

**CHARACTERISATION OF DUST FALLOUT AROUND THE CITY OF
TSHWANE (CoT), GAUTENG, SOUTH AFRICA**

By

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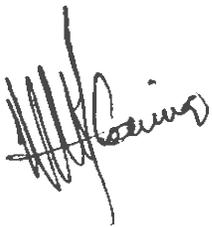
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April 2016

DECLARATION

I, Marks Matee Sebaiwa, declare that “**Characterisation of dust fallout around the City of Tshwane (CoT), Gauteng, South Africa**” is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.



.....

SIGNATURE

(Mr. MM Sebaiwa)

.....

DATE

DEDICATION

I dedicate this research study to:

My parents, who raised, nursed, supported, encouraged and most importantly showed me the way of the Lord: My mother, Jerminah Kwena Sebaiwa and my father, Wilson Tlabo Sebaiwa.

EBENEZER!!!!

My wife, Alvenia Ngwakwana Sebaiwa (the bone of my bone, the flesh of my flesh) for your words of encouragement and personal sacrifices.

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ABSTRACT

The aim of the project was to study the mineral, chemical and morphological characteristics of the fallout dust samples. The dust fallout samples were collected at five different sites following the internationally accepted standard procedure for collection and analysis, South African National Standard and American Standard for Testing Methods (ASTM) D1739-98 (2010). Passive single buckets containing $\frac{3}{4}$ of distilled water and 10.0 ml of sodium hypochlorite (NaOCl) solution, hoisted at a height of about 2.5 m were exposed from March – June 2013 and were collected every month, taken to the laboratory for characterization. First, the samples were filtered and mass concentrations per month were gravimetrically measured. The samples were then prepared for further characterization by the MicroScan Particle Analyser (MSPA)(Microscope UOP UB 100j) which measured the mineral content and the Scanning Electron Microscope - Energy Dispersive X- ray (SEM - EDX) measured the images of different particles (size, shape) and their elemental content.

The results from the MicroScan analysis showed the prevalence of sandy rounded-shaped quartz (SiO_2) particles across all sites. Minerals detected within the crustal material at all sites were quartz (SiO_2), haematite (Fe ; Fe_2O_3 ; Al_2O_3), feldspar (Na , K , Mg , Ca : $\text{Al}_2\text{Si}_2\text{O}_8$), garnet (SiO_4), aluminium silicates ($\text{Al}_2\text{Si}_2\text{O}_8$) and calcium hydroxide [$\text{Ca}(\text{OH})_2$]. Evidently, sites A, B and C dominated the abundance of these minerals. On the other hand, sites D and E showed fine and rounded quartz and quartzite with various trace metal oxides. Measured elements in decreasing concentrations were Si, Ca, P, Al, K, S, Fe, Cu, Ti and Mg. Both coarse particle (2.5 - 10.0 μm) and fine particle sizes ranges (< 1.0 to 2.5 μm) were detected. Large irregular shaped particles sizes were common and were linked to crustal material. The results provide good baseline information which requires further characterization of samples by different analytical techniques and validation of possible sources.

The ICP-MS was used to determine the elemental composition of dust fallout and the mean concentration of the elements of concern ranged from 1.1 - 2.6 for As, 0.2 - 0.6 for Cd, 17.0 - 21.9 for Ni, 449.8 - 751.1 for Pb, 9.9 - 22.3 for V and 101.7 - 293.0 $\mu\text{g}/\text{m}^3$ for Zn. The elements such as Cd exceeded the set limit 0.005 $\mu\text{g}/\text{m}^3$ by OSHA (2015) and NIOSH (2007); Pb exceeded the set standard of 0.5 $\mu\text{g}/\text{m}^3$ set by OSHA (2015), NIOSH (2007), WHO (2000),

USEPA (2012) and DEA (2013). The rest of the elements fell within the set guidelines by various regulatory national and international bodies.

The study concludes that, although, all the sampling sites recorded the dust fallout rates within the SANS 1929 (2011) and DEA (2013) average RESIDENTIAL limit of 600 mg/m²/day, the future accumulation and exceedances cannot be ruled out owing to the increasing developments in urban areas.

ABBREVIATIONS AND ACRONYMS

USEPA	: United States Environmental Protection Agency
PBL	: Planetary boundary layer
PM	: Particulate Matter
PM_{2.5}	: Particles with an aerodynamic diameter of less than 2.5 µm
PM₁₀	: particles with an aerodynamic diameter of less than 10 µm
PAHs	: Polycyclic Aromatic Hydrocarbons
AQA	: Air Quality Act
APPA	: Atmospheric Pollution Prevention Act
AQM	: Air Quality Management
AQMP	: Air Quality Management Plan
APINA	: Air Pollution Information Network for Africa
ASTM	: American Standard for Testing Methods
ATSDR	: Agency for Toxic Substances and Disease Registry
CoT	: City of Tshwane
CAA	: Clean Air act
CAPCO	: Chief Air Pollution Control Officer

DEA	: Department of Environmental Affairs
DEAT	: Department of Environmental Affairs and Tourism
TSP	: Total suspended particles
ICP-MS	: Inductively Coupled Plasma-Optical Emission Spectrometry
IPCC	: Intergovernmental Panel on Climate Change
ISO	: International Standardisation Organisation
IWMP	: Integrated Pollution and Waste Management
NAAQS	: National Ambient Air Quality Standards
NGOs	: Non-Governmental Organisations
NIOSH	: National Institute for Occupational Safety and Health
RPD	: Regional Policy Dialogue
SAWS	: South African Weather Services
SAAQIS	: South African Air Quality Information System
SEM-EDX	: Scanning Electron Microscope-Energy Dispersive X-ray
SPSS	: Statistical Package for the Social Science
SIMRAC	: Safety in Mines Research Advisory Committee
TEOM	: Tapered Element Oscillating Microbalance
WHO	: World Health Organization
OSHA	: Occupational Safety and Health Administration
OC	: Organic carbon
EC	: Elemental carbon
TSP	: Total suspended particles
VOCs	: Volatile organic compounds

TABLE OF CONTENTS

DECLARATION	ii
DEDICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
ABBREVIATIONS AND ACRONYMS	vi
TABLE OF CONTENTS	viii
LIST OF FIGURES	xi
LIST OF TABLES	xiii
CHAPTER 1: INTRODUCTION	1
1.1 THE EARTH’S ATMOSPHERE	1
1.2 OVERVIEW OF AIR POLLUTION	2
1.2.1 Sources and types of air pollutants	3
1.2.1.1 Stationery sources	4
1.2.1.2 Mobile sources	5
1.3 RATIONALE OF THE RESEARCH	6
1.4 PROBLEM STATEMENT	6
1.5 AIMS AND OBJECTIVES	7
1.5.1 Aim of the study	7
1.5.2 Objectives	7
CHAPTER 2: LITERATURE REVIEW	8
2.1 DEFINITION OF AIRBORNE DUST	8
2.2 CLASSIFICATION AND COMPOSITION OF DUST FALLOUT SAMPLES	9
2.2.1 Classification of dust fallout samples	9
2.2.2 Particle size and size distribution	12
2.2.3 Dust fallout sample composition	14
2.3 IMPACTS OF DUST FALLOUT RATES	19
2.3.1 Impacts on human health	20
2.3.2 Impacts on Environment and Ecosystems	21
2.3.3 Impact on climate	22
2.3.4 Impact on visibility reduction	23

2.3.5	Impacts on building materials.....	23
2.4	DUST FALLOUT MONITORING METHODS.....	23
2.4.1	Passive samplers.....	24
2.4.2	Active samplers.....	29
2.5	TRANSPORT AND DISPERSION OF AIR POLLUTANTS.....	32
2.5.1	Wind speed and direction.....	33
2.5.2	Atmospheric stability.....	34
2.6	AIR QUALITY LEGISLATION AND POLICY CONTEXT.....	34
2.6.1	International Context.....	34
2.6.2	Regional/Continental (African State) Context.....	35
2.6.3	National Context.....	36
2.6.4	Local Context.....	38
2.7	AMBIENT AIR QUALITY GUIDELINES AND STANDARDS.....	39
2.7.1	International air quality guidelines and standards.....	39
2.7.2	South African air quality guidelines and standards.....	41
CHAPTER 3: EXPERIMENTAL DESIGN AND METHODOLOGY.....		43
3.1	STUDY AREA.....	43
3.1.1	Sampling sites and sampling periods.....	45
3.2	SINGLE BUCKET PREPARATION AND COLLECTION.....	47
3.3	DATA ANALYSIS.....	49
3.3.1	MicroScan Analysis.....	49
3.3.2	ICP-MS Analysis.....	52
3.3.3	SEM-EDX Analysis.....	53
3.3.4	Statistical Analysis.....	57
3.3.5	Enrichment Factor Analysis.....	58
3.4	QUALITY CONTROL.....	60
CHAPTER 4: RESULTS AND DISCUSSION.....		62
4.1	ANALYSIS OF METEOROLOGICAL DATA.....	62
4.1.1	Maximum and minimum temperature (°C) results.....	62
4.1.2	Rainfall (mm) results.....	64
4.1.3	Humidity (%) results.....	64
4.1.4	Wind velocity (m/s) results.....	65
4.1.5	Wind roses results.....	65

4.2	DUST FALLOUT RATES.....	73
4.2.1	Monthly dust fallout rates	73
4.2.2	Seasonal average dust fallout rates per site	80
4.3	MINERALOGICAL ANALYSIS	82
4.3.1	MicroScan particle analysis.....	82
4.3.2	SEM-EDX analysis.....	85
4.4	CHEMICAL ANALYSIS	100
4.4.1	ICP-MS analysis	100
4.5	STATISTICAL ANALYSIS.....	110
4.5.1	Pearson correlation coefficient analysis	110
4.5.2	One-way ANOVA Analysis	116
4.6	ENRICHMENT FACTOR ANALYSIS.....	117
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS		122
5.1	Conclusions	122
5.2	Recommendations	124
CHAPTER 6: REFERENCES		125
APPENDICES		148
APPENDIX A: Ethical approval to conduct the study		148
APPENDIX B: Annual wind roses for UNISA and EENDRACHT (2012-2013) weather station...149		
APPENDIX C: Elemental analysis of five combined dust samples.		150
APPENDIX D: Turn it in originality report.....		151
APPENDIX E: Conference proceeding and draft manuscript.		152

