Temporal assessment of atmospheric trace metals in the industrialised western Bushveld Complex

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~Abstract~

The presence of trace transition metal species in the atmosphere can be attributed to the emission of particulate matter into the atmosphere by anthropogenic activities, as well as from natural sources. Trace metals emitted into the atmosphere can cause adverse health-related and environmental problems. At present, limited data exists for trace metal concentrations in South Africa. In this investigation, the general aim was to determine the concentrations of trace metals in atmospheric aerosols in the industrialised western Bushveld Igneous Complex, as well as to link the presence of these species in the atmosphere to possible sources in the region.

The measurement site was placed in Marikana, a small rural town situated 35 km east from Rustenburg in the North West Province of South Africa. It is surrounded by numerous industrial and metallurgical operations. MiniVolume^{TM} samplers and Teflon$^{®}$ filters (2 µm pores) were utilised to collect $PM_{2.5}$ and PM_{10} particulate samples. The MiniVolume^{TM} samplers were programmed to filter 5 litres of air per minute for 12 hours per day, over a six-day period. The starting time for sampling was altered every six days, in order to obtain both day and night samples. Sampling was performed for a period of one year.

The collected samples were chemically analysed with inductively coupled plasma mass spectroscopy (ICP-MS). Surface analysis of the sampled filters was performed with a scanning electron microscope (SEM) in conjunction with energy-dispersive spectroscopy (EDS). The dataset was also subjected to factor analysis in an attempt to identify possible sources of trace metal species in the atmosphere.

The concentrations of 27 trace metals (Be, B, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Pd, Cd, Ba, Pt, Au, Hg, Tl, Pb, U) were determined. Pd, Hg, Tl, U, Ca, Co, As, Cd, Ba and Au were above the detection limit 25% or less of the time during the sampling period. With the exception of Ni, none of the trace metals measured at Marikana during the sampling period exceeded local and international standards. Higher Ni levels were possibly due to base metal refining in the region. Pb, which is the only metal species that has a standard prescribed by the South African Department of Environmental Affairs (DEA), did not exceed any of the

standards. It is also significant to refer to Hg that was below the detection limit of the analytical instrument for the entire sampling period.

The impact of meteorological conditions revealed that wet removal of atmospheric PM_{10} trace metals was more significant than the wind generation thereof. During the dry months, the total trace metal concentrations in the PM_{10} fraction peaked, while PM_{10} particles were mostly washed out during the wet season. Wind speed showed an unexpected inverse pattern compared to wet deposition. A less significant seasonal trend was observed for the trace metal concentrations in the $PM_{2.5}$ fraction, which was attributed to a faster replenishment of smaller particles into the atmosphere after rain events.

Separation of trace metal concentrations into $PM_{10-2.5}$ and $PM_{2.5}$ fractions indicated that 79% of the total trace metal levels that were measured were in the $PM_{2.5}$ fraction, which indicated a strong influence of industrial and/or combustion sources. Fractionalisation of each of the trace metal species detected showed that for each metal species, 40% and more of a specific metal was in the $PM_{2.5}$ fraction, with Cr, V, Ni, Zn and Mn occurring almost completely in the $PM_{2.5}$ fraction.

Surface analysis with SEM supported results from the chemical analysis, which indicated that a large fraction of the particles was likely to originate from anthropogenic activities and from wind-blown dust. SEM-EDS also detected non-metallic S that is usually associated with the Pt pyrometallurgical industry that is present in the western Bushveld Igneous Complex.

Correlations between Cr, V, Ni, Zn and Mn revealed that the main sources of these species were pyrometallurgical industries. Explorative factor analysis of the unprocessed and Box-Cox transformed data for all 27 metals detected, resolved four meaningful emission sources, i.e. crustal, vanadium related, base metal related and chromium related. Comparison of trace metal species to other parameters measured (e.g. CO, BC) also indicated pyrometallurgical activities and wind-blown dust to be the main sources of trace metals in this region.

Keywords: Bushveld Igneous Complex, trace metals, aerosols, explorative factor analysis

~Opsomming~

Die teenwoordigheid van spooroorgangsmetale in die atmosfeer kan toegeskryf word aan die emissie van deeltjies in die atmosfeer vanaf antropogeniese aktiwiteite, sowel as vanaf natuurlike bronne. Spoormetale wat vrygestel word in die atmosfeer kan 'n verskeidenheid nadelige gesondheidsverwante en omgewingsprobleme veroorsaak. Tans bestaan daar 'n beperkte hoeveelheid data ten opsigte van spoormetale in Suid-Afrika. Die belangrikste doelwit van hierdie studie was om die konsentrasie van spoormetale in die westelike Bosveld Stollingskompleks te bepaal, asook om die teenwoordigheid van hierdie spesies in die atmosfeer te koppel aan moontlike bronne.

Die meetstasie was geposisioneer by Marikana, 'n klein landelike dorpie wat ongeveer 35 km oos van Rustenburg in die Noordwes Provinsie van Suid-Afrika voorkom. Marikana is omring deur 'n groot aantal industriële en metallurgiese aktiwiteite. MiniVolume™ monsternemers en Teflon® filters (2 µm porieë) was gebruik om $PM_{2.5}$ en PM_{10} deeltjiemonsters te versamel. Die MiniVolume™ monsternemers was geprogrammeer om 5 liter lug per minuut elke 12 uur per dag, oor 'n ses-dag periode te filtreer. Die begintyd vir monsterneming is elke ses dae verander om monsters beide in die dag en nag te neem. Die monsterneming is vir 'n tydperk van een jaar gedoen.

Die monsters wat versamel is, is chemies geanaliseer met 'n induktief-gekoppelde plasma massaspektrometer (IGP-MS). Oppervlakanalise van die monsterbevattende filters was uitgevoer met 'n skandeerelektronmikroskoop (SEM) saam met energie dispersie-spektroskopie (EDS). Faktoranalise is ook op die datastel uitgevoer in 'n poging om moontlike bronne van spoormetaalspesies te bepaal.

Die konsentrasie van 27 spoormetale (Be, B, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Pd, Cd, Ba, Pt, Au, Hg, Tl, Pb, U) is bepaal. Pd, Hg, Tl, U, Ca, Co, As, Cd, Ba en Au was 25% of minder van die tyd tydens die monsternemingsperiode onder die deteksielimiet. Buiten vir Ni het geen van die spoormetale wat gemeet is by Marikana plaaslike en internasionale standaarde oorskry nie. Hoër Ni-konsentrasies kan waarskynlik toegeskryf word aan die basismetaal-raffinaderye in die omgewing. Pb, wat die enigste metaal is waarvoor 'n

standaardkonsentrasie voorgeskryf word deur die Suid-Afrikaanse Departement van Omgewingssake, het geen standaard oorskry nie. Dit is ook belangrik om na Hg te verwys wat onder die deteksielimiet was van die analitiese instrument gedurende die volle monsternemingtydperk.

Die impak van meteorologiese kondisies het daarop gewys dat die verwydering van atmosferiese PM_{10} deur reën meer beduidend was as die opwekking daarvan deur wind. Tydens die droë maande het die totale spoormetaalkonsentrasies in die PM_{10}-fraksie 'n hoogtepunt bereik, terwyl PM_{10} hoofsaaklik uitgewas is gedurende die nat seisoen. Windspoed het 'n onverwagse teenoorgestelde patroon getoon in vergelyking met natdeposisie. Die $PM_{2.5}$-fraksie het 'n minder beduidende seisoenale patroon vir spoormetaalkonsentrasies getoon, wat toegeskryf is aan die vinniger vervanging van kleiner deeltjies in die atmosfeer na reënbuie.

Die opdeling van spoormetaalkonsentrasies in $PM_{10-2.5}$- en $PM_{2.5}$-fraksies het daarop gedui dat 79% van die totale spoormetaalvlakke wat gemeet is in die $PM_{2.5}$-fraksie voorkom, wat 'n sterk invloed van industriële- en/of verbrandingsbronne aantoon. Fraksionering van elk van die spoormetaalspesies wat gemeet is, het aangetoon dat vir elke metaalspesie, 40% of meer van 'n spesifieke spesie in die $PM_{2.5}$-fraksie teenwoordig was, met Cr, V, Ni, Zn en Mn amper uitsluitlik in die $PM_{2.5}$-fraksie.

Oppervlakanalise met SEM het resultate wat verkry is vanaf die chemiese analises ondersteun en het ook daarop gedui dat 'n groot fraksie van die partikels waarskynlik afkomstig is vanaf antropogeniese aktiwiteite en aangewaaide stofdeeltjies. SEM-EDS het ook die nie-metaal S waargeneem wat gewoonlik met die Pt-pirometallurgiese industrie wat teenwoordig is in die westelike Bosveld Stollingskompleks, geassosieer word.

Korrelasies tussen Cr, V, Ni, Zn en Mn het aangetoon dat die hoofbronne van hierdie spesies pirometallurgiese industrieë is. Eksploratiewe faktoranalise van die rou- en die Box-Cox-getransformeerde data vir al 27 metaalspesies wat waargeneem is, het vier sinvolle emissiebronne beslis, d.i. aardkors, vanadium-verwant, basismetaal-verwant en chroom-verwant. Die vergelyking van spoormetaalspesies met ander parameters wat gemeet is (bv. CO, BC) het ook daarop gedui dat pirometallurgiese

aktiwiteite en aangewaaide stofdeeltjies die hoofbronne van spoormetale in die omgewing is.

Sleutelwoorde: Bosveld Stollingskompleks, spoormetale, aërosols, eksploratiewe faktor analise

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~List of Abbreviations~

AR:	Analytical grade
BC:	Black carbon
BIC:	Bushveld igneous complex
DEAT:	Department of Environmental Affairs and Tourism
EAC:	European Aerosol Conference
GHG:	Greenhouse gases
IARC:	International Agency for Research on Cancer
ICP-MS:	Inductively coupled plasma mass spectrometer
IPCC:	Intergovernmental Panel on Climate Change
NAAQS:	National Ambient Air Quality Standards
NACA:	National Association of Clean Air
NWU:	North-West University
OC:	Organic carbon
PAHs:	Polycyclic aromatic hydrocarbons
PM:	Particulate matter
RF:	Radiative forcing
RLM AQMP:	Rustenburg Local Municipality Air Quality Management Plan
ROS:	Reactive oxygen species

SEM-EDS:	Scanning electron microscope – Energy dispersive spectrometer
TSP:	Total suspended particulate matter
UH:	University of Helsinki
US EPA:	United States Environmental Protection Agency
VOCs:	Volatile organic compounds
WHO:	World Health Organization

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~CHAPTER 1~

Introduction

In this chapter, a short background on the relevance of atmospheric aerosols and trace metal species is discussed to emphasise the need and importance for this specific study. This chapter also presents the problem and lists the proposed objectives of the study.

1.1 Background

Aerosols or particulate matter (PM) are solid or liquid particles suspended in a gas (Seinfeld and Pandis, 2006; Brasseur *et al*., 1999). Atmospheric aerosols consist of a mixture of chemical species, which include sulphates, nitrates, organic material, crustal species, sea salt, metal oxides, transition metals, hydrogen ions and water. Within a given parcel of air, the composition of the particles varies significantly. Particles with a diameter larger than 2.5 μm are identified as *coarse* particles, while those with diameters smaller than 2.5 μm are called fine particles. The fine particles include most of the total number of particles and a large fraction of the mass. The fine particles with diameters smaller than 0.1 μm are often called ultra-fine particles (Brasseur *et al*., 1999; Seinfeld and Pandis, 2006). Ultra-fines account for a very large proportion of the number of particles in the atmosphere, although only a modest proportion of the surface area, and a minute proportion of the mass (Brown *et al*., 2003).

The sources of aerosol particles can be subdivided into different categories, viz. area, point and volume sources. The surfaces of oceans and continents act as area sources. Volcanoes and isolated meteorological events such as thunderstorms and

low pressure systems are point sources, while gas-to-particle conversions are considered to be volume sources (Kneip and Lioy, 1980).

Atmospheric aerosols are of significant relevance due to several reasons. Aerosols affect the optical properties of the Earth's atmosphere since they are able to absorb and scatter radiation, which causes variations in the Earth's climate due to an alteration in the amount of sunlight that penetrates the earth's atmosphere (Brasseur *et al*., 1999). The latter depends on more than one property of the particle. Particle size, structure and composition, as well as the wavelength of the radiation are included (Brasseur *et al*., 1999; Mészáros, 1981). Airborne aerosols also act as the nuclei on which cloud or fog drops are formed. PM has a significant effect on the chemical reactions that occur in the Earth's atmosphere (Brasseur *et al*., 1999). Some trace species may be present in the atmosphere in either the gas phase or the particle phase that causes different particle transport rates in the atmosphere.

Although the impacts of atmospheric aerosols on health are wide-ranging, it is predominantly related to respiratory and cardiovascular systems (Brown *et al*., 2003). The entire human population is affected, but the susceptibility may vary with health or age (WHO, 2006). The cut-off size fraction of particles that are considered to have adverse health effects is PM_{10}, since only particles smaller than 10 µm can significantly reach the small airways and alveoli. Studies indicate that $PM_{2.5}$ and ultra-fine $PM_{0.1}$ particles are the most harmful to human health, since larger numbers of these particles exist and due to their ability to penetrate deeper into the lungs (Brown *et al*., 2003).

The presence of various inorganic and trace transition metal species in the atmosphere can be attributed to the emission of particulate matter into the atmosphere by anthropogenic activities. Trace metals emitted into the atmosphere can cause a variety of health-related and environmental problems; depending on the extent and time of exposure (Brown *et al*., 2000). In this investigation the concentrations of trace metals in atmospheric aerosols were determined in a highly industrialised region.

1.2 Problem statement

Marikana is a small rural town situated approximately 35 km east from Rustenburg in a highly industrialised region in the North West Province of South Africa. This region is known as the Western Bushveld Igneous Complex and holds numerous metallurgical operations and different smelters. Marikana itself is surrounded by more than 30 mines and several metallurgical operations (Kaonga and Kgabi, 2009). It is therefore significant to monitor the emissions of chemical species into the atmosphere at Marikana in order to establish their effects on human health and the environment.

At present, limited data exists for atmospheric trace transition metal concentrations in this region, which necessitates the measurement of these species. In this study, the concentrations of trace metals (such as Cr, V, Mn, Fe, Ni, and Pb present in PM samples) will be determined. These values will be compared to standards as stated by the World Health Organization, the US Environmental Protection Agency, and to Government regulations (Brown *et al*., 2003; Seinfeld and Pandis, 2006; DEAT, 2004). The impact of meteorological conditions on the presence of these species in the atmosphere will also be reported. Since the size of PM determines the impact of particles on human health and the environment, the concentrations of trace metals in PM_{10} and $PM_{2.5}$ size fractions will be determined. The size of PM is also an indication of possible sources of these species, since smaller particles are usually associated with anthropogenic activities.

1.3 Objectives

The general aim of this investigation was to determine the concentrations of trace metals in the industrialised western Bushveld Igneous Complex. The specific objectives of this study were to:

- collect $PM_{2.5}$ and PM_{10} samples on filters with mini-volume samplers for a period of one year at Marikana, South Africa.

- develop a method to divide filters to perform two different destructive analytical procedures.
- determine the concentration of trace transitional metals from the collected PM.
- determine the effect of meteorological conditions and other species present in the atmosphere on particle matter- and trace metal concentrations.
- relate the measured trace metal species to possible sources in the region.

~CHAPTER 2~

Literature survey

In this chapter, background information is given on subject matter relevant for this specific study. A discussion on atmospheric pollution is provided to give a better understanding of atmospheric aerosols and trace metal species, which were the main focus of this investigation. The main sources and properties of atmospheric aerosols and trace metals, as well as their impacts on climate, health and the environment, are discussed.

2.1 Atmospheric pollution

2.1.1 Introduction

The Earth's atmosphere can be divided into vertical layers that include the troposphere, stratosphere, mesosphere, thermosphere and exosphere. These different layers are characterised by changes in temperature at different heights and by compositional changes of the layers (Harrison, 1999). The atmospheric layers influenced by air pollution include the stratosphere, troposphere and the boundary layer between the surface of the earth and the troposphere (Figure 2.1). Pollutant species present in these layers have an influence on general air quality and climate change.

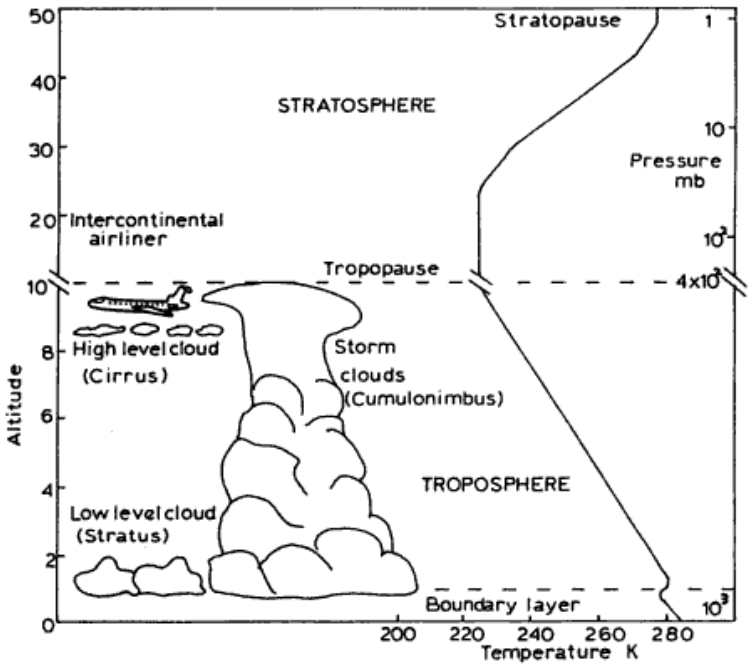

Figure 2.1: The vertical structure of the atmosphere (Harrison, 1999)

The troposphere extends from the surface of the earth to the tropopause at the approximate altitude of 18 km in the tropics, 12 km at midlatitudes, and 6 to 8 km near the poles. It is characterised by a decrease in mean temperature with an increase in altitude due to the declining influence of radiation from the surface of the earth. The troposphere, which contains about 85-90% of the atmospheric mass, is often very unstable due to fast vertical exchanges of energy and mass associated with convective activity. Globally, the time required for these vertical exchanges is in the order of several weeks. Much of the variability observed in the atmosphere occurs within the troposphere, including, for example, the weather patterns associated with the passage of fronts or the formation of thunderstorms (Brasseur *et al.*, 1999). This leads to 'the weather' as the layman experiences it (Harrison, 1999).

The planetary boundary layer is the region of the troposphere where the effects of the surface of the earth are important for atmospheric conditions. It is approximately 1 km deep, but varies significantly with the time of day and with changing meteorological conditions. The exchange of chemical compounds between the surface and the free troposphere is directly dependant on the stability of the boundary layer (Brasseur *et al.*, 1999).

Above the troposphere the atmosphere becomes very stable as the vertical temperature gradient reverses in a second atmospheric region called the stratosphere, which extends between 15 and 50 km in altitude (Brasseur *et al.*, 1999). The stratosphere is relatively cloud-free and considerably less turbulent. In contrast to the decrease in temperature observed in the troposphere, the temperature increases with height in the stratosphere. This turning point is called the tropopause. This condition of a warmer, less dense layer of air over a cooler, dense layer is quite stable (Harrison, 1999).

The earth's atmosphere consists of a variety of constituents and chemical compounds. The most abundant of these species are gaseous nitrogen N_2 (78%) and oxygen O_2 (21%). These gaseous species, together with the noble gases argon, neon, helium, krypton and xenon, are resistant against chemical destruction and have extensive lifetimes in the atmosphere. They are therefore relatively well mixed throughout the entire homosphere (below approximately 90 km altitude). Minor constituents, such as water vapour, carbon dioxide, ozone, and many others species, also play an important role in the troposphere, despite their lower concentration (Brasseur *et al.*, 1999).

Although tropospheric ozone plays an important role in air pollution chemistry, approximately 90% of the total ozone content of the atmosphere is present in the stratosphere (Harrison, 1999). Stratospheric ozone influences the transmission of solar and terrestrial radiation in the atmosphere and is therefore linked to the physical climate system. Stratospheric ozone is a key component of biogeochemical cycles and also determines the "oxidising capacity" of the atmosphere, which consequently affects the atmospheric lifetime of both biogenic and anthropogenic trace gases (Brasseur *et al.*, 1999). A typical residence time for material injected in the lower stratosphere is one to three years (Brasseur *et al.*, 1999).

Also present in the troposphere and stratosphere are aerosols – solid or liquid species suspended in the atmosphere (Kondratyev *et al.*, 2006). Changes in concentrations of stratospheric aerosols, caused by intense, episodic volcanic eruptions, perturb the climate system by warming the lower stratosphere through enhanced absorption of solar and long-wave radiation, and by reducing the solar radiation reaching the surface-troposphere system through increased albedo. The result is negative radiative forcing of the surface-troposphere system. Increases in

stratospheric aerosol concentrations also have the potential to influence cloud formation and maintenance processes in the upper troposphere, circulation in the lower stratosphere, and lower-stratospheric ozone concentrations (via heterogeneous chemical reactions on particle surfaces) (National Research Council, 1996).

