SPATIAL AND TEMPORAL DISTRIBUTION OF TRACE ELEMENTS IN AEROSOLS IN THE VAAL TRIANGLE

Engela Helena Kleynhans
B.Sc Honns
12407690

Dissertation submitted in partial fulfilment of the requirements for the degree *Master of Science* at the Potchefstroom Campus of the North-West University, South Africa

Promotor: Prof. JJ Pienaar
(North-West University, South Africa)
and
Co-promotor: Dr. CE Read
(North-West University, South Africa)

Potchefstroom
January 2008

Abstract

The Vaal Triangle, largely an industrialized area and a so-called *"air pollution hot spot"* in South Africa, was declared as the first air pollution priority area in South Africa on the 21st of April 2006. In such an industrial and highly populated area, concentrations of trace elements and particulate matter are expected to exceed concentration levels that are safe for the environment and for the population. There is very little existing data on trace element concentrations in this region, therefore the purpose of this study was to monitor concentrations of certain harmful trace metals (such as Cr, V, Fe, Ni, and Pb), as well as the total concentration trace elements in the $PM_{2.5}$ and PM_{10} particle fractions.

Three towns in close proximity to one another were selected for sampling, namely Sasolburg, Vanderbijlpark and Vereeniging. The samples were collected using MiniVol Portable Air Samplers (product of Airmetrics) and teflon filters. The MiniVol samplers were set to an air-flow rate of 5 litres per minute. The sampling time was twenty four hours per sample, collected over three days during a winter season (July 2006) and a summer season (March 2007).

Background sampling was conducted at Botsalano game reserve in August 2007. This was essential as a reference for this study, due to the paucity of data on trace metal concentrations in South Africa and data on the trace metal content of various source emissions in the Vaal Triangle.

The samples were analysed using Inductive Coupled Plasma – Mass Spectrometry (ICP-MS) and Scanning Electron Microscopy (SEM). The comparison of the two analytical techniques showed that ICP-MS is the preferred method to determine the concentrations of trace metals in ambient particulate matter.

ICP-MS was used to determine the concentrations of all elements from Li to U for each sample. The average of these concentrations at each site was higher during the winter sampling period than the summer sampling period. This could possibly be attributed to the higher atmospheric stability during the winter and the increase in rainfall during the summer. Another possible reason could be the higher occurrence of field fires and residential combustion (biomass and coal) during the winter. Fe concentrations were higher than most other elements and could possibly be attributed to the activities of numerous steel manufacturing industries in the Vaal Triangle. However, Cr, Ni and Co concentrations were higher during the summer and could be attributed to the influence of local metallurgical industries.

Fe was the most abundant trace element, followed by Zn and Mn. The average Fe concentrations were approximately 1.009 $\mu g.m^{-3}$ ($PM_{2.5}$) and 1.499 $\mu g.m^{-3}$ (PM_{10}) during the winter, and approximately 0.775 $\mu g.m^{-3}$ ($PM_{2.5}$) and 1.071 $\mu g.m^{-3}$ (PM_{10}) during the summer. The average Fe concentrations in the background samples were approximately 0.001 $\mu g.m^{-3}$ ($PM_{2.5}$) and 0.097 $\mu g.m^{-3}$ (PM_{10}). The values in the Vaal Triangle are significantly higher compared to the background concentrations at Botsalano, but it is much lower than values reported for the Rustenburg area.

The most significant observation that could be made from the SEM/EDS results was that carbonaceous particles were the dominant species present and the percentages were higher during the winter months, possibly due to the elevated occurrence of residential biomass burning and residential coal combustion to produce heat, especially in the low-income residential areas.

Further research should be conducted to get clear seasonal trends and annual average concentrations.

Opsomming

Die Vaal Driehoek is grootliks 'n industriële gebied en ook 'n hoogs besoedelde gebied in Suid-Afrika. Daarom was die Vaal Driehoek die eerste gebied wat as 'n lugbesoedeling prioriteitsgebied verklaar was op 21 April 2006. In 'n industriële en dig bevolkte gebied soos hierdie word daar verwag dat die konsentrasies van spoor elemente en atmosferiese deeltjies hoër sal wees as aanvaarbare vlakke vir die voortbestaan van die natuurlike omgewing en vir die gesondheid van die mense in die gebied. Daar is tans baie min inligting rakende die konsentrasie-vlakke van spoor elemente in hierdie gebied. Die doel van die studie was om die konsentrasies van sekere skadelike spoor metale (soos Cr, V, Fe, Ni en Pb) te bepaal en ook om die totale konsentrasie van spoor elemente in die $PM_{2.5}$ en PM_{10} gedeeltes te bepaal.

Drie dorpe (wat naby mekaar geleë is) was gebruik om monsters te versamel, naamlik Sasolburg, Vanderbijlpark en Vereeniging. Die monsters is versamel deur gebruik te maak van "MiniVol Portable Air Samplers" ('n produk van Airmetrics), op teflon filters. Die MiniVols was gestel om lug teen 'n vloeitempo van 5 liter per minuut deur die filters te trek. Die tydsduur van monsterversameling was 24 uur en dit was vir drie agtereenvolgende dae herhaal gedurende die winter (Julie 2006) en die somer (Maart 2007).

Agtergrond monsterneming was by Botsalano natuur reservaat uitgevoer vir drie dae gedurende Augustus 2007. Agtergrond monsterneming was van groot belang vir die betrokke studie as gevolg van die skaarste van inligting oor spoor metaal konsentrasies in Suid-Afrika en ook van die spoor metaal inhoud van verskeie emissie bronne in die Vaal Driehoek.

Die monsters was geanaliseer deur gebruik te maak van induktief-gekoppelde plasma – massa spektrometrie (ICP-MS) en skandeer elektron mikroskopie (SEM). Uit 'n vergelyking wat gedoen is tussen die twee tegnieke het dit vorendag gekom dat ICP-MS die beter tegniek is om spoor metaal konsentrasies in atmosferiese deeltjies te bepaal.

ICP-MS was gebruik om die totale konsentrasie van alle elemente vanaf Li tot U te bepaal vir elke monster. Die gemiddelde waarde van hierdie konsentrasies by elke dorp was hoër gedurende die winter. 'n Moontlike verduideliking hiervoor kan gekoppel word aan die meer stabieler atmosferiese kondisies wat voorkom gedurende die winter en ook die hoër reënval gedurende die somer. Fe konsentrasies was hoër as die meeste ander elemente, moontlik as gevolg van die verskeie staalvervaardigingsmaatskappye in die Vaal Driehoek. Cr, Ni en Co konsentrasies was meer gedurende die somer en dit kan moontlik toegeskryf word aan die invloed van plaaslike metallurgiese industrieë.

Die gemiddelde Fe konsentrasies was ongeveer 1.009 $\mu g.m^{-3}$ ($PM_{2.5}$) en 1.499 $\mu g.m^{-3}$ (PM_{10}) gedurende die winter en ongeveer 0.775 $\mu g.m^{-3}$ ($PM_{2.5}$) en 1.071 $\mu g.m^{-3}$ (PM_{10}) gedurende die somer. Fe was die volopste element teenwoordig in die monsters, gevolg deur Zn en Mn. Die gemiddelde Fe konsentrasies in die agtergrond monsters was ongeveer 0.001 $\mu g.m^{-3}$ ($PM_{2.5}$) en 0.097 $\mu g.m^{-3}$ (PM_{10}). Die waardes in die Vaal Driehoek was noemenswaardig hoër as die agtergrond monsters by Botsalano en tegelykertyd baie laer as waardes wat gerapporteer is vir die Rustenburg area.

Die belangrikste waarneming wat gemaak kon word vanuit die SEM/EDS resultate was dat koolstofagtige verbindinge die mees dominante element teenwoordig was en die konsentrasies hiervan was taamlik hoër gedurende die winter. Dit kan moontlik toegeskryf word daaraan dat daar baie meer veldbrande voorkom in die winter. Nog 'n moontlike rede is die toename in huishoudelike verbrandingsprosesse van steenkool en ander plantaardige brandstowwe gedurende die winter om hitte te voorsien. Die invloed is die duidelikste sigbaar in lae-inkomste behuisingsgebiede, asook plakkerskampe.

Verdere navorsing sal behartig moet word om duideliker seisoenale patrone waar te neem, asook om te bepaal wat die jaarlikse gemiddelde konsentrasies van spoor metale en atmosferiese deeltjies in die Vaal Driehoek is.

* * *

Chapter 1:
Introduction

This chapter will briefly give background information regarding this particular study. Some of the effects of trace metals on human health will also be mentioned. The motivation, as well as specific objectives of this study will be given.

1.1. BACKGROUND

Atmospheric chemistry and the applications thereof in Environmental Management is a relatively new research field in South Africa. Since the field of chemistry and the application thereof in industry is still growing and dominating the modern day lifestyle, it is necessary to continually monitor the concentrations of chemical entities in the atmosphere and to determine the impacts on the population and the environment.

One such area that needs to be monitored is the Vaal Triangle region in South Africa. Historically the Vaal Triangle included an area stretching from Randvaal in the north, to Sasolburg in the southwest, and Deneysville in the east. The towns of Vereeniging, Vanderbijlpark and Meyerton fell within this geographic area, as well as various low income settlements such as Boipatong, Bophelong, Evaton, Orange Farm, Sebokeng, Sharpville and Zamdela. The area spans approximately 3600 km^2, extending across both the Free State and Gauteng provinces and is contained within two district municipalities namely Northern Free State and Sedibeng. Three local municipalities fall within the area, namely Emfuleni (Sedibeng), Midvaal (Sedibeng) and Metsimaholo (Northern Free State).[42] In densely populated, industrial regions such as this, concentrations of particulate matter and trace metals are expected to be higher than other regions.

Particulate matter (PM) is a mixture of multi component particles, the size distribution, composition, and morphology of which can vary significantly in space and time.[1] Particulate matter is composed of tiny airborne solid or liquid particles, other than pure water, held together through intermolecular forces.[2] It includes dust, soot, smoke and other particles emitted by vehicles, power plants, factories, construction, other human activities, and natural processes (e.g. wind-blown dust, soil degradation, and field fires).

PM can also be classified into fine particulate matter, with particles having a diameter equal to or less than 2.5 μm (referred to as $PM_{2.5}$), and coarse particulate matter, with particles having a diameter equal to or less than 10 μm (referred to as PM_{10}).[17] These two types of particulates may differ in chemical composition, source and behaviour in the air. The fine fraction ($PM_{2.5}$) is often generated by combustion processes and by chemical reactions taking place in air. Coarse particles (PM_{10}) usually do not stay in the atmosphere for more than a few hours, but particulates in fine fraction ($PM_{2.5}$) can remain in the atmosphere for days to weeks.[13]

The toxic trace metals found in $PM_{2.5}$ have been linked to illnesses in humans and research animals. The extremely small size of the fine PM promotes entry and adherence to the lungs, from where it can gain access into the blood stream. In terms of health effects of trace metals, the toxicity of the particles is mainly responsible for causing breathing difficulties and/or inflicting permanent lung damage. Exposure to high levels of fine particulates causes an increase in the number of premature deaths and heart disease.[3] Therefore, $PM_{2.5}$ is considered more critical in PM related health impacts than PM_{10}.[4]

1.1.1. Examples of harmful trace elements in atmospheric particulate matter and associated health risks

Some of the trace metals that pose potentially serious health-related risks in a densely populated, industrialised region like the Vaal Triangle are Cr, V, Fe, Ni and Pb.[5-11]

Hexavalent chromium (Cr^{6+}) is a carcinogen and may also lead to severe coughing, asthma, bronchitis, neurological and gastronomical effects, pneumonia, as well as possible effects on the normal functioning of the kidneys, liver, stomach, and immune system.[5,6] Trivalent chromium (Cr^{3+}), however, is not carcinogenic and the health effects are not so severe.[5]

Vanadium pentoxide (V_2O_5) is frequently produced by industry (as a product, a by-product or waste) and the health effects associated with it is more severe than for the free metal. It causes severe irritation of the eyes, throat, lungs and nose when inhaled, and may also lead to bronchitis, pneumonia, asthma, hart-disease, neurological damage and inflammation of the gastrointestinal system.[6,7]

Iron (Fe) is an essential nutrient for humans, since it forms an important part in the production of haemoglobin, which is required to transport oxygen through the veins in red blood cells. If there is an overdose of iron in the body, it can cause lung cancer, heart disease, diabetes, coughing, asthma, and irritation to eyes and throat.[6,8,9]

Nickel (Ni) is commonly used in the industry to reinforce steel and other metals. It has carcinogenic properties and can also lead to dizziness, vomiting, diarrhoea, birth defects, asthma, chronic bronchitis, allergic reactions and heart disease. Nickel is difficult to remove from the atmosphere and can stay in the atmosphere for several years. It also influences plant growth and it damages plant-fibres.[6]

Lead (Pb) is a trace metal that can have serious and long-lasting effects on children below the age of six, and also less serious side effects on adults. Lead poisoning or long-term exposure is dangerous for children younger than six, because they still have to undergo a lot of physical and mental growth. The health effects of lead include damaging of the brain and nervous system, behaviour problems, learning disability, impaired growth, hearing problems and severe headaches. The health effects of lead on adults include complications during pregnancy, reproduction problems, increased blood pressure, indigestion, neurological disorder, concentration and memory problems, muscle-pain, and arthritis. [10,11]

1.2. MOTIVATION

The Air Quality Act 39 of 2004 has made provision for the identification of priority areas where the air quality is regarded as poor and detrimental to human health and the environment. The Vaal Triangle was declared the first priority area in South Africa by the Minister of Environmental Affairs and Tourism on the 21st of April 2006. The area known as the Vaal Triangle Air-shed Priority Area (VTAPA) includes areas contained in four different Local Municipalities over two provincial boundaries. The area includes heavy industrial activities, one power station, several commercial operations, motor vehicles as well as many households utilizing coal as an energy source.[42]

The need has therefore arisen to monitor the concentrations of chemical entities in the atmosphere and the effects of these entities on human health and on the environment. Since there is very little existing data on trace element concentrations in this region, a definite need existed to perform this study. Trace metals and aerosol particles in the fine particle fraction ($PM_{2.5}$) cause a variety of health-related problems, depending on the extent and time of exposure and the concentration of the species.[12] In this study, the concentrations of certain harmful trace metals (such as Cr, V, Fe, Ni, and Pb) were monitored, as well as the total concentration of $PM_{2.5}$ and PM_{10} particles. These values were compared to acceptable standards, as stated by the World Health Organisation (WHO), the Environmental Protection Agency (EPA), and to Government regulations.

In this study data was obtained that will contribute to a better understanding of:

- the seriousness of pollution due to trace metals in the atmosphere;
- the spatial and seasonal distribution of trace metals in the VTAPA (three sites, namely Sasolburg, Vanderbijlpark, and Vereeniging); and
- which analytical technique, or combination of techniques, provides the most useful results for this particular study.

1.3. OBJECTIVES

Taking the afore-mentioned motivation into consideration, the objectives of this study will therefore be to:

- Collect $PM_{2.5}$ and PM_{10} samples once during a winter and once during a summer season at three selected sites in the Vaal Triangle;
- Determine the concentration of trace elements in the different size fractions of the collected atmospheric particulate matter in the study area;
- Compare results from two different analytical techniques to suggest an appropriate atmospheric particulate monitoring method;
- Evaluate the use of portable Minivol Air Samplers (product of Airmetrics) for use in such studies.

This chapter has very briefly given an introduction and stated the need and importance for this particular study. The need for this study is great since there is limited data on trace metals for the Vaal Triangle. Specific health and environmental effects caused by trace metals will be discussed in more detail in the following chapter.

Chapter 2:
Literature Review

This chapter will take a closer look at relevant literature of interest for this particular study. It will start with a description of aerosols, followed by a description of particulate matter, and finally it will describe trace metals in more detail, especially the health and environmental effects of certain trace metals. A brief overview will also be given of some relevant studies that have been conducted at a global scale.

The focus of this particular study was on the chemical composition of atmospheric particulate matter – or more specifically, the chemical composition and contribution of trace metals in atmospheric particulate matter. Therefore, the literature review will focus on aerosols, particulate matter and trace metals.

2.1 AEROSOLS

Aerosols are generally defined as a mixture (or suspension) of solid and/or liquid particles in a gas, with a size range from nanometres to micrometers. From an atmospheric scientific point of view, the focus is more on the suspended particles, in a condensed matter other than water (clouds and water fall under a different phenomena).[13,55,56]

Over the recent years, aerosols have attracted the attention of a variety of scientists from different backgrounds. Even after extensive research has been done in this field, aerosol science is still very complex and the knowledge gained so far is very limited.[13,16]

Some of the more general questions that attract the attention of scientists worldwide include:[13,14,16]

- What kind of processes take place during aerosol formation and growth?;
- What types of reactions take place in the atmosphere?;
- What physical changes occur in aerosol composition in the atmosphere?;
- What causes these physical changes to occur?;
- What is the effect of individual elements of aerosols on human health and the environment?;
- What is the joint effect of various aerosols on human health and the environment?;
- What is the effect of particle size on human health?; and
- What mechanisms cause the adverse health effects of inhaled aerosols?

Aerosols are believed to have effects on climate change (global warming and dimming effects), the energy balance of the Earth, the hydrological cycle, atmospheric circulation, human health and on the environment. Aerosol particles cause these effects because they scatter and absorb radiation from the sun and the earth. They are also involved in the formation of clouds and of "wet precipitation" (as cloud condensation nuclei and ice/snow nuclei).[13]

If a small amount of particles are available as cloud condensation nuclei, large drops are formed and if a large amount of particles are available as cloud condensation nuclei, smaller drops are formed that reflect sunlight more readily, leading to a cooling effect on surface temperature. It is, however, more difficult for the smaller droplets in the clouds to grow to a size where they will form raindrops, and so the number of aerosol particles present in a cloud influences the hydrological cycle and circulation, as well as cloud convection dynamics.[14,15]

Aerosols can influence climate in a direct (interactions of radiation and temperature on particles) or indirect (cloud and precipitation modifications by aerosols) manner, with regards to radiative forcing. Radiative forcing (RF) can be defined as positive or negative changes in the energy balance of solar and terrestrial radiation in the atmosphere. These changes can be caused by a difference in the composition of natural or anthropogenic emissions, the Earth's surface properties, or solar activities. Negative radiative forcing tends to reduce the Earth's surface temperature and positive radiative forcing tends to increase it.[13,15]

However, determining whether a certain aerosol-emitting process has positive or negative radiative forcing properties is very complicated. Combustion-generated aerosols, for instance, have certain entities (i.e. CO_2) that have a positive RF character and others (i.e. particulate matter) that have a negative RF character.[15]

Since the Intergovernmental Panel on Climate Change's Third Assessment Report (IPCC:TAR, 2001), the understanding and quantification of the forcing mechanisms has improved a great deal. This made it possible to give a net anthropogenic radiative forcing estimate for the first time (see Figure 2.1) in 2007, with a very high confidence level. The figure specifies the net estimated contribution (RF values) for various agents (RF Terms) with a 90% confidence interval in 2005, as well as the geographical area affected (spatial scale) and the level of scientific understanding (LOSU) for each agent.[16]

From Figure 2.1, it is clear (from both the level of scientific understanding as well as the error bars) that the total radiative forcing effect of aerosols, especially the aerosol indirect effects (cloud albedo effects) are not as well understood at this point in time as long-lived greenhouse gases (LLGHGs, such as CO_2), which are the dominant, most extensively researched radiative forcing term with the highest level of scientific understanding.[16]

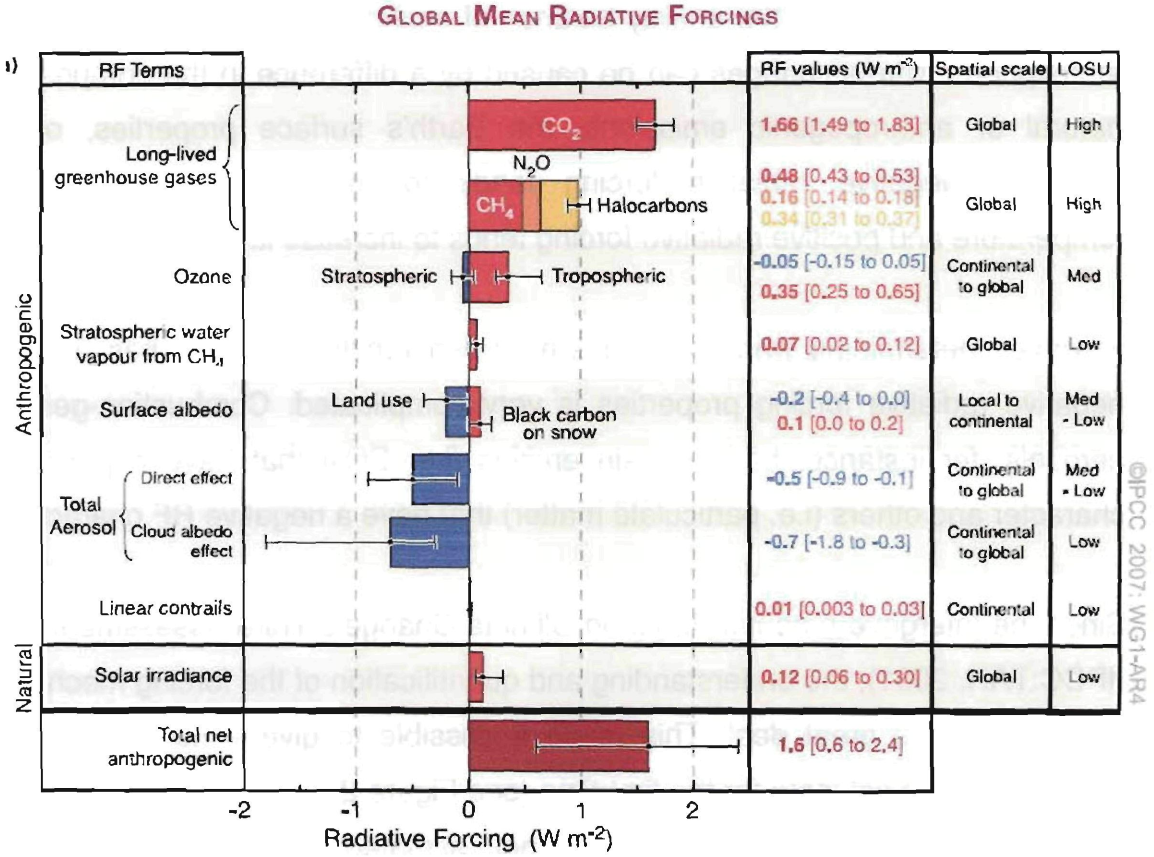


Figure 2.1: *Global mean radiative forcings (RF) and their 90% confidence intervals in 2005 for various agents and mechanisms. (Figure obtained from the IPCC: FAR, 2007)* [16]

Primary particles are emitted directly from a source as a solid or liquid particle, whereas secondary particles are formed by other processes that take place in the atmosphere. Once the particles are airborne, they interact with other particles and undergo atmospheric aging processes. Lifetimes of aerosol particles can vary from as short as a few hours up to several weeks, depending on atmospheric conditions and aerosol composition.[13]

Very small particles (with a diameter ≤ 0.1 μm) normally have large numbers in the atmosphere, small mass, they coagulate very quickly and therefore they have relatively short lifetimes. Intermediate particles (diameter between 0.2 and 2 μm) have smaller numbers, but they still make up a huge fraction of total particulate matter, they do not coagulate as rapidly as smaller particles and therefore they have a longer lifetime. Large particles (diameter ≥ 2 μm) have low numbers and larger masses that cause them to get deposited very rapidly and therefore they have short lifetimes.[14]

Aerosol lifetimes in the atmosphere (a few weeks), is much smaller than the lifetimes of greenhouse gases (several years) and they generally have a negative RF value. Therefore, a drastic reduction in the concentrations of aerosols would possibly result in an increase of surface temperature over a few years, similar to the effect caused by the accumulation of greenhouse gases over the past centuries.[14,15]

Aerosols in the fine particle fraction (diameter of 2.5 µm or less) cause a variety of health-related and environmental problems, depending on certain parameters which are spatially and temporally highly variable. Amongst others, these parameters include: the concentration of the species; the size, structure and chemical composition of the species; the extent and time of exposure; and meteorological conditions (for instance, temperature and relative humidity).[13] It is also generally believed that aerosols in the fine fraction are mainly from anthropogenic origin (for instance, combustion of fossil fuels, traffic emissions, power plants and industrial and mining activities), whereas aerosols in the coarse fraction (diameter larger than 2.5 µm) are believed to be from natural emissions (biomass burning, volcanic eruptions, sea salt, wind-driven soil dust, plant matter, etc.).[13,55,57,58]

Epidemiological research mainly makes use of one of two methods (sometimes both) to evaluate the impact of aerosols on human health. These two methods are the time series method and the cohort method. The time series method is basically a comparison of the actual mortality rate with the mortality calculated by means of the identified impact. A small fraction is unexplainable this way and it has a strong correlation with air pollution events, especially with regards to fine particulate matter.[14]

The cohort method on the other hand, is based on the characterization of a large group of people into groups of various factors, for instance smokers vs. non-smokers, living near emission source vs. living further away, asthmatics vs. non-asthmatics, etc. After these groups have been identified, mortality and frequency of disease are estimated as a function of the various groups and the groups are compared against one another.[14] The main aim of the cohort studies are to quantify or estimate the impact of aerosols on the total population's lifespan, and to differentiate between the impacts of air pollution on the various target groups. Neither one of these methods, nor toxicological studies could thus far reveal what specific compounds (or what combination of compounds) in aerosols are responsible for observed health effects.[14]

Various epidemiological and toxicological studies have identified possible mechanisms by which aerosols may cause adverse health effects, but the biochemical processes in particular that take place and cause a health-related response are not yet satisfactorily resolved or understood. Some of the health effects are inflammation, protein modifications, alterations in immune response and nervous system activities, enhanced response to allergens and suppression of normal defence mechanisms.[13,14]

Particularly little is known about the causes of allergic reactions and the role air pollutants play in this. Before air quality and the related health effects can be efficiently controlled, further studies need to be undertaken to fully understand the various mechanisms that take place, the atmospheric interactions that occur and to identify hazardous air pollutants and their sources and sinks.[13,14] These studies need to include both gaseous and particulate components of aerosols, as well as their reactivity, chemical composition, aging processes and lifetimes. Without a complete understanding of all of the above, guidelines or regulations stands a chance of not being efficient enough. [13]

2.2. PARTICULATE MATTER

2.2.1. Introduction

Particulate matter (PM) is a mixture of primary and secondary aerosols and it can exist in the solid or liquid phase, containing many subclasses of pollutants with each subclass potentially containing many different chemical species.[13,14] The size range spans many orders of magnitude, from molecular clusters (diameters of 1nm) to very coarse particles (diameters up to 100 μm). Particles less than 2.5 μm in aerodynamic diameters are often referred to as fine particles, or $PM_{2.5}$. Particles with aerodynamic diameters larger than 2.5 μm and less than 10 μm are generally referred to as coarse particles, or PM_{10}.[17] Natural PM includes wind-transported geological material, biogenic PM (pollen, spores and secondary PM from volatile organic compounds) and sea salt. Naturally released sulphur and nitrogen compounds produce additional particles, but the anthropogenic emissions of sulphur and nitrogen compounds dominate secondary particle formation in industrial areas.[18] The types of particulate matter can also be classified as organic (soot, polycyclic aromatic hydrocarbons [PAHs], etc.), inorganic (metals, sulphates, nitrates and others), or it can be a combination of both organic and inorganic compounds.[20]

2.2.2. Formation of PM

Fine PM is usually formed during combustion processes where volatilized combustion material condenses to form primary particulate matter, and from the reactions of precursor gases in the atmosphere to form secondary particulate matter. Coarse PM is generally formed during activities that break down large pieces of material into smaller pieces (i.e. crushing, grinding and abrasion of surfaces). These smaller pieces are then suspended by the wind. The chemical and physical properties of particles can change due to the accumulation of atmospheric gas-phase chemical reaction products, or due to heterogeneous reactions with gas-phase species.[17]

The combustion sources of ambient particles include stationary boilers and furnaces, stationary and mobile internal combustion engines, fugitive emissions from industrial processing, domestic fires, open burning, and accidental fires. Combustion particles are multimodal. The finest particles are produced by gas-to-particle conversions and form the nuclei, or nanoparticles. These grow by coagulation and surface growth into the accumulation mode. The larger supermicron particles are produced from the inorganic material that remains in the solid or liquid phase with the fuel and is referred to as residual ash particulate matter. The particle size distribution is determined by the volume fraction of the aerosol that is produced by initial nucleation and by subsequent coagulation and surface growth.[18]

During combustion, the inorganic components associated with fuels goes through complex chemical and physical transformations that leads to the production of primary particles and precursors for secondary particles. It also causes the inorganic components to be transformed into vapours, liquids and solids. These physical transformations depend on the inorganic composition of the fuel and on the combustion conditions. The fuel sources and fuel blending influence the size, morphology, chemical composition and chemical speciation of particulate matter.[20]

The physical transformations involved in primary particle formation include coalescence of individual mineral grains within a char particle, shedding of the ash particles from the surface of the chars, incomplete coalescence due to disintegration of the char, convective transport of ash from char surface during devolatilization, fragmentation of the inorganic mineral particles, formation of cenospheres, and vaporization and subsequent condensation of the inorganic components upon gas cooling. Processes such as ash mineral coalescence, partial coalescence, ash shedding, char fragmentation, and mineral fragmentation all play a role in the size and composition of the final fly ash.[20]

2.2.3. Health and environmental impacts

At present, it is a well-known fact that particulate matter is responsible for the deterioration of visibility, damage to the environment, and serious health-problems. Particles in the fine fraction are of bigger concern than particles in the coarse fraction. The fine particles gain easy access into the bloodstream via the lungs, whereas coarse particles cannot diffuse into the bloodstream and therefore only cause problems in the airways and lungs. It is important to note that all particles (fine and coarse) are potentially harmful to human health and that it is not yet fully known what specific chemical species (or combination) in particulate matter are responsible for adverse health effects.[18,20,21]

Increases in the severity and frequency of asthma attacks and bronchitis are linked to exposures to ambient particulate pollution events. These particulate pollution events may even lead to premature deaths of people with existing cardiac or respiratory disease. The groups of people that are most sensitive to particulate pollution include people with existing cardiac or respiratory diseases, children and the elderly.[17]

The epidemiology and toxicology of ambient particulate matter is an active area of research and recently, efforts to find the causes of adverse health effects of particles have intensified. Initial epidemiological studies were focused on correlating the health effects with the mass concentrations of particles (as a dose-response reaction). Later on the focus was shifted to particle size, or surface area, since stronger associations had been found with fine particles and because the body interacts with the surface area of an insoluble particle. Recently, ultrafine particles have also been extensively studied, because they are deposited deep in the lungs and from there they can easily gain access into the bloodstream via diffusion through the cell walls lining the alveoli of the lungs. [18]

Epidemiologists have not been able to correlate health effects with either ultrafine ambient particles, or with the ambient concentrations of biologically available transition metals. The reason for this is that these substances have not yet been measured routinely over a sufficient geographical area or period of time to show detectable variation. Although epidemiology can show a correlation, it cannot prove causality, because two well-correlated factors may both be individually correlated to a third unknown factor that may be the actual cause.[18]

Combustion-generated secondary sulphates and nitrates are the dominant species of urban fine particulate matter and they correlate the best with epidemiological studies. Acidic particles that are inhaled appear to enhance lung damage biomarkers. The synergistic effects of a mixture of pollutants appear to be more damaging than the effects of one pollutant alone (for example SO_2 + soot, ultrafine PM + ozone, or fly ash + H_2SO_4).[18]

To determine personal exposure to particles, various factors must be taken into consideration, such as physical activity (ventilation rate) and the amount of time spent in various environments indoors, in vehicles and outdoors. When discussing health effects of combustion particles, it must also be considered that people do not inhale combustion emissions directly (with the exception of tobacco smoking and domestic combustion), they inhale particles that have undergone post-combustion atmospheric transformations.[18]

The deposition of supermicron particles by inertial impaction and of submicron particles by diffusion depends on the gas velocity and residence time in various sections of the airways and lungs. Most of the coarse particles are deposited in the nose and throat, while roughly about 60% of inhaled ultrafine particles are deposited in the lungs. The body has defences to rapidly remove inhaled particles.

Mucus is formed in the airways, trapping particles and ciliated cells transport them from the respiratory tract to the throat, where it can be coughed up or swallowed. In the alveoli, macrophage cells take up particles through phagocytosis and transport them into the ciliated airways. Particles can also be removed from the lungs by dissolution and by transport into the lymphatic system. A fraction of inhaled particles is retained for a long time in the respiratory system. The process of clearing particles from the lungs can induce secondary physiological responses, including severe coughing and inflammation.[18]

2.2.4. Air quality

For a targeted reduction of $PM_{2.5}$ and PM_{10} concentrations in the atmosphere, detailed knowledge must be acquired of their sources and their respective contribution to the PM levels must be determined. Unfortunately, there are two essentials that make the estimation of individual source contributions to PM particularly difficult and uncertain. One is that a high fraction of the particles are secondary. The second is that the background levels of PM transported into the areas where the exceeding occurs may be high. Both of these reduce the portion of PM available for control in the exceeded region.[19]

It is not only because of the legal implications that ambient PM levels must be monitored and evaluated, but especially because of the effects of PM on human health that have been observed in a number of studies. Current research trends tend to focus on the fine fraction of particulate matter as a result of its implications on health (ranging from obstructive pulmonary disease to inflammatory potential), and because the majority of the anthropogenic emission sources generate particles mainly in this size range.[21] However, this does not imply that the coarse fraction of particulate matter is innocuous. Thus, the coarse fraction of particulate matter should also be taken into consideration.[21]

The application of effective abatement strategies to reduce PM levels is only possible when the emission sources have been uniquely identified and characterized. Emission inventories initially constitute a useful tool for this purpose, although at times they are not as complete as would be necessary due to the fact that important PM sources are frequently fugitive. PM transport and deposition models based on emission inventory data have greatly improved in recent years, although there is still a need for a better fit between measured data and modelled levels. Among the causes of this disagreement are the presence of water in aerosols and the difficulty of quantifying natural sources and fugitive emissions. A different approach has thus been developed in the form of receptor models, which attempt to identify and quantify the contribution of PM sources at a given study site based on the measured ambient concentrations of different PM fractions and components. A number of methods are currently in use, such as principle component analysis (PCA), chemical mass balance (CMB), positive matrix factorization (PMF), or the multi-linear engine (ME).[21]

2.2.5. Prior research in the Vaal Triangle region

To conclude this section on particulate matter, a closer look will be taken at a study done by Engelbrecht and Swanepoel *et al.* (1997) in South Africa.[22] This study gives a general idea of what the situation in South Africa was at that time (and to some extent still is), with regards to main sources of ambient PM pollution. The study done by Engelbrecht and Swanepoel *et al.* was also of great significance for this particular study, because it was conducted at a location not far from the Vaal Triangle, and also situated in the Vaal Meander (the wetlands and valleys around the Vaal River and Vaal dam). Therefore, the meteorological conditions, vegetation and soil compositions were similar to the sites used in the present study. Another significant factor of importance is that the study was conducted in a township (a low-income settlement, also sometimes referred to as a squatter-camp, where most residents live in lean-to shelters) a great number of which can be found in the Vaal Triangle.

