

CHARACTERISATION OF AMBIENT ATMOSPHERIC AEROSOLS USING ACCELERATOR-BASED TECHNIQUES

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I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of **Master of Science** at the University of the Witwatersrand. It has not been submitted before for any degree or examination in any university.

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ABSTRACT

Atmospheric haze, which builds up over South Africa including our study areas, Cape Town and the Mpumalanga Highveld under calm weather conditions, causes public concern. The scope of this study was to determine the concentration and composition of atmospheric aerosol at Khayelitsha (an urban site in the Western Cape) and Ferrobank (an industrial site in Witbank, Mpumalanga). Particulate matter was collected in Khayelitsha from 18 May 2007 to 20 July 2007 (i.e. 20 samples) using a Partisol-plus sampler and a Tapered Element Oscillating Microbalance (TEOM) sampler. Sampling took place at Ferrobank from 07 February 2008 to 11 March 2008 (6 samples) using a Partisol-plus sampler and an E-sampler. The gravimetric mass of each exposed sample was determined from pre- and post-sampling weighing. The elemental composition of the particulate matter was determined for 16 elements at Khayelitsha using Proton Induced X-ray Emission (PIXE). The concentration of the elements Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, As, Br, Sn, and Pb was determined by analysing the PIXE spectra obtained. In similar manner, the elemental composition of the particulate matter was determined for 15 elements at Ferrobank (Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, As, Br and Pb). The average aerosol mass concentrations for different days at the Khayelitsha site were found to vary between 8.5 $\mu g/m^3$ and 124.38 $\mu g/m^3$. At the Khayelitsha site on three occasions during the sampling campaign the average aerosol mass concentrations exceeded the current South African air quality standard of 75 $\mu g/m^3$ over 24 h. At the Ferrobank

site, there are no single days that exceeded the limit of the South African air quality standard during the sampling campaign.

Enrichment factors for each element of the particles sampled with an aerodynamic diameter of less than $10 \,\mu m \,(PM_{10})$ samples have been calculated in order to identify their possible sources. The analysis yielded five potential sources of PM_{10} : soil dust, sea salt, gasoline emissions, domestic wood and coal combustion. Interestingly, enrichment factor values for the Khayelitsha samples show that sea salt constitutes a major source of emissions, while Ferrobank samples, the source apportionment by unique ratios (SPUR) indicate soil dust and coal emission are the major sources of pollution. The source apportionment at Khayelitsha shows that sea salt and biomass burning are major source of air pollution.

KEYWORDS: atmospheric aerosols, particulate matter, Partisol-plus sampler, E-sampler, proton induced x-ray emission, enrichment factor, sources of atmospheric aerosol emissions, source apportionment by unique ratios.

To my family

PREFACE

Atmospheric aerosol is a mixture of inorganic and organic species that contributes to adverse public health effects, visibility impairment, regional haze, and acid rain (Lee *et al.*, 2005). Atmospheric aerosols are under intense scientific investigation, due to the uncertainty regarding their role in global climate change (Kyoto, 1997). The characterisation of particulate matter is becoming increasingly important to government, regulators and researchers owing to its impact of particulate matter on human health, its ability to travel thousands of kilometres across countries and continents and, more recently, for its influence on climate forcing and global warming.

The main air pollution hotspots in South Africa are Cape Town, Durban, Johannesburg, Pretoria, Richards Bay, Rustenburg, the Vaal Triangle and Witbank. Air pollutants (such as SO₂, NO₂, particulate matter and heavy metals) result from combustion processes in industry, services, agriculture, transport and households. There have been many studies on particulate matter in South Africa (Piketh *et al.*, 2003 and Wicking-Baird *et al.*, 1997). However, only limited studies have been undertaken on a comparison of the characterisation of atmospheric aerosols between urban and industrial sites in South Africa.

The aim of this study is to characterise ambient atmospheric aerosols. More precisely, the study will focus on the characterisation of ambient atmospheric aerosols with respect to soil dust, sea salt, aerosols from diesel and petrol motor vehicle emissions (gasoline emission), wood burning and coal burning. The elemental concentrations of the sampled particulate matter have been determined by Proton induced x-ray emission (PIXE) analysis. The meteorological conditions which promote the accumulation of pollutants have been also investigated.

This study is divided into five chapters. **Chapter 1** presents the background of the study area and effects of atmospheric aerosols on air quality and human health. **Chapter 2** presents a literature review of atmospheric aerosols and the PIXE technique. In **Chapter 3** the description of aerosol sample collection and data analysis methodology used in this study are outlined. The results are presented and discussed in **Chapter 4**. In **Chapter 5**, presents the summary and conclusions of this research study.

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ABBREVIATIONS AND ACRONYMS

μg	microgram(s)
$\mu g/m^3$	microgram(s) per cubic metre
μm	micrometre(s)
AEEs	Anomalously enriched elements
APCA	Absolute Principal Components Analysis
Be	Beryllium
ССТ	City of Cape Town
СМА	Cape Metropolitan Area
СО	Carbon monoxide
CO_2	Carbon dioxide
CPU	Central processing Unit
CRG	Climatology Research Group
D _{ae}	aerodynamic diameter
DEAT	Department of Environmental Affairs and Tourism
ECPSSR	Energy Loss Coulomb-Repulsion Perturbed-Stationary-State Relativistic
EAD	Equivalent Aerodynamic Diameter
EF	Enrichment factor
EPA	Environmental Protection Agency (of the United States of America)
ESKOM	Electricity supply commission
GUPIX	The Guelph PIXE program
h	hour(s)
Hi-Vol	High Volume
ICACS	International Conference on Atomic Collisions in Solids
iThemba	iThemba Laboratory for Accelerator-Based Sciences

LABS	
LOD	Limit of detection
m	metre(s)
MCA	Multi Channel Analyser
MeV	Megaelectron volt(s)
mm	millimetre(s)
nm	nanometre(s)
MV	Megavolt(s)
NEEs	Non-enriched elements
NMP	Nuclear Microprobe
pA	Picoampere(s)
PCA3	Personal Computer Analyser
PIXE	Proton Induced X-ray Emission
PM	Particulate matter
PM_{10}	particles with an aerodynamic diameter of less than 10 μm
PM _{2.5}	particles with an aerodynamic diameter of less than 2.5 μm
ppm	part(s) per million
PSVM	Particulate semi-volatile material
R & P	Rupprecht & Patashnick
S	second(s)
SAWS	South Africa Weather Service
Si(Li)	silicon lithium
SPUR	Source Apportionment by Unique ratios
TEOM	Tapered Element Oscillating Microbalance sampler
TSP	Total suspended particles
VOC(s)	Volatile organic compound(s)
WINS	Well Impactor Ninety Six [a type of impactor]

CHAPTER 1 INTRODUCTION

1.1 Atmospheric aerosols

'Atmospheric aerosols' comprise any solid or liquid matter suspended in the atmosphere (Pilinis and Seinfeld, 1987). Ambient particulate matter (PM) is emerging as a critical component of environmental health. 'Particulate matter' refers to all airborne liquid and solid particles, except pure water, that are microscopic in size. Given the complexity of such particles, it is useful to categorise PM on the basis of three key features: particle size, source, and composition. Most aerosols occur naturally, originating from volcanoes, dust storms, living vegetation, and sea spray. Human activities, such as the burning of fossil fuels and the alteration of natural surface cover, also generate aerosols. These particles may be directly introduced, by natural or anthropogenic sources, into the air as particles (primary aerosol) or produced in the atmosphere by chemical reactions (secondary aerosol). Atmospheric aerosol particles are known to contain organic carbon material in varying amounts, depending on their location (Jacobson et al., 2000). Ambient atmospheric aerosols are typically present in concentrations of between a few micrograms per cubic metre and a few hundred micrograms per cubic metre and are thus a tiny fraction of the total atmosphere, generally below 0.1 ppm by mass (Cahill, 1995). Yet, despite these tiny concentrations, atmospheric aerosols produce relevant health effects and play a large role in many atmospheric processes.

Aerosols contribute both directly and indirectly towards the Earth's radiation budget and climate forcing. As a direct effect, aerosols scatter sunlight directly back into space. They have a 'direct' cooling effect by reducing the amount of solar radiation (insolation) that reaches the Earth's surface (National Aeronautics and Space Administration, 1996). The magnitude of this cooling effect depends on the size and composition of the aerosol particles, as well as the reflective properties of the underlying surface. It is thought that aerosol cooling may practically offset expected global warming that is attributed to increases in the amount of carbon dioxide (CO_2) from human activity (National Aeronautics and Space Administration, 1996). As an indirect effect, aerosols in the lower atmosphere can modify the size of cloud particles, changing how the clouds reflect and absorb sunlight, thereby affecting the Earth's energy budget. Indeed, if there were no aerosols in the atmosphere, clouds would be much less common. It is very difficult to form cloud droplets without small aerosol particles acting as 'seeds' which trigger the formation of cloud droplets by acting as condensation nuclei. According to certain theoretical models (Jacobson et al., 2000), as the aerosol concentration increases within a cloud, the water in the cloud gets spread over many more particles, each of which is correspondingly smaller. Smaller particles fall more slowly in the atmosphere and decrease the amount of rainfall (National Aeronautics and Space Administration, 2007). In this way, changing aerosols in the atmosphere can change the frequency of cloud occurrence, cloud thickness, and amounts of rainfall (National Aeronautics and Space Administration, 2007).

In summary, aerosols catalyse many chemical reactions, enhance erosion processes, influence cloud properties and formation, and modify atmospheric optical properties, producing important effects on the terrestrial radiative balance (planetary albedo).

2

Atmospheric aerosols particle are responsible for most of the reduction of visibility seen in urban and polluted rural setting (as well as colorful sunsets and other effects). Since aerosols carry most of the toxic metals, acids, and nitrates of the atmosphere, atmospheric acids such as sulphates and nitrates act as precursors to acidic rainfall, causing corrosion of materials and they are a major factor in adverse health effects as exemplified by London "killer fogs" of the 1950s (Lippmann, 1989). It has long been known that high concentrations of very small particles in air, such as those experienced during the famous 'killer' fog of London, England in December 1952, can severely affect susceptible people such as the sick and elderly, even causing, or contributing to, death (Lippmann, 1989; Ito and Thurston, 1989; Thurston *et al.*, 1989). In summary, aerosol inhalation by human beings and animals may produce dangerous health effects.

As far as the health impact is concerned, this is connected with different penetration of the particles into the breathing apparatus – smaller particles penetrate deeper into the respiratory system and are potentially more dangerous. The notion that fine particles with aerodynamic diameter (D_{ae}) of less than 2.5 μm ($PM_{2.5}$) are more relevant to adverse health effects than are coarse particles has been widely accepted in recent years (Lin *et al.*, 2002). Particles with aerodynamic diameter (D_{ae}) greater than 10 μm are stopped in the upper respiratory tract and quickly expunged. Particles with aerodynamic diameter between about 10 and 3.5 μm tend to be inhaled and end up in the nose, tract and upper bronchial throat; removal from the body is generally by swallowing. Particles smaller than about 3.5 μm enter the lungs and are retained in the alveoli; removal tends to be through the bloodstream which is generally more hazardous than the gut. The adverse health effects that result from exposure to *PM* are specific to the cardio-respiratory (heart-lung) system. The smaller the particle, the

deeper it can penetrate into the lungs, and the greater the risk of inducing an adverse reaction. Most particles greater than about $10 \,\mu m$ will be caught in the nose and throat, and not reach the lungs. The largest of these particles will be caught by cilia lining the walls of the bronchial tubes, which move particles up and out. $PM_{2.5}$ penetrates deeper into the lungs, into regions where there are no cilia, therefore, particles are removed by other, slower mechanisms. $PM_{2.5}$ is sometimes referred to as 'respirable PM'. The challenge of responding to this concern is great: PM is everywhere, and its sources are diverse and intimately linked to the industrialisation of our society.

The atmospheric dynamics of aerosols are closely tied to their size distribution, which is vital for understanding transport and removal processes and is useful in identifying aerosol sources. For example, sulphate aerosols with a diameter of 0.1 μm are almost transparent to visible light and thus do not cause a reduction in visibility and haze. But particles of the same chemical composition are hygroscopic and thus grow to 0.5 μm in diameter, becoming in the process extremely efficient in scattering light. The atmospheric aerosols are the major component of the brown haze seen in so many cities like that seen in the City of Cape Town. There is a need, therefore, for simultaneous measurements of composition and particle size when studying atmospheric aerosols.

1.2 Study area

1.2.1 Khayelitsha

The City of Cape Town (CCT) was established in December 2000 by the merging of the previous Cape Metropolitan Council and six Metropolitan local councils (Tygerberg, Oostenberg, Blaauwberg, South Peninsula, Helderberg and Cape Town). It is the southernmost metropolitan area of the African continent and covers an area of 2487 km². The Khayelitsha sub-district is a large, predominantly informal settlement located about 30 km from the centre of Cape Town. Khayelitsha was established in 1983 and grew rapidly (Wichmann, 2006). The total number of people living in Khayelitsha is approximate to 27 647 (Cape Town census, 2007).

The residents of Khayelitsha are particularly vulnerable to health implications due to exposure to air pollution. The severity of health outcomes to air pollution increases with vulnerability. Although the CCT is responsible for developing an air quality management plan which should be incorporated into its integrated development plan according to the National Environmental Management Air Quality Act (Act 39 of 2004) (Republic of South Africa, 2004), this study has been performed independently from the CCT. This was done in order to supplement CCT data with PIXE analysis.

Rapid urbanisation and urban growth have resulted in a large population in the CCT and this in turn leads to a larger number of people making use of public and especially private transport to commute to work. During certain periods the capacity of a number of road networks is exceeded and additional road networks are reaching their maximum capacity (Cape Town, 2007). A large proportion of the residents of Khayelitsha live close to the (N2) highway and other busy roads (such as the R310).