LIST OF FIGURES

Figure 1.1: Layers of the atmosphere (Seinfeld & Pandis, 1998)	1
Figure 2.1: Dust Classification (adapted: Petavratzi <i>et al.</i> , 2005).....	9
Figure 2.2: Schematic mass size distribution of particulate matter in an urban environment (EPA, 2012).....	13
Figure 2.3: Dust measurements methods (Soltani, 2011).....	24
Figure 2.4: Single bucket dust fallout monitor (DustWatch.com, 2015).	25
Figure 2.5: Frisbee dust gauge with bird strike preventor and supporting struts	26
(Vallack, 1995).	26
Figure 2.6: BS1747 – Part 5 directional dust gauge (Environmental agency, 2003).	28
Figure 2.7: Schematic representation of TEOM (USEPA, 1999).	30
Figure 2.8: E-Sampler (source: Met One Instruments Inc., 2008).	31
Figure 3.1: The jacaranda trees along Ceiliers street in Muckleneuk suburb.	43
Figure 3.2: City of Tshwane showing the sampling sites of dust fallout rates.....	45
Figure 3.3: The Buchner Funnel vacuum pump filtration system used in the Department of Chemistry laboratory at UNISA.	50
Figure 3.4: UOP UB 100j microscope connected to the computer monitor.	51
Figure 3.5: (a) Scanning Electron Microscope in the Department of Metallurgical Engineering at TUT (b) Prepared dust samples getting loaded for analysis.	54
Figure 3.6: (a) the loading of samples in Quorum system (b) the inside of Quorum (c) The data output of Quorum after coating.....	56
Figure 4.1A: Monthly averaged wind roses for July and August 2012 (winter season) at UNISA (sites A, B and C).	66
Figure 4.1B: Monthly averaged wind roses for November and December 2012 (summer season) at UNISA (site A, B and C).....	67

Figure 4.1C: Monthly averaged wind roses for May and June 2013 (winter season) at UNISA (site A, B and C).....	68
Figure 4.1D: Monthly averaged wind roses for July and August 2012 (winter season) at Pretoria Eendracht (site D and E).....	69
Figure 4.1E: Monthly averaged wind roses for November and December 2012 (summer season) at Pretoria Eendracht (site D and E).....	70
Figure 4.1F: Monthly averaged wind roses for May and June 2013 (winter season) at Pretoria Eendracht (site D and E).....	71
Figure 4.1G: Annual averaged wind roses for July 2012 and June 2013 at UNISA and Pretoria Eendracht sampling sites.	72
Figure 4.2: Comparison of the monthly dust fallout rates at Unisa (Site A, B and C), Sunnyside (site D) and Tshwane CBD (site E) monitoring sites.	79
Figure 4.3: Seasonal variations of average dust fallout rates per site.	80
Figure 4.4 A and B: SEM images and EDX spectra of particles ranging from small clustered spherical to large irregular shapes collected at site A in March 2013.....	85
Figure 4.4 C and D: SEM images and EDX spectra with morphology ranging from small oval-like to irregular shapes collected at site A in June 2013.....	86
Figure 4.4 E and F: SEM images and EDX spectra of particles ranging from small oval to large irregular shape collected at site B during March 2013 sampling period.....	87
Figure 4.4 G and H: SEM images and EDX spectra of particles with round smooth edges and irregular shaped collected at site B during June 2013 sampling period.....	88
Figure 4.4 I and J: SEM images and EDX spectra of particles with smooth rectangular and grossular-shaped collected at site C during March 2013 sampling period.....	89
Figure 4.4 K and L: SEM images and EDX spectra of particles with small spherical and irregular shape collected at site C during June 2013 sampling period.....	90
Figure 4.4 M and N: SEM images and EDX spectra of particles with small spherical and irregular shapes collected at site D during March 2013 sampling period.....	91
Figure 4.4: O and P: SEM images and EDX spectra of particles with large spheroidal to irregular shape collected at site D during June 2013 sampling period.....	92
Figure 4.4: Q and R: SEM images and EDX spectra of particles with large spheroidal and irregular shape collected at site E during March 2013 sampling period.....	93

Figure 4.4: S and T: SEM images and EDX spectra of particles with spheroidal rough surfaces and small irregular shapes collected at site E during June 2013 sampling period. 94

Figure 4.5: Enrichment factors of 18 elements in dust fallout samples around Tshwane. 117

LIST OF TABLES

Table 2.1: National Ambient Air quality Standards for Particulate Matter.....	40
(State of Air Report, 2005; DEA, 2009).....	40
Table 2.2: Dust standards, target, action and alert thresholds for dust deposition (SANS 1929:2011).....	42
Table 2.3: The National Dust Control Regulations (adapted: DEA, 2013).....	42
Table 3.1: Location and characteristics of five (5) monitoring sites around the study area (Tshwane).	46
Table 3.2: Analytical instruments used for analysis of dust fallout and their objectives.	49
Table 3.3: Specifications of SEM-EDX JEOL JSM-7600F	54
Table 3.4: Degree of correlation (r).....	58
Table 3.5: Indeterminate errors for single bucket monitoring system (Adapted: Loans, 2007)	60
Table 4.1: Average meteorological parameters recorded during the sampling period at the UNISA weather station.....	63
Table 4.2: Average meteorological parameters recorded during the sampling period at the Pretoria Eendracht weather station.	64
Table 4.3: Descriptive statistics of dust fallout concentrations at five monitoring sites from July 2012 to June 2013.	73
Table 4.4: Type of 135 analysed dust and their elemental composition particles collected in Tshwane within the radius range of 1.0 – 10.0 μm evaluated by EDX.....	96
Table 4.5: Concentrations of elements ($\mu\text{g}/\text{m}^3$) (Mean \pm SD) ($n = 3$) inf dust fallout	100

Table 4.6: Descriptive statistics of concentrations of 18 elements which were measured at the study area (Tshwane) from July 2012 to June 2013.....	109
Table 4.7: Correlation matrix of dust fallout at site D and E with meteorological parameters.	111
Table 4.8: Correlation matrix of dust fallout at site D and E with meteorological parameters.	112
Table 4.9: Correlation matrix among the 17 elements detected through ICP-MS.	115
Table 4.10: Single-factor ANOVA test for differences in dust fallout of the sampling sites.	116
Table 4.11: Enrichment factor of elemental deposits at the 5 sampling sites around Tshwane.	118

CHAPTER 1: INTRODUCTION

1.1 THE EARTH'S ATMOSPHERE

The Earth's atmosphere is characterized by variations of temperature and pressure with height (Seinfeld & Pandis, 1998). The atmosphere is divided into four regions based on temperature changes with height: the troposphere, stratosphere, mesosphere and thermosphere (see Figure 1.1 below). The troposphere accounts for about three quarters of the mass of the atmosphere and contains nearly all of the water in the atmosphere (in the forms of vapor, clouds, and precipitation). The depth of the troposphere is on average about 16.5 km over the equator and about 8.5 km over the poles. The troposphere also tends to be thicker in summer (when the air is warmer) than in the winter. The depth of the troposphere changes constantly due to changes in atmospheric temperature. The troposphere is the most important layer of the atmosphere with respect to air toxics, because this is the region in which most of the air toxins are released (Pollution (Air), 2006).

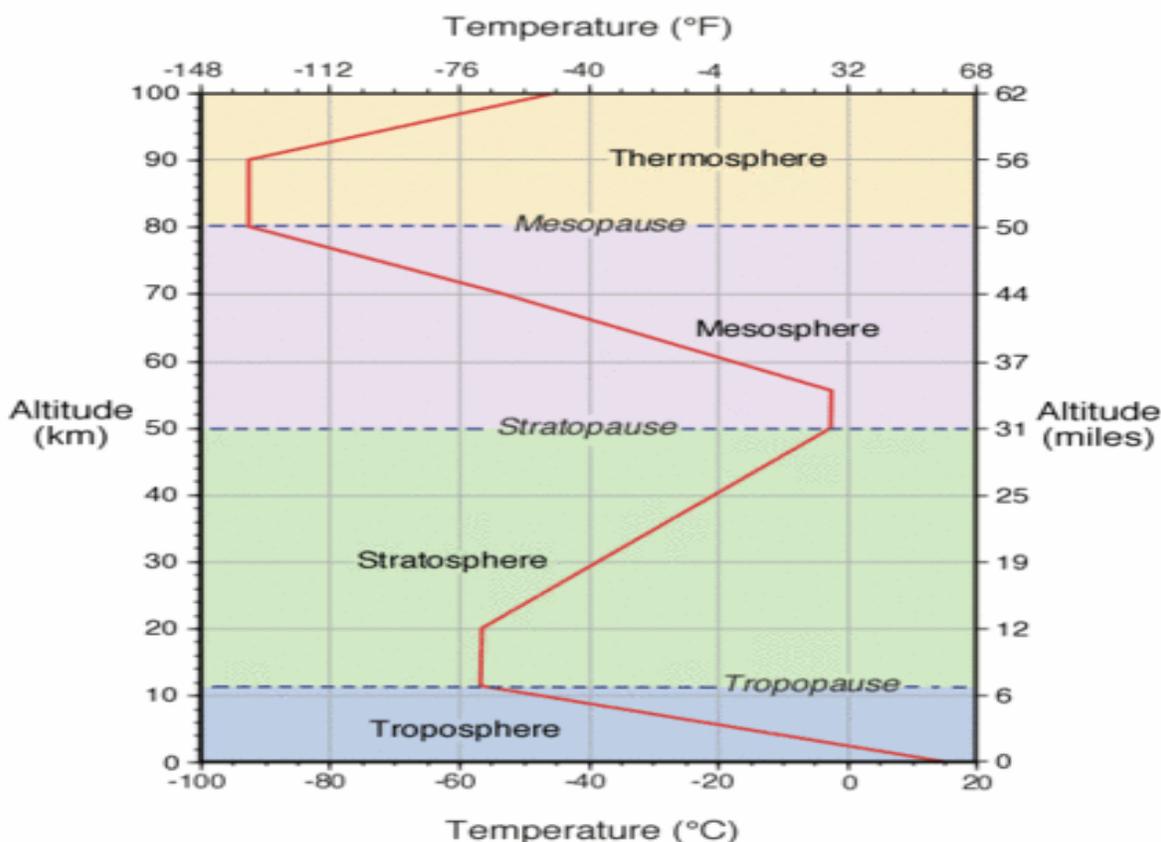


Figure 1.1: Layers of the atmosphere (source: Pidwirny, 2010)

Its importance is underscored by the fact that human actions emit almost all air pollution to the troposphere. It contains the earth's biosphere and nearly all of the atmosphere's water. Approximately 80 % of the atmosphere's mass is contained in troposphere region (Pidwirny, 2010).

Seinfeld & Pandis (1998) indicated that the troposphere is divided into several important layers and the closest to the earth's surface (of obvious importance with respect to emissions, transport and human exposure) is referred to as the planetary boundary layer (PBL). The PBL generally extends to heights of approximately 100 to 3000 m, and is often characterized as the layer through which the atmosphere "feels" the effects of frictional drag at the earth's surface. For high pressure regions over land, the PBL consists of several major parts: a mixed layer, a stable (nocturnal) boundary layer, and a residual layer above the nocturnal boundary layer. This residual layer contains mixed layer air from the previous day time period. The planetary boundary layer is characterized by a capping inversion in which temperature actually increases with height. The region of the troposphere above the PBL is referred to as the "free atmosphere" (Mikkelsen, 2003).

1.2 OVERVIEW OF AIR POLLUTION

Air is one of the single most significant resources available to sustain human life, environment and developmental activities. However, the quality of the air we breathe has been compromised by anthropogenic (man-made) and natural activities particularly in developing countries. Urbanisation and industrialisation have contributed negatively into the surrounding air especially in developing countries. Alahmr *et al.*, (2012) defines urbanisation as the process which involves economic and industrial development and ultimately population growth. This leads to higher energy production and consumption, consequently culminating in a phenomenon known as air pollution.

