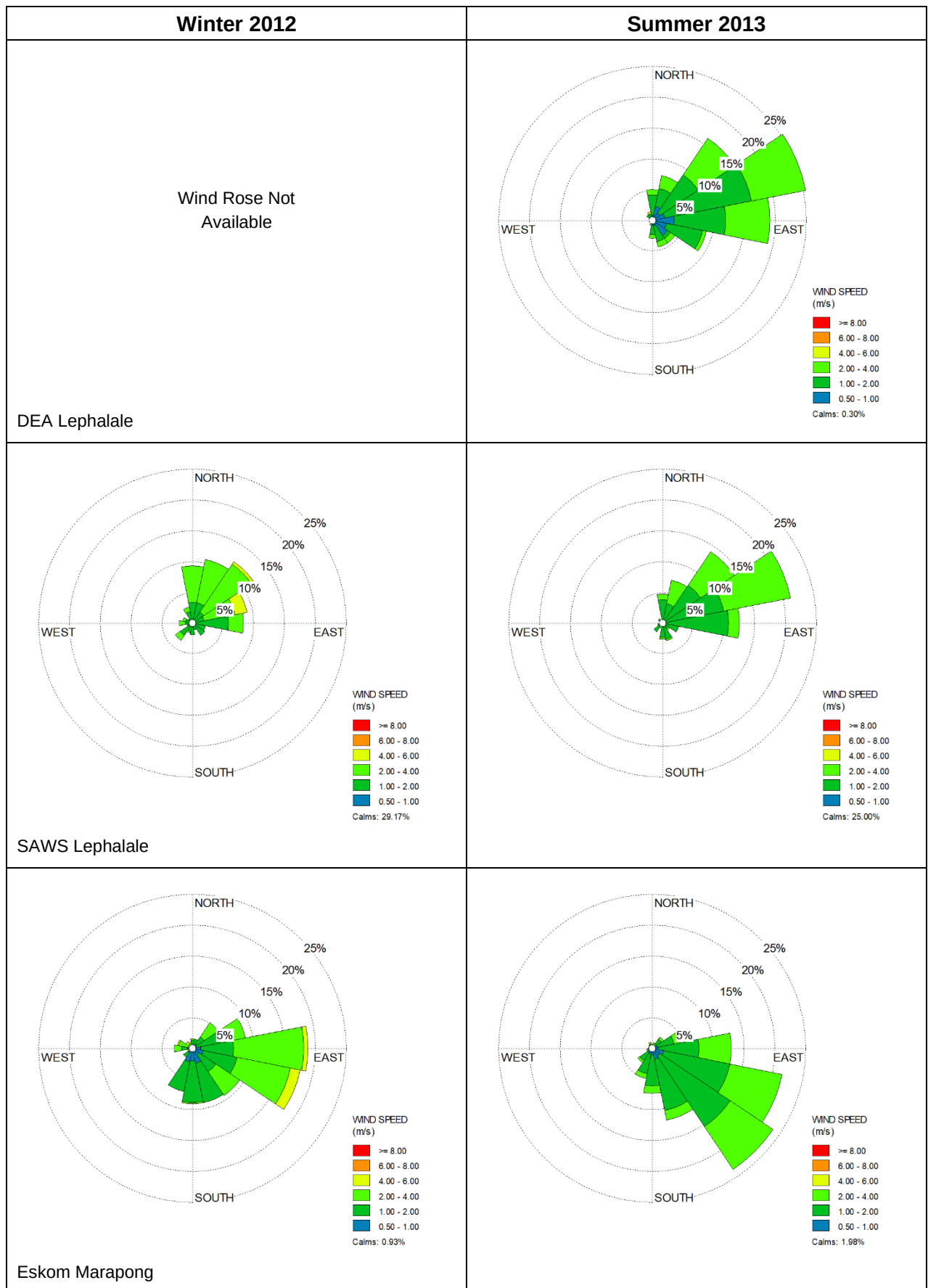


Figure 7.1: Wind field of Lephale during the winter 2012 and summer 2013 sampling campaigns

7.1.2 Highveld Region

7.1.2.1 Kwazamokhule

In Kwazamokhule, a high-pressure system prevailed for the first few days of the winter 2015 sampling campaign, producing fine weather and clear conditions. Daily average temperatures ranged from -5.6 °C to 25.1 °C during the winter sampling campaign (Table 7.1). A passing cold front from 11 July produced very light rain in Kwazamokhule, but this did not have a significant effect on aerosol concentrations. On 14 July, a surface trough was situated over the central interior resulting in light rain in Kwazamokhule for a couple of days. This resulted in a decrease in the coarse fraction concentrations on 14 July, although the effect of the rain was short-lived with aerosol concentrations increasing rapidly again. No other rainfall events occurred during the remainder of the winter sampling campaign. Winds originated predominantly from the south-south east and east-northeast at the Eskom monitoring station and from the east-northeast and east at the DEA monitoring station (Figure 7.2).

During the summer 2016 sampling campaign, light rain was experienced during the first few days of the Kwazamokhule campaign as a surface trough extended over the interior with higher rainfall levels measured on 25 February. A surface trough with a ridging high-pressure system prevailed for the remainder of the campaign, resulting in warm and dry conditions for the remainder of the campaign. Daily average temperatures ranged from 9.6 °C to 31.2 °C during the summer sampling campaign (Table 7.1). A similar wind field was observed at both monitoring stations with winds originating mainly from the easterly sector. Slow to moderate winds from the south-southeast were also recorded at the Eskom monitoring station (Figure 7.2).

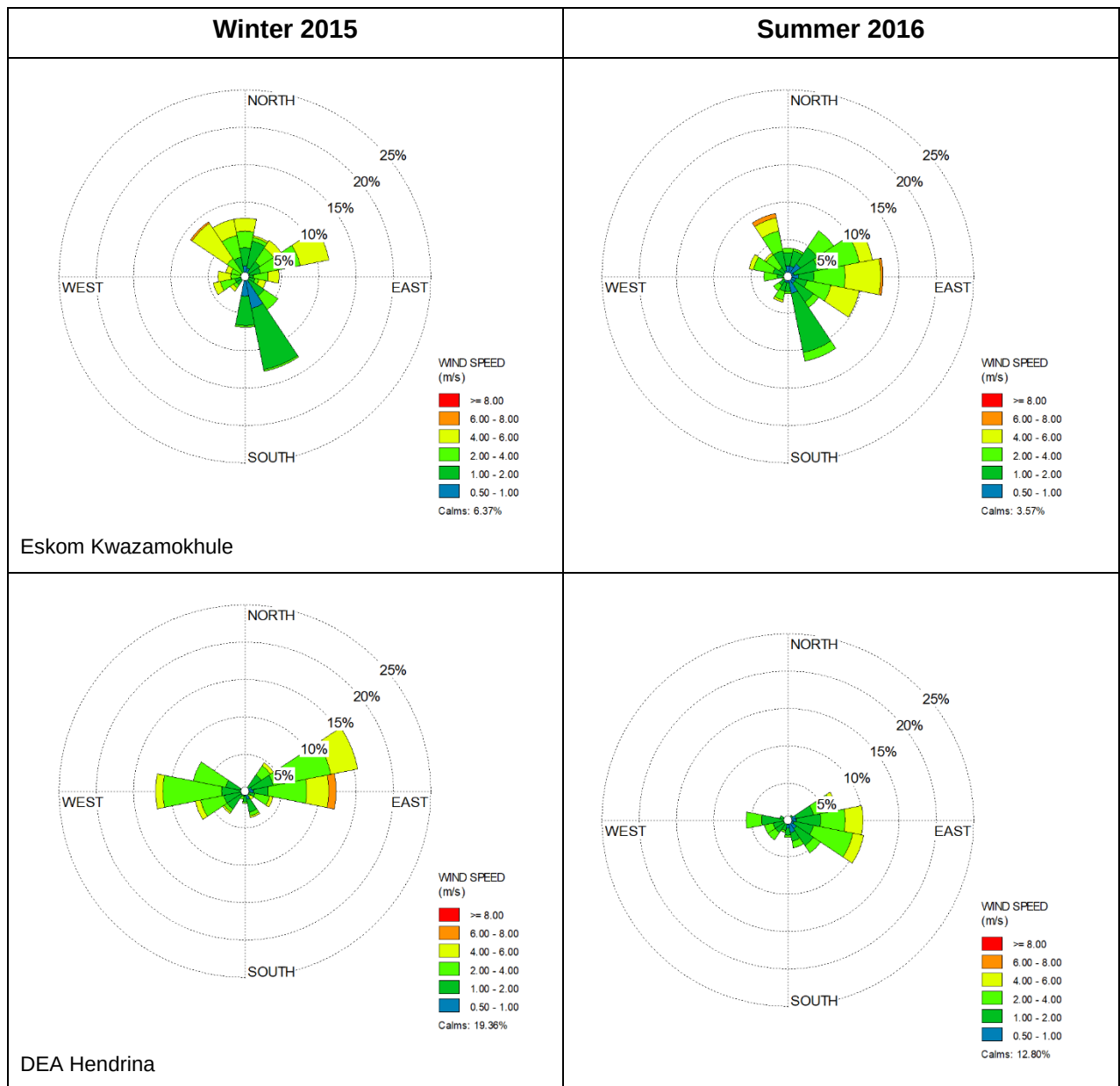


Figure 7.2: Wind field of Kwazamokhule during the winter 2015 and summer 2016 sampling campaigns

7.1.2.2 Embalenhle

The meteorological conditions in Embalenhle were dominated by a high-pressure system for the first part of the winter 2016 sampling campaign with an upper-air cut-off low pressure system prevailing from 24 July. This resulted in rain in Embalenhle from 24 – 27 July and a subsequent reduction in aerosol concentrations. A high-pressure system dominated for most of the August sampling period, causing sunny and cool to warm conditions for most of the sampling period. Light rain was experienced on 8 August 2016 but this did not have a discernible influence on aerosol concentrations. A total of 39 mm of rainfall was recorded during the winter campaign (Table 7.1). Daily average temperatures ranged from -1.0 °C to 26.2 °C during the sampling campaign (Table 7.1). A similar wind field was recorded at all the stations during the sampling campaign with moderate to fast winds originating predominantly from the northeasterly and southwesterly sectors (Figure 7.3).

A low-pressure surface trough prevailed for most of the summer 2017 sampling campaign. For the first few days of the sampling campaign, a tropical storm to the east of the country resulted in rain in Embalenhle on 14 February. Rainfall was also experienced from 19 – 25 February, which is evident in the reduced aerosol concentrations recorded during this period. A total of 145 mm of rainfall was recorded during the summer campaign (Table 7.1). Daily average temperatures were warm to hot and ranged from 11.9 °C to 30.2 °C during the sampling campaign (Table 7.1). Surface winds remained moderate to fast during the summer campaign, with winds originating mainly from the northeast, east-northeast and east at both stations (Figure 7.3).

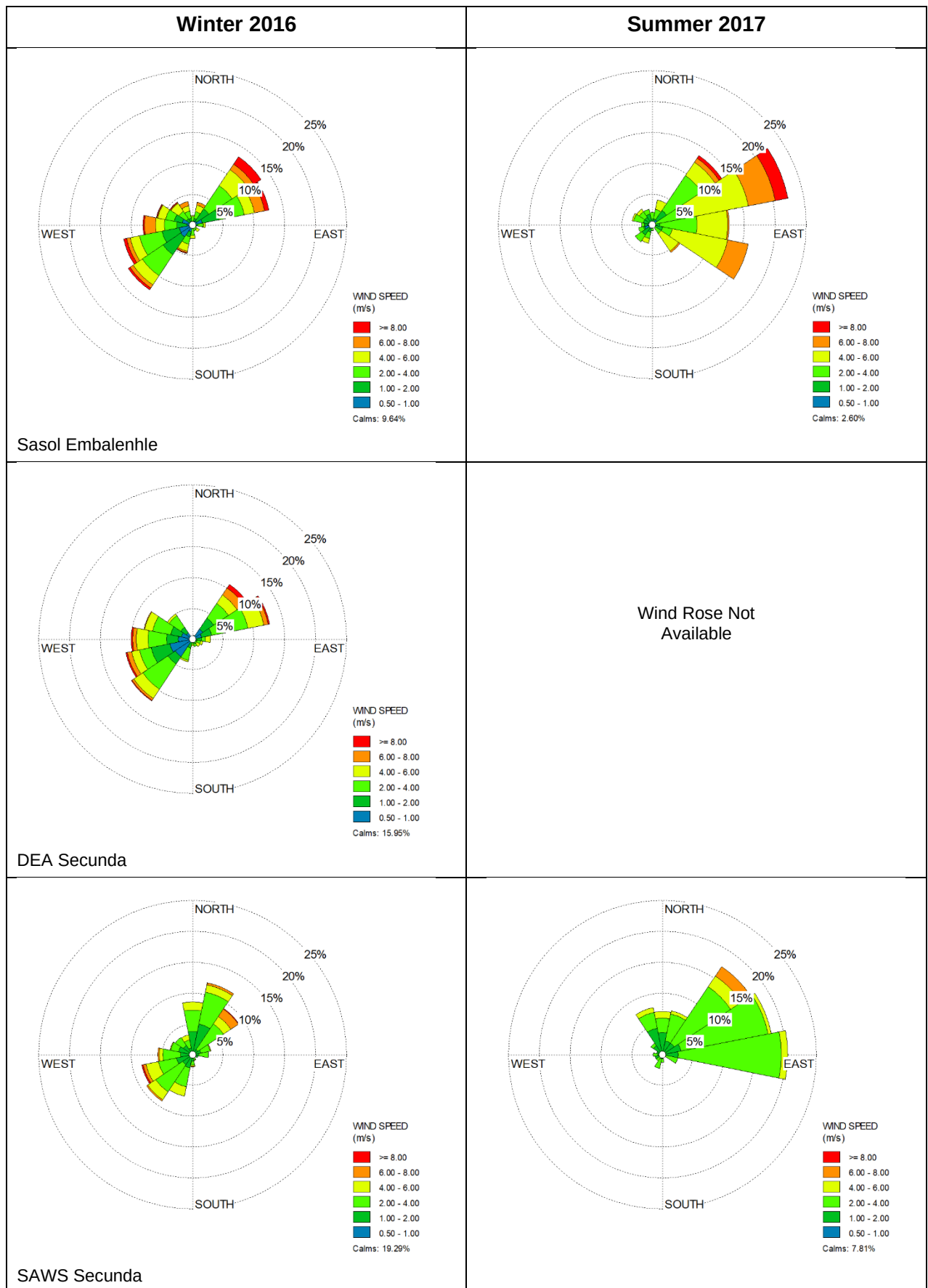


Figure 7.3: Wind field of Embalenhle during the winter 2016 and summer 2017 sampling campaigns

7.1.3 Vaal Triangle

7.1.3.1 Zamdela

During the winter 2016 sampling campaign, a prevailing upper-air cut-off low produced rain on 25 and 26 July in Zamdela, resulting in a reduction in aerosol concentrations. On 17 and 18 September 2016, an upper air trough resulted in rainfall, with a subsequent decrease in aerosol concentrations on these days. A total of 44 mm of rainfall was recorded during the winter sampling period, with daily average temperatures ranging from -2.9 °C to 30.4 °C during the sampling campaign (Table 7.1). A surface trough extended over the interior for the duration of the summer 2017 sampling campaign, producing heaving rain in the region on 20 and 21 February. Light rain was experienced for the remainder of the campaign. A total of 139 mm of rainfall was recorded during the summer campaign with daily average temperatures ranging from 13.2 °C to 28.2 °C (Table 7.1).

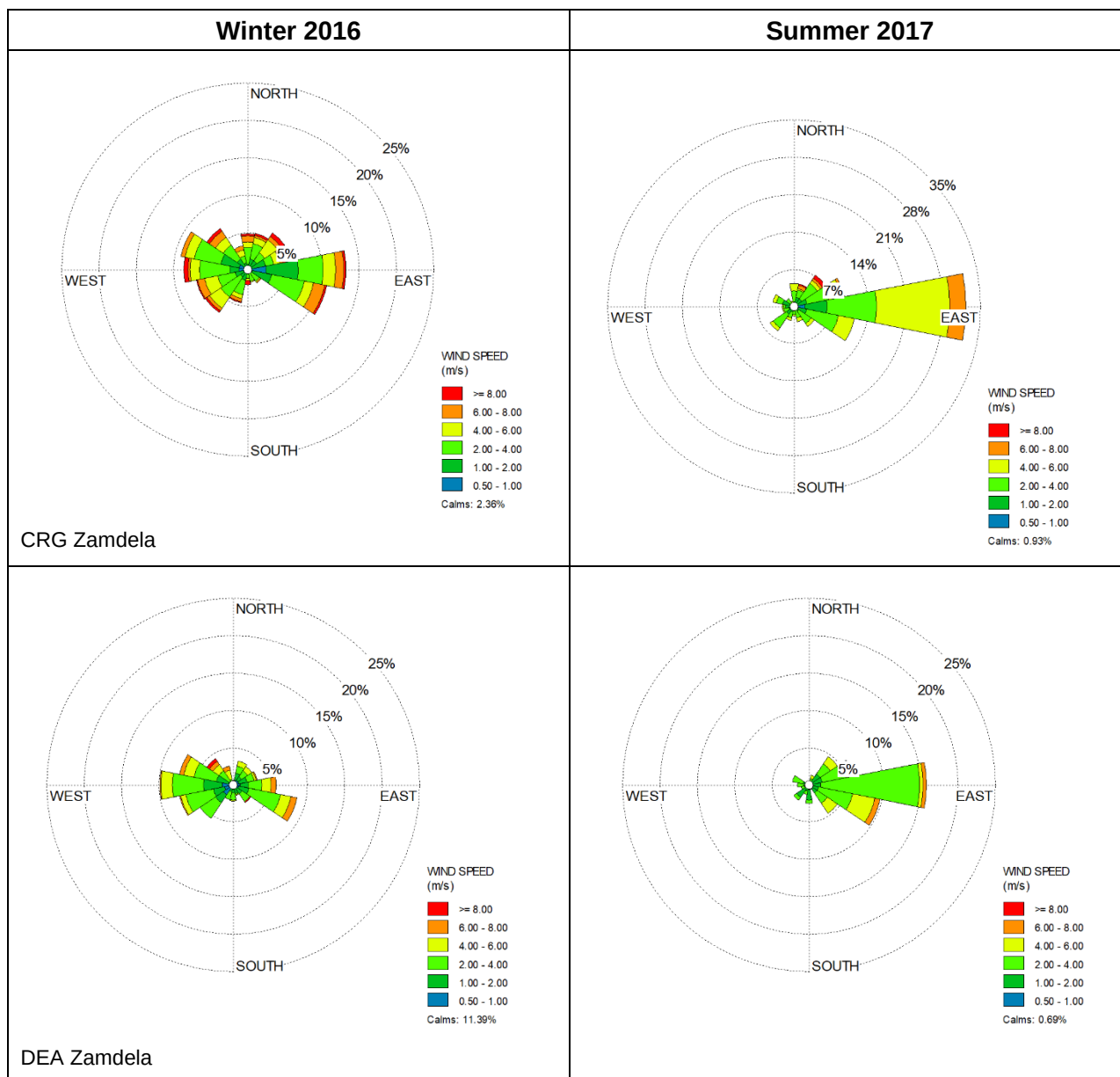


Figure 7.4: Wind field of Zamdela during the winter 2016 and summer 2017 sampling campaigns

Table 7.1: Average, minimum and maximum temperatures (°C) at Lephalale, Kwazamokhule, Embalenhle and Zamdela during the sampling campaigns

Parameter	Lephalale		Kwazamokhule		Embalenhle		Zamdela	
	Winter 2012	Summer 2013	Winter 2014	Summer 2015	Winter 2016	Summer 2017	Winter 2016	Summer 2017
Average	21.6	27.0	10.2	20.4	10.7	17.8	13.4	19.4
Minimum	8.8	18.5	-5.6	9.6	-1.0	11.9	-2.9	13.2
Maximum	35.5	37.5	25.1	31.2	26.2	30.2	30.4	28.2

Table 7.2: Total precipitation (mm) at Lephalale, Kwazamokhule, Embalenhle and Zamdela during the sampling campaigns

Parameter	Lephalale		Kwazamokhule		Embalenhle		Zamdela	
	Winter 2012	Summer 2013	Winter 2014	Summer 2015	Winter 2016	Summer 2017	Winter 2016	Summer 2017
Total	0	5	24	52	39	145	44	139

7.2 Source Identification and Apportionment

Air pollution sources contributing to the aerosol loading in each region are identified using Varimax Rotated PCA and then further refined using PMF and CMB receptor modelling. The detailed Varimax Rotated factor loadings of the fine and coarse fraction aerosol at each site are presented in Appendix A with selected PMF source profiles provided in Appendix B. The CMB modelling results for the Highveld and Vaal Triangle sites are presented in the section below. CMB results for the Lephalale sites in the Waterberg and Kwazamokhule in the Highveld have not been presented as a significant portion of the aerosol fraction could not be accounted for in the modelling, and the available results do not provide a meaningful context.

7.2.1 Source Identification using Varimax Rotated PCA

7.2.1.1 Fine Fraction

In the fine aerosol fraction, factor analysis has identified soil dust, domestic combustion, secondary inorganic aerosols, wood and biomass burning, and industry to be possible contributing sources to the aerosol loading. A possible soil dust profile is identified in the PCA results with high factor loadings of traditional soil elements such as Fe, Mg, Al and Si. Of the identified factors, this factor accounts for the highest total variance in the Waterberg (23 – 35%), Highveld (19 – 54%) and Vaal Triangle (17 – 37%) regions during both seasons. A secondary inorganic aerosol profile is also seen in the PCA results and is identified by high factor loadings of SO_4^{2-} , NH_4^+ and S. The major species of secondary inorganic aerosols include SO_4^{2-} , NH_4^+ and NO_3^- (Crilley *et al.*, 2017). For the most part, this factor is the next most significant during both seasons, with this factor explaining 17 – 21%, 11 – 24% and 8 – 17% of the total variance in the Waterberg, Highveld and Vaal Triangle regions, respectively. High factor loadings of Cl^- are also seen in the datasets for both seasons. Potential sources of Cl^- include coal combustion (Liu *et al.*, 2017; Yang *et al.*, 2018), wood and biomass burning, waste burning and sea salt (Vasconcellos *et al.*, 2007).

A possible biomass burning profile is identified in the PCA results with factor loadings of K^+ which is an excellent tracer for biomass burning (Zhang *et al.*, 2013; Yu *et al.*, 2016). In the Waterberg, this factor accounts for 8 – 10% of the total variance at all three sites. For the Highveld and Vaal Triangle regions, this factor accounts for 6 - 16% and 15 - 22% of the total variance, respectively, during winter. While this species also has high factor loadings during summer in these regions, it is combined into other factors and cannot be resolved into a separate factor. High factor loadings of Na^+ are also seen at all the sites during both seasons although this species tends to be combined into other profiles. Na^+ can be used as a tracer for dust and burning sources (Zhang *et al.*, 2013) and aged sea salt (Cesari *et al.*, 2016). A

possible industry contribution is seen in the Highveld and Vaal Triangle regions with high factor loadings of trace elements such as V, Ni and As. The species V and Ni can be associated with the petrochemical industry (Bosco *et al.*, 2005; de la Campa *et al.*, 2011), residual oil combustion (Moreno *et al.*, 2010) and coke production (Moreno *et al.*, 2007). High factor loadings of Cr are also seen in the three regions which is emitted from coal combustion (Shah *et al.*, 2008), ferrochromium smelting, and other mining and metallurgical refining industries (Venter *et al.*, 2016).

7.2.1.2 Coarse Fraction

In the coarse aerosol fraction, the same sources identified in the fine fraction are also seen with soil dust, domestic combustion, secondary inorganic aerosols, biomass burning, and industry likely contributing sources. In this fraction, the factor containing the traditional soil dust species accounts for the highest total variance in the Waterberg (19 – 58%), Highveld (28 – 47%) and Vaal Triangle (21 – 38%) regions during both seasons. At most sites, this factor is also loaded with additional species associated with other sources and as such, could represent a combined source profile rather than an individual soil dust component only. A secondary inorganic aerosols profile is seen at most sites during both seasons. A separate profile is less distinguishable at the Waterberg sites, especially during summer, while on the Highveld, this factor is only clearly distinguished at Kwazamokhule and accounts for 13 – 16% of the total variance during both seasons. In the Vaal Triangle, this factor explains 13 – 21% of the total variance at Zamdela and Ecopark during both seasons. Higher factor loadings of Cl⁻ and Na⁺ are also seen at most of the sites in this size fraction. While high factor loadings of K⁺ are also seen in the datasets, this species is generally combined into other factors in all three regions. However, the presence of this species, as well as organic acids such as oxalate, suggest that there is a possible biomass burning contribution in this size fraction. A possible industry contribution is again seen at the Highveld and Vaal Triangle sites with high factor loadings of heavy metals such as As, Cd, V and Ni.

7.2.2 Receptor Modelling

7.2.2.1 Fine Fraction

7.2.2.1.1 Waterberg Region

Soil Dust

A soil dust profile is identified in the fine fraction PMF results with the abundance of crustal elements such as Ca, Fe, Mg, Al and Si. While this source has been classified as ‘soil dust’, it is

likely to represent a combined dust profile with contributions from both natural and anthropogenic sources such as paved and unpaved roads.

In this size fraction, soil dust accounts for between 40 - 41% of the reconstructed fine fraction aerosol at the three sites during winter (Figure 7.11). During summer, soil dust accounts for 30 – 45% of the reconstructed fine fraction aerosol (Figure 7.12). During this same season, the fine fraction soil dust is observed to be enriched with Cr (Figure B.2), which has also been observed in crustal/road dust in the Limpopo Province (Tshehla and Djolov., 2018). The soil dust profile at Marapong also shows a Ca^{2+} contribution (Figure B.1). While Ca^{2+} is naturally present in soil dust (Zhang *et al.*, 2012), Ca^{2+} can also be a representative of construction dust as it is the main element in cement or plaster (Kim *et al.*, 2004; Shen *et al.*, 2016). It is likely to have originated from Medupi Power Station, a large-scale construction project which was occurring in the area during the sampling campaigns. During the summertime, construction had been temporarily suspended but this ionic species is still seen in the soil dust profile at this site (Figure B.2).

Domestic Combustion

The domestic combustion profile includes a combination of domestic burning sources including coal combustion and waste burning. In the Lephalale profiles, this mixed source is distinguished by the presence of species such as Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Na and Zn (summer only) in the profiles.

Domestic combustion contributes to 10 - 17% of the reconstructed fine fraction aerosol at all three sites during winter (Figure 7.11). During summer, contributions range from 12 – 23% of the reconstructed fine fraction at all three sites (Figure 7.12). The element, Zn, is seen in the burning profile at Marapong (Figure B.3) which supports a contribution of waste burning at this site as Zn is also emitted from the burning of waste (de Bruin *et al.*, 2006). The uncontrolled and open burning of waste is known to take place in Marapong.

Since coal is not predominantly used as a domestic fuel in Marapong, any coal combustion contribution at these sites is likely to originate from the neighbouring Matimba Power Station (rather than a domestic coal combustion source). This is also supported by the presence of S and SO_4^{2-} at the 'remote' Steenbokpan site which is approximately 25 km west of Matimba Power Station. Further investigation of diurnal SO_2 concentrations in Marapong and Lephalale Town show a characteristic signature typical of tall stack emissions (Figure 7.5). The small increase in SO_2 concentrations seen between 6 – 8 am at both sites is likely due to vehicle emissions rather than domestic fuel burning.