The population at Khayelitsha is exclusively Black. Under Apartheid, South Africans were categorised into one of four socially defined groups: White (mainly European ancestry), Asian (Indian sub-continent ancestry), African or Black (descended primarily from one of a number of Black language groups in southern Africa), and Coloured (general grouping including a mixture of Black, Malay, European and indigeneous Khoisan ancestry) (Wichmann, 2006). Race is very much linked to past access to resources, socio-economic status and educational status. The percentage profiles of types of fuel used by nearly 7 267 households in Khayelitsha (Cape Town census, 2007) for lighting are: paraffin (26.71 %), electricity (67.79 %), gas (0.59 %), candles (4.75 %), solar (0.08 %) and other unspecified fuel (0.08 %). The profile of percentage use of energy for cooking in Black households for the entire CCT (and not specifically just for Khayelitsha) is: electricity (45 %), gas (4 %), paraffin (49 %), coal (1 %) and animal dung (1 %) (Statistics South Africa, Census 2001). The figures for heating are: electricity (33 %), gas (1 %), paraffin (57 %), wood (5 %) and other unspecified fuels (4 %) (Statistics South Africa, Census 2001). It must also be noted that although Khayelitsha is an urban area, it is located close to an industrial area and the Cape Town International Airport.

Every year between March and August the Cape Metropolitan Area (CMA) experiences episodes of pollution which are associated with calm atmospheric conditions and low level inversions (Cape Town, 2006). These conditions give rise to a visible 'brown haze'. Haze pollution has been studied intensively during the last two decades for its impact on the visual environment, climate, and public health (Chen *et al.*, 2003). Haze is an atmospheric phenomenon where dust, smoke and other pollutant particles obscure the normal clarity of the sky. It occurs when dust and smoke particles accumulate in relatively dry air. When weather conditions block the dispersal of smoke and other pollutants they concentrate and form a usually low-hanging shroud that impairs visibility and may become a respiratory health threat. Dense haze caused by industrial pollution is also known as 'smog'. Sources for haze particles include farming (ploughing in dry weather), traffic, industry, forest fires and peat field fires. Seen from afar (for example, from an approaching aeroplane), the haze is brownish, while mist is more bluish-grey. While haze is formed in relatively dry air,

in more humid air mist is formed, and the haze particles can even act as condensation nuclei for the mist droplets (s.v. "Haze", 2007).

The focus areas of this research are Khayelitsha and Ferrobank. The Khayelitsha site shown in figure 1.1 is characterised by the haze during winter which extends over most of the CMA and shifts depending on the wind direction. It is normally most intense in the morning after which it lifts and disperses as the day progresses as a result of the lifting of the inversion layers (Wicking-Baird, de Villiers and Dutkiewicz, 1997; Chiloane, 2005). Previous studies on the Cape Town brown haze (Brown Haze Study I (Wicking-Baird *et al.*, 1997) and Brown Haze Study II (Piketh *et al.*, 2003)) have shown that the haze at Cape Town is due to gaseous and particulate matter.

The main objective of Brown Haze Study I (Wicking-Baird *et al.*, 1997) – which was based on four sites (City Hall, Goodwood, Table View and Wynberg) in the CMA – was to determine the contribution of all major sources to the brown haze and to obtain a better understanding of the mechanism of haze formation. The air pollution and health problems were not addressed in Brown Haze Study I. The summary of Brown Haze I:

- The Brown was sampled over a one year period, from July 1995 to June 1996, using PM2.5 samplers situated at four sites (City Hall, Goodwood, Table view, Wynberg) in the Cape Town Area.
- 2) The Cape Town Brown haze occurs mostly from April to September due to strong temperature inversions and windless conditions that can occur during these moths, which leads to the build-up of pollutants emitted into the atmosphere. The haze extends over most of the Cape Metropolitan

Area and is normally most intense in the morning and then lifts and disperses.

- 3) Generally, in urban areas, particle less than 2.5 microns in size (PM2.5) are the single largest cause of visibility impairment. They are also the most harmful size range of particles to human health. Because of the importance of PM2.5 in the haze the main focus of the study was source apportionment of PM2.5. The apportionment used receptor modeling approach that required chemical data about the main sources and the Brown haze itself.
- 4) Important sources of air pollutants were identified through an emissions inventory of the Cape Town Metropolitan Area. Sources that were included in modeling were soils various soils, road dust, sea salt, coal-fired boilers, oil-fired boilers, Caltex oil-and gas-fired equipment, Caltex's fluidized catalytic cracker unit, Kynoch's ammonium nitrate emissions, diesel combustion, petro combustion, wood fires, grass fires, and tyre burning. Secondary sources for sulphates, nitrates, and carbon were also used in modeling
- 5) During the one year sampling period, internationally recognized health standards for nitrogen dioxide were exceeded during most Brown haze episodes, for sulphur dioxide were very seldom exceeded, and for PM10 were never exceeded. The United States PM2.5 daily standards was not exceeded on the Brown haze episodes measured, but is likely to be exceeded on the worst Brown haze days

The second study on brown haze (Brown Haze Study II) (Piketh *et al.*, 2003) was undertaken by the Climatology Research Group (CRG) from the University of the Witwatersrand which focuses on air quality. The objective of Brown Haze Study II was to characterise the source of the haze which included chemical, physical, spatial and temporal profiles – both particulate and gaseous (Piketh *et al.*, 2003). The main finding of brown Haze Study II:

- The meteorology of the Cape region during the winter is conducive to establishment of highly stable atmospheric conditions close to the surface as well as between 1 and 3km above sea level. Brown haze events have been found to occur on days when the surface inversion layers form over Cape Town particularly under the influence of anticyclonic circulation.
- The dominant wind direction during brown haze is northerly to north westerly.
- Ground based concentrations of pollutants generally rise sharply in the morning and evening.
- High concentrations of aerosols coincide with spatial distribution of stationary sources in the Cape metropolitan area. The majority of sources are located to the south east of the city.
- 5) Airborne and hazemeter observations showed that domestic burning in townships and informal settlements clearly produce considerable concentrations of aerosols relative to the surroundings.
- 6) Morning concentrations of aerosols on Brown haze days are significantly elevated over Khayelitsha, Mitchels Plain and Belville South.
- There is a significant difference in atmospheric aerosol loading between Brown haze and clear days.

Atmospheric aerosols have an impact on the composition and formation of brown haze as they consist of particles that obscure normal clarity of the sky.

Air pollution monitoring sites in Cape Town are located in different types of areas. Figure 1.1 shows the study area and the thirteen (13) monitoring stations of Cape Town. The Cape Town City Council air quality monitoring laboratory maintains an air quality station in Khayelitsha in order to conduct assessments of air quality in the area. Air quality monitoring of Khayelitsha shows that the PM_{10} (particulate matter with an aerodynamic diameter of less than 10 μ m) concentrations exceed air quality limits according to air quality standards in South Africa. The source of these high PM_{10} levels is thought to be mostly from wood- and tyre-burning, along with a large amount of windblown dust due to the presence of unpaved roads and pavements (Cape Town Air Quality, 2007).

The Khayelitsha monitoring station is based within the residential area. Pollutant sources around this area range from fugitive dust, vehicle emissions, paraffin, wood burning as well as influence from regions outside this area (Witi, 2005). Particulate matter represents the most significant critical pollutant in terms of human health risk potential within the CCT (Cape Town, 2006). Elevated PM_{10} concentrations occur over much of the CCT resulting in widespread health risk; with significant health effects anticipated in particular areas (for example, Khayelitsha)(Cape Town Air Quality, 2007). Figure 1.2 shows the source map of pollutants for the CCT, Khayelitsha is dominated by total suspended particles (TSP) (Cape Town Air Quality, 2007). This gives rise to the depth characterisation of particulate matter in Khayelitsha (Cape Town Air Quality, 2007).



Source: I thank Wendy Job, Department of Geography, University of the Witwatersrand, Johannesburg for drawing the map.

Figure 1.1 The study area of Khayelitsha and location of air quality monitoring stations at CMA



Figure 1.2 The industrial sources of TSP map of Cape Town

Figure 1.3 is an aerial photo of Khayelitsha with an arrow indicating the monitoring site in relation to the highway, main roads and surrounding formal and informal settlements.



Figure 1.3 Aerial photo of the Khayelitsha monitoring site (Benson, 2007)

1.2.2 Ferrobank

In contrast to Khayelitsha, Ferrobank at Witbank is a heavy industrial area with intense coal-mining activities. Emalahleni Municipality (previously known as Witbank) is situated in Mpumalanga Province, and it represents one of six local municipalities in the Nkangala District Municipality. It forms part of the western region of Mpumalanga Province and borders onto Gauteng Province. Ferrobank is very close to coal power stations (within radius of 20km), since the southern parts of the Emalahleni Municipality form part of the precinct referred to as the 'Energy Mecca' of South Africa, due to its rich deposits of coal reserves and power stations such as Kendal, Matla, and Duvha. The total population of the Emalahleni Municipality is approximately 276 412 persons, which constitutes 27 % of the total Nkangala District's population (Statistics South Africa Census, 2001).

The types of fuel used by households in Emalahleni Municipality for lighting are paraffin (10%), electricity (73%), candles (16.92%) and other unspecified fuel (0.08%) (Statistics South Africa Census, 2001). The energy use trends for cooking are electricity (57%), paraffin (18.57%), wood (16.43%) and other (8%) (Statistics South Africa Census, 2001). Figure 1.4 shows the location of the Ferrobank study area of the industrial site of Witbank.



Source: I thank Wendy Job, Department of Geography, University of the Witwatersrand, Johannesburg for drawing the map.

Figure 1.4 A map showing the location of Ferrobank

Air quality is an issue of concern in Mpumalanga, as it is in many other parts of South Africa. Air pollution monitoring sites in Mpumalanga are located in different types of areas. These monitoring sites belong to Electricity supply commission (ESKOM), and they are other monitoring sites that belong to Department of Environmental Affairs and Tourism (DEAT) and private monitoring sites, ESKOM monitoring sites have been in operation since 1980s (Eskom, 2002). The monitoring network of ESKOM comprises so many monitoring sites within the Mpumalanga province. The Kendal and Majuba monitoring sites are each located 2 and 3 km from the Kendal and Majuba coal-fired power stations, respectively, in order to assess the local air quality impacts from emissions of these coal-fired power stations. The Elandsfontein monitoring site is located in central Mpumalanga with the aim to assess the long-term air quality impact from various sources (industrial, domestic, mining, agriculture, power stations). The Leandra monitoring site is located at Leandra Junior School to assess the impacts of electrification on air quality at Lebohang. The Verkykkop monitoring site are on the eastern escarpment of Mpumalanga, assessing transportation of pollutants from central Mpumalanga to adjacent regions outside the province (Eskom, 2002).

1.3 Objectives

Since it is well known that air pollution is also one of the prime contributor to endangering the health of the population of urban areas, and since ambient particulate matter is an essential part of this contamination, its characterisation has become an important task. Moreover, atmospheric aerosols are recognised as significant contributors to global climate change (Flores and Aldape, 2001).

In this field, PIXE analysis has demonstrated some its versatility to provide much of the information required to accurately assess the atmospheric pollution problem.

The main objective of this research is to characterise ambient atmospheric aerosols by using PIXE analysis. More precisely, the study will focus on

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characterisation of ambient atmospheric aerosols of soil dust, sea salt, diesel and petrol motor vehicle emissions (gasoline emissions), and wood and coal burning. The intensive sampling campaigns were undertaken from 18 May to 20 July 2007 in Khayelitsha and from 07 February to 11 March 2008 at Ferrobank. The source apportionment study is undertaken to identify the potential source of pollution on our study areas. Gravimetric analysis is being undertaken to quantify our study.

CHAPTER 2

LITERATURE REVIEW OF ATMOSPHERIC AEROSOLS AND THE PIXE CHARACTERISATION TECHNIQUE

2.1 Review of atmospheric aerosols

Atmospheric aerosols have significant local, regional and global impacts. Locally include emissions from industrial processes, vehicles and wood-burning fires that can lead to urban air pollution and possible adverse health effects. Regionally, aerosols can be transported from areas of high emissions to relatively clean remote regions. The word 'aerosol' was introduced in the 1930s as an analogy to the term 'hydrosol', a stable liquid suspension of solid particles (Hinds, 2000). An 'aerosol' is defined in its simplest form as solid or liquid particles suspended in a gas, and it includes a wide range of phenomena such as dust, fumes, smoke, mist, fog, haze, and smog. 'Atmospheric aerosols' are generally considered to be particles that range in size from a few nanometres (nm) to tens of micrometers (μm) in diameter. Particles may be emitted directly into the atmosphere or formed in the atmosphere by the oxidation of precursor gases, such as sulphur dioxide, nitrogen oxides and volatile organic compounds (VOCs). The resulting oxidation products nucleate to form new particles or condense on pre-existing ones. Particles formed through these two routes are referred to as 'primary' and 'secondary' particles, respectively.



Figure 2.1 Ambient particulate matter size distributions (EPA, 1997)

Many studies have shown that there are two rough, size-based categories of particle. Figure 2.1 shows the ambient particulate matter size distributions. These particulate groupings are generally referred to as 'fine' and 'coarse' particles, with median sizes of approximately 1 μm and 10 μm , respectively. This approximate size classification is based on general observations of many studies (Cohen *et al.*, 2004a, and Cahill, 1995). The origin, composition, and properties of ambient particles will be different for each location based on very complex combinations of local and regional geology, climate, and land use. In this dissertation the smaller than 2.5 μm and 2.5 to 10 μm size fractions will be referred to as 'fine' and 'coarse' particulate matter, respectively. Table 2.1 indicates the classification terminology regarding particle size as used by the United States of America Environmental Protection Agency (EPA).