The chemical composition of aerosol particles in the troposphere results from the interaction of many formation and dynamic (e.g. coagulation) processes. For this reason, particles are often composed of several materials and the composition varies as a function of time and location (Mészáros, 1981). The influence of tropospheric aerosols associated with industrial pollution, as well as fossil fuel and biomass burning has only recently been identified and, to some extent, quantified (McGuffie and Henderson-Sellers, 2005).

Aerosols are either emitted directly into the atmosphere or are formed through gas-to-particle conversions due to the following processes:

- heterogeneous homomolecular nucleation (formation of a new stable liquid or solid fine particles from its gaseous phase in the presence of only one gas component);
- heterogeneous heteromolecular nucleation (a similar process to the above, but in the presence of two and more gases); and
- heterogeneous heteromolecular condensation (the growth of the existing particles due to gas adsorption) (Kondratyev *et al.*, 2006).

2.1.2 Types of pollutants

The term pollutant is normally applied to any substance added to the environment in a sufficient concentration to have a measurable effect on humans, animals, and vegetation or building materials. Air pollutants include all natural and artificial substances, including gases, solid particles, liquid droplets, and mixtures of these different items (Degobert, 1995).

Atmospheric pollutant species have received considerable research and regulatory attention in recent times. The exact impacts of atmospheric pollutants are

determined by their physical and chemical properties. Atmospheric pollutant species are mainly categorised into gaseous species and particles. Although the terms *gases* and *particles* are used, pollutants exist in all three phases of matter, i.e. solids, liquids and gases (Godish, 2004).

2.1.2.1 Gaseous

Gaseous pollutant species consist of both organic and inorganic compounds. The organic compounds include volatile organic compounds (VOCs), CH_4 (methane), non-methane hydrocarbons and halogenated organic species. The most abundant inorganic species include NO_2, N_2O, SO_2, O_3, CO, and CO_2, which are present as gases in the atmosphere. All of these species contribute significantly to air pollution. Gaseous compounds can be emitted directly into the atmosphere from natural and anthropogenic sources. Some of the major sources of gaseous pollutants include combustion of fossil fuels and vehicle emissions, which cause NO_x, SO_2, CO, CO_2, VOCs, and heavy metals to be released into the atmosphere (Engelbrecht, 2009; Graedel and Crutzen, 1997). Gaseous pollutants are also formed by chemical reactions taking place in the atmosphere.

2.1.2.2 Aerosols

Aerosols or PM are a complex mixture of solid and liquid particles suspended in air. Aerosols also consist of organic and inorganic species. The most common examples of aerosols present in the atmosphere are clouds, smoke and dust. Natural sources of particular matter include volcanic eruptions, forest fires, dust storms, or spray from seawater, whereas anthropogenic sources comprise traffic, agriculture, chemical, and mining industries. As mentioned previously, aerosols are emitted either directly into the atmosphere as primary aerosols, or are formed through gas-to-particle conversion or chemical reactions as secondary aerosols. The physical and chemical properties of these particles determine their impact on the climate and on health (Engelbrecht, 2009). Aerosols may reduce visibility, impact soil materials, and affect human health (Godish, 2004).

2.1.3 Impacts of pollutants

2.1.3.1 Climate change

Solar energy falling on the surface of the earth is absorbed and transferred to the atmosphere by radiation. At present, the solar energy falling on the earth's surface is approximately 157 W/m^2. Twice this amount enters the stratosphere, but is depleted by reflection from clouds and dust, as well as by absorption by clouds, ozone and water vapour. The infrared energy absorbed by these components is governed by the intensity of infrared emission at the earth's surface and in the lower levels of the atmosphere. The emission of energy from the upper atmospheric levels is reduced as the temperature of the troposphere falls about 5˚C/km, leading to net energy gain and surface warming (Alloway and Ayres, 1993).

Changes in solar radiation, land surface properties and the abundance of atmospheric greenhouse gases and aerosols, alter the energy balance of the climate system. These changes are conveyed in terms of radiative forcing (Figure 2.2) (IPCC, 2007). Radiative forcing is the change in the energy fluxes of solar radiation (maximum intensity in the spectral range of visible light) and terrestrial radiation (maximum intensity in the infrared spectral range) in the atmosphere. These changes in energy fluxes are induced by anthropogenic or natural changes in the atmospheric composition, earth surface properties, or solar activity. Negative forcings caused by scattering and reflection of solar radiation by aerosols and clouds tend to cool the earth's surface, whereas positive forcings caused by absorption of terrestrial radiation by greenhouse gases and clouds tend to warm the surface of the earth (greenhouse effect) (Pöschl, 2005).

Atmospheric concentrations of CO_2 are increasing globally at a rate of about 1% or more annually. Similarly, other greenhouse gases such as O_3, N_2O and NO_x, CO and chlorofluorocarbons are increasing proportionally with increasing industrial emissions; all are linked to population growth.

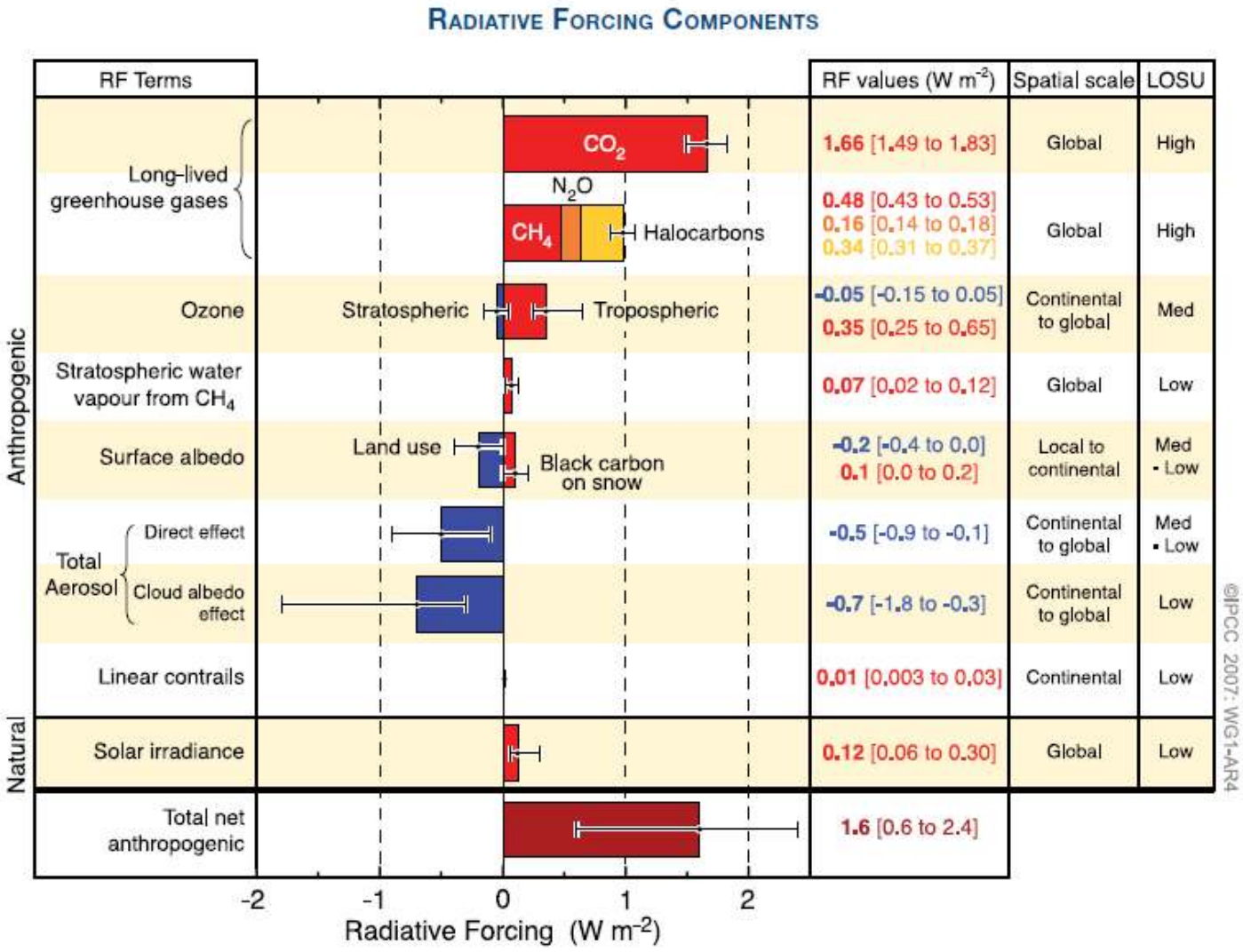

Figure 2.2: Global average radiative forcing (RF) estimates and ranges in 2005 (IPCC, 2007)

The net effect of aerosols on climate change is counteracting of the warming effects of greenhouse gases (GHG) over the past century. This has not only provided some 'climate protection', but also prevented the true magnitude of the problem from becoming evident. In particular, it may have resulted in an underestimation of the sensitivity of the climate system to the effect of GHG (Andreae, 2007). Most aerosols reflect solar radiation back into space, thus reducing the heat absorbed by the earth and thereby lowering its temperature. Alternatively, some aerosols (e.g. soot particles) absorb sunlight, thus warming the atmosphere while still cooling the surface. The atmospheric warming suppresses convection, cloudiness and

precipitation. Shading of the surface by aerosols also reduces evaporation, which leads to less rainfall (Andreae, 2007).

As mentioned, aerosols have the ability to scatter as well as absorb solar radiation, which has a direct influence on climate, as well as an indirect effect through their role as cloud condensation nuclei. The *direct* effect may be observed as the sunlight that is reflected upward from haze when viewed from above. The scattering of sunlight results in an increase in the amount of light reflected by the planet, which leads to a decrease in the amount of solar radiation reaching the surface (Seinfeld, 2006).

The indirect effect arises from increases in aerosol concentrations from anthropogenic sources that lead to increased concentrations of cloud condensation nuclei. This, in turn, leads to clouds with an increased concentration of droplets with smaller radii, which leads to higher cloud albedos (Seinfeld, 2006). When particles become more absorbing than scattering, a point is reached where the overall effect of the particle layer changes from one of cooling to one of heating (Seinfeld, 2006). The *indirect* climate effects of aerosols are more complex and more intricate to assess. The reason being that they depend on a series of phenomena that connect aerosol levels to concentrations of cloud condensation nuclei, which are related to cloud droplet number concentrations (and size), that are subsequently connected to cloud albedo and cloud lifetime (Seinfeld and Pandis, 2006).

It is predicted that in the present century the role of aerosols in opposing global warming will fade, since there are powerful policies to reduce their emissions. The atmospheric lifetimes of aerosols are also short in contrast to GHG (Andreae, 2007). The end of significant climate protection by atmospheric aerosols, combined with the potential very high sensitivity of the climate system, makes rapid reductions in greenhouse gas emissions, especially CO_2, very urgent (Andreae, 2007). A complication arises from combustion as this releases compounds that act to warm the planet, particularly CO_2, and others that have a cooling effect, such as aerosol particles and their precursors (Andreae, 2007).

2.1.3.2 Health and environmental impacts

The evidence on airborne particulate matter (PM) and its public health impact is consistent in showing adverse health effects at exposures that are currently

experienced by urban populations in both developed and developing countries (WHO, 2005). Aerosols can endanger the health of human beings in direct and indirect ways.

Direct effects of aerosols on the health of human beings are significantly more varied than indirect effects, because many single components of an aerosol can trigger specific diseases (Fellenberg, 2000). The range of health effects is broad, but is predominantly to the respiratory and cardiovascular systems. The entire population is affected, but susceptibility to the pollution may vary with health or age (WHO, 2005). Health-effects reported to be associated with PM can be linked with increased daily and annual mortality rates in adults and include cardiopulmonary disorders, symptoms of respiratory dysfunction (e.g. wheeze, cough), asthma attacks, pneumonia, bronchitis, and chronic obstructive pulmonary disease (Martins, 2009; USEPA, 1996).

UV rays are necessary along with the body temperature of human beings in order to form the 7-dehydrocholesterol Vitamin D_3, present in the skin in relatively high concentrations. This is then hydroxylated in the liver and kidneys into physiologically active 1,25-dihydroxycholecalciferol. When there is a lack of UV radiation, the conversion of 7 - Dehydroxycholesterol into vitamin D_3 takes place on too small a scale, so that a deficiency in vitamin D_3 occurs with the resulting symptoms, such as impaired bone formation. This disease became known as vitamin D_3 deficiency rickets (Fellenberg, 2000). Moreover, UV rays also destroy micro-organisms. UV rays, then, have a sterilising effect. Through the reduction of the UV portion, above all, under the smog layers of the big cities, fewer micro-organisms are destroyed, and as a result, the risk of bacterial infection increases (Fellenberg, 2000).

Pollutants that are present in aerosols, especially heavy metals with their high potential toxicity, affect soil processes and lead to the degradation of soil conditions. As a result, plant toxicity is raised and the entry of contaminants into the food chain is inevitable (Vassilakos, 2007). The precipitation of aerosols has adverse environmental impacts and has the potential to alter ecosystem structure and function by altering the nutrient cycling and changing the biodiversity (Martins, 2009; US EPA 1997).

A number of potential harmful substances have been identified in fine mode aerosols, especially $PM_{2.5}$. These include nickel, lead and cadmium, which are all more concentrated in $PM_{2.5}$ than PM_{10} (Kgabi, 2006). Heavy metals such as nickel and chromium(VI) have been defined by the International Agency for Research on Cancer (IARC) as potential cancer causing agents (Martins, 2009; IARC, 1997).

As thresholds have not been identified, and given that there is substantial inter-individual variability in exposure and in the response to a given exposure, it is unlikely that any standard or guideline value will lead to complete protection for every individual against all possible adverse health effects of particulate matter (WHO, 2005).

2.2 Atmospheric aerosols

2.2.1 Introduction

An atmospheric aerosol is formally defined as a suspension of liquid or solid particles in a gas, with particle diameters in the range of 10^{-9}-10^{-4} m (Pöschl, 2005). Aerosols consist of a large number of species originating from natural and anthropogenic sources, which include metallic particles (e.g. Cr, V, Fe and Pb) from industrial and combustion processes, crustal material from erosion of soil and rock, and secondary pollutants such as sulphates, nitrates and organic aerosols (chlorofluorocarbons, hydrofluorocarbons, terpenes and methyl chloroform), among other species (Pekney and Davidson, 2005; Koppmann, 2007).

The distribution of atmospheric particle number concentrations with respect to size exhibits one or more “modes”; that is, particles are grouped within several diameter sub-ranges. The commonly used descriptors for the subpopulations are as follows: nucleation or Aitken (diameter ≤ 0.1 μm), accumulation (diameter between 0.1 and 2.0 μm), and coarse (diameter > 2.0 μm) modes. Additionally, particles with diameters less than approximately 2 μm constitute the fine particle fraction (Brasseur *et al*., 1999; Mészáros, 1981). This division of particle sizes into subpopulations may differ when used in different contexts. For the purpose of this study, particles with diameters ≤ 2.5 μm ($PM_{2.5}$) are considered the fine particle fraction, and diameters

≤ 10 μm (PM_{10}) are considered the coarse particle fraction. In the UK networks, both $PM_{2.5}$ and PM_{10} are measured continuously (Brown *et al*., 2003; Karanasiou *et al.*, 2009).

2.2.2 Sources of aerosols

The sources of aerosols may be divided into anthropogenic sources as well as natural sources. Anthropogenic sources are those determined by human activity: industrial wastes from chimneys, toxic exhausts from cars, fires, explosions, soil erosion in agriculture, and open mining. This gives a global input of (3-4) x 10^8 t yr^{-1} of aerosols to the atmosphere (Kondratyev *et al.*, 2006). The concentration of aerosol smog due to photochemical reactions with exhaust gases in industrial centres, reaches 200 $\mu g.m^{-3}$, which is comparable to dust storm events (Kondratyev *et al.*, 2006). Natural sources include crustal species from erosion of soil and rock, sea spray and windblown dust.

The sources of aerosol particles (natural and anthropogenic) can also be subdivided into different categories. The surfaces of oceans and continents act as *area sources*, volcanoes, and isolated meteorological events such as thunderstorms and low pressure systems are *point sources*, while gas-to-particle conversion is categorised as *volume sources* (Kneip and Lioy, 1980).

Primary particles are directly emitted as liquids or solids from mechanical processes such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, and wind-driven or traffic-related suspension of road, soil, and mineral dust, sea salt and biological materials (plant fragments, micro-organisms, pollen, etc.) (Brasseur *et al.*, 1999; Pöschl, 2005). Secondary particles, on the other hand, are formed by gas-to-particle conversion in the atmosphere (new particle formation by nucleation and condensation of gaseous precursors) (Pöschl, 2005) and can range from small to bigger particles depending on the lifetime of the aerosol and the different physical and chemical transformations they are exposed to in the atmosphere (Figure 2.3). An example of a secondary aerosol is sulphate, which forms downwind of an industrial source, as emitted sulphur gases are chemically converted to condensable

species and then incorporated into particles (gas-to-particle conversion) (Brasseur *et al.*, 1999).

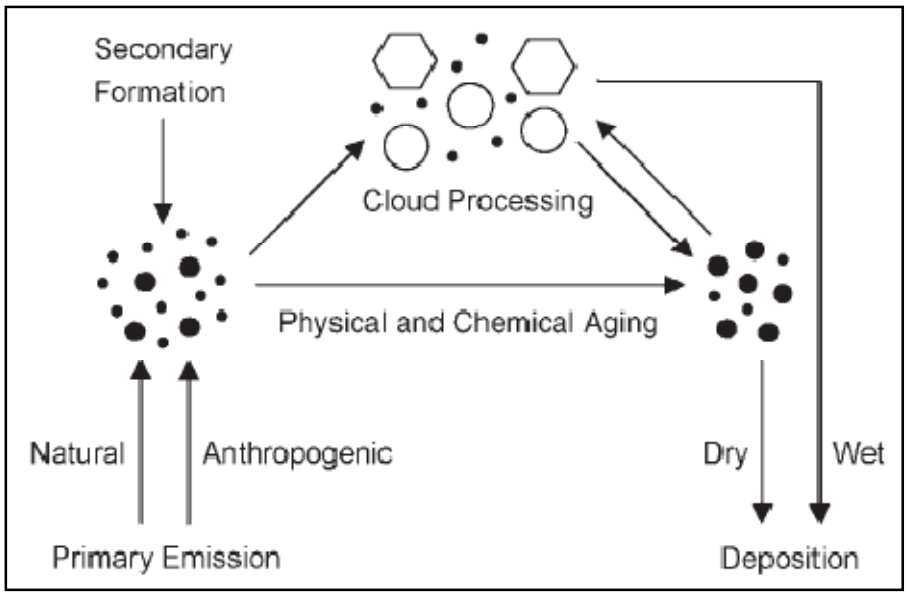

Figure 2.3: Atmospheric cycling of aerosols (Pöschl, 2005)

Natural atmospheric aerosols, depending on their composition or sources, are classified into the following types:

1. products of sea spray evaporation;
2. mineral dust wind-driven to the atmosphere;
3. volcanic aerosol (both directly emitted to the atmosphere and formed due to gas-to-particle conversion);
4. particles of biogenic origin (directly emitted to the atmosphere and formed as a result of condensation of volatile organic compounds, for instance, terpenes, as well as chemical reactions between these compounds);
5. smokes from biota burning on land; and

6. products of natural gas-to-particle conversion (e.g. sulphates resulting from reduced sulphur incoming from the ocean surface with the emissions of dimethyl sulphide) (Kondratyev *et al.*, 2006).

Important types of anthropogenic aerosols are:

1. direct industrial emissions of particles (particles of soot, smoke, road dust, etc.); and

2. products of gas-to-particle conversion.

The estimates of anthropogenic aerosols are more reliable than those of natural aerosols, especially in the oceanic regions and continents that are difficult to access (Kondratyev *et al.*, 2006). The global input of aerosols into the atmosphere from anthropogenic activities is about 20% (by mass) of that from natural sources. For particles with diameters >5 μm, direct emissions from anthropogenic sources dominate over aerosols that form in the atmosphere by gas-to-particle conversion of anthropogenic gases. However, the reverse is the case for smaller particles, where gas-to-particle conversion is the overwhelming source of anthropogenically-derived aerosols (Hobbs, 2000).

2.2.3 Composition of aerosols

Aerosols may consist of a wide variety of species, which include naturally- and anthropologically-derived material (smoke, soot, soil dust etc.) as well as biogenically derived materials (pollens and spores), and within a given parcel of air the composition of the particles varies significantly from place to place as well as particle to particle (Brasseur *et al.*, 1999). Soot, semi-volatile hydrocarbons, and metals are often found in the fine particulate fraction. Soot is a combination of primary emissions of black carbon, which is formed in combustion processes, and organic species that partition to the particles phase as emitted gases cool down. Other semi-volatile organic species, both natural and anthropogenic in origin, may be emitted directly or produced by reactions in the atmosphere; for example, polycyclic aromatic hydrocarbons (PAHs) (Brasseur *et al.*, 1999). Examples of particles

commonly found in the coarse particle mode include sea spray, windblown dust, fly-ash, volcanic ash and particles from tire and break wear. The chemical composition of the coarse fraction reflects these sources: crustal elements (Fe, Ca, Si, Al, etc.) and seawater species (Na, Cl, etc.) are commonly detected (Brasseur *et al*., 1999).