Elsom (1992) defined air pollution as 'the presence in the atmosphere of substances or energy in such quantities and of such duration liable to cause harm to human, plant, or animal life, or damage to human-made materials and structures, or changes in the weather and climate, or interference with the comfortable enjoyment of life or property or other human activities.'

Steyn (2005) further added that it is the presence of one or more contaminants or combinations in quantities in the surrounding or ambient air which may be detrimental to human health, vegetation and biodiversity. Air pollution is a major environmental health problem affecting developed and developing countries around the world. According to Parr *et al.*, (1996), air pollution has become a matter of global concern, particularly in some of the world's largest cities. Air pollutants are usually classified into suspended particulate matter (dusts, fumes, mists, and smokes), gaseous pollutants (sulphur dioxide (SO₂), Nitrogen oxides (NO_x), volatile organic compounds (VOCs), ozone (O₃), and carbon dioxide (CO₂) and odours.

The city of Tshwane is no exception to this global concern. The problem of air pollution is often attributed to poorly regulated emission sources, higher emissions, elevated ambient concentrations of pollutants and inadequate environmental management policies and strategies.

1.2.1 Sources and types of air pollutants

Air pollutants emanate from various sources, for instance, those that are derived from natural sources and those that are anthropogenic (brought about by human activity). Particulate matter (PM) from natural or geogenic sources tends to be coarse, whereas almost all fine particulates are generated as a result of combustion processes, including the burning of fossil fuel for steam generation, heating and household cooking, agricultural field burning, engine combustion, and various industrial processes (Li, 2008). Some of the natural contributors include forest fires, volcanic emissions, dust storms, resuspension of soil material in rural areas, biological sources (bacteria, fungi, pollen) and decaying vegetation (Shandilya *et al.*, 2009). Shandilya *et al.*, (2009) further added that almost ninety percent (90%) of these particulate emissions occur in the troposphere.

Emissions from anthropogenic sources tend to be in fine fractions, i.e. less than 2.5 micrometers (µm) in diameter and include a larger variety of toxic elements than particles emitted by natural sources (Li, 2008). Anthropogenic sources are those pollutants emanating from human activity and can be divided into three categories (Scorgie, 2001; Anon, 1999):

- Industrial sources: these are stationary sources which produce more or less qualities and quantities of pollutants (e.g. manufacturing products from raw materials, converting products to another products);
- Utilities: e.g. electric power plant producing heat and light homes in addition to providing power to household utilities; and
- Personal sources: automobiles, home furnaces, home fireplaces and stoves, open burning of refuse and leaves.

Natural and anthropogenic processes are responsible for the release of emissions into the atmosphere (State of Air Report, 2005). Natural sources include among others, wind-blown dust, uncontrolled veld fires, lightning-induced formation of nitrogen oxides (NO_x). Urban air pollution emanates from a wide variety of natural (biogenic) and anthropogenic sources. Mobile sources such as road (cars) and off-road vehicles (trains, ships and air crafts) and stationery sources (power plants, manufacturing industries, waste deposits and burning facilities household heating systems) are considered as main anthropogenic sources of pollution in urban areas (Bućko, 2012).

1.2.1.1 Stationery sources

The most prevalent stationery sources include industrial and commercial activities; waste treatment and disposal (e.g. waste incineration, landfills etc.) residential activities (e.g. combustion of dung, wood, coal etc.); electricity generating utilities (e.g. coal-fired electricity generating power stations); agriculture (e.g. burning of crop residue and application of fertilizers and pesticides); mining activities (e.g. blasting, drilling etc.) and informal (e.g. tyre burning, construction activities etc.). These sources are regarded as point sources with the exception of residential activities which are considered area sources (Vallius, 2005). Vallius (2005) further elucidated that the physical and chemical characteristics of the particles emitted from these source categories depends on the combustion process itself and the burnt fuel type (solid, liquid or gas).

1.2.1.2 Mobile sources

Traffic is the major contributor of PM in urban environments. Park *et al.* (2003) stated that transportation including automobiles, trains, air planes; ships etc. play a significant role in simplifying the modern human society. Studies of source apportionment to track possible sources of air pollution suggest that primary traffic emissions in a typical urban environment can contribute about a quarter to half of the fine PM mass (WHO, 2005). The further revelation was that traffic contributes to secondary PM, from sulphates to nitrates formed in the atmosphere and resuspended dust, which is mainly associated with PM 10.

Pollutants that are associated with traffic can be grouped into two (2) major groups: exhaust and non-exhaust emissions (Bućko, 2012). Exhaust emissions include CO, NO₂, VOCs, PAHs and PM. These are the by-products of incomplete combustion of vehicle fuel which is made up of hydrocarbon and other compounds which enhance combustion properties. On the other hand, emissions from non-exhaust source are formed through mechanical processes (e.g. braking, clutch usage, tyre wear and road abrasion) and chemical processes (e.g. corrosion of vehicle elements (Bućko, 2012). In spite of where the pollutants emanate, susceptibility of humans and ecosystems to these pollutant sources is still very prevalent in developed and developing countries.

Air pollutants are usually divided into two (2) groups, namely: primary and secondary pollutants. Primary pollutants are emitted directly from the source (Steyn, 2005) and they include: settleable particulate matter (PM) such as dust, soot, smoke, liquid droplets etc. and gaseous pollutants such as carbon dioxide (CO₂), sulphur dioxide (SO₂), carbon monoxide (CO), Nitric oxide (NO) and Nitrogen oxide (NO₂) (Albers, 2011). Secondary pollutants are formed when primary pollutants react chemically with the components of the atmospheric air. For the purpose of this dissertation, attention will only be paid to dust fallout samples.

1.3 RATIONALE OF THE RESEARCH

Numerous studies in South Africa have indicated associations between a variety of respiratory symptoms and air pollution in urban, industrial and informal settlement areas. High prevalence rates for respiratory illness were found in a residential suburb within an industrial area, relative to a suburb further away. Similarly, raised levels of respiratory effects have been identified in informal settlements, where coal and wood were commonly used for domestic purposes when compared with areas using cleaner fuel (WHO, 2000).

Poor air quality causes a nuisance to people living in proximity to the sources, particularly odours, eyes, nose and throat irritations and cleanliness issues (particulates, in the latter case). The effects of PM on health occur at levels of exposure currently being experienced by most urban and rural populations in both developed and developing countries. Chronic exposure to particles contributes to the risk of developing cardiovascular and respiratory diseases, as well as of lung cancer. The mortality in cities with high levels of pollution exceeds that observed in relatively cleaner cities by 15–20%. Even in the European Union (EU), average life expectancy is 8.6 months lower due to exposure to PM_{2.5} produced by human activities (WHO, 2005).

City of Tshwane (CoT) is a great metropolitan city in South Africa characterized by highly dense residential and commercial premises and a very high volume of vehicular traffic. Many industries, including power plants, refineries, and incinerators, chemical and metallurgical factories are located in its skirts. Thus particulate matter (dust fallout) is one of the main pollutants. Therefore, the study seeks to characterize their elemental composition and to measure their concentrations against the standards.

1.4 PROBLEM STATEMENT

Increased awareness of health problems related to air pollution arising from urbanisation and industrialisation has, especially during the last two centuries, gradually created a demand for more efficient emission controls, especially in the developed world, and thus there has been a notable decrease in both the emissions and ambient concentrations of many air pollutants.

Recently, problems caused by atmospheric particulate matter in urban air have received greater attention (Vallius, 2005).

According to Marcazzan *et al.* (2001), aerosol particles of fine dimensions are recognized to have strong impact on the environment and to be of concern in health-related effects. Because these tiny particles are inhalable and they easily reach the deepest recesses of the respiratory systems of human being, scientific studies have linked breathing PM, particularly fine particles (alone or in combination with other air pollutants), with a variety of significant health problems. The United States Environmental Protection Agency (USEPA) summarizes these detrimental health effects as follows: Premature death; Respiratory related hospital admissions and emergency room visits; Aggravated asthma; Acute respiratory symptoms, including aggravated coughing and difficult or painful breathing; Chronic bronchitis; Decreased pulmonary function that can be experienced as shortness of breath; and Work and school absences (EPA, 1997).

1.5 AIMS AND OBJECTIVES

1.5.1 Aim of the study

- The study seeks to characterise the baseline levels of dust fallout rate around the study area (Tshwane)

1.5.2 Objectives

- To undertake physical and chemical characterisation of dust fallout samples.
- To investigate seasonal effects on the concentrations of dust fallout samples.
- To analyse the influence of meteorological parameters on dust fallout rates around the study area.

CHAPTER 2: LITERATURE REVIEW

2.1 DEFINITION OF AIRBORNE DUST

Dust is an airborne suspension of very fine mineral particles derived primarily from surface soils or injected into the atmosphere during volcanic eruptions. Airborne dust is a generic term used to describe fine particles that are suspended in the atmosphere. Dust comes from a wide variety of sources, including soil, vegetation (pollens and fungi), sea salt, fossil fuel combustion, burning of biomass, and industrial activities (Environmental Defender's Office Ltd (NSW) (EDO), 2012). It is an important constituent of tropospheric aerosol, which consists of a mixture of sulphate aerosol, black carbon and organic carbon, nitrate and mixed particles such as sea salt and mineral dust (Durant *et al.*, 2009). It is formed when fine particles are taken up into the atmosphere (entrained) by the action of wind or other physical disturbances or through the release of particulate-rich gaseous emissions (primary particles). In addition, gases such as sulfur dioxide and oxides of nitrogen may react in the atmosphere over time to form fine particles, such as ammonium sulfate and ammonium nitrate (secondary particles).

According to Petavratzi *et al.* (2005), dust can be defined as small solid particles conventionally below 75 μm in diameter, which settle out under its own weight but remain suspended for some time. OSHA (2015) further defined it as finely divided solids that may become airborne from the original state without any chemical or physical change other than fracture. Ji & Huang (2008) defined dust as a generic term describing the particulates that can be found resting on the ground; but also can be resuspended in air and disperses before they return again. ASTM D1739-98 (2010) defined it as any material that is made up of tiny particles that can pass through a 1mm screen and large enough to settle owing to their weight into the container from the ambient air.

2.2 CLASSIFICATION AND COMPOSITION OF DUST FALLOUT SAMPLES

Airborne pollutants may exist in different forms including airborne dusts, mists, fumes, sprays and smokes. Of great interest is dust fallout which has been linked to respiratory diseases including asthma, pneumoconiosis, and allergic alveolitis as well as other non-respiratory diseases such as asthma. It is critical to characterise dust fallout in terms of size and forms in order to fully comprehend its implication with human health.

2.2.1 Classification of dust fallout samples

Airborne dust is classified according to its effects that include: environmental, occupational health and physiological effects (see Figure 2.1) and size distribution (Petavratzi *et al.*, 2005).