EPA description	Particle size
Supercoarse	$D_{ae} > 10 \ \mu m$
Coarse	2.5 $\mu m < D_{ae} \le 10 \mu m$
Fine	0.1 $\mu m < D_{ae} \le 2.5 \mu m$
Ultrafine	$D_{ae} \leq 0.1 \ \mu m$
Source: EPA (2007)	

Table 2.1:EPA terminology for particle sizes

Fine particle pollution in the atmosphere is mainly composed of micron, and sub-micron particles from anthropogenic sources such as motor vehicle emissions, wood-burning and fossil-fuel burning, windblown soils and sea spray. The fine fraction particles, mainly produced by gas-to-particle conversion processes, and direct industrial and combustion emissions, generally contain sulphates, nitrates, organic and elemental carbon, and metal (Pb, Ni, Cu, As, Se, Cd, for example) compounds. The characterisation of these fine particles is becoming increasingly important to governments, regulators and researchers due to their adverse impacts on health, their ability to travel thousands of kilometres across countries and continents and, more recently, for their influence on climate forcing and global warming (Cohen *et al.*, 2004a). These fine particles are small enough to penetrate deep into the human respiratory system and have direct access to the blood-stream with obvious health impacts. Aerosol particles of the fine fraction have longer residence times in the atmosphere (from days to weeks) as they are more resistant to removal, due to physical processes (Raes *et al.*, 2000; Chaloulakou *et al.*, 2005).

The coarse fraction particles are mechanically produced by the breaking down of larger solid particles, and can include wind-blown dust from agricultural processes, uncovered soil, unpaved roads or mining operations, road dust re-suspended by traffic, sea-spray particles, pollen grains, mould spores, and plant and insect parts. The coarse fraction particles, being mainly produced by erosion and other natural processes, generally contain soil-related elements (Al, Si, Ca, Sr, Ti, for example), typically as oxides, sea-spray elements (Na, Cl, S, for example) and organic compounds from pollen grains, mould spores, and plant and insect parts. The amount of energy required to break these particles into smaller sizes increases as the particle size decreases, which effectively establishes a lower limit for the production of coarse particles. Coarse particle removal takes place in general by settling and, since the process is quite efficient, the residence time in the atmosphere is short, typically of the order of hours.

2.1.1 Effects of atmospheric aerosols on air quality and human health

The impact of ambient particles on human health has been known since the early 1950s (Lippman, 1989). Since the 1990s a large number of epidemiological studies have been conducted around the world which have observed associations between ambient particle concentrations and excesses in daily mortality and morbidity (Dockery *et al.*, 1992, 1993; Schwartz and Dockery, 1992; Touloumi *et al.*, 1994; Katsouyianni *et al.*, 1997). These findings have underlined the importance of ambient particles and the need for monitoring PM_{10} (inhalable particles) and $PM_{2.5}$ (respirable particles).

It is widely believed that in the short-term air pollution only anticipates unavoidable deaths. Recent studies have shown, however, that this is not the only reason, and that when air pollution increases, the excess mortality due to the anticipated deaths of particularly vulnerable people – called 'harvesting' – is not followed by a deficit (Schwartz and Dockery, 1992). This implies that air pollution not only kills people in a 'high risk pool', but also recruits new individuals to that pool. This is consistent with the results of a recent study (Molina and Molina, 2002), which showed that short-term inhalation of fine particulate air pollution and ozone at concentrations that occur in the urban environment causes acute conduit artery vasoconstriction in healthy adults. Both within Mexico and in the worldwide literature there is some evidence that criteria air pollutants other than PM_{10} are associated with premature mortality, although this evidence is weaker than it is for particulate matter (Molina and Molina, 2002).

The impact of gaseous and particulate pollutants is gauged by the effect on pollution receptors. For example, deposition of acidic pollutants can speed up the deterioration of building materials, harm vegetation, damage the aquatic ecosystem, cause breathing problems and even increase the mortality rate among humans.

Monitoring of air pollution has a long history within the CMA dating back to 1958 when 'smog' monitors were used. These are the standard 'bubblers' measuring soiling index (expressed as 'smoke') and sulphur dioxide. The results from these instruments are usually used to determine long-term trends. With the introduction of the Air Pollution Prevention Act in 1965, the Cape Town local authority was able to make provision for the control of smoke, dust and vehicle emissions, although this was limited to the control of diesel vehicle emissions (Walton, 2005).

Air quality standards for particulate matter in countries such as the United States of America were expressed some years ago in terms of the mass of total suspended particulate matter (TSP). The standard was then changed to the mass of suspended particulate matter less than 10 μm in size, commonly called PM_{10} , and
more recently was modified to include particulate matter less than 2.5 μm in diameter $PM_{2.5}$ (EPA, 1997). The rationale for basing air quality standards on smaller particles relied on the fact that they can penetrate deeper into the lungs and hence their potential adverse health effect is much greater. In addition, they have larger surface-to-volume ratios and are commonly produced from gas-to-particle conversion or combustion processes, which are known to produce carcinogens such as polycyclic aromatic hydrocarbons. Many epidemiological studies have observed associations between particulate air pollution and human health (Dockery *et al.*, 1993).

2.1.2 Aerosol sampling

The most widely used method for characterisation of mass and chemical composition of PM_{10} and $PM_{2.5}$ is particle sampling on filters. No existing sampling system meets all PM characterisation needs, so it is necessary to chose from a wide variety of filter-based sampling, continuous sampling, and sampling and analysis methodologies to meet the requirements of most PM monitoring programmes (Canadian Chemical Producers' Association, 2001). The challenge with ambient sampling and analysis is to overcome atmospheric conditions and chemical reactions to collect a representative sample and stabilise the sample throughout the sampling and analysis process. Aerosol sampling can be schematically described as follows: Air is pumped through the sampler and particles are collected by 'impaction' and/or 'filtration'. In the 'impaction' process the air stream is forced to make an abrupt change in direction: the heavier particles, due to their higher inertia, cannot follow the air stream and impact onto a surface (impaction foil). As soon as one starts to make cuts than a simple dichotomous cut while retaining ability to perform composition analyses, one moves into particle collection by impaction (Cahill, 1995:p251). There are other methods, but this is the one most used in PIXE sampling programmes. In

'filtration', the air stream is forced (by a pressure gap application) to pass through a filter (or membrane) and particles are collected on the surface and/or in the matrix of the filter itself. This has been the method of choice in the United States of America for particulate matter in high-volume (Hi-Vol) filter samplers. Typical filters are about 500 cm² in area and ion beams sample no more than 0.5 % of the collected matter and occasionally as little as two parts in 10⁵. The PIXE analysis method was greatly improved by mechanically separating mass deposits from substrates; this was a fortunate choice in retrospect, but one that caused early difficulties for air pollution applications using Hi-Vol filter samplers.

Since only particles with $D_{ae} < 10 \mu m (PM_{10})$ are able to penetrate the human respiratory system, most of the samplers used eliminate the larger particles by a pre-impaction stage.

Samplers that separate the aerosol into different size classes are called 'fractionated' or 'multi-mode' samplers, in opposition to the 'single mode' samplers. Multi-mode inertial impactors accomplish size fractionating by arranging several impaction stages in series.

Since the minimum of the atmospheric aerosol bimodal size distribution is around $D_{ae} = 2.5 \,\mu m$, many samplers (dichotomous or two-stage samplers) have a cutoff just in correspondence of this value, thus separating the fine fraction ($PM_{2.5}$) and the coarse fraction ($PM_{10-2.5}$, that is, $2.5 \,\mu m < D_{ae} < 10 \,\mu m$) particles. A $2.5 \,\mu m$ cutoff gives several advantages: (1) it separates particles generally produced by different sources, (2) it roughly divides the PM_{10} fraction that deeply penetrates the lungs from that retained in the upper respiratory system, and (3), it corresponds to the minimum, thus making results less sensitive to the sampler's instabilities and to the shape of the separation function. The sampling time sequence can be discrete or continuous. Cumulative samplers carry out the sampling in discrete periods by repeated changes of filters (or impaction plates); if the changing is automatic the samplers continuously collect the aerosol and deposit it on a spot that is being continuously moved along the collecting substrate, thus producing a 'strip' or 'streak' of pollution. Since the characteristic aerosol temporal variations occur on several scales, from diurnal patterns (hours) through synoptic behaviour (days) to seasonal trends (months), the sampling 'time resolution' can vary from hours to months.

To obtain accurate aerosol characteristics the best approach would be to sample continuously with many size classes and with a time resolution of the order of hours. However, this would produce huge numbers of samples to be analysed and aerosol deposits collected by multi-mode samplers with good time resolution may be too small and require very sensitive analysis methods. As a consequence, when studying long-term behaviours it is convenient to sample with daily or monthly resolution. Sampling strategies (that is, size and time resolution) must be tuned accurately to the specific problem being investigated (for example, air quality monitoring, pollution source identification, climate studies).

2.1.3 Sampler

2.1.3.1 Partisol-plus sampler

The CCT air quality monitoring stations routinely collect particulate matter according to regulations in force that is CCT regulation which uses the United States Environmental Protection Agency (EPA) equivalent monitoring methods in accordance to ISO 17025. The Partisol-plus sampler is a widely used Hi-Vol dichotomous-mode sequential sampler, which collects the particulate matter on standard 47 mm diameter circular filters. The dichotomous Partisol-plus sequential air sampler splits a PM_{10} sample stream into two parts. It samples the fine $PM_{2.5}$ and coarse fractions onto two separate 47 mm diameter filters, which may be of different materials. Filter exchange takes place automatically according to the sampling programmes entered by the user. The sampler has a 16-day capacity for daily sampling which has a fully automatic filter exchange mechanism that provides unattended monitoring (Rupprecht & Patashnick, 2007). The Partisol-plus sampler is designed for a flow rate of 1 m³/h (16.7 L/min). It can be equipped with the EPA standards PM_{10} and $PM_{2.5}$ inlets. The inlet is not heated and air is sampled at ambient temperature and pressure. Figure 2.2 and figure 2.3 show the schematic diagram and picture of a Partisol-plus sampler. But it can also collect using a WINS impactor (located before the filter).

Assuming a typical PM_{10} concentration in an urban environment of 20 to $100 \ \mu g/m^3$, this corresponds to a deposit thickness of 40 to $200 \ \mu g/cm^2$ for the Partisol-plus sampler. Too much sample mass can clog the filters, causing flow changes and precluding quantitative reduction into micrograms per cubic metre (in the impaction stages. Once there are one or two mono-layers of particles, further particles will bounce off the filter membrane). Quantitative collection, sizing and retention of particles set a limit of one or at most a few monolayers to the collected deposit mass. This limit matches rather closely the maximum acceptable areal density for a target to be considered thin for ion beam analysis (Chapter 3 and Chapter 4).



Figure 2.2 Schematic diagram of R & P dichotomous sampler (Rupprecht & Patashnick, 2007)



Figure 2.3 Partisol-plus model 2025 sequential air sampler (a) shows the outside of the sampler and (b) shows the inside of the sampler

2.1.3.2 TEOM sampler

In frequent use are also TEOM samplers, which continuously collect particulate matter on a small glass-fibre membrane; the latter is the oscillating element of a microbalance and resonance frequency directly provides, in real time, the mass concentrations. The particle mass is determined by continuous weighing of the particles deposited onto a filter. The filter is attached to a vibrating hollow tapered glass tube (Charron *et al.*, 2004).

2.1.3.3 E-sampler

The E-sampler uses light scattered from suspended particulate matter to provide a continuous real-time measurement of airborne particulate matter. An internal visible laser diode is collimated and directed through the sample air. This sample air is drawn into the E-sampler by an internal rotary vane pump. The flow rate is controlled by the laser beam in order to match conditions based on actual conditions for accurate cut-points through the sharp-cut cyclone (E-Sampler, 2008). When particulate-laden sampler air intersects the laser beam a portion of the light is scattered. The scattered light is collected at a near forward angle and focused on a photo diode that converts the light to an electric signal proportional to the amount of scattered light. Scattered light is collected by precise glass optics and focused on PIN diode. Rugged state of the art electronics measure the intensity of the focused light and output a signal to the central processing unit (CPU). The output is linear to concentration greater than $100,000 \mu g/m^3$. The E-sampler uses a 47 mm sample filter. In addition, it has two internal filters. One filter protects the optical surfaces and the other prevents damage to the flow controller



Figure 2.4 An E-sampler is a system that provides both real-time monitoring and filter-based sampling capability (E-Sampler1, 2008)

2.1.3.4 Filters

Teflon filters consisting of only carbon and fluorine are hydrogen-free. Teflon filters have the benefit of minimising particle bounce and preserving unstable compounds. It has to be noted that using Teflon as a filter material increases the background in PIXE which, in turn, reduces the PIXE level of detection (International Atomic Energy Agency, 2004). Teflon was chosen as the medium for particle collection, among all the filters commonly used in aerosol sampling, and is suitable for use in a Partisol-plus sampler.

In this study, polycarbonate filters have been used as they are ideal backing material for PIXE analysis because they cause low background atomic bremsstrahlung spectra and incorporate small amounts of contamination (Höller *et al.*, 2003).

2.2 Proton Induced X-ray Emission

2.2.1 Introduction to PIXE

X-rays were first discovered by W.C. Röntgen in 1895 during his experiment with cathode rays (Röntgen, 1895). Although it takes decades usually for a new discovery to have practical applications, this was not the case with X-rays; they were widely applied in medical and industrial radiography within a year of their discovery. Today, X-ray analysis covers a wide range of techniques and fields of applications: from deduction of atomic arrangements by observation of diffraction phenomena to measurements of trace element concentration levels, distributions and maps by measuring fluorescence, X-ray attenuation or scattering (Valcovic, 1996).