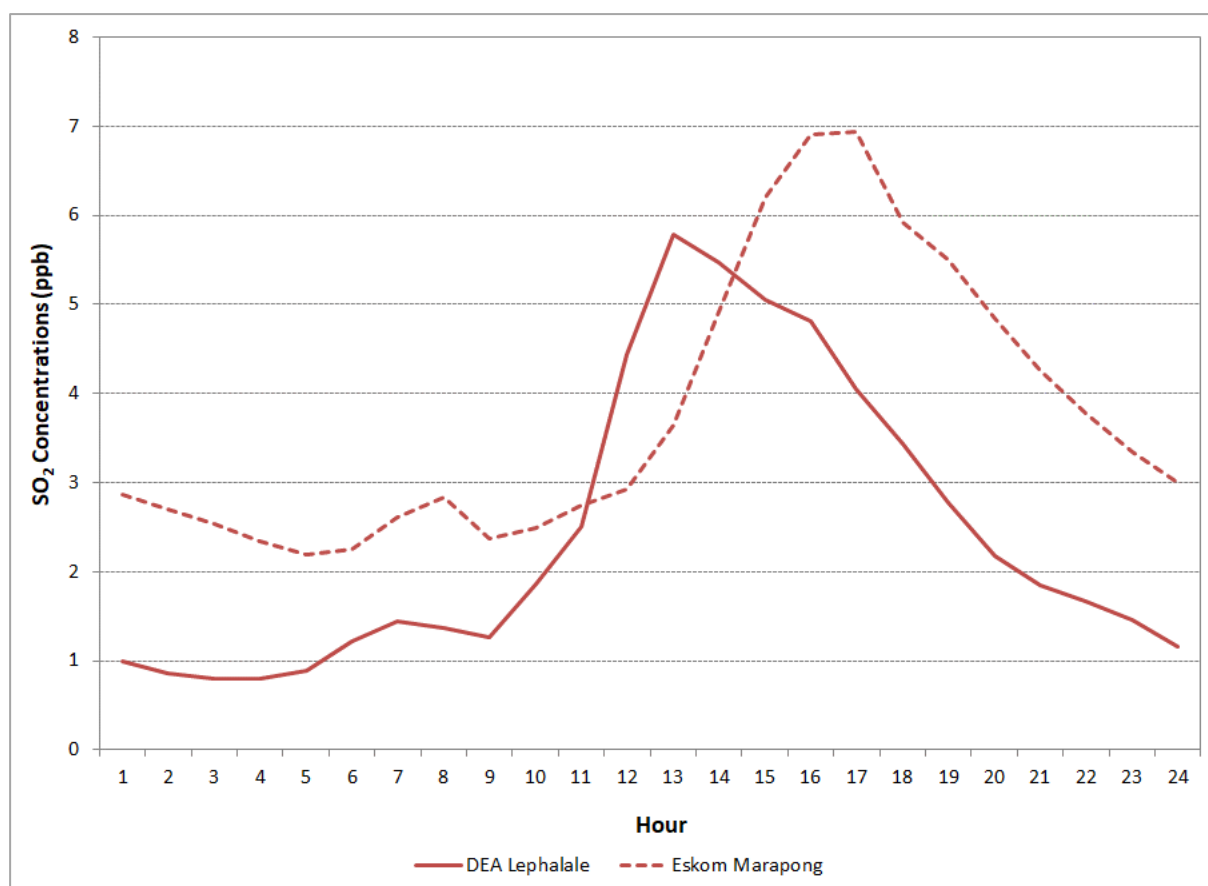


Figure 7.5: Diurnal SO₂ concentrations in Lephale and Marapong for the period January 2012 – December 2013 (Marapong) and January – December 2013 (Lephale)

Secondary Aerosols

A secondary inorganic aerosol profile is detected in the PMF results by the presence of secondary species such as SO₄²⁻, NH₄⁺, NO₃⁻ and S. In the chemical data, SO₄²⁻ is the most abundant species in the ionic fraction during both seasons. NH₄⁺ and NO₃⁻ have similar contributions during winter while NH₄⁺ is the next most abundant species, after SO₄²⁻, during summer. The strong correlations seen between SO₄²⁻ and NH₄⁺ during both seasons supports the secondary origin of these species.

Secondary aerosols contribute to 33%, 18% and 28% of the reconstructed fine fraction aerosol at Lephale Town, Marapong and Steenbokpan, respectively, during winter (Figure 7.11). During summer, secondary aerosols account for 36% of the reconstructed fine fraction aerosol at both Lephale Town and Marapong while Steenbokpan shows a significant increase (58%) in the contribution from secondary aerosols (Figure 7.12). This is also seen in the chemical data for this site which shows elevated SO₄²⁻ (and S) concentrations at this site during the summertime. An increase in relative humidity during this season favours SO₄²⁻ formation (Aurela

et al., 2016; Shikwambana and Sivakumar, 2019). The reduced secondary aerosol contribution observed at Marapong compared to the other two sites is likely a result of the proximity of this site to Matimba Power Station while the elevated contribution seen at Steenbokpan is reflective of its distance downwind of Matimba Power station.

Wood and Biomass Burning

A wood and biomass burning profile is identified by the abundance of K^+ as well as SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , Na^+ and organic acids. A biomass burning profile is seen at all three sites during winter, with this source contributing to 17%, 24% and 16% of the reconstructed fine fraction aerosol at Lephalale Town, Marapong and Steenbokpan, respectively (Figure 7.11). During the summertime, reduced contributions are seen with this source accounting for 7 – 8% of the reconstructed fine fraction aerosol at Lephalale Town and Marapong (Figure 7.12). The biomass burning profile is likely to be representative of combined regional and local sources during winter. Seasonally, emissions from regional biomass burning have the greatest impact on South Africa during the late winter and spring months. Wood is also used as a domestic fuel in Marapong which is also a likely contributor to the aerosol loading. Agricultural burning could also be a contributing source to the biomass burning component seen at Steenbokpan as this site is surrounded by farming and vegetated land.

7.2.2.1.2 Highveld Region

Soil Dust

At Kwazamokhule, soil dust is identified in the PMF model to contribute to 36% and 35% of the reconstructed fine fraction aerosol during winter and summer, respectively (Figure 7.11 - Figure 7.12). At the other two Highveld sites, soil dust contributes to 54% and 35% of the reconstructed fine fraction aerosol at Embalenhle and Kinross, respectively, during winter (Figure 7.11). The soil contribution at Embalenhle during winter seems somewhat elevated for the fine fraction. This profile has high concentrations of Ca^{2+} , Mg^{2+} , Ca, Fe, Mg, Al and Si (Figure B.4). In the fine fraction chemical data for Embalenhle, the contribution of Si is high (35% of the detected elemental species). Strong correlations ($r > 0.93$) are seen between Si and each of these species. Ca^{2+} seen in this profile could indicate a mixed source profile with a possible contribution from the neighbouring petrochemical activities as Ca^{2+} is released from caustic soda and chlor-alkali plants (Luo *et al.*, 2018). During summer, the soil dust contribution decreases to 35% and 18% of the reconstructed fine fraction aerosol at Embalenhle and Kinross, respectively (Figure 7.12). CMB modelling apportions the fine fraction soil dust at Embalenhle into natural soil (19% and 24% during winter and summer, respectively) and paved/unpaved roads (3% and 1% during winter and summer, respectively) (Figure 7.8). At

Kinross, natural soil accounts for 14% and 10% of the fine fraction aerosol during winter and summer, respectively while paved and unpaved roads contribute to 5% of the fine fraction aerosol during summer.

Domestic Combustion

In the Highveld profiles, domestic combustion is distinguished by the presence of species such as Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ and K^+ in the profiles. The presence of Zn is also seen in these profiles, confirming a contribution from waste burning. This likely represents a mixed coal combustion and waste burning source, as also seen in Lephalale.

At Kwazamokhule, domestic combustion in the PMF results accounts for 14 and 12% of the reconstructed fine fraction aerosol during winter (Figure 7.11) and summer (Figure 7.12), respectively.

The diurnal SO_2 signature at Hendrina and Kwazamokhule shows that emissions from domestic coal combustion and surrounding coal-fired power stations both contribute at these sites, although a weaker evening peak in SO_2 concentrations is seen at Hendrina compared to Kwazamokhule (Figure 7.6). This is expected given the predominance of domestic fuel burning in Kwazamokhule compared to the more high-income, urban area of Hendrina. The emissions from the power stations are occurring above 150 m above ground level, and as such, the emissions are trapped above the developing surface stability soon after sunset. This explains why the domestic fuel combustion in the township becomes a more prominent contributor.

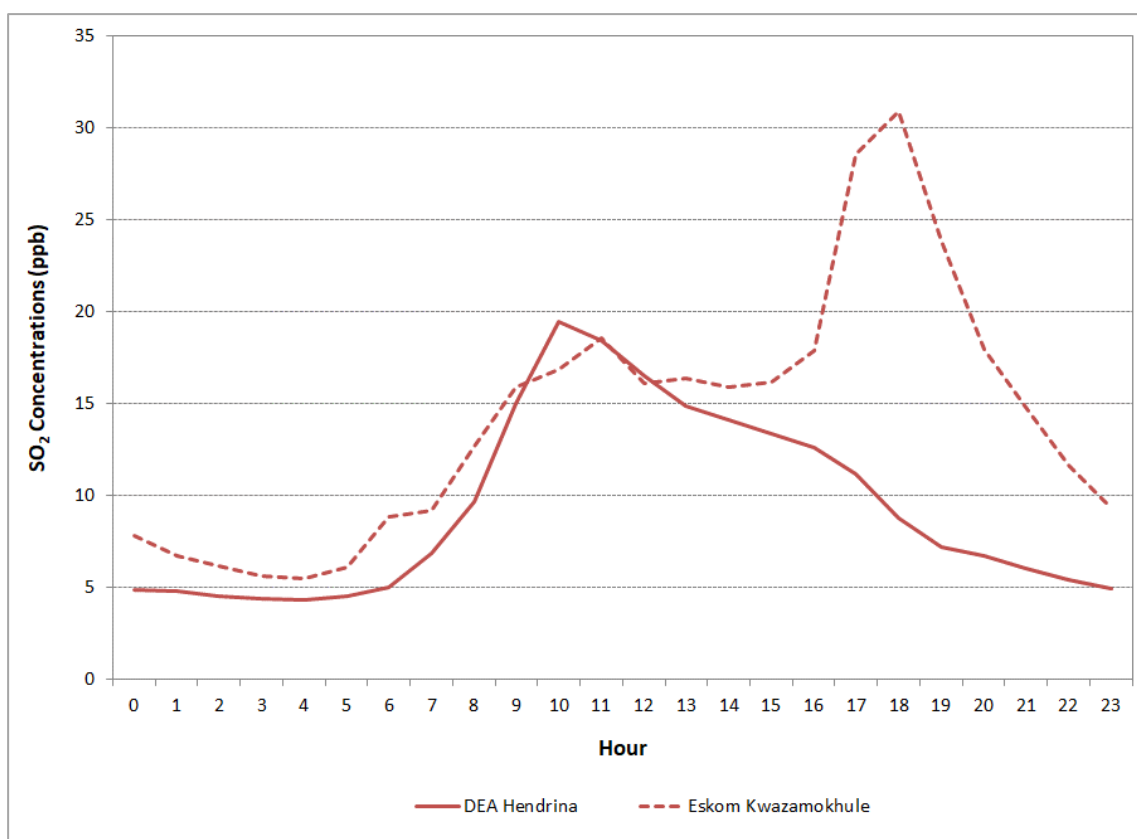


Figure 7.6: Diurnal SO₂ concentrations in Hendrina and Kwazamokhule for the period January 2014 – December 2017 (Hendrina) and January 2015 – March 2016 (Kwazamokhule)

At Embalenhle and Kinross, domestic combustion contributes to 14% and 22%, respectively, of the reconstructed fine fraction aerosol during winter (Figure 7.11 and Figure B.5). During summer, domestic combustion accounts for 24% and 32% at Embalenhle and Kinross, respectively (Figure 7.12). It is interesting that the domestic combustion contribution is higher at Kinross during both seasons (as is also seen in the CMB results). In the CMB model, separate coal combustion (domestic and industrial) and waste burning profiles have been included and as such, the model is able to apportion a separate contribution to these sources. In the CMB model, waste burning contributes between 2 - 12% of the fine fraction aerosol at Embalenhle and Kinross, with similar contributions during the summertime (5 - 11% of the fine fraction aerosol) (Figure 7.8).

Domestic coal combustion accounts for 38% and 8% of the fine fraction aerosol during winter at Embalenhle and Kinross, respectively (Figure 7.8). During summer, the domestic coal contribution decreases with domestic coal combustion accounting for 6% and 2% of the fine fraction aerosol at Embalenhle and Kinross, respectively. Only a small percentage of the fine fraction aerosol is attributed to coal-fired power stations (as fly ash) at both sites for both seasons. Domestic coal combustion is not sufficiently resolved as a separate source in the PMF

model at Embalenhle and Kinross. In the CMB model, the domestic coal combustion profiles have high contributions of the secondary species, NO_3^- , SO_4^{2-} and S which is possibly being resolved to some degree in the secondary aerosol profile in the PMF model (Figure 2.12) which also has high concentrations of these species.

An investigation of diurnal SO_2 concentrations in Embalenhle shows a contribution from both domestic coal combustion and surrounding coal-fired power stations (Figure 7.7). A similar diurnal SO_2 signature is seen at all three monitoring stations, although the evening peak in SO_2 concentrations is much more pronounced at the DEA Embalenhle monitoring station compared to the other two stations.

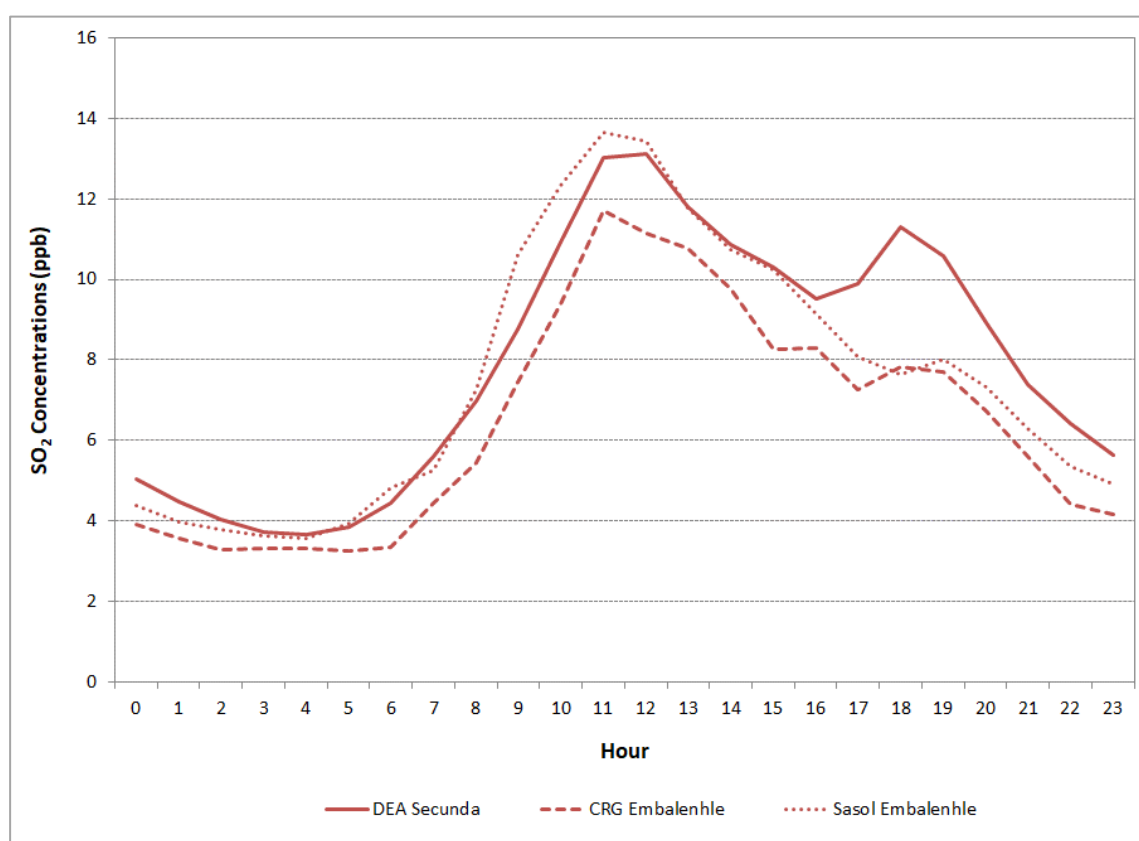


Figure 7.7: Diurnal SO_2 concentrations in Embalenhle for the period January 2014 – November 2016 (DEA), June 2016 – July 2017 (CRG) and January 2014 – December 2017 (Sasol)

Secondary Aerosols

At Kwazamokhule, the PMF findings show secondary aerosols to contribute to 21% and 41% of the reconstructed fine fraction aerosol during winter and summer, respectively (Figure 7.11 - Figure 7.12). At Embalenhle and Kinross, this source accounts for 22% (winter) and 26 – 41% (summer) of the reconstructed fine fraction aerosol at both sites (Figure 7.11 - Figure 7.12). The CMB contribution to this source at Embalenhle and Kinross ranges between 2 – 14% (winter)

and 22 – 26% (summer) (Figure 7.8) which is underestimated given the high contribution of SO_4^{2-} and NH_4^+ seen in the chemical data for this size fraction. However, both models do reflect the summertime increase in the contribution from this source. The discrepancy in the percentage contribution between the two models is likely due to the source profiles included in the CMB model for secondary aerosols which are represented by separate SO_4^{2-} and NO_3^- profiles (Figure 2.12). In the PMF model, SO_4^{2-} , NO_3^- , NH_4^+ and S have been used to identify a secondary aerosol profile. Viana *et al.* (2008a) noted that the inclusion of secondary aerosols as individual chemical compounds rather than complex mixtures with other source profiles in the CMB model can influence contributions from this source.

Wood and Biomass Burning

Source apportionment using PMF has also detected wood and biomass burning to contribute to the aerosol loading at all three Highveld sites. This profile is identified by the abundance of K^+ as well as SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , Na^+ and organic acids. In the chemical data, good correlations are seen between K^+ and oxalate/oxalic acid at all three Highveld sites during both seasons.

At Kwazamokhule, wood and biomass burning has low a contribution during both seasons (17% and 13% during winter and summer, respectively) (Figure 7.11 - Figure 7.12). At Embalenhle and Kinross, the PMF findings also show wood and biomass burning to be a contributing source, with this source accounting for between 10 – 21% during winter (Figure 7.11 and Figure B.6) and 9 - 14% at during summer (Figure 7.12) at both sites. CMB modelling shows some similiarity with biomass burning accounting for 6% of the fine fraction aerosol at Embalenhle during winter but this source is not detected at Kinross. However, a significant percentage of the fine fraction aerosol remains unaccounted for at Kinross. During summer, biomass burning accounts for 10% and 5% of the fine fraction aerosol at Embalenhle and Kinross, respectively (Figure 7.8).

Other Sources

Other sources identified at the Highveld sites include industrial activities and motor vehicles. A minor petrochemical contribution is identified at both sites in the CMB model, with the highest contribution (5%) seen at Embalenhle during winter (Figure 7.8). Motor vehicles are also detected in the CMB model. The highest contributions from motor vehicles are seen at Kinross during the summertime, with this source accounting for 13% of the fine fraction aerosol. At both Embalenhle and Kinross, a high percentage of the fine fraction aerosol cannot be accounted for with almost half (44%) of the fine fraction aerosol undetermined at Kinross during the winter season. As a result, this makes it difficult to make an accurate comparison between the PMF and CMB findings.

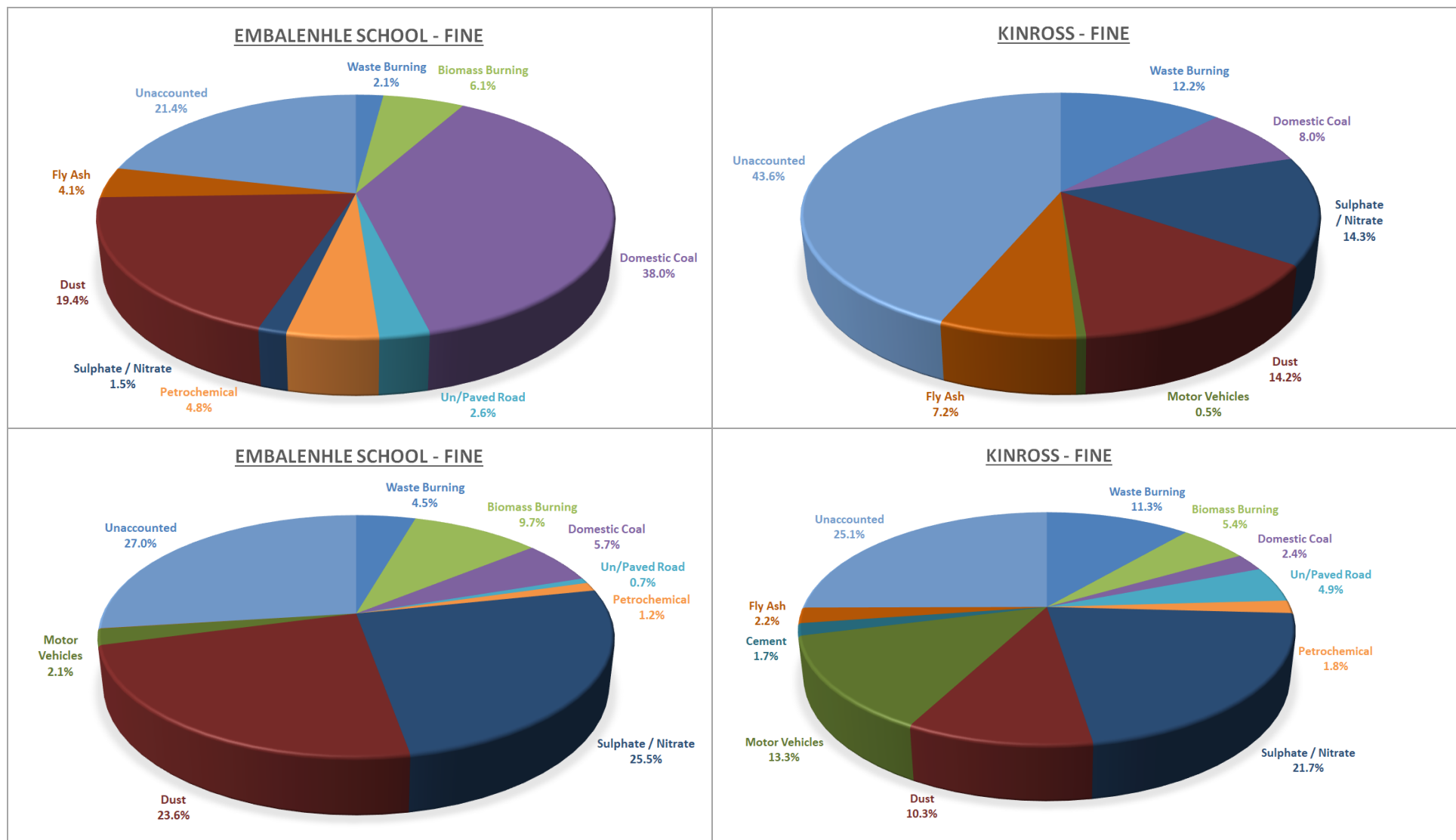


Figure 7.8: CMB source contributions (%) of the fine fraction aerosol at Embalenhle and Kinross for the winter 2016 (top) and summer 2017 (bottom) sampling campaigns

7.2.2.1.3 Vaal Triangle Region

Soil Dust

At the Vaal Triangle sites, soil dust accounts for 26% of the reconstructed fine aerosol fraction during winter (Figure 7.11) and 22% during summer (Figure 7.12). CMB modelling apportions the fine fraction soil dust at Zamdela into natural soil (9% and 21% during winter and summer, respectively) and paved and unpaved roads (2% during both seasons) (Figure 7.10). At Ecopark, higher natural soil contributions are seen during winter, with soil dust contributing to 23% of the fine fraction aerosol. During summer, the natural soil dust contribution decreases to 10% of the fine fraction aerosol. Paved and unpaved roads contribute to 1% and 8% of the fine fraction aerosol during winter and summer, respectively. Both the PMF and CMB models reflect similar percentages and seasonal trends in the soil dust contributions at both sites.

Domestic Combustion

A domestic combustion profile is detected in the PMF findings at both sites during winter (18 – 26%) and summer (16 – 20%) (Figure 7.11). In the CMB model, waste burning ranges between 7 – 12% (winter) and 4 – 9% (summer) of the fine fraction aerosols at both sites (Figure 7.10). Domestic coal combustion contributes to 28% and 15% of the fine fraction aerosol during winter at Zamdela and Ecopark, respectively (Figure 7.10). A small contribution is also seen during the summertime at both sites which reflects the decrease in domestic fuel burning during this season. The CMB model also determines coal-fired power stations (as fly ash) to account for between 6 - 10% of the fine fraction aerosol during winter (with minor contributions during summer).

The diurnal SO₂ concentrations at Zamdela also show a combined domestic coal combustion and coal-fired power station signature (Figure 7.9). An early morning peak in SO₂ concentrations is seen at both monitoring stations with a less pronounced evening peak. This differs from the Highveld sites which show a well pronounced evening peak in SO₂ concentrations.