The chemical composition of particles may change significantly in a given area throughout the year. Photochemically produced species usually have higher concentrations during the summer, for example sulphate, whereas aerosol nitrate concentrations usually peak in the winter even though nitric acid is a secondary species produced photochemically (Seinfeld and Pandis, 2006). It may be true that more nitric acid is available during summer in most locations, but due to the high temperatures during summertime it remains mostly in the gas-phase as nitric acid vapour. During wintertime, almost all available nitric acid is transferred to the particulate matter phase after reaction with ammonia to form ammonium nitrate, which leads to higher aerosol nitrate concentrations (Seinfeld and Pandis, 2006). In particulate form, sulphur mainly occurs as sulphuric acid, H_2SO_4, in the form of droplets, or in the form of ammonium and sodium sulphate, $(NH_4)_2SO_4$ and Na_2SO_4 (Colbeck, 2008).

When the aerosol is released from its source as particles, it is acted upon by numerous processes summarised as *aging*. The aging of aerosols has some major effects, including the formation of the aerosol size distribution with its unique features, the change in chemical composition of the aerosol as well as the formation of rather uniform aerosol bodies summarised as continental, maritime, and background aerosols. Most of these effects affect the time an aerosol particle remains airborne, which is called *residence time* (Kneip and Lioy, 1980).

2.2.4 Removal of aerosols from the atmosphere

The processes that are responsible for aging and residence times of aerosols are called sink processes, which act as *volume sinks* (formation of clouds) and *area sinks* (removal of dry deposition). It can be added that the transport of aerosols into other volumes of the atmosphere are also considered to be sinks (Kneip and Lioy, 1980).

Aerosols are transported through the earth's atmosphere by means of meteorological events where they mix with clean air or other aerosols (dilution). The aerosol particles might collide with each other, which is due to thermal diffusion (coagulation), they can become centre condensation nuclei of cloud droplets (rain-out), they may be collected by falling raindrops (wash-out), or sediment out by their own vertical velocity or by impact on ground obstacles (dry removal). The coagulation process takes place more rapidly in concentrated aerosols (Kneip and Lioy, 1980).

The concentration of trace constituents in the atmosphere would rise rapidly if sink mechanisms did not assure the cleansing of the atmosphere (Mészáros, 1981). The major processes for removing aerosols from the atmosphere are dry deposition or sedimentation and wet deposition.

Dry deposition is the transport of gaseous and particulate species from the atmosphere onto surfaces in the absence of precipitation (Kgabi, 2006). Dry deposition occurs when gases or particles contact a surface and stick to or react with the surface in the absence of precipitation. Dry deposition processes depend on atmospheric stability, chemical properties of the depositing particles and the specific properties of the contacting surface. Sedimentation involves the fall of aerosols under gravity (Kgabi, 2006).

Wet deposition combines all natural processes by which the aerosol particles are scavenged by atmospheric hydrometeors (cloud and fog drops, rain, snow) and are deposited to the earth's surface (Kgabi, 2006). The efficiency of wet removal of gases and particles is due to the fact that the falling speed of precipitation elements greatly exceeds the dry deposition velocity of trace constituents. Wet removal caused by clouds and precipitation is differentiated by processes taking place in the clouds (rain-out) and beneath the cloud base (wash-out). The main phenomena affecting collision efficiency between falling droplets and aerosol particles are inertial impaction, Brownian diffusion, phoresis caused by thermal or concentration gradients, turbulent effects and electrical forces. For particles smaller than 1 μm, Brownian diffusion is the main removal mechanism (Laakso *et al.,* 2002).

2.3 Trace metals

2.3.1 Introduction

Trace metals are usually present in atmospheric aerosols, which is the phase in which the biogeochemistry and transportation of the metal species occur. Gravimetrically, trace metals represent a relatively small proportion of the atmospheric aerosol (generally less than 1%) (Colbeck, 2008). Trace metals that are usually present in the atmosphere include B, Na, Mg, Cu, Zn, Cr, V, Pt, Pd and Pb.

2.3.2. Emission sources

The concentrations of trace metals in atmospheric aerosols are a function of their sources. Trace metals are emitted into the atmosphere naturally or by anthropogenic activities. Natural emissions of trace metals result from different processes acting on crustal minerals (e.g. erosion, surface winds and volcanic eruptions), as well as from natural burning and from the oceans. Na, Mg, Al, K, Ca, Ti, Cr, Fe and Mn are usually associated with mineral dust and crustal species (i.e. geological rock forming minerals) (Rastogi and Sarin, 2009; Eleftheriadis *et al.*, 2001; Al-Momani *et al*., 2005; Kulkarni *et al*, 2007) and are ever present and transported easily into the atmosphere.

The predominant anthropogenic sources are due to high-temperature processes, biomass burning, fossil-fuel combustion, industrial activity and incineration. Metal smelting is regarded as one of the most important anthropogenic heavy metal emission sources. During smelting processes, heavy metals in the ores are evaporated from the matrix, and eventually go into the atmosphere, if no pollution control technology is applied (Zheng *et al.*, 2010). Industrial metallurgical processes produce the largest emissions of As, Cd, Cu, Ni and Zn (Vassilakos *et al*., 2007).

Combustion of fossil fuels is the most important anthropogenic source of atmospheric Be, Co, Hg, Mo, Ni, Sb, Se, Sn and V and also contributes to the emissions of As, Cr, Cu, Mn and Zn. Refuse incineration of fluorescent lights, batteries, electrical switches, thermometers and general waste is the main source of

Hg in the air (Vassilakos *et al.,* 2007). Biomass combustion can contribute to emissions of Cu, Pb and Zn (Rastogi and Sarin, 2009).

Exhaust emissions from gasoline- and diesel-fuelled vehicles contribute to atmospheric Pb, Fe, Cu, Zn, Ni and Cd, while tyre-rubber abrasion emits Zn (Colbeck, 2008). One of the major sources of Pb until almost a decade ago, was vehicular emission (gasoline combustion), but with the world-wide ban on leaded petrol, a decrease is expected in its atmospheric abundance (Rastogi and Sarin, 2009). Despite the fact that Pb-free petrol has become a common choice for most transport facilities, Pb is still found to be an important component of airborne particles around the world (Vassilakos *et al*., 2007).

Atmospheric nickel emissions occur both from natural and anthropogenic sources. Natural nickel sources include windblown soil and dust, volcanoes, vegetation, forest fires, sea salt, and meteoric dust. Anthropogenic nickel emissions occur from two broad categories of sources: direct and indirect sources. The direct category primarily includes sources that either produce nickel or consume nickel or a nickel compound to manufacture a usable product, for example nickel ore mining and smelting, ferrous and nonferrous metals production (nickel alloys and steels, cast irons, stainless steel) etc. Indirect sources are generally those that do not produce nickel or nickel-containing products and only inadvertently handle nickel because it is present as an impurity in a feedstock fuel, e.g. coal and oil combustion, coke ovens, and municipal refuse, sewage sludge incineration etc. (EPA L&E, 1984).

2.3.3. Impacts of trace metals

Heavy metals present in the atmosphere in trace amounts may pose a serious risk to human health and the environment. The potential hazard of several toxic elements such as As, Cd, Cr, Hg and Pb is well known (Krzemiński-Flowers *et al*., 2006:759). Therefore, the WHO gives guidelines for some trace metals.

Trace metals such as Cr, Fe, V, and Co have several oxidation states and can therefore participate in many important atmospheric redox reactions (Colbeck, 2008). Transition metals can catalyse the generation of reactive oxygen species (ROS) that

have been associated with direct molecular damage and with the induction of biochemical synthesis pathways. The amount of bio-available transition metals contained in particles has been associated with acute lung inflammation from both combustion and ambient particles (Kleynhans, 2008; Heal *et al.*, 2005).

Heavy metals can accumulate in street dust from atmospheric deposition by sedimentation interception and may affect population health if they reach a level considered to be toxic. Street dust contaminated by heavy metals poses higher health risks to children because of their low tolerance to toxins as well as the inadvertent ingestion of significant quantities of dust (soils) through hand-to-mouth pathways. Pollutant metals are usually non-degradable and there is no known homeostasis mechanism for them. Therefore, any levels of heavy metals will threaten biological life. They may accumulate in the fatty tissues of the body and affect our circulatory system and disrupt the normal functioning of our internal organs, or they may act as cofactors in other diseases (Zheng *at al.*, 2010).

Iron and its components, present as pollutants in the atmosphere, can cause deleterious effects to humans, animals, and materials. Iron and iron oxides are known to produce a benign siderosis, and iron oxides have been implicated as a vehicle for transporting high concentrations of both carcinogens and sulphur dioxide deep into the lungs, thereby enhancing the activity of these pollutants (Gurzau *et al.*, 2003).

Chromium exists as trivalent (chromite) and hexavalent form (chromate), of which Cr(VI) is considered to be more phytotoxic than the Cr(III) form. Chromite (III) appears to be more toxic to fish than Cr(VI), especially salmon, but toxic concentrations for several species range from 0.2-5 µg/ml. Hexavalent chromium is carcinogenic, causing cancer of the respiratory organs in chromate workers chronically exposed to Cr-containing dusts (Alloway and Ayres, 1993).

On a comparative basis, lead is neither as toxic as many other heavy metals nor as bio-available. Lead is generally more omnipresent in the environment and is a cumulative toxin in the mammalian body; consequently, toxic concentrations can accumulate in the bone marrow, where red blood corpuscle formation (haematopoiesis) occurs (Alloway and Ayres, 1993). This is also the only trace metal with a set standard for ambient air in South Africa.

Airborne Hg concentrations are also of great importance since it has been proven to be of great danger to the human nervous system, kidneys and skin (Vassilakos *et al.* 2007). Mercury is quickly becoming of more importance in environmental studies, and a set standard is said to be documented in the near future for South Africa. Table 2.1 provides air quality standards of some trace metals and particulate matter from different organisations.

Table 2.1: Air quality standards

	WHO[a]		WHO for UK[b]		European Comission[c]		NAAQS[d]		DEAT[e]	
$PM_{2.5}$	10 µg.m^{-3}	annual	-	-	25 µg.m^{-3}	annual	15 µg.m^{-3}	annual	-	-
	25 µg.m^{-3}	24-hour	-	-	-	-	35 µg.m^{-3}	24-hour		
PM_{10}	20 µg.m^{-3}	annual	-	-	40 µg.m^{-3}	annual	-	-	40 µg.m^{-3}	annual
	50 µg.m^{-3}	24-hour	-	-	50 µg.m^{-3}	24-hour	150 µg.m^{-3}	24-hour	75 µg.m^{-3}	24-hour
Cd	-	-	5 ng.m^{-3}	annual	5 ng.m^{-3}	annual	-	-	-	-
Pb	-	-	0.5 µg.m^{-3}	annual	0.5 µg.m^{-3}	annual	1.15 µg.m^{-3}	3-moth average	0.5 µg.m^{-3}	annual
	-	-	-	-	-	-	1.5 µg.m^{-3}	Quarterly average	-	-
Mn	-	-	0.15 µg.m^{-3}	annual	-	-	-	-	-	-
Hg	-	-	1 µg.m^{-3}	annual	-	-	-	-	-	-
V	-	-	1 µg.m^{-3}	24-hours	-	-	-	-	-	-
As	-	-	-	-	6 ng.m^{-3}	-	-	-	-	-
Ni	-	-	-	-	20 ng.m^{-3}	-	-	-	-	-

[a] World Health Organization (WHO), 2005
[b] WHO air quality guidelines for Europe, 2000, 2nd ed
[c] European Commission Air Quality Standards, 2010
[d] National Ambient Air Quality Standards (NAAQS)
[e] Department of Environmental Affairs and Tourism (DEAT) – National Environmental Management: Air Quality Act, 2004

2.3.4. Atmospheric trace metal studies in SA

Recent measurements of trace metals in South Africa include a study conducted by Kleynhans (2008) on the spatial and temporal distribution of trace elements in the Vaal Triangle. 24 hour grab samples were collected over three days during the winter season (July 2006) and the summer season (March 2007). From this investigation it was evident that Fe was the most abundant trace element, followed by Zn and Mn. SEM-EDS results indicated that carbonaceous particles were the dominant species present with higher mass percentages during the winter months. This was attributed to possible elevated occurrences of residential biomass burning

and coal combustion to generate heat, especially in the low-income residential areas (Kleynhans, 2008).

Another study conducted in South Africa, also in the Vaal Triangle area, was by Engelbrecht *et al.* (2002). Source contributions from residential coal and low-smoke fuels were compared by utilising CMB modelling. The study showed that excessively high PM pollution levels were regularly reached in the industrialised regions and informal settlements in the Highveld of South Africa. Source sampling of emissions from regular D-grade residential coal, three low-smoke fuels, wood burning, grass burning, diesel exhausts, as well as metallurgical sinter plants was conducted to characterise source compositions. It was found that lead, bromine and organic carbon (OC) were present in high concentrations in the leaded gasoline fuels. PM_{10} soil had a different profile than that of metallurgical dust, which comprised mainly of silicon, aluminium, iron and OC. The metallurgical profiles were variable, but with iron as the abundant species. Manganese was also high in the coarse fraction. Calcium, sulphate, OC and soluble sodium in the coarse fraction were most abundant in the lime profile (Engelbrecht, 2002).

Burger *et al*. (EAC, 2008) did an assessment of trace elements in ambient aerosols in Sasolburg and found that Si was the most abundant trace element. The elemental PM concentrations showed significant seasonal, temporal, and spatial differentiation. In the PM_{10} fraction, e.g. Si, Ca, Fe, Ni, Cu, Zn, concentrations were higher during the winter, while higher levels of Al, Na, Mg, K and Mn were measured during summer (EAC, 2008). In general, stable meteorological conditions, especially present during winter, lead to higher concentrations of trace pollutants.

Kgabi (2006) completed a study on the levels of toxic trace metals in the coarse fraction (PM_{10}) of particulate matter in the North West Province of South Africa near the Rustenburg municipal area. Rustenburg was identified as one of the biggest mineral producing districts in South Africa, producing approximately 68% of the world's chromium ores. The main elements identified in this study listed in order of decreasing concentrations were: Fe, Ca, Al, Mg, Si, Na, K, Zn, Cr, Ni, Cu, Ti, Mn, Pb, and V, with Cr, Ni, Pb, and V being the major species of concern (Kgabi, 2006).

Brunke *et al*. (NACA, 2010) presented a paper on atmospheric mercury measurements at Cape Point. The study indicated that between 1995 and 2009 the

gaseous elemental mercury (GEM) concentrations have decreased by approximately 0.04 $ng.m^{-3}$ yr^{-1}.at Cape Point. A reduction of the same magnitude was indicated by measurements during intermittent ship cruises, implying a homogeneous distribution of GEM concentrations in the Southern Hemisphere (SH) and a 30% reduction of its atmospheric burden (NACA, 2010).

2.4 Conclusion

From the preceding discussion in Chapter 2 it is evident that the study of aerosols and trace metals present in the atmosphere is both challenging and important. The health and environmental effects associated with aerosols and trace metals are well documented in literature. Only a few studies on the presence and concentrations of trace metals in the South African atmosphere have been conducted up until now. In this study, atmospheric trace metals were collected at Marikana in the North West Province of South Africa, which is part of the highly industrialised western igneous Bushveld Complex. The presence of 27 trace species was analysed, including Be, B, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Pd, Cd, Ba, Pt, Au, Hg, Tl, Pb and U. The importance of these trace species, as well as their relevance in atmospheric chemistry, directly stems from the literature survey completed. A detailed site description and particulars on the procedures and instrumentation utilised in this study will be discussed in Chapter 3.

~CHAPTER 3~

Experimental

In this chapter, the selected sampling site is described, relevant sampling procedures are provided and the analytical techniques used in this study are discussed.

3.1 Reagents and materials

The reagents and standards used were analytical grade (AR) chemicals obtained from different suppliers and used without further purification or processing. Table 3.1 gives a summary of reagents and materials utilised. Deionised water (18.2 MΩ) was used for all dilutions.

Table 3.1: Reagents and materials utilised in this study

Reagents	**Supplier**
Concentrated Nitric Acid (HNO_3)	CJ CHEM
Concentrated Hydrochloric Acid (HCl)	Rochelle Chemicals
Standards for ICP analysis	Sigma Aldrich
Materials	
Teflon filters, 2 micrometer, 46.2 mm. diameter	Whatman Inc.
100 ml. Volumetric flasks A CERT P/S	LASEC
Pipette volumetric A CERT	LASEC
Magnetic stirrers	FMH Instruments

3.2 Site description and selection

The samples were collected at Marikana, which is a small village situated approximately 35 kilometres east of Rustenburg, in the North West Province of South Africa. The atmospheric measurement station is operated in cooperation between the North-West University (NWU) and the University of Helsinki (UH) and is described by Laakso *et al.* (2008). The actual measurements were taken inside the palisade area of this measurement station, which is shown in Figure 3.1. Taking measurements at this station facilitated the use of supporting data (e.g. meteorological parameters), required later for the elucidation of the observed trace metal data. The site was situated on the property of the Marikana Municipal clinic, which provided access to electrical supply, as well as ensured the safe keeping of equipment.

Figure 3.1: Photograph of the measurement station in Marikana

Geologically, the Marikana area forms part of the western Bushveld Igneous Complex (BIC). The western BIC is well known as a highly industrialised area with numerous mining and metallurgical operations. Some of the mining/metallurgical

operations in this area include platinum mining and metallurgical operations (e.g. Anglo Platinum, Impala Platinum, Lonmin Platinum), associated base metal refineries of the same companies, chromite mining and ferrochrome smelting operations (e.g. Xstrata/Merafe Alloys, Hernic Ferrochrome, International Ferrometals, Samancor Chrome), Ferro-Vanadium and Vanadium pentoxide production (Xstrata Rhovan operations), and Omnia Phosphates. Apart from these obvious large point sources, other potential sources of air pollution from these operations include windblown dust from slimes/tailings dams, landfills (RLM AQMP, 2005) and hall roads. Figure 3.2 (a) shows a Google Earth image, covering the area between Marikana (see bottom right of picture) and Rustenburg (see middle left of picture). Figure 3.2 (b) shows a Google Earth image, covering the area between Marikana (see bottom left of picture) and Brits (see top right of picture). The extensive mining/metallurgical operations in this area are evident from this picture. A similar situation exists to the east of Marikana, between Marikana and Brits approximately 38km to the east.

Due to the lure of employment in the above-mentioned sectors, the western BIC is frequented by formal (larger cities and towns, such as Rustenburg and Brits), semi-formal (R&D housing developments, mostly with some form of informal housing additions by the occupants) and informal settlements. Incomplete combustion of coal and wood in ineffective appliances for house-hold heating and cooking are common occurrences in the informal settlement sector.

(a)

(b)

Figure 3.2: Rustenburg west of Marikana (a) and Brits east of Marikana (b)

The Pretoria-Johannesburg mega-city conurbation (with more than 10 million people living in the Gauteng province) may also influence the area, since Pretoria is

approximately 86 km to the east and Johannesburg is approximately 141 km south-east along the N4 highway next to the measurement site (Figure 3.3).

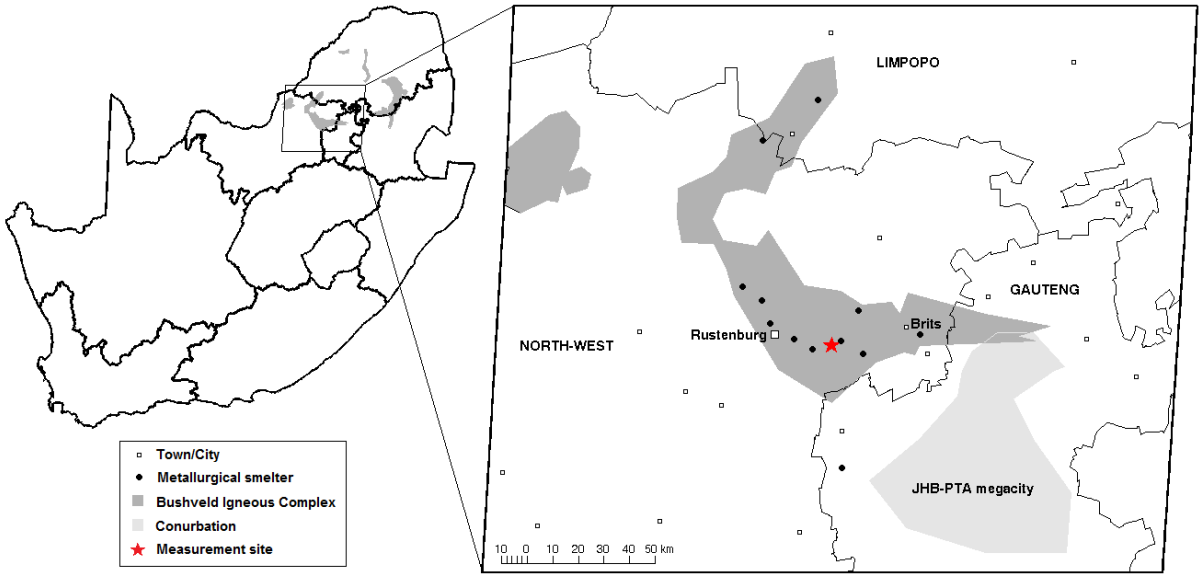

Figure 3.3: Map of Marikana and surrounding towns

Traffic volumes in the area are relatively high, due to the large amounts of raw materials being transported for mining and metallurgical operations by road. Due to an ineffective public transport system in South Africa, private vehicle use is also high. Various tarred and un-tarred roads cross the western BIC, and the N4 highway between Pretoria and Rustenburg passes the measurement site approximately 7.5 km to the south.