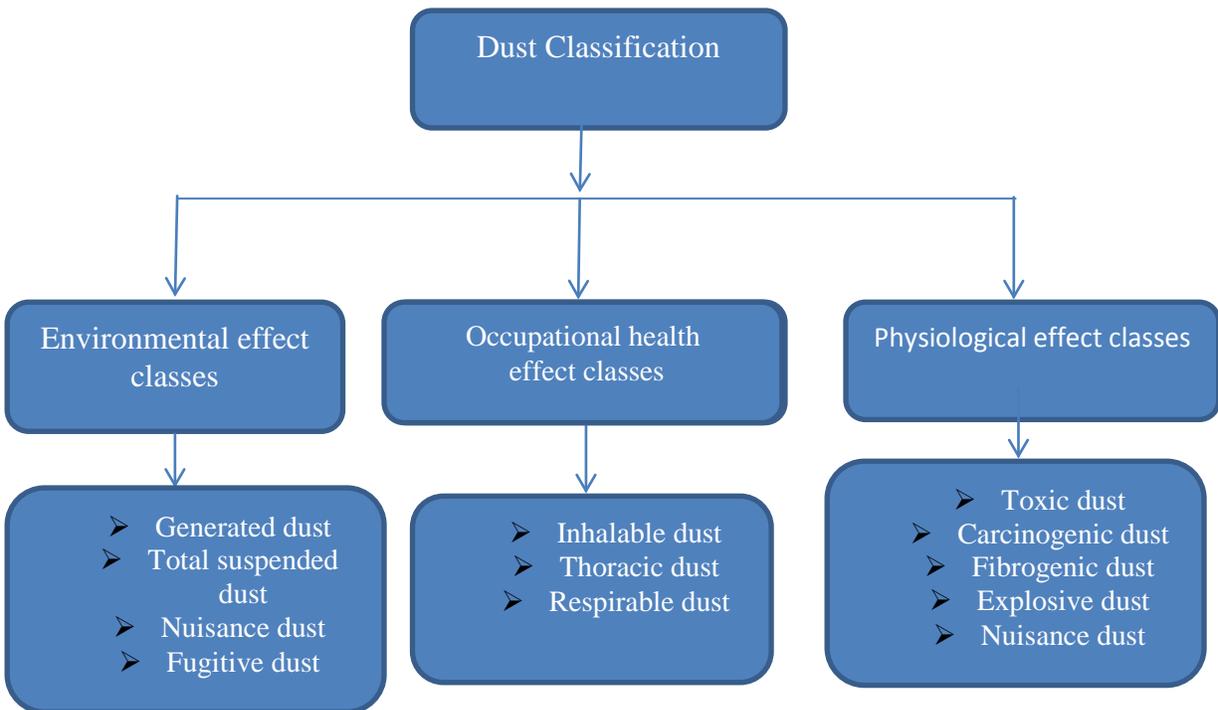


Figure 2.1: Dust Classification (adapted: Petavratzi *et al.*, 2005)

2.2.1.1 Environmental effects class

This class is comprised of generated dust, total suspended dust (TSD), nuisance dust and fugitive dust. Generated dust is the dust that emanates from mechanical processes in which solid material is broken down into smaller pieces (Safety in Mines Research Advisory Committee (SIMRAC), 2003). During the mechanical process, particles of variable sizes (small and large) are formed and smaller particles become airborne. These small particles could stay suspended in air for a long period of time or could grow in size and density by adhering to each other and settle out through gravity. Mining activities such as drilling, bulldozing, cutting and crushing are the primary sources of this dust. Total suspended dust (TSD) is defined as the generated dust which is entrained in the atmosphere (Petavratzi *et al.*, 2005). Nuisance dust becomes nuisance on the basis that it may cause soiling of buildings, diminish visibility and cause respiratory and nasal irritation.

Fugitive dust is the dust which is not emitted from a point source that can be easily defined such as industrial smoke stacks. This kind of dust results from the mechanical disturbance of granular material and is termed “fugitive” owing to confined flow stream which is discharged into the atmosphere (USEPA, 2015). Some of the common sources of fugitive dust include unpaved roads, agricultural tilling operations, aggregate storage piles and heavy construction operations. This dust alone is not toxic, however, its interaction with other air pollutants may pose a serious human health risks (Kentucky Division for Air Quality, 2014).

2.2.1.2 Occupational health effect class

Occupational health effect class is comprised of inhalable, thoracic and respirable dust. Based on the definition by CEN (1993) and International Standardization Organisation (ISO) (1995), the entry of the fraction of airborne substance through the nose and the mouth during breathing and further available for deposition anyway in the respiratory tract is referred to as total inhalable dust. SIMRAC (2003) further elucidated that this kind of dust has an aerodynamic diameter of less than 20microns and may be deposited in the nose, throat and trachea with only part of the respirable fraction reaching the lungs. CEN (1993) as cited by Petavratzi *et al.* (2005) indicated

that the thoracic fraction conforms to the percentage of the inhalable convention, which is to be collected at an aerodynamic, given by a cumulative lognormal distribution, with a median size of 11.64 microns and geometric standard deviation of 1.5 microns. Selenati-Dreyer (2010) substantiated that this fraction (thoracic) refers to particles having the potential to reach to tracheobronchial region as well as the gas exchange region for deposition. The third class is the respirable dust fraction. This fraction has the potential to penetrate the gas exchange region of the lung (Petavratzi *et al.*, 2005). These particles are less than 10 µm and are able to travel beyond the larynx into the lungs (Lenhert *et al.*, 1993).

2.2.1.3 Physiological and Physical effects class

Dust is also classified according to the potential hazards it poses on human health. The physiological effect class is divided into toxic, carcinogenic (cancer-causing), fibrogenic, explosive and nuisance. Toxic dust may initiate chemical reactions with the respiratory tract or allow absorption of poisonous substance into the blood stream through alveolar walls (SIMRAC, 2003). The dust responsible for cancer may emanate from sources such as uranium, asbestos, arsenic or quartz. According to SIMRAC (2003), the microscopic scarring of lung tissue is a consequence of scouring action of many dusts. If this process persists for an extended period of time, a fibrous growth of tissue may develop, resulting in loss of lung elasticity and a greatly reduced area of gas exchange. According to WHO (1997b), fibrous dusts such as asbestos have been shown to present special health problems primarily related to the shape of the particles. From a health point of view, particles with diameter less than (<) 3 µm, length greater than (>) 5 µm, and aspect ratio (length to width) greater than or equal to 3 to 1, are classified as "fibres". Silica (Quartz) and some silicates i.e. asbestos, mica, talc etc. dusts are the most poisonous of the fibrogenic dusts (SIMRAC, 2003).

2.2.2 Particle size and size distribution

Particles vary significantly with size (i.e. their sizes range from few nanometers (nm) to tens of micrometers in diameter). Therefore particle size is an important characteristic of particles which aid in determining the atmospheric lifetime and effects on light scattering (Mehta, 2004). Alade (2010) was of the opinion that the size distribution of atmospheric aerosols plays a fundamental role in order to comprehend extensively their transport, removal and sources. Vallius (2005) further elucidated that size is the single most significant determinant of the properties of particles and it has implications on transformation, physical and chemical properties, transformation, transport, and removal of particles from the atmosphere. The behavioral pattern and resident time of atmospheric particles are determined by their size and further provide the mechanisms which gave rise to the particles (Claes *et al.*, 1998; Seinfeld & Pandis, 1998).

The particle mass size distribution data are usually presented in terms of four modes: the nucleation ($D_p < 0.01 \mu\text{m}$), Aitken ($D_p < 0.1 \mu\text{m}$), accumulation ($0.1 \mu\text{m} < D_p < 1.0 \mu\text{m}$) and coarse ($D_p > 1.0 \mu\text{m}$) particle modes (Finlayson-Pitts & Pitts, 2000). These modes are dependent primarily on diverse main sources, formation mechanisms and chemical composition. Hinds (1999) reported that the modification of particle size distribution around the atmosphere take place through the courses of new particle formation (gas-to-particle conversion and photochemical reactions), growth (coagulation and condensation), evaporation and removal (diffusion, settling, impaction, washout and rainout). The modal structures are represented schematically in Figure 2.2 below:

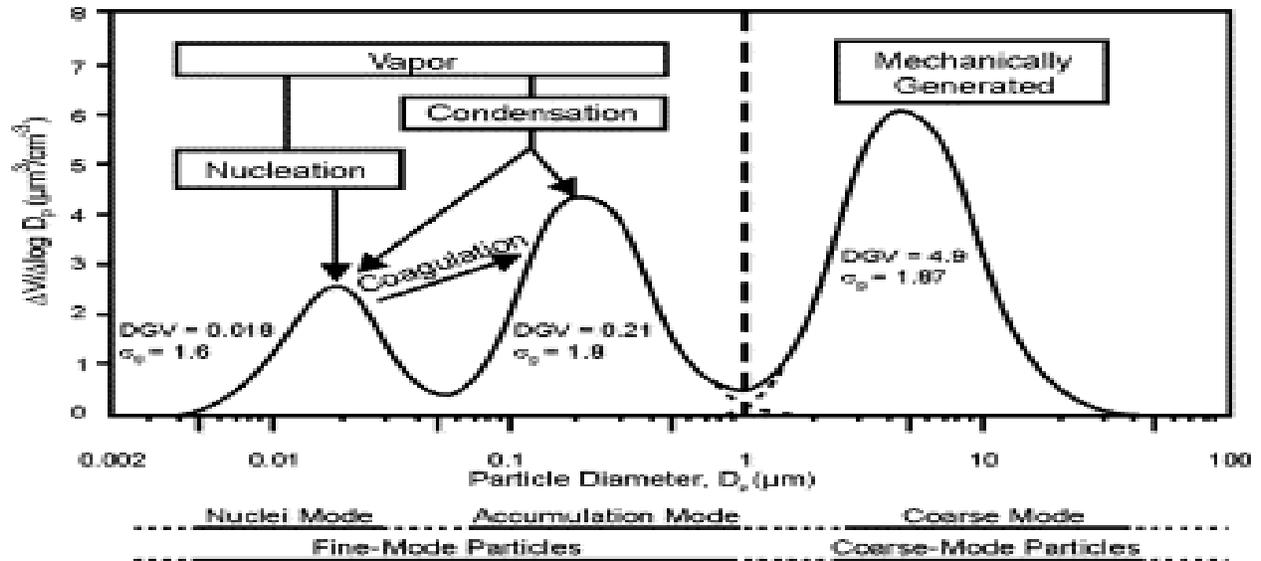


Figure 2.2: Schematic mass size distribution of particulate matter in an urban environment (EPA, 2012).

Particles are classified into fine and coarse particles. According to Seinfeld & Pandis (1998), generally, the fine and coarse particle modes originate separately, are transformed separately, are removed from the atmosphere by different mechanisms, require different techniques for their removal from sources, have different chemical composition, have different optical properties, and differ significantly in their deposition patterns in the respiratory tract. Therefore, it is of great significance to comprehend the difference between the fine and coarse particles and consequently a fundamental one in any discussion of physics, chemistry, measurement, or health effects of aerosols.