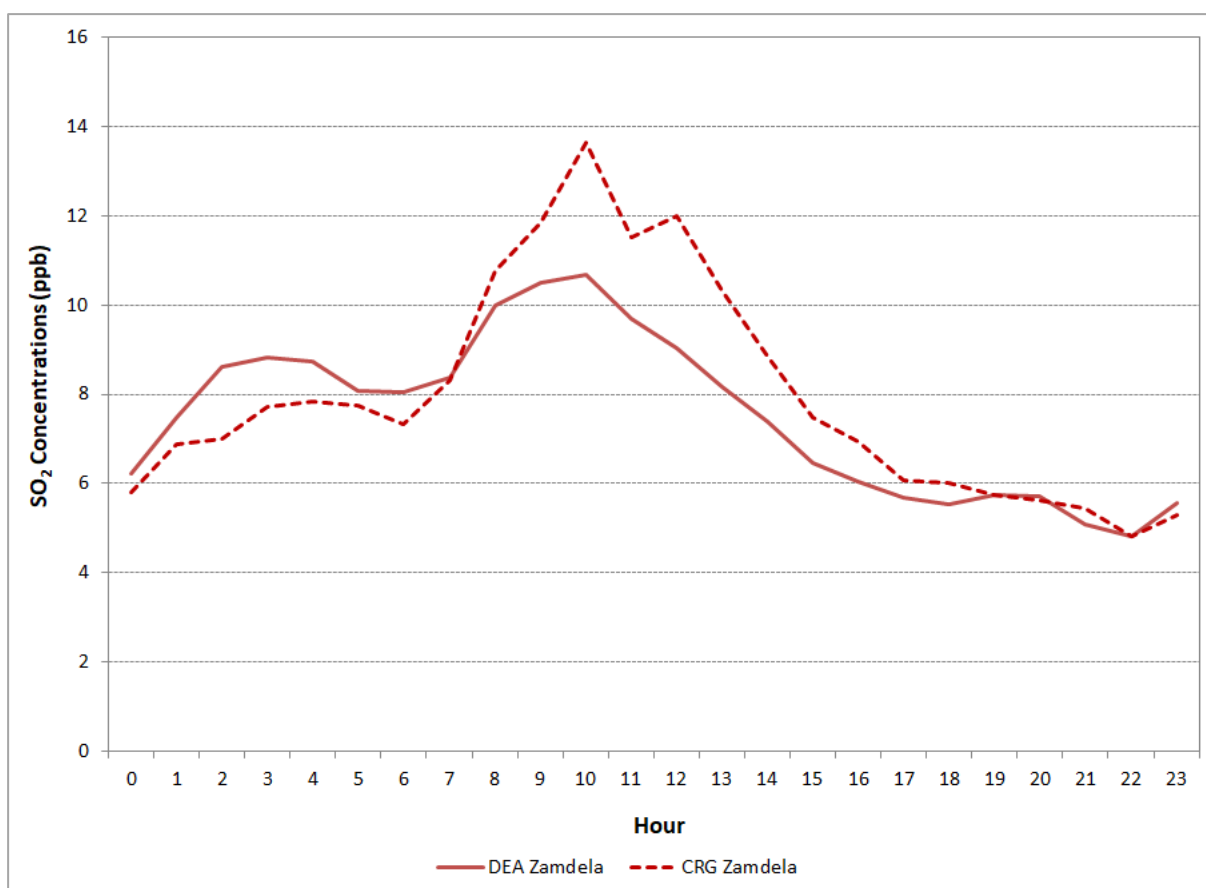


Figure 7.9: Diurnal SO₂ concentrations in Zamdela for the period June 2016 – June 2017 (DEA) and January 2016 – December 2017 (CRG)

Secondary Aerosols

The PMF model has identified secondary aerosols to contribute to 25 – 26% of the reconstructed fine fraction aerosol at both the sites during winter (Figure 7.11), increasing to 52 – 55% during summer (Figure 7.12 and Figure B.7). Lower percentage contributions are predicted by the CMB model (8 – 18% during winter and 28 – 40% during summer) (Figure 7.10) although again, the discrepancy is likely due to the inclusion of secondary species as separate profiles in the CMB model. However, the seasonal change in secondary aerosol concentrations is also observed in the outputs from both models.

Wood and Biomass Burning

Wood and biomass burning is also determined to be a contributing source in the Vaal Triangle. The PMF model also resolves a wood and biomass burning contribution at both Zamdela and Ecopark during winter, with similar contributions observed (21 – 31% of the reconstructed fine fraction) (Figure 7.11). During summer, wood and biomass burning accounts for 3 – 10% of the reconstructed fine fraction at both sites (Figure 7.12). While the CMB model has also identified

biomass burning to be a contributing source at both sites, it is not a significant source with the highest contribution of 10% seen at Zamdela during summer (Figure 7.10).

Other Sources

Other sources identified in the Vaal Triangle include industrial activities and motor vehicles. A minor petrochemical contribution (<3%) is seen at both sites in the CMB model during both seasons (Figure 7.10). In the CMB outputs, motor vehicles have a low contribution, accounting for 1 – 11% (winter) and 2 – 6 (summer) of the fine fraction aerosol at both sites (Figure 7.10). As also seen at Embalenhle and Kinross, a high percentage of the fine fraction aerosol remains unaccounted for in the CMB model at both sites (with the exception of Ecopark during the winter season).

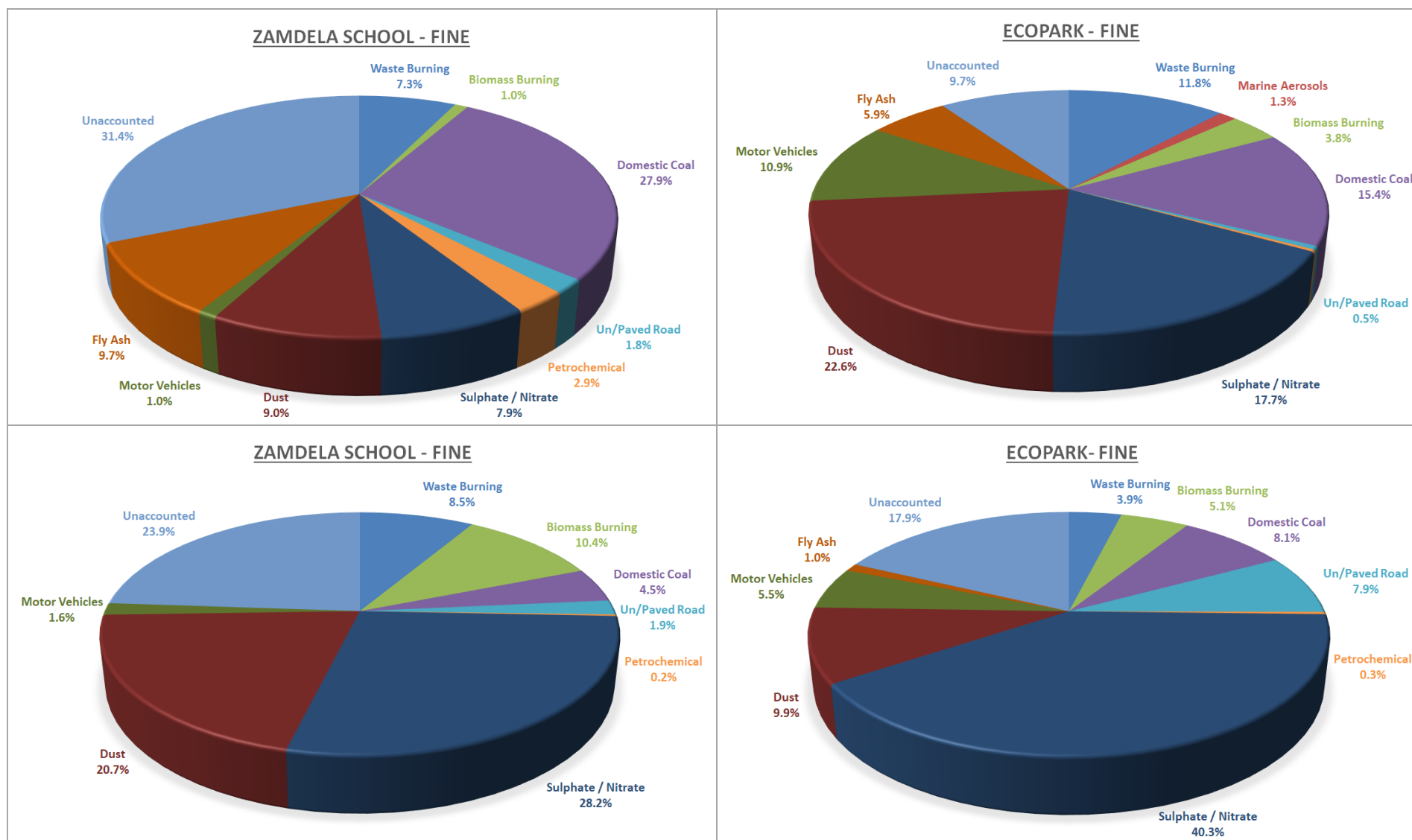


Figure 7.10: CMB source contributions (%) of the fine fraction aerosol at Zamdela school and Ecopark for the winter 2016 (top) and summer 2017 (bottom) sampling campaigns

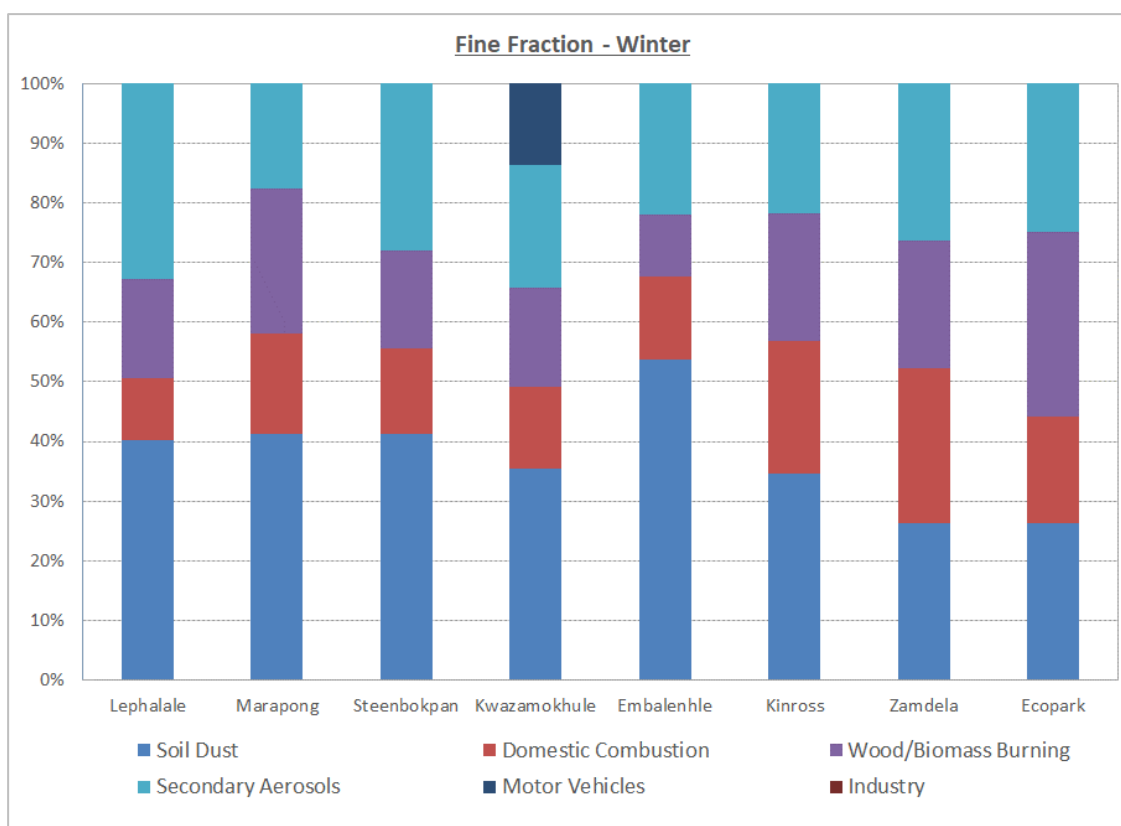


Figure 7.11: PMF source contributions (%) to the fine fraction aerosol at each site in the Waterberg, Highveld and Vaal Triangle regions during winter

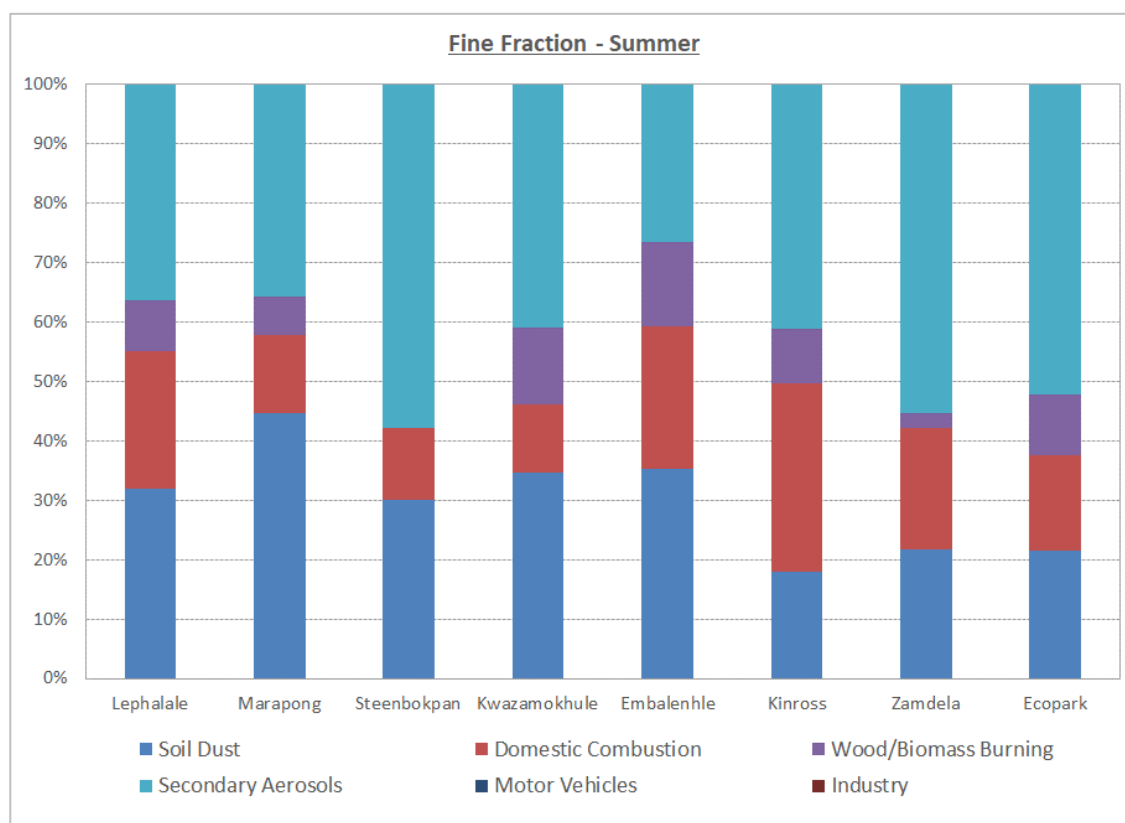


Figure 7.12: PMF source contributions (%) to the fine fraction aerosol at each site in the Waterberg, Highveld and Vaal Triangle regions during summer

7.2.3 Coarse Fraction

7.2.3.1 Waterberg Region

Soil Dust

As also seen in the fine fraction, the soil dust profile for the coarse fraction aerosol includes the crustal elements of Ca, Fe, Mg, Al and Si. In the chemical data, Si and Al are most abundant elements at all three sites during both winter and summer. Soil dust contributes to 37 – 49% of the reconstructed coarse fraction aerosol at the Lephalale sites during winter (Figure 7.18 and Figure B.8) with similar contributions (42 – 57%) seen during the summertime (Figure 7.19).

Domestic Combustion

Domestic combustion (coal combustion and waste burning) is seen at all three sites during both seasons, accounting for between 4 – 12% (winter) and 17 – 24% (summer) of the reconstructed coarse fraction aerosol (Figure 7.18 - Figure 7.19). As seen in the fine fraction, contributions from coal combustion are likely to originate from Matimba Power Station rather than from domestic coal burning in the township. The increase seen during the summer is likely due to the prevailing meteorological conditions during this season which promote improved dispersion and dilution.

Secondary Aerosols

During winter, secondary aerosols account for 15%, 17% and 19% of the reconstructed coarse fraction aerosol at Lephalale Town, Marapong and Steenbokpan, respectively (Figure 7.18) and 14%, 32% and 17% at Lephalale Town, Marapong and Steenbokpan, respectively, during summer (Figure 7.19). Secondary aerosols have a lower contribution in the coarse fraction than the fine fraction, as is also seen in the chemical data for these sites. The contribution of secondary aerosols at Marapong during summer is somewhat inflated as this profile is representative of a mixed source profile. High contributions of crustal elements such as Si, Al, Ca and Fe as well as Zn are also seen in this profile. The presence of secondary aerosols in this size fraction is indicative of aged air masses. An assessment of the air mass history during the sampling campaigns shows that the predominant air masses originate from the east (Figure 7.13). These air masses pass north of the Highveld region and as such, it is likely that these species mainly have a local origin.

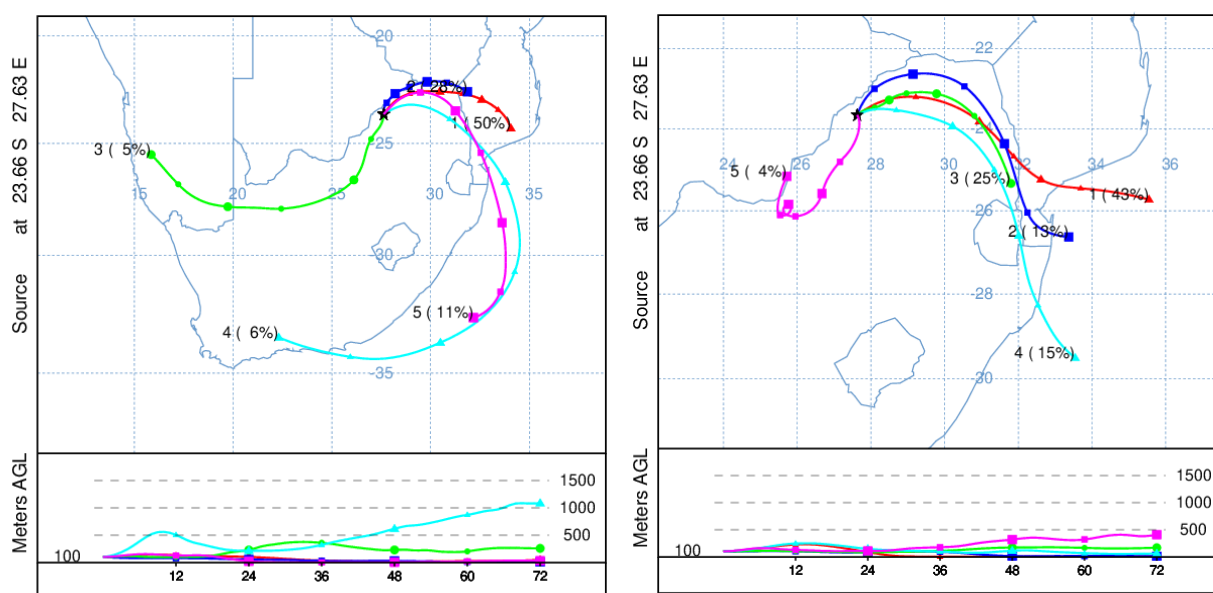


Figure 7.13: 72-hour backward trajectory cluster means for air masses arriving at Marapong during the winter (left) and summer (right) sampling campaigns

Wood and Biomass Burning

Wood and biomass burning is seen to be a contributing source at all three sites during both seasons. The highest contributions (26 – 39%) are observed during winter at all three sites (Figure 7.18) with this source only accounting for 7 – 18% of the reconstructed coarse fraction aerosol during summer (Figure 7.19). The seasonal signature seen at the sites is consistent with the regional trends in biomass burning. Domestic wood burning also decreases in summer as temperatures increase and the need for space heating declines.

7.2.3.2 Highveld Region

Soil Dust

In Kwazamokhule, soil dust contributes to 57% and 40% of the reconstructed coarse fraction aerosol during winter and summer, respectively (Figure 7.18 - Figure 7.19). At Embalenhle and Kinross, soil dust accounts for 35 – 50% of the reconstructed coarse fraction aerosol during winter (Figure 7.18) and 48 – 53% during summer (Figure 7.19). Lower contributions are seen in the CMB model at both sites during both seasons (with the exception of Kinross for winter as no results are available) (Figure 7.15). Natural soil dust and paved and unpaved roads account for 28% and 10%, respectively, of the coarse fraction aerosol at Embalenhle during winter. During summer, natural soil dust accounts for 20% and paved and unpaved roads account for 11% of the coarse fraction aerosol. Kinross also shows a high natural soil dust contribution during

summer, with this source accounting for 28% of the coarse fraction aerosol. Paved and unpaved roads contribute to 5% of the coarse fraction aerosol.

Domestic Combustion

In Kwazamokhule, the contribution from domestic combustion accounts for 21% of the reconstructed coarse fraction aerosol during both seasons (Figure 7.18 - Figure 7.19). At the other two Highveld sites, domestic combustion shows a similar contribution in this size fraction at both sites (8 – 13%) during winter (Figure 7.18). During summer, domestic combustion accounts for 16 - 19% of the reconstructed coarse fraction aerosol at Embalenhle and Kinross (Figure 7.19).

In the CMB model, 13% of the coarse fraction aerosol is apportioned to waste burning at Embalenhle during both seasons. At Kinross, waste burning is less significant, accounting for 2% of the coarse fraction aerosol during summer. Domestic coal combustion also appears to be an insignificant source in the CMB outputs, with contributions ranging from 1 – 4% at both sites during both seasons (Figure 7.15). However, an increase in emissions from power stations is seen at both sites during the summertime (14 – 23% of the coarse fraction aerosol).

Secondary Aerosols

Secondary aerosols at the three Highveld sites contribute to 6 – 19% of the reconstructed coarse fraction aerosol during winter and 8 – 10% during summer (Figure 7.18 - Figure 7.19). The CMB results show a minor contribution of this source at Embalenhle and Kinross, accounting for less than 4% of the coarse fraction aerosol at these sites (Figure 7.15).

An evaluation of the air mass history for Kwazamokhule and Embalenhle during the sampling campaigns shows the dominant air masses originating and passing over the Highveld before being transported to the sampling sites via a short pathway (Figure 7.14). During winter, air masses also originate from the east and pass over the mining and smelting operations in the North-West Province. These air masses are potential contributors to the secondary aerosols in this region.

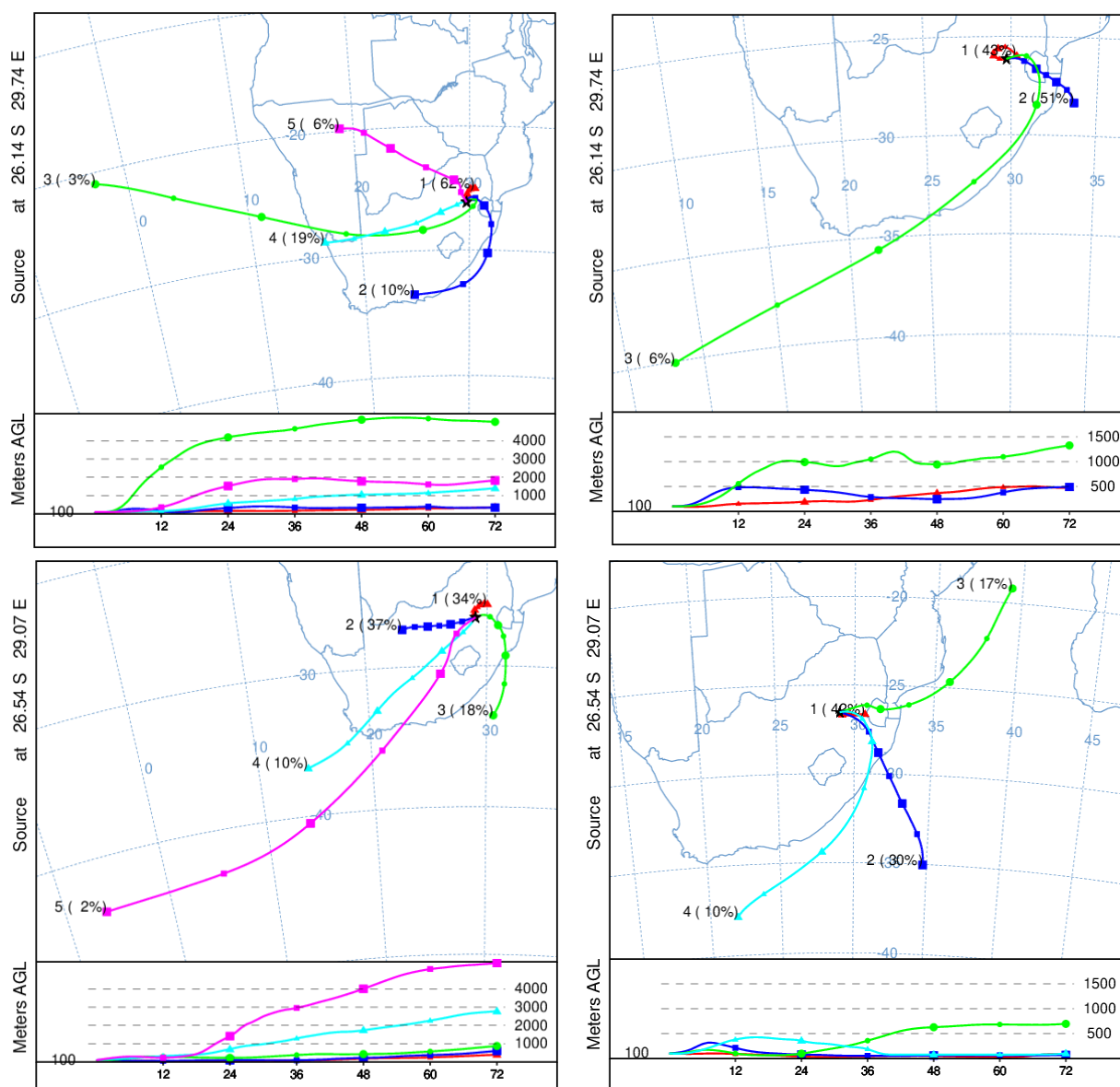


Figure 7.14: 72-hour backward trajectory cluster means for air masses arriving at Kwazamokhule (top) and Embalenhle (bottom) during the winter (left) and summer (right) sampling campaigns

Wood and Biomass Burning

Wood and biomass burning is identified in the PMF results at Kwazamokhule (11%), Embalenhle (3%) and Kinross (11%) during winter (Figure 7.18). In the CMB findings, biomass burning accounts for 12% of the coarse aerosol fraction at Embalenhle during winter (Figure 7.15). Biomass burning shows negligible contributions at both sites during summer in both the PMF and CMB findings.

Other Sources

Industrial activities and motor vehicles are also seen to be contributing sources in the Highveld region. Petrochemical activities are seen in the CMB model outputs at both sites, with contributions ranging from 3 – 9% of the coarse fraction aerosol (Figure 7.15). An industrial profile is also seen in the PMF findings, accounting for 22 - 33% of the reconstructed coarse fraction at both sites during winter. During summer, industry accounts for 18 – 28% at Embalenhle and Kinross, respectively. This profile has high contributions of species such as SO_4^{2-} , NH_4^+ , S, Cr, Ni, V and Pb (Figure B.9). The CMB model shows similar contributions from coal-fired power stations in summer (14% and 23% at Embalenhle and Kinross, respectively). Motor vehicles are identified as a contributing source in the CMB findings at both sites (11 – 12%) during summer.