Particle-Induced X-ray Emission (PIXE) is a method in which X-ray emission is used for elemental analysis. For a long time X-ray emission has been used for analytical purposes, mainly in the form of X-ray fluorescence analysis. It is well known that the cross-sections for X-ray emission by charged particle bombardment are quite high (Johansson and Campbell, 1988). In 1970 it was experimentally shown by Johansson that a combination of X-ray excitation by protons and detection by a silicon detector constitutes a powerful, multi-elemental analysis method of high sensitivity (Johansson and Johansson, 1976; Johansson and Campbell, 1988; Govil, 2001). PIXE therefore, has become a powerful analytical tool for non-destructive trace element analysis with remarkable trace element detection sensitivity of a few parts per million. It is interesting to note that the application of PIXE to atmospheric research makes use of all its advantageous features. One of the inherent limitations of the PIXE technique is its incapability to detect light elements only and therefore elements heavier than aluminum are sought for in the samples analysed.

2.2.2 The principle of PIXE

Among ion beam analysis techniques applied to the characterisation of thin aerosol samples, PIXE holds an outstanding position because of its multi-elemental ability, high sensitivity, and high throughput that allows the analysis of several particulate samples in short times. PIXE analysis of atmospheric aerosols is the major application in about a quarter of the PIXE laboratories around the globe and appears in scientific studies of ambient atmospheric aerosol in the standard aerosol journals.

The main feature that makes PIXE an advantageous technique for atmospheric aerosol is the fact that the sample to be analysed is used a target for the beam of accelerated particles without major sample preparation. The working principle is quite simple. By using an electrostatic accelerator, a particle beam with energy of typically 2 to 4 MeV is produced. Figure 2.5 shows the schematic of the single-ended van der Graaff accelerator of iThemba LABS at Faure. The beam particles usually protons when impinging on a target interact with atoms and nuclei of the target itself. The inner shell of the target atom may be ionised and its vacancy is filled by an outer electron, followed by the emission of an X-ray with energy equal to the difference of the electron binding energies in the outer and inner shells. As atoms of different elements are characterised by unique electron energy states, the emitted X-ray having electron transition represents the unique signature of the element of that particular atom from which they are emitted.



Figure 2.5A schematic of the van der Graaff accelerator and NuclearMicroprobe layout at iThemba LABS (Prozesky *et al.*, 1995)



Atom in the Sample

Figure 2.6 Schematic diagram of PIXE. The top diagram shows an incident proton ejecting an inner shell electron from the specimen atom and the bottom diagram shows an outer shell electron filling the resulting inner shell vacancy and emitting an X-ray

From figure 2.6, protons excite the inner shell electrons in the atoms of the sample and make vacancies. The energies of the X-rays which are emitted when these vacancies are filled again are characteristic of the elements from which they originate.

The angular distribution in the emission of the produced X-ray is isotopic with respect to the beam incidence direction (Garcia, 1970a; 1970b; Johansson and Campbell, 1988). The detection and discrimination of the X-ray is usually performed through the use of solid state Silicon-lithium (Si(Li)) detectors which discriminate the different X-rays by their different energies. Since each element produces a characteristic X-ray spectrum, all the atomic species present in the target can be identified and their concentration can be measured (the number of X-rays produced by the atoms of a given species is obviously proportional to their abundance in the target).

Figure 2.7, taken from Valcovic (1987), shows the origins of the principal K and L X-ray lines in the filling of K and L vacancies, together with the Z-dependence of some of their energies. The K_{α} lines represent the various L-K transitions; the $K'_{\beta 1}$ lines M-K transitions, and the $K'_{\beta 2}$ lines N, O, -K transitions. (Semiconductor detectors resolve only these three gross line groups into their major components in the case of high Z atoms.)



Figure 2.7 Atomic level diagram and the main element electron transitions giving rise to K, L and M X-rays (Aras and Ataman, 2006:p193)

As seen in figure 2.7, as the electron binding energy increases with atomic number (Z), the X-ray energies are also an increasing function of the atomic number.

The ratio of the number of emitted X-rays to the total number of ionisations produced in a given shell is called the 'fluorescence yield' relative to that shell and is usually indicated by the symbol $\omega(\omega_{k}, \omega_{l}, ...)$. The product of ionisation cross-section and fluorescence yield for a given shell gives the cross-section for the production of an X-ray of the corresponding series.

The scaling law, which gives the cross-section σ for any projectile (charge Z_p , nucleon number A_p atomic mass and E_p energy of projectile) in terms of that for a proton of the same velocity is:

$$\sigma_{Z_{p,A_p}}\left(E_{p,Z_p}\right) = Z_p^2 \sigma_{1,1}\left(\frac{E_p}{A_p}, Z\right)$$
(2.1)

That is, the cross-section is simply that for a proton of the same energy per nucleon multiplied by the square of the projectile charge. Of course, this can only be expected to hold to the extent that the ionisation mechanism is the direct Coulombic interaction between projectile charge and bound electron, the rest of the atom being essentially unaltered. In practice the rules breaks down progressively for ions heavier than helium, as multiple vacancies are created by direct ionisation and projectile pick-up; both cross-section and fluorescence yields are then drastically altered (Johannsson and Campbell, 1988). Figure 2.8 shows the K- and L-shell ionisation cross-sections. The values are the theoretical Energy Loss Coulomb-Repulsion Perturbed-Stationary-State Relativistic (ECPSSR) prediction (Cohen and Harrigan, 1985).



Figure 2.8 The K- and L-shell ionisation cross-sections as functions of proton energy E and the target atom (Cohen and Harrigan, 1985:p255)

The inability of PIXE to detect elements lighter than aluminium ($Z \le 13$), which can be major constituents of particulate matter, is precisely because of the Xray attenuation inside the target and in all the materials located between the target and the detector active zone. In most atmospheric aerosols thin targets are used because the X-ray production cross-section is constant through the targets and X-ray absorption inside the sample is negligible. The number of X-rays from a transition j of the element Z, detected during a measurement is:

$$Y_{0X_{j}}(Z) = \sigma_{X}(Z, E_{0})\alpha_{z} \cdot \frac{\Omega}{4\pi} \cdot \mathcal{E}_{det} \cdot \frac{Q}{e} \cdot \frac{N_{AV} \cdot (\rho t)_{z}}{A}$$
(2.2)

where:

 α_z is the fraction of transmitted X-rays from the target to the detector sensitive area

 Ω and ε_{det} are the solid angle covered by the detector and its intrinsic efficiency

- $(\rho t)_z$ is the mean areal density of the element Z in the surface impinged by the beam
- N_{AV} is the Avogadro number
- A is the atomic mass of the element Z
- Q is the integrated beam charge and
- e is the unit charge of the particle.

The equation can be rearranged as:

$$Y_{0X_{i}}(Z) = \eta Q(\rho t)_{z}$$

$$(2.3)$$

By defining the efficiency factor η for a given X-ray, beam energy, detector and geometry:

$$\eta = \eta_X \left(Z \right) = \sigma_{X_j} \left(Z, E_0 \right) \frac{\Omega}{4\pi} \cdot \varepsilon_{det} \cdot \frac{N_{AV}}{A.e}$$
(2.4)

If η is known the areal density $(\rho t)_z$ of a given element can be obtained by measuring the corresponding X-ray yield on the detector and the integrated beam charge on the target. The efficiency factor $\eta(Z)$ is generally obtained experimentally. This is performed by bombarding a series of thin standards containing known quantities $(\rho t)_z$ of the various elements, and measuring the corresponding X-ray yields. The measurements on the standards must be performed exactly in the same geometry and at the same beam energy as those on the sample. The subscript zero reminds us that the specimen is so thin that the proton energy is essentially constant within the target material.

From the known X-ray production cross-section together with the measured or calculated background continua from thin foils, one can calculate the quantity or concentration of a trace element on the foil that is necessary for it to be detectable (Johansson and Campbell, 1988).

2.2.3 Limit of detection

The limit of detection (LOD) is determined by the relationship $N_p \ge 3\sqrt{N_B}$, where N_p the number of counts is characteristics of the X-ray peak and N_B is the number of background counts in the corresponding interval. Thus, detection limits depend crucially on the continuous background. The latter depends on the sample, its matrix components and the specific measuring conditions. Furthermore, detection limits can change dramatically if an interfering X-ray peak from another element coincides with a trace element peak of interest (there are, however, some elemental signals undetectable in the presence of stronger overlapping signals). In several fields of application the sample matrix consists of light elements whose X-rays have energies too low to reach the detector, for example, the organic matrix of soft tissue samples. In such cases detection limits will be due to the secondary electron background. Knowing the X-ray production cross-section one can calculate the amount of certain trace element needed to satisfy the relation of LOD.

2.2.4 Sensitivity

One of the main advantages of the PIXE method is its high sensitivity. It is therefore of considerable importance to discuss what sensitivity can be obtained and how it depends on the various experimental parameters. In the preparation of the sample it is sometimes possible to enhance the sensitivity, for example, by preconcentrating a water solution or ashing an organic sample. There are several ways of defining the sensitivity of an analytical method. The problem is to find small amounts of various trace elements in a certain matrix. The most basic definition of the sensitivity is therefore the minimum detectable concentration. Once this is known one can calculate the minimum detectable absolute amounts of various elements knowing the weight of that part of the sample which is irradiated by the particle beam. If one

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calculates the number of X-ray pulses registered by a Si(Li) detector in a normal geometry when a small amount of trace element is bombarded with protons in the MeV range one finds that a sufficient number for a convenient registration is obtained even with extremely small amounts of matter, of the order of 10^{-16} g (Johansson, Akselsson and Johansson, 1970). The trace elements to be measured are, however, always contained in some matrix.

For lighter elements the sensitivity decreases mainly due to the fall-off of the fluorescence yield. The decreasing sensitivity for the heavier elements depends on the fact that for them the X-ray cross-sections are decreasing while the background is relatively constant. Furthermore, it should be noted that the position of maximum sensitivity depends on the energy of the incident protons. Within certain limits one can therefore adjust the proton energy to give the maximum sensitivity of a particular trace element. Another interesting fact of practical importance is that the highest sensitivity is obtained for $Z \approx 20$ to 30 which happens to be the region of greatest interest in many applications. The most suitable proton energy is then 1 to 3 MeV. For heavier elements with Z > 40, the K X-rays give too small an intensity. Fortunately, in this region one can make use of the L X-rays. Hence using both K and L X-rays in the analysis of a sample one can achieve a minimum detectable concentration which is fairly constant ($\sim 10^{-6}$) over practically the whole periodic table. This important fact distinguishes PIXE favourably from most other analytical methods. However there are some problems in this connection. The simultaneous emission of K and L X-rays sometimes gives rise to accidental coincidences in the recorded spectra. One such example is the L_{β} peak of cadmium (E = 3.317 eV) which coincides with the K_{α} peak of potassium (E = 3.314 eV). Another problem is the detection of very light elements. The low energy of the X-rays from these elements makes it necessary to make special arrangements on the detection side. With a standard Si(Li) detector a

reasonable sensitivity can be maintained down to sulphur or aluminium. By using a windowless detector even lighter elements can be detected. Figure 2.9 shows sensitivity with respect to energy and atomic number of elements.

The analysis of PIXE spectra presents few difficulties when the sample contains only a few elements. However, in many practical situations such as in the analysis of environmental samples, a multitude of trace and minor component elements can be present. Each of these elements may give rise to one or more X-ray peaks due to the K, L and M shell transitions, subdivided to give peaks corresponding to K_{α} , K_{β} , L_{α} , L_{β} , L_{γ} , etc. some of which are capable of being resolved. A large number of both large and small peaks can be expected in such environmental samples. There is a probability that a number of the X-ray peaks will be overlapping and interfering with each other. This can make data reduction and interpretation complicated. Even when the number of samples to be analysed is small, the use of a computer program to unravel overlapping peaks is often useful. When routine analyses are to be performed on a variety of samples of differing compositions, a spectral analysis program is essential. Several programs and The Guelph PIXE program (GUPIX) computer code are useful for this purpose (Maxwell *et al.*, 1989, 1995; Campbell *et al.*, 2000).



Figure 2.9 Minimum detectable concentrations as a function of atomic number and proton energy for thin organic specimens in a typical PIXE arrangement (Johansson and Campbell, 1988:p8)

The X-ray signal from the trace element of interest may be partially or totally masked by an unwanted background (marked A) (figure 2.10) in the spectrum arising from the backing or host material. The background may be in the form of a continuum due to bremsstrahlung or it may contain discrete peaks arising from interfering characteristic X-rays from the matrix material. The figure shows a typical X-ray spectrum obtained with a Si(Li) detector when 1.5 MeV protons are incident on a thin carbon foil. It may be seen that several discrete peaks are sitting on a continuous distribution which has a maximum at low energies. The decrease in the continuum at lowest energies is due to absorption of X-rays in the Be window in front of the Si(Li) detector. The background at low energies prevents easy and precise analysis of the

light elements in the spectrum. The main processes which contribute to the background are incident projectile bremsstrahlung (marked B), secondary electron bremsstrahlung (marked C) and low energy γ -rays (Govil, 2001).



Figure 2.10 An example of an X-ray spectrum of a multi-element specimen (Govil, 2001:p1544)

2.2.5 Application on aerosol samples

PIXE analyses of aerosol particles were among the very first applications of this method. PIXE has established itself as a routine analytical technique in the study of atmospheric aerosols. The reason for this is the advantages of PIXE: it is a multielemental, sensitive, relatively inexpensive technique requiring very little or no sample preparation that provides fast quantitative results. PIXE is non-destructive and there is the possibility to analyse point-by-point the aerosol collected by continuous sampling.

One inherent feature of PIXE is the inability to quantify elements lighter than Al, even though efforts have been made to analyse Mg and even Na. The soft energies of the characteristic X-rays of the low-Z elements make such analysis prone to large errors in the quantification of elements lighter than Al in aerosol samples, since these often consist of micron-sized particles deposited on backing substrate and cannot be considered as homogeneous samples in this respect. This is especially serious in air pollution research since the light elements H, C, N, and O are the main constituents of particulate matter and determine to a great extent its properties and impact on the environment. Numerous attempts have been made to overcome the problem related to the analysis of low-Z elements. Within the PIXE community, such complementary techniques are often based on other types of ion beam analysis which are not part of this study. It is an advantage if PIXE analysis can be made compatible with the various non-nuclear methods used for atmospheric research.