In the areas not affected by industrial activities or human settlements, farming activities are still practiced. Rainfall in the area is relatively low and it is regarded as a semi-arid region. Most of the farming activities are associated with animal grazing, cash crop production (e.g. maze) or game farming. Some citrus and vegetable cultivation also takes place, because the area is almost frost free during winter.

Although the site is almost completely surrounded by mining/metallurgical operations, human settlements, traffic-related emissions and farming activities, a

less anthropogenically affected area occurs towards the south-west of the sampling site in the Magaliesberg.

3.3 Sampling

3.3.1. MiniVol™ portable air sampler

The MiniVol™ portable air sampler, manufactured and supplied by Airmetrics, is generally used for air quality assessments. It is used for sampling of ambient atmospheric particulate matter and non-reactive gases. The patented low flow technology used in the MiniVol™ was developed in cooperation by the US Environmental Protection Agency (US EPA) and the Lane Regional Air Pollution Authority in an effort to address the need for portable air pollution measurement technology. The MiniVol™ sampler is advantageous due to its portability and it is also relatively inexpensive compared to permanent monitoring instrumentation (Kingham *et al*., 2006). Consequently, MiniVol™ samplers are flexible to move or rotate between monitoring sites, can increase the number of monitoring sites in order to improve spatial distribution, and are also capable of measuring contaminant concentrations at almost any location (Baldauf *et al*., 2001).

Figure 3.4: The MiniVol™ portable atmospheric samplers used in this study

The MiniVol™ consists, in essence, of a pump that is controlled by a programmable timer. An elapsed time totaliser is connected in parallel with the pump to record the total pump operation time in hours. The sampler is equipped to operate from either AC or DC power sources. In the DC mode, the sampler operates from a battery pack, making the selection of a sampling site independent of network power supply. The sampler is capable of operating for up to 24 sampling hours on a single charge from a charged battery pack. In the AC mode, the battery pack is connected to a power line and connected to the sampler unit. This configuration charges the battery while using AC power (Airmetrics, 2001).

In the particulate matter sampling mode, air flows through an impactor (particle size selector) and then through a filter medium. Particle size separation is achieved by impactation. The appropriate flow-rate through the impactor is critical in the collection of a specific particle size. The volumetric flow-rate for the MiniVol™ sampler must be 5 L/min. Impactors available for MiniVol™ samplers either have a 10 micron particle cut-off (PM_{10}) or a 2.5 particle micron cut-off ($PM_{2.5}$). Operating the sampler without an impactor allows for the collection of total suspended particulate matter (TSP). The inlet tube downstream from the filter directs the air to a twin cylinder diaphragm pump, after which the air is forced through a standard flow meter to be exhausted into the atmosphere (Airmetrics, 2001).

3.3.2. Procedure

$PM_{2.5}$ and PM_{10} particulate matter samples were collected with MiniVol™ samplers on Teflon® filters. The mini-volume samplers were programmed to filter air at a sampling rate of 5 L/min for 12 hours/day for a period of six days. This implies that each sample contained particulate matter collected for 72 hours. The starting time for sampling was altered every six days in order to obtain diurnal samples. Daytime sampling commenced at 6 am, while night time sampling started at 6 pm. Sampling was performed for one year from November 2008 until October 2009.

3.3.3. Filter handling and storage

The Teflon® filters were carefully inspected prior to sampling to ensure that it was not damaged. Filters were handled with latex gloves and tweezers throughout the investigation, and extra care was taken not to damage or contaminate the filters. The filters were exchanged in the MiniVol™ samplers after each 72-hour sampling period and stored in airtight Petri dishes in a freezer. Samples were removed from the freezer 24 hours before analyses.

3.4 Analyses

Trace metal analyses of the samples were carried out on an inductively coupled plasma mass spectrometer (ICP-MS). In addition to ICP-MS analysis, surface analysis of the samples collected on the filters was also conducted. A scanning electron microscope coupled to an energy dispersive x-ray analysis spectrometer (SEM-EDS) was used. No sample preparation was required for the SEM-EDS analysis, while hot acid extraction of the collected samples from the filters prior to ICP-MS analysis was performed.

3.4.1. Filter preparation

The filters were divided into two equal parts. The one fraction of the filter was used for trace metal analysis, while the other part was stored in the freezer for ionic species analysis. The ionic species analysis is for another study. Partition was achieved by utilising a stainless steel punch, which was specifically designed for this investigation by the instrument maker at the Potchefstroom Campus of the North-West University. The punch stencilled a circle, 36 mm in diameter, from the filter, which was simultaneously split into two halves. A small piece of the remaining rim of each filter was used for SEM-EDS analysis. Figure 3.5 (a) shows the punch, while Figure 3.5 (b) shows a punched out filter.


(a)

(b)

Figure 3.5: (a) Stainless steel punch used for dividing filter (b) Punched out filter with remaining rim

3.4.2. Hot acid extraction

As mentioned previously, collected samples were extracted from the filters for ICP-MS analysis by means of hot acid extraction (Mouli, 2006). The filter was placed in a 100 mL Erlenmeyer flask that contained a mixture of 20 mL concentrated HNO_3 and 40 mL deionised water. The solution was brought to boiling point and kept at this temperature for approximately 5 minutes. 5 mL concentrated HCl was added to the solution, after which the solution was refluxed for 3 hours while stirring it continuously. The solution was transferred into a 100 mL volumetric flask by decantation. The filter material and Erlenmeyer flask was washed twice with deionised water to ensure that all extracted material was collected. The volumetric flask was filled with deionised water up to the 100 ml mark and was stored in a fridge for analysis.

3.4.3. ICP-MS

ICP-MS analysis was conducted with an Agilent 7500c series model. To calculate the concentrations of the metals in ambient particulate matter, the US EPA compendium method IO-3.5 was used.

The Agilent 7500c is the 4^{th} and latest model in the 7500 series and includes a unique Octopole Reaction System (ORS) that offers new analytical possibilities for

ICP-MS. The ORS features an off-axis reaction cell, which effectively removes spectral interferences in even the most complex sample matrices (Analis, 2010).

ICP-MS is a powerful technique for multi-elemental analysis at very low concentrations in sample solutions. A conventional ICP source is used to produce the primary ions, which are then analysed in a quadrupole mass spectrometer (used in this study) in a mass range up to 300 amu. An interface allows the coupling of the ICP source at atmospheric pressure with the mass spectrometer, which is under high vacuum. This consists of a water-cooled outer sampling cone, which is positioned in close proximity to the plasma source. The interface is made from nickel due to its high thermal conductivity, relative resistance to corrosion, and robust nature (see Figure 3.6) (Barker, 1999).

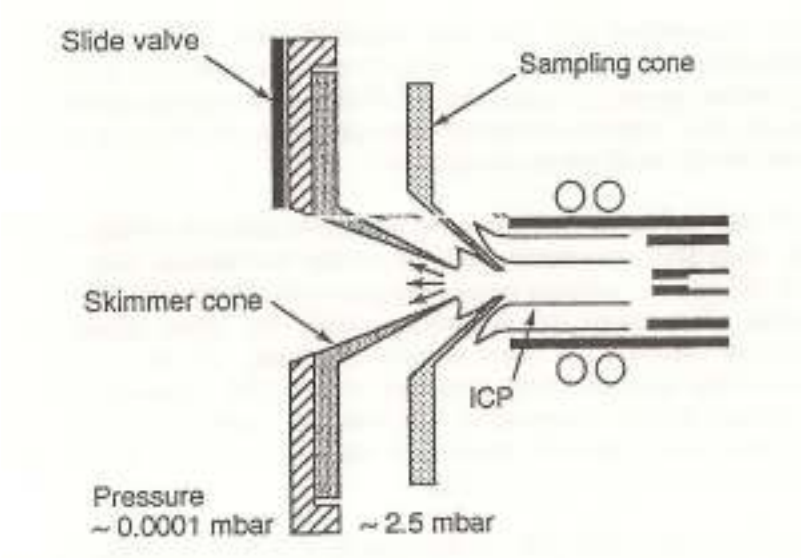

Figure 3.6: Schematic representation of inductively coupled plasma-mass spectrometer interface (Barker, 1999)

This source consists of a flame in which a solution of the sample is introduced as an aerosol mixed with the carrier gas/plasma gas (argon) (Enke, 2001; De Hoffmann *et al*., 1996). The gas that sustains the plasma is initially made electrically conductive by Tesla sparks before a self-sustained plasma results. A coil that surrounds this plasma, once energised with radio frequency (RF) power, induces an electromagnetic field within the torch. This field inductively heats the

formed plasma to temperatures exceeding 10 000K. After penetrating the hot core of the plasma, the sample (gas or aerosol) is desolvated, atomised and ionised. The ionisations attain 100% yield with a majority of singly charged ions, which allows the coupling of this source with a mass spectrometer (De Hoffmann *et al*., 1996).

The transmitted ions are then detected with a channel electron multiplier. Extensive use of computer control and optimised geometry allows for a full elemental analysis within one scan, with measurement times of approximately 10 s per element, even for concentrations as low as ppb levels (Barker, 1999).

10 mL of the extraction solution was used for ICP-MS analysis. The following 27 trace metal species were analysed: Be, B, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Pd, Cd, Ba, Pt, Au, Hg, Tl, Pb and U. The RF power was 1500 W, sample depth was 8 mm and the flow rate of the carrier gas was 1.05 L/min.

3.4.4. SEM-EDS analysis

Scanning electron microscopy (SEM) analysis is used for the examination of the microstructural characteristics of solid objects (Goldstein *et al*., 1981). It provides clear and detailed topographical details of surfaces and is capable to detect surface potential distributions, subsurface conductivity, surface luminescence, surface composition and crystallography (Hayat, 1974).

Surface analysis of sampled filters was performed with an FEI Quanta 2000 scanning electron microscope (SEM) with an integrated Oxford Instruments INCA x-sight 400 EDS microanalysis system. An electron beam is passed over the surface of a sample to cause energy changes in the surface layer. These changes are detected and analysed to give information, which can be displayed in a variety of ways. One of these is an image of the sample produced by several signals resulting from the interaction and detected by appropriate detectors. The signals include low-energy secondary emission, Auger-electron generation, characteristic X-ray emission, *bremmstrahlung*, backscattered electron emission and cathode luminescence (van Zyl, 2007).

X-ray microanalysis yields information about the elemental composition of a sample. The interaction of a high-energy electron with an atom results in the ejection of an electron from an inner shell. When an electron from an outer shell fills the vacancy, a change in energy in the form of an emitted X-ray characteristic of the electronic structure of the atom of the element occurs. A spectrometer collects the characteristic X-rays and counts and sorts these on the basis of energy, a technique known as energy dispersive spectrometry (EDS). The resulting spectrum displays the intensity of X-rays on the vertical axis as a function of their photon energy value ($h\nu$) on the horizontal axis. SEM-EDS analysis gives the mass percentage of the element being analysed in relation to other elements present (van Zyl, 2007).

In this study, SEM-EDS analysis was performed for verification of ICP-MS results. The analysis was conducted under vacuum, with a voltage of 15 kV, and a working distance of 10.2 mm. EDS analysis was performed at a 2400x enlargement, while micrographs were obtained at a 1200x enlargement. Micrographs clearly showed the particle size difference between $PM_{2.5}$ and PM_{10}. Unique surface characteristics of particles could be identified, e.g. rounded particles that indicated the origin from the off-gas of high temperature processes.

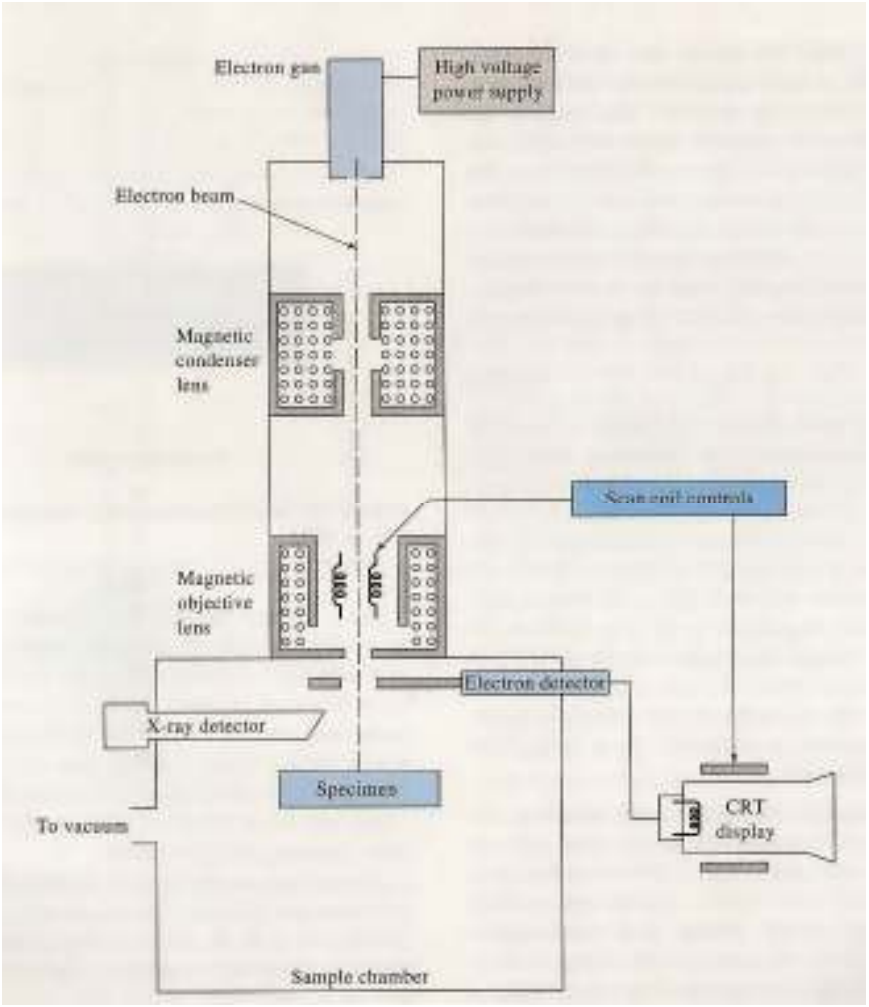

Figure 3.7: Schematic representation of an SEM with both electron and X-ray detection (Holler, 2007)

3.5 Factor analysis

Factor analysis is a branch of statistical science. Due to its development and general use in psychology, the analysis is often mistakenly considered as psychological theory. Initially the method was applied to provide theories of human ability and behaviour. Among the more famous of such theories are those anticipated by Spearman, Burt, Kelley, Thurstone, Holzinger, and Tomson (Harman, 1976).

The factors of the factor analytic-model are basis vectors of the unitary vector space of observed variables (Mulaik, 2010). Furthermore, it is a technique that falls in the same category of classic topics in statistics such as correlation, regression and

multivariate analysis, which are also well developed (Mulaik, 2010). The primary concern of factor analysis is the resolution of a set of variables linearly in terms of categories or "factors." This resolution can be accomplished by the analysis of the correlations among the variables. A suitable solution will yield factors that express all the essential information of the original set of variables and explain the underlying behaviour of the data. Therefore, the chief aim is to achieve scientific parsimony or economy of description (Harman, 1976).

Factor analysis is frequently used in environmental pollution studies to simplify large and complex datasets, with the aim to identify pollution sources and their elemental composition (Mouli *et al*., 2006; Vallius *et al*., 2003). Numerous examples exist of studies performed on collected aerosols and their sources making use of factor analysis. Al-Momani *et al.* (2005) used factor analysis with Varimax rotation to determine pollutant sources in daily collected aerosols in central Jordan. Factor analysis successfully identified four major groups of sources. The same analysis was used by Mouli *et al.* (2006) for a study on trace elemental composition of atmospheric aerosols at a semi-arid urban site. Kulkarni *et al.* (2007) made use of principal component factor analysis (PCFA) with Varimax rotation to quantitatively determine $PM_{2.5}$ emission sources with the trace elements. The PFCA successfully revealed six different groups of emission sources.

Factor analysis is not a method for discovering complete structural theories about a dataset. The more considerable contributions of factor analysis have been made when researchers postulated the existence of certain factors, carefully selected variables from the dataset that would isolate their existence, and then proceeded to factor-analyse in such a way as to reveal these factors as clearly as possible. In other words, factor analysis has been more advantageously used when the researcher knew what he or she was looking for (Mulaik, 2010).

3.6 Supporting data

Since samples were collected at an atmospheric monitoring station equipped with various instruments, trace metal results could be correlated and compared to other atmospheric measurements. These measurements included meteorological data, radiation measurements, inorganic gaseous species concentrations as well as physical and chemical properties of particles. These data assisted in the interpretation and understanding of results obtained. The complete list of instrumentation at the measurement station is:

- Meteorological data including wind direction, wind speed, temperature, and humidity.
- Differential temperature measured at two heights in order to obtain an indication of the stability/instability in the atmosphere.
- PAR – Photo Active Radiation.
- Trace gasses – O_3, NO_x, SO_2 and CO.
- Multi Angle Absorption Photometer for black carbon determination
- AIS air ionisation spectrometer, as well as DMPS deferential mobility particle sizer, which measures secondary particle formation from 10 nm to 1000 nm.
- Total PM_{10} concentration.

~CHAPTER 4~

Results and discussion

In this chapter, the monthly and annual trace metals concentrations measured during the sampling period are compared to ambient air quality standards. The temporal variability and size distribution of the trace metals, as well as the surface analysis of the sampled filters are also discussed. Trace metals with unique characteristics are correlated to each other to recognise likely sources. In a further attempt to identify possible sources of trace metals, explorative factor analysis was performed and trace metals concentrations were also correlated to other parameters measured at the monitoring site.

4.1 Introduction

Results presented in this chapter are mainly ICP-MS analytical results obtained for samples extracted from filters on which $PM_{2.5}$ and PM_{10} particles were collected. During each analysis, the 27 metals described in Chapter 3 were determined. Metal concentrations that were below the detection limit of the ICP-MS were regarded to have concentrations of half the detection limit of the specific metal species considered. This is a precautionary assumption that is frequently used in health-related environmental studies (Polissar *et al.*, 1998).

4.2 Comparison to Ambient Air Quality Standards

The annual average-, three-monthly average- and 72-hours concentrations of all the metals considered with their relevant standards are listed in Table 4.1. Pd, Hg, Tl and U were below the detection limit of the analytical technique for the entire year.

The concentrations of the trace metal species Ca, Co, As, Cd, Ba and Au were only 25% or less of the time during the sampling period above the detection limit. Concentrations reported for these metals (Pd, Hg, Tl, U Ca, Co, As, Cd, Ba, Au) are therefore likely to be an over-estimate due to the precautionary assumption described in Paragraph 4.1. These metals (highlighted in Table 4.1) are therefore not discussed further due to the uncertainties associated with their concentrations.