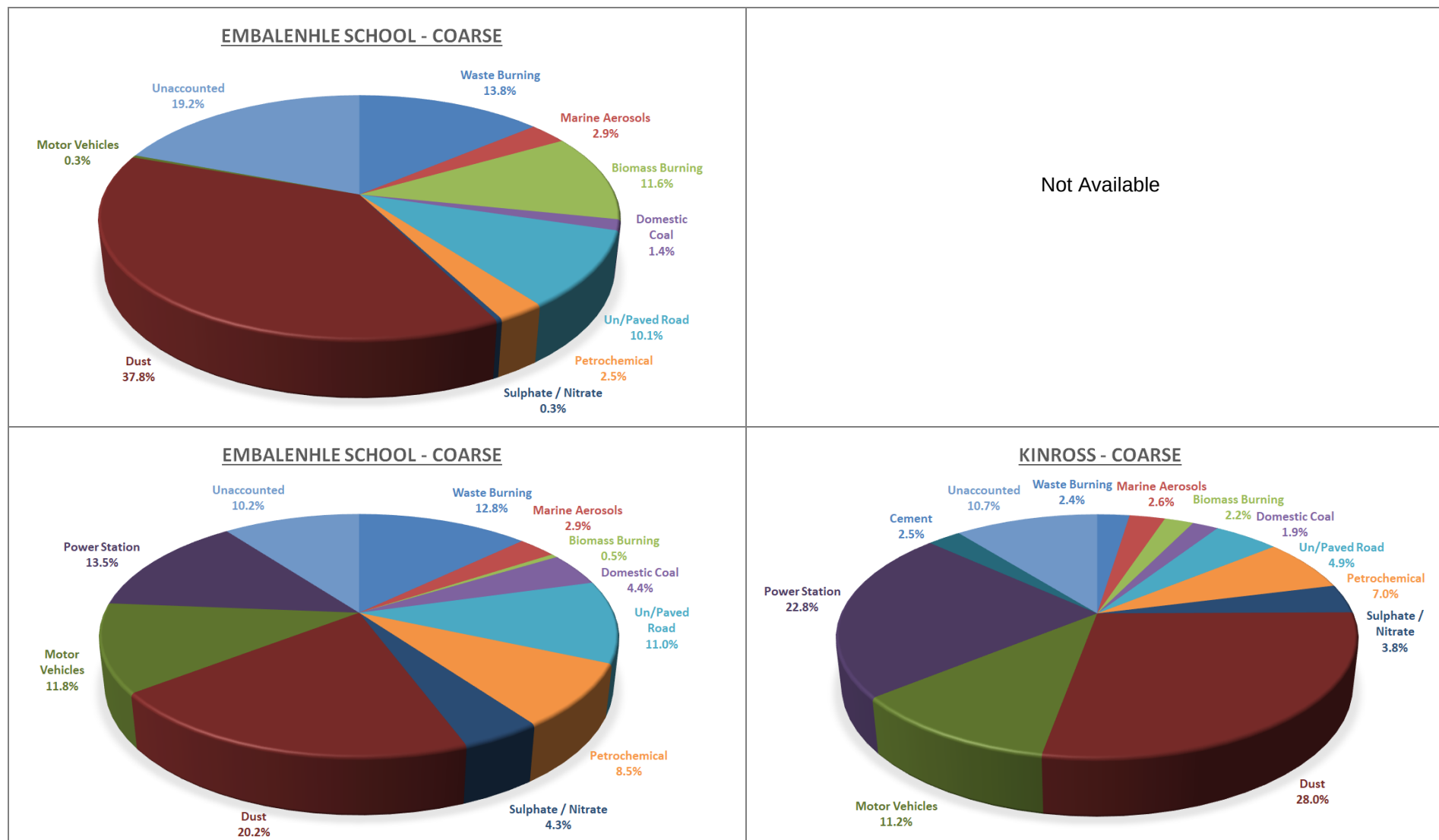


Figure 7.15: CMB source contributions (%) of the coarse fraction aerosol at Embalenhle and Kinross for the winter 2016 (top) and summer 2017 (bottom) sampling campaign

7.2.3.3 Vaal Triangle Region

Soil Dust

At the Vaal Triangle sites, soil dust contributions range from 47 – 65% during winter (Figure 7.18) and 43 - 45% during summer (Figure 7.19). Soil dust is also seen to be a significant source in the CMB results with natural soil dust accounting for 38 – 43% of the coarse fraction aerosol during winter and 21 – 36% during summer (Figure 7.17). Paved and unpaved road contributions range from 8% at both sites during winter and 3 – 11% during summer. The importance of this source at Zamdela and Ecopark is reflected in the outputs from both the PMF and CMB models for this size fraction.

Domestic Combustion

In the PMF outputs, domestic combustion contributes to 7 - 14% of the reconstructed coarse fraction aerosol at Zamdela and Ecopark during winter (Figure 7.18) and 18% at Ecopark during summer. In the CMB results, waste burning is identified to be a contributing source at Zamdela during both seasons (9% during winter and 18% during summer) with only a low contribution (4%) seen at Ecopark during summer. Domestic coal combustion is only observed at Ecopark (8%) during summer (Figure 7.17). A coal-fired power station component (7%) is also seen at Zamdela during the same season which is likely to have originated from Lethabo Power Station, located 17 km to the north-east. A fly ash profile is also distinguished in the CMB outputs which accounts for 5 – 8% of the coarse fraction aerosol at both sites during summer. The detection of this source during the summertime is due to the improved dilution and dispersion conditions associated with the meteorology in this season.

Secondary Aerosols

At Zamdela and Ecopark, the contribution from secondary aerosols is low (12 - 15%) during winter (Figure 7.18), increasing to 12 – 24% during summer (Figure 7.19 and Figure B.10). As seen in the other regions, this follows seasonal trends in the contributions of this source. In the CMB outputs, secondary SO_4^{2-} and NO_3^- is also determined to be low during winter (4 – 7%) and higher during summer (3 – 23%) (Figure 7.17).

The air mass history for Zamdela shows that the dominant air mass pathway originates over the Highveld before being transported to the sampling sites during both seasons (Figure 7.16). This air mass accounts for 49% and 68% of the trajectories during winter and summer, respectively. The next most significant air mass during winter (accounting for 44% of trajectories) originates from the west of the sampling sites, passing over significant mining and smelting operations in the North-West Province.

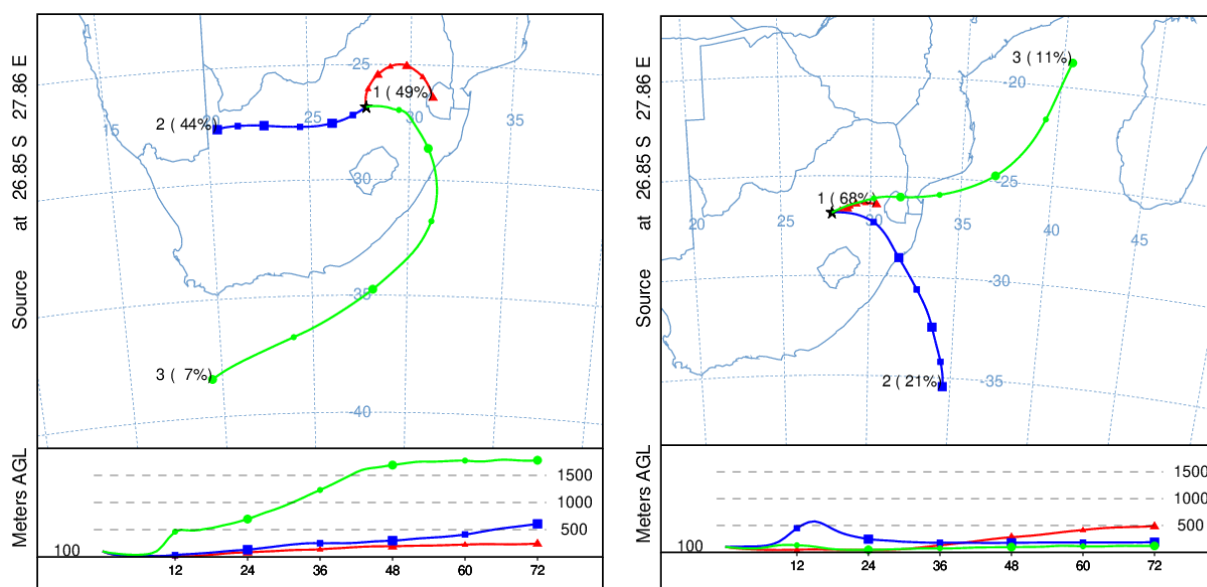


Figure 7.16: 72-hour backward trajectory cluster means for air masses arriving at Zamdela during the winter (left) and summer (right) sampling campaigns

Wood and Biomass Burning

Wood and biomass burning is detected in the PMF findings at both sites during winter accounting for 15% and 18% of the reconstructed coarse fraction aerosol at Zamdela and Ecopark, respectively (Figure 7.18 and Figure B.11). This source is also only identified in the CMB outputs during winter, accounting for 23% and 19% of the coarse fraction aerosol at Zamdela and Ecopark, respectively (Figure 7.17). Both the PMF and CMB findings are in agreement for this source.

Other Sources

Other sources identified in the Vaal Triangle are industrial activities and motor vehicles. The PMF model distinguishes a contribution from industry during winter (6% at Zamdela) and summer (17 – 18% at both sites). This source has high contributions of Fe, Mn and Zn which can be attributed to the presence of a ferromanganese smelter and other industries in the Vaal Triangle (Figure B.12). A minor petrochemical contribution (<2%) is determined during winter in the CMB outputs with similar contributions (5 – 8%) seen for summer (Figure 7.17). Motor vehicles are seen to contribute during summer in both the PMF and CMB findings. In the PMF results, this source accounts for 15% and 7% of the reconstructed coarse fraction aerosol at Zamdela and Ecopark, respectively (Figure 7.19). Motor vehicles account for 9 – 13% of the coarse aerosol fraction in the CMB results (Figure 7.17). In the CMB outputs, between 6% (Zamdela) and 18% (Ecopark) of the coarse aerosol fraction remains unaccounted for at both sites.

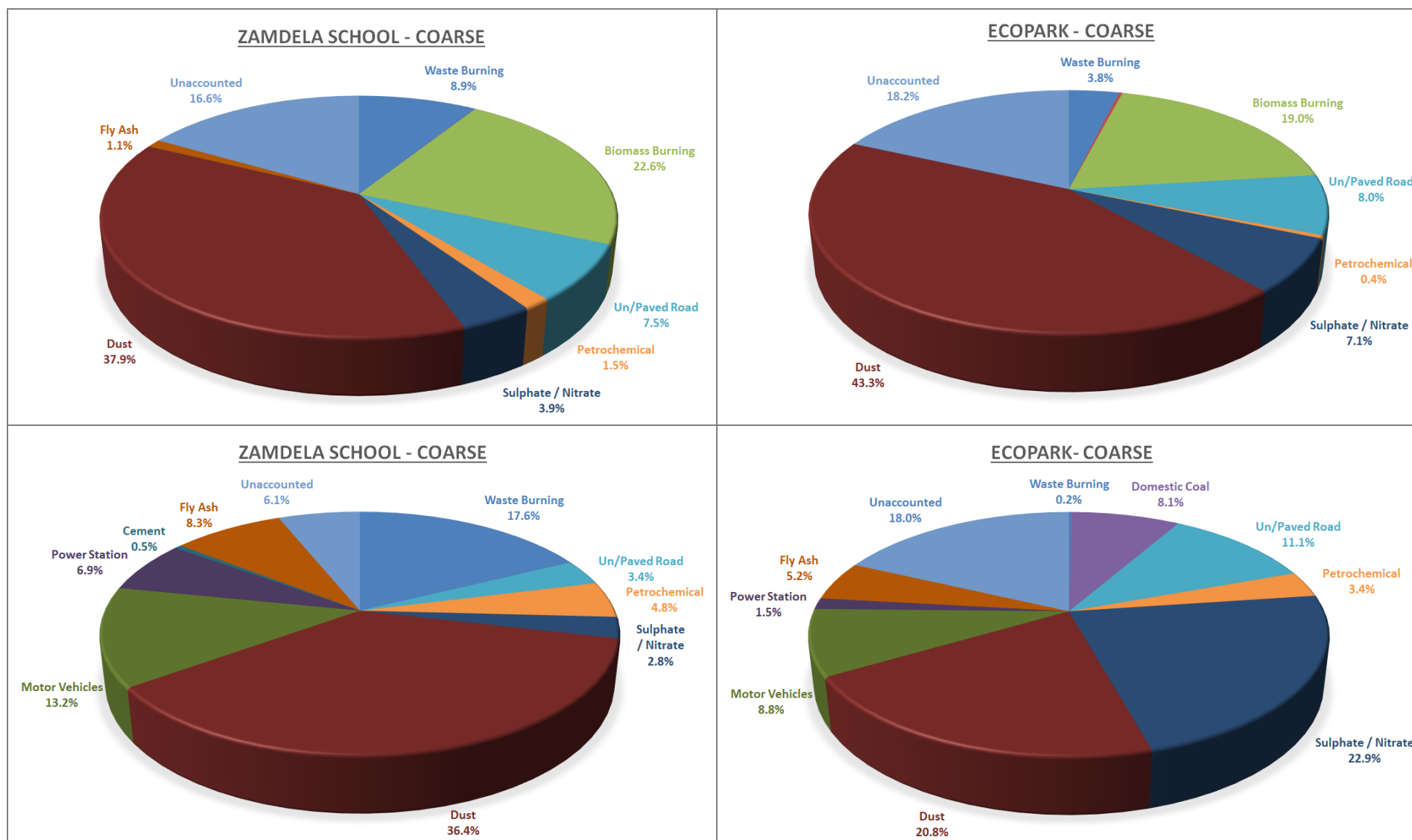


Figure 7.17: CMB source contributions (%) of the coarse fraction aerosol at Zamdela school and Ecopark for the winter 2016 (top) and summer 2017 (bottom) sampling campaign

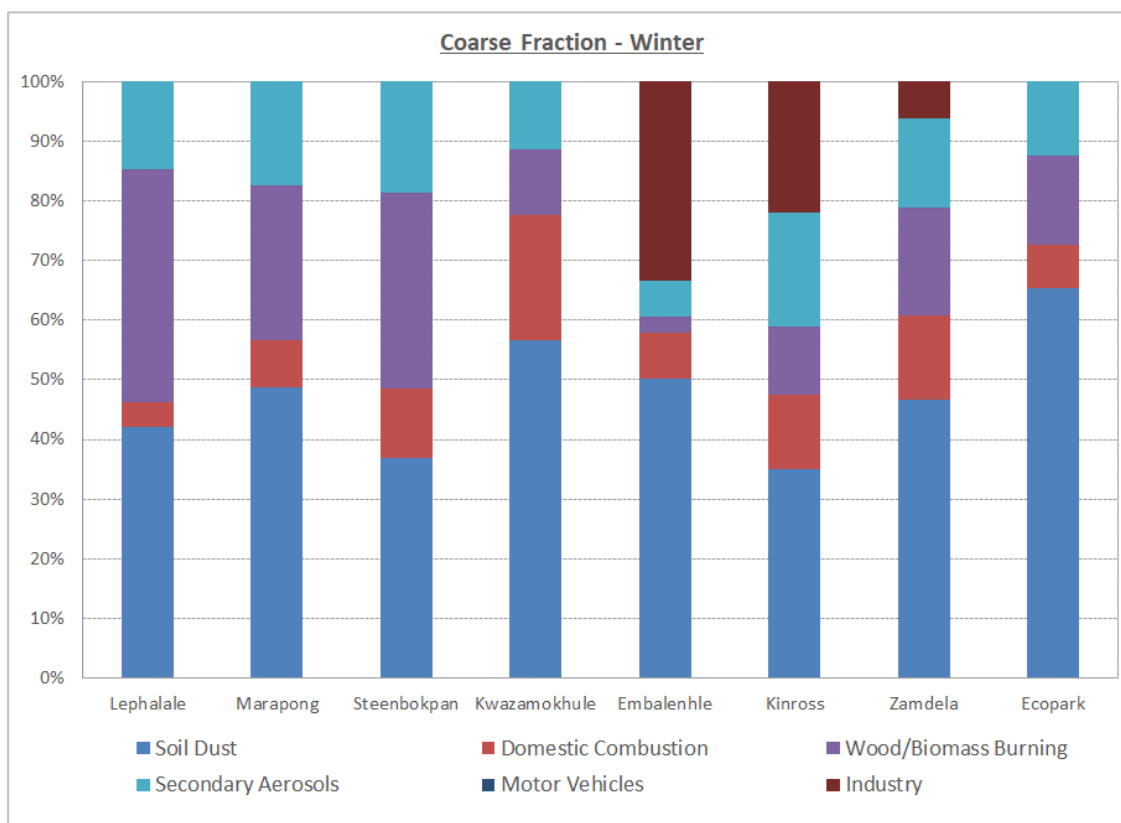


Figure 7.18: PMF source contributions (%) to the coarse fraction aerosol at each site in the Waterberg, Highveld and Vaal Triangle regions during winter

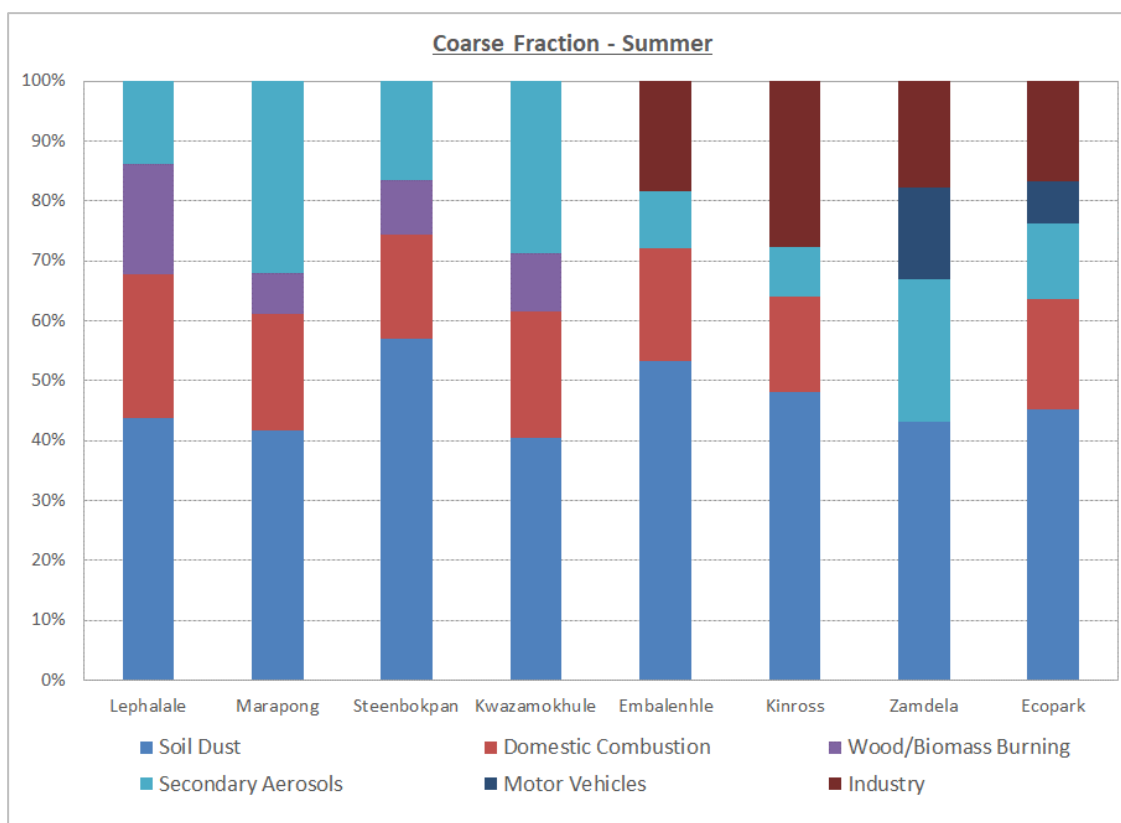


Figure 7.19: PMF source contributions (%) to the coarse fraction aerosol at each site in the Waterberg, Highveld and Vaal Triangle regions during summer

7.2.4 Aerosol Sources in the Waterberg, Highveld and Vaal Triangle Regions

The variability in the composition of each of the airsheds in the three regions is seen in the type of sources identified at each site and their relative contributions. In the Waterberg region, the airshed is well understood and the sources characterised. Source apportionment using PMF shows soil dust (natural and anthropogenic), secondary aerosols, domestic combustion (coal combustion and waste burning) and wood and biomass burning to be contributing sources to the fine and coarse fraction aerosol in all three regions. The other two regions have more diverse airsheds with the Vaal Triangle region representing the most complex airshed of all three regions. In addition to the same sources identified in the Waterberg, other contributing sources in these two regions include motor vehicles and industrial activities.

In all three regions, soil dust and secondary aerosols are identified to be the two most significant contributing sources to the fine and coarse aerosol fractions. Soil dust has a significant contribution in the Waterberg (30 – 45% in the fine fraction and 37 – 57% in the coarse fraction), Highveld (18 – 54% in the fine fraction and 35 – 57% in the coarse fraction), and Vaal Triangle (22 – 26% in the fine fraction and 43 – 65% in the coarse fraction) regions. A distinct seasonal difference in the contribution of this source is not seen in the three regions. Potential sources of soil dust at the sites include windblown dust from the surrounding open, exposed areas as well as from vehicle entrainment on unpaved roads (and paved roads to a lesser extent). Unpaved roads can constitute a significant portion of the road network in the township sites. Secondary aerosols contributions in the Waterberg (18 – 58% in the fine fraction and 14 – 32% in the coarse fraction), Highveld (21 – 41% in the fine fraction and 6 – 29% in the coarse fraction), and Vaal Triangle (25 – 55% in the fine fraction and 12 – 24% in the coarse fraction) reflect the importance of this source to the aerosol loading in all three regions. An evident seasonal signature is observed in the contributions of this source with a noticeable increase seen during the summer months. This seasonal trend has also been reported in other studies undertaken locally (Aurela *et al.*, 2016; Shikwambana and Sivakumar, 2019). Coal combustion is the dominant source of secondary aerosols as the burning of coal releases significant quantities of the precursor gases, SO_2 , NO_x and NH_3 which then oxidize in the air to form secondary particles such as H_2SO_4 , NH_4HSO_4 , NH_4SO_4 and NH_4NO_3 (Seinfeld, 1986; Watson *et al.*, 1994). Domestic coal combustion has a greater contribution in the Highveld and Vaal Triangle regions during winter compared to summer while emissions from coal-fired power stations have a greater influence in summer as pollutants are more effectively dispersed. In the Waterberg region, the main coal combustion source is coal-fired power stations as coal is not predominantly used a domestic fuel in the township.

Biomass burning also generally shows a seasonal signature with emissions from this source having a greater influence during the winter season. The winter sampling campaigns were undertaken during winter and early spring which coincide with peak emissions from biomass burning both regionally and locally. The use of wood as a domestic fuel in the townships, particularly in the Waterberg region, may also contribute to this source.

Other sources such as industrial activities, motor vehicles and waste burning do not show such a distinctive seasonal variability in their contributions. However, greater variability is evident in the type of sources contributing during the summertime which is likely due to the prevailing atmospheric conditions during this season, which allows for better dispersion and dilution of pollution. During winter, stable conditions inhibit such dispersion and dilution. This is particularly evident for emissions from tall stack sources such as coal-fired power stations and petrochemical activities.

7.2.5 Applicability of Receptor Models

Three source apportionment methods, namely, PCA, PMF and CMB modelling, have been applied to the datasets for source apportionment of the aerosol loading in each of the three regions.

The application of PCA to the datasets shows that this technique can be used as an effective preliminary tool to identify the contributing sources in an airshed prior to further refinement using receptor modelling techniques. This approach has been suggested by Hopke (2015) and Hopke and Jaffe (2020) rather than applying this method for receptor modelling purposes. While this method can be used for source identification, it is difficult to extract meaningful contributions of each source to the aerosol loading in an airshed given that sources are often combined into the same factors and cannot be separated into individual factors. As such, further refinement using PMF or CMB modelling is needed to corroborate the findings of PCA as well as to determine the relative contribution of each source to the aerosol loading in each of the airsheds.

The other multivariate method of PMF has an added advantage over PCA as this technique is able to differentiate between similar sources such as coal combustion and secondary inorganic aerosols which are reflected as separate sources in the PMF model. The PMF model also takes into account the individual data uncertainties and non-negativity of the loadings and scores factors. Missing data and BDL values can also be accounted for in the PMF model (Agarwal *et al.*, 2020). As seen with other receptor models, there are limitations associated with the application of the PMF model and the subsequent findings. A sample size of at least 100 samples is recommended to reduce instability in the solution (Brown *et al.*, 2015). Smaller sample sizes (such as the Waterberg region datasets) are on the extreme lower end of viability

for a PMF solution and as such, caution needs to be applied to the interpretation of the model findings for these sites.

While the multivariate methods of PCA and PMF do not require detailed source profiles for inclusion into the model, CMB modelling requires this input. In the absence of local, site-specific source profiles for each site, available source profiles from the USEPA SPECIATE database have been used. However, there is significant variability in the chemical composition of the contributing sources in each geographical region and as such, the CMB model cannot always be accurately resolved without the inclusion of local, site-specific sources. Also, the chemical data obtained for the receptor sites does not always include the same species present in the SPECIATE source profiles (and vice versa) which can also lead to source apportionment challenges. The utilised SPECIATE coal-fired power station profiles do not include NH_4^+ in their chemical speciation which has a potential influence on the estimated contributions for this source. The inclusion of secondary aerosols as individual source profiles for SO_4^{2-} and NO_3^- has also resulted in this source being underestimated in the CMB model at most of the sites. Secondary aerosols are easily identified in the PMF model by the presence of SO_4^{2-} , NO_3^- and NH_4^+ (and S) in the profiles. Organic acids are also not included in the SPECIATE vegetative burning (and other) source profiles. At most of the sites, a high percentage of the fine and coarse fraction aerosol remains accounted for in the CMB modelling. The variability in the chemical composition of the local sources and the available SPECIATE profiles used in the CMB modelling is one of the reasons for this discrepancy and is considered to be a limitation of this source apportionment approach. The CMB model is also not able to effectively resolve samples with low PM mass concentrations. For samples where the measured PM mass is very low ($< 5 - 10 \mu\text{g}/\text{m}^3$), the percent mass can potentially be outside of the acceptable 80 – 120% range, as the uncertainty of the mass measurement is on the order of $1 - 2 \mu\text{g}/\text{m}^3$ (Coulter, 2004). The inclusion of OC and EC in both the PMF and CMB models would also assist with source identification, especially for vehicular emission sources.

The complexity of applying three different receptor models to a single dataset is also seen in this study, consistent with other findings in literature (Almeida *et al.*, 2006; Ilacqua *et al.*, 2007; Vallius *et al.*, 2008; Viana *et al.*, 2006; Viana *et al.*, 2008b). The challenge in obtaining concurring results with the application of different receptor models to the same dataset is as a result of the different theoretical approaches behind each of the models. Specifically, the rotational ambiguity (where the output matrices may be linear combinations of the true ones which produces a solution that is not unique) together with the subjective choice of model dimension is considered to be the main issue with the different methods (Viana *et al.*, 2008b).

The main aerosol sources and their contributions within each of the three regions have been presented in this section using three different source apportionment methods. The main findings of the study are described in Chapter 8.

CHAPTER 8 CONCLUSION

Southern Africa is recognised to be a significant source of aerosols in the southern Hemisphere with South Africa, and especially the industrial Highveld, a major contributing source to the atmospheric aerosol loading over the sub-continent. South Africa has also recognised the importance of localised air quality and its impact on human health with the declaration of the Vaal Triangle, Highveld and Waterberg-Bojanala regions as Air Quality Priority Areas. This study aimed to assess the composition and sources of the aerosol loading at selected sites in each of these regions, namely, Lephalale (in the Waterberg-Bojanala), Kwazamokhule and Embalenhle (in the Highveld), and Zamdela (in the Vaal Triangle). Domestic fuel burning is a significant contributor to air pollution in the townships, with other key sources of air pollution, such as coal-fired power stations, also located in proximity to the sampling sites. Fine and coarse aerosol samples were collected at each selected site during summer and winter spanning the period 2012 to 2017. WD-XRF and IC analysis was used to identify the elemental and ionic species contributing to the fine and coarse aerosol fraction at each site. Source apportionment of the aerosol loading at each site was then undertaken using PCA as an initial means to identify potential sources and was then further refined using PMF and CMB receptor modelling.