Coarse particulate matter (PM₁₀)

Coarse particulate matter (PM₁₀) have aerodynamic diameter between 2.5 and 10 μm. This type is formed from mechanical disruption (e.g. crushing, grinding, abrasion of surfaces; evaporation of sprays, and suspension of dust). Particles in this mode consist of man-made (anthropogenic) and natural dust particles. Scott (2010) added that bio aerosols (such as pollen, spores, leaf-litter decay and viruses) may also be found in the coarse particle mode.

Coarse particles do not remain in the atmosphere for long periods as high sedimentation rates lead to quick removal (Seinfeld and Pandis, 1998). The lifetime of PM₁₀ is from minutes to hours, and its travel distance varies from < 1km to 10 km (Fierro, 2000).

Fine particulate matter (PM_{2.5})

Fine particulate matters (PM_{2.5}) have an aerodynamic diameter less than 2.5 µm. These particles are formed from gas and condensation of high-temperature vapours during combustion, and they are composed of various combination of sulphate compounds, nitrate, carbon compounds ammonium, hydrogen ion etc. Crist *et al.* (2008) reported that the vast majority of PM_{2.5} constituents are secondary materials which were derived directly from chemical reactions of gaseous precursors such as SO₂, NO_x, volatile organic compounds (VOCs), organic and elemental carbon and a number of trace metals. Their lifetime is from days to weeks and travel distance ranges from hundreds (100s) to greater than thousands (>1000s) of kilometres (km) (Fierro, 2000). Fine particles remain in the atmosphere for extended periods of time than the coarse particles and are ultimately removed through the process of dry deposition (settling) or wet deposition (rain-out). Accumulation of fine particles in the air leads to a reduction in visibility, an increase in cloud formation and also changes in our climate (Krupa *et al.*, 2001).

2.2.3 Dust fallout sample composition

The composition of dust can be explained in terms of chemical and mineralogical content. The major components of airborne particulate matter are sulphate, nitrate, chloride, elemental and organic carbon, crustal and biological material. Trace elements usually constitute less than 1% of total particle mass (Lung Institute of Western Australia, 2007). The study conducted by Jacobson (2001) showed that PM at lower atmosphere is comprised of highly water soluble inorganic salts e.g. sulphate (SO₄²⁻), nitrates (NO₃⁻) and ammonium (NH₄⁺) emanating from anthropogenic activities. The study further revealed the presence of insoluble mineral dust such as metal oxides and silicates, clay minerals derived from soil dust etc. Therefore, the make-up of dust fallout samples with mineralogical and chemical species is of great interest in understanding its

behavioral pattern. Moja and Mnisi (2013) added that the determination of composition of dust fallout material aid in tracking its origin and the attached dangers it may pose.

Seasonal variability is also an important parameter in determining the dust fallout sample composition and concentration. Heintzenberg (2003) found that coarse particles during the summer season constituted 47% of insoluble dust and water and 11% of water soluble inorganic salts were discovered during the winter season. This implies that the winter seasons contribute elevated concentrations of insoluble dust and water than summer seasons. This phenomenon may be explained in terms of high frequency of ground inversions in winter and high wind velocity in summer (Pandey *et al.*, 2007).

2.2.3.1 Chemical composition and particle origin

According to Xiong and Friedlander (2001) as cited by Henyo (2011), the chemical composition of any particulate matter is determined by its source (either it originated from a primary or a secondary source) and further determined by the area and daily activities, as well as local and distant sources. Its composition is of great significance to source apportionment and receptor modeling showing the need for accurate source profile so that the results can be useful to regulatory agencies that rely heavily on modeling (Krupa *et al.*, 2001). The study conducted by Warneck (1988) as cited by Alade (2010) classified particulate matter into three broad categories according to their chemical composition i.e. water-soluble inorganic salts, water-insoluble minerals of crustal origin and organic compounds. Metals, insoluble minerals and ammonium are the examples of inorganic primary particles while the secondary particles are comprised primarily of sulphates and nitrates. Organic primary particles are soot (impure graphite), polar organics (alkanoic acids) and non-polar organics (PAH, alkanes). The secondary particles are mainly polar organics (multifunctional compounds) (Alade, 2010).

Elemental carbon (EC) and organic carbon (OC)

Carbonaceous species, organic carbon (OC) and elemental carbon (EC) are the major constituents of atmospheric fine particulate matter (Khillare & Singh, 2013). EC which is also

known as black carbon, graphitic carbon or soot emanates from combustion processes which directly inject it into the surrounding atmosphere. The main sources are road traffic, (mainly diesel motors), power generation, specific industrial processes, biomass combustion and residential and domestic emissions (Lozano, 2007). Elemental carbon is the principal light absorbing species in the atmosphere, playing an important role in the aerosol climatic forcing. Khillare & Singh (2013) further reported that owing to its surface characteristics, it provides a good adsorption site for many semi volatile compounds such as polycyclic aromatic hydrocarbons (PAHs).

On the other side, OC gets introduced into the atmosphere through burning of biomass or alternatively through atmospheric condensation of low volatility organic gases (Alfarra, 2004; Seinfeld and Pandis, 2006). Organic carbon is an effective light scatterer and may contribute significantly to both visibility reduction and direct aerosol climatic forcing.

According to Shah *et al.* (2004), elemental carbon (EC) and organic carbon (OC) are the predominant components emitted from diesel engine. The elemental fraction stems from fuel droplet pyrolysis, while the organic fraction originates from unburned fuel, lubricating oil, and combustion by-products.

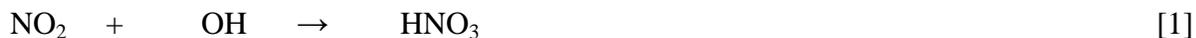
Inorganic ions (NO_3^- , SO_4^{2-} , NH_4^+)

Inorganic ions including nitrates (NO_3^-), sulphates (SO_4^{2-}) and ammonium (NH_4^+) are all secondary particulate species formed by chemical reactions in the atmosphere (Scott, 2005). Sillanpää (2006) and Lozano (2007) further added that sulphate, nitrate and ammonium in the particulate phase are known as secondary inorganic ions, since they are mainly formed from their precursor gases (SO_2 , NO_x and NH_3) through gas-to-particle conversion. The secondary inorganic compounds represent around 5% of the global planetary emissions (Intergovernmental Panel on Climate Change (IPCC), 2001).

The chemical composition of atmospheric aerosols plays a fundamental role in identifying and predicting their sources and their effect on a number of atmospheric activities. According to Alfarra (2004), a thorough comprehension of the formation, composition and behaviour of ambient aerosol particles is of great significance in order to better quantify the effects of aerosols on issues like human health and global climate.

Nitrates (NO₃⁻) ions

When vehicular and industrial activities take place under a high temperature combustion process, particulate nitrate is formed from the oxidation of NO_x (NO and NO₂) as a by-product (Seinfeld and Pandis, 1998). They also originate naturally from soil and lightning and anthropogenically from combustion of fossil fuels. The formation process of a fine mode nitrate involves the conversion of NO₂ to HNO₃ in the gaseous phase which subsequently reacts with NH₃ to form ammonium nitrate (NH₄NO₃) (Zhuang *et al.*, 1999). The process is represented by the equation below:



Sulphate (SO₄²⁻) ions

Sulphates are water-soluble inorganic ions that usually exist in the fine particle fraction (Scott, 2005). Andreae and Rosenfield (2008) as cited by Alade (2010) mentioned that large quantities of sulphur dioxide (SO₂) entering the atmosphere each year is primarily from burning of fossil fuels, particularly coal, with trace quantities from smelting and biomass burning. In many developed countries, the atmospheric aerosols containing sulphate ions are at the center stage of environmental and energy-related programmes. Once in the atmosphere, it is oxidized to form sulphuric acid aerosol which subsequently reacts with ammonia to form particulate ammonium sulphate (Lozano, 2007).

According to Roessler *et al.* (1965); Lundgren, (1970); Kadowaki, (1976); Whitby (1978) and Chy'lek *et al.* (1983) as cited Igbafe (2007) elucidated that sulphates have a characteristic size range of 0.1 to 1.0 µm making them efficient in scattering light in hot and humid weathers typical of summer periods, creating very low visibility covering several thousands of kilometers. A number of studies including that by Winter Haze Intensive Tracer Equipment (WHITEX) hold the view that visibility degradation is a consequence of sulphate plumes from coal-fired power

plants (Eatough *et al.*, 1991). Moreover, studies have shown a close correlation between the concentration of sulphate ions and a number of hospital admissions for respiratory disease.

Ammonium (NH₄⁺) ions

Ammonium sulfate ((NH₄)₂SO₄), ammonium bisulfate (NH₄HSO₄), and ammonium nitrate (NH₄NO₃) are the most common compounds containing ammonium from irreversible reactions between sulfuric acid and ammonia gas.

Essential and non-essential elements

Trace elements are vital for human body to maintain normal yet complex physiological functions related to body's growth and development. These elements are called trace owing to their concentration in the body which is few milligrams per kilogram or less (Trace elements, 2015). According to Liebshar and Smith (1968), trace elements including heavy metals may be categorized into two classes depending on whether or not the biological processes keep them in the correct level in our bodies. They are called essential or non-essential based on their biological effect, diseases that occur because of their deficiency and toxicity due to overdose. Fe, Zn, Cu, Co, Cr, F, I, Mn, Mo and Se are called essential trace elements. The border line or probably essential are Ni, Ti, V, Si and B. Elements such as Al, As, Ba, Bi, Br, Cd, Au, Pb, Li, Hg, Rb, Ag, Sr, Ti and Zr are called non-essential. An element is considered essential when its reduction below the required concentration affect the physiological state of an organism's body (WHO, 2002). Non-essential elements show adverse health effects to organisms irrespective of their concentration level.

Heavy metals, as part of trace elements, are of great concern owing to their persistence and potential toxicity to human health. The long-term effect of heavy metals on human health is based upon their non-biodegradability and long biological half-lives for elimination. Although heavy metals occur naturally in various concentrations in the ecosystem, anthropogenic activities have contributed to their elevated concentrations beyond the required limit. Some of these heavy metals (e.g. Zn, Cu, Fe, Se, Co, Mo, I and Cr) are nutritionally essential and required in minute

quantities for the normal functioning of the body, however, at elevated concentrations, they may be toxic (Okonkwo *et al.*, 2006). Vernet (1992) and Coen *et al.* (2001) further substantiated that the large amounts of these metals may cause acute or chronic toxicity. According to Rimmer *et al.* (2006), a wide variety of toxic effects including neurological, hepatic renal and hematopoietic ones may be exerted by heavy metals. Children and the elderly people are more susceptible to the direct effect of heavy metals (Olowoyo *et al.*, 2013).