A compositional analysis of atmospheric aerosols can range from a determination of a few specific constituents, often present at trace levels, to an almost complete chemical and elemental characterisation including trace, minor and major constituents. It is interesting to note that the application of PIXE to atmospheric research makes use of all its good features. It is important in atmospheric research that the ambient aerosol is collected in an efficient manner. An aerosol sample is a mixture of particles of different size and composition, collected by filtration or impaction on a substrate. These samples do not need preliminary manipulation though not all the substrates commonly used are suited for PIXE. High volume samplers are widely used in air pollution research. The air flow is large (1500 L/min) and the filters are less well suited for PIXE analysis. The mass loading is often very high, the glass a large background and the depth distribution on the filter is uneven.

Thin filters are used to collect particles on their surface. Glass-fibre filters should be avoided due to their fibrous structure, the tremendous concentration of Si, which saturates Si(Li) detectors, and the high levels of other impurities. Nucleopore or

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Millipore filters are suitable and are widely employed with different pore sizes and can hence be used for separating the aerosol into different size fractions.

In most of the cases the aerosol deposit consists of very few layers of particles with $D_{ae} < 10 \mu m$, as a consequence it can be considered a 'thin target' with good approximation, thus strongly simplifying the quantitative analysis. The size and concentration of environmental aerosols are governed by processes occurring on time scales from a few seconds to months (Tapper *et al.*, 1995; Johansson and Campbell, 1988). An ideal particle depends on the size of the particle and should be capable of particle separation more specific of this study on PM_{10} and PM_{25} .

CHAPTER 3 DATA AND METHODOLOGY

3.1 Sampling

3.1.1 Sampling at Khayelitsha

Sampling of the air particulate matter followed the criteria established by the EPA (Quality Assurance Handbook, 1994). The Khayelitsha samples were collected during a continuous period of 12 hrs (night samples were collected between 18h00 and 6h00 while daytime sample were collected between 06h00 and 1800) using a Partisol-plus sampler and for 24 hrs using a TEOM. Sampling was done from 18 May to 20 July 2007 at the Khayelitsha air quality monitoring station. At this site two concurrently operating samplers were employed, one collecting particulate matter and the other for radiocarbon analysis (radiocarbon analysis was not part of this study). The Khayelitsha sampling site is in an urban residential area located near the Cape Town International airport, a busy highway (N2) and other busy roads (such as the R310). The samplers were placed inside a caravan which belongs to Scientific Service, Air Quality Division of the CCT at the Khayelitsha Fire Station. The roof of the caravan was flat and the sampling inlet was placed 2 m above the roof. The sampling time was varied in order to ensure that the flow rate remained within prescribed limits.

The TEOM sampler is a high-volume collector of airborne particles that are smaller than $10 \,\mu m$. Millipore filters were used as collection substrates for TEOM sampling. Details about the particle collection mechanism using Millipore filters can be found in Keith (1996). The dichotomous ($PM_{10-2.5}$) sampler separates the air

particles into two different fractions, coarse and fine (Chapter 2). The entrance of the dichotomous sampler allows only particles smaller than 10 μm to enter after which they are separated into the fractions and collected on a Teflon filter (47 mm in diameter and with pore size of 2 μm). The Partisol-plus Hi-Vol sampler is capable of collecting air particulate samples in PM_{10} and $PM_{2.5}$ size fractions. In order to correct size fractionation, the sampling time was varied to ensure that the flow rate remained within the prescribed limits. In each sampling period one coarse particulate sample was obtained using 47 mm diameter Teflon filters. Particulate matter of 2.5 to 10 μm equivalent aerodynamic diameter (EAD) was collected on the coarse filter. The original plan was to collect six (6) sets of samples per week but this could not always be achieved due to regional electricity power cuts during the sampling period. The sampling site was selected so that it provided average pollution levels representative of the urban site in which it was located.

The concentration of particulate matter was obtained by weighing the filters before and after the sampling, always after a storage period (24 h) in a temperature and humidity controlled room, by an analytical balance (with sensitivity $\pm 0.1 \ \mu g$).

3.1.2 Sampling at Ferrobank

The Ferrobank samples were collected during continuous periods of 12 h using Partisol-plus sampler and for 24 h aerosol concentrations were measured using an Esampler. Sampling was performed from 07 February to 11 March 2008 at the Ferrobank Transnet office. The Partisol-plus sampler was placed outside the caravan on the ground and the E-sampler was placed on top of the caravan. The site was selected so that it provided average pollution levels representative of the industrial area in which it was located.

3.2 Methods of analysis

3.2.1 PIXE analysis

Accelerator-based ion beam analysis techniques have been applied to studies of particulate matter (Cohen *et al.*, 2004b) using Teflon filters to determine the composition of the particulate matter collected by the dichotomous sampling device. Following the EPA standards procedures, such filters were previously identified and left in the weighing chamber, before and after collection, for a continuous period of 24 h in order to prevent hydration of the filter's surface. Similar procedures were followed in the present study after sample collection.

The elemental composition of the particulate matter was determined for 16 elements at Khayelitsha using Proton Induced X-ray Emission (PIXE). The concentration of the elements Al, Si, S, Cl, K, Ca, T, Cr, Mn, Fe, Cu, Zn, As, Br, Sn, and Pb was determined by analysing the PIXE spectra obtained. In similar manner, the elemental composition of the particulate matter was determined for 15 elements at Ferrobank (Al, Si, S, Cl, K, Ca, T, Cr, Mn, Fe, Cu, Zn, As, Br and Pb). The measurements were carried out at iThemba LABS, Faure, Cape Town, using the single-ended van der Graaff 5 MV accelerator. A PIXE experimental setup facility is available within the so-called Nuclear Microprobe (NMP) facility shown in figure 3.1. In this, an accelerated proton beam can be focused down to micrometre size and scanned over a particular sample under investigation. Although a micro-beam was not necessary for the present measurements, it could be used in the future to focus within rather large particles of between 2.5 µm and 15 µm in diameter, and determine their composition down to ppm sensitivity levels. All measurements were performed using a 3 MeV proton beam with an average current of between 100 and 300 pA. The beam spot at the target position was about 7.2 x 4.1 μm , and was scanned over the sample

to avoid beam damage to filters and reduce elemental losses. The acquisition time (counting time) for each sample ranged between 212 s and 3648 s.

Table 3.1 and table 3.2 show the identification of the samples analysed from Khayelitsha and Ferrobank, respectively with their start and stop date. On the same tables the gravimetric mass and air volume are shown. Note that 'day-time sampling (between 06:00 and 18:00) and night-time sampling (between 18:00 and 06:00).

Sample ID	Start date- Stop date	Start time- Stop time	Gravimetric mass (mg)	Air volume (m ³)
BLK0002	18 May - 18 May	06:00-18:00	0.64	12
BLK00016	18 May - 19 May	18:00-06:00	0.41	12
BLK0003	23 May - 23 May	06:00-18:00	0.89	12
BLK0004	23 May - 24 May	18:00-06:00	0.69	12
BLK0005	29 May - 29 May	06:00-18:00	0.32	12
BLK0010	29 May - 30 May	18:00-06:00	0.36	12
BLK0009	30 May - 30 May	06:00-18:00	0.63	12
BLK0008	30 May - 31 May	18:00-06:00	0.28	12
BLK0006	31 May - 31 May	06:00-18:00	0.53	12
BLK0007	31 May - 01 June	18:00-06:00	2.32	12
BLK0015	20 June - 20 June	06:00-18:00	1.17	12
BLK0001	20 June - 21 June	18:00-06:00	2.05	12
BLK0014	03 July - 03 July	06:00-18:00	1.05	12
BLK0017	03 July - 04 July	18:00-06:00	2.05	12
BLK0012	04 July - 04 July	06:00-18:00	0.77	12
BLK0013	04 July - 05 July	18:00-06:00	0.52	12
BLK0018	18 July - 18 July	06:00-18:00	0.82	12
BLK0020	18 July - 19 July	18:00-06:00	1.3	12
BLK0011	19 July - 19 July	06:00-18:00	0.72	12
BLK0019	19 July - 20 July	18:00-06:00	1.12	12

Table 3.1Summary of the analysed samples at Khayelitsha

Sample ID	Start date- Stop date	Start time- Stop time	Gravimetric mass (mg)	Air volume (m ³)
wgs0011	07 Feb - 07 Feb	06:00-18:00	1.037	12
wgs0012	07 Feb - 08 Feb	18:00-06:00	0.386	12
wgs0013	10 Feb - 10 Feb	06:00-18:00	0.111	12
wgs0014	10 Mar - 10 Mar	06:00-18:00	0.995	12
wgs0015	10 Mar - 11 Mar	18:00-06:00	0.311	12
wgs0017	11 Mar - 11 Mar	06:00-18:00	1.099	12

Table 3.2Summary of the analysed samples at Ferrobank



Figure 3.1 The Nuclear Microprobe (NMP) beam line of iThemba LABS

The filters (that is the filters containing the aerosol samples and the blank filters of each lot used in the collection) and the calibration targets were placed in a target holder accommodating up to five (5) specimens. Each batch of unexposed filters was examined for blank concentrations (Chow, 1995) and found to have no significant concentration of elements that could interfere with the present analysis. Before the measurement setup, a calibration was carried out using standard samples. Blank levels for PIXE were determined. Figure 3.2 shows beryllium transmission at various photon energies.



Figure 3.2 Beryllium transmission at various photon energies

The characteristic X-ray induced by the proton beam passed through a 125 μm thick Be absorber was detected by a Si(Li) detector with an energy resolution of 172 eV at 5.9 keV. The detector was positioned at an angle of 45° relative to the beam direction. Standard signal-processing electronics, such as a Canberra 2024 amplifier and a PCA3 multi-channel analyser (MCA) (Oxford nucleus) running on a PC-compatible computer were used. The standardisation procedure was carried out using several thin Micromatter standards of about 50 $\mu g/cm^2$ consisting of single or composed elements evaporated and covered an energy range from Si (1.74 keV) up to Pb (74.97 keV) (MicroMatter, 1994). The standardisation procedures as well as the data analysis were performed using the GUPIX code in the thin target approximation mode (Maxwell *et al.*, 1989, 1995; Campbell *et al.*, 2000).

The raw data from the GUPIX spectrum for the Fe standard are given in Figure 3.3.



Figure 3.3 PIXE spectrum from an Fe standard

Results from fitting theoretical models to X-ray spectra using GUPIX are summarised in table 3.3 (Khayelitsha) and table 3.4 (Ferrobank). Then the results are converted from ng/cm^2 to ppm and then to $\mu g/m^3$ by using the equation:

$$\mu g / m^3 = \frac{p p m \times M W}{0.02445} \tag{3.1}$$

where MW is molecular weight.

Figures 3.4 and 3.5 are a PIXE spectrum from an atmospheric aerosol sampling filter at Khayelitsha and Ferrobank, respectively.



Figure 3.4 A PIXE spectrum from an atmospheric aerosol sampling filter at the Khayelitsha site



Figure 3.5 A PIXE spectrum from an atmospheric aerosol sampling filter at the Ferrobank site

Element	Mean μg/m ³	Median μg/m ³	STD μg/m ³	Minimum µg/m ³	Maximum µg/m ³
Al	0.202	0.004775	0.347	LOD	0.83
Si	4.906	0.185	8.317	0.05	22.46
S	15.165	2.31	24.099	0.25	86.15
Cl	107.576	4.575	188.754	0.29	554.97
K	33.886	1.85	57.847	0.47	152.86
Ca	122.779	5.07	204.033	1.19	530.69
Ti	5.565	0.275	9.296	0.11	25.03
Cr	1.086	0.03	1.92	0.02	6.52
Mn	6.811	0.325	11.707	0.08	33.79
Fe	125.604	5.78	211.682	1.33	572.02
Cu	24.223	3.765	42.836	0.26	158.72
Zn	18.358	1.705	33.795	0.23	124.12
As	3.395	0.245	6.488	LOD	54.45
Br	6.426	0.425	13.633	LOD	50.05
Sn	33.182	0.58	123.149	LOD	554.37
Pb	7.297	0.75	16.137	LOD	64.24

Table 3.3:Descriptive statistics of the concentrations of the 16 elements as
determined by PIXE measured at the Khayelitsha sampling site

Table 3.4:Descriptive statistics of the concentrations of the 15 elements asdetermined by PIXE measured at the Ferrobank sampling site

Element	Mean μg/m ³	Median μg/m ³	STD μg/m ³	Minimum µg/m ³	Maximum μg/m ³
Al	0.3583	0.286	0.3373	LOD	0.927
Si	0.8217	0.651	0.7817	0.078	2.229
S	0.848	0.557	1.1553	0.029	3.123
Cl	0.0392	0.012	0.0514	LOD	0.108
K	0.17	0.14	0.1575	LOD	0.432
Ca	0.425	0.415	0.3488	LOD	1.033
Ti	0.2038	0.0935	0.2995	0.0059	0.787
Cr	0.1912	0.066	0.3277	0.0043	0.851
Mn	0.1004	0.026	0.1839	0.0045	0.472
Fe	1.0457	0.6325	1.1261	0.0069	2.832
Cu	0.0117	0.0104	0.008	0.0026	0.026
Zn	0.0787	0.028	0.1275	0.001	0.334
As	0.0024	0	0.0035	LOD	0.0092
Br	0.0133	0.0075	0.0141	LOD	0.033
Pb	0.0397	0.0255	0.0439	LOD	0.102

3.2.2 Enrichment factor analysis

Calculation of the enrichment factor (EF) values helps decide whether a certain element has additional sources other than its major source. EF values were calculated (Hobbs, 2000) for the PM_{10} samples using the equation:

The enrichment factor (EF) = $([X]_{air}/[Ref]_{air})/([X]_{source}/[Ref]_{source})$ (3.2)

Where [X] is the element of interest and [Ref] is the reference element for the particular source of interest (Hobbs, 2000). EF values near unity for a certain reference element [X] suggest that the source of interest is the primary source of element [X] and that it has not been altered by emissions from other sources. An EF much less than 1, or much higher than 1, indicates the presence of sources other than

the source of interest (Senaratne and Shooter, 2004). Table 3.5 shows the average of the crustal elements that were used in the study. Table 3.6, 3.7, 3.8, 3.9 are elemental composition of sea salt, domestic wood burning, coal burning and gasoline emission, respectively.