D-grade residential coal is widely used as a fuel source for heating and cooking by most of the lower-income urban communities in South Africa, due to its abundant availability and low cost. Smoke from residential coal combustion in townships was found to contribute up to 30% of the particulate pollution in the industrialized areas of South Africa. The adverse health effects resulting from exposure to residential coal combustion emissions have been for many years (and still are), a major public concern. Although electricity has been available in most of these townships for some time, the cost thereof is high compared with coal.[22]

It was envisaged that coal stoves and braziers would still be used for cooking and heating in townships for several decades to come. This study showed that excessively high PM pollution levels were regularly being reached in the industrialized regions and townships in the Highveld of South Africa. It also showed what the major sources of air pollutants were. To protect public health, low-smoke fuels were developed as an alternative source of energy for residential use.[22]

To address the public concern for health with regards to coal combustion emissions, the Department of Minerals and Energy of South Africa conducted a macro-scale experiment whereby three brands of low-smoke fuels were tested in the township of Qalabotjha (approximately 15 000 inhabitants), situated along the southern banks of the Vaal river in the Free State Province. This area was selected for the experiment because it represented a small, low-income township in suburban South Africa, and because it was located generally upwind in relation to the polluted and industrialized Vaal Triangle and Mpumalanga Highveld regions. The objective of this experiment was to assess the technical, health, and social benefits of low-smoke fuels, in contrast to D-grade residential coal. The ambient $PM_{2.5}$ and PM_{10} particulate monitoring and source apportionment study was conducted over a 30-day period during the winter of 1997.[22]

Elevated PM mass was found when D-grade coal was combusted during the first 10 days of the experiment. 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 were conducted to characterize source compositions. It was found that lead, bromine and organic carbon (OC) were highly abundant in the leaded gasoline fuels. PM_{10} soil reported a different profile than that of metallurgical dust with an abundance of silicon, aluminium, iron and OC. The metallurgical profiles were variable, but with iron as the abundant species. Manganese in the coarse fraction was also high. Sodium, chloride and potassium in the fine fraction were enriched in the metallurgical sinter plant emission. Calcium, sulphate, OC and soluble sodium in the coarse fraction were abundant in the lime profile.[22]

Results of this study showed that residential coal combustion was the largest contributing source of particulate matter, accounting for 62% of $PM_{2.5}$ and 42% of PM_{10}. Biomass burning had also contributed significantly, accounting for 13% of $PM_{2.5}$ and 19% of PM_{10}. Crustal material was only found to be significant in coarse particles, accounting for 1% in $PM_{2.5}$ and 11% of PM_{10}. Minor contributions were found from power plant fly ash, leaded petrol vehicle emissions, and agricultural lime. A large portion of total source contributions was attributed to unidentified sources. More than 90% of the mass of PM_{10} was in fact found to be the $PM_{2.5}$ fraction.[22]

Besides the unidentified sources, the largest contributors for $PM_{2.5}$ were residential coal combustion (32%), ammonium sulphate (17%), and biomass burning (10%). The largest contributors for PM_{10} were crustal material (30%), residential coal combustion (14%), ammonium sulphate (13%), and biomass burning (9%). According to the authors, their measurements were sufficient to determine that residential coal combustion is the major contributor to elevated particulate matter concentrations and the aerosol measurements were insufficient to distinguish D-grade coal emissions from low-smoke fuel emissions.[22]

2.3 TRACE METALS

2.3.1 Emission sources

This section will focus on some possible emission sources of trace metals into the atmosphere, as well as the elements that can be used as tracers for these sources.

Residential and commercial boilers and furnaces, as a combustion application, generate fine particles consisting of sulphates, elemental carbon (EC), organics, nitrates and other ionic and oxidized trace species (mainly SiO_2, Al_2O_3, Fe_2O_3 and Na^+).[18] In coal-fired steam generation boilers, metals may partition into three major emission streams, namely the stack, the bottom ash and the fly ash collected during gas cleaning.[18] The toxic trace metals in the emissions are the result of fuel combustion, combustion conditions and downstream cleanup. Large-scale biomass combustion has a unique characteristic, namely the high alkali content, especially K, compared to fossil fuel combustion ash. The supermicron particles are predominantly Ca, but also contain Fe, Al, Mn and Si. With domestic combustion (combustion taking place indoors, for example tobacco smoking, natural gas appliances, oil-fired furnaces, fireplaces and wood stoves), the particles were predominantly EC and OC, but also contained K, Cl, S and Al, Si, P, Zn, Pb and Fe.[18]

In terms of tracers, As and Se are used as tracers for emissions from coal-fired power plants, and Zn and Pb, though not specific to coal combustion, are still present in source profiles from coal-related emissions.[23] Al and Ti are generally used as tracers for soil dust particles. As is generally used as a tracer for coal combustion particles.[25]

Zr, Zn, Pb, and As may be considered as tracers of ceramic emissions. The ceramic pigments are prepared by the calcinations of inorganic raw materials containing a wide variety of metals, such as V, Cr, Mn, Fe, Co, Ni, Ti, Pb, Sb, Nb, W, Sn, Cu, Pr, Zr, Al, Zn, Cd, Se or Ce in batch or continuous kilns at a temperature around 1000°C.[26] Rb is used as a typical tracer component for clay minerals and feldspars. Ni, V and sulphate could come from oil fired power plants, and possibly to a lesser extend petrochemical plants (Ni and V are widely used as tracers of emissions from petroleum coke fired power plants). Mineral tracers are mainly Al, Fe, Ti, Ca, Mg, Mn Y, Sr, Li, Rb and K.[26]

Emissions from burning coal and oil, and steel production can increase chromium(III) levels in the air. Stainless steel welding, chemical manufacturing and use of other compounds containing chromium(VI) can increase chromium(VI) levels in the air.[32]

In a study done in Northern Spain by Viana *et al.*[21], in which the authors combined principal component analysis (PCA) with multi-linear regression (MLRA) and wind direction data, the following sources and main tracers were identified: Crustal source (Al_2O_3, Rb, Sr, Ti and Ba as main tracers and also Mg, K and Ca); Marine source or sea spray (Na as tracer, as well as Cl); Pigment manufacture (Cr, Mo, Pb and Fe oxides).[21] Sources for coarse particles were found to be the re-suspension of road dust generated by the abrasion of vehicle-parts and pavement (Fe, Ba, and Cd). For fine particles it was steel manufacturing (main tracers are Pb, Cd, Mn, Fe and Cu) and exhaust emissions (main tracers are P, organic carbon (OC) and elemental carbon (EC)). Biomass burning could also be included (main tracers are K, OC and EC).[21]

2.3.2. Some important metals focussed on in this study

2.3.2.1. Mercury

Mercury is an element in the earth's crust, and can be found in many rocks including coal. When coal is burned, mercury is released into the environment. Burning hazardous waste, producing chlorine, breaking mercury products (i.e.

thermometers, switches, some light-bulbs) and spilling mercury, as well as the improper treatment and disposal of products or waste containing mercury, can also release it into the environment. Mercury in the air eventually settles into water, or onto land where it can be washed into water. Once deposited, certain micro organisms can change it into methyl mercury which is a highly toxic form.[27]

Typically, mercury is released into the atmosphere in one of three forms. Elemental mercury can travel a range of distances and may remain in the atmosphere up to one year and may travel globally before undergoing transformation. Particle-bound mercury can fall out of the air over a range of distances. Oxidized mercury, sometimes called reactive gaseous mercury (RGM), found predominantly in water-soluble forms, may be deposited at a range of distances from sources depending on a variety of factors including topographic and meteorological conditions downwind of the source.[27] After the elimination of mercury from most products and controlling the emissions from incinerators, coal-fired utilities are now the largest single source of mercury in the United States, estimated to account for one-third of anthropogenic emissions.[20]

Setting a uniformly high control requirement for all utility sources does not appear to be practical or achievable at the present state of control technology, and it would pose special difficulties for certain coals that emit elemental mercury vapour, which is more difficult to control than oxidized forms of mercury. The most problematic coals are those that contain the element chlorine, which promotes the oxidation of mercury. There are some preliminary indications suggesting that elemental mercury may be the more prevalent form being transported and deposited, even where oxidized mercury is emitted.[20,59,60]

Since long-distance atmospheric transport of elemental mercury can take place, control is a global problem that requires the cooperation of countries from around the world to achieve some significant measure of improvement. As much as one-third to half of the world's atmospheric mercury is estimated to be of anthropogenic origins, with over 75% of this coming from Asia, Europe and Africa.[20]

2.3.2.2. Lead

Lead is a highly toxic metal that was used for many years in products found in and around our homes. Research suggests that the primary sources of lead exposure for most children are deteriorating lead-based paint, lead contaminated dust, and lead contaminated residential soil.[27]

Lead is a naturally occurring metal found in the earth's crust. It rarely occurs in its elemental state, but rather its +2 oxidation state in various ores throughout the earth. Levels of lead in the environment (not contained in ore deposits) have increased over the past three centuries as a result of human activity. Human exposure to lead is common and results from the many uses of this metal due to its exceptional properties.[28]

2.3.2.3. Nickel

Nickel, combined with other elements, occurs naturally in the earth's crust. It is found in all soil, and is also emitted from volcanoes. In the environment, it is primarily found combined with oxygen or sulphur. Nickel is also found in meteorites and on the ocean floor in lumps of minerals called seal floor nodules. Nickel is released into the atmosphere during nickel mining and by industries that make or use nickel, nickel alloys, or nickel compounds.[29,30]

Nickel is also released into the atmosphere by oil-burning power plants, coal-burning power plants, combustion of fuel oil, and municipal incinerators. The nickel that comes out of stacks of power plants attaches to small particles of dust that settle to the ground or are taken out of the air in rain or snow. It usually takes many days for nickel to be removed from the air. If the nickel is attached to very small particles, it can take more than a month to settle out of the air. The form of nickel emitted to the atmosphere is dependent upon the source. Complex nickel oxides, nickel sulphate, and metallic nickel are associated with combustion, incineration, and smelting and refining processes.[29,30]

Food is a major source of exposure to nickel, but a person can also be exposed by breathing air, drinking water, or smoking tobacco, containing nickel. Unborn children are exposed through the transfer of nickel from the mother's blood to fetal blood. Nursing infants are exposed through the transfer of nickel from the mother into her breast milk.[29]

2.3.2.4. Vanadium

Vanadium is a white to grey metal with compounds widely distributed at low concentrations in the earth's crust. Vanadium is released naturally to air through the formation of continental dust, marine aerosols, and volcanic emissions. Anthropogenic sources include the combustion of fossil fuels, particularly residual fuel oils, which constitute the single largest overall release of vanadium to the atmosphere. These releases are generally in the form of vanadium oxides and contribute approximately two-thirds of atmospheric vanadium. Other anthropogenic emission sources include leachates from mining tailings, vanadium-enriched slag heaps, municipal sewage sludge, and certain fertilizers.[31]

2.3.2.5. Chromium

Chromium is a naturally occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases. Chromium is present in the environment in several different forms. The most common forms are chromium (Cr^0), trivalent (Cr^{3+}), and hexavalent (Cr^{6+}).[32]

Cr^{3+} occurs naturally in the environment and is an essential nutrient required by the human body to promote the action of insulin in body tissues so that the body can use sugar, protein, and fat. Cr^{6+} and Cr^0 are generally produced by industrial processes.[32]

Common uses of chromium include steel and alloy manufacture, brick-lining for high-temperature industrial furnaces, chrome plating, chemical compounds, dye and pigment manufacture, leather tanning, wood preserving, and small amounts are used in drilling muds, rust and corrosion inhibitors, textiles, and toner for copying machines. Chromium enters the air, water, and soil mostly in the trivalent and hexavalent chromium forms as a result of natural processes and human activities.[32]

2.3.3. Environmental and health impacts of trace metals

Toxicological studies have frequently implicated the metal content (particularly water-soluble metal) as a possible harmful component of PM. There is a gap in linking identified potential hazards of soluble metal, and putative risks from actual human exposure to trace metals (i.e. its airborne concentration).[24]

Particles provide a vehicle for metals to enter the body in inappropriately high amounts. There is increasing evidence that the same element has very different behaviour when inhaled than when ingested. The dose of a particle-bound element that is available to the body depends on the entry route, particle size and morphology, and the mineral species in the particle. Transition metals on inhaled particles may act as biochemical catalysts that can induce other biochemical responses.[18]

Transition metals, such as V, Cu, Fe, Ni and Pt can catalyze the generation of reactive oxygen species (ROS) that have been associated with both direct molecular damage and with the induction of biochemical synthesis pathways.[18]

Metals that generate ROS has also been found to switch on cellular pro-inflammatory response pathways in vitro and in vivo.[24]

Coal fly ash and residual oil fly ash have been studied as examples of combustion particles enriched in transition metals. Residual oil fly ash has been shown to induce inflammatory cytokines in bronchial epithelial cells, lung inflammation, and cardiac arrhythmia. Coal fly ash has been shown to be a source of bio-available iron and can also induce inflammatory cytokines in lung epithelial cells. Generation of ROS and induction of cytokines in bronchial cells has also been reported in studies of diesel exhaust particles. The amount of bio-available transition metals contained in particles has been associated with acute lung inflammation from both combustion and ambient particles.[18]

In the following paragraphs, environmental and health impacts of specific trace elements will be discussed.

2.3.3.1. Mercury

Mercury – especially methyl mercury – has a bio-accumulative effect in the ecosystem. Methyl mercury builds up more in some types of fish and shellfish than in others. At high levels of exposure, methyl mercury's harmful effects on these animals may include death, reduced reproduction, slower growth and development, and abnormal behavior.[27]

Human exposure to mercury commonly results from eating fish containing methyl mercury that has accumulated in the food chain.[27] Significant exposure also occurs for persons affected by small gold-mining operations that use mercury amalgamation methods. Precautions to limit mercury exposure have arisen because of evidence of serious harm to the developing nervous system of unborn and growing children.[20,61]

Major studies of mercury's health effects in humans have reported contradictory results. All of these studies were well conducted using scientifically reliable methods, indicating that unrecognized factors in these locations may have caused different responses to similar levels of mercury exposure. A number of past studies suggest that one such factor may be the level of selenium in the diet.[20] Selenium-containing proteins (selenoproteins) detoxify free radicals generated during normal cellular respiration and perform other still unknown functions. When too much selenium is lost to formation of precipitates, brain cells can be damaged, resulting in impaired neurological developments in the fetus.[20,62]

Mercury exposure at high levels can harm the brain, heart, kidneys, lungs, and immune system of people of all ages. High levels of methyl mercury in the bloodstream of unborn babies and young children may harm the developing nervous system, making the child less able to think and learn. It became clear that the developing nervous system of the foetus may be more vulnerable to methyl mercury than is the adult nervous system.[27]

In addition to the subtle impairments noted above, symptoms of methyl mercury exposure may include impairment of peripheral vision; disturbances in sensations ("pins and needles" feelings in hands, feet and around the mouth); lack of coordination of movements; impairment of speech, hearing, and walking; and muscle weakness.[27]

Elemental mercury primarily causes health effects when it is breathed as a vapour where it can be absorbed through the lungs. Symptoms include tremors, emotional changes (e.g. mood changes, irritability, nervousness, and excessive shyness), insomnia, neuromuscular changes (weakness, muscle atrophy, twitching), headaches, disturbances in sensations, changes in nerve responses and performance deficits on tests of cognitive function. At higher exposures there may be kidney effects, respiratory failure and death.[27]

High exposures to other forms of inorganic mercury compounds may result in damage to the nervous system, the gastrointestinal tract, and the kidneys. Other symptoms include skin rashes, dermatitis, memory loss, and mental disturbances.[27]

2.3.3.2. Lead

Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains.[6] Lead does not degrade easily and is strongly absorbed to soil. Lead released from historical uses still remains in the soil. The atmospheric concentration of lead varies greatly, with the highest levels observed near stationary sources such as lead smelters.[28]

Lead accumulates in the bodies of water organisms and soil organisms. These organisms will experience health effects from lead poisoning. Health effects on shellfish can take place even when small concentrations of lead are present and body functions of phytoplankton can be disturbed. Phytoplankton is an important source of oxygen production in seas and many larger sea-animals eat it. It is hypothesized that lead pollution can therefore influence global balances.[6]

Soil functions are disturbed by lead intervention, especially near highways and farmlands, where extreme concentrations may be present. Soil organisms can suffer from lead poisoning as well.[6]

If not detected early, children with high levels of lead in their bodies can suffer from damage to the brain and nervous system, behaviour and learning problems (such as aggression, impulsiveness, and hyperactivity), slowed growth and development, hearing problems and severe headaches.[6,27] In children 8 to 10 years of age, lead accelerates skeletal maturation, which might predispose to osteoporosis in later life.[28] Lead has also been associated with increased occurrence of dental caries in children and periodontal bone loss, which is consistent with delayed mineralization in teeth.[28]

Adults can suffer from difficulties during pregnancy, other reproductive problems in men and women, digestive problems, nerve disorders, brain damage, and muscle and joint pain.[6,27] Symptoms develop following prolonged exposure and include dullness, irritability, poor attention span, epigastric pain, constipation, vomiting, convulsions, coma, and death.[28]

The most sensitive targets for lead toxicity are the developing nervous system, the haematological and cardiovascular systems, and the kidneys. Lead could potentially affect any system or organs in the body. Long-term exposure to lead may be associated with increased mortality due to cerebrovascular disease. Blood lead levels (PbB) have been associated with small elevations in blood pressure.[6,27,28] Studies of children have shown associations between PbB and growth, delayed sexual maturation in girls, and decreased erythropoietin production. Some studies have observed associations between PbB and abortion and pre-term delivery in women, and alteration in sperm and decreased fertility in men. Studies of cancer in lead workers have been inconclusive, but there is limited evidence of increased risk of lung cancer and stomach cancer. The EPA has determined that lead is a probable human carcinogen.[28]

Lead has long been known to alter the haematological system by inhibiting the activities of several enzymes involved in heme biosynthesis. Anaemia induced by lead is primarily the result of both inhibition of heme synthesis and shortening of erythrocyte lifespan.[6,28]

Altered serum levels of reproductive hormones, particularly follicle stimulating hormone (FSH), luteinizing hormone (LH), and testosterone have been observed at increased blood lead levels. Lead also has been shown to decrease circulation levels of the active form of vitamin D.[28]

2.3.3.3. Nickel

Nickel does not accumulate to a great extent in animals. Results of observations of the accumulation of nickel in plants are contradictory.[6,29,30] Growth retardation has been reported in some species, at high nickel concentrations. There is no evidence that nickel may undergo biotransformation, though it does undergo complexation. Nickel is considered essential based on reports of nickel deficiency in several animal species.[29,30]

Nickel deficiency is manifested primarily in the liver. Effects include abnormal cellular morphology, oxidative metabolism, and increases and decreases in lipid levels. Decreases in growth and haemoglobin concentration, impaired glucose metabolism, adverse effects in the male reproductive system, and decreases in the survival of the offspring of animals exposed have also been observed.[29,30]

It is known that high nickel concentrations on sandy soils can damage plants and high concentrations in surface waters can diminish the growth rates of algae and micro organisms.[6] It is an essential foodstuff in small amounts for animals, but it can also be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer.[6]

The most common harmful effect of nickel in humans is an allergic reaction when nickel is in direct contact and prolonged contact with the skin. The most common reaction is a skin rash. In some sensitized people, dermatitis may develop in an area of the skin that is away from the site of contact. Some workers exposed to nickel by inhalation can become sensitized and have asthma attacks.[16,29] The most serious harmful effects from exposure to nickel, such as chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus, have occurred in people who have breathed dust containing certain nickel compounds while working in nickel refineries or nickel-processing plants. Exposure to high levels of soluble nickel compounds may also result in cancer. The EPA has determined that nickel-refinery dust and nickel-sub-sulphide are human carcinogens.[29]

An uptake of too large quantities of nickel has the following consequences: higher chances of developing nose cancer, lung cancer, larynx cancer and prostate cancer; sickness and dizziness after exposure to nickel gas; lung embolisms; birth defects; heart disorders.[6] Other symptoms of nickel exposure include chronic bronchitis, emphysema, pulmonary fibrosis, and impaired lung function. Inhalation exposure to some nickel compounds can induce lung cancer. The carcinogenicity of nickel has been well documented in occupational exposed individuals. The potential for nickel compounds to induce reproductive effects has not been firmly established.[29]

In terms of human health, nickel carbonyl is the most toxic nickel compound. The effects include frontal headache, vertigo, nausea, vomiting, insomnia, and irritability, followed by pulmonary symptoms similar to those of a viral pneumonia. Pathological pulmonary lesions include haemorrhaged, oedema, and cellular derangement. The livers, kidneys, adrenal glands, spleen and brain are also affected.[30] Chronic effects such as rhinitis, sinusitis, nasal septal perforations, and asthma have also been reported. In addition, nasal dysplasia has been reported in nickel refinery workers.[6,30]

2.3.3.4. Vanadium

Vanadium can be found in the environment in algae, plants, invertebrates, fish and many other species. Vanadium strongly bioaccumulates in mussels and crabs. Vanadium causes the inhibition of certain enzymes with animals, which has several neurological effects. Next to the neurological effects, vanadium can cause breathing disorders, paralysis and negative effects on the liver and kidneys. Vanadium can also damage the reproductive system of male animals, and it accumulates in the female placenta. Vanadium has also been found to cause DNA alterations in some cases, but it cannot cause cancer in animals.[6]

Vanadium is not metabolized when it is ingested. However, in the body, there is an inter-conversion of two oxidation states of vanadium, the tetravalent form, vanadyl (V^{4+}), and the pentavalent form, vanadate (V^{5+}). Vanadium can reversibly bind to transferring protein in the blood and then be taken up into erythrocytes. These two factors may affect the biphasic clearance of vanadium that occurs in the blood. Vanadate is considered more toxic than vanadyl, because it is reactive with a number of enzymes and is a potent inhibitor of the Na+K+ATPase of plasma membranes.[31]

The only other significant, clearly documented, effect in humans is mild to moderate respiratory distress and mucosal irritation from exposure to vanadium dusts. Symptoms include coughing, wheezing, chest pain, runny nose and sore throat. Symptoms are believed to be reversible within days or weeks after exposure ceases.[31]

The other significant peripheral finding in some workers was a green discoloration of the tongue attributed to direct deposition of vanadium. Workers exposed to vanadium ore dust also reported skin rashes and weight loss. Neurological effects of vanadium dust include dizziness, depression, headache, and tremors of the fingers and arms.[6,31]

The acute effects of vanadium are irritation of lungs, eyes, throat, and nasal cavities. Other health effects of vanadium uptake are cardiac and vascular disease, inflammation of stomach and intestines, damage to the nervous system, bleeding of livers and kidneys, severe trembling and paralysis, nose bleeds and throat pains, weakening, sickness and headaches, dizziness, and behavioural changes.[6]

2.3.3.5. Chromium

There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water, and soil in the Cr^{3+} and Cr^{6+} forms through natural processes and human activities. Cr^{3+} is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions if the daily dose is too low. Cr^{6+} is mainly toxic to organisms. It can alter genetic materials and cause cancer.[6]

Acidification of soil can influence chromium uptake by crops. Plants usually absorb only Cr^{3+}. This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects might occur.[6]

Chromium is not known to accumulate in the bodies of fish. High concentrations of chromium in surface waters can damage the gills of fish. In animals, chromium can cause birth defects, infertility, tumour formation, respiratory problems , and lower their ability to fight disease,.[6]

In general, Cr^{6+} is absorbed by the body more easily than Cr^{3+}. Once inside the body, Cr^{6+} is changed to Cr^{3+}. Chromium particles can be deposited in the lungs. Particles deposited deep in the lungs are likely to remain long enough for some of the chromium to pass through the lining of the lungs and enter the bloodstream. Once in the bloodstream, chromium distributes to all parts of the body.[32]

Breathing in high levels of Cr^{6+} can cause irritation to the nose, such as runny nose, sneezing, itching, nosebleeds, ulcers, and holes in the nasal septum. Long-term exposure to chromium has been associated with lung cancer.[6,32] High levels of chromium in the workplace have caused asthma attacks in sensitized people. Breathing in Cr^{3+} however, does not cause irritation to the nose or mouth in most people.[32]

Exposure to Cr^{3+} is less likely to cause skin rashes in chromium sensitive people than exposure to Cr^{6+}.[6,32] Other respiratory effects that have been observed include a decrease in the forced expiratory volume of the lungs, accompanied by erythema of the face, nasopharyngeal pruritis, nasal blocking, coughing, and wheezing.[6,32]

Cr^{6+} is also known to cause various health effects that include upset stomachs and ulcers, weakened immune systems, kidney and liver damage, alterations of genetic material and death.[6]

2.3.3.6. Iron

Iron is an essential part of haemoglobin. Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer. A more common problem for humans is iron deficiency, which leads to anaemia.[6]

It is hypothesized that particles generate free radicals (also referred to as reactive oxygen species [ROS]) at their surface in reactions involving iron. PM_{10} particles showed significant free radical activity by their ability to degrade supercoiled DNA. This occurs by an iron dependent process and hydroxyl radicals could play a part in the pathogenicity of PM_{10} particles. Iron may be mobilized inside macrophages after phagocytosis, leading to oxidative stress in the macrophages.[39,40]

The inflammation that can be caused by ROS can exacerbate pre-existing ailments and has been implicated in a variety of diseases, including atherosclerosis. Combustion conditions in mobile and stationary sources can affect the reactivity of aerosols and their ability to generate ROS. The presence of Fe significantly increases the production of ROS.[40]

$Fe(AsO)_3.5H_2O$ may be hazardous to the environment. Special attention should be given to plants, air and water. It is strongly advised not to let the chemical enter into the environment because it has accumulative character.[6]

2.3.4. Relevant studies

2.3.4.1. Analytical techniques and elemental speciation of trace metals

Joseph A. Caruso and Maria Montes-Bayon reviewed elemental speciation as a new approach to trace metal analysis.[37] The importance of metal speciation relative to total metal analysis was considered and various types of chromatographic separation methods using ICP-MS detection were discussed. A brief introduction to the instrumental techniques was included with an emphasis on liquid chromatography (LC). Gas Chromatography (GC) and capillary electrophoresis (CE) were also discussed. Advantages and disadvantages of ICP-MS were compared with other detection methods.[37]

According to the authors[37], it was no longer adequate to consider only the total trace metal or metalloid. Rather, it was necessary to determine the chemical form (species) of the element, primarily the oxidation state or the organometallic nature, because different species of the same metal can range from essential, to innocuous, to toxic. Depending on the metal of interest, ICP-MS afforded as much as a thousand times lower detection limits for LC than non-element-specific detectors such as ultraviolet (UV). Metal-specific detectors had the advantage of “seeing” only the species of a particular metal, whereas the more universal detectors such as UV and refractive index are responsive to a variety of compounds.[37]

ICP-MS was the technique of choice for a wide range of samples with metal concentrations in the ppm to sub-ppb range. It became a highly versatile technique with low detection levels and high sensitivity. Coupled with metal specificity, it was a technique of choice for chromatographic detection including GC, LC, size exclusion chromatography (SEC) and CE. ICP-MS also offered a wide linear dynamic range, low limits of detection, high throughput, multi-element capability, relatively simple spectra, and the ability to conduct isotopic analysis.[37]

In conclusion, the authors[37] stated that GC, LC and CE in their various modes were commonly coupled with ICP-MS for detection of the separated analytes. This ability to provide speciation analyses was consistent with the ever-growing need for speciation of toxicological information for environmental, biological, and clinical samples.[37]

A major concern in metal speciation analysis is whether or not species interconversion takes place during any of the steps of the analysis. Quantifiable conversions can be compensated for, but those that go undetected pose serious problems. The chromatography must also be well characterized with speciation standards. Unfortunately, relatively few of these standards are available.[37]

2.3.4.2. Determination of trace metals in particulate matter

In a study done by Heal *et al.* to determine the total and water-soluble trace metal content of particulate matter and black smoke (BS) in Edinburg in the UK, they collected 24 hour samples of $PM_{2.5}$, PM_{10} and BS over a one year period, and analyzed for Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd and Pb with ICP-MS. The following results were obtained:[24]

Table 2.1: *Summary of annual total metal concentration in 24 h samples of urban background PM_{10}, $PM_{2.5}$ and BS in Edinburg,UK.*[24]

Component	**PM_{10}**		**$PM_{2.5}$**		**BS**	
	Median ($ng.m^{-3}$)	**(5–95)%**	**Median**	**(5–95)%**	**Median ($ng.m^{-3}$)**	**(5–95)%**
Ti	3.66	0.64–13.7	0.37	0.00–1.83	1.68	0.00–22.9
V	1.14	0.38–5.9	0.72	0.21–3.80	0.76	0.17–3.47
Cr	1.60	0.57–7.4	0.49	0.04–2.07		
Mn	2.94	0.74–8.2	0.69	0.21–3.18		
Fe	183	50.2–486	27.6	8.92–80.6	94.2	8.50–433
Ni	3.43	0.89–37.9	0.97	0.16–5.47		
Cu	4.93	1.78–13.6	1.39	0.52–4.61		
Zn	13.3	2.21–38.6	7.49	1.08–27.1		
As	0.37	0.13–1.49	0.30	0.10–1.24	0.30	0.08–1.11
Cd	0.34	0.00–10.1	0.38	0.00–7.98		
Pb	14.1	1.28–130	13.6	0.65–103		

Heal *et al.*[24] found that for all metals analyzed, a greater portion of the metals were water-soluble in the fine fraction than in the coarse fraction, presumably in part as a consequence of the increase in particle surface area to volume ratio with decrease in diameter. In general, a higher proportion of water-soluble metal is indicative of anthropogenic rather than crustal sources. Metals in anthropogenic particles consist of metal-dominated abrasion or hot-vapour condensation particles or metals that have condensed onto the surface of other particles, and thus tend to be more labile than metal bound within crustal material.[24]

Heal *et al.*[24] also found that across all the particle size fractions, over 90% of the water-soluble or total mass of metals analyzed was always contributed by the four metals Fe, Cu, Zn and Pb. The other metals each constituted only approximately

2% on average of the total metal concentration measured in each size fraction. About one-third to one-quarter of $PM_{2.5}$ trace metal content was water-soluble, and only about one-seventh to one-eighth of PM_{10} trace metal content was water-soluble.[24]

In conclusion they found that, in the absence of major point-source influences, there is a reasonable commonality in the general source contributions of particle-associated trace metals. Particle-associated trace metals at particular receptor locations will depend on the relative influences of particular local sources such as road traffic, and/or the extent by which long-range transport from different geographical sectors changes source contributions.[24]

Correlation and factor analysis indicated three main source contributions for trace metals, namely traffic, static combustion and crustal. It seems likely that emissions of metals most associated with traffic (Cu, Fe, Mn, Pb and Zn) is probably more related to suspension or re-suspension of vehicle wear or crustal dust than to direct exhaust emission.[24]

Okuda *et al.*[25] conducted a study that describes the daily concentrations of trace metals and ionic constituents in the aerosol of Beijing, China from March 2001 to August 2003. In their study, the trace metal concentrations were analyzed by using inductively coupled plasma mass spectrometry equipped with laser ablation sample introduction (LA/ICP-MS) and the source identification was carried out by using the chemical mass balance (CMB) receptor model with the daily concentration of metals in the aerosol.[25]

The primary sources of the aerosol of Beijing were considered to be soil dust and coal combustion and vehicle exhaust contribution tended to increase over the study period. In the Chinese urban area, a large amount of aerosol is emitted from anthropogenic sources (e.g. coal combustion and vehicle exhaust) and natural sources (e.g. soil dust).[25] From the strong correlation between Al and Ti, and the fact that these metals showed the same seasonal trends, they concluded that it is mainly caused by desert dust transport, since Al and Ti are generally used as tracers for soil dust particles. They also identified As as a tracer for coal combustion particles.[25]

In a study conducted by Wang *et al.*[34], the concentrations of trace metals in aerosols of different sizes in the suburban area of Kanazawa, Japan, were determined with ICP-MS. The area was chosen for an airborne trace metals study since there were no local or proximal industrial activities on its western region. Furthermore, it is a suitable place to monitor atmospheric pollution by long distance transport from the Asian continent. The study area proximity to the Japan Sea may also provide an insight into the contribution of airborne trace elements from sea salts.[34]

Aerosol particles were collected with a low-volume sampling system equipped with a nine-stage standard cascade impactor placed on top of a 25m high sampling tower. Teflon filters were used for all stages. Sixty three samples were collected over 7 sampling periods from May to June 2003. The samples were refrigerated before analysis. Concentrations of V, Ca, Cd, Fe, Mg, Mn, Pb, Sr, Zn, Co and Cu were measured with ICP-MS.[34]

The results indicated that, among the anthropogenic elements, the ambient concentration of Zn in the total suspended particles (TSP) was the highest. High enrichment factors (EFs) were obtained for Zn, Cd, Pb, and Cu, reflecting the importance of anthropogenic inputs. In contrast, the EFs calculated for V, Ca, Mg, Mn, Sr and Co were low, suggesting that they were primarily of natural sources. The concentration ratios of natural sources derived elements (V, Ca, Mg, Mn and Sr) to Fe, and anthropogenic elements (Cd, Pb and Cu) to Zn are quite close in each particle size range.[34]

According to the authors[34], the results revealed that Fe could be a fine indicator for the prediction of ambient concentrations along with their size distributions of other elements mainly from natural processes. Elements from natural sources are primarily associated with coarse particles, while metals from anthropogenic sources are accumulated mainly in fine particles.[34]

2.3.4.3. Trace elements in South African coal

South Africa is a country rich in mineral resources and had approximately 75% of the coal resources of Africa. The USA Clean Air Act Amendment of 1990 (Title III) lists 189 potentially hazardous air pollutants, 15 of which are inorganic elements potentially originating form coal utilization.[38] Coal combustion and the use of coal in the industry and in homes significantly contributes to PM levels in South Africa. For this reason, this section on trace elements in South African coal is included.

Wagner and Hlatshwayo[38] investigated the occurrence of potentially hazardous trace elements in five Highveld coals of South Africa. Fourteen trace elements (As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, V and Zn) were selected for this study, based on the global perception that these elements may be hazardous to human health and/or the environment when they are released during coal utilization. South Africa is the world's 6th largest producer of coal. Relatively poor quality coal is used for combustion and gasification processes in South Africa. Trace elements occur at ppm (or ppb) levels in coals, and the large tonnages of coal utilized produce significant quantities of potentially toxic trace elements to accumulate and become a concern in the environment and to human health.[38]

The coals from the Highveld coal field are typically low rank bituminous with a moderate to high ash content. Permian coals of the southern hemisphere generally contain lower sulphides, chlorine, and trace elements, and have higher ash and inert organic matter than Carboniferous coals of the northern hemisphere.