Table 4.1 Annual average-, three-month average- and 72-hour concentrations of metal species detected

Metal	Annual Standard* / µg.m^{-3}	Annual concentration value / µg.m^{-3}	Exceeded	3-Month Standard / µg.m^{-3}	Max 3-month concentration value / µg.m^{-3}	Number of exceedances	24-Hour Standard / µg.m^{-3}	Max 72-hour concentration value/ µg.m^{-3}	Number of actual exceedances
Be	-	0.015	-	-	0.021	-	-	0.067	-
B	-	1.299	-	-	1.883	-	-	14.530	-
Na	-	1.410	-	-	2.014	-	-	7.226	-
Mg	-	2.036	-	-	2.779	-	-	13.572	-
Al	-	1.277	-	-	1.983	-	-	2.859	-
K	-	0.682	-	-	1.119	-	-	3.252	-
Ca	-	1.082	-	-	1.375	-	-	4.527	-
Ti	-	0.120	-	-	0.279	-	-	0.449	-
V	-	0.044	-	-	0.084	-	1[b]	0.395	None
Cr	-	0.238	-	-	0.683	-	-	1.257	-
Mn	0.15[b]	0.058	None	-	0.102	-	-	0.162	-
Fe	-	2.543	-	-	4.694	-	-	19.006	-
Co	-	0.135	-	-	0.298	-	-	2.420	-
Ni	0.02 [c]	0.328	Yes	-	0.376	-	-	1.920	-
Cu	-	0.183	-	-	0.281	-	-	0.804	-
Zn	-	0.494	-	-	0.640	-	-	1.481	-
As	0.006 [c]	0.256	Yes	-	0.333	-	-	1.077	-
Se	-	0.583	-	-	0.741	-	-	2.393	-
Pd	-	0.410	-	-	0.521	-	-	1.684	-
Cd	0.005[b],[c]	0.029	None	-	0.037	-	-	0.159	-
Ba	-	0.139	-	-	0.174	-	-	0.727	--
Pt	-	0.345	-	-	0.461	-	-	1.585	-
Au	-	0.383	-	-	0.482	-	-	1.671	-
Hg	1[b]	0.553		-	0.703	-	-	2.270	-
Tl	-	0.273	-	-	0.346	-	-	1.120	-
Pb	0.5[b],[c],[e]	0.084	None	0.15[d]	0.141	None	-	0.368	-
U	-	0.473	-	-	0.601	-	-	1.942	-

[a] World Health Organization (WHO), 2005
[b] WHO air quality guidelines for Europe, 2000, 2nd ed.
[c] European Commission Air Quality Standards, 2010
[d] National Ambient Air Quality Standards (NAAQS)
[e] Department of Environmental Affairs and Tourism (DEAT) – National Environmental Management: Air Quality Act, 2004

It is evident form Table 4.1 that there are currently only ambient air quality standards for seven trace metal species listed by the World Health Organization (WHO), the European Commission, the United States Environmental Protection Agency (US EPA), the National Ambient Air Quality Standards (NAAQS) and the South African Department of Environmental Affairs (DEA). Comparison of the annual average-, three-month average- and 72-hour concentrations to the appropriate standards listed in Table 2.1 indicates that only As and Ni exceeded an existing standard set by the European Commission of Air Quality Standards during the sampling period. The 0.256 $\mu g.m^{-3}$ annual concentration exceeded the 0.006 $\mu g.m^{-3}$ annual standard. This result, however, has to be brought into perspective since As was detectable less than 25% of the duration of the sampling period as mentioned previously. The annual average concentration of 0.313 $\mu g.m^{-3}$ measured for Ni exceeded the set standard of 0.02 $\mu g.m^{-3}$ by an order of magnitude. This can possibly be attributed to the metallurgical activities, especially those associated with base metal refining, in the region as described in Paragraph 2.3.2. This will be explored further in subsequent discussions later in this chapter.

It is important to note that Pb, which is the only metal species that has a standard prescribed by the South African DEA, did not exceed any of the standards. Deleading of petrol in South Africa could be considered to be partially responsible for these low concentrations. It is also significant to refer to the concentrations of Hg. Measurement of the ambient Hg concentrations is receiving increasing attention in South Africa and it is likely that a standard for Hg levels will be prescribed in the near future. As mentioned previously, Hg was below the detection limit of the analytical instrument for the entire sampling period.

4.3 Temporal variations

4.3.1 Seasonal trends

Since measurements were conducted for 12 consecutive months, it was possible to make some deductions with regard to seasonal variations. In Figures 4.1 and 4.2 the

monthly total trace metal concentrations in the PM_{10} and $PM_{2.5}$ fractions are shown, respectively.

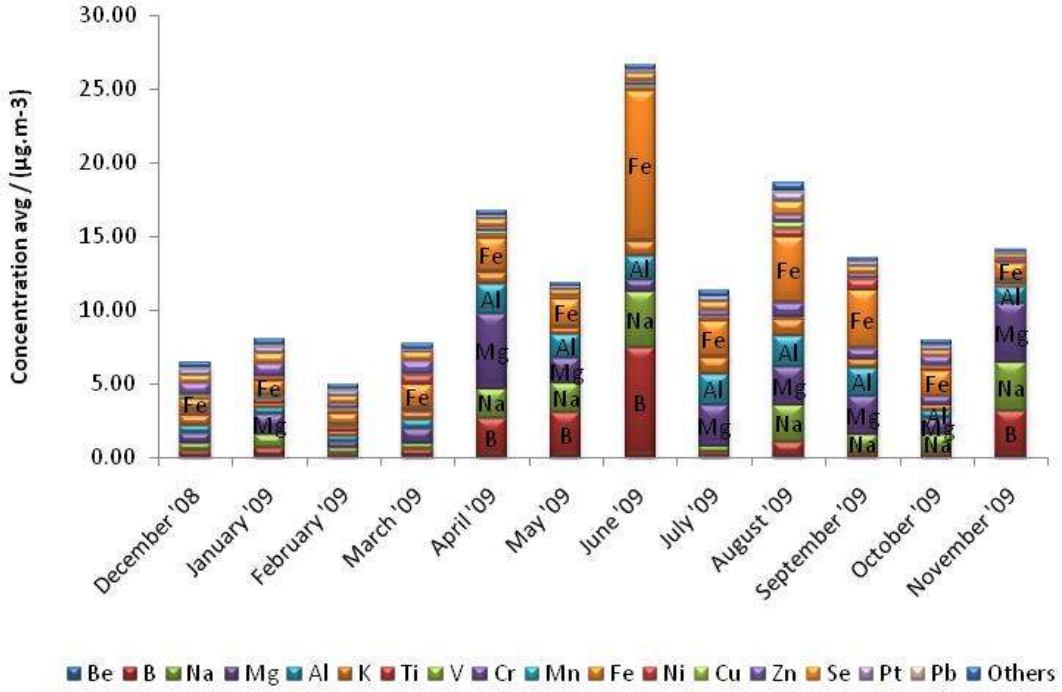

Figure 4.1: Monthly total trace metal concentration in the PM_{10} fraction

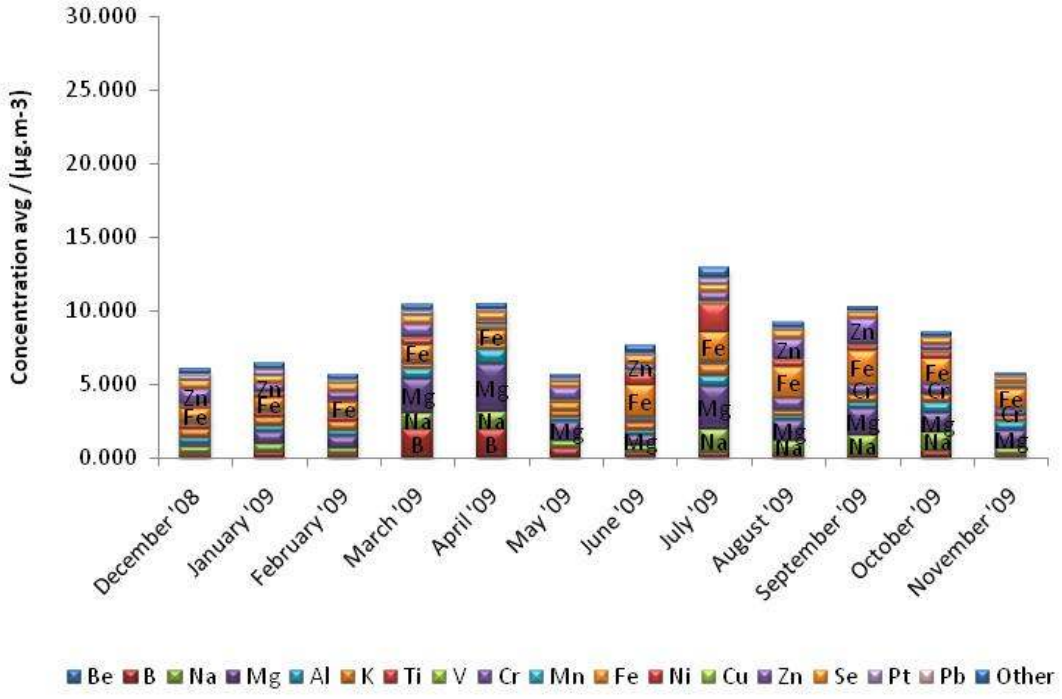

Figure 4.2: Monthly total trace metal concentration in the $PM_{2.5}$ fraction

The total trace metal concentrations in the PM_{10} fraction peaked during the months of April to September, with the highest level recorded during June. This can at least partially be ascribed to seasonal variations in meteorological parameters. In Figure 4.3, precipitation patterns for the corresponding sampling period are given. Although not perfectly correlated, there seems to be a clear relationship between periods of precipitation and low total atmospheric PM_{10} trace metal concentrations. In the period December 2008 to mid March 2009, frequent rain events occurred resulting in significant atmospheric removal of PM_{10} particles. This relatively wet period was followed by a dry period from the beginning of April 2009 to the middle of October 2009. Rain events again increased from October 2009 up until the end of the sampling period in November 2009.

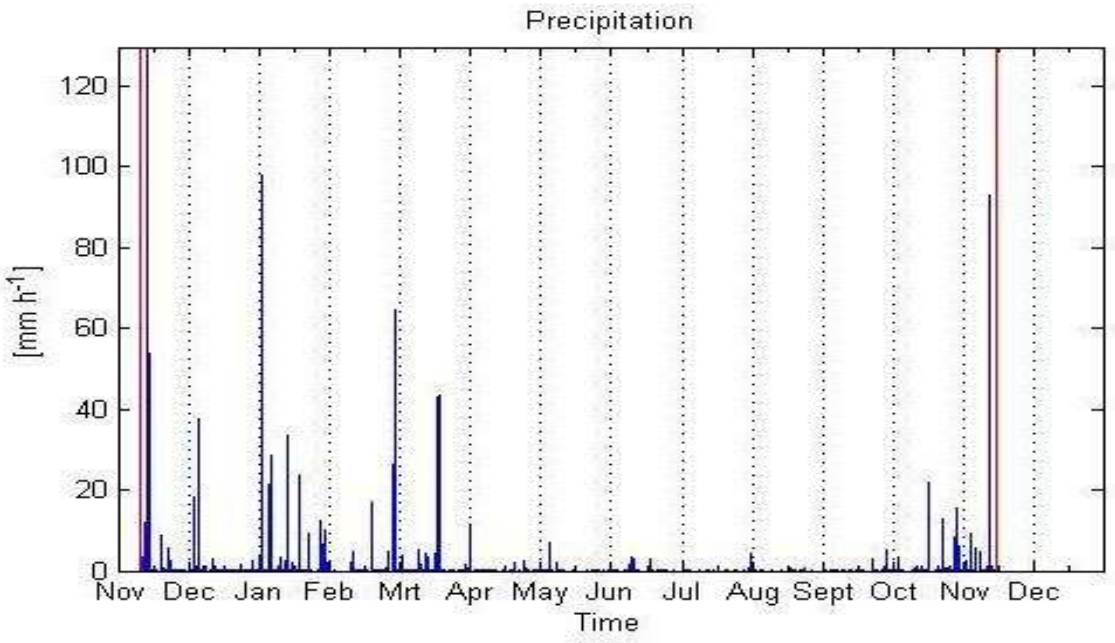

Figure 4.3: Precipitation events during the sampling period

In Figure 4.4, the average monthly wind speeds is presented. The lowest wind speeds were measured from the beginning of May 2009 up until the end of August 2009. This seasonal wind pattern was expected, since it is well known that more stable tropospheric conditions occur during the winter months, while more unstable conditions are associated with summer. Considering strict mono-variance conditions, i.e. only wind variations, it can be expected that higher wind velocities would lead to

higher PM_{10} trace metal concentrations, especially of dust from crustal species (Al-Momani, 2005; Krzemiński-Flowers, 2006; Rastogi and Sarin, 2009). Considering the presented precipitation and wind velocity data, it seems that wet removal processes of atmospheric PM_{10} trace metals are more significant than wind generation thereof. The wind speeds almost followed an inverse pattern compared to the precipitation. This is also illustrated in Figure 4.5 where the total PM_{10} concentrations are correlated to the wind speed measured during the sampling period. The results show that PM_{10} concentrations were the highest with lower wind speeds prevailing.

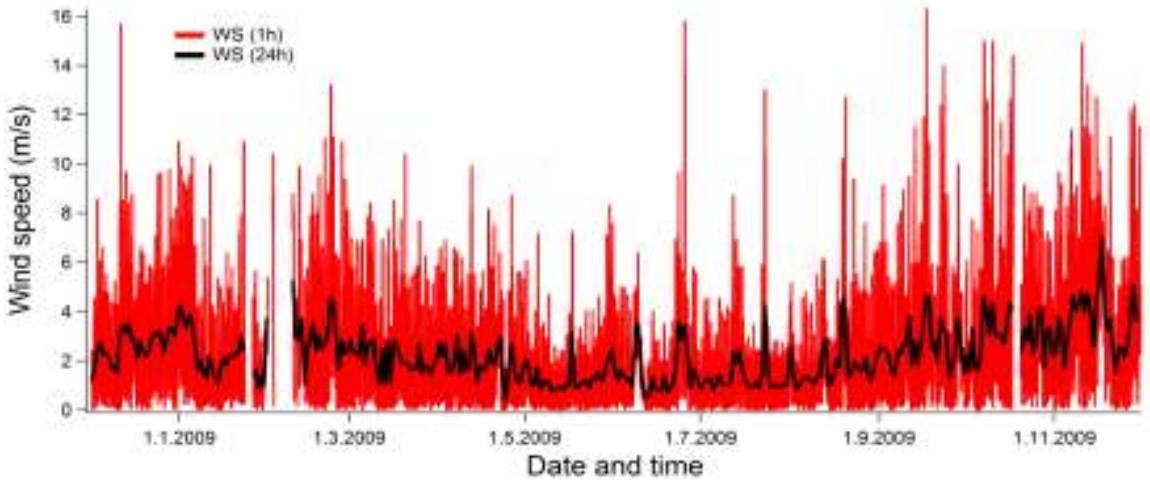

Figure 4.4: Total wind velocities measured for the entire year of sampling

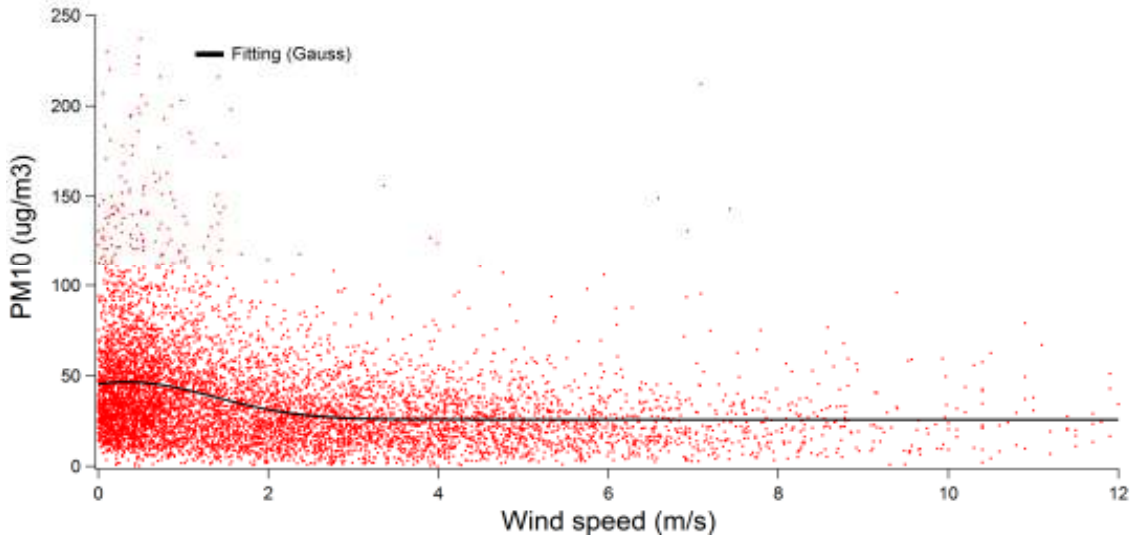

Figure 4.5: Correlation of total PM_{10} concentrations with wind speed measured during the sampling period

A less significant seasonal trend is observed for the trace metal concentrations in the $PM_{2.5}$ fraction. The highest concentrations were determined during the winter month of July. Compared to the chemical composition of atmospheric PM_{10}, a larger fraction of $PM_{2.5}$ usually consists of species associated with chemical processes (natural or anthropogenic). PM_{10} is, for instance, usually strongly associated with windblown dust of crustal species. This implies that dust suppression in the wetter months has a significant influence on PM_{10} concentrations in the atmosphere. Fractionally a larger portion of the $PM_{2.5}$ composition will originate from processes such as biomass burning, fossil fuel combustion, pyrometallurgical processes and secondary particle formation. Due to the nature of $PM_{2.5}$ sources, smaller particle concentrations are replenished faster than larger particles after wash-out events. Smaller particles also have a longer lifetime in the atmosphere prior to deposition than larger aerosols. In Figure 4.6 and Figure 4.7, normalised graphs with a breakdown of the composition of trace metal species present in PM_{10} and $PM_{2.5}$ are shown, respectively. From these figures no obvious seasonal variations in the trace metals composition in both particle size fractions are observed. Species that were dominant in both fractions were Fe, Mg, Al, Na and B. It also seems that Zn and Ni are more prevalent in the $PM_{2.5}$ fraction. This size resolved distribution, together with the possible sources of these species, will be discussed further in paragraph 4.7.

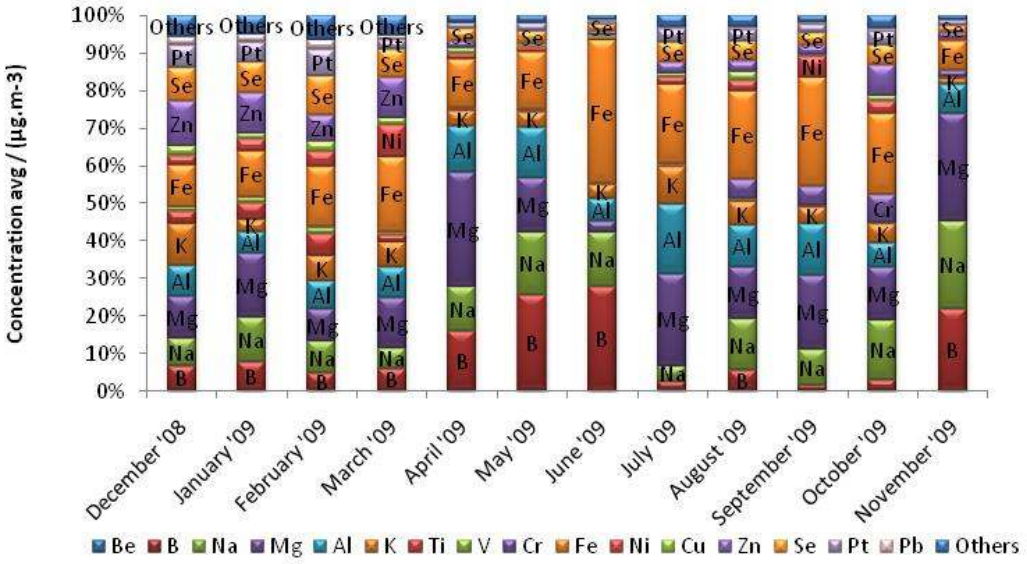

Figure 4.6: Normalised trace metal distribution in the PM_{10} size fraction

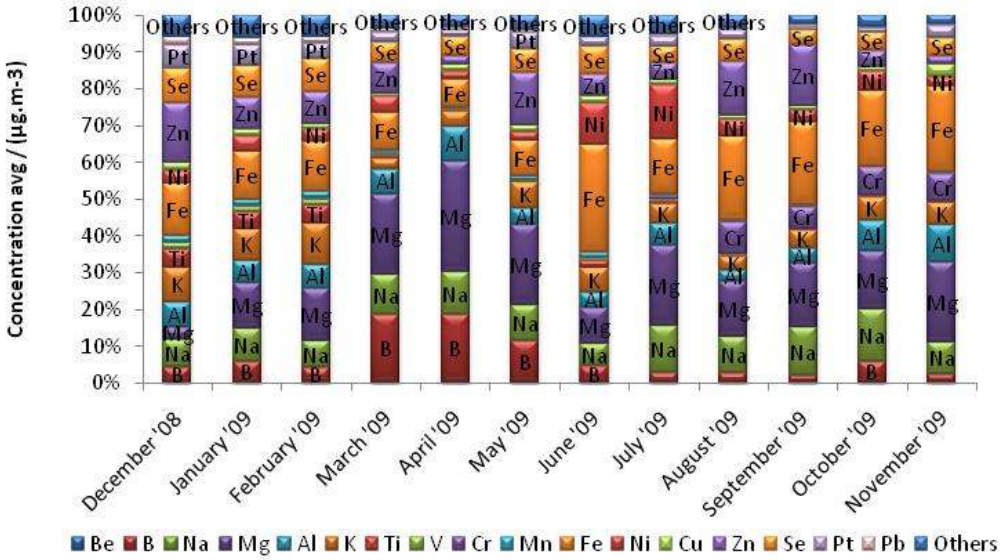

Figure 4.7: Normalised trace metal distribution in the $PM_{2.5}$ size fraction

4.3.2 Diurnal variations

Figure 4.8 (a) and (b) represent the total fractional trace metal concentration for PM_{10} and $PM_{2.5}$ during day- and night time respectively. From this data it is apparent that the total trace metal concentrations were the highest in the daytime for PM_{10}, while the highest $PM_{2.5}$ total trace metal concentrations were prevalent during night time.