The main findings of the study can be summarised as follows:

Fine and coarse aerosol concentrations are elevated during winter in all three regions, with an evident decrease in aerosol concentrations during summer. Aerosol concentrations tend to be highest in the township sites of Marapong (Waterberg), Kwazamokhule and Kinross (Highveld), and Zamdela (Vaal Triangle).

- In Lephalale, mean fine fraction aerosol concentrations ranged from 13.9 – 26.9 $\mu\text{g}/\text{m}^3$ during winter and 11.2 – 19.7 $\mu\text{g}/\text{m}^3$ during summer. In the coarse fraction, mean concentrations ranged from 14.6 – 89.8 $\mu\text{g}/\text{m}^3$ during winter and 10.7 – 35.8 $\mu\text{g}/\text{m}^3$ during summer.
- In Kwazamokhule, mean fine fraction aerosol concentrations were 35.1 $\mu\text{g}/\text{m}^3$ in winter and 23.8 $\mu\text{g}/\text{m}^3$ in summer. Coarse fraction aerosol concentrations were 68.9 $\mu\text{g}/\text{m}^3$ during winter and 15.8 $\mu\text{g}/\text{m}^3$ during summer.
- In Embalenhle and Kinross, mean fine fraction aerosol concentrations ranged from 16.3 – 34.1 $\mu\text{g}/\text{m}^3$ during winter and 7.4 – 19.0 $\mu\text{g}/\text{m}^3$ during summer. Mean coarse fraction aerosol

concentrations ranged from 10.3 – 114.2 $\mu\text{g}/\text{m}^3$ during winter and 5.9 – 11.2 $\mu\text{g}/\text{m}^3$ during summer.

- In Zamdela and Ecopark, mean fine fraction aerosol concentrations ranged from 17.1 – 35.7 $\mu\text{g}/\text{m}^3$ during winter and 7.9 – 17.2 $\mu\text{g}/\text{m}^3$ during summer. Mean coarse fraction aerosol concentrations ranged from 21.1 – 58.4 $\mu\text{g}/\text{m}^3$ during winter and 6.3 – 8.7 $\mu\text{g}/\text{m}^3$ during summer.

The chemical speciation data for each of the sites indicates that:

- Al and Si (and S in the fine fraction) are the dominant species in the elemental fine and coarse aerosol fractions at the Lephalale sites during both seasons. In the ionic component, SO_4^{2-} , NH_4^+ , F^- and Na^+ have substantial contributions.
- Al, Si and S are the dominating species in the elemental fine fraction at Kwazamokhule and Al, Si and Fe in the elemental coarse fraction during both seasons. SO_4^{2-} and NH_4^+ are the most abundant species in the ionic fine aerosol fractions during both seasons. In ionic coarse aerosol fraction SO_4^{2-} and F^- were the dominant ions.
- Si and Na are the most abundant species in the elemental fine and coarse fractions (and Al) at Embalenhle and Kinross during winter. During summer, Si, Ca and S dominate in the elemental fine fraction at both sites with Si the most abundant species in the elemental coarse fraction. SO_4^{2-} is the most abundant species in the ionic component in both aerosol size fractions for both seasons.
- Si and Na are the most abundant species in the elemental fine and coarse fractions (and Al) at Zamdela and Ecopark during winter. During summer, S, Ca and Si are the most abundant elements in the elemental fine fraction and Si, Al and Ca in the elemental coarse fraction at both sites. SO_4^{2-} , NH_4^+ and F^- are the most abundant ionic species.

Source apportionment using PMF identified soil dust (natural and anthropogenic), secondary aerosols (mainly derived from coal combustion), domestic combustion (coal combustion and waste burning) and wood and biomass burning to be contributing sources in each region. Motor vehicles and petrochemical activities were also identified in the Highveld and Vaal Triangle regions. Of these sources, soil dust and secondary aerosols were determined to be the main contributing sources. The contribution from secondary aerosols reflects a clear seasonal signature, with an increase in the contribution from this source during the summer season due to an increase in relative humidity. Measures to mitigate particulate air pollution in South Africa should consider these key sources.

Waterberg Region

In the Waterberg, soil dust accounts for 30 – 45% of the fine fraction aerosol and 37 – 57% of the coarse fraction aerosol. Secondary aerosols contribute to 18 – 58% of the fine fraction aerosol and 14 – 32% of the coarse fraction aerosol. Domestic combustion and wood and biomass burning were also identified to be contributing sources at the three sites.

Highveld Region

In the Highveld, soil dust contributes to 18 – 54% of the fine fraction aerosol and 35 – 57% of the coarse fraction aerosol. Secondary aerosols account for 21 – 41% of the fine fraction aerosol and 6 – 29% of the coarse fraction aerosol. Domestic combustion, wood and biomass burning and motor vehicles were also seen to contribute at the Highveld sites. At Embalenhle and Kinross, industrial activities were also identified to contribute to the aerosol loading.

Vaal Triangle Region

In the Vaal Triangle, soil dust accounts for 22 – 26% of the fine fraction aerosol and 43 – 65% of the coarse fraction aerosol. Secondary aerosols account for 25 – 55% of the fine fraction aerosol and 12 – 24% of the coarse fraction aerosol. Domestic combustion, wood and biomass burning, industrial activities and motor vehicles were also identified in the region.

The variability in the composition of each airshed in each of the three regions is seen in the type of sources identified at each site and their relative contributions. In Lephalale in the Waterberg, the local contributing sources are less numerous and far better understood, while the Highveld and more specifically, the Vaal Triangle regions, have a more complex and diverse emission source profile.

While the PMF and CMB models show good agreement in terms of the type of sources identified at each site and the source contributions relative to each other, the actual percentage contribution of each source is not always concurrent with each other. This discrepancy is likely a result of the inherent limitations associated with each of the modelling approaches as well as inadvertent errors. Despite this, these methods provide valuable information about the air pollution sources in a given airshed and their respective contributions which facilitates the implementation of appropriate strategies to control and mitigate air pollution.

Within the South African context, several considerations need to be taken into account when selecting receptor models for aerosol source apportionment purposes. The ease of application of the CMB receptor model within South Africa is limited as local, site-specific source profiles are needed for inclusion into the CMB receptor model. The need for local source profiles, together with varying degrees in the complexity of the airsheds within each region does not

support the widespread use of this model for aerosol source apportionment purposes within South Africa. The multivariate method of PMF does not require detailed source profiles for inclusion into the model and can be more easily applied in complex emission source airsheds. Consideration of the limitations associated with the available datasets and each of the source apportionment techniques needs to be recognised when undertaking aerosol source apportionment. Based on the findings of this research, the simultaneous use of PCA and PMF is the recommended approach for aerosol source apportionment studies in South Africa where local, site-specific source profiles are not available for the contributing sources.

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APPENDIX A VARIMAX ROTATED FACTOR ANALYSIS

Table A.1: Varimax rotated factor loadings of the fine aerosol fraction at Lephalale Town, Marapong and Steenbokpan for the winter 2012 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Lephalale Town					Marapong					Steenbokpan				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
F ⁻	0.13	0.50	0.62	-0.07	-0.24	0.81	0.08	0.19	-0.27	-0.08	0.54	-0.18	0.48	0.45	0.15
Cl ⁻	0.12	0.22	-0.61	-0.36	-0.47	-0.22	0.19	-0.01	0.85	0.01	-0.06	-0.30	0.57	0.23	0.29
NO ₃ ⁻	-0.08	-0.10	0.89	0.05	-0.01	0.54	0.48	0.49	0.29	-0.10	0.11	0.14	0.84	0.23	-0.19
SO ₄ ²⁻	0.07	0.96	-0.02	-0.06	0.12	0.25	0.91	0.26	0.07	0.05	0.10	0.94	0.02	0.14	0.16
Na ⁺	0.30	-0.46	0.60	-0.26	-0.29	-0.02	0.29	0.88	-0.03	0.03	0.01	0.25	0.86	0.02	0.22
NH ₄ ⁺	-0.16	0.92	-0.02	-0.28	-0.01	0.13	0.90	0.31	-0.14	0.10	-0.08	0.94	-0.01	-0.03	0.18
K ⁺	0.12	0.13	-0.10	-0.17	0.87	-0.04	0.28	0.17	-0.22	0.76	-0.08	0.22	0.18	0.64	-0.15
Ca ²⁺	0.35	-0.15	0.17	0.86	-0.01	0.47	0.48	0.33	-0.49	0.12	0.24	-0.26	0.00	0.79	0.19
Mg ²⁺	0.66	-0.57	0.20	-0.01	-0.02	0.25	0.36	0.79	-0.35	0.07	-0.18	0.11	0.90	0.18	0.18
Formate	-0.36	-0.15	-0.01	0.74	-0.23	0.06	0.48	0.54	0.06	0.04	0.18	0.80	0.17	-0.05	-0.15
Oxalate	0.25	-0.30	0.01	-0.03	0.04	0.22	-0.08	-0.10	0.35	0.74	0.43	-0.02	0.09	0.48	-0.42
S	0.14	0.94	-0.03	-0.15	0.09	0.30	0.92	0.12	0.13	0.07	0.22	0.92	0.03	-0.12	0.10
Fe	0.97	0.03	-0.10	0.04	0.09	0.85	0.27	-0.07	-0.06	0.18	0.91	0.04	-0.07	-0.04	0.27
Na	-0.46	0.09	0.71	0.05	-0.06	0.39	0.35	0.55	0.24	-0.35	0.11	-0.29	0.72	-0.19	-0.40
Mg	0.71	-0.01	0.64	0.11	-0.02	0.84	0.07	0.39	-0.06	-0.08	0.47	0.24	0.69	-0.38	-0.18
Al	0.98	-0.01	-0.07	0.04	0.04	0.91	0.18	0.00	-0.13	0.03	0.95	0.24	0.03	0.03	0.09
Si	0.98	0.01	-0.09	0.00	0.05	0.94	0.19	0.00	-0.14	0.05	0.95	0.23	0.05	0.02	0.07
K	0.61	-0.06	-0.17	-0.12	0.63	0.67	0.16	-0.17	0.44	0.30	0.86	-0.03	0.02	0.22	-0.24
Ti	0.42	-0.35	-0.18	0.49	-0.45	0.25	0.24	-0.49	-0.50	-0.10	0.29	0.27	0.15	-0.02	0.83
% Variance	26.76	19.97	15.62	9.95	9.56	27.91	20.29	15.95	10.53	7.61	23.03	20.69	20.53	9.83	8.34
% Cumulative	26.76	46.73	62.35	72.29	81.86	27.91	48.20	64.15	74.68	82.29	23.03	43.72	64.25	74.08	82.42

Table A.2: Varimax rotated factor loadings of the fine aerosol fraction at Lephalale Town, Marapong and Steenbokpan for the summer 2013 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Lephalale Town						Marapong					Steenbokpan				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
F ⁻	0.24	0.06	0.76	-0.04	0.09	0.21	0.72	0.26	-0.04	0.56	0.08	0.69	0.47	-0.26	0.14	-0.16
Cl ⁻	0.10	0.80	-0.25	-0.11	0.19	0.11	0.06	-0.85	-0.02	0.09	0.05	0.00	-0.08	0.12	0.16	0.88
NO ₃ ⁻	-0.18	0.77	-0.05	0.26	-0.31	-0.07	0.14	0.46	0.68	-0.38	-0.05	-0.40	0.30	-0.49	0.37	-0.14
SO ₄ ²⁻	0.31	0.00	0.92	0.11	0.06	0.08	0.42	0.69	0.34	0.31	0.24	0.43	0.37	0.74	-0.11	0.21
Na ⁺	0.07	0.98	-0.07	-0.03	-0.11	-0.05	-0.17	-0.18	0.93	-0.13	-0.09	-0.05	0.95	-0.11	0.00	-0.04
NH ₄ ⁺	0.33	-0.08	0.91	0.08	0.07	0.08	0.49	0.68	0.27	0.33	0.19	0.47	0.35	0.71	-0.07	0.24
K ⁺	0.56	0.25	0.09	0.48	0.24	0.38	0.03	0.13	0.08	0.05	0.97	0.24	0.28	-0.49	0.35	0.22
Ca ²⁺	0.72	0.41	0.39	0.08	-0.09	-0.05	0.86	0.28	-0.09	0.27	0.21	0.53	0.40	0.38	0.29	0.34
Mg ²⁺	0.31	0.81	0.37	0.13	0.10	-0.01	0.41	0.35	0.49	0.41	0.10	0.24	0.72	0.24	0.28	-0.29
Formate	0.11	-0.09	-0.14	-0.89	0.02	0.08	-0.26	0.29	0.71	0.06	0.27	-0.02	0.56	-0.01	-0.37	0.29
Acetate	-	-	-	-	-	-	0.64	0.04	0.20	-0.12	-0.25	-	-	-	-	-
Oxalate	-	-	-	-	-	-	-	-	-	-	-	0.05	-0.06	0.04	0.79	0.05
Cl	-0.08	0.72	-0.52	-0.19	-0.06	0.24	-0.13	-0.88	0.26	-0.13	-0.18	-0.17	0.22	-0.73	-0.08	0.06
S	0.29	0.03	0.93	0.10	0.08	0.05	0.44	0.67	0.34	0.32	0.27	0.45	0.36	0.73	-0.09	0.23
Ca	-	-	-	-	-	-	0.92	0.21	-0.11	0.21	0.16	-	-	-	-	-
Fe	0.95	0.09	0.21	-0.11	0.06	-0.05	0.92	0.16	-0.16	0.23	0.12	0.96	0.09	0.17	0.01	0.00
Na	0.05	0.96	0.09	0.06	-0.11	-0.04	-0.06	-0.14	0.94	-0.01	0.05	0.09	0.96	0.01	-0.02	-0.09
Mg	0.29	0.88	0.21	0.08	0.04	-0.01	0.84	0.29	0.24	0.30	0.15	0.34	0.89	0.14	-0.01	0.08
Al	0.93	0.13	0.28	-0.12	0.04	-0.04	0.91	0.19	-0.21	0.25	0.14	0.93	0.13	0.28	-0.09	-0.06
Si	0.93	0.10	0.27	-0.14	0.05	-0.05	0.91	0.18	-0.19	0.25	0.13	0.94	0.12	0.27	-0.08	-0.03
P	0.60	-0.22	0.05	0.27	-0.07	0.24	0.86	-0.21	0.03	-0.06	0.06	0.10	0.65	0.05	-0.53	0.03
K	0.85	0.14	0.14	0.14	0.16	-0.15	0.38	0.17	0.02	0.12	0.89	0.80	0.31	0.08	-0.02	-0.04
Ti	0.88	0.01	0.38	-0.11	-0.12	-0.08	0.92	0.16	-0.21	0.22	0.12	0.88	-0.04	0.34	0.06	0.02
Mn	-	-	-	-	-	-	0.29	0.10	-0.34	0.76	-0.05	0.69	-0.16	-0.16	0.29	0.05
Zn	-0.19	0.00	0.31	-0.06	-0.08	0.86	0.39	-0.02	0.09	0.65	0.26	0.15	0.02	0.30	0.39	-0.55
Cr	0.03	-0.14	0.19	0.01	0.92	-0.06	0.37	0.53	-0.39	-0.16	0.18	-0.07	0.07	0.71	0.28	-0.30
% Variance	27.02	24.66	19.61	6.18	5.30	5.09	35.01	16.55	15.53	9.90	9.41	26.61	21.04	15.95	7.85	7.22
%Cumulative	27.02	51.68	71.29	77.48	82.78	87.87	35.01	51.56	67.10	76.99	86.41	26.61	47.65	63.60	71.45	78.67

Table A.3: Varimax rotated factor loadings of the fine aerosol fraction at Kwazamokhule for the winter 2015 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Kwazamokhule Fine				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
F ⁻	-0.14	-0.02	0.81	-0.13	-0.07
Cl ⁻	-0.14	0.14	0.87	0.01	-0.23
NO ₃ ⁻	-0.19	0.02	-0.20	0.88	-0.10
SO ₄ ²⁻	-0.18	0.84	-0.23	0.25	-0.09
Na ⁺	-0.05	-0.20	0.06	-0.06	-0.92
NH ₄ ⁺	-0.03	0.92	0.23	0.09	0.14
K ⁺	0.10	0.09	-0.08	0.89	0.32
Ca ²⁺	0.99	0.00	-0.03	-0.04	0.04
Formate	0.52	-0.07	0.78	-0.14	0.11
Acetate	-0.16	0.12	0.78	-0.23	0.15
Oxalate	-0.09	0.24	-0.14	0.84	-0.07
Cl	0.95	-0.14	-0.10	0.03	0.05
S	0.03	0.95	0.15	0.04	0.17
Ca	0.99	-0.03	-0.01	-0.07	0.00
Fe	0.99	-0.04	-0.03	-0.04	0.01
Na	0.71	0.47	0.01	0.03	0.26
Mg	0.98	0.04	-0.03	-0.06	0.05
Al	0.99	-0.02	-0.04	-0.05	0.02
Si	0.99	-0.02	-0.03	-0.05	0.01
P	0.99	0.00	-0.03	-0.06	0.03
K	0.78	0.13	-0.09	0.34	0.27
Ti	0.99	-0.04	-0.02	-0.05	0.00
Mn	0.97	-0.04	-0.02	0.03	0.00
Zn	0.94	0.11	0.06	-0.15	0.01
Cr	0.85	-0.13	-0.13	-0.04	0.08
V	0.99	-0.03	0.01	-0.04	-0.01
Ni	0.93	-0.11	0.03	-0.02	-0.08
% Variance	54.29	10.81	10.63	9.69	4.72
% Cumulative	54.29	65.10	75.73	85.41	90.13

Table A.4: Varimax rotated factor loadings of the fine aerosol fraction at Kwazamokhule for the summer 2016 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Kwazamokhule			
	Factor 1	Factor 2	Factor 3	Factor 4
F ⁻	0.85	0.47	-0.08	0.09
NO ₃ ⁻	0.25	0.63	0.08	0.58
SO ₄ ²⁻	0.09	0.97	0.12	-0.05
Na ⁺	0.79	-0.36	0.07	0.23
NH ₄ ⁺	0.11	0.89	0.05	0.11
K ⁺	0.67	0.18	-0.01	0.58
Ca ²⁺	0.82	0.44	0.07	-0.05
Mg ²⁺	0.91	0.31	0.08	0.21
Oxalate	0.43	0.69	0.30	0.27
Cl	0.40	-0.03	0.07	0.88
S	0.11	0.95	0.18	-0.09
Fe	0.94	0.22	0.11	0.14
Na	0.83	-0.23	0.12	0.27
Mg	0.93	0.27	0.12	0.20
Al	0.95	0.15	0.11	0.14
Si	0.96	0.13	0.09	0.13
P	0.83	0.52	0.09	0.10
K	0.82	0.08	0.11	0.49
Ti	0.97	0.13	0.07	0.14
Mn	0.10	0.20	0.93	0.01
Zn	-0.03	0.39	0.87	-0.18
Cr	0.19	0.78	0.30	0.06
V	0.22	0.06	0.78	0.30
% Variance	45.28	23.87	11.21	9.61
% Cumulative	45.28	69.15	80.36	89.97

Table A.5: Varimax rotated factor loadings of the fine aerosol fraction at Embalenhle and Kinross for the winter 2016 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Embalenhle							Kinross						
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
F ⁻	0.86	0.36	0.15	0.22	0.07	0.12	-0.01	0.86	-0.07	0.11	0.35	0.15	0.10	0.07
Cl ⁻	0.17	0.95	-0.07	0.07	0.14	-0.07	0.08	-0.23	-0.04	-0.08	-0.03	-0.06	0.92	-0.05
NO ₃ ⁻	0.01	-0.02	0.17	0.36	0.54	0.29	0.10	0.53	0.14	0.30	0.21	0.33	0.06	-0.19
SO ₄ ²⁻	0.08	-0.02	0.95	0.16	0.01	0.13	-0.09	0.02	0.16	-0.07	0.97	-0.02	0.12	-0.03
Na ⁺	0.26	0.03	0.29	0.87	-0.01	-0.01	-0.04	0.29	0.64	-0.07	0.33	0.11	0.48	0.05
NH ₄ ⁺	0.10	0.01	0.96	0.14	0.07	0.14	-0.06	0.09	0.09	-0.03	0.98	0.01	0.07	-0.01
K ⁺	0.21	0.48	0.33	0.45	0.47	0.05	-0.06	0.02	0.91	0.00	0.33	-0.05	0.04	-0.07
Ca ²⁺	0.95	0.14	0.11	0.07	0.01	0.07	0.06	0.27	0.08	0.27	0.40	-0.06	0.64	-0.23
Mg ²⁺	0.93	0.14	0.11	0.11	0.17	0.11	-0.07	0.23	0.28	0.00	0.31	0.05	0.71	0.16
Formic	0.55	0.17	0.14	-0.10	0.61	0.03	0.28	0.13	0.76	-0.08	-0.17	-0.10	-0.10	-0.29
Acetic	0.41	0.45	0.00	-0.20	0.49	-0.21	-0.16	-	-	-	-	-	-	-
Oxalate	0.16	0.19	0.62	-0.19	0.38	0.32	0.10	-0.08	0.79	-0.11	0.17	-0.06	-0.01	0.43
Cl	0.20	0.92	-0.04	0.04	0.17	-0.10	0.17	0.15	-0.46	-0.23	-0.38	-0.52	-0.12	-0.04
S	0.14	-0.01	0.94	0.15	0.00	-0.12	0.04	0.13	0.32	-0.01	0.89	-0.10	0.16	0.10
Ca	0.97	0.15	0.04	0.07	-0.06	-0.01	0.08	0.82	0.01	0.40	-0.04	-0.10	0.00	-0.13
Fe	0.92	0.17	0.10	0.11	0.10	0.20	0.08	0.22	0.04	0.96	0.00	-0.02	0.00	-0.02
Na	0.50	0.51	0.05	0.64	0.02	-0.18	0.04	0.48	0.71	-0.06	0.10	-0.04	0.30	0.11
Mg	0.96	0.11	-0.05	0.08	0.07	-0.02	-0.04	0.92	0.24	0.16	-0.08	-0.14	0.06	0.00
Al	0.96	0.14	0.09	0.14	-0.02	-0.02	0.04	0.89	0.12	0.01	0.10	-0.11	0.01	-0.04
Si	0.96	0.17	0.09	0.11	0.01	0.00	0.10	0.89	0.04	0.00	-0.03	-0.18	-0.02	-0.01
P	0.82	0.11	-0.03	-0.01	0.33	-0.13	0.02	0.39	-0.12	0.86	-0.03	-0.13	0.05	-0.10
K	0.59	0.43	0.22	0.44	0.29	-0.07	0.06	0.19	0.94	0.07	0.17	-0.10	0.06	0.00
Ti	0.87	0.14	0.27	0.05	-0.11	-0.11	0.20	0.73	0.26	0.06	0.05	-0.03	0.01	0.43
Mn	0.69	0.17	0.04	0.05	0.18	-0.17	0.36	0.10	-0.38	0.10	0.02	0.69	0.33	0.12
Zn	0.19	0.97	0.02	0.05	0.01	-0.03	0.05	0.37	-0.19	0.26	0.27	-0.06	-0.12	0.61
Cr	0.04	0.03	0.17	0.07	0.21	0.79	0.11	0.10	0.01	0.98	-0.03	-0.03	0.01	0.02
V	0.42	0.22	0.19	0.08	-0.03	-0.05	0.64	-0.11	0.19	-0.32	-0.22	-0.23	0.08	0.64
Pb	0.41	0.66	0.27	0.08	-0.43	-0.03	0.00	-0.06	-0.11	-0.21	-0.03	0.85	-0.09	-0.09
As	0.53	0.51	0.13	0.12	-0.33	0.12	-0.22	-0.30	0.03	-0.09	-0.18	0.77	-0.17	-0.11
Ni	0.02	0.01	-0.22	-0.07	0.14	0.32	0.83	0.01	0.01	0.96	-0.03	-0.06	0.01	0.02
Sr	0.00	-0.17	0.03	-0.08	-0.09	0.68	0.05	0.12	0.14	-0.38	-0.03	-0.17	0.07	-0.34
% Variance	35.26	15.34	12.07	6.53	6.42	5.38	5.00	19.08	15.67	14.62	12.56	8.13	7.81	5.22
% Cumulative	35.26	50.59	62.67	69.19	75.61	81.00	86.00	19.08	34.75	49.37	61.94	70.07	77.88	83.10

Table A.6: Varimax rotated factor loadings of the fine aerosol fraction at Embalenhle and Kinross for the summer 2017 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Embalenhle						Kinross					
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
F ⁻	0.06	0.19	0.80	0.05	-0.07	-0.09	0.79	-0.08	-0.03	0.41	0.34	0.02
Cl ⁻	-0.09	-0.13	-0.13	0.96	-0.01	0.06	0.03	-0.06	-0.05	0.43	-0.03	0.76
NO ₃ ⁻	0.97	0.08	-0.03	0.03	-0.08	-0.09	0.21	0.06	-0.07	0.39	0.76	-0.02
SO ₄ ²⁻	0.33	0.90	-0.03	-0.02	-0.07	0.09	0.14	0.97	-0.05	0.00	0.05	0.00
Na ⁺	-0.04	0.08	0.23	0.92	-0.04	-0.08	0.77	0.25	-0.18	-0.20	0.12	0.30
NH ₄ ⁺	0.37	0.89	-0.02	-0.02	-0.06	0.09	0.18	0.96	-0.09	-0.01	0.13	0.02
K ⁺	0.14	0.37	0.77	0.11	-0.04	-0.09	0.91	0.10	0.00	0.08	0.24	0.07
Ca ²⁺	0.04	-0.09	0.75	0.02	0.29	0.13	0.52	-0.08	0.00	0.72	0.34	0.00
Mg ²⁺	-0.05	0.14	0.92	0.02	0.08	0.14	0.90	0.14	0.03	0.27	0.25	0.00
Formic	0.05	0.55	0.21	-0.11	0.04	0.07	0.56	-0.25	0.08	-0.21	0.57	0.19
Acetic	-	-	-	-	-	-	0.22	0.26	0.15	0.03	0.67	0.15
Oxalate	0.00	0.80	0.34	0.10	-0.15	-0.16	0.64	0.41	-0.17	-0.02	0.38	0.10
Cl	0.30	-0.03	0.08	0.88	0.12	-0.05	-0.21	0.04	-0.19	0.63	-0.01	0.05
S	0.00	0.74	0.11	-0.01	-0.12	-0.18	0.16	0.97	-0.05	-0.01	0.02	0.01
Ca	0.21	-0.12	0.07	0.04	0.95	-0.03	0.43	-0.02	0.06	0.76	0.16	0.05
Fe	0.95	0.01	0.03	0.01	0.14	0.24	0.05	-0.07	0.97	-0.03	-0.04	0.00
Na	0.90	0.11	0.26	0.17	-0.05	0.08	0.91	0.04	-0.09	-0.13	0.13	0.06
Mg	0.98	0.07	0.08	0.02	-0.03	0.12	0.97	0.17	0.01	0.07	0.11	-0.03
Al	0.97	0.12	0.07	0.02	0.03	0.12	0.81	0.30	0.03	0.11	-0.17	-0.22
Si	0.97	0.10	0.11	0.03	0.05	0.11	0.96	0.08	0.03	0.08	0.13	-0.02
P	0.82	0.38	-0.09	0.02	0.06	0.06	0.70	0.47	-0.11	0.11	0.17	-0.11
K	0.90	0.09	0.23	0.06	0.31	0.08	0.95	-0.01	0.08	0.08	0.12	-0.01
Ti	0.84	0.01	0.01	0.03	0.51	0.10	-	-	-	-	-	-
Mn	0.97	-0.08	-0.03	0.04	0.02	0.07	0.54	-0.40	0.18	0.11	0.14	-0.48
Zn	0.87	0.12	-0.03	-0.09	-0.08	-0.08	0.45	0.04	0.02	0.22	0.43	-0.29
Cr	0.11	-0.12	0.03	-0.01	-0.04	0.93	-0.08	-0.04	0.98	-0.05	0.02	0.04
V	0.76	0.27	-0.17	-0.02	0.06	-0.07	0.08	0.02	0.29	-0.12	0.19	0.71
As	-0.01	-0.15	0.11	0.02	0.97	-0.06	-	-	-	-	-	-
Ni	0.19	0.06	0.05	-0.05	-0.03	0.95	-0.06	-0.10	0.92	-0.09	0.10	0.11
%Variance	37.34	13.11	11.09	9.41	8.62	7.38	35.19	13.95	11.28	8.54	8.41	6.09
%Cumulative	37.34	50.45	61.54	70.95	79.57	86.95	35.19	49.13	60.41	68.96	77.36	83.45