Samples were obtained from five different mines in relative close proximity at various times during 2002 and 2003. Six sample sets were analyzed, including a screening middlings product from one of the mines, totalling 32 samples.[38] According to the authors[38], ICP-AES or ICP-MS were regarded as the preferred analytical techniques for the determination of trace elements in solution and that Cold-Vapour Atomic Absorption Spectrometry (CVAAS) was the most common technique used for mercury determinations. Therefore, ICP-AES and CVAAS were used during this study.[38]

A major concern in trace element assessments was the sample preparation techniques. Typically coals can be ashed to remove the organic fraction, and the remaining inorganic fraction dissolved in an acid solution to extract the elements of interest for analysis. However, due to their volatility, some elements are lost as volatile gases; Hg for example is likely to be released between 100 to 150°C. Several sample preparation methods were tested during this study, in order to determine the most appropriate preparation technique for South African coals. Certified reference materials (SARM 18, 19 and 20) were used as controls for each investigation.[38]

For the Highveld coals, standard dry coal crushing, milling and screening were employed to obtain particle size of less than 250μm. The results obtained are presented in Table 2.2:

Table 2.2: *Mean values and ranges for Highveld coal samples, and a comparison with average global mean values.*[38]

Mean values for Highveld coal samples (ppm)

Trace element	Highveld coals (excl. et 6 and USGS data)		USGS data means (excl set 6)	SARM 19 and 20				Average global values (Zhang et al., 2004)	Average global values (Ketris, in press)[b]
	mean values	Range		LOQ[a]	Obtained	Actual	Range		
Sb	<0.136 ± 0.06	<0.094–0.3	0.32		<0.094	(0.4)	Uncertified	3.0	1.0 ± 0.11
As	2.7 ± 1.0	1.0–4.7	3.14	0.0013	6.9	4.7	4.6–65.0	5.0	9.0 ± 0.8
Cd	0.24 ± 0.17	0.05–0.51	0.44	0.056			Uncertified	0.6	0.2 ± 0.05
Cr	43.2 ± 12.0	23–69	70.5	0.15	45	50	47–58	10	17.0 ± 1
Co	6.9 ± 1.6	5–12	6.3	0.062	8	5.6	5.0–6.6	5	6.0 ± 0.2
Cu	12.6 ± 1.6	9–16	13.2	0.024	13	13	11–14	15	17.0 ± 1
Pb	7.0 ± 2.6	4.2–11	7.51	0.94	292	304	295–318	25	9.0 ± 0.9
Mn	99.1 ± 8.4	84–117	19.6	0.0076	138	157	143–168	50	70.0 ± 6
Hg	0.15 ± 0.05	0.04–0.27	0.20	0.003	0.19	0.25	0.18–0.27	0.12	0.1 ± 0.01
Mo	2.09 ± 1.06	0.4–<5	1.18	0.24	2	(2)	Uncertified	5	2.0 ± 0.1
Ni	16.6 ± 3.4	12–23	21.1	0.18	16	16	13–20	15	16.0 ± 1
Sc	0.99 ± 0.24	<0.5–1.5	1.05	0.0015	0.58	0.8	0.7–1	3	1.4 ± 0.1
V	31.2 ± 3.9	23–37	33.5	0.068	34	35	33–37	25	29.0 ± 1
Zn	11.6 ± 3.4	8–19	17.9	0.066	16	12	12–16	50	29.0 ± 2

[a] LOQ=3.333 limit of detection.

[b] In prep. Translated by Dr Yudovich (personal communication): hard coals.

Concentrations of As, Cd and Cu were lower compared to global average values, and Mo, Pb, Se, Zn and Sb could be considered low to very low. Arsenic is ten times lower than typical USA values. Concentrations of Co and Ni are similar to global averages, with V and Hg being very slightly higher. However, Cr and Mn values were found to be much higher in the Highveld coals compared to typical USA values and cited average global values.[38]

Risk-based health studies in the USA on coals with similar or higher Hg and significantly higher As contents have not reported negative health effects, and therefore it could be assumed that the values reported for these five Highveld coals should not be of concern to human health. On utilization, certain elements will vaporize rapidly (Hg, Se, As) and other elements (including As, Cd, Pb, Mn) are likely to become bound to fly ash and could be emitted via stacks.[38]

To effectively reduce, mitigate, and/or prevent negative environmental and human health impacts from coal utilization, it is crucial to understand the geological origin of coal, its mineralogical and elemental content, as well as the mode of occurrence of this elements.[38]

2.3.4.4. *Trace metal composition of aerosols in South Africa*

Kgabi[51] completed a study on the levels of toxic trace metal in the coarse fraction (PM_{10}) of particulate matter in the North West Province of South Africa, especially in the Rustenburg municipality area. Rustenburg was identified as one of the biggest mineral producing districts in South Africa, producing approximately 68% of the world's chromium ores. In this study, the composition of atmospheric particulate matter was determined using ICP-MS. The main elements identified were Fe, Ca, Al, Mg, Si, Na, K, Zn, Cr, Ni, Cu, Ti, Mn, Pb and V.[51]

The following concentration levels of Cr, Ni, Pb and V were found at two chosen sites in this study:[51]

Table 2.3: *Summary of the concentrations of the potentially toxic trace metals in the Rustenburg area.*[51]

Metal		**Site A (Monthly) (µg.m^{-3})**	**Site B (Monthly) (µg.m^{-3})**
Cr	Range	0.36 – 5.2	0.03 – 0.5
	Mean	2.55	0.18
	SD	1.42	0.08
Ni	Range	0.34 – 2.8	0.03 – 0.46
	Mean	1.41	0.13
	SD	0.73	0.07
V	Range	0.04 – 0.4	0.01 – 0.05
	Mean	0.28	0.03
	SD	0.12	0.01
Pb	Range	0.06 – 0.5	0.02 – 1.4
	Mean	0.35	0.48
	SD	0.15	0.28

In general, the elements identified in this study in order of decreasing abundance were: Fe, Ca, Al, Mg, Si, Na, K, Zn, Cr, Ni, Cu, Ti, Mn, Pb, and V. The trace metals of concern are found to be in decreasing order Cr, Ni, Pb, and V.[51]

PCA were used to identify possible sources of atmospheric particles in the Rustenburg area. In decreasing abundance, the sources identified were: Soil dust (30%); Mining activities (24%); Traffic emissions and biomass burning (18%); Industry (9%); and Smelting (8%).[51]

The overview presented in this chapter clearly indicates that trace metal analysis in ambient particulate matter can be complicated and challenging. The reviews showed that many environmental and health risks are associated with trace metals. The overview also showed that relatively few studies have been reported on trace metals in particulate matter in South Africa, and especially in the Vaal Triangle. This study will contribute significantly in this regard.

Recent studies have shown that trace metals as pollutants play an important role in causing health and environmental impacts. It is very difficult, however, to determine the effects of a single element. Some of the trace metals that have been found to be associated with environmental and health effects include Hg, Cr, V, Fe, Ni and Pb. The effects of these metals (that are known at this stage) were briefly described.

Chapter 3:
Experimental Procedures

In this chapter, a description of the study area and the sampling sites are presented. The sampling procedures, followed by a brief description of the MiniVol Portable Air Samplers are given. Lastly, the analytical techniques used are described.

3.1. DESCRIPTION OF THE STUDY AREA

The most common physical aspects used for the demarcation of regions are topographical and hydrographical barriers, geology, nature areas and the occurrence of natural resources.[41] The various physical aspects of the Vaal Triangle are subsequently discussed.

The Vaal Triangle is surrounded by open hills, lowlands and mountains to the north, east and west of the region. The relief varies between 130 – 450 m. The drainage density is medium (0.5 – 2 km^{-2}) and the stream frequency is 0 – 6 streams per square kilometre. Between 20 – 50% of the surface has a slope angle of less than 5%. The Vredefort dome structure lies to the west of the region. The border to the north-west of the region is formed by a prominent hill, named the "Gatsrand".[41] Elevation across the Vaal Triangle is relatively uniform, with elevations of approximately 1550 m in the east, decreasing slightly to 1452 m above mean sea level in the west. The Vaal River runs through the region and forms the natural boundary between the Gauteng and Free State provinces.[42]

Slightly undulating plains with a low relief occur in the central parts of the Vaal Triangle. These plains are associated with sandstone, shale and coal deposits. The drainage density is low and more than 80% of the surface has a slope of less than 5%. Mudstone and sandstone occur in the south of the region. The geology causes slightly undulating plains with hills with a relief of 30 – 210 m. The drainage density is low, and more than 80% has a slope of less than 5%.[41]

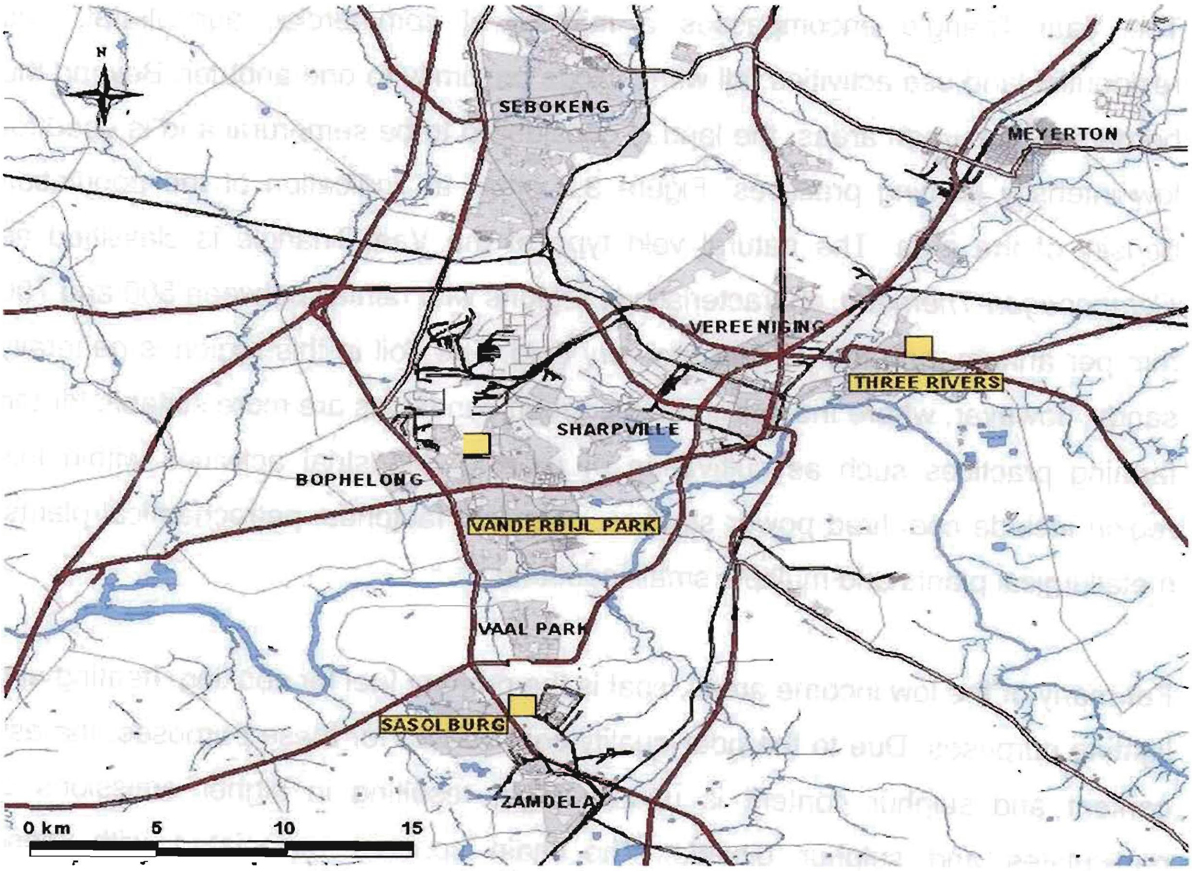


Figure 3.1: *Map of the study area. The yellow squares indicate the approximate location of the sampling sites.*

There are two main mineral deposits of importance in the Vaal Triangle. Firstly, intermitted coal occurrences are found in the area between Vredefort and Vrede. The coal field measures about 180 x 60 km and the long dimension lies west-northwest. The whole area cannot be called a coal field, but several sectors may qualify as such in future, based on increased prospecting currently taking place. In 1993, the SA Geological Survey in Pretoria determined that the total recoverable reserves in these coal fields are in the order of 2 100 million tons.[41] Clay is the second most important mineral deposit in the Vaal Triangle. Mainly four types of clay are mined, namely flint clay, semi-flint clay, plastic clay and fire clay. Extensive deposits are found in the region.[41]

The Vaal Triangle encompasses a mixture of commercial, agricultural, and residential land use activities, all within close proximity to one another. Beyond the borders of the urban areas, the land is considered to be semi-rural and is used for low intensity farming practices. Figure 3.2 gives an indication of the population density of the area. The natural veld type of the Vaal Triangle is classified as *Cymbopogon-Themeda,* characteristic of regions with rainfall between 500 and 700 mm per annum, and the winters are very cold. The soil in this region is generally sandy; however, where the soil is deep enough conditions are more suitable for the farming practices such as cultivation or grazing. Industrial activities within this region include coal fired power stations, chemical factories, petrochemical plants, metallurgical plants and multiple small industries.[42]

For many of the low income areas, coal is the primary fuel for cooking, heating and lighting purposes. Due to the poor quality coal utilized for these purposes, the ash content and sulphur content is usually high, resulting in higher emissions of particulates and sulphur dioxide. The main concern associated with these emissions is the breathing levels at which these are emitted and hence impacted. Various health studies have been conducted in the Vaal Triangle in the past decade to establish an understanding of the human health impacts associated with the ambient air concentrations of various chemical entities.[42]

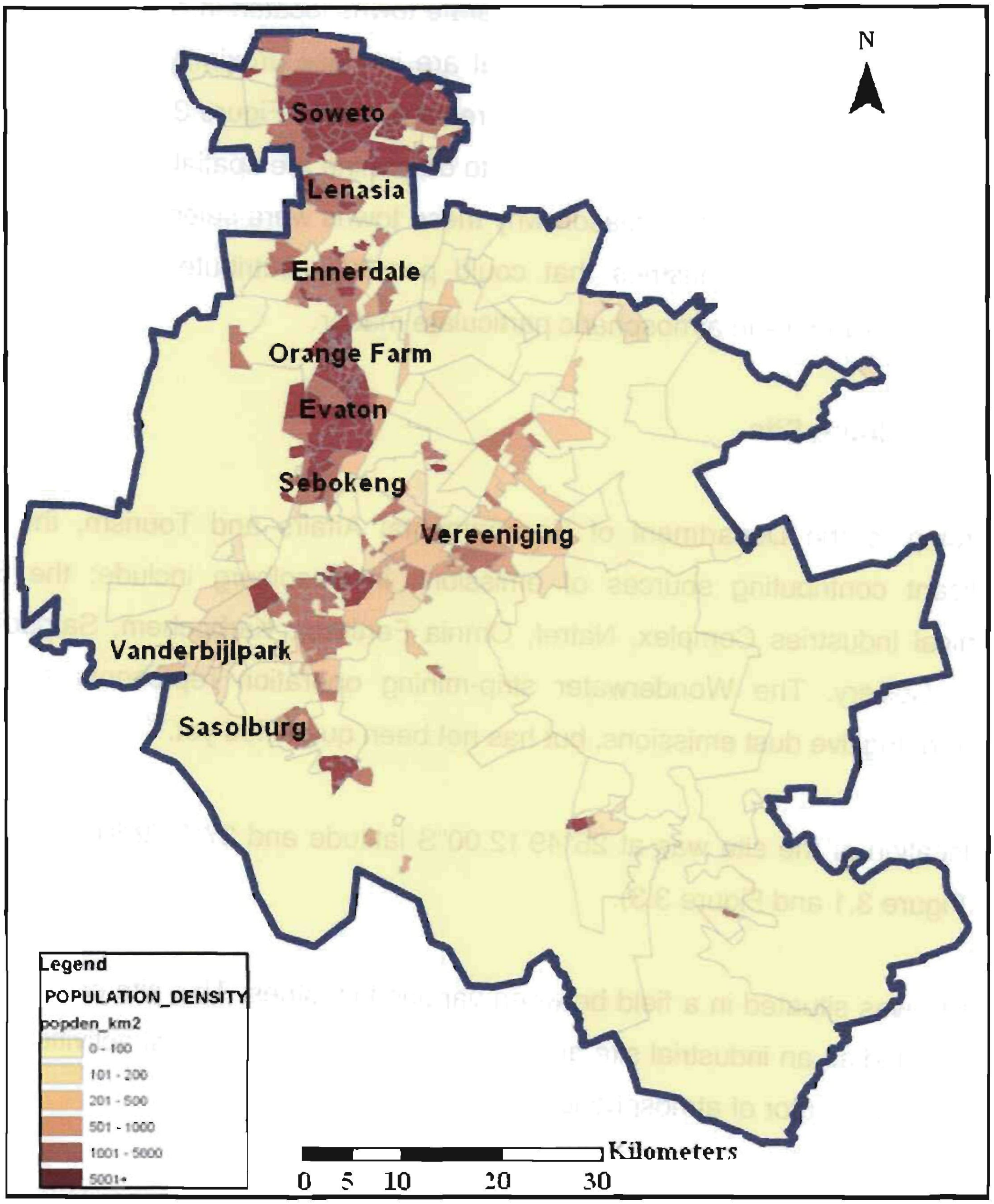


Figure 3.2: *Population density of the Vaal Triangle Air-shed Priority Area.*[42]

3.2. SITE SELECTION

The Vaal Triangle consists of various separate towns located in two provinces. For this study, three towns were selected that are in close proximity to one another, namely Sasolburg, Vanderbijlpark and Vereeniging (see Figure 3.1). One site was selected for each of these towns in order to determine the spatial variation of trace metals in the region. Another reason why these towns were selected was because they all had various industries that could possibly contribute to the levels of different trace metals in atmospheric particulate matter.

3.2.1. Sasolburg Site

According to the Department of Environmental Affairs and Tourism, the main significant contributing sources of emissions in Sasolburg include: the Sasol Chemical Industries Complex, Natref, Omnia Fertilizer, Karbochem, Safripol and Sigma Colliery. The Wonderwater strip-mining operation represents a further source of fugitive dust emissions, but has not been quantified yet.[42]

The location of the site was at 26°49'12.00"S latitude and 27°51'9.81"E longitude (see Figure 3.1 and Figure 3.3).

The site was situated in a field between various industries. This site can therefore be classified as an industrial site and it is suspected that industrial activities will be the main contributor of atmospheric particulate matter at this site.

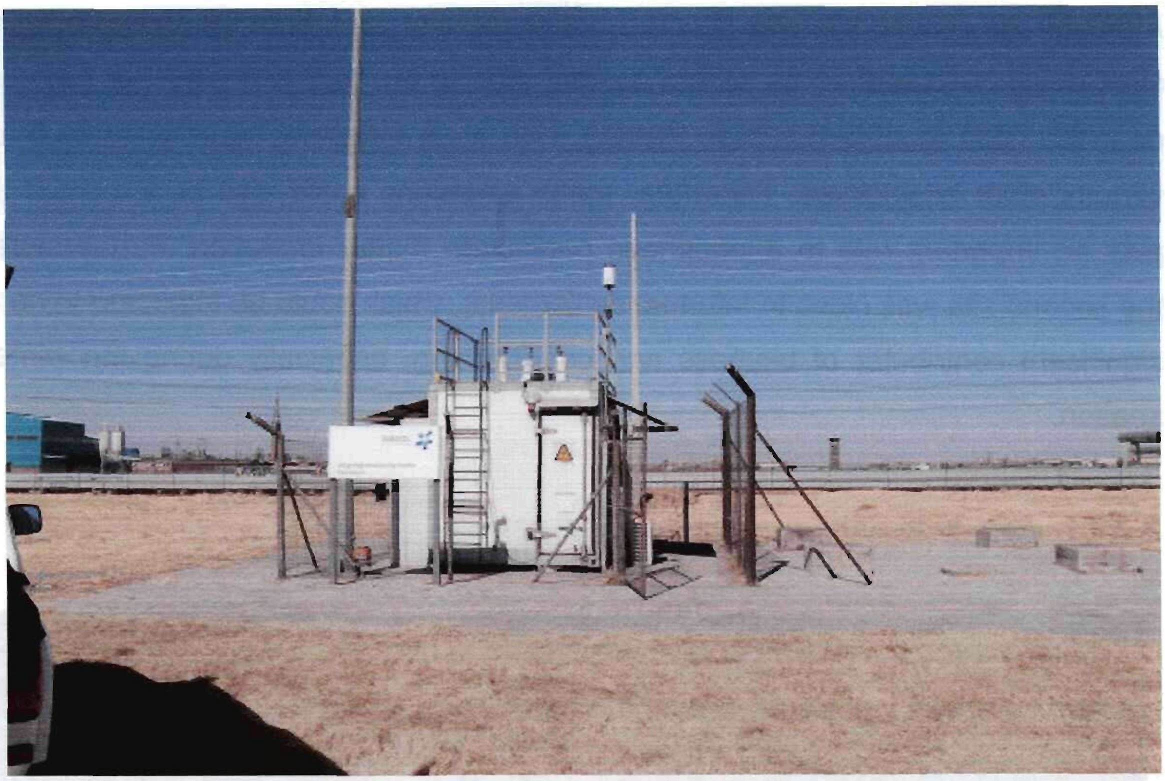


Figure 3.3: *Photo of the Sasolburg site – the MiniVol samplers are on the roof of the sampling station.*

3.2.2. Vanderbijlpark Site

The site that was used during July 2006 could unfortunately not be used during March 2007, since the ground on which the site was located had been sold for housing development. Therefore, an alternative site was chosen, which was as near as possible to the original site (see Figure 3.1)

According to the Department of Environmental Affairs and Tourism, the main contributing sources of particulates in Vanderbijlpark include: Mittal Steel Vanderbijlpark, Vitro Building Products and Davesteel (Cape Gate). Other potentially significant sources include Africa Cables, Dorbyl Heavy Engineering and Slagment. Potentially significant sources that have not been quantified, include Heckett Multiserv, Sharon Wire Mill, Van Riels Stene and Zeekoeistene.[42]

Although the second site was situated in a residential area, both the Vanderbijlpark sites could be classified as semi-industrial, due to the fact that they are situated near the CBD (central business district), with main industries nearby, as well as various other businesses. Therefore, traffic emissions could also be expected to play an important role to atmospheric particulate matter formation. Furthermore, the second site was close to informal settlements, which could be expected to be a significant contributor of biomass and coal burning, especially during the winter season.

3.2.2.1. July 2006 Site

Figure 3.4: *Photo of the Vanderbijlpark site used during July 2006 – the MiniVol samplers are on the roof of the sampling station.*

The location of the site featured in Figure 3.4 was at 26°41'16.61"S latitude and 27°49'18.21"E longitude. The site was situated in a field, used at that time for sports practices.

3.2.2.2. March 2007 Site

The location of the site was at 26°41'16.10"S latitude and 27°48'48.63"E longitude. The site was situated next to a church, in a residential area.

3.2.3. Vereeniging Site

According to the Department of Environmental Affairs and Tourism, the main contributing sources of particulate matter for Vereening include: Mittal Vereeniging (Vaal Works), Rand Water Board and the New Vaal Colliery. Other sources include Brickveld Stene, SCAW, Coverland Roof Tiles and Lime Distributers. It is anticipated that Vereeniging Refractories and Vereeniging Foundaries would represent significant sources of particulate emissions, although emission data are not available for these plants.[42]

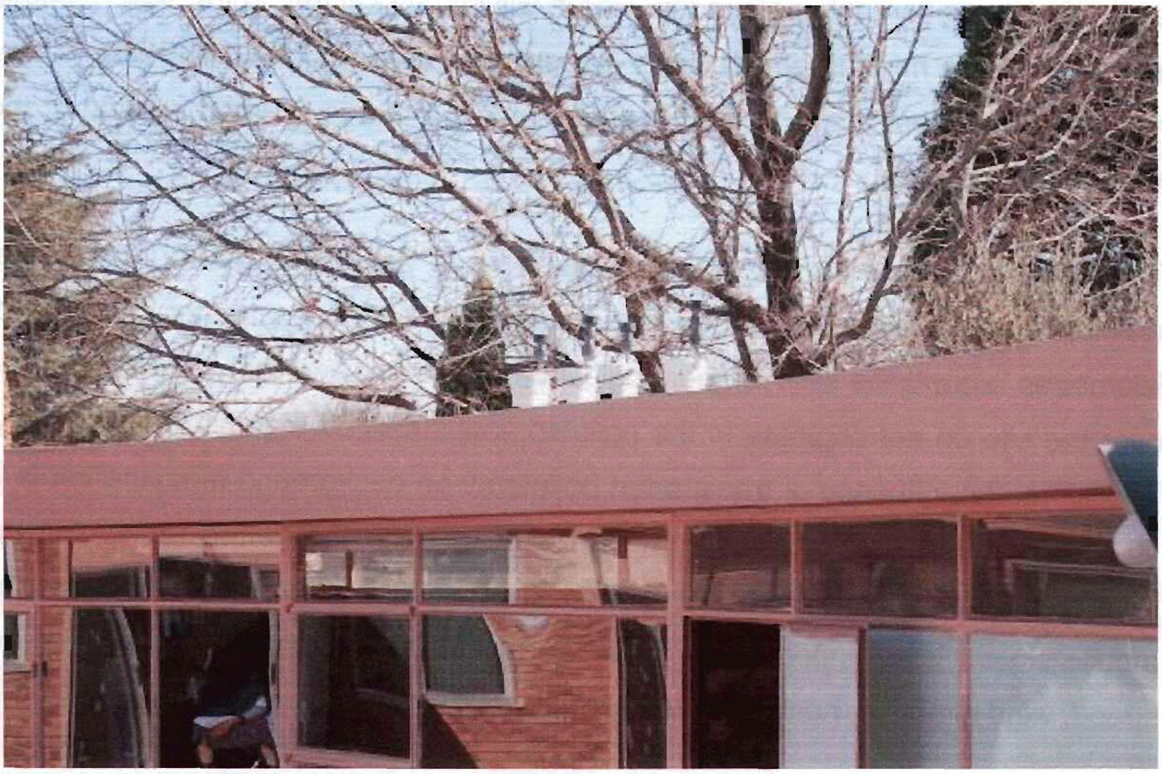


Figure 3.5: *Photo of the Vereeniging sampling site, with the MiniVol samplers on the roof of the building.*

The location of the site in Figure 3.5 was at 26°39'14.21"S latitude and 27°59'24.01"E longitude.

The site is situated in a residential area of Vereeniging called Three Rivers. There are no major industries in the area, therefore the site can be classified as a residential site, with the main contributing sources expected to be traffic and other household activities.

3.3. BACKGROUND SAMPLING (BOTSALANO SITE)

Background, or "clean air", sampling is essential as a reference for this study, since the data available on trace metal concentrations in South Africa are limited and because there are no data available of the trace metal content of various source emissions in the Vaal Triangle. The Vaal Triangle is surrounded by topographical boundaries (described in more detail in Section 3.1.). It is therefore reasonable to expect that pollution hot spots in this region will impact sectors in the Vaal Triangle where there are no emission sources (except natural emissions). Therefore it was necessary to select a site for background sampling that is situated outside of the Vaal Triangle region.

The Botsalano-site was chosen because there is almost no direct influence of anthropogenic activities at the site. There are no industries located for a number of kilometres around the site. Meteorological data also showed that wind trajectories over the site do not originate in the polluted, industrialized regions of the country. Therefore, the influence of transported pollutants on background measurements is minimal. A mobile air monitoring station is situated in the nature reserve, away from picnic areas and areas where there is a lot of activities from visitors. The mobile station is equipped with a weather station that continually measures wind speed, wind direction, humidity, precipitation, temperature, pressure and radiation.

The coordinates for the Botsalano-site were the following:
North-western coordinates: 25º6.69”E longitude and 25º5.44”S latitude;
South-eastern coordinates: 25º7.39”E longitude and 25º5.88”S latitude.

Botsalano was selected as a suitable site for background sampling for various reasons. The site is already in use as a background monitoring station in a long term project between the North-West University (South Africa), the University of Helsinki (Finland), and the local provincial government (Northwest Province, South Africa).

Botsalano is a 5 800 ha game reserve, situated in the Northwest Province, approximately 40 km from Mafikeng and 18 km north from the Ramatlabama border post, on the Botswana border. The reserve is located in open Kalahari thornveld. It is used for the breeding of antelope species and other mammals for the stocking of reserves throughout the province.

Even though Botsalano is situated far to the northwest of the Vaal Triangle (approximately 350 km), the climate conditions are nearly similar. The texture of the soil, upon visual inspection, has the same texture, but there is a slight difference in the colour. The vegetation is approximately the same as in the Vaal Triangle region. Even though the elemental compositions of the vegetation and soil are expected to be slightly different than in the Vaal Triangle, important information is expected to be gained as to what the general elemental composition of natural sources are, and what fraction of fine particles are in the PM_{10} fraction.

3.4. FILTER SELECTION

The SEM/EDS analytical technique required that the filters to be used have as smooth a surface as possible. The use of quarts filters was ruled out, since the quarts fibres have a woven, thread-like structure when viewed under the scanning electron microscope, making the analyses of samples with the SEM/EDS technique very difficult. It was therefore decided to use teflon filters.

Two different filter types were used during the study, namely:

- PALL life sciences
  Zefluor^{TM} 47 mm diameter, 0.5 μm pore size, supported PTFE filter
  (P/N P5PQ047; Lot 32631)
- Whatman Inc.
  2 μm pore-size, 46.2 mm PTFE filter, PP ring supported for $PM_{2.5}$
  (Cat.No. 7592-104; Lot 5256011)

The PALL life sciences filters were used during the July 2006 sampling period. It became clear from the SEM/EDS analyses of these samples that some of the filters had a rough surface, making analyses with this technique impossible. During the March 2007 sampling period, both filters were used as a comparison. The Whatman Inc. filters seemed to eliminate the problems that were encountered with the SEM/EDS analyses. For the background sampling during August 2007, only the Whatman Inc. filters were used.

3.5. SAMPLING

The samples were collected for two different size fractions of atmospheric particulate matter, namely the fine fraction (particles with a diameter of 2.5 μm and smaller - $PM_{2.5}$) and the coarse fraction (particles with a diameter up to 10 μm - PM_{10}). MiniVol Portable Air Samplers (product of Airmetrics) and teflon filters were used to obtain samples (see Figure 3.6). The MiniVol samplers were set to an air-flow rate of 5 litres per minute. The sampling time was twenty four hours per sample, and sampling was conducted over three days during a winter season (July 2006), three days during a summer season (March 2007) and three days for background sampling (August 2007).

3.5.1 MiniVol Portable Air Samplers

The MiniVol Portable Air Sampler is an ambient air sampler for particulate matter and non-reactive gases. The patented low flow technology used in the MiniVol was developed jointly by the U.S. Environmental Protection Agency (EPA) and the Lane Regional Air Pollution Authority in an effort to address the need for portable air pollution sampling technology.[43]

Figure 3.6: *A picture of the MiniVol Portable Air Samplers that were used in this study.*

The MiniVol (see Figure 3.6) is not a reference method sampler, but it is both accurate and precise and it gives results that closely correlate with reference method air quality data. The MiniVol features a seven day programmable timer, a constant flow control system, an elapsed time totalizer, rechargeable battery packs, and all-weather PVC construction.[43]

The MiniVol is basically a pump that is controlled by a programmable timer. An elapsed time totalizer is linked in parallel with the pump to record the total time in hours of pump operation. 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 line power supply. A charged battery pack is capable of operation the sampler for up to 24 sampling hours on a single charge. In the AC mode, the battery pack is connected to line power and mated to the sampler unit. This configuration charges the battery while using AC power.[43]

In the particulate matter sampling mode, air is drawn through a particle size selector (also referred to as an impactor) and then through a filter medium. Particle size separation is achieved by impaction. It is critical to the collection of the correct particle size that the correct flow rate move through the impactor. For the MiniVol, the actual volumetric flow rate must be 5 litres per minute.[43]

Impactors are available with a 10 micron cut-point (PM_{10}) and a 2.5 micron cut-point ($PM_{2.5}$). Operating the sampler without an impactor allows for the collection of total suspended particulate matter (TSP). The inlet tube downstream from the filter takes the air to the twin cylinder diaphragm pump. From the pump, air is forced through a standard flow meter where it is exhausted to the atmosphere inside the sampler body.[43]

The MiniVol sampler is a popular choice of use in air quality assessments because it is portable and inexpensive relative to fixed site monitors. Advantages of the MiniVol sampler include the flexibility to move or rotate monitoring sites, the ability to increase the number of monitoring sites to improve spatial distribution of data collected, and the ability to measure contaminant concentrations at almost any location.[44]

Baldauf *et al.*[44] conducted a performance evaluation of the MiniVol Portable Air Sampler. They concluded that the MiniVol operated reliably and yielded statistically similar concentration measurements when co-located with another MiniVol. Also, the characterization of spatial distributions of $PM_{2.5}$ and PM_{10} mass concentrations can be accomplished with a high level of confidence. They also found that the MiniVol produced statistically reliable results when co-located with a Versatile Air Pollutant Sampler (VAPS) and a Tapered Element Oscillating Microbalance (TEOM). Further, the authors mentioned that environmental factors such as ambient concentration, wind speed, temperature, and humidity influence the relative measurement comparability between these sampling systems. Results also indicated that passive airborne particulate matter collection occurred at the MiniVol inlet during non-sampling conditions.[44]

3.5.2. Filter handling and sampling procedures

Visual inspection of the filters was made over a light before each sampling period, to make sure that the filters did not have any flaws or weak spots. The filters were always handled with plastic tweezers and whilst wearing surgical gloves. After visual inspection was completed, the filters were weighed and stored in airtight centrifuge tubes until sampling. The filters were exchanged after each day of sampling on the site, taking care not to let any of the loose particles fall from the filter.

After the filters had been collected at the sites, the tubes/Petri dishes were sealed with masking tape, bagged and refrigerated. The samples were taken out of the refrigerator 24 hours before the samples were analysed. Note should be taken that the filters were weighed again before analyses, but since there were no facilities to weigh filters under controlled temperature and relative humidity, the weight difference before and after sampling cannot be regarded as accurate.

3.6. ANALYSES

After the samples were collected, the filters were analysed first by using Scanning Electron Microscopy, coupled with Energy Dispersive Spectroscopy (SEM/EDS) because this is a non-destructive method, and then using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), which is a destructive analytical method. For SEM/EDS no treatment of the filters was necessary. The filters were fixated to the sampling disk in the specimen chamber by using carbon tape. For ICP-MS, the filters were digested in concentrated HNO_3 for a period of 24 hours. Afterwards, it was diluted before injecting into the instrument.

3.6.1. SEM/EDS

The ESEM FEI QUANTA 200 instrument, coupled with the OXFID ENCA 200 EDS was used for the SEM/EDS analyses during this study. It operated under a high vacuum, with a voltage of 15 kV, and a working distance of 10 mm.