2.2.3.2 Mineralogical Composition

Based on the findings by Chow & Watson (1992) as cited by Chow and Watson (1998), the primary components of dust fallout are oxides of iron, silicon, calcium, aluminium, titanium etc. Lozano (2007) further added that the main mineral composition of PM is quartz (SiO_2), calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), clay minerals, mainly kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), illite ($\text{K}(\text{Al,Mg})_3\text{SiAl}_3(\text{OH})_2$), smectite ($(\text{Na,Ca})\text{Al}_4(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) and palygorskite ($(\text{Mg,Al})_5(\text{OH})_2[(\text{Si,Al})_4\text{O}_{10}]_2 \cdot 8\text{H}_2\text{O}$), and feldspars like the microcline/orthoclase (KAlSi_3O_8) or the albite/anorthite ($(\text{Na,Ca})(\text{AlSi})_4\text{O}_8$). Minerals are found in combinations that are determined by the geology of a particular area and the industrial processes (steel-making, smelting, mining, and cement production) connected to it. Houck *et al.* (1990) as cited by Chow and Watson (1998) mentioned that the geological material is in the coarse particle mode. Watson *et al.* (1995) further pointed out that ~50% of PM_{10} is found in geological material while contributing 5 to 15% of $\text{PM}_{2.5}$.

2.3 IMPACTS OF DUST FALLOUT RATES

According to Mehta (2004) particulate matter e.g. dust fallout material causes a wide spectrum of health and environmental impacts. Several epidemiological studies have linked both PM_{10} and $\text{PM}_{2.5}$ with significant health problems, including: premature mortality, chronic respiratory disease, respiratory emergency room visits and hospital admissions, aggravated asthma, acute respiratory symptoms, and decreased lung function. These studies further proved that there is a link between particulate matter ($\text{PM}_{2.5}$ and PM_{10}) with adverse health effects.

For the purpose of this study, dust fallout as an example of PM will be dealt with extensively. Dust fallout has potential adverse effects on human health, environment, climate, ecosystems, visibility reduction and degradation of building materials.

2.3.1 Impacts on human health

The association between the adverse health effects and air pollution has been an issue of global concern. The effects of air pollutants on health vary depending on the level of exposure and the susceptibility of the exposed population. The susceptibility of the population is affected by factors such as the numbers of young children and older people, as well as the proportion of people suffering from asthma and other chronic respiratory conditions (Hicks *et al.*, 2004).

According to Pope and Dockery (1999); Pope *et al.* (2002) and (2004) and WHO (2003) as cited Lozano (2007) reported that atmospheric particulate matter effects on health have been evaluated by means of epidemiological studies carried out since 1980s proving that elevated PM concentrations are associated with an increase in mortality and other serious health effects.

Pope III (1996) conducted a study and showed a strong correlation between PM_{10} and mortality rate due to cardiopulmonary and lung cancer diseases. He further alluded to the fact that 36% increase in death from lung cancer and 26% cardiopulmonary deaths are attributed to $PM_{2.5}$. This implies that $PM_{2.5}$ contributed to high mortality rate while PM_{10} had none. Fierro (2000) further substantiated that $PM_{2.5}$ is of great concern owing to its high proportion of various toxic metals and acids. Aerodynamically, $PM_{2.5}$ can penetrate deeper into the respiratory tract.

A study conducted by Atkinson *et al.* (1999) showed a close link between emergency hospital admissions for respiratory and cardiovascular disease and PM_{10} . Furthermore, in the study conducted in Utah by Pope III (1989), results showed a relationship between elevated PM_{10} levels and reduction in lung function as measured by peak respiratory flow (PEF). For the past thirty (30) years epidemiologists have been able to demonstrate that there is a strong exposure-response relationship between PM for short-term effects (premature mortality, hospital

admissions etc.) and long-term or cumulative health effects (morbidity, lung cancer, cardiovascular and cardiopulmonary diseases, etc.) (Valavanidis *et al.*, 2008).

In the South African context, air pollution and adverse health impacts studies showed that people exposed to air pollution encounter health problems including respiratory conditions such as runny nose, shortness of breath, hay fever etc. (Robins *et al.*, 2002).

Humans are exposed to dust fallout through three (3) main routes: ingestion, inhalation and dermal absorption (Cao *et al.*, 2011). Leug *et al.* (2008) as cited by Al-Aawadhi (2012) pointed out that an estimated 100.0 mg of dust/day may be ingested by an adult in dusty places. Dust fallout components such as soot, fly ash, organics or metals are believed to maximize the potential of risk of catching a disease (Jacobson, 2001). The groups that are likely to be susceptible to adverse health effects caused by ingestion or inhalation of dust fallout are the elderly and children. Based on the physiological state deterioration on the elderly (because of age), they are at risk of contracting cardiorespiratory diseases. Children, by virtue of their developing respiratory system and spending more time outdoors, they are at risk of exposure to dust fallout.

Sibanda (2009) further added that the groups that are at the highest risk are infants, children and teens, the elderly and pregnant women; people with asthma, bronchitis, emphysema, or other respiratory conditions; people with heart disease; and healthy adults working or exercising outdoors.

2.3.2 Impacts on Environment and Ecosystems

The potential effects of dust fallout on vegetation and ecosystems encompasses a full range, scales, and properties of biological organisations with exposures to occurring sites to vegetation surfaces, via the soil, or both and include many uncertainties (Grantz *et al.*, 2003). Dust fallout may cause reduced photosynthesis on vegetation owing to reduced light penetration through the leaves (Martins, 2014). It may lead to reduced growth rates, growth of fungal diseases and plant vigour. It should be noted that several factors play a significant role on the effects of dust on

environment and ecosystems. Martins (2014) mentioned that the concentration of dust particles, their size distribution, the deposition rate as well as the chemistry are of great significance. The effects of dust fallout on ecosystems could potentially cause substantial modification to community composition and ecosystem functioning. It could further change the course of evolution within species and cause loss of biological activity (Tyson *et al.*, 1988). From the 1970s, researchers have been studying acid rain and showed through their studies that in lakes and oceans, the alteration of living conditions of various species has led to their death as a consequence of the acidification of the environment (Lozano, 2007). The study of Lozano (2007) further revealed that in land, acid rain reacts with soil nutrients preventing their absorption by plants and dissolves toxic metals facilitating their absorption and producing damage even perceptible on the surface.

2.3.3 Impact on climate

Aerosol particles i.e. dust fallout have substantial impact on climate and its variations (Busec & Posfai, 1999). Both authors have pointed out to the potential of dust fallout in intensifying or moderating the effects of greenhouse gases through the scattering or absorption of solar and thermal radiation emanating from the earth's surface.

According to Lozano (2007), these absorption and scattering of incoming solar radiation depends on chemical composition or refractive index. The scattering and absorption of solar radiation leads to the cooling and warming effects of the space respectively. These effects are called direct aerosol forcing of climate (IPCC, 2007; Rashki, 2012). The conclusion made by Rashki (2012) suggested that it is based on the type of aerosol i.e. scattering or absorbing properties, reflecting property of the surface, altitude distribution of aerosols, solar declination, geographical latitude and distribution of clouds for the aerosols to solely have an effect on the earth radiation budget.

2.3.4 Impact on visibility reduction

Dust fallout impacts the regional air quality through the visibility impairment (Propero, 1999). According to Lozano (2007), the anthropogenic activities which contribute to dust fallout pollution can reduce visibility to a few meters, particularly in urban environments. Rashki (2012) alerted that reduction in visibility as a result of dust storms poses severe hazard to aviation, rail and road transport. Horizontal reduction in visibility owing to the dust storms leads to vehicle accidents. All these visibility related effects may lead to economic decline. Martins (2014) lamented that dust fallout may inhibit people's ability to have joyous outdoor leisure time such as sports and other activities.

2.3.5 Impacts on building materials

In urban areas, the building materials such as cement, bricks, metallic structures and monuments are susceptible to degradation caused by the interaction between dust fallout and their surfaces (Lozano, 2007). All these effects may lead to costly reconstructions of degraded buildings (Martins, 2014). Maeda *et al.* (2001) as cited by Martins (2014) gave an indication that the presence of sulfur and chlorine in dust fallout may lead to serious damage to copper. Chloride and sulphate pollutants, naturally breakdown the protective corrosion products that may be formed under pollution-free conditions (Tyson *et al.*, 1988).

2.4 DUST FALLOUT MONITORING METHODS

Dust fallout monitoring is undertaken for health, epidemiological and environmental purposes, therefore, monitoring techniques differ tremendously (sustainableaggregates, 2015). Hall *et al.* (1994) further indicated that dust monitoring is an important practical activity for pollution control activities. Monitoring methods can be divided into two (2) categories, namely: passive and active systems. Active monitoring methods require electricity or pump to run. Examples include manual methods and reading instruments (see Figure 2.3 below). On the other, passive monitoring methods require no source of power poor electricity. The dust particles settle passively through gravity, adhesion and electrostatic attraction (see Figure 2.3).

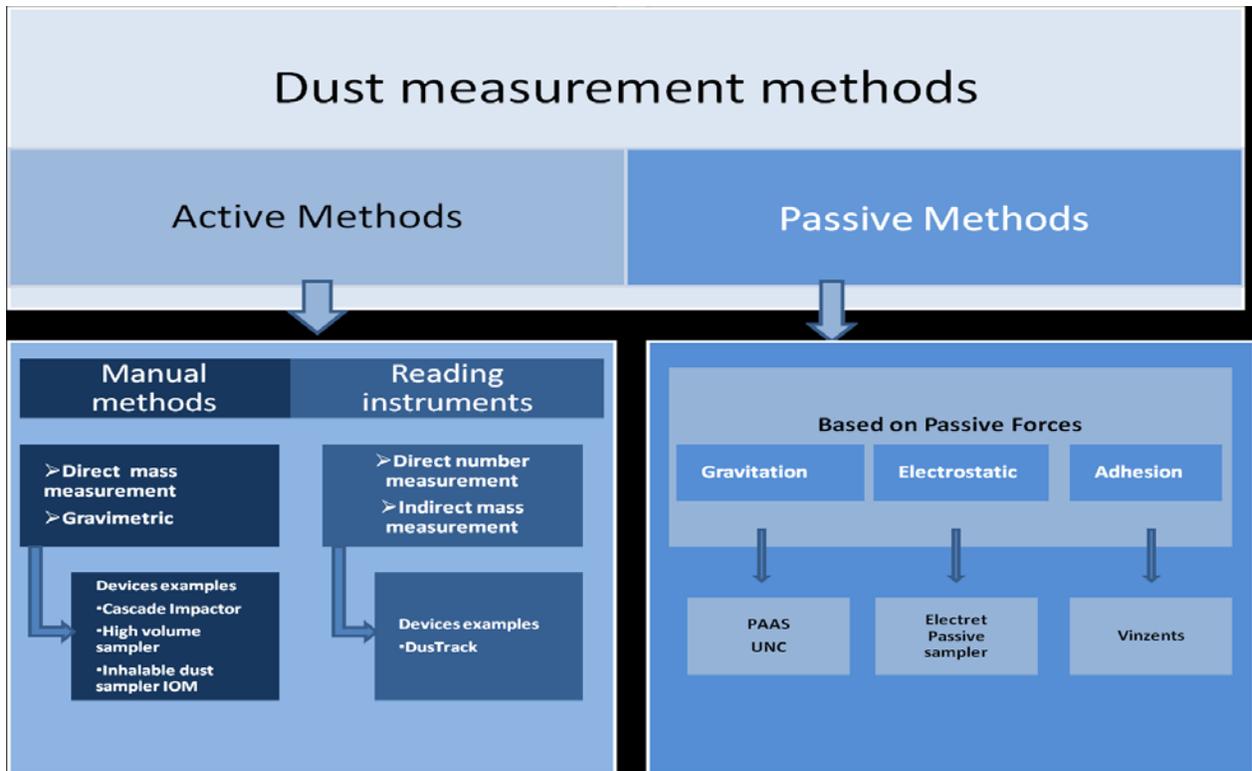


Figure 2.3: Dust measurements methods (Soltani, 2011)

2.4.1 Passive samplers

Passive samplers are designed to collect dust fallout naturally through mass transfers (Yamamoto *et al.*, 2006). According to USEPA (1998), the operational costs associated with these samplers are extremely low which implies several numbers can be installed. Sampling of dust fallout using these samplers can be over days, weeks and months. Passive samplers can be divided into non-directional (BS 1747 Part 5 and Dustcan) and directional techniques (e.g. single bucket dust fallout monitors, Frisbee gauge and Dustwatch).