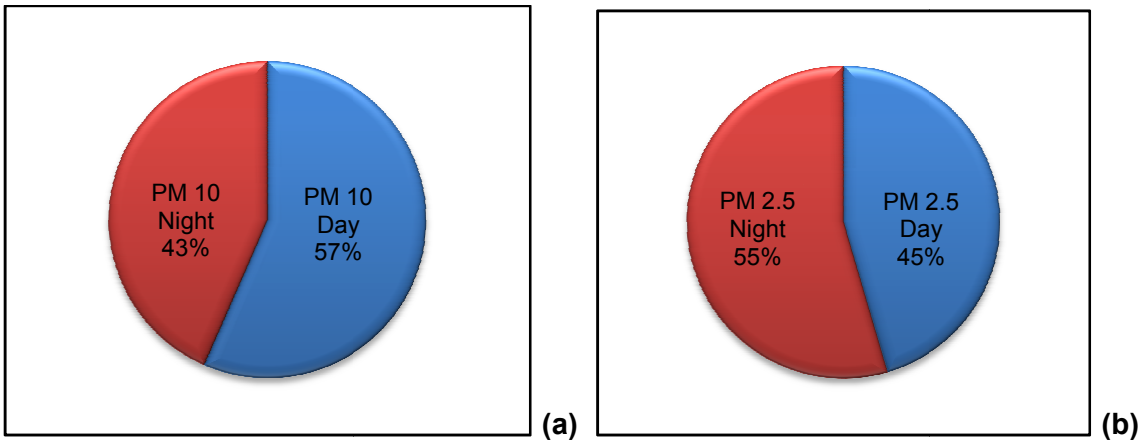

Figure 4.8 (a) and (b): Total trace metal concentrations for day- and night time for PM_{10} and $PM_{2.5}$ respectively

Considering the fact that atmospheric PM_{10} load is expected to be mainly generated by crustal wind blow dust, the daytime peak of total PM_{10} trace metal concentration can be explained by the fact that daytime wind speed (WS) was significantly higher than night time throughout the one-year sampling period. This is illustrated in Figure 4.9.

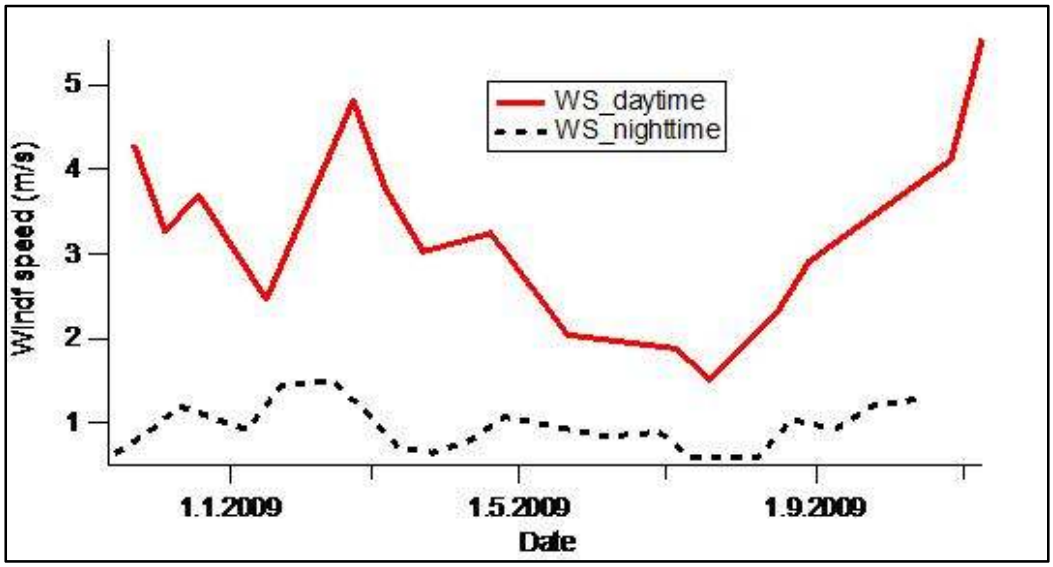

Figure 4.9: Daytime wind speed (WS) vs. night time winds peed (WS)

The night time peak of total $PM_{2.5}$ trace metal concentrations can possibly be explained by the formation of low level inversion layers trapping smaller atmospheric particles. The Highveld of South Africa is well known for its cold and dry winters, with associated formation of strong low level inversion layers during the night time and early morning. These inversion layers usually dissipate in the mid morning, resulting in the dispersal of PM. The effect (trapping of PM by the inversion layer) is expected to be stronger on smaller particles, since they are more persistent in the atmosphere than larger particles. Additionally, household combustion for space heating and cooking occurs more during night time and early mornings, especially during winter when the low level inversion layers are still prevalent.

Thus far, PM_{10} was defined as particles smaller than 10 µm, which also included the fraction of particles smaller than 2.5 µm i.e. $PM_{2.5}$. In Figure 4.10 (a) and (b) the total trace metal concentrations determined for day and night are separated into the $PM_{10-2.5}$ and $PM_{2.5}$ fractions. $PM_{10-2.5}$ values were calculated by subtracting the $PM_{2.5}$ total trace metal concentrations from the PM_{10} total trace metal concentrations. From

these figures it is evident that $PM_{2.5}$ is more persistent during night time. This implies that the previously reported PM_{10} night time trace metal concentrations consisted almost exclusively (96%) of trace metals present in the $PM_{2.5}$ fraction.

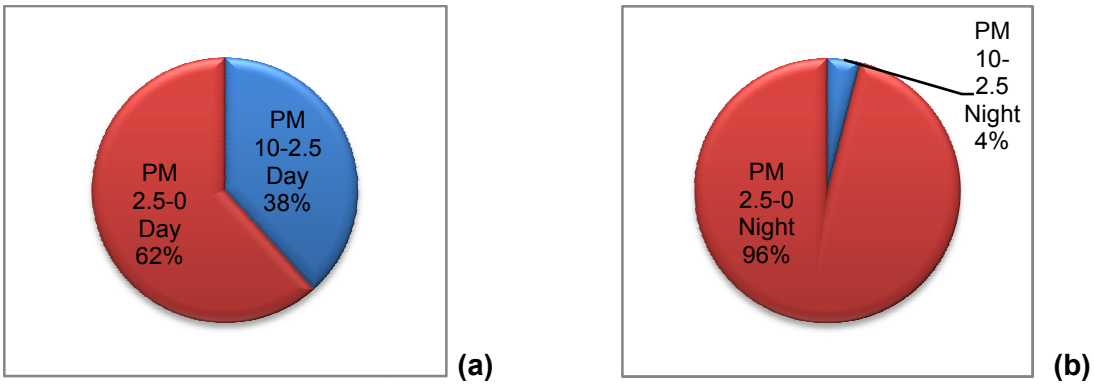

Figure 4.10: Total trace metal concentrations for day and night separated into the $PM_{10-2.5}$ and $PM_{2.5}$ fractions

4.4 Size distribution of trace metals

In paragraph 4.3.2, the total trace metal concentrations were divided into the $PM_{10-2.5}$ and $PM_{2.5}$ fractions for day and night respectively (Figure 4.9). In Figure 4.11 the total trace metal contributions (day and night combined) of the $PM_{10-2.5}$ and $PM_{2.5}$ fractions are shown. 79% of the total trace metal concentrations that were determined were present in the $PM_{2.5}$ fraction. This prevalence of trace metals in the $PM_{2.5}$ section is indicative of the existence of significant combustion and/or industrial sources in addition to natural processes.

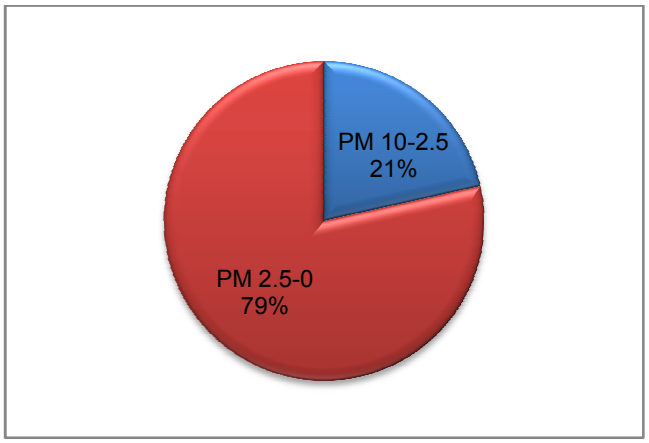

Figure 4.11: Size distribution of total trace metal species

In addition to the size distribution showed in Figure 4.11 for the total trace metals composition, each trace metal species (detected above the detection limit) was also fractionalised separately between $PM_{10-2.5}$ and $PM_{2.5}$. These distributions are shown in Figure 4.12. For each of the metal species, 40% and more of the specific metal were present in the $PM_{2.5}$ fraction. The results also indicate that the $PM_{10-2.5}$ fraction comprised of Al, B, Fe, Na, K, Pt, Cu, Mg, Be, Pb Se and Ti. As mentioned previously, the $PM_{10-2.5}$ fraction is usually associated with windblown dust. Cr, Mn, V, Zn and Ni occurred almost exclusively in the $PM_{2.5}$ fraction. The absence of these species in the coarse fraction implies the improbability of these species originating from windblown dust. It is significant to note that pyrometallurgical industries related directly to the production of Cr, V and Ni, are common anthropogenic activities in the Western Igneous Bushveld Complex. It is also well known that Zn and Mn are volatilised during pyrometallurgical smelting processes (Kemink, 2000). These possible mining and metallurgical sources are described in Paragraph 3.2.

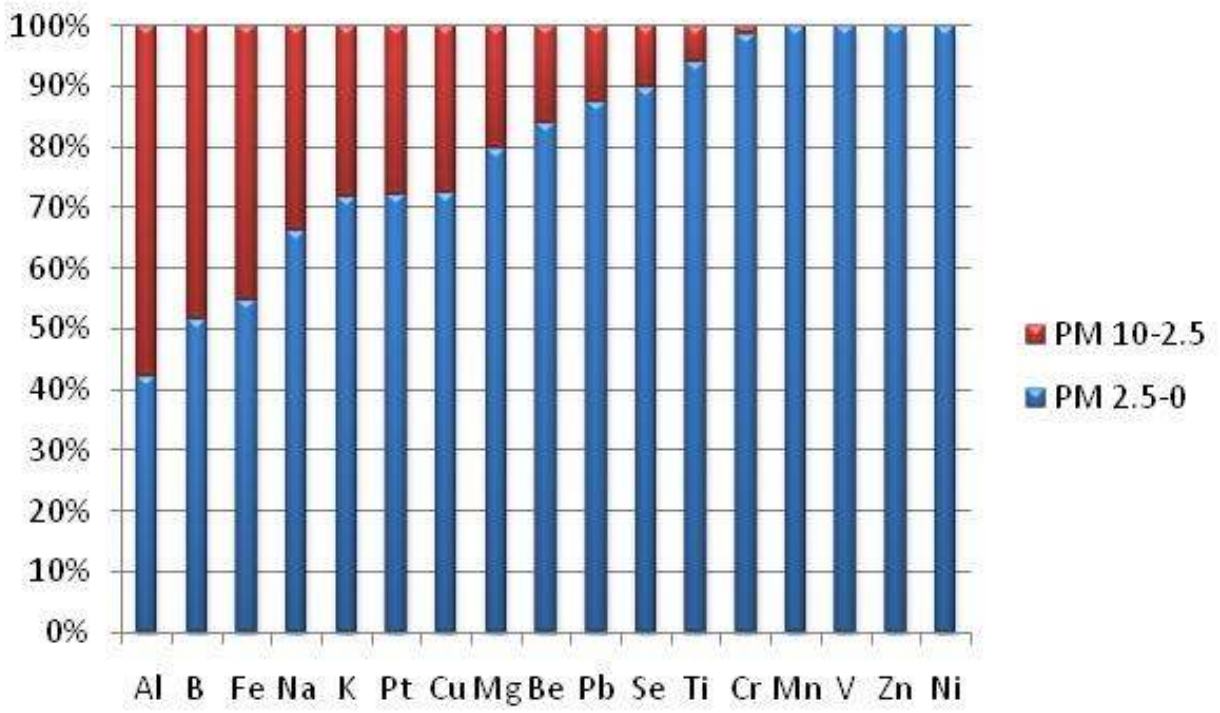

Figure 4.12: Size distributions of individual metal species detected

4.5 SEM-EDS analysis

SEM is a surface analysis technique that allows for visible inspection of samples. Backscatter micrographs of a typical PM_{10} sampled filter is shown in Figure 4.13 (a) and (b). Particles collected are clearly visible in these micrographs. The shapes of particles can be used as an indicative method or observation to distinguish between windblown particles and particles originating from pyrometallurgical processes. Beukes *at al.* (1999) and Beukes *et al.* (2010) indicated that small atmospheric rounded particles are likely to originate from the off-gas of pyrometallurgical processes. In Figure 4.12 (b), typical rounded and uneven shaped particles are indicated with white circles and white squares, respectively. This visual observation emphasises the deductions made from chemical analyses described in previous paragraphs that particles are likely to originated from anthropogenic activities (e.g. pyrometallurgical processes), as well as from windblown dust.

In addition to visual inspection, SEM-EDS was used to obtain surface chemical composition. This is a semi-quantitative technique. This technique confirmed the presence of most of the trace metal species identified with ICP-MS analysis. Additionally, non-metallic species were also detected, of which S was the most significant. The pyrometallurgical industry associated with the large Pt industry in the Western Bushveld Igneous Complex is well known for high SO_2 emissions. In general, the S content was more than 6% of the total elemental weight percentage, excluding C and F, which are the elements associated with the Teflon filter media. This relatively high S content clearly indicates the strong influence of pyrometallurgical activities on the PM sampled. This is another confirmation of conclusions made previously with regard to the influence of anthropogenic activities on the trace metal species measured.

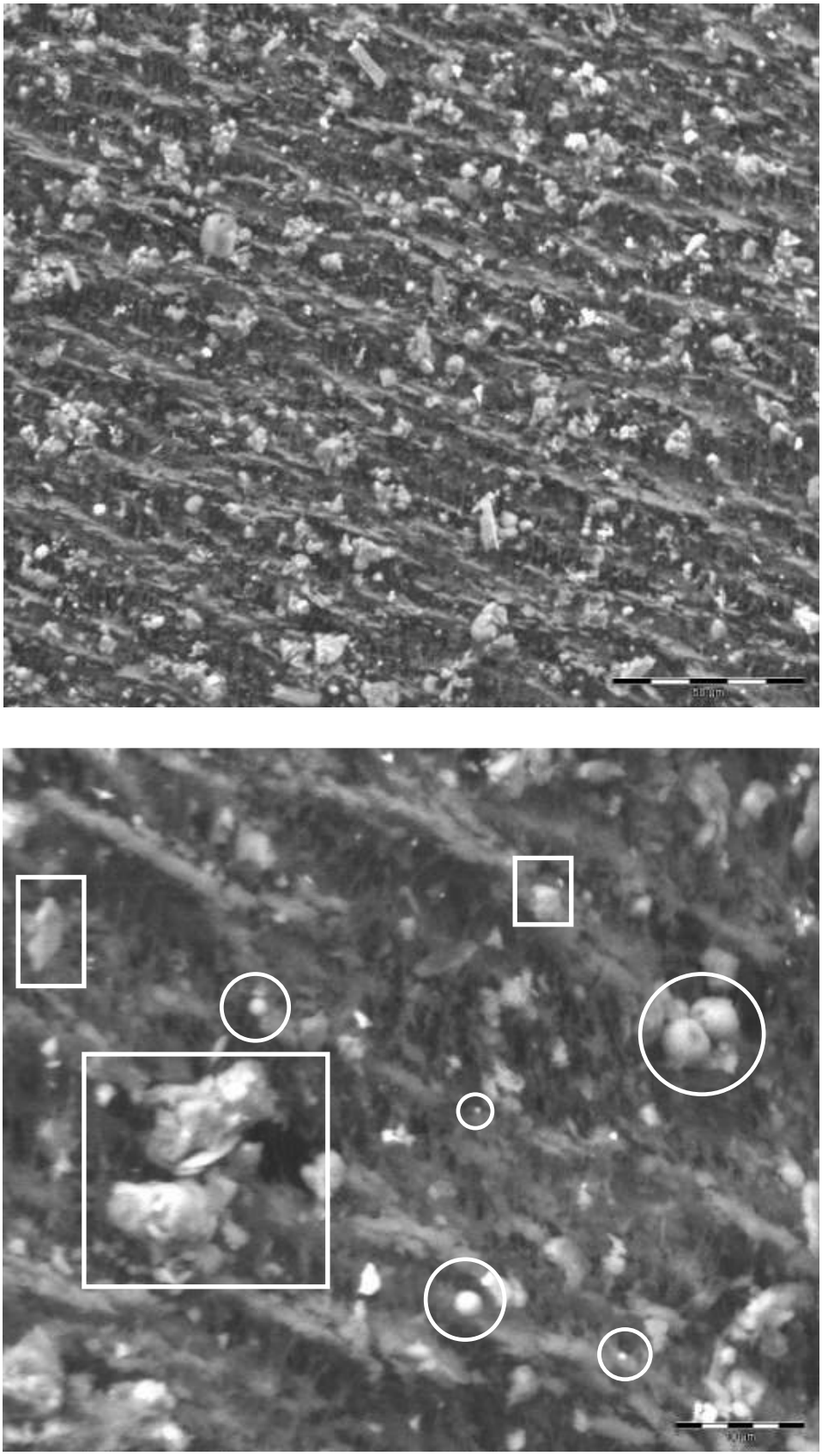

Figure 4.13: Backscatter micrographs of a typical PM_{10} filter

4.6 Cr, Mn, V, Zn and Ni correlations

The characteristics of Cr, Mn, V, Zn and Ni were found to be unique, i.e. occurring almost exclusively in the $PM_{2.5}$ fraction and seemingly associated with anthropogenic activities relatively unique to this region. As indicated in paragraph 3.6, various other atmospheric parameters were also measured during the sampling period. In subsequent paragraphs the measured concentrations of these species (Cr, Mn, V, Zn and Ni) were correlated with each other and other trace metals.

When performing these types of calculations it is important to note that a few outliers can have a large effect on the correlations. Also, if the correlations are not statistically significant, it does not necessarily imply that there is no correlation. Therefore, correlations were scientifically scrutinised and in the subsequent paragraphs only possible significant correlated relationships are discussed.

4.6.1 Cr correlations

A correlation between Fe and Cr was anticipated due to the presence of ferrochromium smelters in the region as described in paragraph 3.2. This correlation was especially expected in the smaller particulate fraction, since smaller particles in the atmosphere are usually associated with chemical and pyrometallurgical processes. In Figures 4.14 and 4.15, the relationships between Fe and Cr in the PM_{10} and $PM_{2.5}$ fractions measured during night time are shown, respectively. These graphs illustrate a distinct correlation between Fe and Cr during night time in both size fractions. As shown previously, approximately 96% of the night time PM_{10} consisted of $PM_{2.5}$ particles (Figure 4.10 (b)). Daytime measurements did not show a clear correlation between Fe and Cr in both particulate matter size fractions. This could possibly be attributed to less stable conditions, such as higher wind velocities (Figure 4.9), which occur during daytime. In addition, the daytime PM_{10} fraction also consisted of approximately 38% larger particulates ($PM_{2.5-10}$) as described in paragraph 4.3.2. In the larger particulate matter fraction, an additional source of Fe is wind-blown dust, which will lead to dissimilar correlations between Cr and Fe.