The SEM permits the observation of materials in macro and submicron ranges. The instrument is capable of generating three-dimensional images for analysis of topographic features. When used in conjunction with EDS the analyst can perform an elemental analysis on microscopic sections of the material or contaminants that may be present. SEM generates high energy electrons and focuses them on a specimen. The electron beam is scanned over the surface of the specimen in a motion similar to a television camera to produce a rasterized digital image.[45]

Electrons are speeded up in a vacuum until their wavelength is extremely short, only one hundred-thousandth that of white light. Beams of these fast-moving electrons are focused on a sample and are absorbed or scattered by the specimen and electronically processed into an image. Most electron microscopes used to study materials can image down to about 10 angstroms (0.001 microns). It is often necessary to identify the different elements associated with a specimen. This is accomplished by using a built-in spectrometer called an Energy Dispersive X-ray Spectrometer, featured in Figure 3.7.[45]

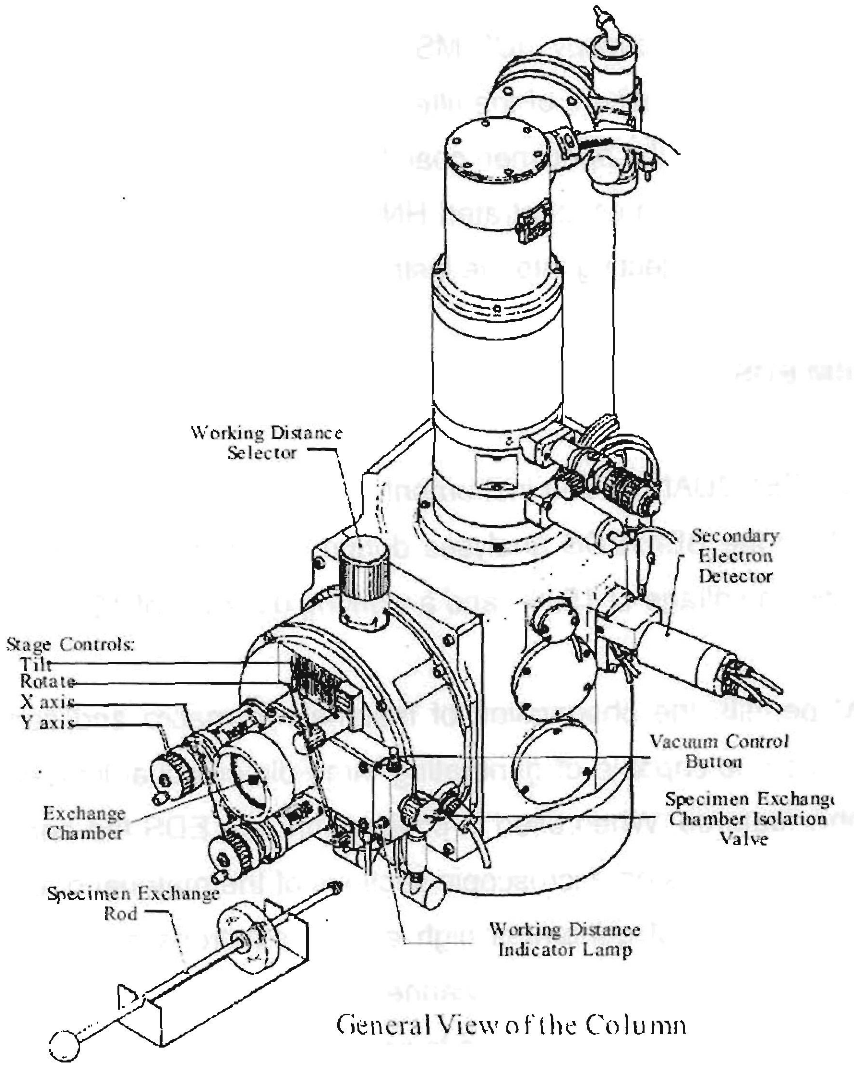


Figure 3.7: *Schematic drawing of the SEM instrumentation.*[46]

EDS is an analytical technique which utilizes x-rays that are emitted from the specimen when bombarded by the electron beam to identify the elemental composition of the specimen.[45] X-rays are generated as a result of the ejection of an inner level electron (low energy) from the sample, by an energetic electron from an electron column. The ejected electron is replaced by an electron from a higher energy shell. The energy lost as it moves from a high energy shell to a low energy shell is released in the form of x-rays.[46]

Each element has many energy levels and therefore many potential vacancy-filling mechanisms. Consequently, even pure elements emit x-rays at a variety of energies. Because the atomic structure of each element is different, it follows that each element will emit a different pattern of x-rays.[46]

These x-rays can be analyzed either by wavelength dispersive methods or energy dispersive methods. EDS systems use a semiconductor detector, which is basically a single crystal of silicon which has been treated with lithium (lithium-drifted silicon). An x-ray photon first creates a charge pulse in a semiconductor detector; the charge pulse is then converted into a voltage pulse, the amplitude of which reflects the energy level of the detected x-ray. This voltage pulse is then converted into a digital signal which causes one count to be added to the corresponding voltage channel of a multi-channel analyzer. Counting over a period results in an x-ray spectrum.[46]

If the primary electron interacts with the nucleus of a sample atom, it may be scattered in any direction with little loss of energy. Some are directed back out of the sample, allowing them to be detected. These backscattered electrons are much more energetic than the secondary electrons and so may escape from a greater depth within the sample. They do not carry the topographic information of the secondary electrons but the main influence on the strength of the backscattered signal is the mean atomic number within the interaction volume. The higher the atomic number of an atom, the more protons present and the higher the backscattered signal.[46]

The biggest advantage of the SEM/EDS analytical technique is that it is a non-destructive method. Disadvantages of the technique are that it is mainly a "surface" analysis method. Since the entire volume of a sample is not analysed, the results may differ from that of a complete chemical analysis of the samples.

3.6.2. ICP-MS

Inductive Coupled Plasma Mass Spectrometry is a very powerful tool for trace (ppb-ppm) and ultra-trace (ppq-ppb) elemental analysis. In ICP-MS, a plasma or gas consisting of ions, electrons and neutral particles is formed from Argon gas. The plasma is used to atomize and ionize the elements in a sample. The resulting ions are then passed through a series of apertures (cones) into the high vacuum mass analyzer. The isotopes of the elements are identified by their mass-to-charge ratio and the intensity of a specific peak in the mass spectrum is proportional to the amount of that element in the original sample.[47]

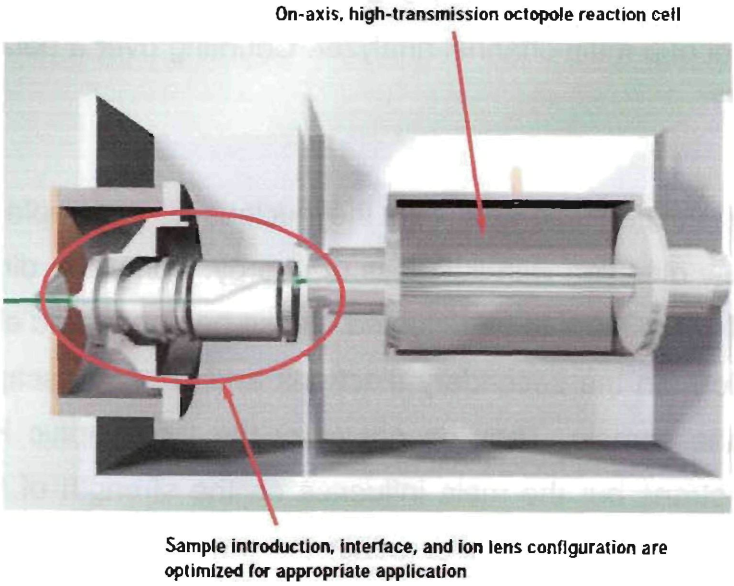


Figure 3.8: *Sample introduction system of the ICP-MS.*[49]

The ICP-MS instrument is an ion source and the MS requires a rich and stable source of positively charged ions. Therefore, the ICP must operate at high temperatures. Plasma temperatures can be increased in several ways: use of low sample uptake rates, a chilled spray chamber, a wide diameter torch injector, and finally by the correct choice of generator frequency. Ions produced by the plasma enter the mass spectrometer via a vacuum interface. The interface consists of a sample cone and a skimmer cone, with the volume between the two at a low pressure. Ions are extracted through the sample cone orifice and accelerate into the low pressure interface. The beam of ions and neutrons come into contact with the skimmer cone and are further extracted into the mass spectrometer (high vacuum) region through the skimmer cone orifice.[48]

Ion lenses transfer and focus the ions efficiently into the mass filter. Some neutral species also get introduced into the mass spectrometer and if they reach the detector the background noise will increase. The mass spectrometer is a Quadrupole Mass Filter. It can be controlled to allow a single mass to charge ration pass through at a given time. By changing the control, the quadrupole can sweep across the whole mass range of the Periodic Table.[48]

Most ICP-MS use electron multiplier detectors to count the ions passing through the quadrupole mass filter. The Agilent 7500 Series (the Agilent 7500c ICP-MS was used in this study) features a discrete dynode type detector with unique fast amplification electronics. This combination allows the detector to operate over 9 orders of magnitude linear dynamic range, without compromising speed.[48]

The procedure for ICP-MS analysis involved filter digestion, dilution, and measurements. Air particulates collected on the filters were exctracted into a dilute nitric acid solution (5 ml Nitric Acid, 65% GR for analyses ISO, Merck) at room temperature for a period of 24 hours. A 10x dilution was made from the extracted solution and it was stored at room temperature until analysis by ICP-MS.

Three sites were selected for sampling in the Vaal Triangle , to determine the spatial distribution of trace metals in this region , namely Sasolburg, Vanderbijlpark and Vereeniging. Background sampling was done at a game reserve in the North-west Province, namely Botsalano. The samples were collected on teflon filters by using MiniVol Portable Air Samplers. The samplers were set (according to the manufacturers specification) at a flow rate of 5 litres air per minute, for a period of 24 hours and for three days per sampling period. After the samples were collected, they were analysed firstly by using SEM/EDS (a non-destructive method, no pre-treatment of filters necessary) and then the filters were digested with a concentrated acid, diluted and analysed using ICP-MS (a destructive method).

Chapter 4:
Results and discussion

In this chapter, the results obtained from the analyses are given and discussed. A brief discussion of the meteorological conditions and the possible implications thereof on this study are given, followed by some key-observations and discussion from the SEM/EDS analyses. A few general observations from the ICP-MS results are given, followed by a discussion of the daily and seasonal variations that were observed.

The results obtained from the two different analytical techniques are discussed in the order that the analyses were done. SEM/EDS analyses, a non-destructive method, were done first, followed by the ICP-MS analyses of the samples (a destructive method). Before the results of the two techniques are discussed, a brief overview of the meteorological conditions of the Vaal Triangle will be given.

4.1. METEOROLOGICAL CONDITIONS OF THE VAAL TRIANGLE

Meteorological data used for July 2006 and March 2007 were obtained from the Sasolburg site, since this was the only site equipped to measure meteorological conditions. It can be assumed that the wind directions and wind speeds were approximately the same at the Vanderbijlpark and Vereeniging sites. The meteorological data for the background sampling site (August 2007) was obtained from the meteorological equipment at the site (see Appendix C for the data Tables for each sampling period, giving the hourly measurements of Wind Speed, Wind Direction, Temperature and Relative Humidity).

South Africa is situated in the subtropical high pressure belt and it is influenced by several high pressure cells, in addition to various circulation systems prevailing in the adjacent tropical and temperature latitudes. The mean circulation of the atmosphere over South Africa is anti-cyclonic throughout the year, due to the dominance of three high pressure cells (the South Atlantic HP off the west coast, the South Indian HP off the east coast, and the continental HP over the interior).[42]

The winter weather of South Africa is largely dominated by perturbations in the westerly circulation. Such perturbations take the form of a succession of cyclones or anti-cyclones moving eastwards around the coast or across the country. During the summer months, the anti-cyclonic belt weakens and shifts southwards, allowing the tropical easterly flow to resume its influence over South Africa.[42]

The impact of various synoptic systems and weather disturbances on the dispersion potential of the atmosphere largely depends on the effect of such systems on the height and persistence of elevated inversions. The most important of these synoptic situations are the semi-permanent, subtropical continental anticyclones which dominate 70% of the time during winter and 20% of the time during summer.[53] Elevated inversions suppress the diffusion and vertical dispersion of pollutants by reducing the height to which such pollutants are able to mix, and consequently result in the concentration of pollutants below their bases. Such inversions therefore play an important role in controlling the long-range transport and recirculation of pollution.[42]

During winter months, the first elevated inversion is located at an altitude of around 3 km over the plateau. In summer months this inversion is known to increase to between 4 and 5 km over the plateau. The lower level subsidence inversion, which occurs at about 1200 – 1400 m above ground level within the VTAPA, is significant in that it represents a persistent cap impending the upward mixing of air pollutants. Cloudlessness (experienced for most winter months over the region) ensures full intensity of incoming solar radiation, which enhances photochemistry and results in the accumulation of photochemical smog in some areas.[42]

Wind roses (a visual representation of the wind speed and wind direction for a given time period) were compiled for each sampling period (see Appendix D). The wind speed and wind direction were measured at hourly intervals for each day. The ADMS 3.2 model was used to obtain the wind roses.

The wind roses are comprised of 36 spokes that represents the direction from which the winds blew during the time period. The different colours represent the different categories of wind speeds (ranging from 0 m/s – 10 m/s, or more). The concentric circles provide information regarding the frequency of occurrence (in hours) of winds in a given direction at a given speed.

Atmospheric stability is frequently categorised into one of six stability classes. Wind roses can be used to estimate the class of atmospheric stability for a certain time period (period that is represented by the wind rose). The categories can be identified as follows:[42]

A	Very unstable	calm wind, clear skies, hot daytime conditions
B	Moderately unstable	clear skies, daytime conditions
C	unstable	moderate wind, slightly overcast daytime conditions
D	neutral	high winds or cloudy days and nights
E	stable	moderate wind, slightly overcast night-time conditions
F	very stable	low winds, clear skies, cold night-time conditions

The highest concentrations due to ground-level sources, such as furnace fugitive emissions, occur during periods of low wind speed and stable atmospheric conditions. Under these conditions, the pollutant remains in the vicinity of its sources. Peak ground level concentrations due to elevated source emissions typically occur during unstable conditions.[42]

The wind roses (see Appendix D) showed that the average wind direction for the different sampling periods were 300º, 220º, and 80º for July 2006, March 2007 and August 2007, respectively. It also showed that the average wind speeds were 3.1-5.1 m/s, 5.1-8.2 m/s, and ≥ 8.2 m/s for July 2006, March 2007 and August 2007, respectively. The atmospheric stability in the Vaal Triangle can therefore be classified as stable during winter and unstable during summer. The atmospheric stability at the background sampling site during an intermediate season can be classified as neutral.

The average temperature for July 2006 was approximately 10ºC, ranging from a minimum of 0.24ºC to a maximum of 22ºC (see Appendix C for temperatures). During March 2007, the average temperature was approximately 22ºC, with a minimum of 9.9ºC and a maximum of 32.02ºC. For the intermediate season at the background sampling site, the average temperature was approximately 12ºC, ranging between 2.3ºC minimum and 19.4ºC maximum.

The average relative humidity for the different sampling seasons were approximately 43%, 28%, and 56% for July 2006, March 2007 and August 2007, respectively (see Appendix C).

4.2. SEM/EDS RESULTS AND DISCUSSION

All the results obtained from the SEM/EDS analyses are attached as Appendix A. It is important to mention that not all of the field samples obtained from the first sampling period in July 2006 could be analysed with the SEM/EDS. This was due to the fact that some of the filters had a rough surface, which made the determination of the elemental composition of the samples impossible with this technique.

Visual inspection of the filters before sampling did not show any differences or flaws. The problem was first picked up while the analyses were done, when the filters were viewed under the scanning electron microscope. A different type of Teflon filter was used for PM_{10} samples during the next sampling period (March 2007) as a possible means to eliminate this problem. Analyses of blank filters of each type did not show any significant differences in the filter composition (see Appendix A, Section A.1).

It became clear from the analyses of samples in July 2006 and March 2007 that an accurate weight percentage contribution of trace metals was generally not picked up by the SEM/EDS. It did however give an idea as to what the main elemental compositions of the samples were. A few exceptions included elements mostly associated with wind-blown dust (namely Na, Al, Si, Mn, Mg, K, Ca). The contribution of each element individually did not exceed 1% of the filter composition. Some elements that may be associated with anthropogenic activities (Fe, Cu, S) were occasionally observed. Fe and Cu could possibly be from the steel manufacturing industries in the area, and S could possibly be attributed to coal combustion processes.

Since it seemed logical that the concentrations of the trace elements in the background samples would be significantly lower than for the samples taken in the Vaal Triangle, it was decided not to do SEM/EDS analyses on the background samples. This limited the risk of some of the particles being lost due to the handling of filters, or being lost due to the working conditions under which the SEM/EDS operates that might deflect some particles from the filter when coming into contact with the high-energy electron beam.

An important observation that was made when looking at the summer results, were that the C and F levels were very similar to the composition of the blank filters. Since SEM/EDS are a surface analytical method, it could possibly mean that the layer of particulate matter was much thinner during the summer than the winter, and that this caused the electron beam to penetrate and analyse the filter medium. There is also no industry in the area that could have produced these high contributing levels of F. Even if it could be attributed to some degree to industrial activities, F would have been observed for the winter samples as well.

The most significant observation that could be made from the SEM/EDS results was that carbonaceous particles were the dominant species present. During the winter sampling period, the weight percentages of carbon per sample ranged between 24% and 94%. The average value was 52% during the winter.

The high percentages of carbon during the winter sampling period could possibly be attributed to the elevated occurrence of residential biomass burning and residential coal combustion to produce heat, especially in the low-income residential areas. Since the winter season in South-Africa is the dry-season, the occurrence of field fires would also have contributed to the higher carbon levels. The occurrences of residential biomass and coal combustion, as well as field fires are much lower in the summer (wet-season). This could therefore explain the lower carbon levels that were observed during the summer.

4.3. ICP-MS RESULTS AND DISCUSSION

The raw results obtained from the ICP-MS analyses of the samples gave the elemental concentrations in ppb. To calculate the concentrations of the metals in ambient particulate matter, the US EPA compendium method IO-3.5 were used. The results given in Appendix B are after the blank filters were subtracted and divided by the volume of air sampled. The final concentrations are given as $\mu g.m^{-3}$. Elemental concentrations that were below the detection limit are not included, and in the tables of results (see Appendix B) these elements are highlighted.

Due to a malfunctioning of the MiniVol Portable Air Samplers at the Sasolburg site, on the 20th of March 2007, the results could not be accurately calculated to represent the concentrations in air for this particular day. Therefore, the data for Sasolburg on this day was omitted (Table B.4, Section B.2.1 of Appendix B).

From the results obtained, the percentage of $PM_{2.5}$ in PM_{10} was calculated for the average of each sampling period per site (the average total concentration $PM_{2.5}$ divided by the average total concentration PM_{10}, calculated separately for the various sampling sites). It is important to mention that the total concentrations for elements from Li to U were used (as determined by ICP-MS), and not the concentrations of total atmospheric particulate matter. The concentrations of the total atmospheric particulate matter could not be determined, since the filters could not be weighed accurately (i.e. the temperature and relative humidity could not be accurately controlled).

For the average values elements from Li to U for the July 2006 sampling period, the percentage of $PM_{2.5}$ in PM_{10} was 56% for Vanderbijlpark, 76% for Sasolburg, and 63% for Vereeniging. For the average values of March 2007, the percentage of $PM_{2.5}$ in PM_{10} was 58% for Vanderbijlpark, 93% for Sasolburg, and 117% for Vereeniging. The percentage of $PM_{2.5}$ in PM_{10} was also calculated for the background sampling in August 2007, namely 6%.

Since the amount of $PM_{2.5}$ in the PM_{10} fraction can logically not exceed 100%, the percentage of $PM_{2.5}$ in PM_{10} at Vereeniging during March 2007 could not be correct. Closer examination of all the March data indicated that the $PM_{2.5}$ levels exceeded the total PM_{10} levels only on the 21st of March 2007.

A possible explanation for the higher $PM_{2.5}$ values could be the following: The flow rate of the MiniVol sampler is adjusted manually to 5 litres per minute. Human error could occur when setting the flow rate and this 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 litres per minute, and/or the flow rate of the $PM_{2.5}$ sampler could have been slightly higher than 5 litres per minute. All sample concentrations are calculated by using the time sampled at a flow rate of 5 litres per minute. Small deviations in the actual flow rate over a 24 hour sampling time could therefore have made a significant impact on the calculations of the concentrations. The above should be taken into consideration when the reported percentage ratios are viewed.

The average concentrations (for all elements from Li to U) at Botsalano were 0.0453 $\mu g.m^{-3}$ ($PM_{2.5}$) and 0.7919 $\mu g.m^{-3}$ (PM_{10}). The average concentrations in the Vaal Triangle ranged between 8.2505-9.2329 $\mu g.m^{-3}$ ($PM_{2.5}$) and 10.8982-16.3298 $\mu g.m^{-3}$ (PM_{10}) during the winter and between 1.8739-2.3758 $\mu g.m^{-3}$ ($PM_{2.5}$) and 2.0465-3.8674 $\mu g.m^{-3}$ (PM_{10}) during the summer.

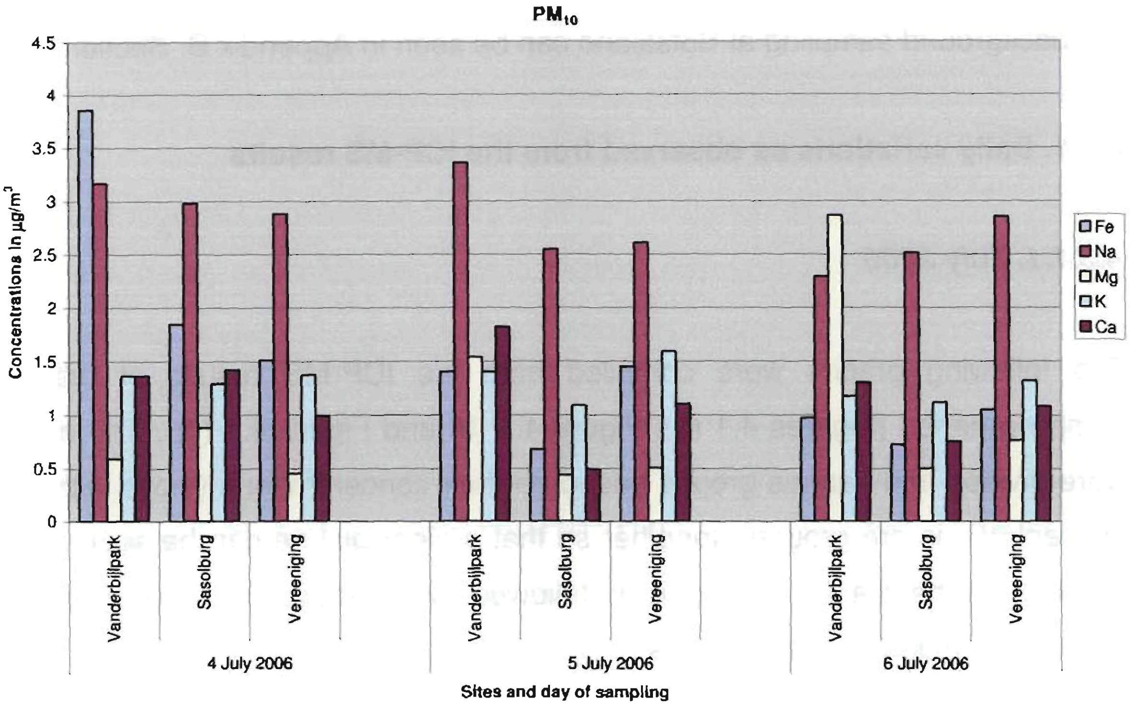
Fe was the most abundant trace element, followed by Zn and Mn. The average Fe concentrations were approximately 1.009 $\mu g.m^{-3}$ ($PM_{2.5}$) and 1.499 $\mu g.m^{-3}$ (PM_{10}) during the winter, and approximately 0.775 $\mu g.m^{-3}$ ($PM_{2.5}$) and 1.071 $\mu g.m^{-3}$ (PM_{10}) during the summer. The average Fe concentrations in the background samples were approximately 0.001 $\mu g.m^{-3}$ ($PM_{2.5}$) and 0.097 $\mu g.m^{-3}$ (PM_{10}). The values in the Vaal Triangle are significantly higher compared to the background concentrations at Botsalano.

More elements were lower than the detection limit of the ICP-MS in the samples from Botsalano than the samples from the Vaal Triangle. The results obtained from the background sampling at Botsalano can be seen in Appendix B, Section B.3.

4.3.1. Daily variations as observed from the ICP-MS results

4.3.1.1. July 2006

The following graphs were compiled from the ICP-MS results of the winter sampling period (Figures 4.1 (a), Figure 4.1 (b) and Figure 4.1 (c)). The elements were divided into various groups based on their concentrations (those with similar concentrations are grouped together so that a clear picture can be seen from the graphs). All the graphs will be given, followed by a discussion of the observations that can be made from the graphs.



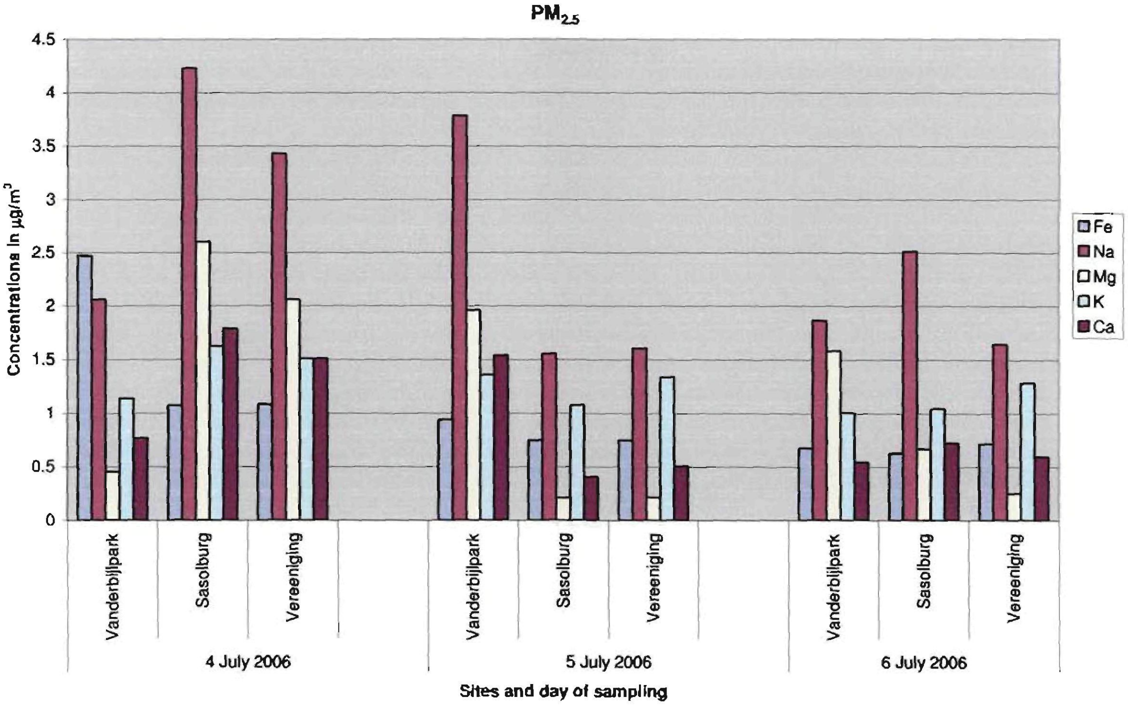
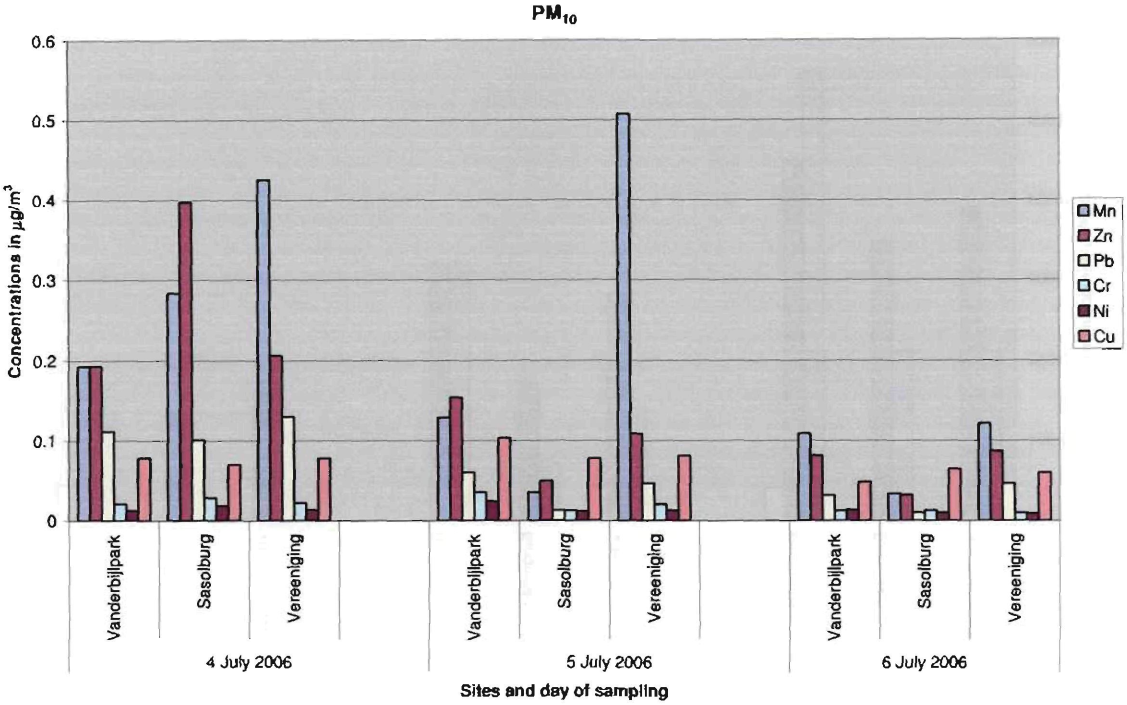


Figure 4.1 (a): *Comparison of the trace metal composition in* $PM_{2.5}$ *and* PM_{10} *during the winter sampling period (4-6 July 2006).*



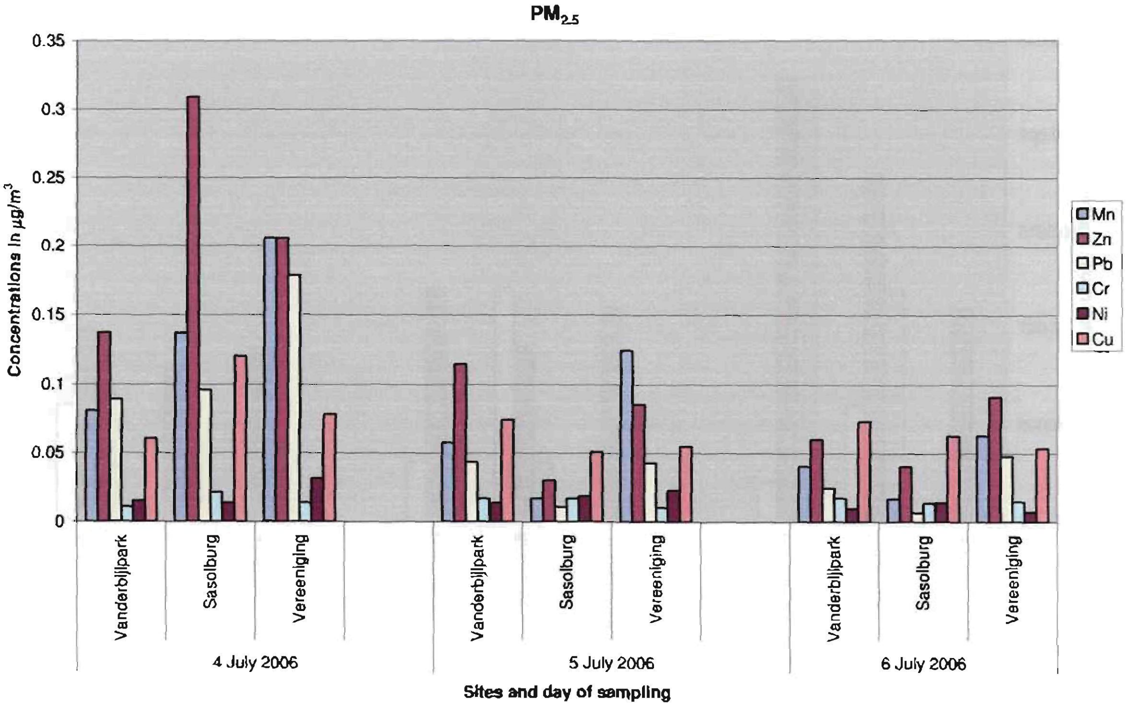


Figure 4.1 (b): *Comparison of the trace metal composition in PM$_{2.5}$ and PM$_{10}$ during the winter sampling period (4-6 July 2006).*

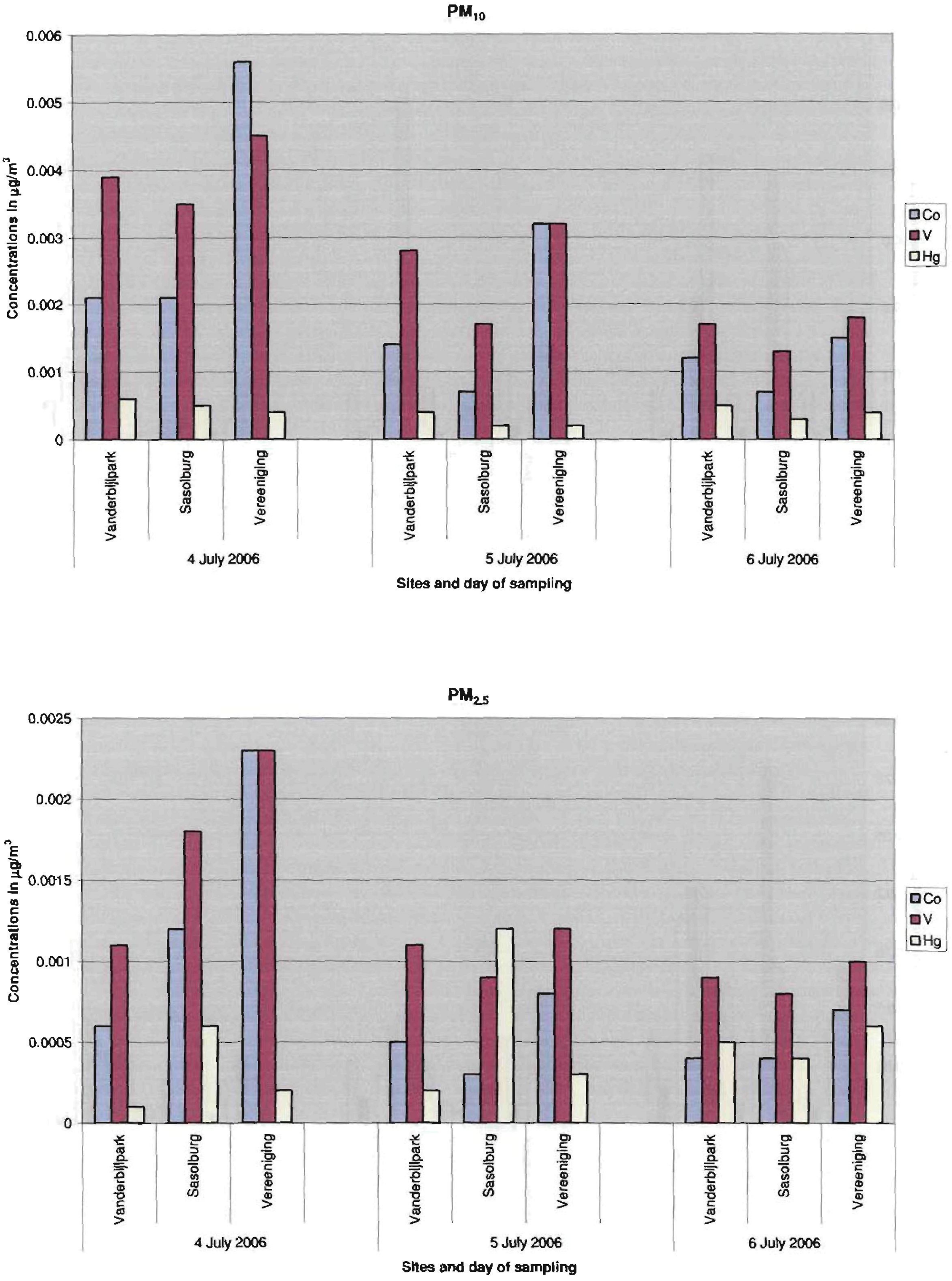


Figure 4.1 (c): *Comparison of the trace metal composition in PM$_{2.5}$ and PM$_{10}$ during the winter sampling period (4-6 July 2006).*

The high concentrations of Fe at all three sites could possibly be attributed to various sources in the region (Vaal Triangle), such as domestic coal combustion, biomass burning, road dust, steel manufacturing and mineral dust.[18,21,26] Since the concentration of Fe was the greatest at the Vanderbijlpark site, the dominating source contribution was estimated to be due to steel manufacturing industries in this area. The $PM_{2.5}$ concentrations of Fe were generally more than half of the percentages for PM_{10}, and it was the highest at Vanderbijlpark. This could possibly also be attributed to the steel manufacturing industry close to this site.