2.4.1.1 Non-directional samplers

Single bucket dust fallout monitor

Figure 2.4 below shows the single bucket dust fallout monitor. The monitor is deployed according to the American Society for Testing and Materials (ASTM) D1739 standard method which deals with measurement of vertical dust fallout (ASTM D1739:98, 2004). This method employs single or double bucket units which are half-filled with de-ionised water and 10.0 mL of 3.5% bleach (hypochloride) solution. The unit is comprised of a cradle with a 2.2 m stand above the ground and a bird ring to prevent birds from perching inside the buckets. According to Kwata (2014), the most recent version (ASTM D1739:98) has a wind shield which aids in maximizing the laminar flow across the top of the collecting container, thereby, stimulating ground level conditions as compared to previous versions (ASTM D1739:70 and ASTM D1739:82). After the collection of dust, the buckets are sent to the laboratory for filtration and gravimetric analysis. Furthermore, these methods are cost-effective, easy to operate, electricity-independent and allow multiple sampling stations to be established. However, only nuisance dust can be measured and the process is labour intensive.



Figure 2.4: Single bucket dust fallout monitor (DustWatch.com, 2015).

Frisbee gauge monitor

The Frisbee-shaped collecting bowl consists of anodized spun aluminium. It is mounted on a pole with an opening of 1.7 m above the ground level and has an opaque drain pipe leading from the pole down a rainwater collecting bottle on the ground (Vallack, 1995). Figure 2.5 below shows a Frisbee gauge with bird-strike preventor in the form of a ring of fine (1.0 mm thick) plastic fishing line supporting 5.0 cm above the collecting bowl on six stainless steel struts. After a one month period, the Frisbee (with foam disc still in place) and the collecting bowl are removed and sent to the laboratory for analysis. The insoluble matter is dried and determined gravimetrically and the deposition rate is expressed as $\text{mg/m}^2/\text{day}$ (Environmental agency, 2003).



Figure 2.5: Frisbee dust gauge with bird strike preventor and supporting struts (Vallack, 1995).

Dustwatch

Dustwatch is a method which employs a series of monitoring units that have developed practical and almost failure-proof devices. This method, like Frisbee gauge, is independent of external power supply and is functional even under severe climatic conditions and requires minimal maintenance. This method is wind-dependent in order to rotate a horizontal plate which makes it an ideal choice for isolated locations and for both temporary and permanent installations (Kuhn & Loans, 2012). It has an advantage of allowing site-specific directionality adjustment to suit required monitoring. The manufacturers claim that its results are comparable to ATSM D1739; however, Kwata (2014) found no results to compare both methods.

2.4.1.2 Directional samplers

Directional monitoring techniques are employed to monitor nuisance through dust fallout or soiling surface. Kwata (2014) defined directional monitors as horizontal flux gauges designed to measure the particulate matter passing through a particular monitoring sampling station. According to Environmental agency (2003), the dust deposit gauges are designed in such a way that dust collection period may range from one week to a month. The gauges are governed by the principle that airborne coarse material is deposited through the gravity (dry deposition) or washing down by rain (wet deposition). BS 1747 Part 5 and directional sticky pads (Dustcan) are some of the samplers that will be explained in this section.

BS 1747 Part 5 samplers

It is a technique which uses a grouping of four (4) vertical tubes with slots on the vertical surface facing the main direction which the wind blows (Kwata, 2014) or towards the pollution source (Sibanda, 2009) (see Figure 2.6). The South African National Power Utility, ESKOM, is the first company to employ this gauge in “insulators pollution survey undertaken in the country from 1974 to 1976”. Despite the limitations of this gauge, Environmental agency (2003) alludes that it continues to be preferred technique for routine directional dust monitoring.

The duration of the sampling may be short-term (10.0 days to 1.0 month) and long-term (up to 1 year). Aqueous suspension of dust placed in a water-filled glass cell and the estimation of dust loading can be achieved through the amount of obscured beam light which passes through its cell (Environmental agency, 2003). The results are expressed in $\text{mg}/\text{m}^2/\text{day}$ for each direction. Despite limited efficiency of this gauge in dust collection, Mace Technology (2008) as cited by Kwata (2014) indicated its advantage of being electricity-independent, cost-effective and minimal skill required by personnel.



Figure 2.6: BS1747 – Part 5 directional dust gauge (Environmental agency, 2003).

Directional Sticky Pads (Dustcan)

It is a purpose-made adhesion slide which provides a comprehensive method of directional nuisance dust monitoring (Environmental agency, 2003). The slide is mounted on a collection cylinder on a stand of 2.0 m above the ground. The slides are exposed in the field for 1 to 2 weeks sampling period. The collection dust in flux can be analysed using a standard flat-bed scanner with relevant software.

Results are expressed as loss of reflectance through soiling (Effective Area Coverage, EAC %). A combination of both EAC and AAC or as the density of coverage of dust (Abrolite Area Coverage, AAC %). A combination of both EAC and AAC is extremely useful in accessing the quality of dust present and define whether the levels are nuisance or not.

2.4.2 Active samplers

Active sampling involves the active pulling or sucking of air through a collection device using a sampling pump. According to Colls (1997), these types of samplers operate by sucking a precise volume of air through a filter or chemical solution for a specified period of time. The examples of Active samplers include amongst others; PM₁₀ Tapered Element Oscillating Microbalance (TEOM) samplers, E-Sampler, PM₁₀ High volume air samplers.

PM₁₀ tapered element oscillating microbalance (TEOM)

These samplers are comprised of size-selective PM₁₀ inlet to monitor PM₁₀ particulates (see Figure 2.7). The air is drawn into filter which is mounted on a vibrating glass (EPA, 2006). The oscillating frequency is changed and affected by the additional weight which emanates from the trapped PM₁₀ particulates. The change in frequency is translated into a particulate mass which subsequently can be divided by the volume of the air drawn into the instrument to produce PM₁₀ concentration. The results are expressed in the units of $\mu\text{g}/\text{m}^3$.

TEOM samplers are more advantageous to high volume samplers on the basis of continuous operation without changing the filters (EPA, 2006). They can further give additional information e.g. time of the day which recorded the highest concentrations. This kind of information is critical when used in line with meteorological information in order to identify the source of emission.

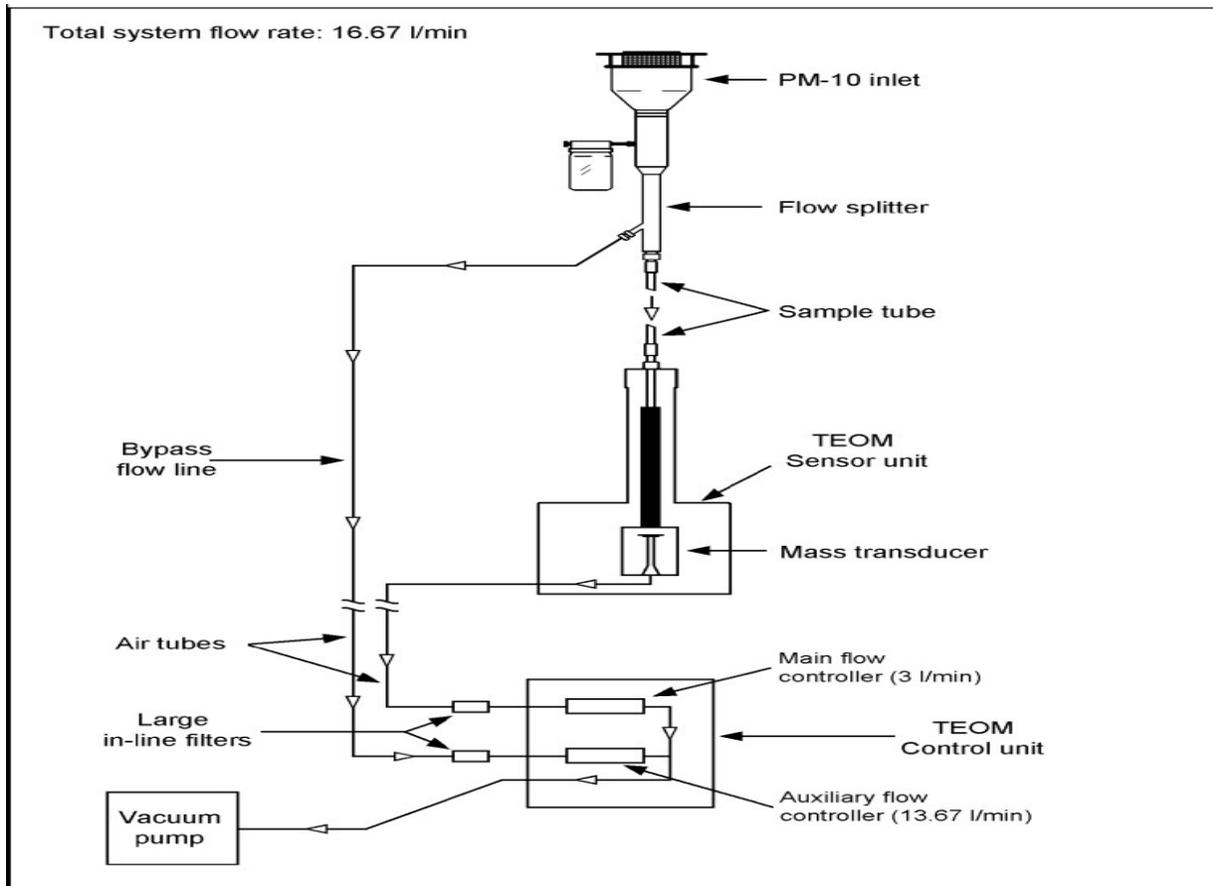


Figure 2.7: Schematic representation of TEOM (Abdullah *et al.*, 2011.).