Table A.7 Varimax rotated factor loadings of the fine aerosol fraction at Zamdela and Ecopark for the winter 2016 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Zamdela						Ecopark				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
F ⁻	0.79	0.36	0.23	0.29	0.05	0.15	0.90	-0.01	0.18	0.08	0.07
Cl ⁻	-0.03	-0.09	-0.01	0.20	0.84	0.02	0.08	0.98	-0.03	0.02	0.02
NO ₃ ⁻	-0.11	0.02	0.76	-0.05	0.09	-0.04	-0.04	0.28	0.70	0.21	0.00
SO ₄ ²⁻	0.06	0.04	0.96	0.06	-0.10	0.02	0.05	0.02	0.96	-0.04	0.08
Na ⁺	0.44	0.62	0.04	0.08	-0.15	-0.25	0.54	0.80	-0.07	-0.08	-0.07
NH ₄ ⁺	0.03	-0.02	0.98	0.09	-0.01	0.03	-0.05	-0.10	0.96	0.02	0.11
K ⁺	0.34	0.76	0.41	0.15	-0.08	0.08	0.79	0.34	0.29	-0.13	-0.27
Ca ²⁺	0.89	0.30	0.02	0.16	0.07	0.05	0.44	0.86	0.04	0.09	0.08
Mg ²⁺	0.82	0.29	0.03	-0.02	-0.14	0.13	0.23	0.95	-0.04	0.00	0.03
Formic	0.24	0.80	-0.24	0.16	0.17	0.14	0.21	0.94	-0.07	0.00	-0.07
Acetic	0.11	0.87	-0.23	0.00	0.16	-0.13	0.22	0.95	-0.08	-0.02	-0.05
Oxalate	0.30	0.79	0.39	0.04	-0.23	0.00	0.84	0.26	-0.03	-0.15	-0.22
Cl	-0.11	-0.02	-0.05	0.09	0.88	0.14	-0.32	0.33	-0.46	0.35	0.09
S	0.12	0.00	0.94	0.16	-0.04	0.02	0.05	-0.07	0.95	-0.07	0.11
Ca	0.93	0.18	0.01	0.23	0.07	0.06	0.92	0.25	0.17	0.01	0.14
Fe	0.90	0.22	0.05	0.17	0.16	0.19	0.90	0.24	0.05	0.24	0.04
Na	0.56	0.64	-0.08	0.08	-0.19	-0.15	0.78	0.49	-0.10	-0.15	-0.02
Mg	0.92	0.21	-0.14	0.09	-0.11	0.07	0.90	0.24	-0.13	-0.01	0.15
Al	0.95	0.14	0.03	0.18	0.00	0.01	0.94	-0.04	-0.04	0.10	0.16
Si	0.96	0.10	0.00	0.18	-0.01	0.04	0.91	-0.03	-0.09	0.14	0.22
P	0.74	0.08	-0.05	0.04	-0.09	0.11	0.41	-0.06	0.11	-0.08	0.79
K	0.57	0.65	0.32	0.22	-0.06	0.10	0.87	0.33	0.26	-0.09	-0.12
Ti	0.90	0.12	0.16	-0.07	-0.07	-0.12	0.85	0.12	0.07	0.12	0.28
Mn	0.56	0.19	0.04	0.62	0.20	0.03	0.70	0.39	0.22	-0.12	0.09
Zn	0.19	0.37	0.13	0.68	-0.04	0.10	0.40	0.69	0.22	-0.31	0.00
Cr	0.05	0.11	-0.02	-0.29	0.60	0.54	0.19	-0.07	0.00	0.78	-0.05
V	0.51	0.11	0.05	0.52	0.16	0.33	0.20	0.07	0.51	-0.52	0.24
Pb	0.19	0.01	0.10	0.75	0.19	0.35	0.14	-0.15	0.76	0.10	0.10
As	0.19	-0.05	0.16	0.38	0.11	0.66	0.01	-0.03	0.39	-0.13	0.75
Ni	0.19	0.04	0.13	0.12	0.47	0.73	0.07	-0.04	0.19	0.84	-0.05
Sr	0.01	-0.18	-0.33	0.27	-0.09	0.66	0.25	-0.34	0.01	0.05	0.07
% Variance	31.11	14.65	13.52	7.96	7.93	7.14	32.83	21.79	15.70	6.82	5.40
% Cumulative	31.11	45.76	59.28	67.24	75.18	82.32	32.83	54.62	70.32	77.14	82.54

Table A.8 Varimax rotated factor loadings of the fine aerosol fraction at Zamdela and Ecopark for the summer 2017 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Zamdela					Ecopark					
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
F ⁻	0.54	0.23	-0.02	0.24	0.56	0.45	0.40	0.52	0.30	-0.15	0.16
Cl ⁻	0.11	-0.53	0.57	0.15	-0.02	-0.01	0.10	-0.03	-0.16	0.93	0.05
NO ₃ ⁻	0.01	0.21	0.53	0.06	0.54	0.41	0.07	0.59	0.01	0.26	0.30
SO ₄ ²⁻	0.34	0.90	-0.04	0.07	0.14	0.97	0.12	0.11	0.00	0.11	-0.04
Na ⁺	0.72	0.49	0.05	-0.15	0.04	0.24	0.19	0.07	0.09	0.91	-0.03
NH ₄ ⁺	0.32	0.92	-0.03	0.08	0.14	0.97	0.11	0.09	-0.01	0.11	-0.03
K ⁺	0.87	0.24	0.06	0.11	0.15	0.63	0.20	0.22	0.62	-0.04	0.06
Ca ²⁺	0.00	0.24	-0.13	0.67	-0.21	0.26	0.06	0.90	0.11	-0.02	0.04
Mg ²⁺	0.79	0.36	-0.19	0.10	0.25	0.68	0.44	0.20	0.48	0.01	-0.02
Acetic	0.34	0.04	0.04	0.67	0.03	-0.14	0.26	0.26	-0.02	-0.22	0.76
Oxalate	0.59	0.67	0.10	0.02	0.23	0.84	0.27	0.31	0.27	-0.02	0.03
Cl	0.09	0.18	-0.11	-0.05	0.79	0.08	0.16	0.69	0.35	-0.07	-0.20
S	0.34	0.90	-0.01	0.08	0.12	0.96	0.12	0.10	0.01	0.11	-0.05
Ca	-0.32	0.11	0.50	0.38	-0.42	0.05	-0.21	0.84	-0.05	0.07	-0.05
Na	0.82	0.27	0.06	-0.06	0.09	0.55	0.37	0.22	0.61	-0.09	-0.01
Mg	0.89	0.25	-0.16	-0.06	0.11	0.66	0.57	0.02	0.43	-0.08	0.00
Al	0.93	0.20	-0.11	-0.01	-0.04	0.36	0.77	-0.06	0.40	-0.11	0.06
Si	0.91	0.14	-0.16	-0.07	0.09	0.35	0.79	-0.03	0.39	-0.10	0.06
P	0.83	0.29	0.22	0.02	0.32	0.76	0.41	0.23	0.30	-0.11	0.13
K	0.93	0.22	0.03	0.07	0.11	0.61	0.33	0.17	0.63	-0.12	0.13
Ti	0.88	0.01	-0.07	-0.03	-0.28	0.13	0.82	-0.04	0.19	0.03	0.09
Mn	0.64	-0.21	0.15	0.07	0.09	0.00	0.14	0.03	0.79	0.04	-0.06
Zn	0.69	0.32	0.22	0.09	0.06	0.64	0.05	0.47	0.48	0.03	-0.02
V	-	-	-	-	-	-0.48	-0.03	-0.41	0.34	0.24	0.28
Pb	0.11	-0.18	0.69	-0.43	-0.07	0.08	-0.17	-0.19	-0.01	0.10	0.80
Cd	0.19	0.20	-0.05	-0.73	-0.20	0.13	-0.26	0.38	-0.02	0.25	0.07
As	-0.03	0.04	0.80	0.01	-0.01	-0.11	-0.26	0.07	0.04	0.47	-0.07
Sr	-	-	-	-	-	-0.18	-0.67	-0.03	0.13	-0.22	0.19
% Variance	36.60	16.78	8.58	7.44	7.36	27.01	14.20	12.95	11.88	8.37	5.60
% Cumulative	36.60	53.38	61.96	69.40	76.76	27.01	41.21	54.15	66.03	74.39	79.99

Table A.9: Varimax rotated factor loadings of the coarse aerosol fraction at Lephalale Town, Marapong and Steenbokpan for the winter 2012 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Lephalale Town					Marapong				Steenbokpan				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
F ⁻	0.13	-0.04	0.24	0.07	0.91	-0.25	0.86	0.19	-0.07	0.61	0.74	-0.06	-0.12	-0.02
Cl ⁻	-0.08	-0.03	-0.11	0.97	-0.05	0.11	-0.07	0.98	0.00	0.05	0.98	0.11	0.00	-0.09
NO ₃ ⁻	0.53	-0.16	0.19	0.56	0.38	0.83	0.23	0.25	0.21	0.32	0.76	0.07	-0.35	0.21
SO ₄ ²⁻	0.85	0.05	0.07	-0.06	0.41	0.16	0.89	-0.23	0.10	0.65	0.58	-0.13	0.15	0.28
Na ⁺	-0.04	0.61	-0.34	-0.19	-0.16	0.19	0.37	-0.19	0.74	-0.04	-0.06	-0.01	0.04	0.94
NH ₄ ⁺	-0.06	0.93	-0.06	-0.07	-0.12	0.86	0.00	0.08	0.17	-0.01	0.12	0.48	-0.63	0.22
K ⁺	-0.11	0.97	-0.06	-0.09	-0.07	0.92	0.19	0.06	0.24	0.01	0.12	0.94	0.07	0.02
Ca ²⁺	-0.01	0.89	-0.13	0.12	0.04	0.91	0.09	0.15	0.31	-0.04	-0.05	0.96	-0.07	-0.12
Mg ²⁺	-0.04	0.83	-0.16	-0.08	0.27	0.52	0.25	-0.01	0.76	0.08	0.24	0.51	0.60	0.33
Formate	-	-	-	-	-	0.24	-0.05	0.38	0.83	0.17	-0.12	0.27	0.72	-0.06
Oxalate	0.84	-0.21	0.27	-0.02	-0.04	0.73	0.56	-0.04	-0.09	0.83	0.02	0.21	0.04	-0.09
Cl	-0.13	-0.03	-0.13	0.95	-0.03	0.15	-0.15	0.95	0.10	0.12	0.97	0.06	-0.01	-0.08
S	0.96	0.04	-0.05	-0.03	0.09	0.16	0.89	-0.27	0.16	0.68	0.58	-0.11	0.15	0.27
Ca	-0.05	-0.15	0.66	0.00	0.22	0.57	0.69	-0.18	0.35	-	-	-	-	-
Fe	0.42	-0.14	0.85	-0.06	0.15	0.61	0.71	-0.12	0.24	0.86	0.23	0.06	-0.15	-0.33
Na	-0.11	-0.05	-0.07	0.98	0.12	-0.06	-0.11	0.98	-0.04	0.08	0.97	0.09	-0.16	-0.04
Mg	0.29	-0.17	0.58	0.67	0.23	0.52	0.73	0.25	0.20	0.55	0.82	-0.01	-0.04	-0.05
Al	0.59	-0.10	0.78	-0.04	0.06	0.53	0.69	-0.29	0.32	0.97	0.10	-0.03	0.09	0.10
Si	0.50	-0.15	0.82	-0.05	0.09	0.55	0.70	-0.25	0.30	0.97	0.15	-0.02	0.05	0.05
P	0.70	-0.16	0.62	-0.08	-0.06	0.60	0.71	-0.08	0.24	-0.09	-0.14	-0.17	0.43	0.18
K	0.89	-0.01	0.34	-0.08	-0.09	0.68	0.65	-0.18	0.20	0.86	0.27	-0.08	-0.02	0.06
Ti	-0.06	-0.19	0.51	-0.18	-0.33	0.65	0.45	-0.13	0.49	0.96	0.14	-0.02	0.00	-0.08
% Variance	23.03	18.60	18.59	17.50	7.37	31.59	29.78	16.22	13.04	31.92	26.60	11.99	8.15	6.85
% Cumulative	23.03	41.63	60.22	77.72	85.09	31.59	61.37	77.59	90.63	31.92	58.51	70.51	78.66	85.51

Table A.10: Varimax rotated factor loadings of the coarse aerosol fraction at Lephalale Town, Marapong and Steenbokpan for the summer 2013 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Lephalale Town					Marapong				Steenbokpan					
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
F ⁻	0.75	0.13	-0.04	-0.29	-0.10	0.97	0.02	0.06	0.02	0.37	0.44	-0.09	0.15	0.20	-0.59
Cl ⁻	-0.10	0.92	-0.16	0.13	-0.01	-0.28	0.82	-0.41	-0.21	-0.29	0.71	0.40	-0.25	-0.27	-0.05
NO ₃ ⁻	0.12	0.34	0.75	-0.21	0.00	0.15	0.39	0.64	0.58	0.17	0.83	0.02	0.06	0.21	0.17
SO ₄ ²⁻	0.52	-0.03	0.53	-0.02	-0.40	0.81	-0.05	-0.19	0.38	0.10	0.34	-0.15	0.17	0.21	0.76
Na ⁺	-0.05	0.98	0.10	-0.08	0.08	-0.13	0.99	0.07	0.03	-0.15	0.93	0.10	-0.19	-0.01	0.08
NH ₄ ⁺	0.56	-0.52	0.27	0.28	0.15	0.79	-0.32	-0.08	0.46	0.53	-0.04	-0.17	0.63	0.12	0.18
K ⁺	0.28	0.42	0.48	0.13	0.57	0.78	0.00	0.32	0.13	-0.12	0.10	0.96	-0.03	0.06	-0.02
Ca ²⁺	0.86	-0.03	-0.02	0.16	-0.06	0.94	-0.21	0.18	0.12	0.71	0.37	-0.05	0.49	-0.03	-0.09
Mg ²⁺	0.17	0.93	0.08	-0.12	0.07	0.80	0.54	0.13	0.16	0.02	0.95	-0.03	0.15	0.04	0.02
Formate	-0.18	-0.17	0.07	-0.04	-0.82	-0.09	0.31	-0.78	0.00	-	-	-	-	-	-
Oxalate	0.39	-0.05	0.74	0.04	0.02	0.55	-0.04	0.57	-0.21	-0.16	-0.23	0.02	0.64	-0.24	-0.03
Cl	-0.14	0.94	-0.25	0.01	0.02	-0.20	0.83	-0.39	-0.27	-0.41	0.77	0.25	-0.25	-0.23	0.05
S	0.62	0.03	0.55	0.10	0.36	0.86	-0.16	0.06	0.42	0.64	0.48	0.08	0.47	0.09	0.21
Ca	0.85	0.12	0.00	0.07	0.09	0.93	-0.30	0.11	0.16	0.86	0.15	-0.06	0.29	-0.01	-0.19
Fe	0.93	-0.02	0.26	0.10	0.11	0.96	-0.19	0.12	0.09	0.99	-0.07	-0.01	-0.01	0.07	-0.04
Na	-0.05	0.97	0.17	-0.11	0.08	-0.12	0.98	0.05	0.08	-0.18	0.97	-0.02	-0.08	0.00	-0.04
Mg	0.24	0.87	0.33	-0.02	0.15	0.93	0.12	0.15	0.26	0.37	0.90	-0.07	0.06	0.02	-0.10
Al	0.93	-0.06	0.24	0.11	0.11	0.95	-0.24	0.09	0.09	0.98	-0.06	0.03	0.06	0.04	0.06
Si	0.92	-0.09	0.25	0.09	0.12	0.96	-0.20	0.09	0.07	0.98	-0.07	0.03	0.03	0.03	0.04
P	0.46	-0.14	0.41	0.02	0.45	0.92	-0.24	0.21	0.06	0.86	0.07	0.30	-0.03	0.17	-0.13
K	0.86	0.14	0.34	0.10	0.20	0.96	-0.17	0.14	0.09	0.40	0.03	0.89	-0.03	0.04	-0.04
Ti	0.92	0.00	0.31	0.08	0.09	0.92	-0.31	0.11	0.08	0.97	-0.11	0.01	-0.04	0.04	0.05
Mn	0.59	-0.12	0.36	-0.29	0.19	0.92	-0.11	0.23	0.15	0.76	-0.18	0.04	-0.21	-0.29	0.08
Zn	0.08	0.53	0.36	0.06	-0.43	0.50	-0.30	-0.01	0.63	0.12	-0.01	0.16	0.12	-0.66	0.08
Cr	-0.08	-0.32	-0.09	0.72	0.03	0.77	-0.02	0.42	0.24	0.23	-0.13	0.09	0.19	0.73	0.01
V	0.44	0.22	0.02	0.78	0.13	0.92	-0.03	0.08	0.00	0.62	0.00	-0.05	0.30	0.27	-0.39
Ni	0.19	0.00	0.64	0.59	-0.11	0.72	-0.05	0.27	0.17	0.00	0.09	0.15	-0.12	0.51	0.12
% Variance	33.58	23.85	10.76	7.70	33.58	58.18	16.86	8.61	6.42	32.12	23.65	8.35	6.94	6.83	4.98
% Cumulative	33.58	57.42	68.18	75.88	33.58	58.18	75.04	83.65	90.07	32.12	55.77	64.13	71.07	77.90	82.88

Table A.11: Varimax rotated factor loadings of the coarse aerosol fraction at Kwazamokhule for the winter 2015 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Kwazamokhule				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
F ⁻	0.91	0.08	-0.03	0.11	0.14
Cl ⁻	0.19	0.90	0.05	0.06	0.12
NO ₃ ⁻	0.11	0.28	0.56	0.41	0.42
SO ₄ ²⁻	0.04	0.05	0.95	0.23	0.09
Na ⁺	-0.08	-0.01	0.23	0.92	0.17
NH ₄ ⁺	0.11	0.06	0.98	-0.01	0.02
K ⁺	0.55	0.58	0.19	0.08	0.49
Ca ²⁺	0.81	0.41	0.20	0.25	-0.03
Mg ²⁺	0.80	0.13	0.30	0.36	0.17
Formate	0.39	0.78	0.24	-0.01	0.20
Acetate	0.43	0.70	0.08	0.09	-0.09
Oxalate	0.48	0.04	0.26	0.35	0.72
Cl	0.38	0.87	0.06	-0.01	0.05
S	0.31	0.24	0.89	0.15	0.03
Ca	0.82	0.45	0.11	0.21	-0.06
Fe	0.93	0.24	0.11	0.01	0.19
Na	0.21	0.13	0.15	0.92	0.09
Mg	0.91	0.29	0.14	0.11	0.14
Al	0.92	0.34	0.11	0.09	0.06
Si	0.93	0.32	0.09	0.09	0.08
P	0.84	0.45	0.18	0.08	-0.04
K	0.85	0.43	0.11	0.07	0.24
Ti	0.91	0.34	0.11	0.14	0.04
Mn	0.89	0.16	0.11	-0.13	0.22
Zn	0.63	0.59	0.21	0.09	-0.28
Cr	0.69	0.21	0.01	0.00	0.42
V	0.91	0.27	0.17	0.10	0.00
Ni	0.49	-0.03	-0.03	0.50	-0.20
% Variance	44.19	17.56	12.68	9.48	5.62
% Cumulative	44.19	61.75	74.43	83.91	89.53

Table A.12: Varimax rotated factor loadings of the coarse aerosol fraction at Kwazamokhule for the summer 2016 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Kwazamokhule				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
F ⁻	0.89	0.32	0.19	-0.13	0.03
Cl ⁻	0.02	-0.20	0.25	0.14	0.91
NO ₃ ⁻	0.53	-0.16	0.74	-0.07	0.17
SO ₄ ²⁻	0.35	0.92	-0.01	-0.02	-0.09
Na ⁺	0.05	-0.06	0.94	-0.22	0.20
NH ₄ ⁺	0.37	0.89	-0.10	0.01	-0.12
K ⁺	0.83	0.14	0.00	-0.11	0.31
Ca ²⁺	0.90	0.22	0.12	0.23	-0.13
Mg ²⁺	0.80	0.27	0.48	0.04	0.04
Oxalate	0.77	0.09	-0.10	0.30	-0.08
Cl	0.29	0.01	0.52	0.02	0.69
S	0.33	0.92	-0.01	0.01	-0.10
Ca	0.94	0.16	0.05	0.22	-0.09
Fe	0.89	0.32	0.10	-0.14	0.16
Na	0.03	-0.08	0.94	-0.16	0.13
Mg	0.83	0.20	0.43	0.19	0.08
Al	0.95	0.14	0.15	-0.08	0.05
Si	0.94	0.16	0.16	-0.09	0.09
P	0.92	0.26	-0.06	0.09	-0.13
K	0.94	0.08	0.13	-0.14	0.19
Ti	0.94	0.15	0.13	-0.12	0.05
Mn	0.80	0.42	-0.03	-0.18	0.10
Zn	0.02	-0.13	-0.16	0.84	0.09
Cr	0.19	0.79	-0.15	0.50	0.17
V	0.77	0.22	0.08	-0.11	0.39
Ni	-0.11	0.30	-0.16	0.65	0.00
% Variance	47.40	15.68	12.74	7.15	7.05
% Cumulative	47.40	63.09	75.82	82.98	90.03

Table A.13: Varimax rotated factor loadings of the coarse aerosol fraction at Embalenhle and Kinross for the winter 2016 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Embalenhle						Kinross				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
F ⁻	0.18	0.85	0.38	-0.01	0.13	0.10	0.09	0.89	0.34	-0.12	-0.04
Cl ⁻	0.15	0.10	0.22	0.00	0.11	0.92	-0.19	0.80	0.05	0.01	-0.02
NO ₃ ⁻	0.27	0.03	-0.09	-0.01	0.84	0.17	0.29	0.38	0.72	-0.22	0.28
SO ₄ ²⁻	0.55	0.39	0.14	0.02	0.54	0.17	0.01	0.50	0.81	-0.11	-0.04
Na ⁺	0.19	0.32	0.07	-0.07	0.80	0.01	0.36	0.19	0.69	0.18	0.31
NH ₄ ⁺	0.33	0.36	0.40	0.00	0.25	0.71	0.02	0.52	0.76	-0.17	-0.08
K ⁺	0.30	0.68	0.22	0.01	0.36	0.45	0.09	0.72	0.56	-0.25	-0.04
Ca ²⁺	0.30	0.85	0.19	0.06	0.28	0.15	-0.01	0.95	0.24	-0.09	-0.05
Mg ²⁺	0.24	0.90	0.06	-0.01	0.16	-0.01	-0.08	0.90	0.23	0.01	0.04
Formic	0.24	0.88	-0.10	0.00	0.00	0.12	0.01	0.94	0.13	-0.14	0.00
Acetic	0.35	0.72	-0.15	-0.02	-0.09	-0.04	-	-	-	-	-
Oxalate	0.32	0.62	0.30	0.07	0.35	0.12	-	-	-	-	-
Cl	0.31	0.25	0.75	-0.03	-0.02	0.11	0.33	-0.33	0.20	0.10	-0.31
S	0.72	0.19	0.05	0.00	0.48	0.31	0.79	0.04	0.24	0.20	0.42
Ca	0.92	0.27	0.13	0.10	0.16	0.09	0.91	-0.04	0.01	0.23	-0.07
Fe	0.37	0.08	0.05	0.92	0.04	0.03	0.97	-0.04	0.04	0.04	-0.02
Na	0.81	0.21	0.23	0.04	0.33	0.02	0.34	0.04	0.85	-0.03	-0.24
Mg	0.87	0.31	0.10	0.10	0.16	0.09	0.92	-0.04	0.32	0.03	-0.12
Al	0.93	0.22	0.16	0.11	0.17	0.10	0.95	0.07	0.08	-0.18	-0.13
Si	0.92	0.23	0.16	0.11	0.17	0.10	0.97	0.03	-0.01	-0.12	-0.08
P	0.75	0.38	-0.05	0.02	-0.07	-0.08	0.40	-0.09	-0.02	0.65	-0.13
K	0.91	0.20	0.21	0.08	0.22	0.10	0.95	-0.05	0.11	-0.04	0.17
Ti	0.94	0.19	0.15	0.09	0.16	0.10	0.95	0.19	0.05	0.06	-0.08
Mn	0.38	0.05	0.09	0.92	0.02	0.05	0.45	0.01	-0.20	0.71	0.27
Zn	0.06	0.05	0.92	0.00	0.04	0.12	0.04	-0.11	0.12	0.32	0.78
Cr	-0.10	-0.04	-0.02	0.99	-0.05	-0.03	0.57	-0.01	0.19	0.01	-0.15
V	0.86	0.17	0.24	0.29	0.09	0.11	-0.13	-0.08	0.01	0.93	-0.05
Pb	0.30	-0.06	0.87	0.04	-0.05	0.11	-0.15	-0.40	0.34	-0.22	0.36
As	0.03	0.10	0.93	0.07	0.08	0.10	0.16	0.58	-0.02	0.10	0.07
Ni	-0.07	-0.03	-0.02	0.99	-0.05	-0.02	-0.23	-0.05	-0.13	0.89	0.06
Sr	0.85	0.13	0.02	-0.09	-0.02	0.11	0.19	-0.06	0.11	0.18	-0.72
% Variance	31.72	17.70	12.51	12.36	8.49	6.17	28.43	20.58	13.70	10.91	6.85
% Cumulative	31.72	49.42	61.93	74.29	82.77	88.94	28.43	49.01	62.71	73.62	80.47