Main sources of Na were expected to be metallurgical dust and lime.[22] There might also have been some contribution of sea spray (even though the study area is situated in the central regions of South Africa) since there was a great deal of cold fronts that frequently moved in over the country from the Atlantic ocean (the cold fronts usually took about 2-3 days to move from the Cape Province over the Vaal Triangle region). However, it is not known what the magnitude of the contribution of sea spray was.

Mg is generally believed to be a tracer for crustal (mineral) sources, such as wind-blown dust.[21,26] This could explain why the concentrations of Mg showed great fluctuations between the sites on the different days of the sampling period. The occurrence of K, and to a lesser extent Ca, in ambient particulate matter is generally used as a tracer for the identification of crustal sources (wind-blown dust) and biomass burning.[18,21,26] Since both these events occurred on a regular basis during the sampling period, these sources are believed to have the biggest contributions.

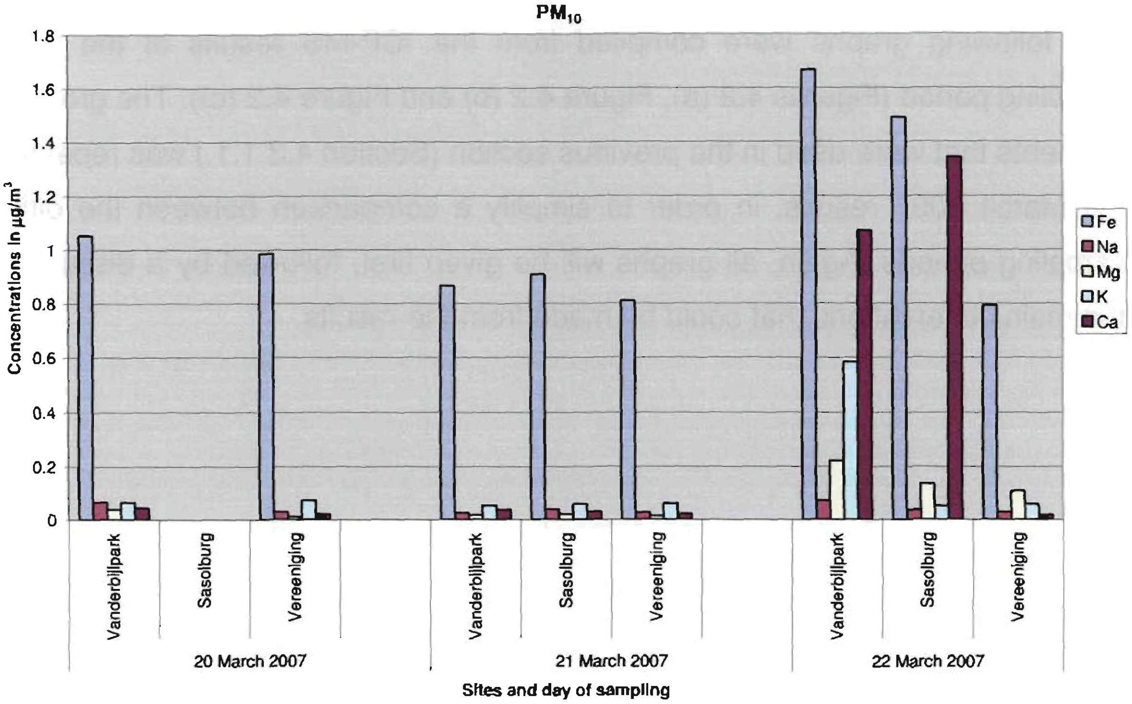
The elevated concentrations of Mn at Vereeniging can possibly be attributed to wind-blown dust.[26] Another possible source could be steel manufacturing[21], since the local steel manufacturer is located to the west of the sampling site, and the average wind direction for the sampling period was from the northwest. Mn is also a tracer element for biomass burning and has a high occurrence in South African coal (see Chapter 2, Section 2.3.4.3 for the levels of Mn in SA coal).[18,38] Therefore, biomass burning and coal combustion could also have contributed to the levels of Mn in the particulate matter. The higher levels of Pb, Cr and Cu at Vanderbijlpark and Vereeniging could also possibly be from the steel manufacturing industries, since both these towns have these industries in the vicinity.[21,32]

The occurrence of nickel and vanadium can possibly be attributed to the petrochemical industries, and/or the coal-fired power plant in the area.[23,26] The concentrations of Ni and V for $PM_{2.5}$ was also higher at the Vereeniging site. On the first day, however, the concentrations were higher at Sasolburg. This can also possibly be explained from the meteorological data. The average wind speed on the first day was lower than for the other sampling days, and the pollutants might not have reached as far as Vanderbijlpark or Vereeniging. These two sites would, however, be more strongly influenced by the coal-fired power plant. Cobalt is a natural occurring element found in rocks, soil, water, plants and animals. It can be released into the atmosphere through coal combustion.[50]

Mercury concentrations are generally very low, just above the detection limit of the ICP-MS. The levels of Hg for the fine particulate fraction were slightly higher at the Sasolburg site. Coal combustion processes (including the coal-fired power plant) are believed to be the main contributing source. Since the literature suggests that there is no safe limit value for Hg, even though the concentrations in the area are very low they still pose a great concern for health and environmental impacts.[27,38]

4.3.1.2. March 2007

The following graphs were compiled from the ICP-MS results of the summer sampling period (Figures 4.2 (a), Figure 4.2 (b) and Figure 4.2 (c)). The grouping of elements that were used in the previous section (Section 4.3.1.1.) was repeated for the March 2007 results, in order to simplify a comparison between the different sampling periods. Again, all graphs will be given first, followed by a discussion of the main observations that could be made from the results.



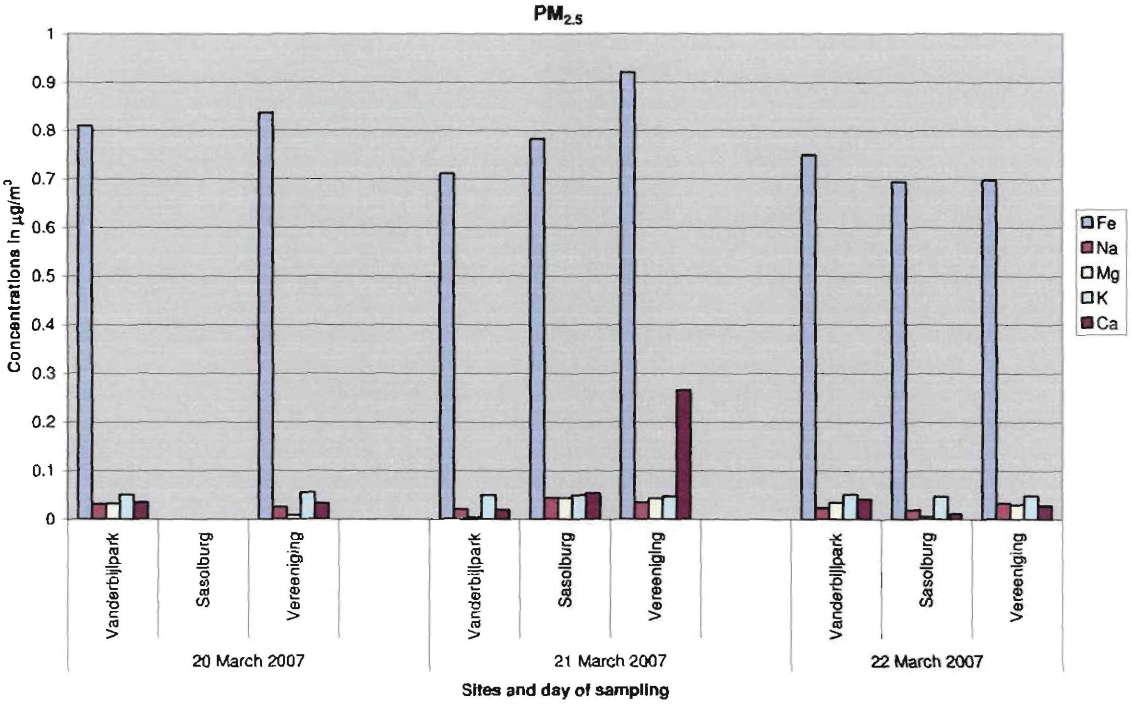
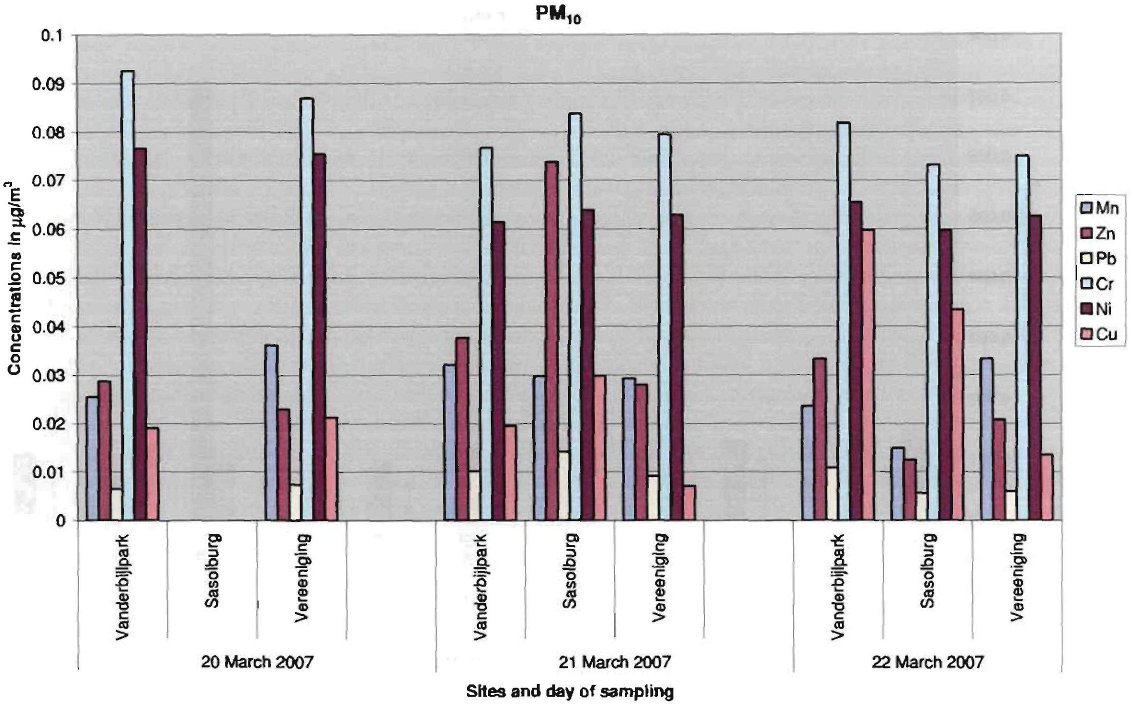


Figure 4.2 (a): *Comparison of the trace metal composition in $PM_{2.5}$ and PM_{10} during the summer sampling period (20-22 March 2007)*



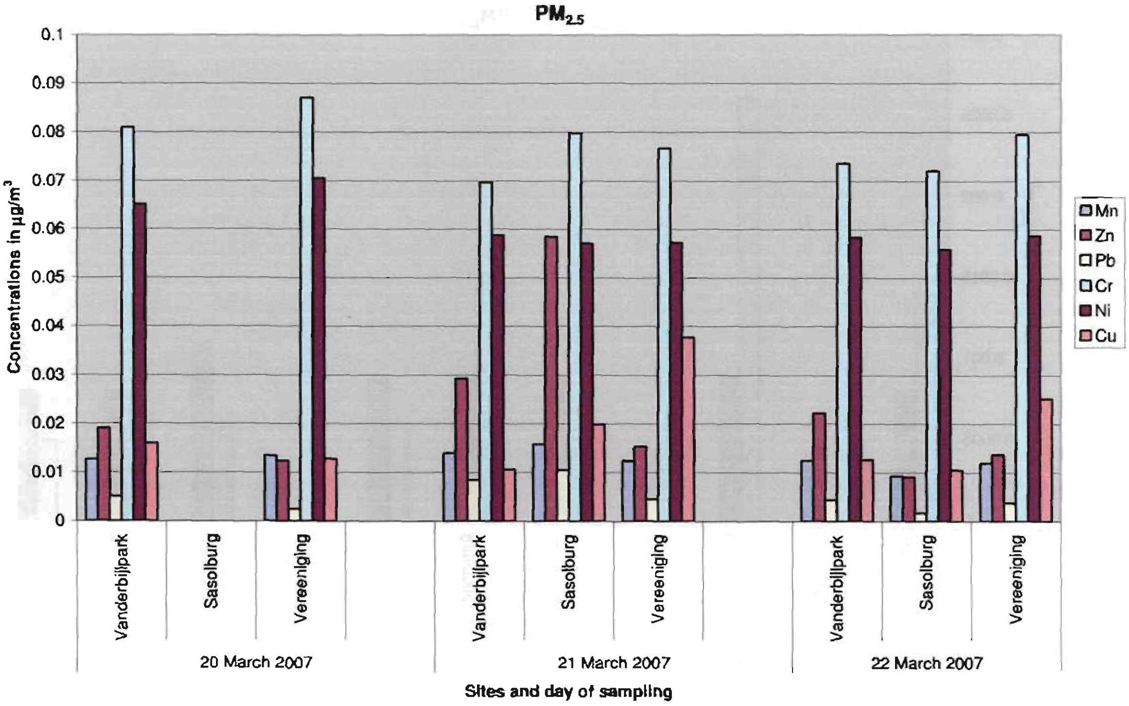
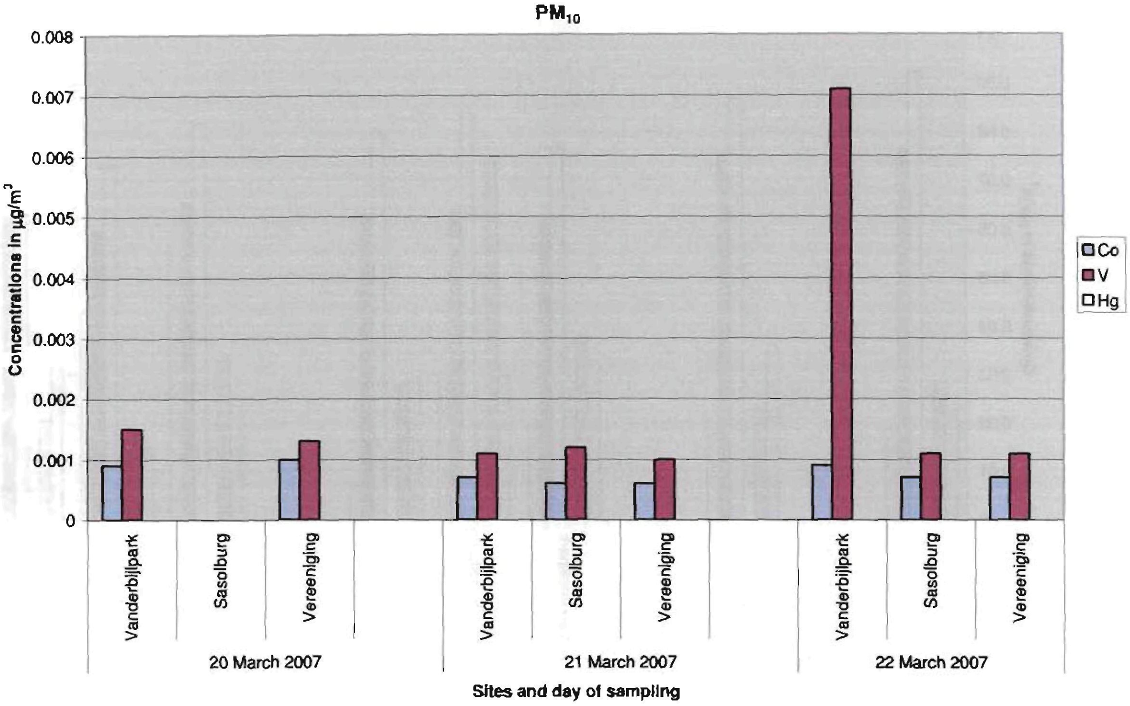


Figure 4.2 (b): *Comparison of the trace metal composition in PM$_{2.5}$ and PM$_{10}$ during the summer sampling period (20-22 March 2007)*



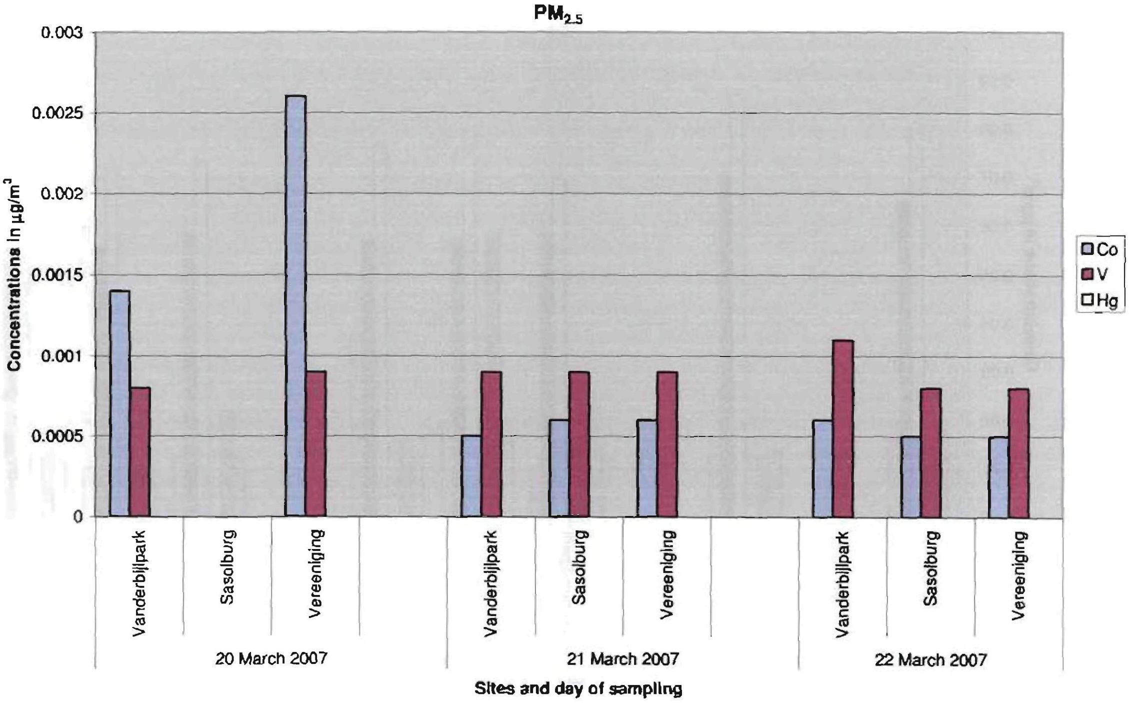


Figure 4.2 (c): *Comparison of the trace metal composition in PM$_{2.5}$ and PM$_{10}$ during the summer sampling period (20-22 March 2007)*

In general, Fe concentrations were the highest for Vanderbijlpark and Vereeniging. Possible sources that might have contributed to the Fe levels include road dust, mineral, and steel manufacturing.[2,22,26] Steel manufacturing was suspected to be the main contributing source, especially since the percentages of fine particles in the coarse fraction for Fe was high.

The occurrence of Na was expected to be due to metallurgical dust and lime.[22] Mg, K and Ca are all believed to be associated with crustal elements (wind-blown dust as source).[21,26] All these elements generally showed increased concentrations on the third day at all sites. This variation from the other sampling days might be seen as a confirmation that these elements could possibly be attributed to this source, also since the $PM_{2.5}$ levels of these elements were less than 50% of the PM_{10} levels.

Ni concentrations stayed approximately the same for the entire sampling period at all sites, possibly suggesting that the main contributing source is from a process that has relatively constant outputs. Following this estimation, the main contributing sources were expected to be the coal-fired power plant and the petrochemical industry.[23,26] Ni concentrations did not vary significantly between the different sites. Therefore, meteorological data and the locations of the two possible sources could not be used to make a more calculated estimation.

The main contributing source of Mn was estimated to be steel manufacturing industries,[21,22] especially because the levels were generally higher for Vanderbijlpark and Vereeniging. Wind-blown dust was expected to be the second most contributing source.[22,26]

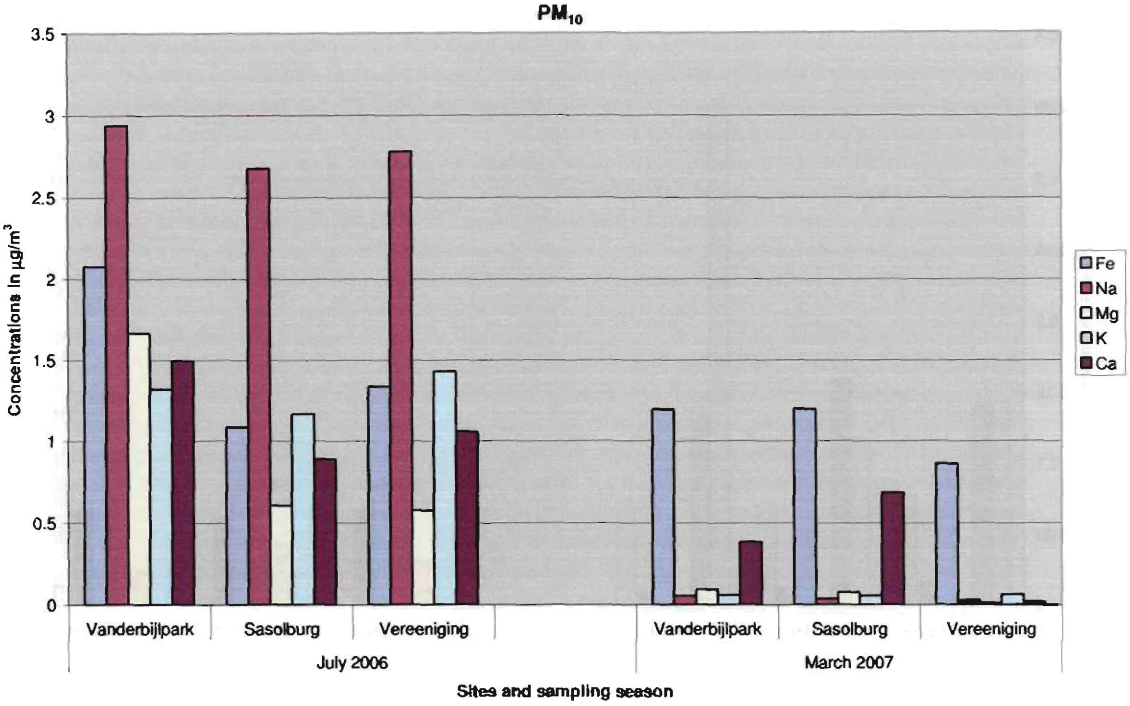
A possible contributing source for Cr could have been steel manufacturing.[22,32] This source was also estimated to have contributed to Cu and Pb concentrations.[21] Road dust and the coal-fired power plant could have been two more possible contributing sources for Pb.[21,23]

Co concentrations can be associated with coal combustion processes.[50] The concentrations for the fine particulate matter on the first day showed significantly higher concentrations at Vereeniging compared with the other sites. A possible elucidation for this could be given by using the meteorological data for that day. The average wind direction was 230°, and since the coal-fired power plant is situated approximately in that direction of the sampling site, it could mean that the power plant was the major contributing source.

Vanadium is used as a tracer for petrochemical industrial emissions, and also as a tracer for emissions from coal-fired power plants.[26,38] The petrochemical industries in the area are situated in Sasolburg. Therefore, it would be estimated that the concentrations of V should be higher at that site. However, the concentrations were significantly higher at Vanderbijlpark compared to the other sites on the third sampling day. Meteorological data showed that the average wind direction on that day was from the southwest. Vanderbijlpark is located to the northeast of Sasolburg. Therefore, the petrochemical industries at Sasolburg could have contributed to the concentrations observed at Vanderbijlpark.

4.3.2. Seasonal variations as observed from the ICP-MS results

The following graphs, compiled from the ICP-MS results (and the average concentrations of the winter and summer sampling) are given to determine the seasonal variations of the trace elements in the Vaal Triangle (Figures 4.3 (a), Figure 4.3 (b) and Figure 4.3 (c)).



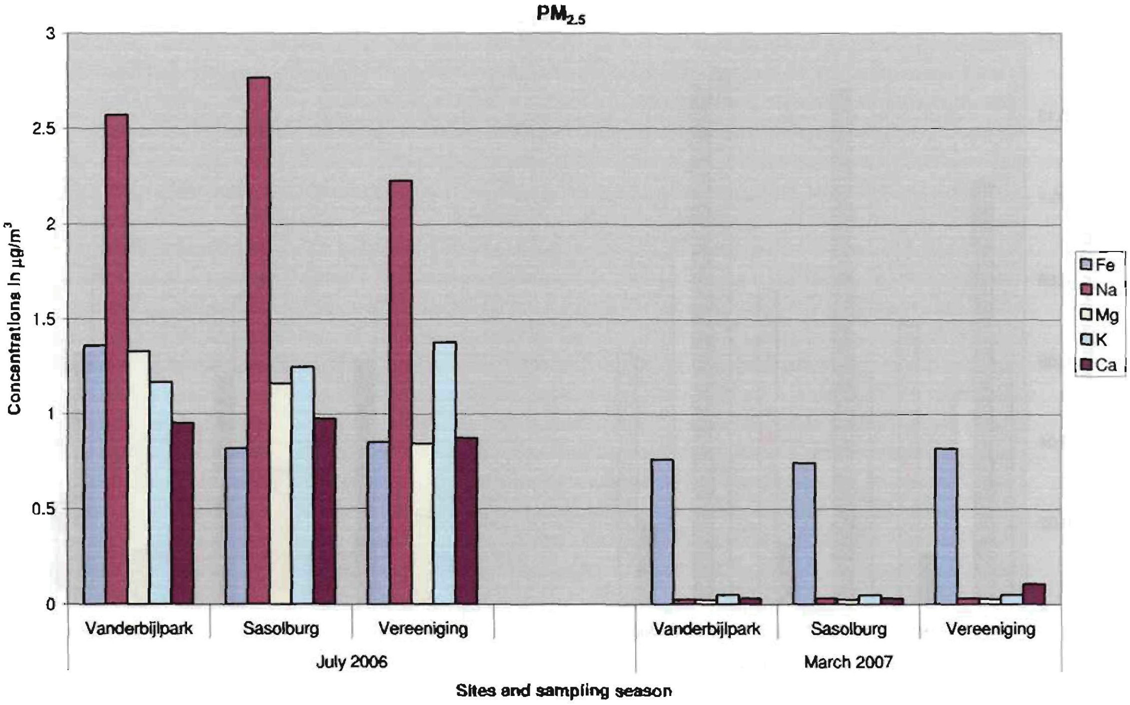
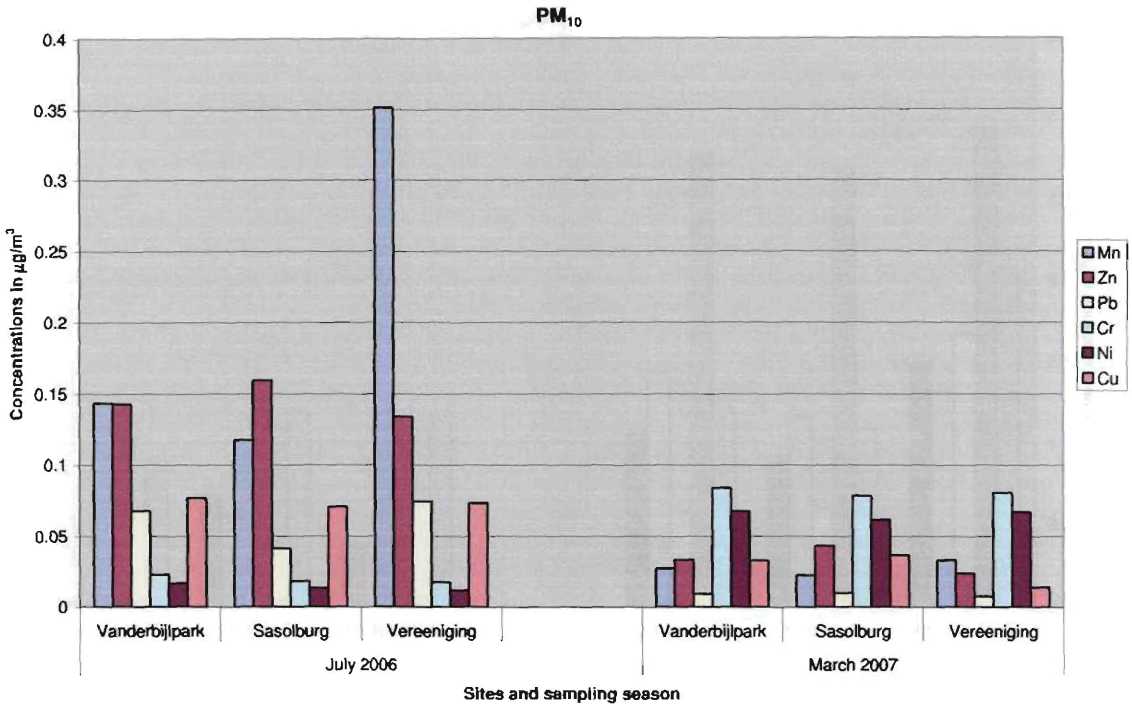


Figure 4.3 (a): *Comparison of the trace metal composition in $PM_{2.5}$ and PM_{10} between the winter and the summer sampling period.*



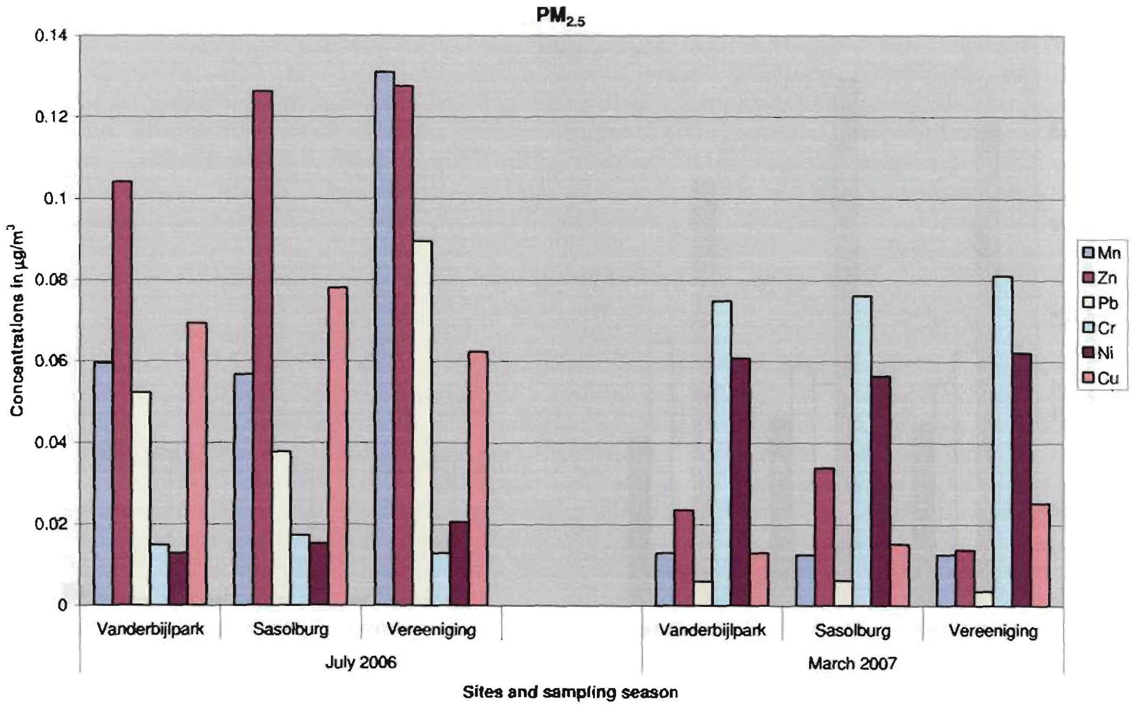


Figure 4.3 (b): *Comparison of the trace metal composition in PM$_{2.5}$ and PM$_{10}$ between the winter and the summer sampling period.*

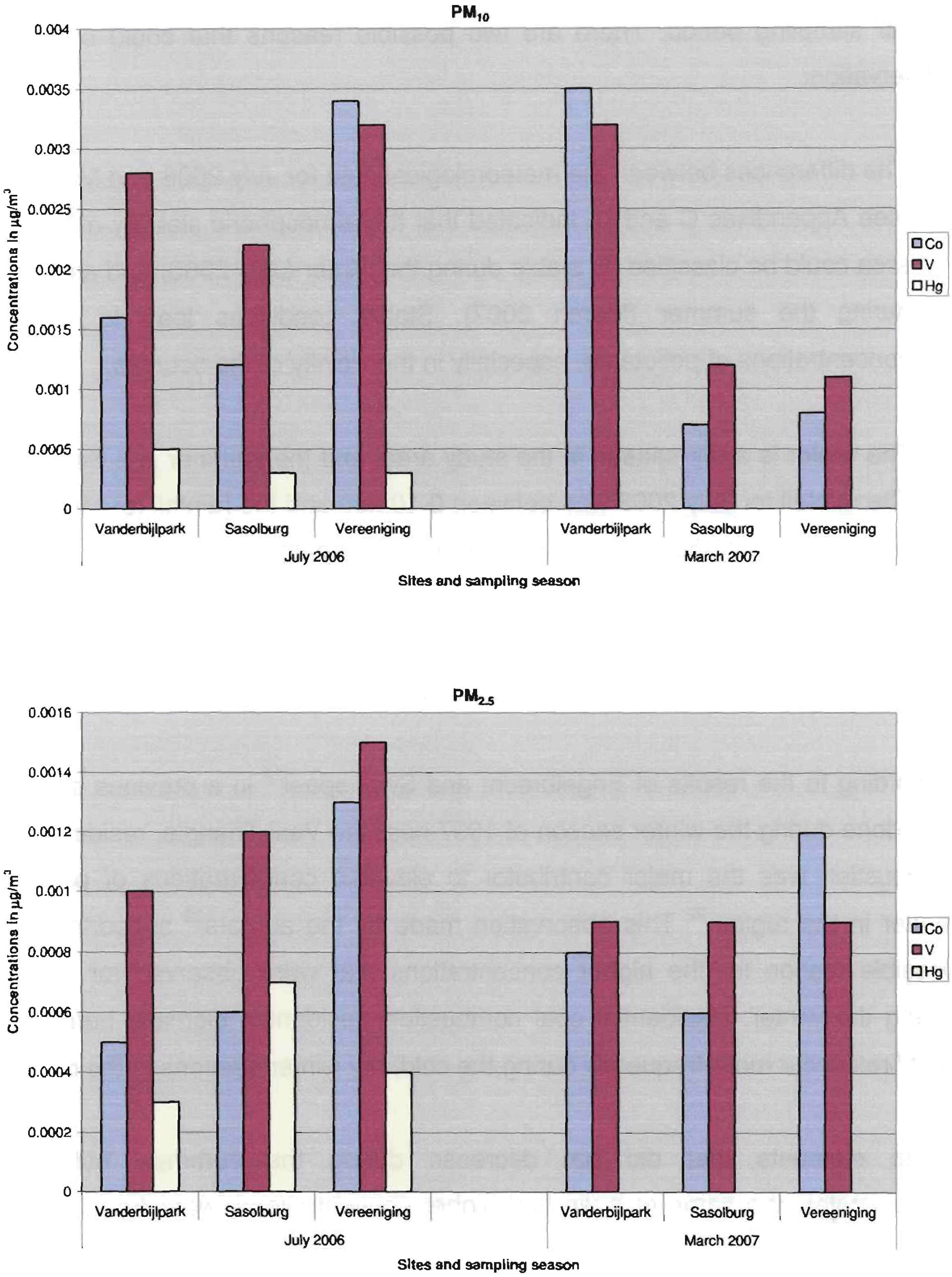


Figure 4.3 (c): *Comparison of the trace metal composition in $PM_{2.5}$ and PM_{10} between the winter and the summer sampling period.*

An important observation that could be made from the seasonal variations in the study area was that almost all of the elements had higher concentrations during the winter sampling period. There are two possible reasons that could explain this observation:

- The differences between the meteorological data for July 2006 and March 2007 (see Appendixes C and D) indicated that the atmospheric stability of the study area could be classified as stable during the winter (July 2006) and as unstable during the summer (March 2007). Stable conditions lead to increased concentrations of pollutants, especially in the vicinity of the sources.