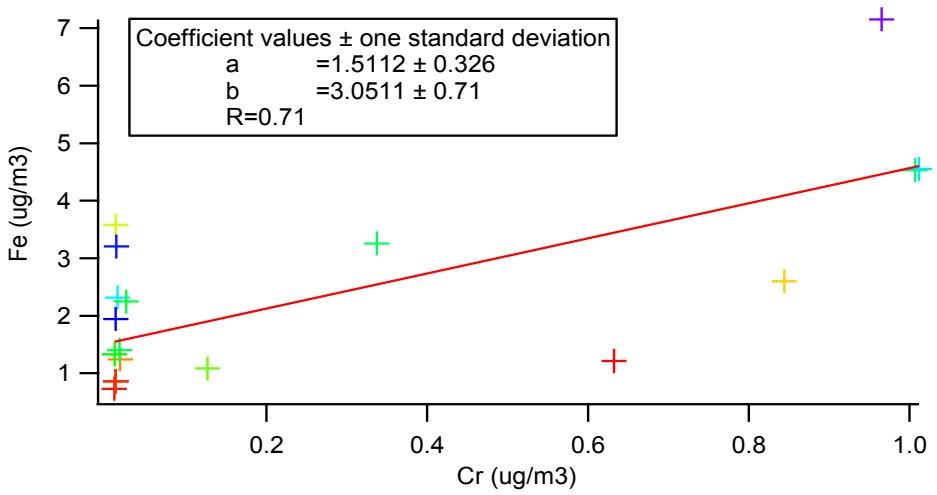

Figure 4.14: Night time Fe PM_{10} concentration correlated with night time Cr PM_{10} concentration

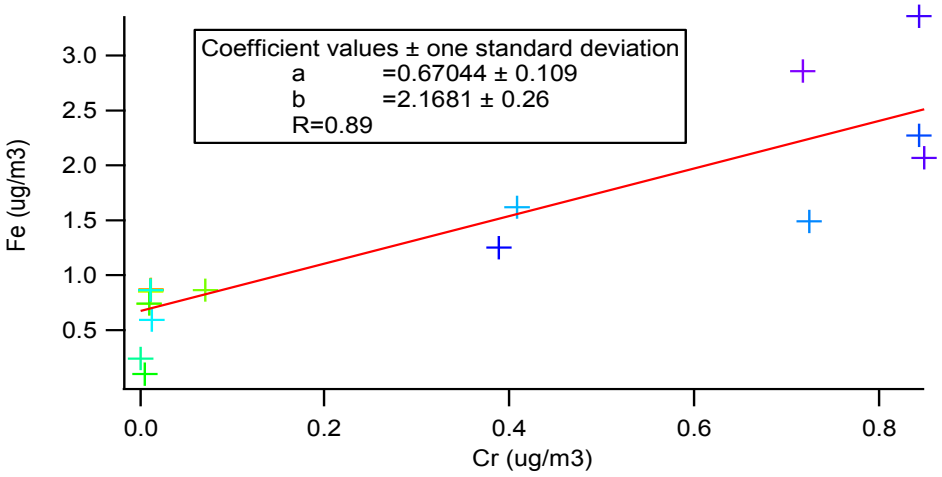

Figure 4.15: Night time Fe $PM_{2.5}$ concentration correlated with night time Cr PM_{10} concentration

4.6.2 V correlations

The presence of V in the atmosphere in this region can also be ascribed to pyrometallurgical processes. A correlation that was expected for atmospheric V was its association with Ti, since titaniferous magnetite deposits are used for V recovery and have relatively high titanium content (Kennedy, 1990). In Figures 4.16 and 4.17, a clear correlation between V and Ti is observed in both particulate size fractions measured during night time. The daytime measurements did not correlate as

noticeably, which could possibly be ascribed to the same reasons given in the previous paragraph.

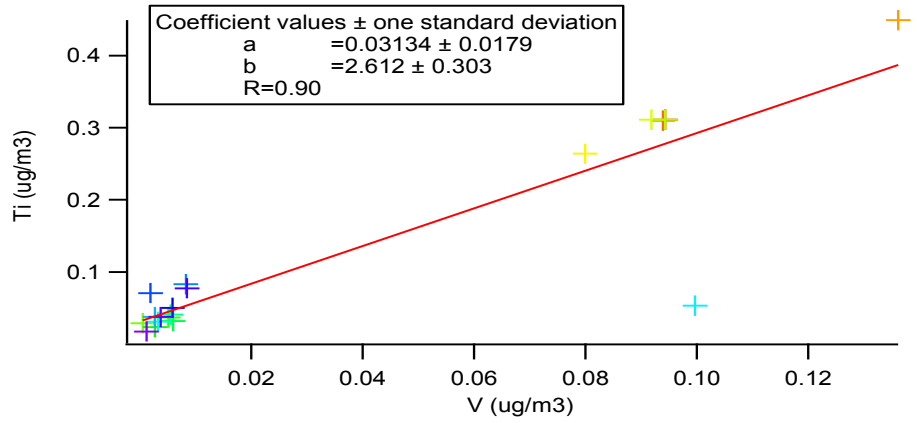

Figure 4.16: Night time V PM_{10} concentration correlated with night time Ti PM_{10} concentration

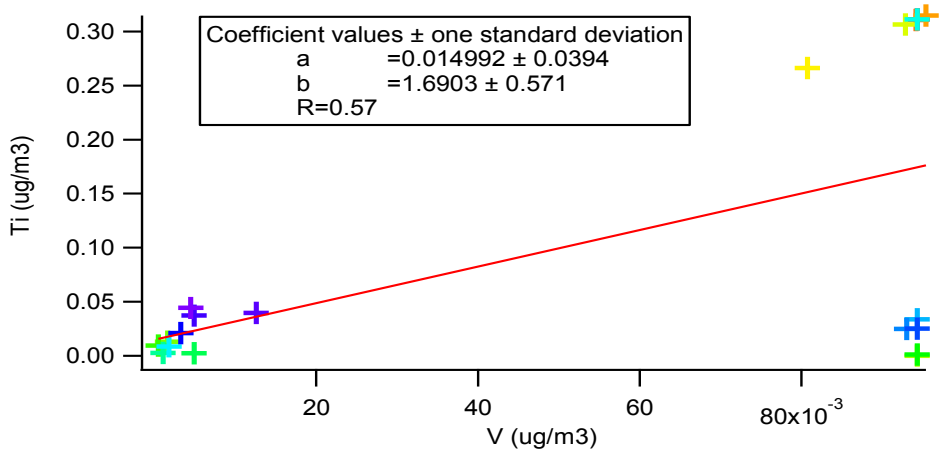

Figure 4.17: Night time V $PM_{2.5}$ concentration correlated with night time Ti PM_{10} concentration

4.6.3 Mn correlations

Mn is present in most of the ores from which metals (e.g. Cr, V, etc.) are produced in the western Bushveld Igneous Complex. Mn has a substantially higher vapour pressure than metals produced in this region and are therefore more volatile

(Kemink, 2000). Many of the pyrometallurgical industries will therefore be sources of atmospheric Mn. A correlation between Mn and Ti was observed in the night time PM_{10} and $PM_{2.5}$ measurements. These correlations are showed in Figures 4.18 and 4.19, respectively. Although it is difficult the give an exact explanation for this observation, due to the complexity of sources in this region, a correspondence to pyrometallurgical sources is indicated.

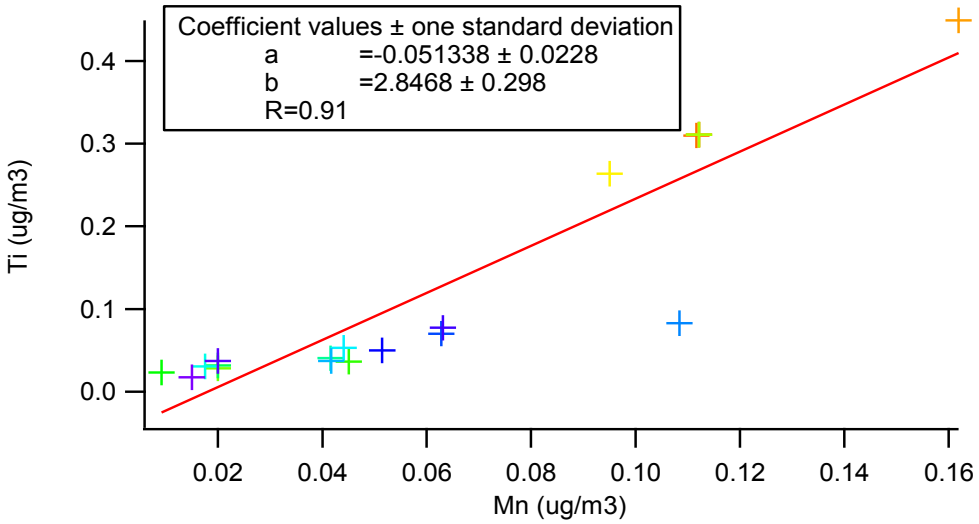

Figure 4.18: Night time Mn PM_{10} concentration correlated with night time Ti PM_{10} concentration

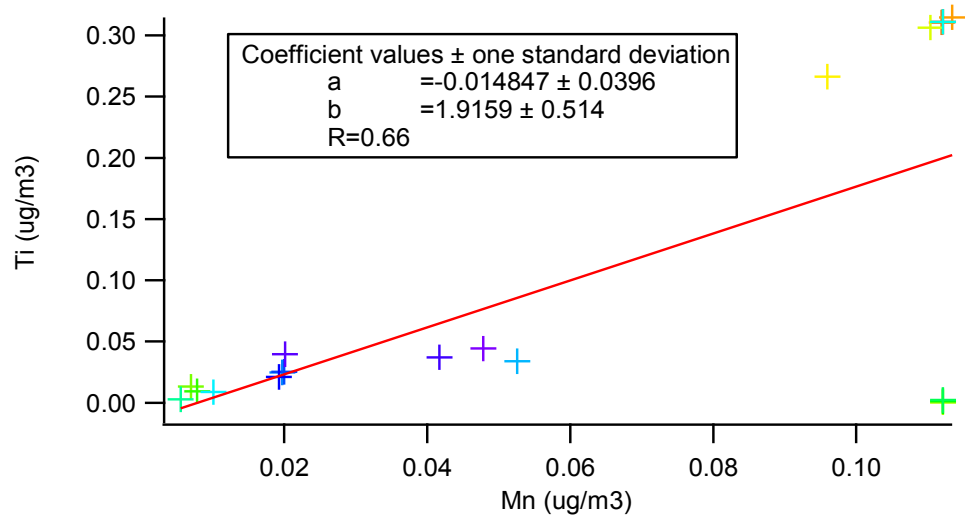

Figure 4.19: Night time Mn $PM_{2.5}$ concentration correlated with night time Ti $PM_{2.5}$ concentration

4.6.4 Zn and Ni correlations

Zn and Ni are two base metals that are produced in the western Bushveld Igneous Complex. In Figure 4.20, the night time correlation between Ni and Zn in the PM_{10} fraction is shown. Higher Zn concentrations coincided with higher levels of Ni, which can at least partially be attributed to similar sources, i.e. base metal refineries

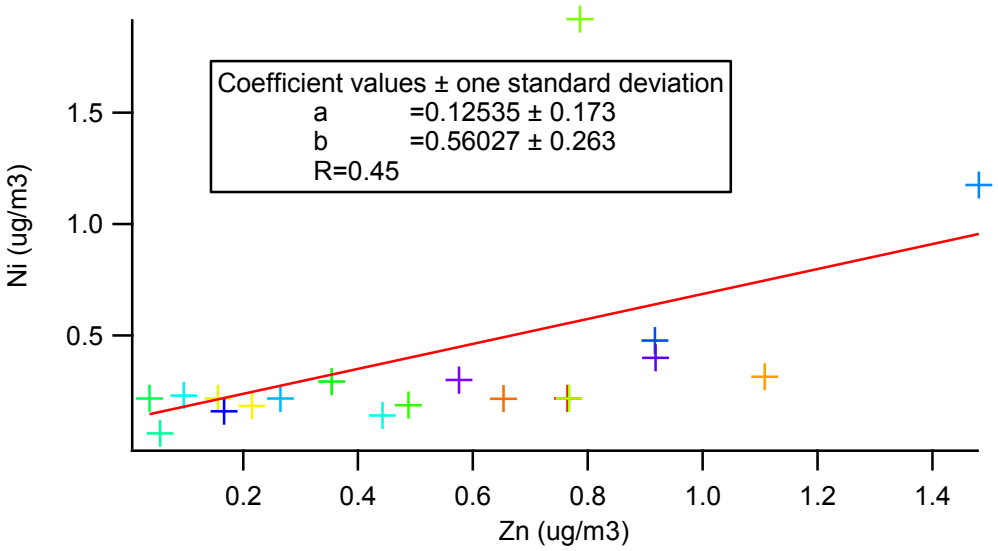

Figure 4.20: Night time Zn PM_{10} concentration correlated with night time Ni PM_{10} concentration

4.7 Sources

4.7.1 Factor analysis

In a further attempt to identify possible sources of trace metals measured in this area, principle component factor analysis (PCFA) with Varimax rotation (v. 13.0 SPSS Inc., Chicago, IL, USA) was performed on the dataset. PCFA has been used widely in receptor modelling to identify major source categories affecting a given receptor site. The technique operates on sample-to-sample fluctuations of the normalised concentrations. It does not directly yield concentrations of species from various sources, but identifies a minimum number of common factors whose

variance often accounts for most of the variance of species (Al-Momani *et al.*, 2005; Koutrakis and Spengler, 1987).

PCFA was applied as an explorative tool in this investigation, since the dataset obtained during the sampling period was not large enough for definitive source apportionment with PCFA. Factor analysis of smaller datasets is more susceptible to statistical artifacts, such as autocorrelation or the influence of outliers. This implies that some correlations are not necessarily considerable. Therefore, explorative PCFA was applied to the dataset and only the most apparent groupings of metal species relating to expected sources in the region were identified.

The dataset used for PCFA was the combined ambient concentrations determined for all 26 metal species in both the $PM_{2.5}$ and PM_{10} fractions. The dataset was also subjected to Box-Cox transformation in an effort to eliminate some possible artifacts. There are no well-defined rules on the number of factors to be retained. Generally, factors that are either meaningful or with eigenvalues larger than one are kept (Al-Momani *et al.* 2005; Kulkarni *et al*., 2007; Hosiokangas *et al.*, 1999). Factor loadings obtained for the unprocessed and transformed datasets are given in Figures 4.22 and 4.23 respectively. Five factors were obtained for PCFA of the unprocessed dataset with a total variance of 80.2%, while six factors were retained from the transformed dataset that explained 78.9% of the variance.

Factor 1 obtained for the unprocessed data is mostly loaded with the metal species Pd, Hg, Tl, U, Ca, Co, As, Cd, Ba and Au, which were species that were 25% or less of the time above the detection limit. Therefore, this factor was excluded in the elucidation of possible sources of trace metal species. This factor explained 45.3% of the total system variance. The other four factors calculated with PCFA of the unprocessed dataset resolved four meaningful sources of trace metals in the region, which is discussed in subsequent paragraphs.

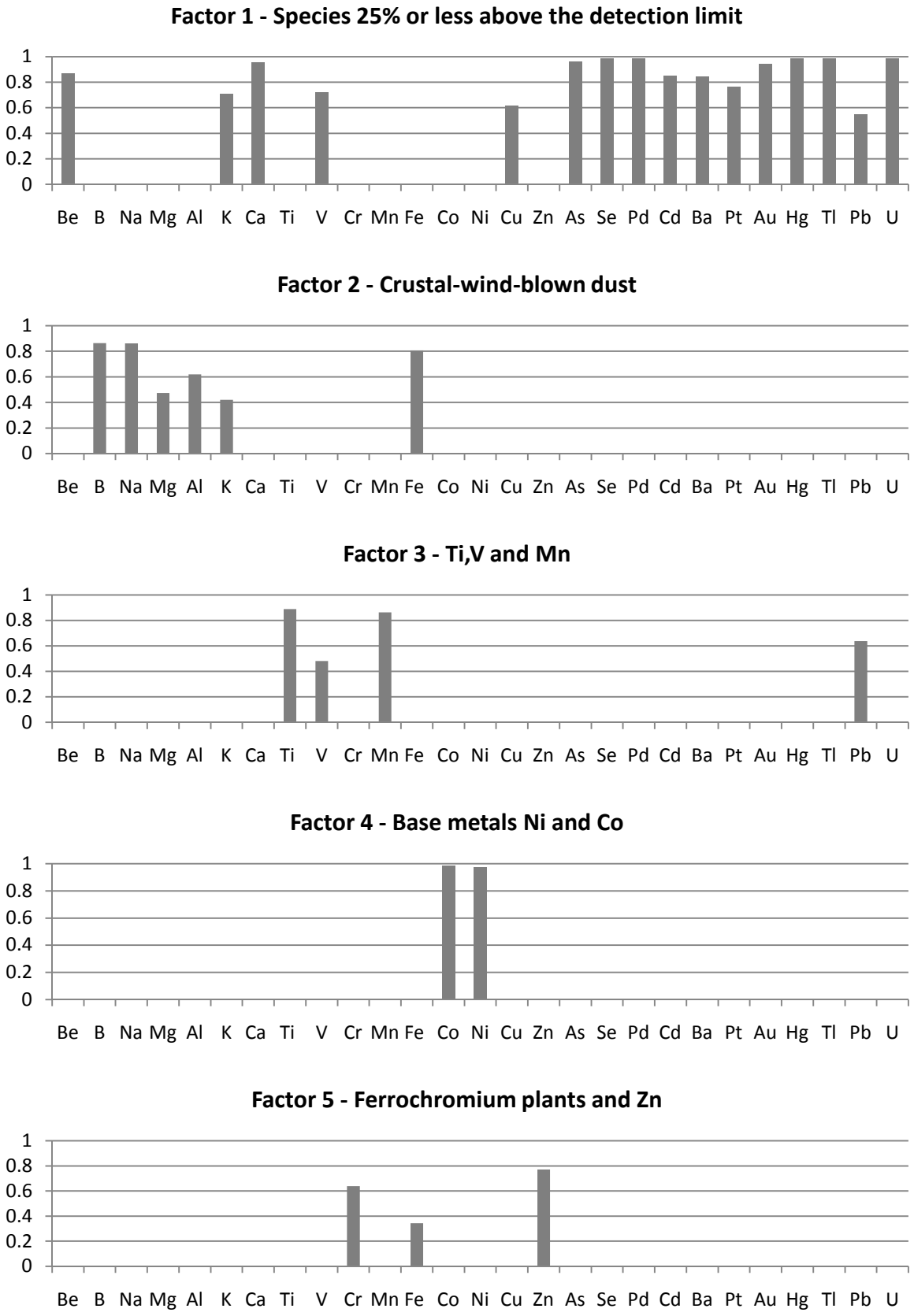

Figure 4.21: Principal component factor analysis with Varimax rotation of the raw data, i.e. atmospheric concentrations of all metal species

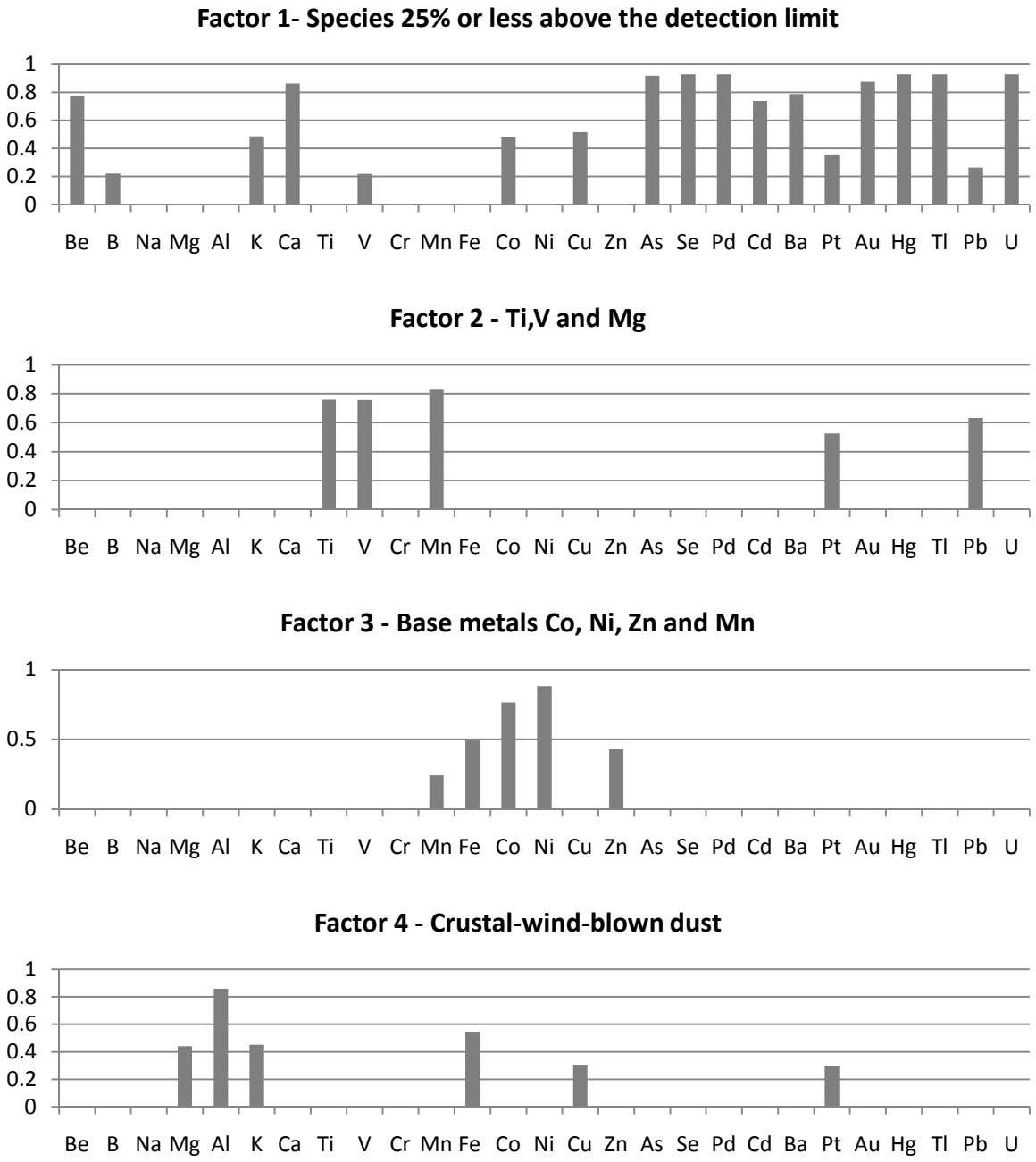

Figure 4.22: Principal component factor analysis with Varimax rotation of Box-Cox transformed data