Table A.14: Varimax rotated factor loadings of the coarse aerosol fraction at Embalenhle and Kinross for the summer 2017 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Embalenhle						Kinross					
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
F ⁻	0.15	0.95	0.18	-0.03	0.06	-0.03	0.91	-0.12	-0.07	0.14	-0.19	0.17
Cl ⁻	0.37	-0.05	0.81	0.01	-0.02	0.18	-0.05	0.24	-0.17	0.47	0.12	0.52
NO ₃ ⁻	0.36	0.56	0.30	0.47	0.21	-0.20	-0.04	-0.06	0.70	0.05	0.03	-0.13
SO ₄ ²⁻	-0.14	0.95	-0.12	0.15	0.00	0.03	0.21	-0.07	0.94	-0.10	0.15	0.03
Na ⁺	0.41	0.44	0.65	0.15	0.23	-0.09	0.32	-0.17	0.03	0.83	-0.16	0.07
NH ₄ ⁺	-0.19	0.89	-0.24	0.20	0.02	0.06	0.13	-0.08	0.96	-0.14	0.07	0.09
K ⁺	0.20	0.93	0.02	0.14	0.15	-0.05	0.77	-0.13	0.43	0.13	-0.12	0.09
Ca ²⁺	0.17	0.94	0.19	-0.04	0.00	-0.05	0.93	-0.10	0.01	-0.03	-0.06	0.11
Mg ²⁺	0.09	0.93	0.21	-0.04	0.03	-0.05	0.98	-0.09	0.09	0.09	-0.01	0.00
Formic	0.90	0.22	0.14	-0.10	-0.11	-0.04	-0.17	-0.02	0.20	-0.46	0.62	0.14
Acetic	-0.02	0.85	-0.05	0.11	0.01	0.10	-	-	-	-	-	-
Oxalate	0.14	0.95	0.02	0.10	0.15	-0.01	-	-	-	-	-	-
Cl	0.50	0.11	0.63	0.00	0.17	0.09	-0.18	0.15	-0.06	0.74	-0.08	0.01
S	-0.15	0.67	-0.26	-0.07	0.20	0.05	0.32	-0.07	0.83	-0.05	0.16	0.04
Ca	0.96	-0.01	0.20	0.09	-0.05	0.04	-0.02	0.98	-0.11	-0.01	0.10	0.00
Fe	0.91	-0.11	0.15	-0.11	0.08	-0.08	0.84	0.36	0.01	-0.10	-0.17	0.12
Na	0.65	-0.11	0.62	0.23	0.07	0.03	0.38	-0.15	-0.01	0.83	-0.17	-0.01
Mg	0.93	0.04	0.27	0.14	0.04	0.04	0.95	-0.10	0.18	0.18	-0.02	-0.02
Al	0.98	0.07	0.11	0.05	-0.01	-0.02	0.94	-0.07	0.13	0.01	0.13	-0.14
Si	0.97	0.07	0.17	0.08	0.02	0.01	0.98	-0.04	0.11	0.02	-0.02	0.00
P	0.69	0.35	-0.17	0.46	-0.02	0.14	0.73	-0.10	0.27	-0.02	0.26	-0.20
K	0.96	0.08	0.09	0.16	-0.03	0.01	0.83	0.48	0.17	0.06	-0.05	0.03
Ti	0.06	0.49	0.13	-0.10	0.61	-0.11	0.66	0.71	-0.01	-0.07	0.18	-0.07
Mn	0.80	-0.06	0.00	0.04	-0.07	0.21	0.69	0.18	0.02	-0.06	0.05	0.54
Zn	-0.44	0.02	0.34	0.18	-0.24	0.43	-0.05	0.13	-0.04	0.06	-0.03	-0.92
V	0.00	-0.01	-0.24	0.02	-0.67	-0.07	0.34	0.28	0.01	-0.12	0.71	-0.05
Pb	0.28	0.09	-0.16	0.75	0.13	0.33	-0.13	0.06	0.05	-0.22	0.60	0.06
Cd	0.12	-0.04	0.10	-0.02	0.03	0.83	-0.30	-0.13	-0.21	0.43	0.27	-0.22
As	-0.16	0.18	-0.28	0.05	0.68	0.00	-0.12	0.97	-0.09	-0.04	-0.01	0.02
Ni	0.03	-0.11	-0.26	-0.67	0.19	0.17	-0.04	-0.01	0.30	0.35	0.73	0.00
Sr	0.17	0.24	-0.43	0.35	0.26	0.39	-0.11	0.98	-0.11	-0.01	0.10	0.00
% Variance	29.13	27.00	9.63	6.07	5.51	4.41	32.87	14.11	12.38	9.91	7.64	5.67
% Cumulative	29.13	56.13	65.76	71.83	77.34	81.75	32.87	46.97	59.35	69.26	76.90	82.57

Table A.15: Varimax rotated factor loadings of the coarse aerosol fraction at Zamdela and Ecopark for the winter 2016 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Zamdela						Ecopark				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
F ⁻	0.67	0.66	0.02	0.21	0.19	0.10	0.72	0.60	0.27	0.02	0.06
Cl ⁻	0.14	0.87	-0.07	0.28	-0.12	-0.02	0.29	-0.06	0.80	-0.12	0.41
NO ₃ ⁻	0.38	0.69	0.01	0.16	0.52	0.09	0.86	0.23	0.39	0.01	0.04
SO ₄ ²⁻	0.28	0.90	0.15	-0.04	0.09	0.12	0.21	0.31	0.91	0.09	-0.02
Na ⁺	0.49	0.10	-0.01	0.19	0.80	0.05	0.83	0.15	0.30	-0.10	0.33
NH ₄ ⁺	0.11	0.97	0.10	0.03	0.01	0.09	0.02	0.34	0.86	0.02	-0.26
K ⁺	0.48	0.52	-0.01	0.66	0.17	0.08	0.63	0.49	0.51	0.00	0.17
Ca ²⁺	0.85	0.35	0.07	0.15	0.17	0.14	0.55	0.45	0.59	0.28	0.09
Mg ²⁺	0.54	0.27	0.04	0.73	0.16	0.11	0.46	0.20	0.63	-0.01	0.44
Formic	0.72	0.21	-0.10	0.50	0.14	-0.04	0.49	0.09	0.63	-0.09	0.45
Acetic	0.75	0.11	-0.09	0.20	0.21	-0.03	0.47	0.06	0.58	-0.08	0.57
Oxalate	0.63	0.33	0.10	0.24	0.51	0.19	0.73	0.44	0.40	-0.17	0.11
Cl	0.21	0.81	-0.07	0.32	-0.15	-0.03	0.88	-0.10	0.04	0.10	0.14
S	0.37	0.85	0.19	-0.01	0.13	0.08	0.16	0.30	0.87	0.17	-0.16
Ca	0.89	0.27	0.10	0.15	0.19	0.13	0.49	0.51	0.44	0.46	-0.06
Fe	0.16	0.08	0.98	0.01	0.02	-0.03	0.00	0.07	0.04	0.98	0.03
Na	0.53	0.09	0.00	0.19	0.76	0.02	0.66	0.36	0.08	-0.06	0.44
Mg	0.73	0.29	0.09	0.53	0.20	0.05	0.49	0.63	0.27	0.34	0.24
Al	0.91	0.32	0.10	0.07	0.10	0.07	0.24	0.92	0.21	0.10	0.06
Si	0.92	0.30	0.10	0.10	0.07	0.07	0.25	0.94	0.10	0.06	0.08
P	0.25	0.07	0.03	0.94	0.02	0.06	0.01	0.59	0.26	0.00	-0.09
K	0.77	0.38	0.06	0.43	0.19	0.11	0.60	0.68	0.33	0.03	0.18
Ti	0.94	0.01	0.11	0.08	0.13	0.14	0.33	0.84	0.18	0.07	-0.06
Mn	0.20	0.16	0.91	0.02	0.21	0.04	0.12	0.05	0.05	0.97	-0.02
Zn	0.62	0.57	0.00	0.23	0.23	0.23	0.81	0.16	0.02	-0.01	-0.42
Cr	-0.06	0.00	0.99	-0.01	-0.02	-0.06	-0.06	0.00	0.02	0.98	0.02
V	0.64	0.06	0.52	0.19	0.22	0.35	-0.02	0.04	-0.03	0.88	0.01
Pb	0.05	0.05	0.00	0.04	0.07	0.92	-0.11	0.77	0.02	-0.10	-0.24
As	-0.03	0.15	-0.22	0.09	-0.44	-0.20	-	-	-	-	-
Ni	-0.05	0.00	0.99	0.00	-0.01	-0.04	-0.06	0.00	0.02	0.99	0.02
Sr	0.33	0.22	-0.12	0.10	0.18	0.73	0.07	-0.15	-0.07	0.09	0.78
% Variance	31.10	20.59	13.68	10.20	8.10	5.85	23.32	20.43	19.20	17.31	7.75
% Cumulative	31.10	51.69	65.38	75.57	83.67	89.52	23.32	43.74	62.94	80.25	88.00

Table A.16: Varimax rotated factor loadings of the coarse aerosol fraction at Zamdela and Ecopark for the summer 2017 sampling campaign. Factor loadings > 0.6 are highlighted in blue bold

Species	Zamdela						Ecopark					
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
F ⁻	0.95	-0.22	0.14	0.01	0.09	-0.02	0.75	0.46	-0.08	0.33	0.27	0.09
Cl ⁻	0.47	-0.04	-0.29	-0.09	0.76	-0.08	-0.16	-0.17	-0.04	0.14	0.73	-0.27
NO ₃ ⁻	0.65	0.16	-0.04	0.38	-0.14	0.20	0.53	0.58	-0.07	0.13	0.41	-0.13
SO ₄ ²⁻	0.21	0.02	0.94	-0.05	-0.12	-0.10	0.12	0.96	-0.12	0.15	-0.02	-0.02
Na ⁺	0.59	-0.36	0.00	0.63	0.03	-0.13	0.33	0.17	-0.06	-0.01	0.88	0.12
NH ₄ ⁺	0.05	0.02	0.95	-0.05	-0.04	-0.18	0.10	0.94	-0.17	-0.03	-0.09	-0.04
K ⁺	0.93	-0.09	0.22	0.11	0.13	-0.08	0.49	0.62	0.06	0.49	0.26	0.05
Ca ²⁺	0.80	-0.12	0.21	-0.26	0.14	0.17	0.64	0.41	-0.02	0.59	0.14	-0.06
Mg ²⁺	0.93	-0.15	0.24	0.07	0.09	0.00	0.68	0.49	-0.05	0.40	0.25	0.08
Formic	0.81	-0.04	-0.32	-0.09	0.03	0.08	0.41	0.56	0.35	0.19	0.03	0.23
Acetic	-	-	-	-	-	-	-0.06	0.49	0.11	0.61	-0.02	0.07
Oxalate	0.49	-0.10	0.72	0.15	0.14	-0.01	0.55	0.56	-0.05	0.41	0.13	0.10
Cl	0.12	-0.07	-0.06	0.01	0.90	-0.10	0.46	-0.39	-0.03	0.42	0.54	-0.10
S	0.24	0.03	0.94	-0.04	-0.11	-0.11	0.18	0.94	-0.10	0.14	-0.02	-0.01
Ca	-0.03	0.98	0.00	0.02	-0.03	0.03	-0.02	-0.08	0.97	0.01	-0.08	0.01
Fe	0.87	0.41	0.15	0.02	0.07	-0.02	0.76	0.20	0.41	0.41	0.09	-0.03
Na	0.48	-0.37	-0.01	0.67	0.07	-0.16	0.45	0.15	-0.01	-0.08	0.79	0.19
Mg	0.94	-0.09	0.16	0.14	0.10	-0.03	0.78	0.43	-0.01	0.28	0.27	0.08
Al	0.97	-0.04	0.15	-0.03	0.07	-0.02	0.94	0.09	0.04	0.04	0.08	0.03
Si	0.96	0.01	0.03	0.00	0.09	-0.08	0.94	0.11	0.06	0.05	0.08	0.03
P	0.89	-0.01	0.37	0.14	0.10	-0.06	0.32	0.58	0.23	-0.32	0.04	-0.35
K	0.83	0.51	0.04	0.04	0.14	-0.02	0.70	0.13	0.65	0.15	0.07	0.03
Ti	0.42	0.88	0.04	0.05	0.00	0.04	0.46	-0.01	0.86	0.00	-0.09	0.10
Mn	0.75	0.14	0.24	0.04	0.17	-0.10	0.51	0.07	0.01	0.65	0.20	-0.31
Zn	0.55	0.01	0.29	0.02	0.47	0.35	0.41	0.04	0.09	0.79	-0.07	-0.12
Cr	0.08	0.46	0.10	0.39	0.08	0.58	0.18	0.36	-0.08	0.33	0.12	0.25
V	-0.33	0.31	0.06	0.55	-0.23	0.32	0.06	0.02	0.66	0.14	0.14	0.12
Pb	-0.09	0.28	-0.08	0.59	0.00	0.29	0.13	0.13	0.32	-0.02	-0.03	0.63
Cd	-0.20	0.11	-0.31	-0.01	0.00	0.70	-0.22	-0.22	0.24	0.09	-0.16	0.58
As	-0.12	0.91	-0.03	-0.01	-0.08	0.04	-0.07	-0.15	0.95	-0.06	-0.07	0.04
Ni	0.21	-0.14	-0.27	0.12	-0.25	0.62	0.10	0.01	-0.09	-0.13	0.09	0.66
Sr	-0.14	0.98	-0.02	0.03	-0.03	0.03	-0.10	-0.10	0.96	-0.05	-0.10	0.02
% Variance	38.01	15.51	13.17	6.41	6.31	5.65	22.95	18.63	15.57	10.27	9.00	5.47
% Cumulative	38.01	53.52	66.70	73.11	79.41	85.06	22.95	41.59	57.16	67.43	76.43	81.89

APPENDIX B SELECTED PMF SOURCE PROFILES

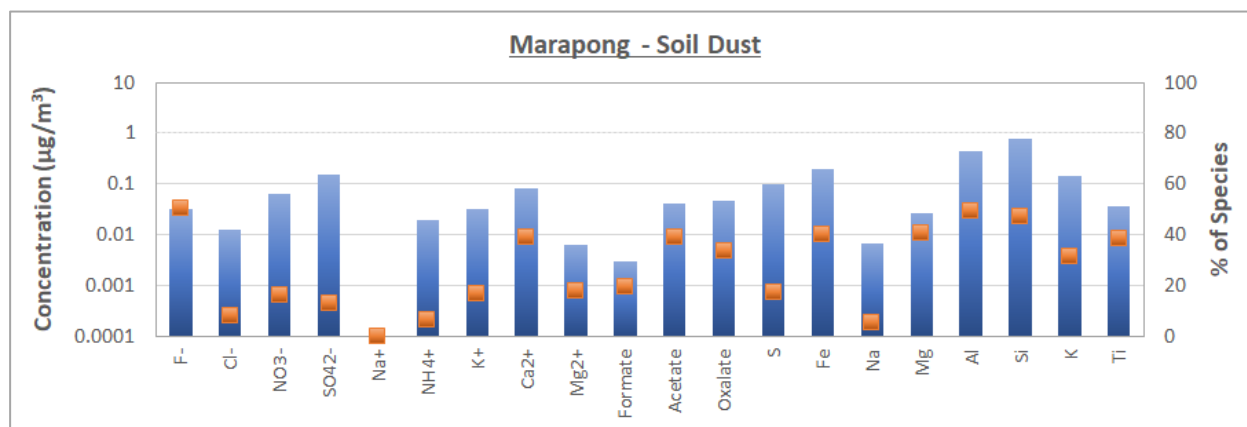


Figure B.1: PMF fine fraction source profile for soil dust at Marapong for the winter 2012 sampling campaign

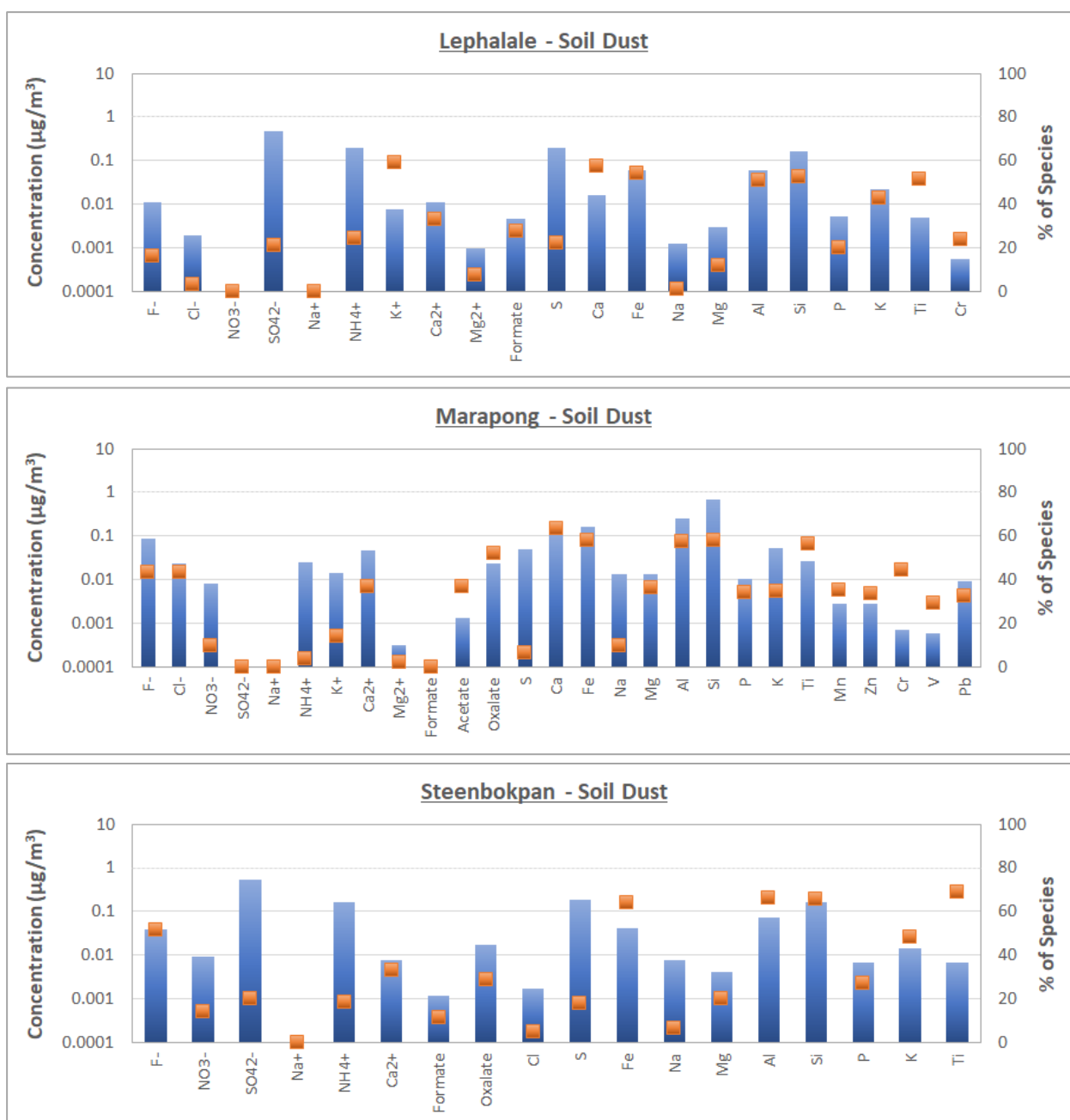


Figure B.2: PMF fine fraction source profiles for soil dust at Lephalale Town, Marapong and Steenbokpan for the summer 2013 sampling campaign

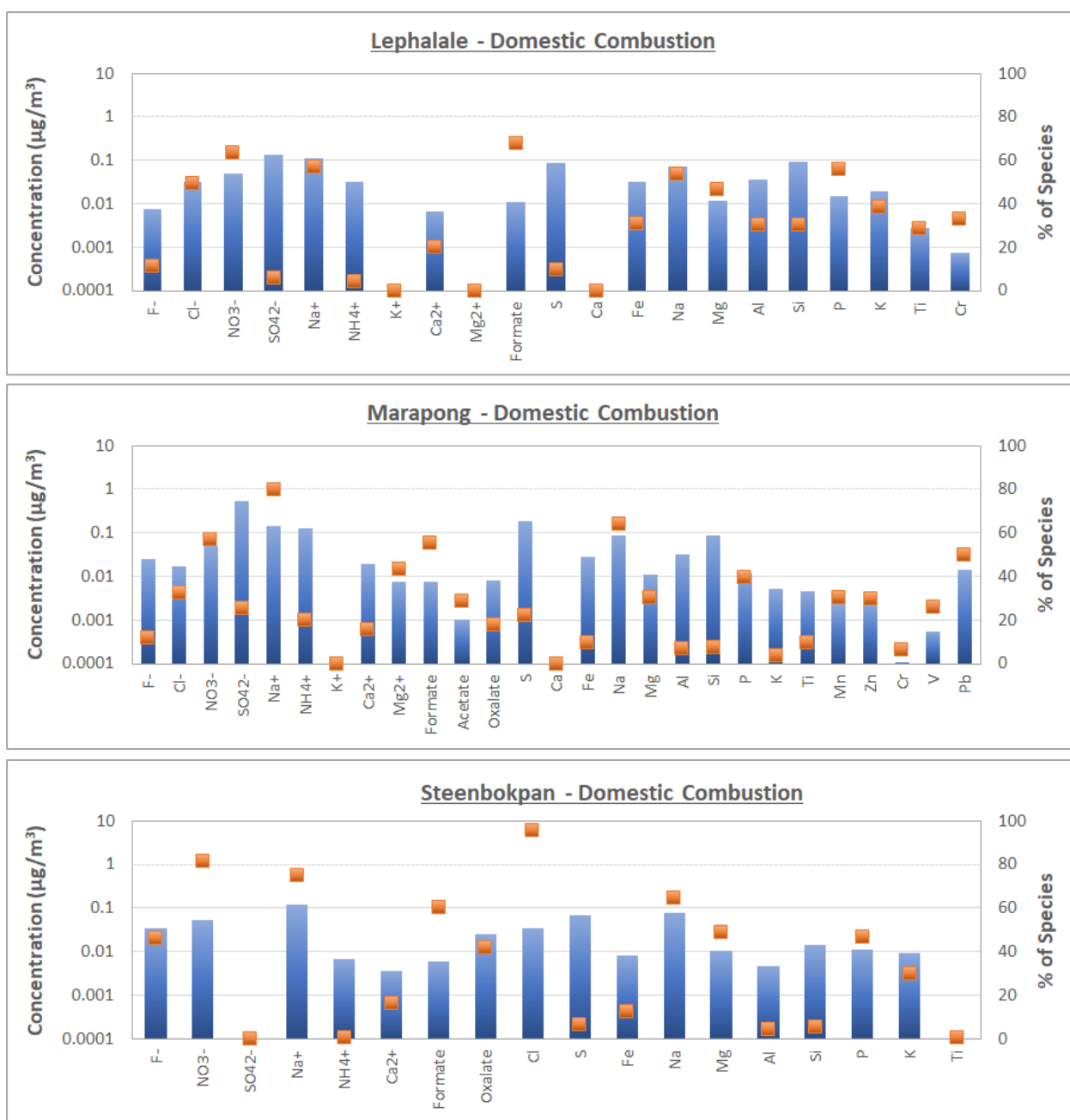


Figure B.3: PMF fine fraction source profiles for domestic combustion at Lephalale Town, Marapong and Steenbokpan for the summer 2013 sampling campaign

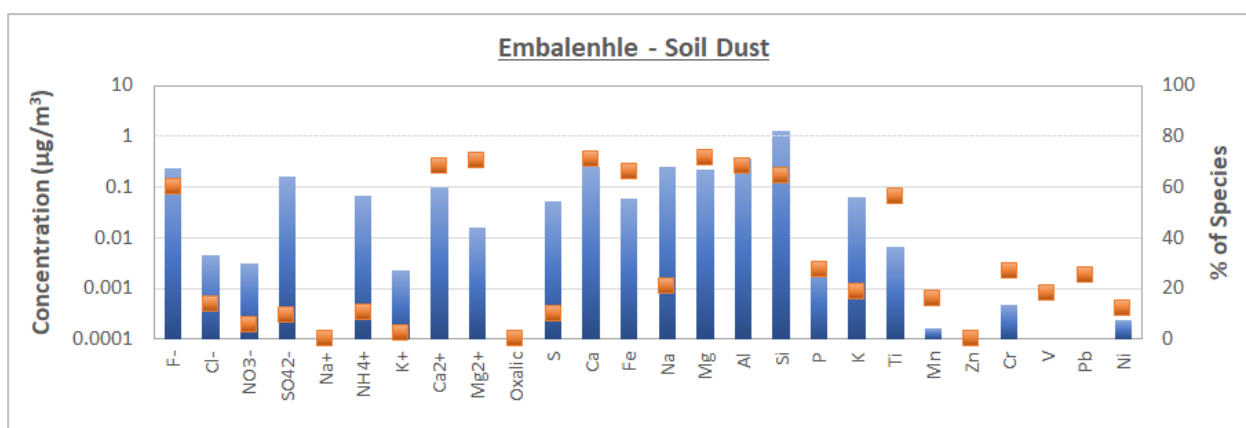


Figure B.4: PMF fine fraction source profiles for soil dust at Embalenhle for the winter 2016 sampling campaign

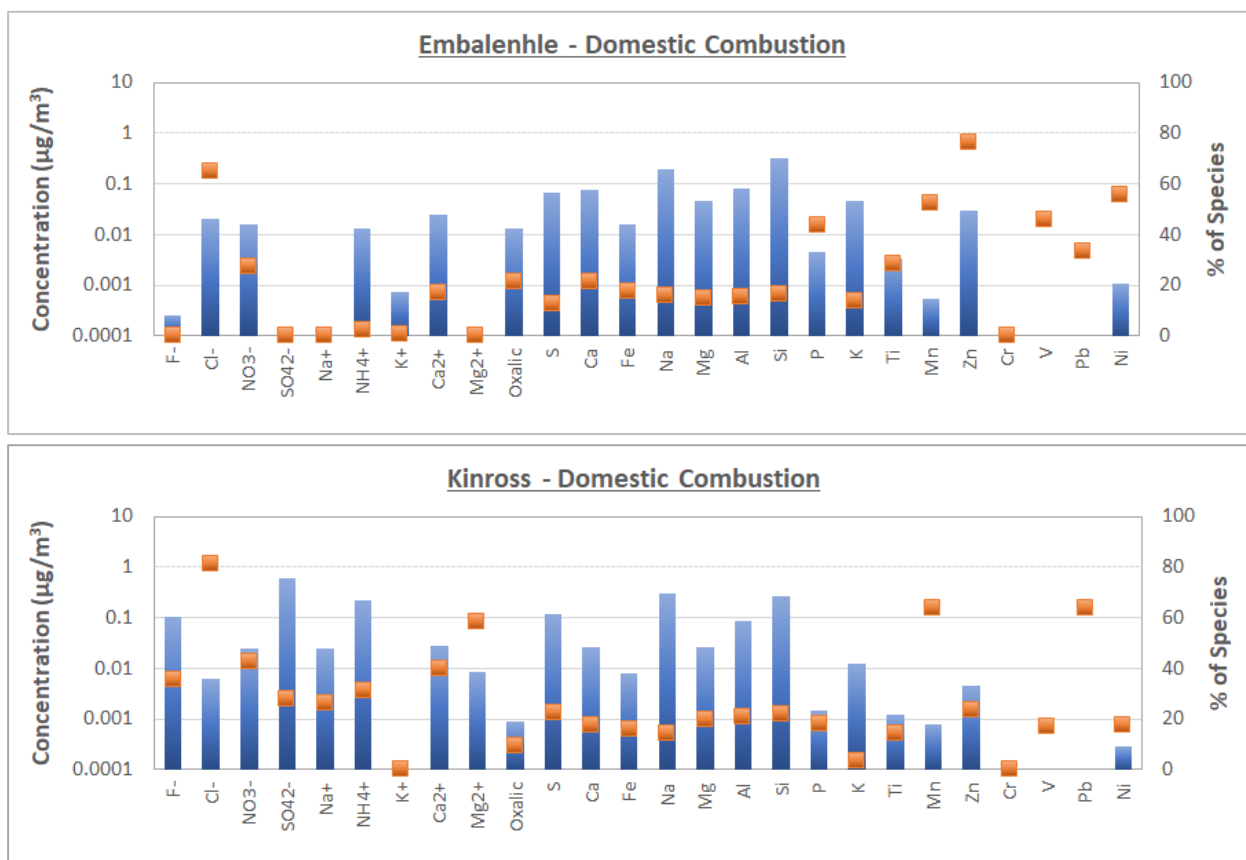


Figure B.5: PMF fine fraction source profiles for domestic combustion at Kwazamokhule, Embalenhle and Kinross for the winter 2015 (Kwazamokhule) and 2016 (Embalenhle and Kinross) sampling campaigns