- The winter is a dry-season in the study area, and the summer is a wet-season. The rainfall for July 2006 was between 0-10 mm and the rainfall for March 2007 was between 25-50 mm (the rainfall measurements given here are based on preliminary data obtained from the website of the South African Weather Service [www.weathersa.co.za]). The higher rainfall during the summer could have led to pollutants being washed out of the atmosphere.

According to the results of Engelbrecht and Swanepoel[22] in a previous study that was done during the winter season of 1997 near the Vaal Triangle, residential coal combustion was the major contributor to elevated concentrations of particulate matter in the region.[22] This observation made by the authors[22] supports another possible reason for the higher concentrations that were observed for elements during the winter. Residential coal combustion, residential biomass burning and field fires occur more frequently during the cold, dry winter seasons in the region.

Some elements that did not decrease during the summer, but stayed approximately the same or even had higher concentrations, were Fe, Cr, Ni and Co.

The possibility that interferences during the analyses of the samples could have contributed to the elevated concentrations of Cr and Ni in the summer were investigated. The only interference that could have made a contribution was found for Cr. It is the interference of the polyatomic ions of ArC. The carbon ions could have made an impact due to the fact that carbonaceous particles made up a large percentage of the ambient particulate matter (see the results obtained from SEM/EDS analyses, Appendix A). However, Cr and Ni showed similar trends and polyatomic ions of ArC do not interfere with the detection of Ni isotopes. Therefore, an assumption could be made that the concentrations of these elements were, in fact, higher during the summer.

The major contributing source of Fe was probably the steel manufacturing industries in the study area. The output of these industries was expected to remain constant throughout the year and therefore the concentrations were expected to stay approximately the same. Cr and Ni, as well as Co (used as catalysts) are generally associated with the metallurgical industry, specifically the manufacturing of stainless steel. The local metallurgical industries were expected to significantly influence the Cr and Ni concentrations in the Vaal Triangle.

Even though the atmospheric stability was unstable and the rainfall increased during the summer and therefore the concentrations of these elements were also expected to be lower, the influence and close proximity of the steel manufacturing and metallurgical industries to the sampling sites could have caused these elements to accumulate faster than the other elements.

Another observation that could be made from the seasonal variations was that the concentrations of Na were significantly lower during the summer. This could mean that the major contributing sources of Na might be from natural sources, since the influence of anthropogenic sources are expected to remain fairly constant (with the exception of residential coal and biomass combustion that was generally higher during the winter season). Therefore, the cold fronts that frequently move in from the Atlantic Ocean during the winter (reaching the Vaal Triangle within a few days) could have carried sea spray (and therefore Na)[21] to the study area. The dryer conditions during the winter could also have caused the increased contribution of lime sediments that contained Na.[22]

4.4. COMPARISON OF ICP-MS RESULTS WITH OTHER STUDIES

The average concentrations (for both size fractions) for each sampling period were calculated for the Vaal Triangle (average concentrations for each site was combined and divided by 3).

These average concentrations were compared to annual averages for:

- Edinburg, UK (Heal *et al.*)[24]
- Vienna, Austria (Puxbaum *et al.*)[19]
- Beijing, China (Okuda *et al.*)[25] and
- Rustenburg, South Africa (N.A Kgabi)[51]

The results for all studies compared are given in Table 4.1. It should be noted that the scope of the sample duration was limited for this study (i.e. three days for summer and three days for winter). Therefore, comparisons and deductions were made with due care and consideration.

The concentrations of the elements given in the table were generally higher in the Vaal Triangle than at Edinburg, UK and at Vienna, Austria. The only exceptions were Ti, Cd and Pb that were lower than the annual average at Edinburg, UK for the summer sampling period.

A direct comparison cannot be made with the results for Beijing, China, since these results are for total suspended particles (TSP). The Cr levels in the Vaal Triangle during July 2006 were higher than the TSP annual average in China. This indicated that the concentration of Cr in the Vaal Triangle was significant. Although the major chromium industries in South Africa are not in this region, the levels of Cr in the Highveld coal are higher than global averages.

The study done by N.A Kgabi[51] in Rustenburg is one of the very few studies that measured the trace metal concentrations in ambient particulate matter. For a more general overview of the study, refer to Chapter 2, Section 2.3.4.4. The concentrations of all elements were lower in the Vaal Triangle than for Rustenburg, South Africa, for both sampling periods. Even Fe concentrations – that would initially be expected to have higher concentrations in the Vaal Triangle – were significantly higher in the Rustenburg area. This might be due to the large number of chromium smelters in the Rustenburg area.

Chromium ore, which is burned in the smelters, is a ferrochrome mixture (approximately 50% Cr, 38% Fe and the remaining 12% a variety of other metals). Therefore, the large number of smelters in the area would contribute to Fe concentrations in the atmospheric particulate matter (the reason for the increased Fe concentrations in Rustenburg was given by Dr. Paul Beukes from his experience in the ferrochrome industry).

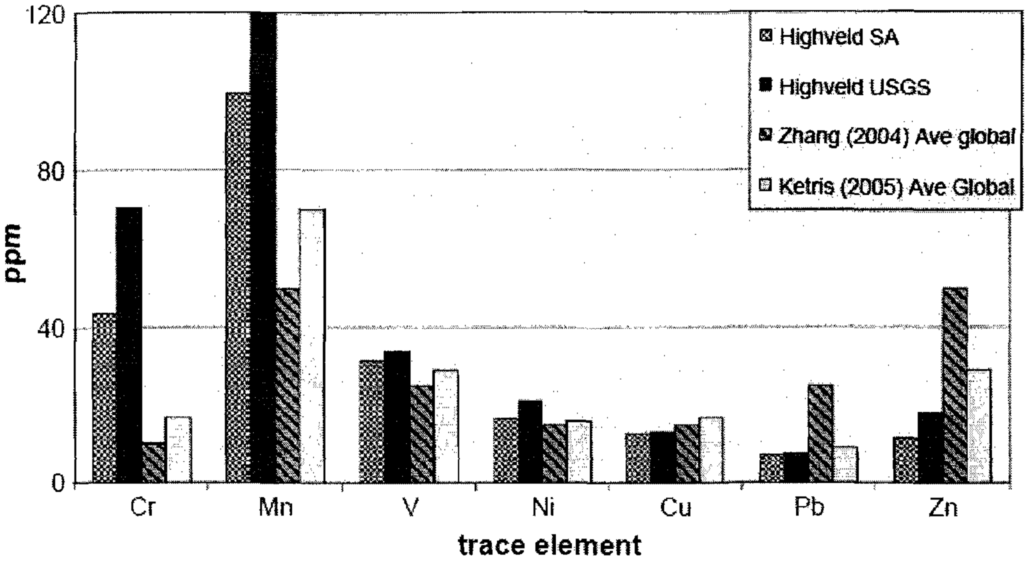
Thus, although the Vaal Triangle was declared by the South African government as a priority air pollution area and the Rustenburg area not, it would seem that the Rustenburg area is more heavily polluted (with respect to trace metal concentrations).

Table 4.1: *Comparison of the results of various studies with the results of the Vaal Triangle (this particular study) (all results given as µg.m^{-3}).*

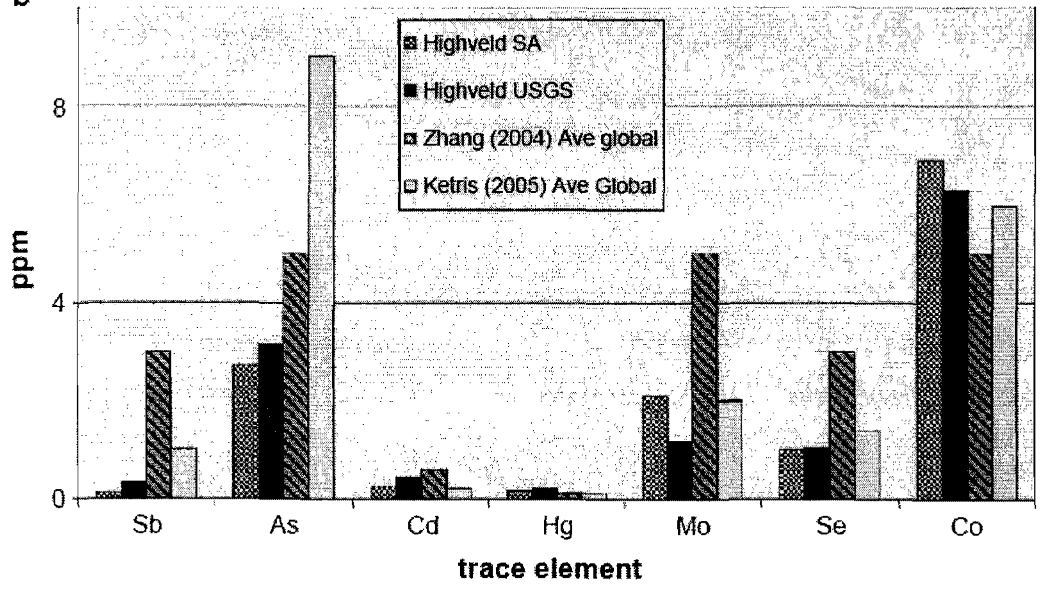
Element	**Edinburg, UK**		**Vienna, Austria**				**Beijing, China**	**Rustenburg, South Africa**		**Vaal Triangle, South Africa**			
	1999 – 2000		**1999 – 2000**				**2001 – 2003**	**2005**		**July 2006**		**March 2007**	
			PM_{10} – $PM_{2.5}$		**$PM_{2.5}$**			**PM_{10}**					
	PM_{10}	**$PM_{2.5}$**	**AU1**	**AU2**	**AU1**	**AU2**	**TSP**	**Site A**	**Site B**	**PM_{10}**	**$PM_{2.5}$**	**PM_{10}**	**$PM_{2.5}$**
Ti	0.00366	0.00037					0.47	0.17	0.19	0.02	0.0066	0.0005	0.0002
V	0.00114	0.00072	0.00053	0.00049	0.0013	0.00074	0.013	0.28	0.03	0.0027	0.0012	0.0018	0.0009
Cr	0.00160	0.00049	0.00039	0.00017	0.0004	0.00035	0.019	2.55	0.18	0.0194	0.0149	0.0808	0.0771
Mn	0.00294	0.00069	0.0043	0.0022	0.0024	0.002	0.24	8.47	0.31	0.2054	0.0819	0.0264	0.0123
Fe	0.183	0.0276	0.146	0.03	0.035	0.023	5.5	12.83	6.69	1.5057	1.0105	1.0444	0.8426
Ni	0.00343	0.00097	0.0004	0.0003	0.012	0.044	0.022	1.41	0.13	0.0138	0.0164	0.0657	0.0605
Cu	0.00493	0.00139	0.0079	0.0018	0.0031	0.0017	0.11	0.22	0.2	0.0736	0.0692	0.0257	0.0237
Zn	0.0133	0.00749	0.013	0.011	0.022	0.017	0.77	0.34	0.33	0.1460	0.1169	0.0299	0.0219
As	0.00037	0.0003	0.00028	0.00023	0.00066	0.00049	0.048			0.006	0.005	0.0011	0.0006
Cd	0.00034	0.00038	0	0.00011	0.00044	0.00023	0.0068			0.001	0.0012	0	0
Pb	0.0141	0.0136	0.0051	0.0055	0.017	0.012	0.43	0.35	0.48	0.0617	0.0594	0.0079	0.0049

The occurrence of potentially hazardous trace elements in the Highveld coals of South Africa were compared to average global concentrations found in coal.[38]

a



b



These figures show that South African coal is rich in Cr and Mn and that the levels of Co, Ni and V are slightly higher, but very comparable to global average concentrations.[38]

The majority of emission sources in the Vaal Triangle (especially during the winter season) could possibly have been related to coal combustion processes. Therefore, it could be estimated that the high occurrence of Cr and Mn in coal would influence the concentrations of these elements, and possibly also (to a lesser extent) the levels of Co, Ni and V.[38]

The results obtained from the SEM/EDS analyses for the July 2006 sampling period were not complete for all size fractions at all the sites, due to the rough texture of the teflon filters that were used. For the next sampling period, other teflon filters were used for PM_{10} measurements. SEM/EDS results showed that the dominant species in ambient particulate matter is carbon and other elements contributed only a small fraction of the weight percentage of each sample.

ICP-MS was used to determine the concentrations of all elements from Li to U for each sample. The results showed that the concentrations were generally much higher during the winter season than the summer season, and very low concentrations of all elements analysed were obtained for the background sampling. The ICP-MS results also showed that a large fraction of the concentrations of elements from Li to U in PM_{10} samples are, in fact, contributed by particles in the fine fraction (less than 2.5 µm in diameter). For the background sampling, only a very small fraction of the PM_{10} samples were contributed by fine particles.

Comparison of the results obtained in this study with other studies showed that the concentrations of elements were higher in the Vaal Triangle than Edinburg (UK) and Vienna (Austria), but lower than Rustenburg (SA) and not comparable with Beijing (China). A comparison of the levels of trace elements in South African coal with global average values showed a very high enrichment of Cr and Mn in South African coal. This could possibly influence the levels of these elements in the Vaal Triangle, due to the high use of coal and coal combustion processes.

Meteorological measuring equipment were only available at the Sasolburg site, but since the sites in the Vaal Triangle are relatively close to one another, it may be assumed that the same meteorological conditions will apply to all sites.

Chapter 5:
Conclusions

This chapter will give a brief summary of the scientific achievements in the previous chapters, through a critical evaluation of each objective. General conclusions are made from the comparison of the results with other studies, with guideline values and with government regulations. Lastly, limitations of the study are mentioned and recommendations are made for future studies.

5.1. EVALUATION OF THE FIRST OBJECTIVE

The first objective of this study was to collect samples once during an winter and once during a summer season at three selected sites in the Vaal Triangle. This objective was completed successfully. However, a few problems were encountered with the sampling.

One of the problems occurred with the site selection for Vanderbijlpark. The site that was used for the collection of samples during the winter season could not be used again for the summer season (see Chapter 3 for the reasons). Therefore, a new site had to be chosen for the summer sampling period, as close as possible to the original site, and other factors had to be taken into consideration (safety on the site, and accessibility). The new site complied with all these criteria. However, there remained the possibility that the data obtained from the new site could not be compared directly with that of the first site.

Another problem that occurred with the sampling was the type of filter used during the winter sampling period. Whilst doing the SEM/EDS analyses on the samples collected for this period, it became clear that some of the filters had a rough surface that had not been apparent from the visual filter inspection before sampling. This made the determination of the elemental composition of the filters impossible by using SEM/EDS. Only eleven of the eighteen samples collected during the winter were analysed using this technique.

The last problem with the sampling occurred during the summer sampling period. Both of the MiniVols used at the Sasolburg site had malfunctioned and shut down on the first day of sampling. The exact time that the sampler was operational could not be determined. Therefore, the concentrations could not be determined and the results had to be omitted.

In addition to the winter and summer sampling periods in the Vaal Triangle, it was decided to collect background samples at a suitable site in the Botsalano Game Reserve in the Northwest Province. The background samples could give a general idea as to what the contributions of natural emissions might be. Since it was not possible to collect background samples on the exact times that samples were collected in the Vaal Triangle, it was decided to do the sampling during an intermediate season. Samples for both the winter and summer periods would then be comparable to some degree with the background samples.

5.2. EVALUATION OF THE SECOND OBJECTIVE

The second objective of this study was to determine the concentrations of trace elements in different size fractions of the collected atmospheric particulate matter in the Vaal Triangle. This has also been successfully completed for $PM_{2.5}$ and PM_{10}. The results obtained from the ICP-MS analyses were used to achieve this objective.

The concentrations of all elements from Li to U were determined for each sample. The total concentrations of all these elements were calculated for each sampling site and for each day of sampling. The average total values were also calculated for each sampling period at each site. The average total concentrations at each site were higher during the winter sampling period than the summer sampling period. This could possibly be attributed to the higher occurrence of residential coal combustion, residential biomass burning and field fires during the dry winter season than in the wet summer season.

Fe concentrations were higher than most other elements, possibly due to the numerous steel manufacturing industries in the Vaal Triangle. Cr and Mn levels were higher, possibly because these elements are higly enriched in South African coal and the Vaal Triangle is a region in South Africa that is known for the high usage of coal (including coal mining).

The stable atmospheric conditions during the winter and the unstable atmospheric conditions during the summer could be the main reason why the concentrations of the elements were higher during the winter sampling period. Another possible reason for the higher concentrations during the winter could be that the pollutants were washed out of the atmosphere more frequently during the wet summer season than during the dry winter season.

5.3. EVALUATION OF THE THIRD OBJECTIVE

The third objective was to compare the results from two different analytical techniques to suggest an appropriate atmospheric particulate monitoring method. The two analytical techniques that were used was SEM/EDS and ICP-MS. After some difficulties had been experienced, a comparison between the two techniques was made successfully.

As it was mentioned in previous chapters, the SEM/EDS technique is usually used to analyse the surface of a substance. The total concentrations of particulate matter in the study area was lower during the summer season (attributed to unstable meteorological conditions, increased mixing of pollutants, higher mixing depth, better transportation of pollutants from the emission sources, and wash-out of pollutants by wet events). Since the concentrations of particulate matter was lower during the summer, the layer of particulate matter that covered the filter was considerably thinner. This caused the electron beam to penetrate the sample further, resulting in the filter components being picked up by the SEM/EDS and influencing the analyses.

Another problem with the SEM/EDS analyses was that the results generally gave an idea as to what the elemental composition of the sample might be in weight percentage. Since the filters could not be accurately weighed before and after sampling (the temperature and relative humidity could not be controlled), the contribution of each element that was picked up by this technique could not be calculated.

Due to the reasons mentioned above, the use of ICP-MS for the determination of the concentrations of trace elements is preferred (in this case) above SEM/EDS. Even if the filter mass could have been accurately determined, the SEM/EDS would still only give a general idea of what the filter composition might be. In contrast, the ICP-MS technique was found to be more accurate and precise, and it measured the concentrations of all the elements from Li to U.

5.4. EVALUATION OF THE FOURTH OBJECTIVE

The fourth objective of this study was to evaluate the use of MiniVol Portable Air Samplers. This objective was completed successfully.

The MiniVol Portable Air Samplers are very user-friendly. It is easy to clean the impactors before sampling, relatively simple to assemble and to change the filters after each sampling day. The fact that they can run from line power supply or from a battery made the sampling more convenient. The samplers were run from line power at each sampling site (with the exception of the first site at Vanderbijlpark). The batteries of the samplers are then a back-up in case of a power failure. The samplers automatically changes to battery in case of a power failure when the samplers are run from line power. Therefore, it is not necessary for someone to be present to switch from line power to battery operation.

Another advantage of the samplers are that they are relatively small compared to measuring equipment at fixed sampling stations. Therefore, the MiniVols can be placed almost anywhere, and they are heavy enough not to be blown over by low to moderate winds.

Another great advantage of the samplers is that they come equipped with a programmable timer. If the sampling site is remote and access is limited (like for instance the background sampling site), the timers can be set to start and stop sampling at given times. The only thing left to be done after programming, is to ensure that the filters get changed before the next sampling cycle begins.

The only problem that occurred from the use of the MiniVols were the failure of both MiniVols at the Sasolburg site on the first day of sampling during the summer period. The samplers had shut down after the low flow fault circuit was activated. This problem occurs if excessive accumulation of particulate matter takes place, or if some restriction in the tubing cause the air flow to fall below a specified rate.[43]

Overall, the MiniVol Portable Air Samplers was found to be very reliable and easy to handle.

5.5. GENERAL CONCLUSIONS

From the comparisons done in Chapter 4 between the results obtained at the Vaal Triangle and results from other studies, it became clear that the concentrations of trace elements in the study area was higher than the concentrations found in other cities around the world. This is a cause of great concern, especially since some trace metals could potentially cause serious health-related problems, as well as negative impacts on the environment. The concentrations were lower in the Vaal Triangle than in Rustenburg, but the Vaal Triangle is only one of two areas proclaimed as a priority area in South Africa (the other one is the Highveld).

The concentrations of lead in the study area never exceeded the Air Quality Standard[52] on any given day. The standard is for a one-month average and since the sampling was only done for three days during July 2006 and three days during March 2007, the possibility that Pb might exceed this value at some point during the year cannot be ruled out.

The contribution of trace elements analysed in particulate matter never exceeded the 24-hour average of 180 μg.m^{-3} for total concentration of PM$_{10}$. The SEM/EDS analyses showed, however, that trace elements only made up a small fraction of the total sample. The maximum concentration of trace elements observed for PM$_{10}$ (obtained from the ICP-MS analyses) was for Vanderbijlpark, 4 July 2006 (the concentration was 24 μg.m^{-3}). The SEM/EDS analyses for Vanderbijlpark PM$_{10}$ on that day showed that the contribution of trace elements would only account for about 7% of the weight of the filter. This shows that the possibility exists that the total PM$_{10}$ concentrations could have exceeded the 24-hour average Air Quality Standard[52].

5.6. RECOMMENDATIONS FOR FUTURE STUDIES

The number of studies done on the trace metal content of ambient particulate matter in South Africa are limited, especially in the Vaal Triangle. Even though the study was completed successfully, there existed a few limitations in this particular study. Future studies will be significantly improved and the elucidation of results simplified if these limitations are dealt with.

The first recommendation that can be made for future studies is to make sure that the filters are weighed before and after sampling, at the same temperature and relative humidity, to accurately determine the mass of the particles. Since the concentration range is in μg.m^{-3}, the slightest change in temperature and relative humidity can cause a significant difference in the filter mass due to the higher or lower adherence of water vapour molecules.

Secondly, it is highly recommended to do more frequent sampling. With more samples per season, it would become possible to get better seasonal trends. With more samples it would also become possible to do source apportionment analyses of the results. This would enable more accurate estimations as to what the main contributing sources might have been.

Another possibility to distinguish between natural and anthropogenic sources would be to calculate the enrichment factors (EFs) of the various elements in the soil at the various sampling sites in the Vaal Triangle. These EFs would also give an indication as to what elements are more correlated with each other, also possibly helping with the estimation of the contributing sources.

As it was previously mentioned, the SEM/EDS analyses gave a rough estimate as to what the main elemental composition of the samples might have been. ICP-MS analyses gave more precise concentrations of the various elements. The majority of studies worldwide on the trace metal content of ambient particulate matter also tends to use either ICP-MS or ICP-AES for the determination of the concentrations. Therefore, it would be recommended to use SEM/EDS analyses to get an initial idea of the composition of the samples, and then to do a comparative study between ICP-MS and ICP-AES to determine the best analytical method between these techniques.

In general, it can be concluded that the study was successful according to the objectives that had been set. The comparison of the two analytical techniques showed that ICP-MS are the preferred method to determine the concentrations of trace metals in ambient particulate matter. A few limitations were identified that would have improved the quality of the research, and it would be recommended that these be taken into consideration in future studies. Since there is a paucity of data available on trace metal concentrations in the Vaal Triangle priority pollution area, it would be recommended that further studies be done to get clear seasonal trends and annual average concentrations.

References

1. Khlystov A: *"Quality Assurance Project Plan for Pittsburgh Air Quality Study (PAQS)";* February 2001; Carnegie Mellon University.
2. Ministry of Water, Land and Air Protection: *"Environmental Indicator: Air Quality Impacts from Inhalable Particulates and Ozone";* 2002; British Columbia.
3. http://www.etcentre.org/publication; February 2006.
4. Lee SW, He I, Herage T, Young B, Razbin V, Kelly E, Pomalis R: *"Fuel Sulfur Effects on Particulate Emissions from Fuel Oil Combustion Systems Under Accelerated Laboratory Conditions";* March 2002; REPORT CETC 02-09(CF).
5. Ministry for the Environment: *"Ambient Air Quality Guidelines, Air Quality Report No 32";* 2002; Wellington, New Zealand. (www.mfe.govt.zn).
6. Lenntech water treatment and air purification holding B.V, the Netherlands; www.lenntech.com/Periodic-chart-elements/; November 2007.
7. Agency for toxic Substances and Disease registry: *"Vanadium";* www.atsdr.cdc.gov/facts58.htm/; February 2006.
8. Material safety data sheet Nr 17500, May 2006.
9. Dr. Joseph Mercola: *"Iron can have devastating effects on your health";* www.mercola.com/2002/; 2002
10. Environmental Protection Agency; www.epa.gov; February 2006.
11. Environmental Department, General Directorate of Environmental Quality, Commission of the European Communities Directorate-General XI: *"Air Quality Daughter Directives Position Paper on Lead"*; 1997
12. Des W. Connell: *"Basic Concepts of Environmental Chemistry"*
13. Ulrich Pöschl: *"Atmospheric Aerosols: Composition, Transformation, Climate and Health Effects"*; 2005; Angewandte Chemie Int. Ed.; Vol 44; pp. 7520-7540.

14. S.Slanina and Y.Zang: *"Aerosols: connection between regional climate change and air quality (IUPAC Technical Report)"*; 2004; Pure and applied chemistry; Vol 76; pp. 1241-1253.

15. Meinrat O.Andreae: *"Atmospheric aerosols versus greenhouse gases in the twenty-first century"*; 2007; Philosophical Transactions of the Royal Society A; Vol 365; pp. 1915-1923.

16. S.Solomon, D.Quin, M.Manning, R.B.Alley, T.Berntsen, N.L.Bindoff, Z.Chen, A.Chidthaisong, J.M.Gregory, G.C.Hegerl, M.Heimann, B.Heuritson, B.J.Hoskins, F.Joos, J.Jousel, V.Kattsov, U.Lohmann, T.Matsuno, M.Molina, N.Nicholis, J.Overpeck, G.Raga, V.Ramaswamy, J.Ren, M.Rusticucci, R.Somerville, T.F.Stocker, P.Whetton, R.A.Wood, and D.Wratt: *"Technical Summary. In: Climate change 2007: the Physical Science Basis. Contribution of working group 1 to the Fourth Assesment Report of the Intergovernmental Panel on Climate Change [S.Solomon, D.Quin, M.Manning, Z.Chen, M.Marquis, K.B.Averyt, M.Tignor, and H.L.Mills (eds.)]"*; 2007; Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA; pp. 20-91.

17. www.arb.ca.gov/aqd/weekendeffect/arb-final/wee_tsd_ch3_1.pdf; *"Analysis of variations in Particulate Matter"*; 30 June 2003; downloaded on 5 Nov 2007.

18. JoAnn Slama Lighty, John M.Verranth, and Adel F.Sarofim: *"Combustion Aerosols: Factors governing their size and composition and Implications to Human Health"*; 2000; Journal of the Air & Waste Management Association; Vol 50, pp. 1565-1618.

19. H.Puxbaum, B.Gomiscek, M.Kalina, H.Bauer, A.Salam, S.Stopper, O.Preiring, and H.Hauck: *"A dual site study of $PM_{2.5}$ and PM_{10} aerosol chemistry in the larger region of Vienna, Austria"*; 2004; Atmospheric Environment; Vol 38; pp. 3949-3958.

20. E.A.Sondreal, S.A.Benson, J.H.Pavlish, and N.V.C.Ralston: *"An overview of Air Quality III: Mercury, trace elements, and particulate matter"*; 2004; Fuel processing technology; Vol 85; pp. 425-440.

21. M.Viana, X.Querol, A.Alastuey, J.I.Gil, and M.Menéndez: *"Identification of PM sources by principal component analysis (PCA) coupled with wind direction data"*; 2006; Chemosphere; Vol 65; pp. 2411-2418.

22. J.P.Engelbreght, L.Swanepoel, J.C.Chow, J.G.Watson, and R.T.Egami: *The comparison of source contributions from residential coal and low-smoke fuels, using CMB modelling in South Africa";* 2002; Environmental Science & Policy; Vol 5; pp. 157-167.
23. E.A.Weitkamp, E.M.Lipsky, P.J.Pancras, J.M.Ondov, A.Polidori, B.J.Turpin, and A.L.Robinson: *"Fine particulate emission profile for a large coke production facility based on highly time-resolved fence line measurements";* 2005; Atmospheric Environment; Vol 39, issue 36; pp. 6719-6733.
24. M.R.Heal, L.R.Hibbs, R.M.Agius, and I.J.Beverland: *"Total and water-soluble trace metal content of urban background PM_{10}, $PM_{2.5}$ and black smoke in Edinburgh, UK";* 2005; Atmospheric Environment; Vol 39, issue 8; pp. 1417-1430.
25. T.Okuda, J.Kato, J.Mori, M.Tenmoku, Y.Suda, S.Tanaka, K.He, Y.Ma, F.Yang, X.Yu, F.Duan, and Y.Lei: *"Daily concentrations of trace metals in aerosols in Beijing, China, determined by using inductive coupled plasma mass spectrometry equipped with laser ablation analysis, and source identification of aerosols";* 2004; Science of The Total Environment; Vol 330, issues 1-3; pp. 145-158.
26. X.Querol, M.C.Minguillón, A.Alastuey, E.Monfort, E.Mantilla, M.J.Sanz, F.Sanz, A.Roig, A.Renau, C.Felis, J.M.Miró, and B.Artíñano: *"Impact of the implementation of PM abatement technology on the ambient air levels of metals in a highly industrialized area";* 2007; Atmospheric Environment; Vol 41; pp. 1026-1040.
27. United States Environmental Protection Agency (www.epa.gov): *"Lead"* and *"Mercury";* February 2006.
28. U.S. Department of Health and Human Services, Public Health Service, Agency for toxic Substances and Disease Registry (www.atsdr.cdc.gov): *"Draft toxicological profile for lead";* September 2005.
29. U.S. Department of Health and Human Services, Public Health Service, Agency for toxic Substances and Disease Registry (www.atsdr.cdc.gov): *"Toxicological profile for nickel";* August 2005.

30. The International Programme on Chemical Safety (first draft prepared by R.F.Hertel, T.Maass, and V.R.Muller): *"Environmental Health Criteria 108: Nickel";* 1991; www.inchem.org/documents/ehc/ehc/ehc108.htm; downloaded February 2006.
31. U.S. Department of Health and Human Services, Public Health Service, Agency for toxic Substances and Disease Registry (www.atsdr.cdc.gov): *"Toxicological profile for vanadium and compounds";* July 1992.
32. U.S. Department of Health and Human Services, Public Health Service, Agency for toxic Substances and Disease Registry (www.atsdr.cdc.gov): *"Toxicological profile for chromium";* September 2000.
33. H.Hou, T.Takamatsu, M.K.Koshikawa, and M.Hosomi: *"Trace metals in bulk precipitation and throughfall in a suburban area of Japan";* 2005; Atmospheric Environment; Vol 39, issue 20; pp. 3583-3595.
34. X.Wang, T.Sato, B.Xing, S.Tamamura, and S.Tao: *"Source identification, size distribution and indicator screening of airborne trace metals in Kanazawa, Japan";* 2005; Journal of Aerosol Science; Vol 36, issue 2; pp. 197-210.
35. M.Koçak, M.Nimmo, N.Kubilay, and B.Herut: *"Spatio-temporal aerosol trace metal concentrations and sources in the Levantine Basin of the Eastern Mediterranean";* 2004; Atmospheric Environment; Vol 38, issue 14; pp. 2133-2144.
36. I.F.Al-Momani: *"Trace elements in atmospheric precipitation at Northern Jordan measured by ICP-MS: acidity and possible sources";* 2003; Atmospheric Environment; Vol 37, issue 32; pp. 4507-4515.
37. Joseph A.Caruso and Maria Montes-Bayon: *"Elemental speciation studies – new directions for trace metal analysis";* 2003; Ecotoxicology and Environmental Safety; Vol 56, issue 1; pp. 148-163.
38. Nicola J.Wagner, and Bafana Hlatshwayo: *"The occurrence of potentially hazardous trace elements in five Highveld coals, South Africa";* 2005; International Journal of Coal Geology; Vol 63; pp. 228-246.
39. P.S.Gilmour, D.M.Brown, T.G.Lindsay, P.H.Beswick, W.MacNee, and K.Donaldson: *"Adverse health effects of* PM_{10} *particles: involvement of iron in generation of hydroxyl radical";* 1996; Occupational and Environmental Medicine.