Atomic number	Element	Crustal average (ppm)	Crustal average (µg/m ³)
13	Al	81300	89.72
14	Si	277200	318.42
16	S	260	0.34
17	Cl	130	0.19
19	K	25900	41
20	Ca	36300	59.51
22	Ti	4400	8.62
24	Cr	100	0.21
25	Mn	950	2.1
26	Fe	50000	114.21
29	Cu	55	0.14
30	Zn	70	0.19
33	As	1.8	0.0055
35	Br	2.5	0.0082
50	Sn	2	0.0097
82	Pb	13	0.11
Source: Mason, 1982	:p46-47.		

 Table 3.5:
 The average of the elements in crustal rocks

Atomic number	Element	Concentration (ppm)	Concentration (µg/m ³)
13	Al	0.001	0.0000011
16	S	904	1.185
17	Cl	19400	28.13
19	К	392	0.627
20	Ca	411	0.674
22	Ti	0.001	0.00000196
24	Cr	0.0002	0.00000043
25	Mn	0.0004	0.00000899

Fe	0.0024		
10	0.0034	0.00000777	
Cu	0.0009	0.00000234	
Zn	0.005	0.0000134	
As	0.0026	0.00000797	
Br	67.3	0.22	
Sn	0.00081	0.00000392	
Pb	0.00003	0.00000254	
Source: Mason, 1982:p236-237.			
	Cu Zn As Br Sn Pb 2:p236-237.	Cu 0.0034 Cu 0.0009 Zn 0.005 As 0.0026 Br 67.3 Sn 0.00081 Pb 0.00003 2:p236-237. 2	

Table 3.7: Elemental Composition of biomass burning

Atomic number	Element	Concentration (ppm)	Concentration (µg/m ³)
13	Al	1345	1.484
14	Si	3815	4.382
16	S	980	1.285
17	Cl	392	0.568
19	K	1480	2.367
20	Ca	2017	3.306
22	Ti	77	0.151
25	Mn	90	0.202
26	Fe	702	1.603
29	Cu	3	0.0078
30	Zn	45	0.12
Source: Formenti e	t al., 2000:p24-7.		

 Table 3.8:
 Concentrations of some metallic elements in fossil fuels (Coal)

Atomic number	Element	Coal (ppm)	Concentration (µg/m ³)
13	Al	10000	11.035
16	S	6300*	8.261
22	Ti	500	0.98
24	Cr	10	0.021
25	Mn	50	0.112
26	Fe	10000	22.842
29	Cu	15	0.039
30	Zn	50	0.134
33	As	35	0.107
50	Sn	2	0.01
82	Pb	25	0.212
Source: Vouk et al.			

*Data taken from Gaus-Liu (Gaus-Liu, 2008)
Atomic number	Element	Gasoline (ppm)	Concentration (µg/m ³)
13	Al	0.01	0.00011
16	S	50*	0.0656
24	Cr	0.017	0.0000362
25	Mn	0.016	0.000036
26	Fe	1.07	0.0024
29	Cu	0.14	0.000364
30	Zn	0.16	0.000428
33	As	0.0015	0.0000046
82	Pb	400	3.39
Source: Vouk et al.			

Table 3.9: Concentrations of some metallic elements in fossil fuels (Gasoline)

*Data taken from DEAT (DEAT, 2007: Boroughs, 2007)

3.2.3 Source Apportionment by Unique ratios (SPUR)

The identification of sources contributing to the aerosols deposited on the collected samples is known as receptor modeling. Through PIXE analysis between 8 and 13 elements are detected on each analysed sample. Annegarn et al., 1988, showed that the combination of the limited number of elements can be counteracted by having time resolved samples. No attempt is made in this apportionment technique to account for the total sampled mass. Instead, there is an attempt to derive the contribution of a given number of sources and to calculate relative concentrations for each source from the detected elements. This is similar to the technique used for source apportionment by Absolute Principal Component Analysis (Annegarn *et al.*, 1992 and Maenhaut and Cafmeyer, 1987). By comparing the detected elements with time and size fraction it is possible to separate the contributing sources from stand alone key elemental indicators, for example Al for soil dust. The impact of a source allows one to determine unique ratios between elements for given sources, or alternatively, known ratios of each element to known elements for that source are utilised to extract the contribution of that source from the detected inorganic mass. This type of source

apportionment requires a good knowledge of the local and regional meteorology as well as the possible contributing sources. The contributing sources from both Cape Town and the Witbank area are fairly well understood (Piketh et al., 2003 and Held et al., 1994). SPUR is based on receptor modelling principles which have been used extensively for identifying contributing sources to receptor site samples (Gordon, 1980; Artaxo, *et al.*, 1988 and Rheingrover *et al.*, 1988).

Based on the elemental composition of the sources identified at Khayelitsha and Ferrobank a Source Apportionment by Unique Ratios (SPUR) has been attempted. The principle of SPUR is that the elemental ratios do not change over time in the atmosphere. SPUR analysis has been successfully employed by Annegarn et al. (1988) and Piketh, Tyson and Anne.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Meteorological conditions

In Cape Town the climate is characterised by low temperature and high humidity most of the year, and by distinctly marked seasonal variations in precipitation. Cape Town has a Mediterranean climate. The year can be divided into four seasons according to meteorological conditions: summer is from December to February with the day-time temperature averaging 23 °C. The prevailing wind during October to March (spring to autumn) is from SSE to SSW. It brings very little rain with it. Occasionally during summer the Cape will experience northerly 'berg winds' with an associated increase in ambient temperature. The 'South Easter' subsides slightly during February to March. The prevailing wind between May and August (autumn and winter) blows from N to NW. This wind is not as strong as the 'South Easter' and occurs less frequently. It precedes a cold front and is therefore followed by much-needed rain. The rainy season peaks during June and July (winter). During March to August the area has calm atmospheric conditions and low-level inversions (Wichmann, 2006). Cape Town experiences what is known as 'low-level temperature inversions'. This meteorological (weather) condition means that cooler air just above the surface of the ground – air that is full of city pollutants – becomes trapped by a layer of warm air above it. Sometimes this trapped layer of concentrated pollution can be as low as 30 m above ground or sea level, particularly in winter (Cape Town Air Quality, 2007). Weather data consisting of wind direction, wind speed, temperature, and relative humidity for Khayelitsha site was obtained from weather service at Cape

Town International Airport. Figures 4.1 and 4.3 shows the temperature data and descriptive statistics of the temperature at Khayelitsha.

Mpumalanga experiences distinct weather patterns in summer and winter that affect the dispersal of pollutants in the atmosphere. In the summer months, unstable conditions result in the mixing of air and rapid dispersion of pollutants in the atmosphere. Summer rainfall also removes pollutants through wet deposition. In contrast, the winter months are characterised by atmospheric stability caused by a persistent high-pressure system. This high-pressure system results in subsidence, causing clear skies and pronounced temperature inversions at night. The temperature inversion layer keeps the air pollutants trapped in the lower atmosphere, causing increasingly poor air quality (Environment, 2003). Weather data consisting of wind direction, wind speed, temperature, and relative humidity for Ferrobank site was obtained from South Africa Weather Service at Pretoria. Figures 4.2 and 4.4 shows the temperature data and descriptive statistics of the temperature at Ferrobank.

Plumes emitted from tall stacks during stable conditions at night can be transported thousands of kilometres downwind of the source before reaching ground level in a well-diluted state. During day-time, however, strong convection currents transport plumes upward and downward. Pollutants reach ground level close to the point of emission and are well diluted due to convective mixing (Turner, 2001).



Figure 4.1 Temperature data corresponding to sampling days at Khayelitsha



Figure 4.2 Temperature data corresponding to sampling days at Ferrobank



Figure 4.3 Time series of ambient temperature at Khayelitsha between 18 May and 19 July 2007



Figure 4.4Time series of ambient temperature at Ferrobank between
07 February and 11 March 2008

Wind roses for the duration of each sampling campaign were constructed to illustrate the differences in wind speeds and directions at the sampling site. For particulate matter concentrations, hourly averages were calculated. Then, for each hour, the concentrations were averaged across all the days to correspond with the sampling duration of the Partisol-plus sampler.

Wind roses are radial graphs for a specific location that summarises the occurrence of winds by direction and speed. The length of each direction line shows the percentage of time (frequency) that the wind blew from a particular wind direction; connecting the ends of the direction lines produces the characteristics pattern of the wind rose. The direction lines are divided into segments that represent the frequency of different wind speeds for that wind direction. The color of the wind rose line segments depicts speed categories. Wind roses were used to visualize the frequency of the incoming winds for the sampler for the duration of all the sampling days at our sampling sites.

The Khayelitsha site was classified as being in an urban setting by the South Africa Census. The weather conditions were mostly cloudy for the sampling periods with brief periods of clear skies on few days of our sampling periods. The average temperature was 15 °C for the twenty (20) days sampling. The prevailing winds during the sampling were light to moderate winds (6.7 to 13.6 m/s) from N to NW direction. The wind was calm 21.73 % of the time. Wind rose diagram for Khayelistha is shown in figures 4.5.



Figure 4.5 Wind rose showing the wind directions and speeds between 18 May and 19 July 2007 at Khayelitsha



Figure 4.6Wind rose showing the wind directions and speeds between
07 February and 11 March 2008 at Ferrobank

The Ferrobank site was classified as being in an industrial setting by the South Africa Census. The weather conditions were mostly clear skies for the sampling periods with brief period of cloudy sky on one day of our six sampling periods. The average temperature was 19 °C for the six (6) days sampling. The prevailing winds during the sampling were light (0.4 to 6.2 m/s) and predominantly from the western sector (~47 %). The wind was calm 16 % of the time. Wind rose diagram for Ferrobank is shown in figures 4.6.

4.2 Median elemental composition



The median elemental composition of PM_{10} from Khayelitsha and Ferrobank is presented in figure 4.7

Figure 4.7Median elemental composition of PM_{10} deduced by PIXE analysis
of the Partisol-plus samples for Khayelitsha and Ferrobank

In figure 4.7 the elemental composition for Khayelitsha is higher than for Ferrobank except for Al and Cr. At Khayelitsha, in most cases, Al concentration was below detection limit. Some elements are more common in both sampling sites with different concentrations due to the location of the sampling site. S, Cl, K, Ca, Fe, Zn, As, Br, Sn and Pb are on higher concentration at Khayelitsha than at Ferrobank. Al, Si, S, Ca, Cr, and Fe are on high concentration at Ferrobank, but only Al, Si and Cr are on high concentration at Ferrobank than Khayelitsha.

4.3 TEOM analysis at Khayelitsha

The hourly concentrations for each 24 h period were obtained for at least 20 days of samples taken at 1 h intervals in accordance with ISO 17024 guidelines. If these requirements were not met, a 24 h average was set as a missing value (that is, shows 'm' on the TEOM). PM_{10} concentrations exceeded the South African limit of $75 \ \mu g/m^3$ for 24 h three times during the Khayelitsha sampling period (figure 4.8). Since hourly limits for PM_{10} have not been set in South Africa, the 24 h limit is used. Figure 4.8 shows the diurnal TEOM results obtained from daily average concentrations of PM_{10} sampling at Khayelitsha for the entire sampling period (18 May to 20 July 2007). The daily average concentrations shown in figure 4.10 of ambient PM_{10} standard was exceeded on three occasions, on 20 June 2007 (day) $(124.38 \ \mu g/m^3)$, 20 June 2007 (night) $(102.71 \ \mu g/m^3)$ and 03 July 2007 (day) $(88.88 \ \mu g/m^3)$. These three periods were also characterised by very low temperature (figure 4.1). Low-level temperature inversions in the morning combined with evening wood-fires and re-circulation were the major contributor of PM_{10} pollution events. This is also confirmed by higher concentration of PM_{10} during the night and early hours of the morning. The highest concentrations were observed on the early morning

(i.e. between 3 and 5 am) of the 05 July and the night of 20 June between 9 and 10 pm with concentration of about $348 \,\mu\text{g/m}^3$. The temperature data corresponding to sampling days are shown in figure 4.1 (Khayelitsha) and figure 4.2 (Ferrobank).

Sampling day	Concentration $(\mu g/m^3)$		
18 May 2007	42.75		
19 May 2007	9.38		
23 May 2007	12.42		
29 May 2007	23.75		
30 May 2007	31.83		
31 May 2007	32.21		
20 June 2007	124.38		
21 June 2007	102.71		
03 July 2007	88.88		
04 July 2007	59.38		
05 July 2007	57.17		
18 July 2007	74.58		
19 July 2007	65.46		
20 July 2007	41.45		

Table 4.1:The average TEOM samples concentrations of PM_{10} at Khayelitsha



Figure 4.8 TEOM 24-hour samples concentration of *PM*₁₀ at Khayelitsha



Figure 4.9 E-sampler 12-hour concentrations of *PM*₁₀ at Ferrobank

4.4 Gravimetric analysis

The mass concentrations were obtained from the mass of particulate matter deposited on the filter on individual days, with a fixed the volume flow-rate of aerosol and total time of sampling. An electronic microbalance with a maximum attainable precision of $\pm 0.1 \ \mu g$ was used to weigh the aerosol samples. Note that 'D' represents day-time sampling (between 06:00 and 18:00) and 'N' represents night-time sampling (between 18:00 and 06:00). The mass concentration measured at Khayelitsha during the sampling campaign ranged from 23 to 193 μ g/m³ between 18 May to 19 July 2007 (figure 4.10). In most cases the mass concentration during the day-time was lower than the night-time concentration. The mass concentration measured at Ferrobank during the sampling campaign ranged from 11.1 to 103.7 μ g/m³ between 07 February and 11 March 2008 (only six samples) (figure 4.11).