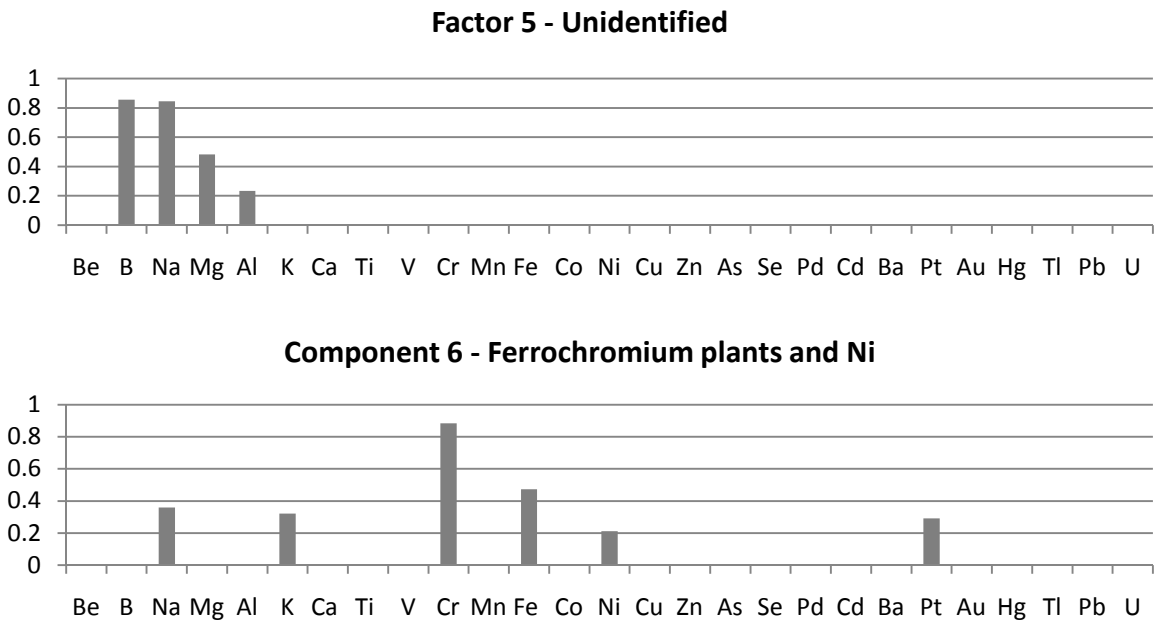

Figure 4.22 (continued): Principal component factor analysis with Varimax rotation of Box-Cox transformed data

Factor 1 of the Box-Cox transformed dataset also correlates with the metal species that were 25% or less of the time above the detection limit. Factor 5 obtained for this dataset has high loadings of B and Na, as well as moderately high loadings of Al and Mg. These trace metals might be indicators of crustal sources, which is more likely to be correlated in Factor 4. Therefore, Factor 5 was considered as an unidentified source. Factor 1 and Factor 5 explained 34.5% and 6.1% of the total system variance, respectively. Similar to the PCFA performed for the raw data, four meaningful sources were identified from factor analysis of the transformed dataset and discussed below.

Factor 2 of the unprocessed dataset explains 11.8% of the variance and correlates with B, Na, Mg, Al, K and Fe. Explorative investigation revealed that this factor is mainly loaded with metal species that are considered to be from wind-blown dust, i.e. Mg, Al, K and Fe. Therefore, this factor was identified as the crustal factor. Similar loadings were obtained for Factor 4 of the Box-Cox transformed dataset, which was loaded with Mg, Al, K, Fe, Cu and Pt. This factor explained 10.0% of the total system variance and also gives correlations between Mg, Al, K and Fe.

Factor 3 of the raw dataset and Factor 2 of the modified dataset were highly loaded by Ti, V, Mn and Pb. These factors explain 10.3% and 13.9% of the variances respectively. This compared to the correlations observed in Paragraphs 4.6.2 and 4.6.3 where V and Mn correlated to Ti. In these paragraphs, possible explanations for the relationship between these metal species are also discussed.

Factor 4 of the untreated dataset accounts for 7.6% of the total variance and were only loaded by Ni and Co, which are base metals produced in this region. This factor compared to Factor 3 of the transformed dataset, which correlated to Mn, Fe, Co, Ni and Zn, with Zn also a base metal produced in this area. This factor explains 10.2% of the variances of the data. These factors were identified as the base metal industry-related sources.

Another factor identified was chromium-related pyrometallurgical sources. This factor was calculated in Factor 5 of the unprocessed dataset and in Factor 6 of the Box-Cox transformed dataset. These factors have high loadings of Cr and Fe. Factor 5 of the raw dataset also correlates to Zn, while Factor 6 of the Box-Cox transformed dataset also correlates to Ni, Pt, Na and K. Factor 5 explains 5.3% of the total variances in the raw dataset, while Factor 6 accounts for 4.2% of the variances in the modified dataset.

4.7.2 Correlations to other parameters

As described in Paragraph 3.1, the western Bushveld Igneous Complex is a highly industrialised region with many different sources contributing to pollutant species in the atmosphere. This was also evident in the correlations of trace metal species concentrations and other parameters measured at the monitoring station. These parameters included global radiation, temperature, relative humidity, atmospheric pressure, total PM_{10} concentration, black carbon (BC) concentration and concentrations of trace gaseous species, i.e. O_3, SO_2, NO, NO_x and CO.

No distinct correlation was observed between trace metals and other pollutant species, such as SO_2 and NO_2. It is also interesting that no distinct correlation was observed between trace metals and CO or BC. In Figures 4.24 and 4.25, the diurnal

concentrations for CO and BC during the four seasons are shown respectively. These figures clearly illustrate higher CO and BC levels during winter, as well as concentration peaks in the morning and late afternoon. These diurnal peaks are most probably attributable to household combustion in the morning and late afternoons for cooking and heating from the relatively large informal settlement in the western part of the monitoring site (paragraph 3.2). It is evident that household combustion has a negative impact on air quality in general. However, since there were no correlations between any trace metals and CO or BC it is unlikely that it is a major source of the 17 trace metals that were mostly above the detection limit. It can therefore be partly concluded that atmospheric trace metals in the western Bushveld Igneous Complex were primarily emitted from wind-blown dust and pyrometallurgical processes during the sampling period.

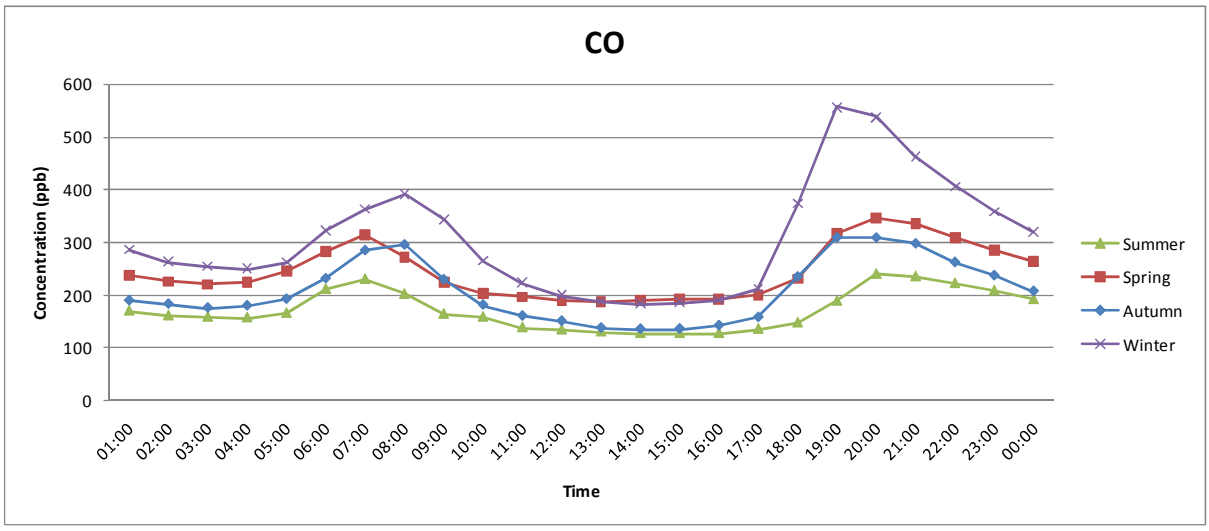

Figure 4.23: CO seasonal diurnal concentrations measured during the sampling period

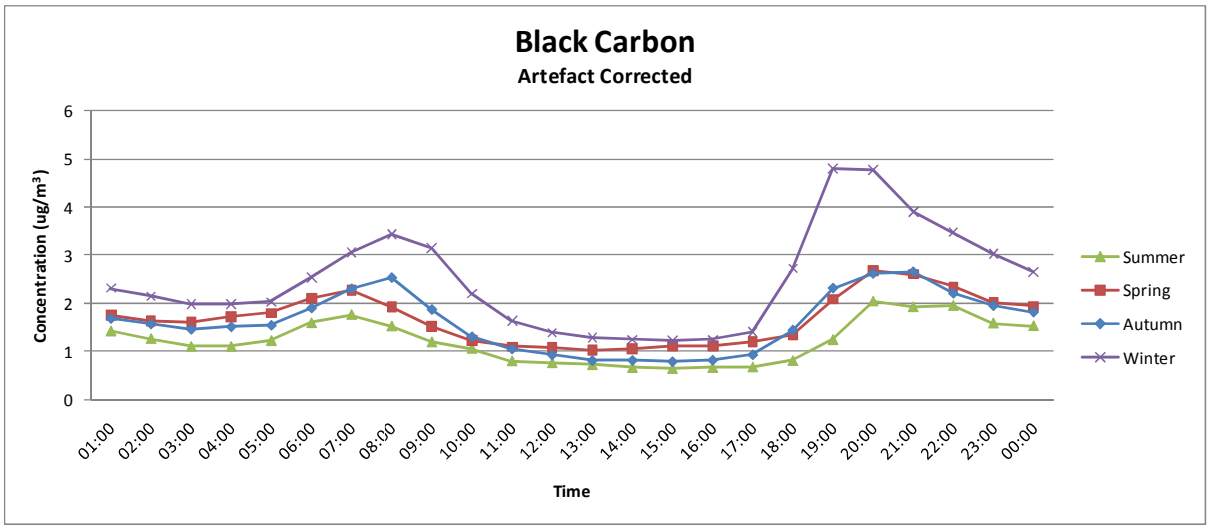

Figure 4.24: BC seasonal diurnal concentrations measured during the sampling period

The complexity of this region can also be illustrated by the pollution rose determined for SO_2 at the monitoring site. In Figure 4.25, the pollution rose for SO_2 measured during the sampling period is shown. SO_2 is emitted from many of the pyrometallurgical industries in the region due to the high sulphur content of the ores from which many of the metals are produced. Figure 4.25 clearly illustrates that SO_2 concentrations cannot be linked to a specific area and corresponding source. The SO_2 measured at the trailer came from most of the surrounding areas.

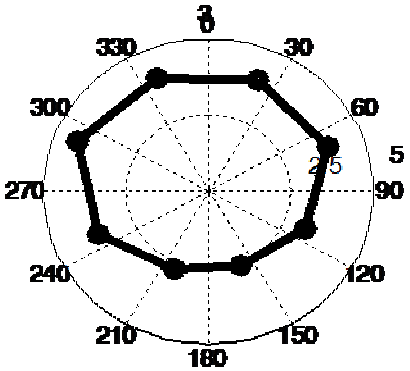

Figure 4.25: Pollution rose for SO_2 determined during the sampling period

4.8 Conclusions

From the results and discussions presented in this chapter, the following conclusions can be made:

- With the exception of Ni, none of the trace metals measured at Marikana during the sampling period exceeded local and international standards. This was possibly due to base metal refining in the region. Pb, which is the only metal species that has a standard prescribed by the South African DEA, did not exceed any of the standards. It is also significant to refer to Hg that was below the detection limit of the analytical instrument for the entire sampling period.
- The wet removal processes of atmospheric PM_{10} trace metals were more significant than wind generation thereof. Total trace metal concentrations in the PM_{10} fraction peaked during the dry months and were mostly washed-out during the wet season. Wind speed showed an unexpected inverse pattern compared to wet deposition. A less significant seasonal trend is observed for the trace metal concentrations in the $PM_{2.5}$ fraction, which was attributed to a faster replenishment of smaller particles into the atmosphere after rain events. This indicates the possible anthropogenic origin of the smaller particles.
- Separation of trace metal concentrations into $PM_{10-2.5}$ and $PM_{2.5}$ fractions indicated that 79% of the total trace metal levels that were measured were in the $PM_{2.5}$ fraction, which indicated a strong influence of industrial and/or combustion sources. Fractionalisation of each of the trace metal species detected showed that for each metal species, 40% and more of a specific metal was in the $PM_{2.5}$ fraction, with Cr, V, Ni, Zn and Mn occurring almost completely in the $PM_{2.5}$ fraction.
- Surface analysis with SEM emphasised results from chemical analysis, which indicated that a large fraction of the particles were likely to originate from anthropogenic activities and from wind-blown dust. SEM-EDS also detected non-metallic S that is usually associated with the Pt pyrometallurgical industry that is large in the western Bushveld Igneous Complex.
- Correlations between Cr, V, Ni, Zn and Mn revealed that the main sources of these species were pyrometallurgical industries in the western Bushveld Igneous Complex. Explorative factor analysis of the unprocessed and Box-Cox

transformed data for all 26 metals detected resolved four meaningful emission sources, i.e. crustal, vanadium related, base metal related and chromium related.

- Comparison of trace metal species to other parameters measured (e.g. CO, BC, etc.) also indicated that the main source of trace metals were pyrometallurgical activities and wind-blown dust.

~CHAPTER 5~

Project evaluation and future perspectives

In this chapter, the study is evaluated in terms of its achievement of objectives, based on the results discussed in Chapter 4. Each objective is evaluated by considering and weighing the success and shortcomings of this investigation. General conclusions are drawn from the results and recommendations are made for future studies.

5.1 Project evaluation

The general aim of this investigation was to measure trace metal species present in aerosols at a polluted site in a highly industrialised area. Specific objectives were set out to achieve this goal.

Objective 1

Collect $PM_{2.5}$ and PM_{10} samples on filters with mini-volume samplers for a period of one year at Marikana, South Africa.

Successes:

$PM_{2.5}$ en PM_{10} samples were collected successfully for a period of one year utilising MiniVolume^{TM} samplers. It was undertaken to collect samples for six-day, 12-hour periods, which were alternated between day and night. Although there existed periods in which sampling was not possible mostly due to instrumentation failure, 83% of the intended samples were collected. The data collected provided sufficient

information to make adequate scientific conclusions and obtain valuable information with regard to trace metals in this area.

Shortcomings:

During the interpretation of the data, it was observed for a few minor instances that the $PM_{2.5}$ concentration was higher than the PM_{10} concentration, which is realistically not possible. This phenomenon may be explained by the fact that the flow rate of the MiniVol^{TM} samplers is adjusted manually to 5 L/min. Human error may occur when setting the flow rate, which would influence the calculations of the concentrations. For instance, the actual flow rate of the PM_{10} sampler could have been slightly less than 5 L/min, and/or the flow rate of the $PM_{2.5}$ sampler could have been slightly higher than 5 L/min. All sample concentrations were calculated by using the sampling time and the flow rate of 5 L/min. Small deviations in the actual flow rate over a 72-hour sampling period could therefore have made a significant impact on the concentrations (Kleynhans, 2008).

Although there were not many gaps in the dataset, there were months in which sampling was not conducted for the entire month. This complicated the interpretation and elucidation of results for specific months.

Future Perspective:

It is recommended that high-volume samplers with one inlet equipped with impactors to separate particles into the different size fractions are used for future aerosol sampling. It is also recommended to collect and investigate the PM_1 size fraction, especially with regard to human health impacts. Gaps in the collected data should also be prevented and the logistics of sampling can be improved.

Objective 2

Develop a method to divide filters to perform two different destructive analytical procedures.

Successes:

The procedure developed proved to be successful in dividing the sampled filters into two equal parts. The remaining half was stored for another type of analysis, while the other part was used effectively for ICP-MS to determine trace metal concentrations. The analysis of blank filters with the ICP-MS showed no evidence of stainless steel, which is the material from which the division apparatus was made.

Another advantage of this separation technique was that the rim of the filter that remained after the division of the filters could be used for SEM-EDS analysis. Surface analysis could therefore be conducted to support chemical analysis.

Future perspective:

The procedure developed for separating sampled filters can be used in future studies. The partitioning of the filter into two parts has the advantage of conducting two destructive analytical techniques.

Objective 3:

Determine the concentration of trace transitional metals from the collected particulate matter.

Successes:

The concentrations of the trace metals in the $PM_{2.5}$ and PM_{10} size fractions could be detected with ICP-MS analysis. The measured concentrations could be used to make plausible conclusions, as well as give a verdict on the air quality in the region. Results showed that, with the exception of Ni, none of the trace metals measured at Marikana exceeded local and international standards. The impact of meteorological

conditions on trace metal concentrations could also be observed. The presence of trace metals in the $PM_{2.5}$ and PM_{10} size fractions could also be fractionalised. Surface analysis was effectively employed to support chemical analysis of the sampled filters.

Shortcomings:

A significant deficiency encountered with the ICP-MS technique was that several trace metal species concentrations were below the detection limit. This can be attributed to various reasons. The fact that only one half of each of the filters was used could have contributed to this occurrence. However, the main reason for this phenomenon was considered to be the fact that lower calibration ranges were not obtained for metal species with much lower concentrations on the ICP-MS. Since the samples were analysed for 26 metal species at once, the same calibration line range was used for all the species measured. Two point calibrations were also applied for all the measurements, which could also contribute to below detection limit values.

Future Perspective:

ICP-MS can be used efficiently to determine the concentrations of trace metals in aerosol samples. It is recommended that higher resolution calibration lines with different concentration ranges for each metal species are used. This should significantly reduce the problem of concentrations below the detection limit. Analysis of samples can also be repeated to verify measured concentrations. The use of a high-volume sampler, described previously, could also possibly yield higher concentrations of metals that were below the detection limit of the ICP-MS. This will also contribute to retain the advantages of separating the filters.

Objective 4:

Determine the effect of meteorological conditions and other species present in the atmosphere on particle matter- and trace metal concentrations.

Successes:

It could be shown that wet removal processes of atmospheric PM_{10} trace metals were more significant than wind generation thereof. PM_{10} concentrations peaked during the dry months. A less significant seasonal trend is observed for the trace metal concentrations in the $PM_{2.5}$ fraction, which was attributed to a faster replenishment of smaller particles into the atmosphere after rain events. No distinct correlation was observed between trace metals and other pollutant species.

Future Perspective:

It is recommended that the remaining part of the filter is used for analysis to determine ionic species such as SO_4, NO_3 and Cl^-. These results could show correlation to other species present in the aerosol samples.

Objective 5:

Relate the measured trace metal species to possible sources in the region.

Successes:

From the separation of the trace metal concentrations into $PM_{10-2.5}$ and $PM_{2.5}$ it was possible to determine that the majority (79%) of the collected particles were present in the $PM_{2.5}$ size fraction, and that most of these species present (Cr, V, Ni, Mn, Zn) were related to anthropogenic sources, which is typical of the sampling area.

Pyrometallurgical sources of trace metal species were also supported by correlations between Cr, V, Ni, Mn and Zn, as well as by surface analysis with SEM. The SEM analysis also indicated the presence of non-metallic sulphur, which may be

associated with the platinum pyrometallurgical industry found in excess in the Bushveld Igneous Complex.

Further confirmation of trace metal sources was done by means of explorative factor analysis of the unprocessed data and Box-Cox transformed dataset for the 26 metals detected. This analysis revealed four significant sources of trace metals in the western Bushveld Igneous Complex, which include crustal sources, base metal-related sources, vanadium-related sources and chromium-related sources. In general, anthropogenic- and wind-blown sources were identified as the two main sources for the presence of the trace metal species.

Shortcomings:

Factor analysis was only applied as an explorative tool in this investigation, since the dataset obtained was not large enough for definitive source apportionment. Factor analysis of smaller datasets is more susceptible to statistical artifacts, such as autocorrelation or the influence of outliers. Therefore, some correlations were not necessarily considerable. Therefore, only the most apparent groupings of metal species relating to expected sources in the region were identified.

Future Perspective:

It is recommended that a larger dataset is obtained in order to enhance the utilisation of factor analysis to obtain more definitive source apportionment.

~References~

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