40. Ian M.Kennedy: *"The health effects of combustion-generated aerosols";* 2007; Proceedings of the Combustion Institute; Vol 31; pp. 2757-2770.

41. www.vaal.co.za/info/bos report/positioning of the vaal triang.php; *"Physical aspects";* downloaded from site on 1st October 2007.

42. Department of Environmental Affairs and Tourism of South Africa, Environmental quality and protection, Chief Directorate: Air quality management and climate change: *"Draft:Vaal Triangle Priority Area Air Quality Management Plan – Baseline Characterization";* May 2007; [Report Authors: H.Liebenberg-Enslin; R.Thomas, N.Walton, M.Van Nierop].

43. Minivol Portable Air Sampler: Operation Manual version 4.2c; June 2001; Airmetrics U.S.A.

44. R.W.Baldauf, D.D.Lane, G.A.Marotz, and R.W.Wiener: *"Performance evaluation of the portable MiniVol particulate matter sampler";* 2001; Atmospheric Environment; Vol 35; pp. 6087-6091.

45. W.R.Herguth, and G.Nadeau: *"Applications of Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM/EDS) to practical tribology problems";* Herguth Laboratories Inc.; California.

46. D.Briggs, J.Brady, and B.Newton: *"Scanning electron microscopy and x-ray microanalysis"; 2000.*

47. ICP-MS – The Quadrupole Mass Analyzer; www.missouri.edu/~murrwww/pages/ac icpms.shtml; downloaded: Febr 2006.

48. *"Fundamentals of Inductive Coupled Plasma Mass Spectrometry (ICP-MS)";* 2002; Agilent Technologies.

49. *"Make the change to ICP-MS: Agilent 7500 Series ICP-MS";* Agilent Technologies; www.agilent.com/chem/icpms; downloaded November 2007.

50. U.S. Department of Health and Human Services, Public Health Service, Agency for toxic Substances and Disease Registry (www.atsdr.cdc.gov): *"ToxFAQs^{TM} for Cobalt";* April 2004.

51. Nnenesi Anna Kgabi: *"Monitoring the levels of toxic metals of atmospheric particulate matter in the North West province";* Thesis submitted in fulfilment of the requirements for the degree Philosophiae Doctor in Environmental Science, North-West University, May 2006, South Africa.

52. Government Gazette, Republic of South Africa, Vol 476, Cape Town, February 2005, No. 27318.
53. P.D.Thyson, M.Garstang, R.J.Swap, M.Edwards and P.Kallberg: *"An air transport climatology for subtropical southern Africa";* 1996; International Journal of Climatology; Vol 16; pp. 151-163.
54. Lenntech: *"Bromine – Chemical properties, Health and Environmental effects"*, www.lenntech.com/Periodic-chart-elements/Br-en.htm; December 2007.
55. J.H. Seinfeld and S.N. Pandis: *"Atmospheric Chemistry and Physics"*; 1998; Wiley; New York.
56. W.C. Hinds: *"Aerosol Technology";* 1999; Wiley, New York.
57. B.J. Finlayson-Pitts and J.N. Pitts: *"Chemistry of the upper and lower atmosphere";* 2000; Academic Press; San Diego.
58. J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell and C.A. Johnson: *"Climate change 2001: The scientific basis (Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change)";* 2001; Cambridge University Press, Cambridge.
59. E. Brown: *"Current policy developments and directions concerning mercury control of air emissions, Proceedings of the Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference, Arlington, VA, Sept 9 – 12, 2002.*
60. Recommendations for the Utility Air Toxics MACT; Final Working Group Report, Oct; 2002.
61. A. Yumang, I.Makalinao, N. Cortes-Maramba and A. Rivera: *"Health and environmental assessment from mercury exposure among gold miners in Compostela Valley Province, Phillippines, Proceedings of the Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference, Arlington, VA, Sept 9 – 12, 2002.*
62. D. Behne, H. Hilmert, S. Scheid, H. Gessner and W. Elger: *"Evidence for specific selenium target tissues and new biologically important selenoproteins";* 1998; Biochim, Biophys. Acta 966, pp. 322 – 328.

Appendix A:
SEM/EDS results

A.1. Blank filters

Table A.1: Elemental composition of the blank filters (in weight %).

PALL LIFE SCIENCES TEFLON FILTERS		WHATMAN INC. TEFLON FILTERS	
Element	**Weight %**	**Element**	**Weight %**
C	19.31	C	19.51
F	80.69	F	80.69
Total	**100.00**	**Total**	**100.00**

Table A.2: Oxides of the elements of the blank filters (in weight %).

PALL LIFE SCIENCES TEFLON FILTERS		WHATMAN INC. TEFLON FILTERS	
Element	**Weight %**	**Element**	**Weight %**
C	9.31	C	9.31
F	65.90	F	65.90
0	24.80	C	24.80
Total	**100.00**	**Total**	**100.00**

A.2. July 2006

A.2.1. 4 July 2006

Table A.3: Elemental composition of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}	
Element	Weight%	Element	Weight%	Element	Weight%	Element	Weight%	Element	Weight%	Element	Weight%
C	51.65	C	51.14	C	51.66			C	52.66	C	24.27
O	40.67	O	42.11	O	43.39			O	43.01	O	6.46
										F	66.23
Na	0.32	Na	0.26							Na	0.13
Al	0.53	Al	0.84	Al	0.49			Al	0.80	Al	0.66
Si	0.94	Si	1.55	Si	0.90			Si	1.07	Si	1.08
S	0.95	S	0.70	S	1.43			S	0.77	S	0.38
Cl	1.15	Cl	0.98	Cl	0.92			Cl	0.69	Cl	0.30
K	0.42	K	0.35	K	0.20			K	0.45	K	0.16
Ca	0.31	Ca	0.44	Ca	0.33					Ca	0.08
Fe	2.49	Fe	1.63	Fe	0.68			Fe	0.56	Fe	0.25
Cu	0.57										
Total	**100.00**	**Total**	**100.00**	**Total**	**100.00**			**Total**	**100.00**	**Total**	**100.00**

Table A.4: Oxides of the elements of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}	
Element	**Weight %**	**Element**	**Weight %**	**Element**	**Weight %**	**Element**	**Weight %**	**Element**	**Weight %**	**Element**	**Weight %**
C	25.68	C	25.76	C	26.07			C	26.28	C	11.84
										F	53.74
Na	0.17	Na	0.14							Na	0.07
Al	0.27	Al	0.44	Al	0.26			Al	0.40	Al	0.34
Si	0.47	Si	0.79	Si	0.46			Si	0.52	Si	0.55
S	0.47	S	0.35	S	0.71			S	0.37	S	0.19
Cl	0.56	Cl	0.48	Cl	0.45			Cl	0.33	Cl	0.15
K	0.21	K	0.17	K	0.10			K	0.21	K	0.08
Ca	0.15	Ca	0.21	Ca	0.16					Ca	0.04
Fe	1.21	Fe	0.79	Fe	0.33			Fe	0.26	Fe	0.13
Cu	0.32										
O	70.49	O	70.85	O	71.46			O	71.63	O	32.86
Total	**100.00**	**Total**	**100.00**	**Total**	**100.00**			**Total**	**100.00**	**Total**	**100.00**

A.2.2. 5 July 2006

Table A.5: Elemental composition of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
PM$_{2.5}$		PM$_{10}$		PM$_{2.5}$		PM$_{10}$		PM$_{2.5}$		PM$_{10}$	
Element	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**
C	91.60	C	46.11	C	93.32						
		O	47.58								
Na	0.60										
Al	0.42	Al	0.69								
Si	1.26	Si	1.97	Si	0.59						
S	1.43	S	1.42	S	1.23						
K	0.56	K	0.63								
		Ca	0.75								
		Fe	0.86								
				Mn	1.21						
Cu	4.14			Cu	3.65						
Total	**100.00**	**Total**	**100.00**	**Total**	**100.00**						

Table A.6: Oxides of the elements of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
PM$_{2.5}$		PM$_{10}$		PM$_{2.5}$		PM$_{10}$		PM$_{2.5}$		PM$_{10}$	
Element	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**
C	26.23	C	25.49	C	26.56						
Na	0.18										
Al	0.11	Al	0.39								
Si	0.31	Si	1.10	Si	0.13						
S	0.33	S	0.77	S	0.26						
K	0.13	K	0.34								
		Ca	0.40								
		Fe	0.46								
				Mn	0.25						
Cu	1.43			Cu	1.14						
O	71.28	O	71.04	O	71.66						
Total	**100.00**	**Total**	**100.00**	**Total**	**100.00**						

A.2.3. 6 July 2006

Table A.7: Elemental composition of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}	
Element	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**
				C	91.77	C	94.06			C	52.72
										O	42.39
										Al	0.88
						Si	1.27			Si	1.62
				S	1.60	S	1.58			S	1.03
				Cl	2.29	Cl	2.12				
				K	0.69	K	0.54			K	0.45
				Ca	0.34	Ca	0.43			Ca	0.42
										Fe	0.49
				Cu	3.31						
				Total	**100.00**	**Total**	**100.00**			**Total**	**100.00**

Table A.8: Oxides of the elements of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}	
Element	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**
				C	26.37	C	26.62			C	26.07
										Al	0.44
						Si	0.33			Si	0.78
				S	0.40	S	0.39			S	0.48
				Cl	0.56	Cl	0.50				
				K	0.17	K	0.13			K	0.21
				Ca	0.08	Ca	0.10			Ca	0.19
										Fe	0.23
				Cu	1.20						
				O	71.22	O	71.93			O	71.62
				Total	**100.00**	**Total**	**100.00**			**Total**	**100.00**

A.3. March 2007

A.3.1. 20 March 2007

Table A.9: Elemental composition of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}	
Element	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**
C	20.15	C	12.75	C	19.10	C	18.62	C	20.00	C	18.94
		O	2.15					O	1.22	O	5.08
F	78.59	F	71.87	F	80.90	F	80.75	F	77.64	F	72.22
		Al	0.37							Al	0.75
Si	0.24	Si	0.72					Si	0.22	Si	1.26
								S	0.17	S	0.30
Cl	0.13	Cl	0.22							Cl	0.28
K	0.13	K	0.27					K	0.20	K	0.40
										Ca	0.15
Fe	0.30									Fe	0.62
Mn	0.04	Mn	11.65								
Mo	0.43										
						Cu	0.63	Cu	0.55		
Total	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**

Table 4.10: Oxides of the elements of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}	
Element	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**
C	9.47	C	7.59	C	9.17	C	8.99	C	9.64	C	9.75
F	64.38	F	57.30	F	66.42	F	66.66	F	63.77	F	60.66
		Al	0.23							Al	0.41
Si	0.11	Si	0.45					Si	0.11	Si	0.68
								S	0.08	S	0.16
Cl	0.06	Cl	0.14							Cl	0.15
K	0.06	K	0.17					K	0.10	K	0.22
										Ca	0.08
Fe	0.14									Fe	0.34
Mn	0.02	Mn	10.19								
Mo	0.21										
						Cu	0.31	Cu	0.27		
O	25.53	O	23.94	O	24.42	O	24.03	O	26.03	O	27.54
Total	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**

A.3.2. 21 March 2007

Table A.11: Elemental composition of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}	
Element	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**
C	18.80	C	17.78	C	22.82	C	19.44	C	19.98	C	20.05
		O	2.49			O	3.47	O	1.38	O	4.20
F	80.75	F	76.84	F	76.73	F	73.66	F	77.39	F	71.97
		Na	0.22			Na	0.25			Na	0.20
		Al	0.47			Al	0.69	Al	0.10	Al	0.84
		Si	0.71	Si	0.13	Si	0.94	Si	0.22	Si	1.03
		S	0.16	S	0.15	S	0.32	S	0.16	S	0.22
		Cl	0.29	Cl	0.18	Cl	0.39	Cl	0.07	Cl	0.24
K	0.10	K	0.22			K	0.28	K	0.26	K	0.36
		Ca	0.39			Ca	0.15				
						Ti	0.11				
		Fe	0.44			Fe	0.29			Fe	0.49
Cu	0.35							Cu	0.43	Cu	0.39
Total	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**

Table A.12: Oxides of the elements of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}	
Element	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**
C	9.06	C	8.99	C	10.35	C	9.67	C	9.66	C	10.00
F	66.54	F	64.53	F	61.72	F	61.44	F	63.61	F	59.97
		Na	0.12			Na	0.13			Na	0.11
		Al	0.25			Al	0.37	Al	0.05	Al	0.44
		Si	0.38	Si	0.06	Si	0.49	Si	0.11	Si	0.54
		S	0.09	S	0.07	S	0.17	S	0.08	S	0.12
		Cl	0.15	Cl	0.08	Cl	0.20	Cl	0.03	Cl	0.13
K	0.05	K	0.11			K	0.15	K	0.13	K	0.19
		Ca	0.21			Ca	0.08				
						Ti	0.06				
		Fe	0.23			Fe	0.15			Fe	0.26
Cu	0.17							Cu	0.21	Cu	0.21
O	24.18	O	24.95	O	27.73	O	27.08	O	26.11	O	28.03
Total	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**

A.3.3. 22 March 2007

Table A.13: Elemental composition of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}	
Element	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**
C	19.14	C	16.38	C	19.69	C	18.62	C	20.59	C	19.74
O	2.16	O	4.47			O	2.88	O	1.89	O	5.41
F	77.83	F	74.26	F	79.44	F	76.31	F	76.33	F	71.50
		Na	0.27								
Mg	0.45	Mg	0.98								
		Al	0.55			Al	0.46			Al	0.86
		Si	0.83	Si	0.06	Si	0.83	Si	0.14	Si	0.99
S	0.23	S	0.28	S	0.07	S	0.31	S	0.28	S	0.41
		Cl	0.13								
K	0.19	K	0.31	K	0.09	K	0.23	K	0.19	K	0.43
		Ca	0.29							Ca	0.28
		Fe	0.65			Fe	0.35			Fe	0.37
		Cu	0.60	Cu	0.65			Cu	0.36		
								Br	0.20		
Total	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**

Table A.14: Oxides of the elements of the filters (in weight %).

Vanderbijlpark				Sasolburg				Vereeniging			
PM$_{2.5}$		PM$_{10}$		PM$_{2.5}$		PM$_{10}$		PM$_{2.5}$		PM$_{10}$	
Element	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**	**Element**	**Weight%**
C	9.51	C	8.72	C	9.33	C	9.32	C	9.96	C	10.13
F	64.36	F	63.55	F	65.23	F	63.67	F	62.55	F	59.56
		Na	0.16								
Mg	0.23	Mg	0.56								
		Al	0.31			Al	0.24			Al	0.46
		Si	0.47	Si	0.03	Si	0.43	Si	0.07	Si	0.53
S	0.12	S	0.16	S	0.03	S	0.16	S	0.14	S	0.22
		Cl	0.07								
K	0.10	K	0.17	K	0.04	K	0.12	K	0.09	K	0.23
		Ca	0.16							Ca	0.15
		Fe	0.37			Fe	0.18			Fe	0.20
		Cu	0.34	Cu	0.32			Cu	0.18		
								Br	0.10		
O	25.69	O	24.98	O	25.02	O	25.87	O	26.90	O	28.51
Total	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**	**Total**	**100.00**

Appendix B:
ICP-MS results

B.1. July 2006

B.1.1. 4 July 2006

Table B.1: Concentrations of elements in μg.m^{-3}

Mass	Vdb(10)	Ver(10)	Sas(10)	Vdb(2.5)	Ver(2.5)	Sas(2.5)
Li 7	0.0048	0.0043	0.0047	0.0032	0.0032	0.0037
Be 9		0.0003	0.0002			
B 11	0.0427	0.0329	0.0298	0.0132	0.0165	0.0179
Na 23	3.1680	2.8807	2.9787	2.0576	3.4294	4.2276
Mg 24	0.5923	0.4527	0.8794	0.4527	2.0576	2.6016
Al 27	0.4545	0.5350	0.5248	0.1111	0.2743	0.1350
K 39	1.3636	1.3717	1.2908	1.1385	1.5089	1.6260
Ca 43	1.3636	0.9877	1.4184	0.7682	1.5089	1.7886
Sc 45	0.0018	0.0018	0.0020	0.0013	0.0016	0.0016
Ti 47	0.0289	0.0192	0.0241	0.0070	0.0080	0.0073
V 51	0.0039	0.0045	0.0035	0.0011	0.0023	0.0018
Cr 53	0.0207	0.0219	0.0284	0.0107	0.0137	0.0211
Mn 55	0.1928	0.4252	0.2837	0.0809	0.2058	0.1366
Fe 57	3.8567	1.5089	1.8440	2.4691	1.0837	1.0732
Co 59	0.0021	0.0056	0.0021	0.0006	0.0023	0.0012
Ni 60	0.0124	0.0133	0.0184	0.0151	0.0316	0.0135
Cu 63	0.0785	0.0782	0.0695	0.0604	0.0782	0.1203
Zn 66	0.1928	0.2058	0.3972	0.1372	0.2058	0.3089
Ga 69	0.0044	0.0059	0.0054	0.0021	0.0030	0.0033
Ge 72	0.0047	0.0027	0.0038	0.0053	0.0023	0.0041
As 75	0.0138	0.0096	0.0088	0.0102	0.0091	0.0107
Se 82	0.0220	0.0206	0.0255	0.0086	0.0151	0.0163
Br 79	12.3967	8.6420	8.2270	1.7833	1.5089	1.2033
Rb 85	0.0036	0.0048	0.0038	0.0025	0.0049	0.0033
Sr 88	0.0275	0.0151	0.0468	0.0104	0.0106	0.0163
Y 89	0.0012	0.0016	0.0027	0.0003	0.0005	0.0008
Zr 90	0.0028	0.0027	0.0031	0.0027	0.0023	0.0023
Nb 93	0.0002	0.0001	0.0002		0.0001	
Mo 95	0.0045	0.0021	0.0020	0.0036	0.0015	0.0018

Ru 101	0.0036	0.0034	0.0024	0.0006	0.0012	0.0006
Rh 103	0.0003	0.0002	0.0003	0.0001	0.0002	
Pd 105	0.0003	0.0003	0.0018	0.0004	0.0040	0.0005
Ag 107	0.0018	0.0014	0.0028	0.0011	0.0033	0.0018
Cd 111	0.0019	0.0026	0.0026	0.0014	0.0055	0.0014
In 115	0.0001	0.0001	0.0004	0.0011	0.0004	0.0001
Sn 118	0.0275	0.0274	0.1121	0.3155	0.1372	0.0244
Sb 121	0.0152	0.0219	0.0156	0.0130	0.0233	0.0163
Te 125						
I 127	0.0120	0.0082	0.0094	0.0086	0.0096	0.0104
Cs 133	0.0002	0.0002	0.0006	0.0001	0.0002	0.0002
Ba 137	0.0386	0.0809	0.0496	0.0134	0.0343	0.0163
Ce 140	0.0030	0.0058	0.0135	0.0009	0.0026	0.0042
Hf 178			0.0002	0.0002	0.0002	0.0002
Ta 181						
W 182	0.0004	0.0006	0.0005	0.0002	0.0063	0.0005
Re 185						
Os 189		0.0004	0.0007	0.0004	0.0006	0.0003
Ir 193	0.0001	0.0001				0.0001
Pt 195	0.0029	0.0027	0.0026	0.0011	0.0016	0.0015
Au 197	0.0002	0.0007	0.0028	0.0003	0.0078	0.0004
Hg 202	0.0006	0.0004	0.0005	0.0001	0.0002	0.0006
Tl 205	0.0015	0.0011	0.0005	0.0002	0.0004	0.0003
Pb 208	0.1116	0.1303	0.1007	0.0892	0.1783	0.0959
Bi 209	0.0010	0.0009	0.0021	0.0008	0.0010	0.0020
U 238	0.0003	0.0003	0.0005	0.0001	0.0007	0.0003
Total:	24.0847	17.5469	18.4511	9.6057	12.4090	13.5262

B.1.2. 5 July 2006

Table B.2: Concentrations of elements in μg.m^{-3}

Mass	Vdb(10)	Ver(10)	Sas(10)	Vdb(2.5)	Ver(2.5)	Sas(2.5)
Li 7	0.0043	0.0048	0.0034	0.0029	0.0029	0.0025
Be 9	0.0003					
B 11	0.0294	0.0188	0.0138	0.0154	0.0126	0.0103
Na 23	3.3613	2.6087	2.5424	3.7815	1.6064	1.5537
Mg 24	1.5406	0.5072	0.4379	1.9608	0.2142	0.2119
Al 27	0.4762	0.4928	0.1412	0.1331	0.1205	0.0523
K 39	1.4006	1.5942	1.0876	1.3585	1.3387	1.0734
Ca 43	1.8207	1.1014	0.4944	1.5406	0.5087	0.4096
Sc 45	0.0017	0.0017	0.0014	0.0013	0.0013	0.0014
Ti 47	0.0308	0.0246	0.0088	0.0078	0.0055	0.0054
V 51	0.0028	0.0032	0.0017	0.0011	0.0012	0.0009
Cr 53	0.0350	0.0203	0.0129	0.0168	0.0102	0.0169
Mn 55	0.1289	0.5072	0.0353	0.0574	0.1245	0.0169
Fe 57	1.4006	1.4493	0.6780	0.9384	0.7497	0.7486
Co 59	0.0014	0.0032	0.0007	0.0005	0.0008	0.0003
Ni 60	0.0238	0.0126	0.0113	0.0137	0.0228	0.0184
Cu 63	0.1036	0.0812	0.0777	0.0742	0.0549	0.0508
Zn 66	0.1541	0.1087	0.0494	0.1148	0.0857	0.0297
Ga 69	0.0028	0.0043	0.0009	0.0014	0.0019	0.0006
Ge 72	0.0029	0.0022	0.0024	0.0025	0.0019	0.0017
As 75	0.0050	0.0064	0.0020	0.0041	0.0040	0.0020
Se 82	0.0182	0.0174	0.0141	0.0098	0.0074	0.0089
Br 79	3.0812	3.1884	1.4124	0.9524	1.3387	0.7627
Rb 85	0.0035	0.0051	0.0014	0.0022	0.0037	0.0010
Sr 88	0.0224	0.0159	0.0049	0.0095	0.0044	0.0027
Y 89	0.0013	0.0014	0.0005	0.0003	0.0003	0.0002
Zr 90	0.0032	0.0030	0.0021	0.0015	0.0020	0.0011
Nb 93	0.0002	0.0001	0.0001	0.0002		
Mo 95	0.0073	0.0017	0.0013	0.0056	0.0008	0.0014
Ru 101	0.0022	0.0019	0.0014	0.0007	0.0004	0.0006
Rh 103	0.0002	0.0002	0.0002	0.0003	0.0001	0.0001
Pd 105	0.0002		0.0004			0.0007
Ag 107	0.0097	0.0014	0.0014	0.0017	0.0012	0.0024
Cd 111	0.0009	0.0016		0.0011	0.0013	
In 115	0.0010	0.0004	0.0002	0.0003	0.0004	0.0001
Sn 118	0.2241	0.1043	0.0466	0.0700	0.1004	0.0141
Sb 121	0.0045	0.0055	0.0016	0.0035	0.0050	0.0014
Te 125						
I 127	0.0073	0.0106	0.0066	0.0064	0.0088	0.0073

Cs 133	0.0002	0.0003	0.0001	0.0001	0.0002	
Ba 137	0.0350	0.0580	0.0123	0.0102	0.0174	0.0052
Ce 140	0.0028	0.0048	0.0016	0.0007	0.0013	0.0005
Hf 178					0.0001	
Ta 181						
W 182	0.0002	0.0003	0.0001	0.0002	0.0006	0.0002
Re 185						
Os 189	0.0004	0.0003	0.0003	0.0002	0.0003	
Ir 193			0.0001	0.0001		
Pt 195	0.0020	0.0019	0.0014	0.0009	0.0007	0.0008
Au 197	0.0003	0.0004	0.0004	0.0002	0.0004	0.0003
Hg 202	0.0004	0.0002	0.0002	0.0002	0.0003	0.0012
Tl 205	0.0003	0.0004	0.0002	0.0001	0.0001	0.0004
Pb 208	0.0602	0.0464	0.0130	0.0434	0.0428	0.0106
Bi 209	0.0005	0.0011	0.0002	0.0004	0.0010	0.0009
U 238	0.0002	0.0002	0.0002	0.0002	0.0002	0.0001
Total:	14.0168	12.0262	7.1283	11.1494	6.4088	5.0324

B.1.3. 6 July 2006

Table B.3: Concentrations of elements in µg.m^{-3}

Mass	Vdb(10)	Ver(10)	Sas(10)	Vdb(2.5)	Ver(2.5)	Sas(2.5)
Li 7	0.0040	0.0038	0.0026	0.0029	0.0027	0.0025
Be 9						
B 11	0.0143	0.0149	0.0114	0.0112	0.0115	0.0093
Na 23	2.2890	2.8529	2.5105	1.8678	1.6442	2.5105
Mg 24	2.8612	0.7658	0.5021	1.5805	0.2541	0.6695
Al 27	0.3577	0.2402	0.1395	0.0934	0.0852	0.0921
K 39	1.1731	1.3213	1.1158	1.0057	1.2855	1.0460
Ca 43	1.3019	1.0811	0.7531	0.5460	0.5979	0.7252
Sc 45	0.0016	0.0015	0.0014	0.0014	0.0015	0.0014
Ti 47	0.0243	0.0113	0.0077	0.0080	0.0049	0.0053
V 51	0.0017	0.0018	0.0013	0.0009	0.0010	0.0008
Cr 53	0.0123	0.0096	0.0126	0.0172	0.0148	0.0138
Mn 55	0.1087	0.1216	0.0335	0.0402	0.0628	0.0167
Fe 57	0.9728	1.0511	0.7252	0.6753	0.7175	0.6276
Co 59	0.0012	0.0015	0.0007	0.0004	0.0007	0.0004
Ni 60	0.0134	0.0092	0.0100	0.0098	0.0075	0.0139
Cu 63	0.0486	0.0601	0.0642	0.0733	0.0538	0.0628
Zn 66	0.0815	0.0871	0.0321	0.0603	0.0912	0.0404
Ga 69	0.0044	0.0021	0.0011	0.0032	0.0014	0.0005
Ge 72	0.0021	0.0018	0.0022	0.0029	0.0030	0.0024
As 75	0.0033	0.0030	0.0018	0.0020	0.0019	0.0012
Se 82	0.0157	0.0150	0.0109	0.0144	0.0082	0.0098
Br 79	1.4306	1.3964	1.0321	0.7759	0.8670	0.8089
Rb 85	0.0019	0.0030	0.0017	0.0014	0.0024	0.0013
Sr 88	0.0186	0.0120	0.0066	0.0080	0.0045	0.0036
Y 89	0.0010	0.0008	0.0005	0.0002	0.0003	0.0002
Zr 90	0.0021	0.0027	0.0015	0.0012	0.0016	0.0013
Nb 93	0.0001	0.0001	0.0001		0.0001	
Mo 95	0.0039	0.0011	0.0026	0.0032	0.0010	0.0544
Ru 101	0.0009	0.0007	0.0009	0.0006	0.0004	0.0006
Rh 103	0.0002	0.0001	0.0002		0.0001	0.0001
Pd 105		0.0002			0.0004	0.0003
Ag 107	0.0016	0.0015	0.0009	0.0012	0.0022	0.0009
Cd 111	0.0008	0.0009		0.0006	0.0008	
In 115	0.0001	0.0008	0.0003	0.0001	0.0005	0.0001
Sn 118	0.0186	0.1952	0.0948	0.0560	0.1211	0.0251
Sb 121	0.0027	0.0042	0.0009	0.0029	0.0034	0.0009
Te 125						
I 127	0.0062	0.0089	0.0064	0.0075	0.0109	0.0049

Cs 133	0.0002	0.0002		0.0001	0.0002	
Ba 137	0.0672	0.0375	0.0123	0.0402	0.0138	0.0053
Ce 140	0.0029	0.0026	0.0013	0.0007	0.0009	0.0006
Hf 178						
Ta 181						
W 182	0.0002	0.0002	0.0002		0.0002	0.0002
Re 185						
Os 189	0.0002		0.0004	0.0002		0.0002
Ir 193		0.0001				
Pt 195	0.0014	0.0013	0.0011	0.0012	0.0009	0.0007
Au 197	0.0004	0.0002	0.0002	0.0003	0.0001	0.0003
Hg 202	0.0005	0.0004	0.0003	0.0005	0.0006	0.0004
Tl 205	0.0002	0.0002	0.0001	0.0001	0.0002	0.0001
Pb 208	0.0315	0.0465	0.0098	0.0244	0.0478	0.0067
Bi 209	0.0008	0.0006	0.0003	0.0004	0.0008	0.0007
U 238	0.0001	0.0001	0.0001		0.0001	0.0001
Total:	10.8878	9.3749	7.1152	6.9437	5.9337	6.7700

B.2. March 2007

B.2.1. 20 March 2007

Table B.4: Concentrations of elements in $\mu g.m^{-3}$

Mass	Vdb(10)	Sas(10)	Ver(10)	Vdb(2.5)	Sas(2.5)	Ver(2.5)
Li 7	0.0000		0.0000	0.0000		0.0000
Be 9						
B 11	0.0159		0.0148	0.0105		0.0099
Na 23	0.0654		0.0279	0.0317		0.0246
Mg 24	0.0383		0.0102	0.0317		0.0084
Al 27	0.1228		0.0870	0.1349		0.1527
Si 29	0.7656		0.7882	0.7460		0.7882
K 39	0.0638		0.0706	0.0508		0.0558
Ca 43	0.0431		0.0197	0.0349		0.0328
Sc 45	0.0002		0.0002	0.0002		0.0002
Ti 47	0.0006		0.0001	0.0002		0.0001
V 51	0.0015		0.0013	0.0008		0.0009
Cr 53	0.0925		0.0870	0.0810		0.0870
Mn 55	0.0255		0.0361	0.0127		0.0135
Fe 57	1.0526		0.9852	0.8095		0.8374
Co 59	0.0009		0.0010	0.0014		0.0026
Ni 60	0.0766		0.0755	0.0651		0.0706
Cu 63	0.0191		0.0213	0.0159		0.0128
Zn 66	0.0287		0.0230	0.0190		0.0123
Ga 69	0.0000		0.0000	0.0000		0.0000
Ge 72	0.0009		0.0009	0.0008		0.0007
As 75	0.0016		0.0012	0.0012		0.0009
Se 82	0.0070					
Br 79	0.0009		0.0020	0.0012		0.0009
Rb 85	0.0000		0.0001	0.0000		0.0000
Sr 88	0.0002		0.0001	0.0001		0.0002
Y 89	0.0000		0.0000	0.0001		0.0000
Zr 90	0.0001		0.0000	0.0000		0.0000
Nb 93			0.0000			
Mo 95	0.0002		0.0001	0.0002		0.0001
Ru 101	0.0000		0.0000			
Rh 103	0.0000		0.0000	0.0000		0.0000
Pd 105	0.0000		0.0000	0.0000		0.0000
Ag 107	0.0000		0.0000	0.0000		0.0000
Cd 111						
In 115						
Sn 118	0.0001		0.0002	0.0001		0.0005

Sb 121	0.0000		0.0001	0.0000		0.0000
Te 125						
I 127	0.0002		0.0003	0.0001		0.0001
Cs 133						
Ba 137	0.0040		0.0057	0.0022		0.0026
Ce 140	0.0000		0.0001	0.0001		0.0001
Hf 178						
Ta 181						
W 182						
Re 185						
Os 189						
Ir 193						
Pt 195	0.0000		0.0000	0.0000		0.0000
Au 197	0.0000		0.0000	0.0000		0.0000
Hg 202	0.0000		0.0000	0.0000		0.0000
Tl 205	0.0012		0.0010	0.0003		0.0003
Pb 208	0.0065		0.0074	0.0051		0.0025
Bi 209	0.0000		0.0000	0.0000		0.0000
U 238	0.0000		0.0000			
Total:	2.4364		2.2687	2.0582		2.1189

B.2.2. 21 March 2007

Table B.5: Concentrations of elements in $\mu g.m^{-3}$

Mass	Vdb(10)	Sas(10)	Ver(10)	Vdb(2.5)	Sas(2.5)	Ver(2.5)
Li 7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Be 9						
B 11	0.0123	0.0113	0.0116	0.0089	0.0084	0.0088
Na 23	0.0251	0.0383	0.0265	0.0209	0.0442	0.0349
Mg 24	0.0167	0.0199	0.0126	0.0042	0.0442	0.0432
Al 27	0.1381	0.0624	0.0976	0.0349	0.0997	1.0181
Si 29	0.6695	0.6809	0.6974	0.6834	0.7123	0.7113
K 39	0.0530	0.0582	0.0600	0.0502	0.0499	0.0474
Ca 43	0.0363	0.0298	0.0209	0.0195	0.0541	0.2650
Sc 45	0.0001	0.0001	0.0001	0.0002	0.0002	0.0002
Ti 47	0.0002	0.0003	0.0002	0.0001	0.0001	0.0001
V 51	0.0011	0.0012	0.0010	0.0009	0.0009	0.0009
Cr 53	0.0767	0.0837	0.0795	0.0697	0.0798	0.0767
Mn 55	0.0321	0.0298	0.0293	0.0139	0.0157	0.0124
Fe 57	0.8647	0.9078	0.8089	0.7113	0.7835	0.9205
Co 59	0.0007	0.0006	0.0006	0.0005	0.0006	0.0006
Ni 60	0.0614	0.0638	0.0628	0.0586	0.0570	0.0572
Cu 63	0.0195	0.0298	0.0071	0.0106	0.0199	0.0377
Zn 66	0.0377	0.0738	0.0279	0.0293	0.0584	0.0153
Ga 69	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001
Ge 72	0.0007	0.0006	0.0007	0.0007	0.0007	0.0007
As 75	0.0014	0.0008	0.0009	0.0012	0.0008	0.0010
Se 82						
Br 79	0.0010	0.0010	0.0013	0.0013	0.0011	0.0009
Rb 85	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000
Sr 88	0.0002	0.0002	0.0001	0.0001	0.0003	0.0015
Y 89	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
Zr 90	0.0000	0.0000	0.0015	0.0001	0.0000	0.0003
Nb 93			0.0000	0.0000	0.0000	0.0000
Mo 95	0.0000	0.0000	0.0001	0.0001	0.0001	0.0001
Ru 101	0.0000		0.0000			
Rh 103	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Pd 105	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000
Ag 107		0.0000	0.0000	0.0000	0.0000	0.0001
Cd 111		0.0004				
In 115						
Sn 118	0.0001	0.0001	0.0001	0.0003	0.0001	0.0003
Sb 121	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000
Te 125						
I 127	0.0001	0.0002	0.0001	0.0001	0.0001	0.0004