Figure 4.10 PM_{10} mass concentrations (12 h average) determined from gravimetric analysis of the collected samples at Khavelitsha



Figure 4.11 PM_{10} mass concentrations (12 h average) determined from
gravimetric analysis of the collected samples at Ferrobank

The advantage of having several different methodologies for aerosol measurements is that it is possible to compare parameters measured by two different techniques. Figure 4.12 shows the aerosol mass concentration measured by gravimetric analysis of the Partisol-plus samples and with the real-time TEOM aerosol mass monitor (Khayelitsha). It is important to note that the data does not represent a continuous time series. The TEOM data were reduced to the same 12 h collection time as the Partisol-plus data. The overall comparison between the two methodologies is fairly good. The TEOM results show slightly lower concentrations, possibly because the TEOM has to heat up the air before collection to about 40 °C which results some volatile organic mass being lost. For the most part the nighttime concentrations are

higher than those recorded during the day. This is almost certainly associated with the decreasing dispersion potential at night. Aerosols collect in the Cape Town area over night as a result of the development of highly stable surface inversion conditions. During the morning the surface inversion lifts and the particulates are allowed to disperse (Piketh *et al.*, 2004). The one exception to the higher nightime concentrations of particulates was observed on 4 July. The ambient temperatures were found to be higher on this day which indicates a change in the synoptic scale circulation over Cape Town.



Figure 4.12 Temporal series of two different measurements of aerosol mass concentrations. The Partisol-plus plot is the PM_{10} concentration obtained by gravimetric analysis of Teflon filters. The TEOM plot is the PM_{10} concentration obtained by the TEOM real-time aerosol mass monitor at Khayelitsha in 2007

Figure 4.13 shows the aerosol mass concentration measured by gravimetric analysis of the Partisol-plus samples and of the real-time E-sampler data (Ferrobank). The E-sampler data were reduced to the same 12 h collection time as the Partisol-plus data. The key thing is the pattern of impact which is identical in both sampling methodologies despite the measured concentration being significantly different. The high night time concentrations of aerosols at Ferrobank are associated with atmospheric stability.



Figure 4.13 Temporal series of two different measurements of aerosol mass concentrations. The Partisol-plus plot is the PM_{10} concentration obtained by gravimetric analysis of polycarbonate filters. The Esampler plot is the PM_{10} concentration obtained by the E-sampler real-time aerosol mass monitor at Ferrobank in 2008

4.5 Enrichment factor

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Table 4.2 (Khayelitsha) and table 4.3 (Ferrobank) show the enrichment factor values for the particulate matter at both sites at the two monitoring sites respectively. As indicated in the methodology EF's were calculated for all the elemental data using a tracer element each potential source.

Elements	Si	Cl	Pb	K
	(Soil)	(Sea salt)	(Gasoline)	(Wood)
Al	0.149	48076.72727	8536.636364	0.00950628
Si	1			0.078204989
S	2894	3.346401772	107.3973704	0.824360708
Cl	36748.07	1		13.22954804
K	53.642	14.13229665		1
Ca	133.931	47.63402315		2.594174548
Ti	41.9	742431.0714		2.574386821
Cr	335.65	660727.907	13937.39503	
Mn	210.51	1980677.419	87895.16667	2.355282178
Fe	71.379	4227030.296	24313.50555	5.473282938
Cu	11229.82	2706851.325	30915.86868	216.9264462
Zn	6271.112	358237.6493	19926.78435	10.685427
As	40063.59	111390.5646	340916.087	
Br	50862.73	7.637295		
Sn	222025.9	2213443.495		
Pb	4305.51	7512038.976	1	

Table 4.2:Enrichment factors for particulate matter analysed with PIXE
(Khayelitsha)

At Khayelitsha all elements the detected elements are highly enriched relative to soil dust (Si). These are referred to as the enriched or anomalously enriched elements (AEEs). With the exception of Al due to the PIXE setup at iThemba LABS, Al on this setup is below detection limit in most cases. Overall the enrichment factors at Khayelitsha indicate major enrichment for Chlorine (tracer for sea salt) Pb and Br (both tracers for gasoline) and Cu, Zn, As and Sn. The sources of the later elements are more difficult to pin to a specific source. Lesser enrichment is observed for K (tracer for wood burning). Relative to the tracer element of K other elements such as

Ca, Ti, Mn, and Fe have values that range from 1 and 10, indicating that they are present in the aerosol in roughly wood proportions. These are termed the wood or non-enriched elements (NEEs).

Elements	Si	Pb	Fe
	(Soil)	(Gasoline)	(Coal)
Al	1.58	2781399.13	2.42029
Si	1		
S	966.5	1103.817	5.3173E-06
Cl	79.95		1.03545E-08
K	1.61		2.01462E-06
Ca	2.78		4.6854E-06
Ti	9.16		0.77261
Cr	352.82	451012.428	3.30395
Mn	18.53	238144.417	0.82983
Fe	3.55	37205.321	1
Cu	32.29	2744.692	0.03715
Zn	160.51	15701.464	0.04364
As	169.1	44551.528	0.00224
Br	628.53		4.49203E-07
Pb	139.86	1	1.16137

Table 4.3:Enrichment factors for particulate matter analysed with PIXE
(Ferrobank)

For Ferrobank, the detected aerosol soil dust element is Si. The EF for Al (1.58) as an element of soil dust is close to unity. The EF for K (1.61) is also close to unity with respect to Si. The enrichment factor of Al, K, Ca, Ti, Fe are less than 10, suggesting that they are present in the aerosol in crustal proportions which implies that they are non-enriched elements relative to soil dust.

For gasoline, Pb is the reference element. All the elements are highly enriched. Indicating that gasoline is unlikely to have been responsible for the bulk of the aerosols detected at Ferrorbank.

Interestingly, Fe exhibited a contribution from Mn (0.829), Cr (0.773)and Pb (1.161) in addition to coal combustion emissions, both of which were close to unity, suggesting that, in addition to coal combustion emissions, industry emission also contributes to the Fe loading, since Cr and Mn are elements of industrial emission.

The EF value for Pb (1.161) as an element of gasoline, is close to unity, suggesting that gasoline also contributes to coal combustion emissions.

The days with a low concentration of particulate matter at the Khayelitsha site are 18 May (night) (figure 4.14), 23 May (day) (figure 4.15) and 29 May (day) (figure 4.16). The days with a high concentration of particulate matter at the Khayelitsha site are 20 June (day) (figure 4.17), 20 June (night) (figure 4.18) and 03 July (day) (figure 4.19). All these days show lower (higher) concentrations on PIXE analysis. They also show a lower (higher) concentration on TEOM analysis.



Figure 4.14 Enrichment factor of Si on 18 May (N) at Khayelitsha



Figure 4.15 Enrichment factor of Si on 23 May (D) at Khayelitsha



Figure 4.16 Enrichment factor of Si on 29 May (D) at Khayelitsha



Figure 4.17 Enrichment factor of Si on 20 June (D) at Khayelitsha



Figure 4.18 Enrichment factor of Si on 20 June (N) at Khayelitsha



Figure 4.19 Enrichment factor of Si on 03 July (D) at Khayelitsha

Figures 4.14, 4.15 and 4.16 show the enrichment factor of Si at **Khayelitsha** on days with lower concentrations of particulate matter and figures 4.17, 4.18 and 4.19 shows the enrichment factor of Si at **Khayelitsha** on days with higher concentrations of particulate matter. S and Cl are the dominant elements with higher concentrations on all days with lower and higher concentrations of particulate matter. The concentration of Fe remains stable on days with lower and higher concentrations of particulate matter.

Figures 4.20, 4.21, 4.22, 4.23, 4.24and 4.25 show the enrichment factor of Si at **Ferrobank** on all sampling days. S, Cl, Cr, Br and Pb are the dominant elements on all days with higher concentrations of particulate matter.

Figures 4.26 show that all elements are highly enriched with respect to soil dust at **Khayelitsha**. S, Cl, Cu and As are dominant elements with very high concentrations.

Figures 4.27 show the enrichment factor of Si on all sampling days at **Ferrobank**. The elements S, Cr, Cu, Zn, and Br are highly enrich on all sampling days. Al and Fe are close to unity in most of the days.



Figure 4.20 Enrichment factor of Si on 07 February (D) at Ferrobank



Figure 4.21 Enrichment factor of Si on 07 February (N) at Ferrobank



Figure 4.22 Enrichment factor of Si on 10 February (D) at Ferrobank



Figure 4.23 Enrichment factor of Si on 10 March (D) at Ferrobank



Figure 4.24 Enrichment factor of Si on 10 March (N) at Ferrobank



Figure 4.25 Enrichment factor of Si on 11 March (D) at Ferrobank



Figure 4.26 Enrichment factor of Si on days with lower and higher concentration at Khayelitsha



Figure 4.27 Enrichment factor of Si on all sampling days at Ferrobank

4.6 SPUR results

The source apportionment of aerosols study at Khayelitsha and Ferrobank are presented. Elemental concentrations will be used to apportion the aerosols between four identifiable source categories of soil dust, sea salt, domestic wood burning (coal burning at Ferrobank) and gasoline. The elemental concentration are taken from table 3.3 and 3.4 for Khayelitsha and Ferrobank respectively. Table 3.5, 3.6, 3.7, 3.8 and 3.9 are used to obtain the ratio to Si, Cl, K, Fe, and Pb for crustal average, sea salt, domestic wood burning, coal burning, and gasoline, respectively.

The ratios of elemental concentrations in standard crustal material with respect to Si, standard sea salt composition w.r.t. Cl, domestic wood burning w.r.t. K, coal burning w.r.t. Fe and gasoline w.r.t. Pb are shown in table 4.4

	Crustal elemental composition	Sea salt	Domestic wood burning	Coal burning	Gasoline
Elements	Ratio to Si	Ratio to Cl	Ratio to K	Ratio to Fe	Ratio to Pb
Ca	0.13	0.0212	1.363		
Fe	0.18	1.753x10 ⁻⁷	0.474		0.0027
Cu	0.000198	4.639x10 ⁻⁸	0.002	0.0015	0.00035
Zn	0.0002525	2.57x10 ⁻⁷	0.0304	0.005	0.0004
Cr	0.00003606	1.031x10 ⁻⁸		0.0001	
S	0.000938	0.0466	0.6622	0.0063	0.125
Cl	0.000496				

Table 4.4:Ratios of elemental concentrations

Soil dust

Soil has previously been identified as a significant component of South African aerosol in many studies (Piketh, 1999a). In order to obtain a reliable estimate of the soil mass associated with PM_{10} for major crustal components associated with soil fingerprints for the Khayelitsha site and the Ferrobank site, the seven elements, Ca, Fe, Cu, Zn, Cr, S and Cl were used. The source profile derived from atmospheric aerosol samples is used to apportion appropriate to soil dust. The total soil component is made of the following equation:

$$[Soil]_{i} = [Si]_{i} + [Ca]_{soil} + [Fe]_{i} + [Cu]_{i} + [Zn]_{i} + [Cr]_{i} + [S]_{i}$$
(4.1)

The equation is breakdown into individual concentrations of elements as follows:

$$[Ca]_{res1} = [Ca]_i - [Ca/Si]_{soil} x [Si]_i$$
 (4.2)

$$[Fe]_{res1} = [Fe]_i - [Fe/Si]_{soil} \times [Si]_i$$

$$(4.3)$$

$$[Cu]_{res1} = [Cu]_i - [Cu/Si]_{soil} x [Si]_i$$
(4.4)

$$[Zn]_{res1} = [Zn]_i - [Zn/Si]_{soil} x [Si]_i$$
(4.5)

$$[Cr]_{res1} = [Cr]_i - [Cr/Si]_{soil} x [Si]_i$$
 (4.6)

Sea salt

Sea salts are detected through the presence of Cl in sampled aerosols. Strictly speaking, Cl is not the best indictor for identifying sea-salt aerosols owing to its loss during transport (Piketh, 1999b). Frequently Cl in sea-salt particles is observed with deficit with respect to elements such as Na and Mg, specifically in the sub-micron range. Na and Mg are considered better indicators but, due to the limitation of the PIXE system at iThemba LABS, Na and Mg cannot be detected. The six elements, Ca, Fe, Cu, Zn, Cr and S were used to define the 'sea-salt fingerprint' at Khayelitsha. No sea salt fingerprint at Ferrobank. In the absence of another key trace element, chlorine is used for the detection of sea-salt aerosols using the relationship:

$$[Sea salt] = [Cl]_i + [Cl]_i \times (S/Cl)_{sea salt} + [Cl]_i \times (Ca/Cl)_{sea salt} + [Cl]_i \times (Fe/Cl)_{sea salt} + [Cl]_i \times (Cu/Cl)_{sea salt} + [Cl]_i \times (Zn/Cl)_{sea salt} + [Cl]_i \times (Cr/Cl)_{sea salt}$$

$$(4.8)$$

Then the equation is breakdown into the following to obtain the residual:

$$[Ca]_{res2} = [Ca]_{res1} - [Ca/Cl]_{sea salt} x [Cl]_i$$

$$(4.9)$$

$$[Fe]_{res2} = [Fe]_{res1} - [Fe/Cl]_{sea salt} x [Cl]_i$$

$$(4.10)$$

$$[Cu]_{res2} = [Cu]_{res1} - [Cu/Cl]_{sea salt} x [Cl]_i$$
(4.11)

$$[Zn]_{res2} = [Zn]_{res1} - [Zn/Cl]_{sea salt} x [Cl]_i$$

$$(4.12)$$

$$[Cr]_{res2} = [Cr]_{res1} - [Cr/Cl]_{sea salt} \times [Cl]_i$$
(4.13)

$$[S]_{res2} = [S]_{res1} - [S/Cl]_{sea salt} x [Cl]_i$$
(4.14)