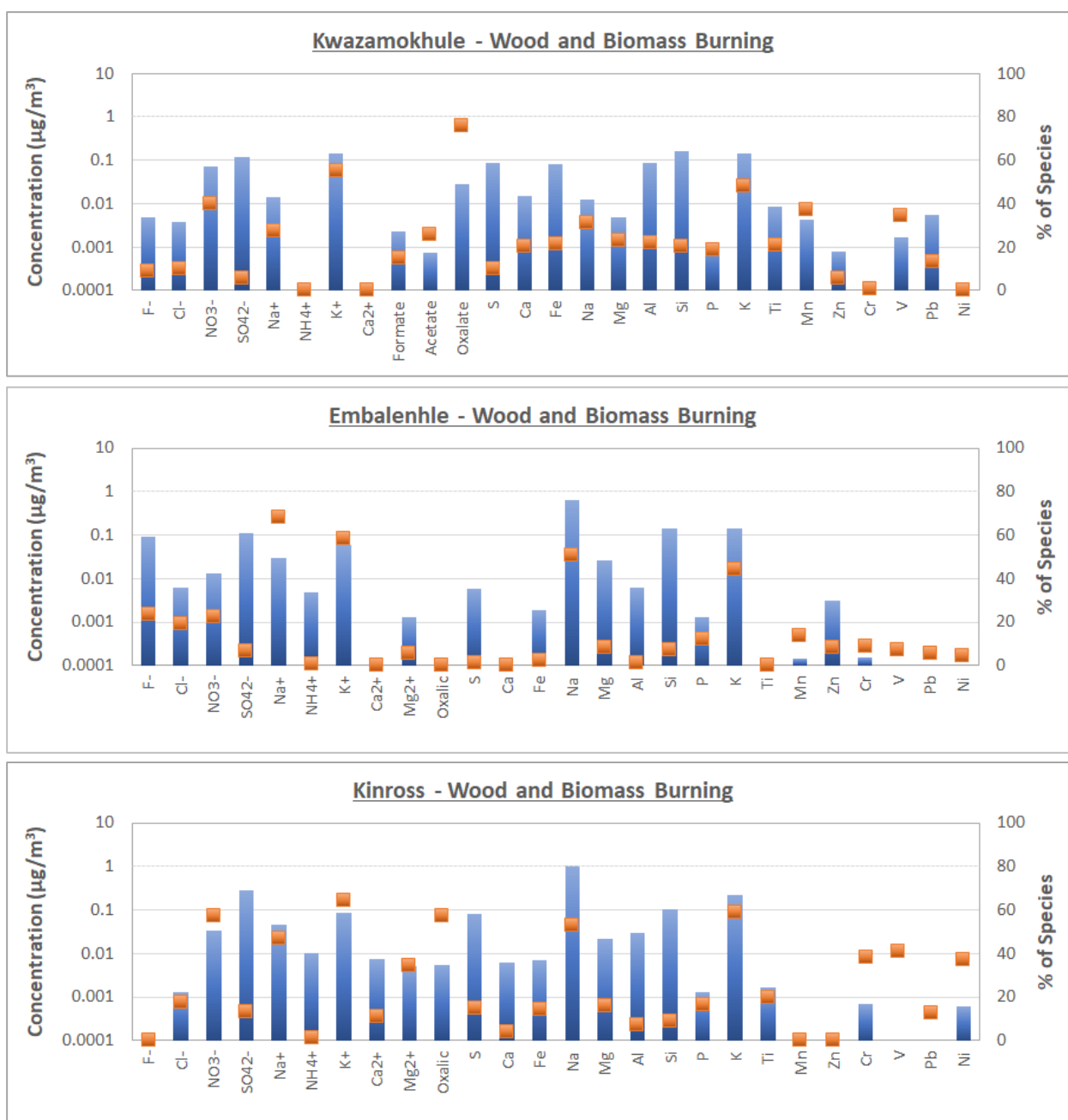


Figure B.6: PMF fine fraction source profiles for wood and biomass burning at Kwazamokhule, Embalenhle and Kinross for the winter 2015 (Kwazamokhule) and 2016 (Embalenhle and Kinross) sampling campaigns

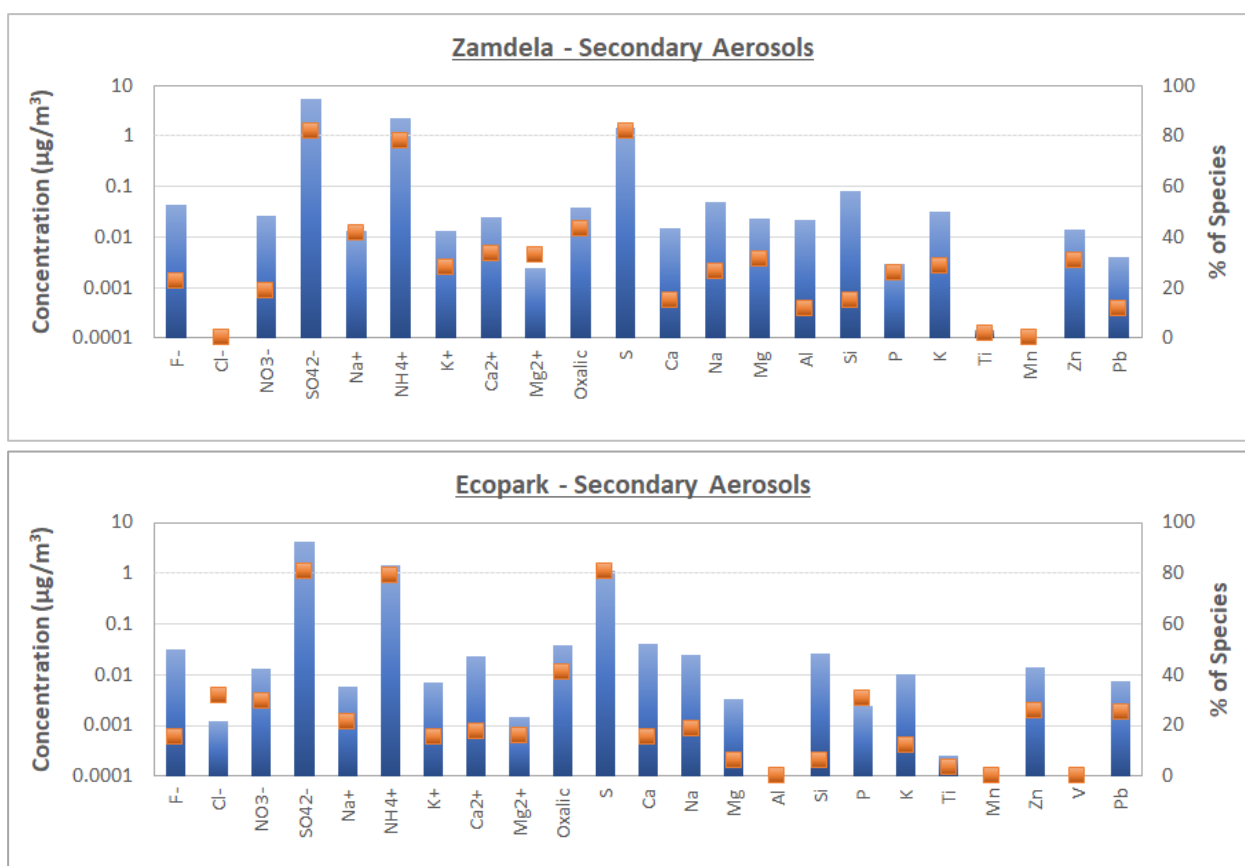


Figure B.7: PMF fine fraction source profiles for secondary aerosols at Zamdela and Ecopark for the summer 2017 sampling campaign

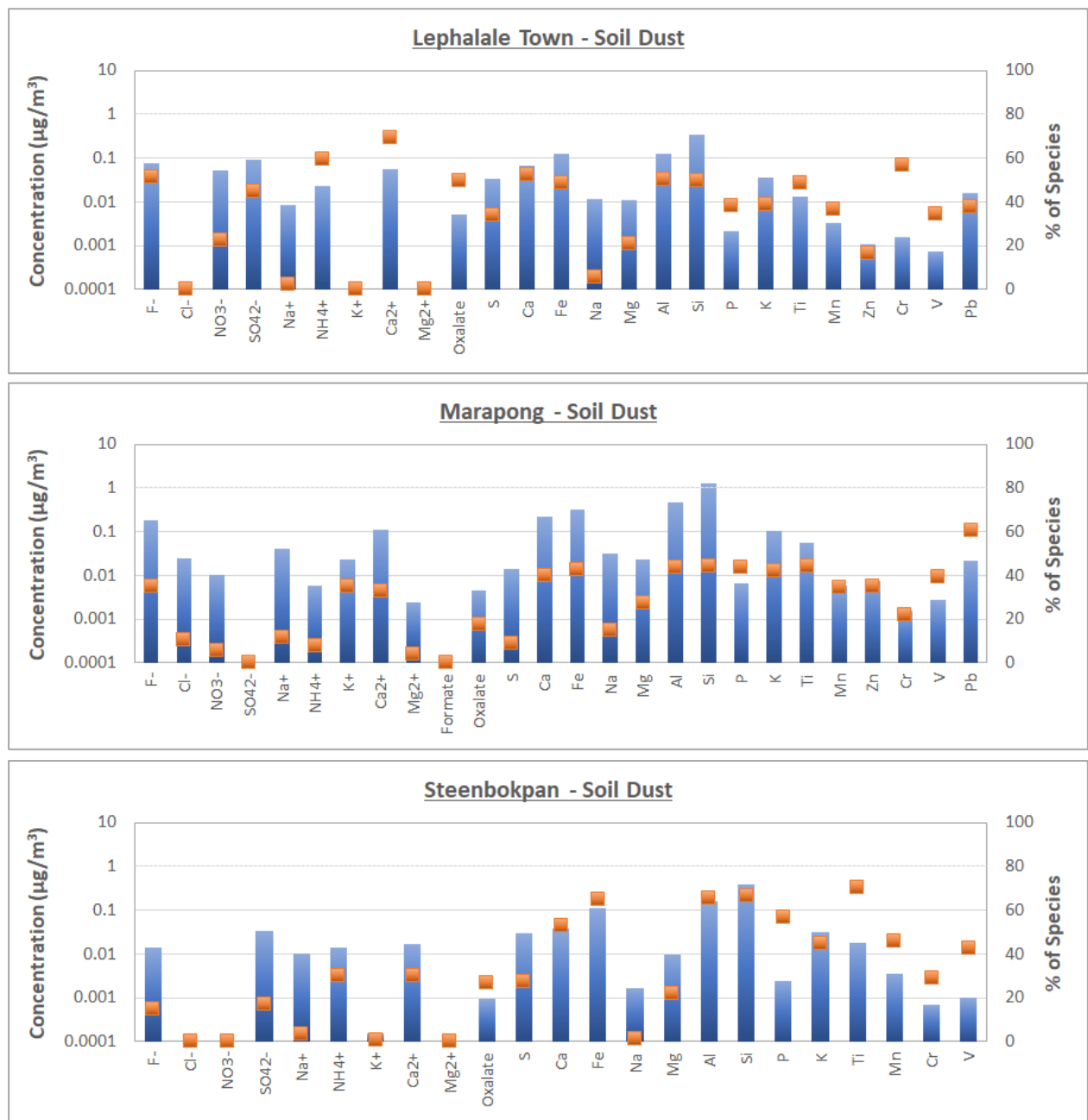


Figure B.8: PMF coarse fraction source profiles for soil dust at Lephalale Town, Marapong and Steenbokpan for the summer 2013 sampling campaign

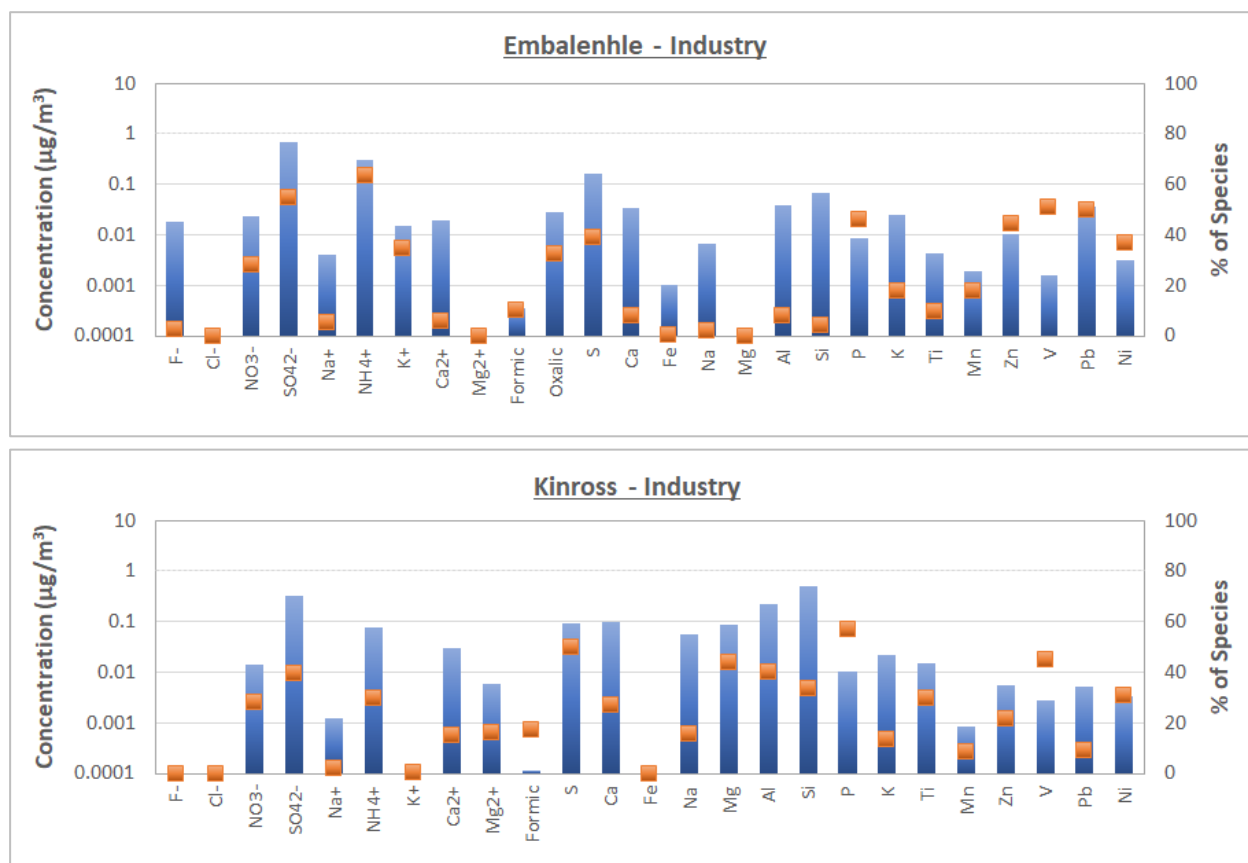


Figure B.9: PMF coarse fraction source profile for industry at Embalenhle and Kinross for the summer 2017 sampling campaign

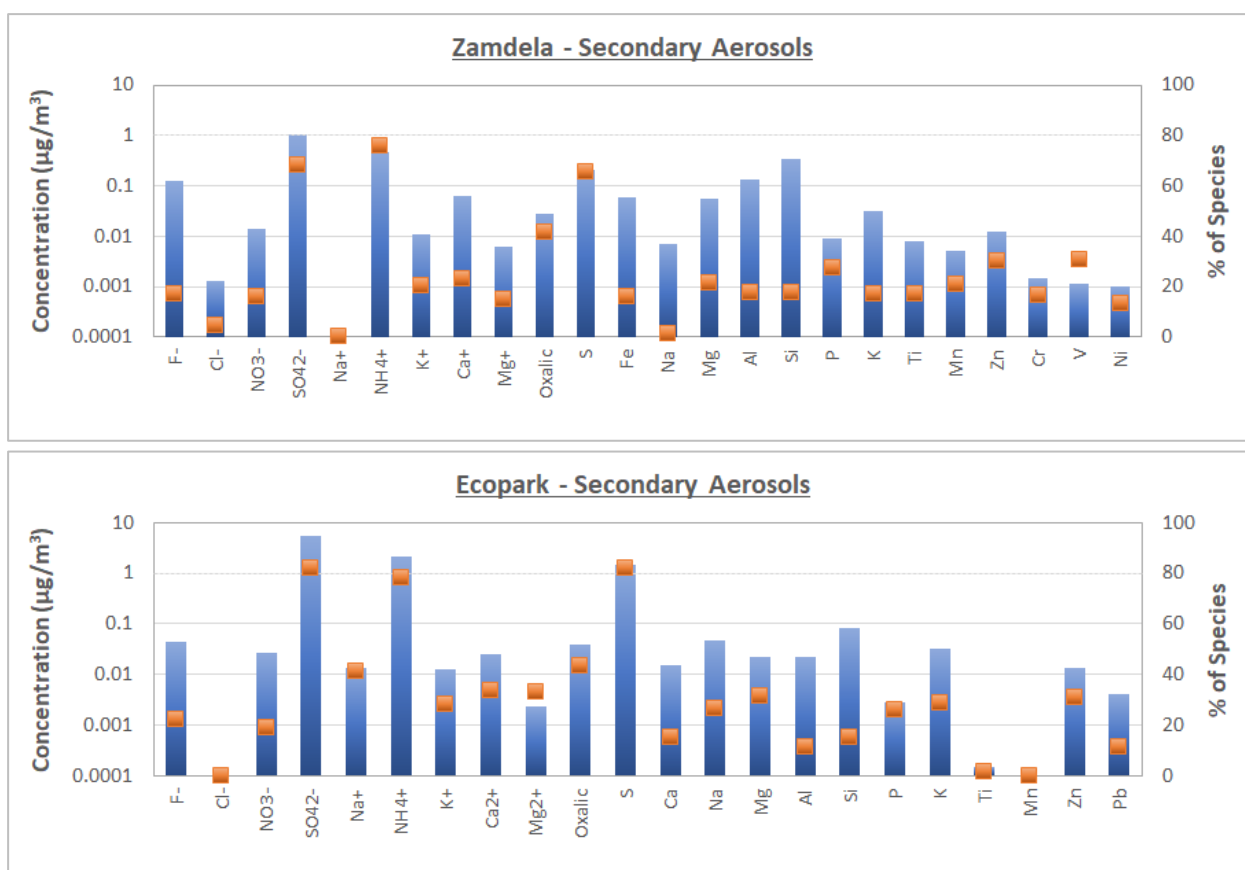


Figure B.10: PMF coarse fraction source profiles for secondary aerosols at Zamdela and Ecopark for the summer 2017 sampling campaign

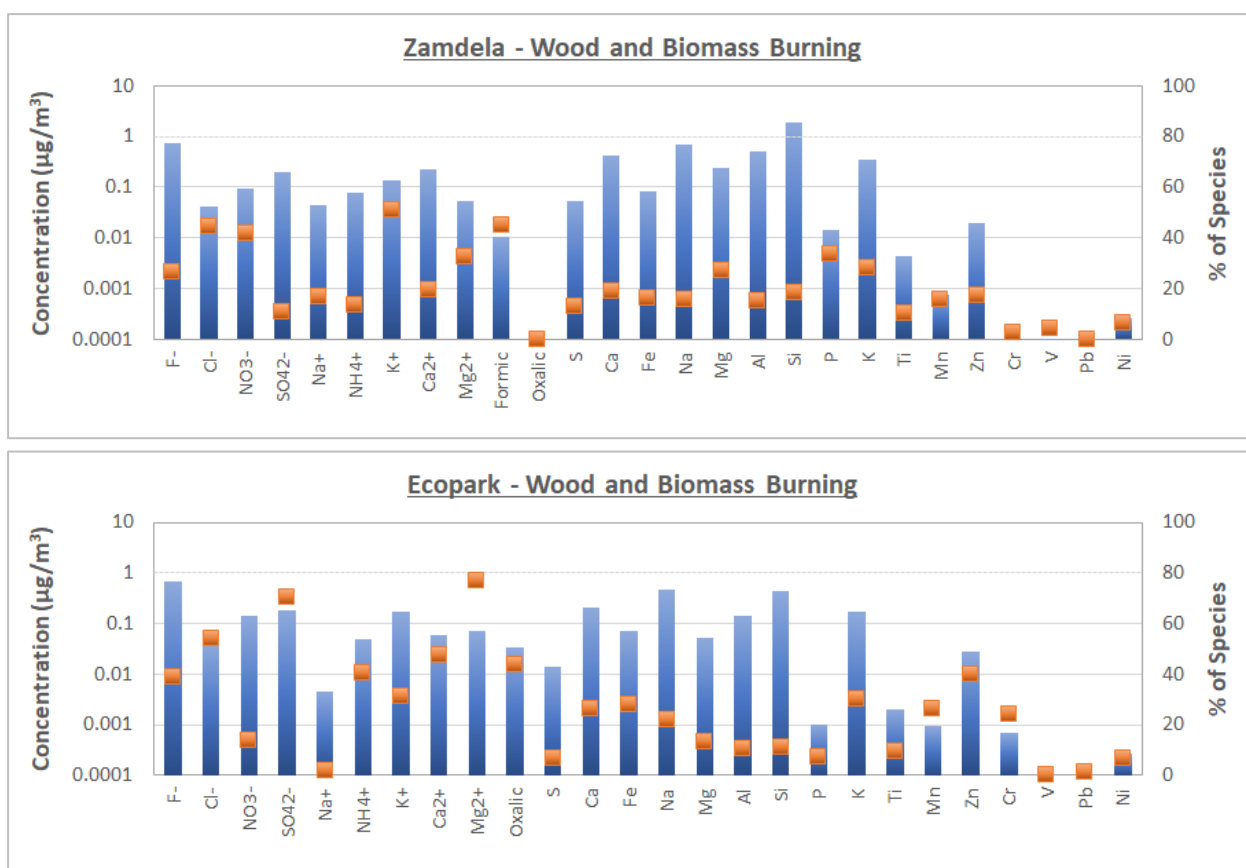


Figure B.11: PMF coarse fraction source profiles for wood and biomass burning at Zamdela and Ecopark for the winter 2016 sampling campaign

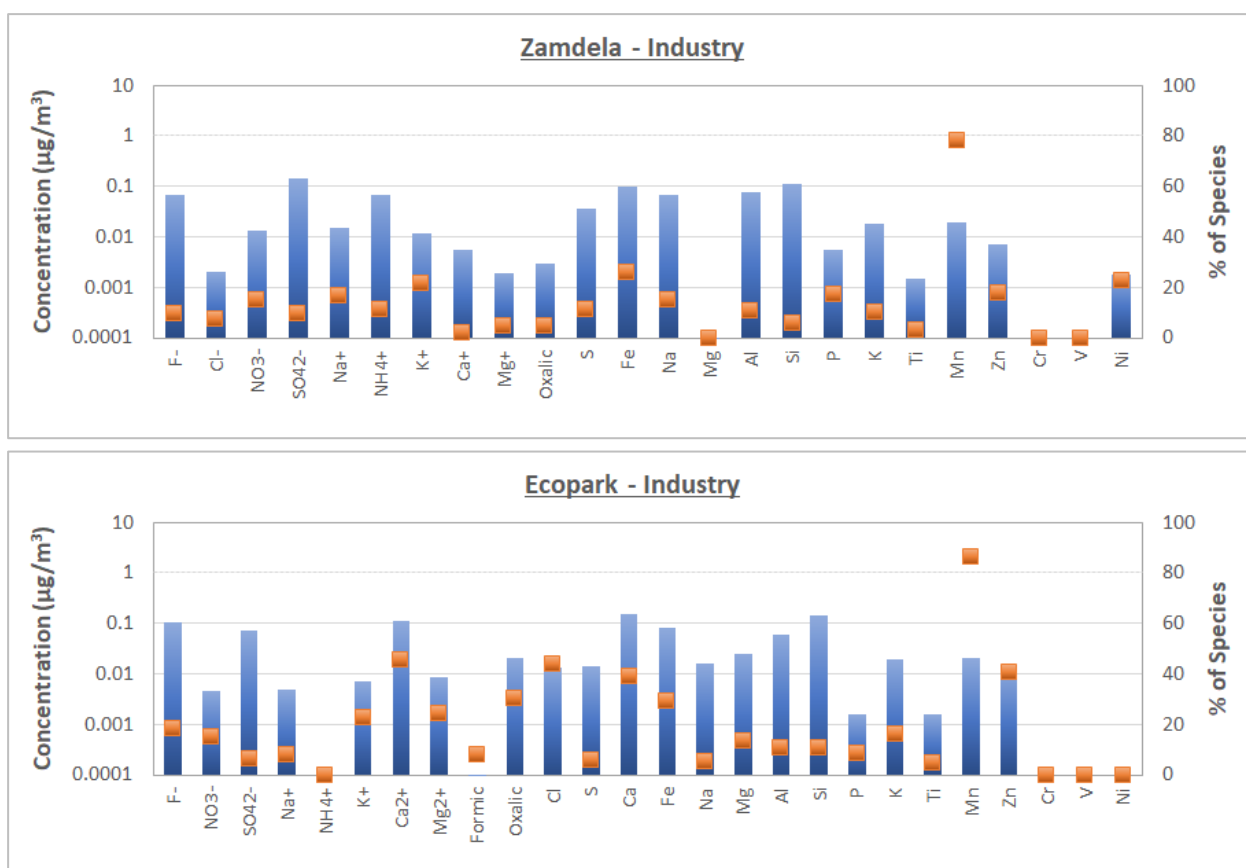


Figure B.12: PMF coarse fraction source profiles for industry at Zamdela and Ecopark for the summer 2017 sampling campaign