Cs 133		0.0000	0.0000			
Ba 137	0.0025	0.0041	0.0046	0.0014	0.0034	0.0181
Ce 140	0.0002	0.0001	0.0002	0.0000	0.0000	0.0000
Hf 178			0.0001			0.0000
Ta 181						
W 182						
Re 185						
Os 189						
Ir 193						
Pt 195	0.0000	0.0000	0.0001	0.0000	0.0001	0.0000
Au 197	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Hg 202		0.0000	0.0000	0.0000	0.0000	0.0000
Tl 205	0.0008	0.0005	0.0007	0.0003	0.0004	0.0003
Pb 208	0.0102	0.0142	0.0091	0.0084	0.0105	0.0045
Bi 209	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
U 238		0.0000				0.0000
Total:	2.0627	2.1143	1.9639	1.7315	2.0464	3.2787

B.2.3. 22 March 2007

Table B.6: Concentrations of elements in µg.m^{-3}

Mass	Vdb(10)	Sas(10)	Ver(10)	Vdb(2.5)	Sas(2.5)	Ver(2.5)
Li 7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Be 9					0.0001	
B 11	0.0106	0.0108	0.0097	0.0089	0.0087	0.0099
Na 23	0.0708	0.0366	0.0278	0.0236	0.0190	0.0335
Mg 24	0.2222	0.1341	0.0106	0.0347	0.0054	0.0307
Al 27	1.1528	1.6260	0.0903	0.1347	0.0789	0.0139
Si 29	0.6944	0.6775	0.6806	0.6667	0.6667	0.6695
K 39	0.0583	0.0515	0.0583	0.0514	0.0476	0.0488
Ca 43	1.0694	1.3415	0.0181	0.0417	0.0109	0.0279
Sc 45	0.0007	0.0005	0.0001	0.0002	0.0001	0.0002
Ti 47	0.0017	0.0009	0.0002	0.0001	0.0001	0.0002
V 51	0.0071	0.0011	0.0011	0.0011	0.0008	0.0008
Cr 53	0.0819	0.0732	0.0750	0.0736	0.0721	0.0795
Mn 55	0.0236	0.0149	0.0333	0.0125	0.0093	0.0120
Fe 57	1.6667	1.4905	0.7917	0.7500	0.6939	0.6974
Co 59	0.0009	0.0007	0.0007	0.0006	0.0005	0.0005
Ni 60	0.0653	0.0596	0.0625	0.0583	0.0558	0.0586
Cu 63	0.0597	0.0434	0.0135	0.0126	0.0105	0.0251
Zn 66	0.0333	0.0125	0.0208	0.0222	0.0091	0.0137
Ga 69	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000
Ge 72	0.0008	0.0006	0.0007	0.0007	0.0006	0.0007
As 75	0.0013	0.0015	0.0005	0.0006	0.0007	
Se 82	0.0082				0.0060	
Br 79	0.0009	0.0011	0.0006	0.0008	0.0007	0.0011
Rb 85	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sr 88	0.0031	0.0028	0.0001	0.0001	0.0000	0.0001
Y 89	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000
Zr 90	0.0014	0.0011	0.0000	0.0000	0.0000	0.0000
Nb 93	0.0000					0.0000
Mo 95	0.0002	0.0001	0.0000	0.0001	0.0000	0.0001
Ru 101		0.0000				
Rh 103	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Pd 105	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ag 107	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
Cd 111						
In 115						
Sn 118	0.0001	0.0000	0.0001	0.0001	0.0004	0.0003
Sb 121	0.0005	0.0000	0.0000	0.0001	0.0000	0.0000
Te 125						
I 127	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001

Cs 133	0.0000		0.0000	0.0000		
Ba 137	0.0292	0.0312	0.0038	0.0050	0.0010	0.0014
Ce 140	0.0004	0.0001	0.0000	0.0002	0.0001	0.0000
Hf 178	0.0001	0.0000				0.0000
Ta 181						
W 182				0.0000		
Re 185						
Os 189						
Ir 193						
Pt 195	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Au 197	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Hg 202	0.0000	0.0000		0.0000	0.0000	0.0000
Tl 205	0.0006	0.0005	0.0005	0.0004	0.0003	0.0002
Pb 208	0.0108	0.0056	0.0060	0.0044	0.0018	0.0038
Bi 209	0.0000	0.0000	0.0000	0.0000		
U 238	0.0000	0.0000	0.0000	0.0000		0.0000
Total:	5.2775	5.6204	1.9069	1.9059	1.7014	1.7298

B.3. August 2007

Table B.7: Concentrations of elements in μg.m^{-3}

MASS	Day1 2.5	Day2 2.5	Day3 2.5	Day1 10	Day2 10	Day3 10
Li 7	0.0000	0.0000	0.0000		0.0000	0.0000
Be 9						
B 11	0.0017	0.0000	0.0022	0.0011	0.0029	0.0083
Na 23	0.0033	0.0014	0.0264	0.0021	0.0216	0.0417
Mg 24	0.0002	0.0001	0.0014	0.0001	0.0006	0.0038
Al 27	0.0002	0.0001	0.0269	0.0000	0.0131	0.0264
Si 29	0.0000	0.0000	0.0000	0.0000	0.0000	1.8056
K 39	0.0000	0.0014	0.0014	0.0007	0.0007	0.0569
Ca 43	0.0040	0.0000	0.0049	0.0016	0.0031	0.0065
Sc 45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002
Ti 47	0.0001	0.0000	0.0000	0.0000	0.0000	0.0002
V 51	0.0000	0.0000	0.0002	0.0000	0.0002	0.0005
Cr 53	0.0017	0.0001	0.0006	0.0006	0.0011	0.0026
Mn 55	0.0007	0.0000	0.0024	0.0004	0.0013	0.0069
Fe 57	0.0000	0.0000	0.0278	0.0000	0.0000	0.2917
Co 59		0.0001	0.0002		0.0001	0.0001
Ni 60	0.0033	0.0000	0.0167	0.0007	0.0063	0.0264
Cu 63	0.0005	0.0000	0.0027	0.0002	0.0008	0.0032
Zn 66	0.0000	0.0001	0.0028	0.0000	0.0003	0.0049
Ga 69				0.0000		0.0000
Ge 72	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001
As 75			0.0001	0.0007		0.0006
Se 82	0.0000	0.0050	-0.0061	0.0077	0.0049	0.0133
Br 79	0.0003	0.0000	0.0000	-0.0001	0.0001	0.0011
Rb 85						
Sr 88	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Y 89						
Zr 90			0.0004		0.0002	0.0004
Nb 93						
Mo 95						
Ru 101			0.0000			
Rh 103			0.0000			
Pd 105					0.0000	0.0000
Ag 107			0.0000			
Cd 111						
In 115						
Sn 118			0.0000		0.0000	
Sb 121						
Te 125						
I 127	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001

Cs 133						
Ba 137						0.0003
Ce 140			0.0000		0.0000	0.0000
Hf 178			0.0000		0.0000	0.0000
Ta 181						
W 182						
Re 185						
Os 189						
Ir 193						
Pt 195			0.0000	0.0000	0.0000	0.0000
Au 197						
Hg 202	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Tl 205			0.0001		0.0001	0.0001
Pb 208	0.0001	0.0000	0.0002	0.0000	0.0001	0.0002
Bi 209						
U 238			0.0000		0.0000	
Total:	0.0162	0.0083	0.1113	0.0159	0.0575	2.3023

Appendix C:
Meteorological data

C.1. July 2006

Date& Hour	WD Deg	WS m/s	T Deg C	RH %
4/7/06 01:00	171.65	0.80	4.60	59.50
4/7/06 02:00	152.97	0.66	3.12	67.76
4/7/06 03:00	32.48	0.20	2.20	73.17
4/7/06 04:00	85.44	0.24	1.89	71.70
4/7/06 05:00	212.83	0.87	1.01	77.75
4/7/06 06:00	183.54	0.69	0.32	83.16
4/7/06 07:00	146.06	0.60	0.24	84.51
4/7/06 08:00	293.84	0.50	2.33	80.01
4/7/06 09:00	189.08	0.43	7.91	62.34
4/7/06 10:00	126.34	1.50	12.33	42.62
4/7/06 11:00	152.52	2.33	14.49	32.11
4/7/06 12:00	168.39	3.23	15.74	27.56
4/7/06 13:00	167.77	2.75	17.31	23.01
4/7/06 14:00	186.36	2.63	17.87	20.41
4/7/06 15:00	226.61	1.49	18.39	18.44
4/7/06 16:00	270.82	2.07	18.30	18.06
4/7/06 17:00	273.07	2.38	17.46	18.70
4/7/06 18:00	251.84	1.99	15.09	22.56
4/7/06 19:00	205.58	1.71	14.35	24.07
4/7/06 20:00	200.35	1.68	13.62	25.91
4/7/06 21:00	197.75	1.69	10.60	31.88
4/7/06 22:00	115.69	1.10	8.53	38.51
4/7/06 23:00	124.40	0.46	6.29	44.25
4/7/06 24:00	224.71	0.13	6.80	41.97
5/7/06 01:00	53.59	1.16	5.60	46.78
5/7/06 02:00	75.07	0.98	2.88	59.81
5/7/06 03:00	219.49	1.37	1.50	66.81
5/7/06 04:00	178.02	0.84	2.27	62.40
5/7/06 05:00	64.88	2.38	1.18	69.50
5/7/06 06:00	60.06	1.75	1.71	64.65
5/7/06 07:00	79.37	1.66	1.38	64.56
5/7/06 08:00	75.01	1.68	2.35	63.13
5/7/06 09:00	65.11	1.71	5.32	58.75
5/7/06 10:00	121.81	1.33	10.59	43.55
5/7/06 11:00	295.78	2.76	14.91	29.61

5/7/06 12:00	297.16	3.97	16.89	25.26
5/7/06 13:00	280.39	4.91	18.46	23.28
5/7/06 14:00	274.66	4.69	19.06	21.95
5/7/06 15:00	277.89	4.56	19.59	21.01
5/7/06 16:00	282.96	4.09	19.65	20.88
5/7/06 17:00	291.50	3.75	18.42	21.29
5/7/06 18:00	295.31	2.29	16.41	23.88
5/7/06 19:00	284.30	2.57	15.34	26.09
5/7/06 20:00	297.60	2.63	13.64	29.55
5/7/06 21:00	327.30	3.91	8.29	44.86
5/7/06 22:00	326.28	3.58	6.20	54.05
5/7/06 23:00	310.23	3.24	6.39	53.77
5/7/06 24:00	294.36	3.16	6.08	56.01
6/7/06 01:00	316.84	2.94	5.57	58.44
6/7/06 02:00	316.58	3.31	4.22	63.04
6/7/06 03:00	310.55	2.99	4.82	61.18
6/7/06 04:00	302.05	3.34	3.45	66.79
6/7/06 05:00	299.15	3.10	3.60	65.87
6/7/06 06:00	300.73	3.10	3.50	66.93
6/7/06 07:00	295.69	3.74	4.43	64.01
6/7/06 08:00	304.23	3.25	5.53	64.91
6/7/06 09:00	329.80	2.68	8.75	59.56
6/7/06 10:00	299.16	4.42	13.64	37.42
6/7/06 11:00	298.07	4.79	17.14	29.07
6/7/06 12:00	280.97	4.94	19.81	21.97
6/7/06 13:00	258.61	4.65	21.02	19.37
6/7/06 14:00	256.55	4.54	21.32	18.12
6/7/06 15:00	273.78	4.05	22.00	17.07
6/7/06 16:00	282.19	4.60	21.49	17.20
6/7/06 17:00	280.48	4.64	20.70	17.87
6/7/06 18:00	290.41	2.54	18.38	21.17
6/7/06 19:00	281.88	2.70	15.95	27.02
6/7/06 20:00	281.32	2.92	13.54	29.39
6/7/06 21:00	274.51	3.38	13.11	31.60
6/7/06 22:00	301.98	3.50	9.41	38.77
6/7/06 23:00	295.93	3.31	9.48	39.06
6/7/06 24:00	315.83	3.29	6.45	49.60

C.2. March 2007

Date& Hour	WD Deg	WS m/s	T Deg C	RH %
20/3/07 01:00	196.00	2.81	14.28	34.05
20/3/07 02:00	89.00	1.45	10.94	42.57
20/3/07 03:00	231.00	0.84	10.89	44.30
20/3/07 04:00	224.00	0.75	12.03	41.76
20/3/07 05:00	264.00	1.47	11.32	45.99
20/3/07 06:00	184.00	1.52	11.13	47.26
20/3/07 07:00	159.00	1.14	9.90	51.97
20/3/07 08:00	71.00	1.41	11.15	55.58
20/3/07 09:00	19.00	0.76	16.50	41.10
20/3/07 10:00	295.00	1.91	20.60	28.01
20/3/07 11:00	287.00	2.65	22.82	20.65
20/3/07 12:00	299.00	4.27	24.66	16.84
20/3/07 13:00	304.00	3.99	25.72	13.97
20/3/07 14:00	293.00	4.36	26.59	12.69
20/3/07 15:00	280.00	4.91	27.65	11.40
20/3/07 16:00	252.00	5.55	28.13	11.17
20/3/07 17:00	256.00	5.59	27.70	11.69
20/3/07 18:00	250.00	4.89	26.49	12.91
20/3/07 19:00	225.00	4.60	24.05	14.99
20/3/07 20:00	222.00	3.77	22.62	17.44
20/3/07 21:00	226.00	3.88	21.80	19.28
20/3/07 22:00	225.00	3.59	21.31	20.14
20/3/07 23:00	230.00	2.35	18.60	25.52
20/3/07 24:00	311.00	1.27	15.40	31.92
21/3/07 01:00	318.00	2.06	14.86	32.95
21/3/07 02:00	312.00	1.83	15.73	32.07
21/3/07 03:00	303.00	1.90	14.90	33.41
21/3/07 04:00	76.00	1.27	12.54	44.43
21/3/07 05:00	20.00	0.82	11.89	49.07
21/3/07 06:00	31.00	0.83	11.57	50.43
21/3/07 07:00	46.00	0.79	10.34	54.64
21/3/07 08:00	50.00	0.99	15.57	41.60
21/3/07 09:00	70.00	1.54	21.18	25.96
21/3/07 10:00	34.00	1.75	25.17	18.14
21/3/07 11:00	261.00	2.23	27.51	14.67
21/3/07 12:00	263.00	3.74	28.75	13.21
21/3/07 13:00	229.00	4.73	29.91	12.47
21/3/07 14:00	229.00	5.13	30.31	12.35
21/3/07 15:00	232.00	5.20	31.19	12.04
21/3/07 16:00	237.00	5.92	31.18	12.57
21/3/07 17:00	233.00	5.56	30.71	12.93
21/3/07 18:00	221.00	4.31	29.63	13.74
21/3/07 19:00	201.00	2.84	26.83	16.80
21/3/07 20:00	189.00	2.00	25.25	19.15

21/3/07 21:00	173.00	1.67	23.87	20.70
21/3/07 22:00	85.00	1.05	21.75	24.04
21/3/07 23:00	60.00	1.79	19.17	28.47
21/3/07 24:00	27.00	0.63	18.42	33.13
22/3/07 01:00	45.00	1.33	17.39	35.28
22/3/07 02:00	56.00	2.20	16.79	39.86
22/3/07 03:00	44.00	1.75	15.09	45.44
22/3/07 04:00	92.00	2.12	16.31	43.94
22/3/07 05:00	95.00	2.69	16.15	47.25
22/3/07 06:00	78.00	3.23	15.57	52.57
22/3/07 07:00	80.00	2.18	15.72	47.15
22/3/07 08:00	68.00	2.38	18.77	34.29
22/3/07 09:00	36.00	3.77	21.96	32.43
22/3/07 10:00	9.00	6.63	26.17	28.77
22/3/07 11:00	357.00	7.52	28.83	21.11
22/3/07 12:00	341.00	8.26	30.49	17.46
22/3/07 13:00	325.00	9.03	31.69	14.79
22/3/07 14:00	331.00	9.73	31.92	14.84
22/3/07 15:00	329.00	8.23	32.02	14.64
22/3/07 16:00	313.00	8.13	31.75	14.42
22/3/07 17:00	313.00	6.16	30.79	16.89
22/3/07 18:00	314.00	4.75	29.33	19.72
22/3/07 19:00	331.00	2.17	26.70	24.16
22/3/07 20:00	343.00	1.90	26.72	26.35
22/3/07 21:00	343.00	1.94	25.64	29.63
22/3/07 22:00	290.00	2.74	25.34	32.29
22/3/07 23:00	255.00	5.55	25.03	30.64
22/3/07 24:00	220.00	5.60	23.72	36.04

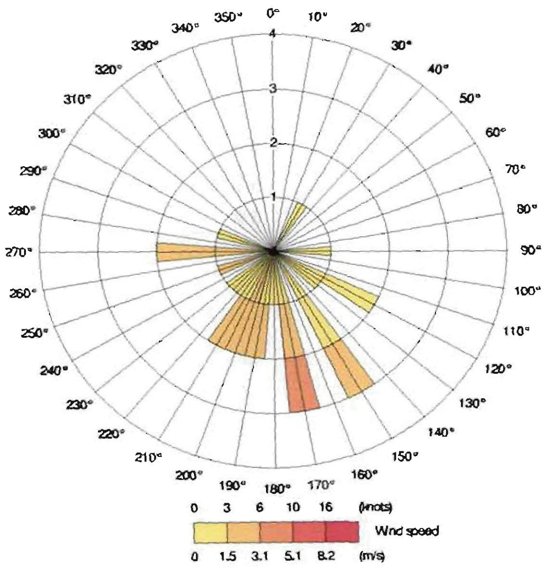
C.3. August 2007

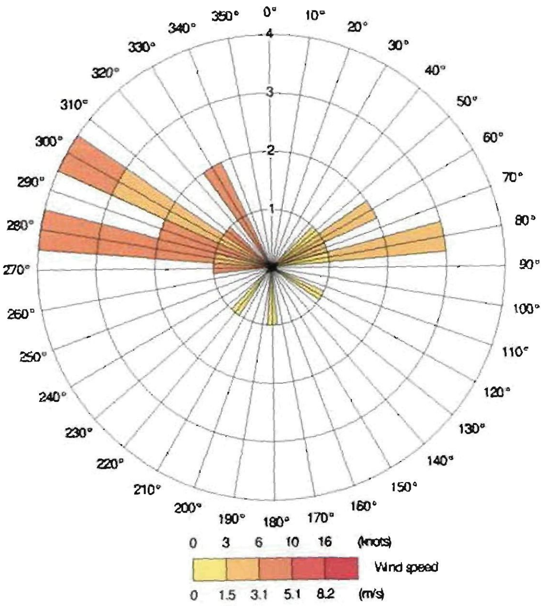
Date& Hour	WD Deg	WS m/s	T Deg C	RH %
6/8/07 01:00	85	13.9	9.9	85.6
6/8/07 02:00	73	6.4	9.1	90.2
6/8/07 03:00	92	6.7	9.5	88.3
6/8/07 04:00	93	9.5	9.2	87.9
6/8/07 05:00	78	9.4	8.7	89
6/8/07 06:00	95	10.3	8.9	86.5
6/8/07 07:00	79	7.8	8.7	86.5
6/8/07 08:00	69	9.1	8.9	86.8
6/8/07 09:00	76	10.6	9.8	82.8
6/8/07 10:00	82	8.2	11.3	76.2
6/8/07 11:00	100	7.1	13.2	67.8
6/8/07 12:00	88	3.9	14.3	62.2
6/8/07 13:00	73	6	15.8	56.2
6/8/07 14:00	69	12.8	17.2	50.8
6/8/07 15:00	31	7	17.7	47.2
6/8/07 16:00	71	10.8	17.5	48.9
6/8/07 17:00	66	5.7	16.7	50.9
6/8/07 18:00	49	6	15.3	54.5
6/8/07 19:00	82	5.1	14.2	57.8
6/8/07 20:00	80	5.9	12.3	65.3
6/8/07 21:00	93	6.2	12	68.6
6/8/07 22:00	89	6.6	10.9	74.5
6/8/07 23:00	103	4.8	10.3	78.6
6/8/07 24:00	78	5.9	9.3	83.2
8/8/07 01:00	167	3.8	3.3	43.6
8/8/07 02:00	167	2.3	3.1	46.2
8/8/07 03:00	158	3.2	2.3	48.9
8/8/07 04:00	151	1.6	2.4	49.6
8/8/07 05:00	143	3.2	3.6	50.7
8/8/07 06:00	148	3.4	3.5	54.1
8/8/07 07:00	130	2.3	2.9	58.3
8/8/07 08:00	99	3.9	6.4	55.8
8/8/07 09:00	109	11.1	10.1	58.8
8/8/07 10:00	68	8.9	12.5	56.8
8/8/07 11:00	76	10	14.3	54.7
8/8/07 12:00	89	9.2	15.3	48.3
8/8/07 13:00	80	8.3	16.2	45.6
8/8/07 14:00	80	8.8	17.3	43.2
8/8/07 15:00	79	5.5	17.2	44
8/8/07 16:00	107	4.6	17.5	43
8/8/07 17:00	66	4.9	16.7	44.4
8/8/07 18:00	80	2.8	14.9	47.9
8/8/07 19:00	97	2.4	12.9	53.8
8/8/07 20:00	75	1.6	11.4	57.7

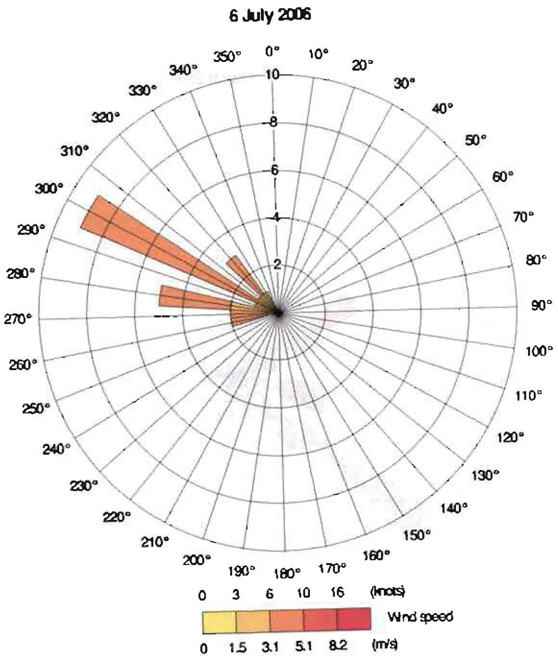
8/8/07 21:00	92	0.7	10.8	59.7
8/8/07 22:00	99	1.2	10.1	62.3
8/8/07 23:00	97	0.9	9.3	67
8/8/07 24:00	130	1.1	8	72.7
10/8/07 01:00	143	0	9.2	60.8
10/8/07 02:00	147	1.1	8.1	63.2
10/8/07 03:00	171	0	8.4	62.1
10/8/07 04:00	160	0.6	7.2	65.3
10/8/07 05:00	150	1.5	5	73.6
10/8/07 06:00	151	1.8	5.7	70.9
10/8/07 07:00	144	0.5	6.3	69.2
10/8/07 08:00	110	1.1	11.7	54.2
10/8/07 09:00	0	3.5	14.2	44
10/8/07 10:00	25	7.1	15.2	39.4
10/8/07 11:00	82	5	15.9	37
10/8/07 12:00	71	6.4	17.2	32.3
10/8/07 13:00	99	2.9	18.4	29.5
10/8/07 14:00	38	6.4	19.1	21.5
10/8/07 15:00	58	4.2	19.4	20.9
10/8/07 16:00	82	3.9	19.4	20.8
10/8/07 17:00	35	5	18.7	21.9
10/8/07 18:00	86	1.5	15.9	26.1
10/8/07 19:00	93	1.1	12.3	32.6
10/8/07 20:00	120	1.3	11.4	36
10/8/07 21:00	116	1.8	11.2	37.7
10/8/07 22:00	114	1.5	11.1	38.5
10/8/07 23:00	133	1.2	10.6	38.9
10/8/07 24:00	138	1.8	9.3	42

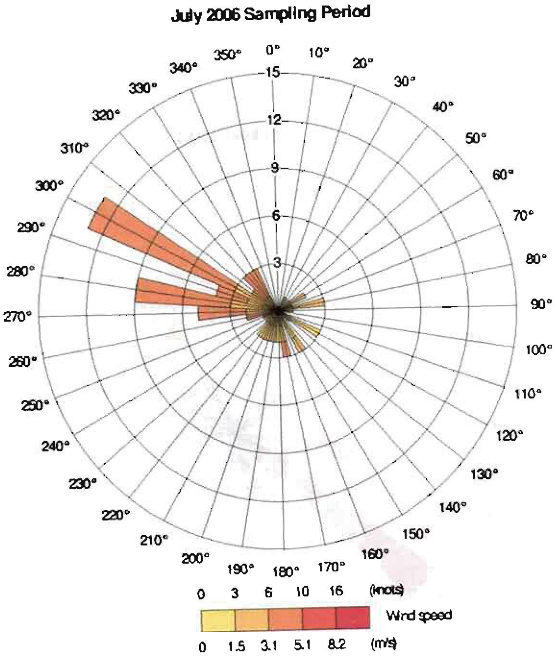
Appendix D:
Wind roses

D.1. Wind roses for July 2006


4 July 2006

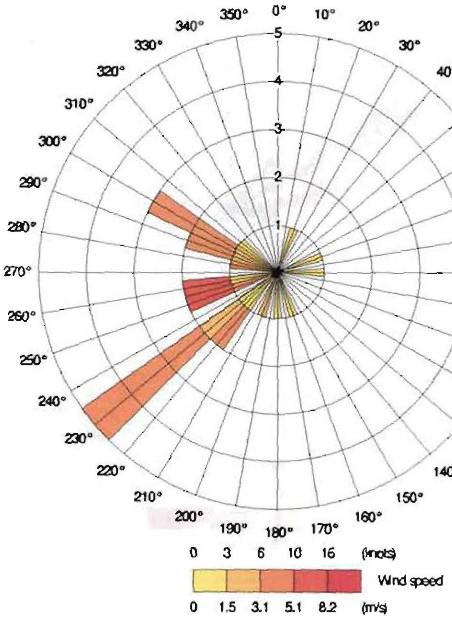

5 July 2006


6 July 2006

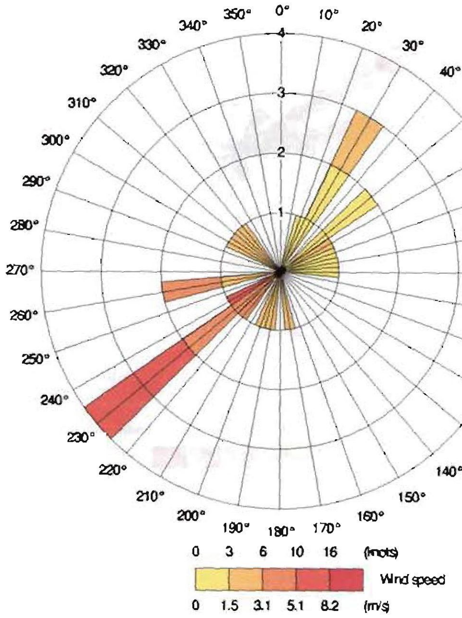

July 2006 Sampling Period

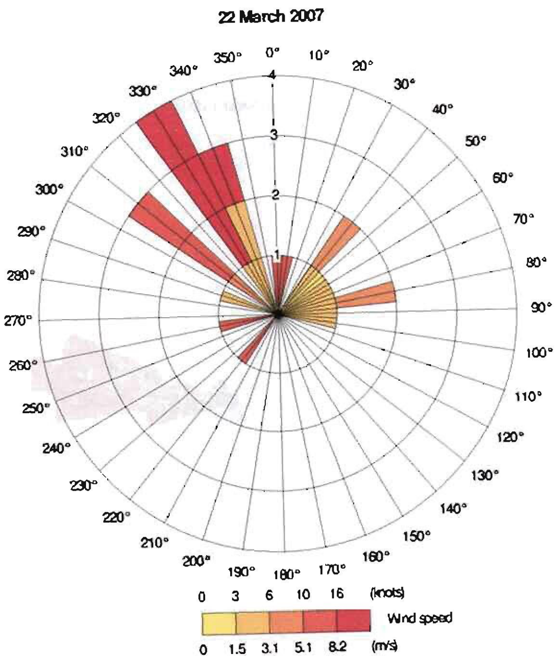
D.2. Wind roses for March 2007

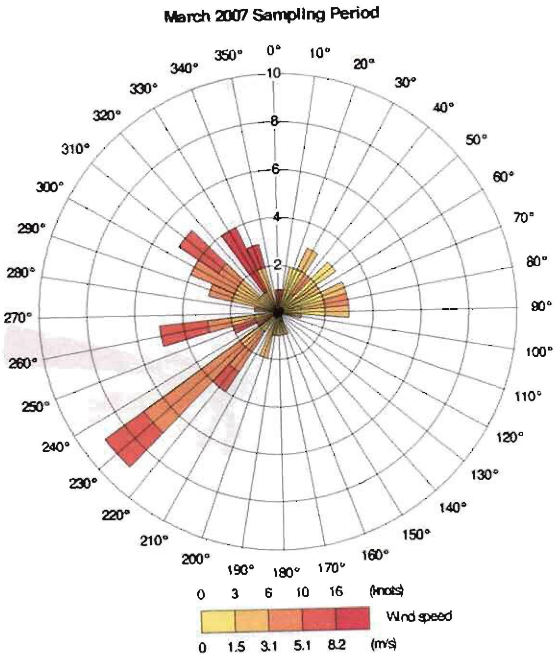
20 March 2007



21 March 2007

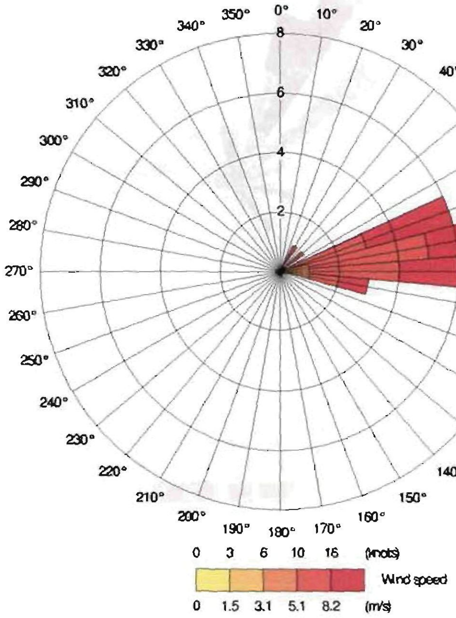



22 March 2007

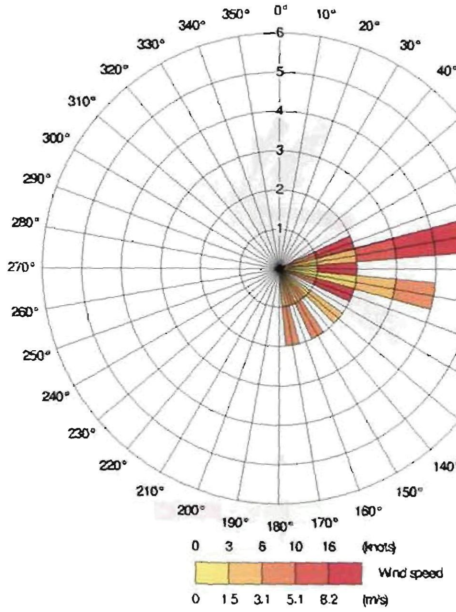

March 2007 Sampling Period

D.3. Wind roses for August 2007

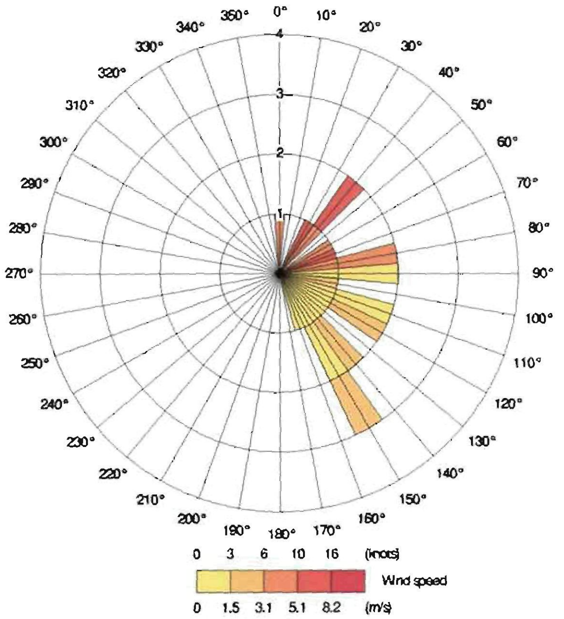
6 August 2007



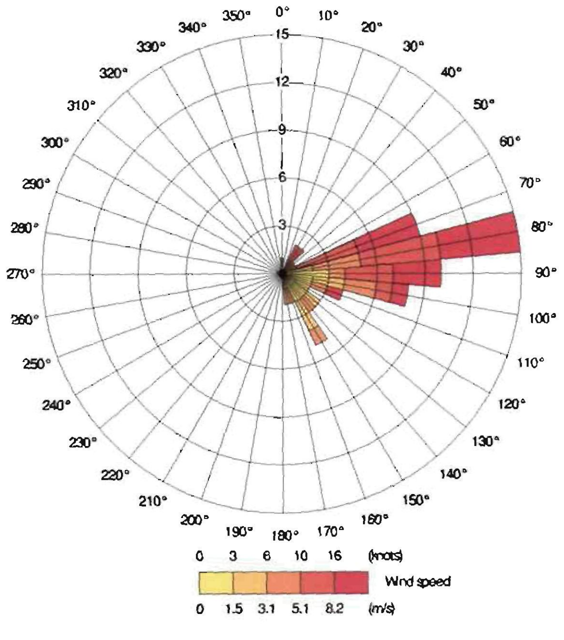
8 August 2007



10 August 2007



August 2007 Sampling Period



Acknowledgements

Firstly, I would like to thank the Lord God Almighty for giving me the opportunity to study and to do research. It meant a great deal to me personally and I have learned a lot about myself as well as this particular subject.

I also want to give thanks to my promoter (Kobus Pienaar) and co-promoter (Colin Read) for their willingness to help and their guidance throughout the duration of the study. Thanks also to Paul Beukes and various other persons in the research group for their help, and guidance when needed.

I would like to give a special word of thanks to my parents (Manie and Wilma), my sisters (Izet and Suné) and my boyfriend (Kobus Conradie) for their love and support and for encouraging me to keep on giving my best.

I would also like to thank Liezl Jonker for all her help with the text editing, it is greatly appreciated.

Without all of your help the study would have been much more difficult to complete. I appreciate your support very, very much! Thanks from the bottom of my heart.

Table of contents