Domestic wood burning

At Khayelitsha, domestic wood burning also contributes to air pollution due to burning of dead vegetation. This includes the human-initiated burning of vegetation for clearing land and land-use change as well as natural, lighting-induced fires. Scientists has estimate that humans are responsible for about 90 % of domestic wood burning with only small percentage of natural fires contributing to the total amount of vegetation burned (NASA, 2009). Domestic wood burning is a seasonal source with its highest intensity between June and October. Domestic wood burning particulates impact climate and can also affect human health when they are inhaled, causing respiratory problems. Wood burning is source of energy for fire burning at Khayelitsha and whereas at Ferrobank they are using coal. It is very difficult to obtain coal at Khayelitsha in Western Province of South Africa than Mpumalanga Province due to transportation of coal. K has been used as the indicator of domestic wood burning. The apportionment equation is:

$$[wood burning] = [K]_i + [Ca/K]_{wood} x [K]_i + [Fe/K]_{wood} x [K]_i + [Cu/K]_{wood} x [K]_i + [Zn/Cl]_{wood} x [Cl]_i + [S/K]_{wood} x [K]_i$$
(4.15)

Then the equation is breakdown into the following to obtain the residual:

$$[Ca]_{res3} = [Ca]_{res2} - [Ca/K]_{wood} x [K]_i$$
(4.16)

$$[Fe]_{res3} = [Fe]_{res2} - [Fe/K]_{wood} x [K]_i$$
 (4.17)

$$[Cu]_{res3} = [Cu]_{res2} - [Cu/K]_{wood} x [K]_i$$
(4.18)

$$[Zn]_{res3} = [Zn]_{res2} - [Zn/Cl]_{wood} \times [Cl]_i$$
(4.19)

$$[S]_{res3} = [S]_{res2} - [S/K]_{soil} x [K]_i$$
(4.20)

Mpumalanga is energy mecca of South Africa on which there are so many coal power stations. Burning coal is a leading cause of smog, acid rain, global warming, and air toxics. Coal pollutes when it is mined, transported to the power plant, stored, and burned. A typical (500 megawatt) coal plant burns 1.4 million tons of coal each year. Fe has been used as indicator for coal burning at Ferrobank. The apportionment equation is:

 $[\text{coal burning}] = [\text{Fe}]_i + [\text{Fe}]_i \times [\text{Cu/Fe}]_{\text{coal}} + [\text{Fe}]_i \times [\text{Zn/Fe}]_{\text{coal}} + [\text{Fe}]_i \times [\text{Cr/Fe}]_{\text{coal}}$ (4.21)

Then the equation is breakdown into the following to obtain the residual:

$$[S]_{res2} = [S]_{res1} - [S/Fe]_{coal} x [Fe]_i$$
(4.22)

$$[Cu]_{res2} = [Cu]_{res1} - [Cu/Fe]_{coal} x [Fe]_i$$
(4.23)

$$[Zn]_{res2} = [Zn]_{res1} - [Zn/Fe]_{coal} x [Fe]_i$$
(4.24)

$$[Cr]_{res2} = [Cr]_{res1} - [Cr/Fe]_{coal} x [Fe]_i$$
 (4.25)

Gasoline

Again, S can serve as a tracer for traffic exhaust (petrol and diesel engines) at Khayelitsha, as there are no coal-fired plants around Khayelitsha. In South Africa, ultra-low sulphur diesel with only 50 ppm of S is available at some Sasol, Shell, Total and Bp filling stations, though not yet from Engen filling stations (Boroughs, 2007). Diesel emissions account for 42 % of Cape Town infamous brown haze, more than any other source measured by the University of Cape Town's landmark Brown Haze 1 study undertaken by Wicking-Baird *et al.* in 1997 (Boroughs, 2007). Since Ferrobank is situated at Witbank where there are many coal-fired power stations, S could not be used as a tracer – so, for both sites, Pb was used as a tracer. The four elements, Fe, Cu, Zn, and S were used to define the 'gasoline fingerprint' at Khayelitsha and at Ferrobank only Zn and Cu are the only elements that used for gasoline. The apportionment equation is:

$$[Gasoline] = [Pb]_i + [Pb]_i x (Fe/Pb) + [Pb]_i x (Cu/Pb) + [Pb]_i x (Zn/Pb)$$
(4.26)

Then the equation is breakdown into the following to obtain the residual:

$$[Fe]_{res4} = [Fe]_{res3} - [Fe/Pb]_{gasoline} x [Pb]_i$$
(4.27)

$$[Cu]_{res4} = [Cu]_{res3} - [Cu/Pb]_{gasoline} x [Pb]_i$$
(4.28)

$$[Zn]_{res4} = [Zn]_{res3} - [Zn/Pb]_{gasoline} x [Pb]_i$$

$$(4.29)$$

$$[S]_{res4} = [S]_{res4} - [S/Pb]_{gasoline} x [Pb]_i$$

$$(4.30)$$

Table 4.5:Elemental co	oncentrations to	or each	identified	source c	alculated

	Soil	Sea salt	Domestic wood burning	Coal burning	Gasoline	Residual
	Khayelitsha					
Ca	0.6378	2.281	46.187			73.7
Fe	0.8831	0.0000215	16.012		0.0197	108.628
Cu	0.0009714	0.0000538	0.0678		0.00255	24.1507
Zn	0.001769	0.000323	1.03		0.00292	17.324
Cr	0.004602	0.0000111				
S	0.002434	5.013	24.439		0.9121	
Cl	0.0023					
			Ferrobank			
Ca	0.1068					
Fe	0.1479					
Cu	0.0001627			0.00157	0.000139	0.0016
Zn	0.0002075			0.00523	0.0000159	0.0052
Cr	0.002963			0.0001046		0.0001
S	0.00077			0.0066	0.005	

from source apportionment by unique ratio

Contribution to the detected elemental mass by PIXE has been calculated for each source, for soil, sea salt, domestic wood burning, coal burning and gasoline:

$$[Soil]_{detected} = [Si]_{i} + \Sigma [Si]_{i} \times \{[Ca/Si] + [Fe/Si] + [Cu/Si] + [Zn/Si] + [Cr/Si] + [S/Si] \}$$
(4.31)

 $[Sea salt]_{detected} = [Cl]_i + \Sigma [Cl]_i x \{[Ca/Cl] + [Fe/Cl] + [Cu/Cl] + [Zn/Cl] + [Cu/Cl] +$

$$Cr/Cl] + [S/Cl] \}$$
 (4.32)

 $[Domestic wood burning]_{detected} = [K]_i + \Sigma [K]_i x \{ [Ca/K] + [Fe/K] + [Cu/K] + K \}$

$$[Zn/K] + [S/K]$$
 (4.33)

$$[Coal]_{detected} = [Fe]_i + \Sigma [Fe]_i x \{ [Cu/Fe] + [Zn/Fe] + [Cr/Fe] \}$$
(4.34)

$$[Gasoline]_{detected} = [Pb]_i + \Sigma [Pb]_i \times \{[Fe/Pb] + [Cu/Pb] + [Zn/Pb] + [S/Pb]\}$$

(4.35)

So that the percentage contribution for each source has been calculated from equation 4.36 for soil dust and other calculation has been done in similar manner with respect to each source. The results are being presented on table 4.5.

$$[Soil]_{detected} / [Total_{elements}] \times 100 \%$$
(4.36)

Source	Soil	Sea salt	Domestic wood burning	Coal burning	Gasoline	Residual
		L	Khayeltsha			
%	1.246	22.24	23.17		1.594	51.75
			Ferrobank			
%	24.77			24.18	0.913	50.137

Table 4.6:Source apportionment of filter samples

The source apportionment reveals that soil dust, sea salt, domestic wood burning and gasoline account for 48.25 % of the detected source at Khayelitsha. The domestic wood burning dominated the contribution in percentage with 23.17 % and sea salt with 22.24%. The domestic wood burning is a source with a strong seasonal signature. It can be expected that the contribution of wood burning in the samples collected for this study are representative of winter, the period of highest wood usage. The significant contribution of sea salt was expected as a result of the proximity of the site to the ocean. The soil dust and gasoline contribute very little at Khayelitsha. The biggest contribution was found to be from a residual source. This source could be made-up of many sources and it was beyond the scope of this research to try and break this down into all the contributing sources

At Ferrobank, the source apportionment indicates that the soil dust, coal burning and gasoline emissions account for about 49.863 % of detected source. The soil dust and coal are dominates factor with 24.77 % and 24.18 % respectively. Since this sampling period happen during summer season, the higher percentages of soil dust may be coming from unpaved roads which were very close to our sampling area. The main source of energy in Mpumalanga Province is coal, so it is not surprise to obtain high percentages of coal which at the sampling site is likely to be mostly from domestic coal combustion. The gasoline contribute very close to 1 %, this may due to the petrochemical company was located approximately 2 km from the sampling site. Similar to Khayelitsha the biggest contribution to the particulate load was from an unidentified source or sources. Ferrobank is an industrial area with a large Ferrochrome company directly opposite the monitoring site. The residual source contribution was highly enriched in element like Fe, Cr, and Ti are typically associated with the smelting industry. It is therefore likely that the main contribution of particulate matter to the collected samples was from the Ferrochrome industry.
CHAPTER 5 SUMMARY AND CONCLUSIONS

Particulate matter concentrations were measured at Khayelitsha (an urban site in Cape Town) and at Ferrobank (an industrial site at Witbank). The study of PM_{10} particles in the air of the Khayelitsha and Ferrobank sampling sites revealed the presence of Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, As, Br, Sn, and Pb, leading to the characterisation of different sources of these elements: soil dust, sea salt, gasoline emissions and wood and coal burning. Although these elements (with the exception of Sn) were found in the particulate matter collected at Ferrobank, their mass concentrations were not above the daily limit (75 $\mu g/m^3$) of air quality standards recommended by the South African legislation. Since we have 20 samples, the particulate matter concentrations exceeded the air quality standards regulation three times at Khayelitsha with concentrations of 124.38 $\mu g/m^3$, 102.71 $\mu g/m^3$ and 88.88 $\mu g/m^3$ on 20 June 2007 (day), 20 June 2007 (night) and 03 July 2007 (day), respectively.

The main findings of the study are summarise as follows:

• Source apportionment show that the major sources of atmospheric aerosols at the Khayelitsha sampling site were sea salt and wood burning. The soil dust and gasoline emission contributes little percentages. This is also in agreement with the previous study undertaken at the site, which shows that PM_{10} contributes to air pollution (Wicking-Baird *et al.*, 1997; Walton, 2005). The township of Khayelitsha is an important source of aerosol with reduced visibility in the early morning due to burning of wood for heating and cooking.

- Most of the contribution which accounted for 51.75 % may be coming from industrial emission which was not account for in this study. The biggest contribution was found to be from a residual source. This source could be made-up of many sources and it was beyond the scope of this research to try and break this down into all the contributing sources
- Source apportionment shows that the main contributor of air pollution at the Ferrobank site are soil dust and coal burning. Gasoline contributes only 0.913 %.
- The residual contribution accounted for 50.137 %. The residual source contribution was highly enriched in element like Fe, Cr, and Ti are typically associated with the smelting industry Ferrochrome is a significant source of Cr emissions as it was adjacent to the sampling site
- Enrichment factor of industrial elements of Cr and Mn contributes to Fe emission as there values are close to unity. This shows that the Cr and Mn are coming from neighbouring industry. For the Pb it suggests that its value close to unity shows that it comes from the nearest petrochemical industry.

The advantage of having several different methodologies of aerosol measurements is that it is possible to compare parameters measured by two different techniques. The aerosol mass concentration measured by gravimetric analysis of the Partisol-plus samples and with the real TEOM data were reduced to the same 12 h collection time as the Partisol-plus sampler at Khayelitsha. Similarly the aerosol mass concentration was established for the Partisol-plus samples and the E-sampler samples

from Ferrobank. The TEOM results show slightly lower concentrations, possibly because the TEOM has to heat up the air to 40 °C before collection. In standard operation the TEOM maintains a constant air stream temperature of 50 °C. A number of studies have argued that operation at this temperature causes volatilization of particulate semi-volatile material (PSVM) component of PM, leading to systematic under-measurement of the true PM mass in the sampled air (Allen *et al.*, 1997; Chung *et al.*, 2001; Cyrys *et al.*, 2001; Eatough *et al.*, 2003; Price *et al.*, 2003;). The mass of volatile material lost is associated with type of volatiles within the sampled aerosol, which are site-specific and may vary from day-day (Cyrys *et al.*, 2001). As a consequence no standardized correction factors have been developed for use with the TEOM (Meyer *et al.*, 2000; Price *et al.*, 2003). In this study, the TEOM air stream was heated to 40 °C.

Specific meteorological conditions are necessary for the accumulation of pollutants in the atmosphere. Measurements of ambient temperature, wind speed and direction, relatively humidity and rainfall were made continuously during the particle sampling period, and recorded as hourly averages. At Khayelitsha during particle sampling, the daily average of air temperature and wind speed were 15 °C and 2.56 m/s, respectively. At Ferrobank the corresponding values were 19 °C and 3 m/s. The frequent passage of cold fronts over Khayelitsha brings rain and results in cleansing of the atmosphere. Low temperature inversions occurred during the night at Khayelitsha which affected the mass concentrations. The most of the highest PM_{10} concentrations were observed between 06:00 to 08:00 which coincides with increased traffic volumes and human activity during this period.

The primary limitation of this study was to use of concentrations from 12-hour integrative sampling in association with wind data averaged over 1 min interval. A more accurate portrayal of the influence of wind on the concentrations in the sampling area would be obtained by using real time sampling of the concentrations along with wind data. Another limitation of the study was the reliance on information from local airport for wind data at Cape Town International Airports for Khayelitsha and SAWS for Ferrobank data.

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