E-Sampler

E-SAMPLER is a type of nephelometer which automatically measures and records real-time airborne PM_{10} , $PM_{2.5}$, or TSP particulate concentration levels using the principle of forward laser light scatter. In addition, it has a built-in 47mm filter sampler which can optionally be used to collect the particulate for subsequent gravimetric mass or laboratory evaluation. The E-Sampler combines the excellent real-time response of a nephelometer with the accuracy and traceability of a manual gravimetric sampler (Met One Instruments Inc., 2011).

The air is drawn through the MD laser optical module or “laser engine”, where an internal visible laser diode beam is collimated and directed through the sample air stream. The particulate in the sample air stream scatters the laser light through reflective and refractive properties. This scattered light is collected onto a silicon photodiode detector at a near-forward angle, and the resulting electronic signal is processed to determine a continuous, real-time measurement of

airborne particulate mass. The forward light scatter method allows for a more accurate total mass estimate compared to right-angle light scatter, which is better suited for counting and sizing individual particles. These samplers are expensive, labour intensive and need to be mounted in a secured place to minimise vandalism/theft.



Figure 2.8: E-Sampler (source: Met One Instruments Inc., 2008).

PM₁₀ High-Volume air samplers

These samplers operate by the air sample through a size-selective inlet. The particles which are larger than 10.0 μm are removed by impaction while the particles less than 10 pass through the inlet onto the filter paper (EPA, 2006). These samplers are programmed to capture airborne particulate every 24-hours at six day intervals. Filters are weighed before the sampling to determine the mass of particles.

2.5 TRANSPORT AND DISPERSION OF AIR POLLUTANTS

To comprehend the mechanisms that govern the transport and dispersal of pollutants, these processes need to be differentiated. Transportation of pollutants refers to processes such as winds that cause pollutants to be moved over a certain distance from one place to the other while dispersion refers to the spread or distribution of air pollutants from the source with a decrease in concentration away from the source. The latter process is influenced by factors such as characteristics of the source, pollutant and the surrounding atmospheric conditions.

Topography, climate, and physical processes in the atmosphere play an important role in transport, concentration, dispersal, and removal of many air pollutants. After pollutants are emitted from the source, they are dissipated in the surrounding environment and ultimately get absorbed in the atmosphere. The potential of the atmosphere to disperse and transport pollutants varies geographically and further depends on atmospheric conditions, i.e. wind speed and direction; atmospheric stability; chemical transformation and precipitation (DEAT, 2003).

Sankaran *et al.* (2012) further reported that the dispersion of pollutants in the atmosphere from point, line, and area sources depends on the meteorological conditions of that particular region. Kumar (1999) was of the opinion that the prevailing meteorological conditions such as wind speed and direction; mixing height, atmospheric stability and inversion have significant influence on the dispersion and transportation of air pollutants once they are emitted into the atmosphere.

Moreover, the transport and dispersion of air pollutants in the ambient air are influenced by many complex factors. Global and regional weather patterns and local topographical conditions affect the way that pollutants are transported and dispersed. The primary factors affecting transport and dispersion of pollutants are wind and atmospheric stability or differential heating.

2.5.1 Wind speed and direction

According to Turner *et al.*(1995) as cited by Steyn (2005) the atmospheric conditions determines the rate and means through which air pollutants are dispersed around the atmosphere, particularly within the earth's boundary layer where thermal (convective) and mechanical processes dominate. DEAT (2003) further elucidated the fact that knowledge of how the atmosphere behaves aid in understanding movement of pollutants and also determining concentrations at particular locations. Air pollutants can move horizontally and vertically depending on the surrounding factors such as wind speed, wind direction, mechanical and thermal turbulence; and mixing depth. Vertical movement of pollutants is dependent on wind speed and direction while their movement vertically is governed by atmospheric stability (DEAT, 2003).

Wind direction determines the path that air pollutants will take, while wind speed influences how fast they disperse. Windy condition can cause soil erosion and stir up particulate matter and is capable of transporting pollutants to great distances. According to Sankaran *et al.* (2012), wind speed and direction are fundamental parameters in the distribution of particulate matter and are interrelated with the vertical and horizontal temperature gradients in the atmosphere, both large and small scale.

According to DEAT (2008), the vertical movement of pollutants is governed by atmospheric stability and the horizontal movement of pollutants is dependent on wind speed and direction. The higher the wind speed the greater the dispersion of pollution. Direction is also important as it determines where the pollution moves and hence governs the downwind impact areas. When air is displaced vertically, atmospheric behavior is a function of atmospheric stability. Vertical air circulation depends on the compressibility of gases, which cools upon expansion and heat upon compression. During the day, differential heating of the earth's surface by the sun generate thermal turbulence. Warm air rises and is replaced by cold air, in this way the vertical air currents are created and pollutants are dispersed. In winter and at night, atmospheric pressure drops and there is little wind, less mixing and dilution and pollution becomes enhanced.

2.5.2 Atmospheric stability

The concept of atmospheric stability is of great significance in determining whether air pollutants will rise or whether they will accumulate near the source (DEAT, 2008). Atmospheric stability affects vertical movements of air. During a temperature inversion, the atmosphere becomes very stable and vertical movement of pollutants is inhibited. Warm air overlying cooler air acts as a lid and prevents upward movement, which leaves pollutants trapped near the ground (Cossience, 2013).

During unstable atmosphere, vertical movement of pollutants becomes conducive and the concentration of pollutants gets lowered as pollution is spread over a larger volume of air. In neutral atmosphere pollutants are neither up nor down, they remain at the level which they were released.

2.6 AIR QUALITY LEGISLATION AND POLICY CONTEXT

2.6.1 International Context

The Clean Air Act (CAA) was first passed into law in 1963 and revised in 1990 (Cote *et al.*, 2007). The Act addresses the two main categories of air pollutants referred to as “criteria pollutants” i.e. particulate matter (PM), tropospheric ozone (O₃), sulfur dioxide [SO₂], nitrogen oxides (NO), carbon monoxide (CO) and lead (Pb) and the “hazardous air pollutants,” (a group of toxic and carcinogenic pollutants specifically designated by the CAA).

The Clean Air Act (CAA) requires Environmental Protection Agency (EPA) to set national ambient air quality standards (NAAQS) for particulate matter and five other pollutants considered harmful to public health and the environment (the other pollutants are ozone, nitrogen oxides, carbon monoxide, sulfur dioxide and lead). The law also requires EPA to periodically review the standards to ensure that they provide adequate health and environmental protection and to update those standards as necessary (EPA, 2012).

Air quality guidelines for particulates are given by various countries and organizations for various particle sizes, including total suspended particulates (TSP), inhalable particulates (PM₁₀), and respirable particulates (PM_{2.5}, defined as particulates with an aerodynamic diameter of less than 2.5 μm).

2.6.2 Regional/Continental (African State) Context

The problem of air pollution is being recognized as a growing source of socio-ecological concern for many African countries. Significantly higher levels of air pollution are currently being experienced in major urban centers. Countries are now recognizing air pollution as having significant adverse impacts on national economies. There is therefore need to strengthen existing partnership programmes on air quality in Africa in order to tackle the air pollution problem (Hicks *et al.*, 2004).

The Air Pollution Information Network for Africa (APINA) was established in order to deal with issues pertaining to Air pollution in southern Africa (Simukanga *et al.*, 2003). APINA is a multi-stakeholder network which is comprised of scientists, policy-makers, industry and non-governmental organisations (NGOs). Some of the air pollution identified problems in Southern Africa, which require focused attention include:

- To fill the gaps in knowledge in southern Africa concerning the extent and impacts of air pollution
- To ensure that current knowledge about air pollution is adequately reflected by national and regional policy development.

A regional multi-stakeholder policy dialogue on air pollution which was organized by APINA in September 1998 came with ‘Harare resolution on prevention and control of regional air pollution in Southern Africa and its likely transboundary effects’ outcome.

The second Regional Policy Dialogue (RPD) organized by APINA was held in September 2003.

The specific objectives of the dialogue were to:

- Define the stages to move towards policy formulation in Southern Africa;
- Translate and transfer scientific information to the policy process in the region;
- Define the information gaps; and
- Define the structures that can be developed to facilitate the regional policy process.

The major outcomes of the dialogue were:

The draft of ‘Maputo Draft Declaration on the Prevention and Control of Air Pollution in Southern Africa and its likely Transboundary Effects’ in which the delegates from different countries declared they shall: *‘Endeavor to promote national reporting systems and strengthen scientific and academic efforts in the understanding and tackling of air pollution issues; Continue this process in a coordinated manner and in stages with mutual consultation to draw up and implement national and regional action plans and protocols based on a fuller understanding of transboundary air pollution issues; Endeavour to promote the philosophies and practices of cleaner production, waste management to enhance sustainable development in the region.’*

The mechanisms of how scientific information on air pollution issues can reach policy makers both at national and regional levels which led to the agreement on new APINA structure. The main purpose of the structure was to promote constant dialogue with the ministries of environment through the appointment of national focal points within the ministries (Simukanga *et al.*, 2003).

2.6.3 National Context

Prior to 1965, South Africa did not have massive industrial activities until the fall of 19th century (Brown & Brown, 1929). From 1939, there was steady industrial growth and after World War II, the industrialization began to increase rapidly owing to the cut-off in the supply of goods from Europe (Scott, 2010). This resulted in an outcry in 1955 about the pollutants which were emitted in the atmosphere (Boegman, 1979). Since 1965, the approach to air quality management in South Africa was informed and driven by Atmospheric Pollution Prevention Act (APPA) (Act No. 45 of 1965).

2.6.3.1 Atmospheric Pollution Prevention Act 45 of 1965

The main aim of APPA was the control of noxious and offensive gases emitted by industrial processes (through registration certificate), the control of smoke and wind borne dust pollution, and emissions from diesel vehicles. Under APPA, all industries undertaking scheduled processes were controlled by the Chief Air Pollution Control Officer (CAPCO) through Best Practicable

Means (BPM) using permits (known as Registration Certificates). The APPA approach, with regard to industrial emissions, was largely based on point source emission control. Over the years major shortcomings in the regulation of industrial emissions under APPA were discovered. Amongst others is that APPA largely focuses on point source emission control that does not fully address the cumulative impacts of air pollution (DEA, 2009).

Owing to the shortcomings of APPA, the introduction of a new policy in Integrated Pollution and Waste Management (IP&MW) marked a new era and a complete paradigm shift from the APPA approach (DEAT, 2005). Furthermore, there were set standards or targets by APPA that would consequently permit the achievement of an environment that is not harmful to health or well-being. This requirement now forms part of the South African Constitution which came into existence in 1996.

2.6.3.2 South African Constitution, 1996

The Constitution is thus the pivotal piece of legislation that informs all environmental legislation (DEA, 2013). In 1996, the South African Constitution (Act No. 108 of 1996) was promulgated and contained within it the Bill of Rights (Lazarus, *et al.*, 1997). Section 24 of the Bill of Rights in the South African Constitution, states that everyone has the right to an environment that is not harmful to their health and well-being. It further states that the environment should be protected for the benefit of the present and further questions, through reasonable legislative and other measures that:

- (i) Prevent pollution and ecological degradation;
- (ii) Promote conservation; and
- (iii) Secure ecologically sustainable development and use of natural resources.

2.6.3.3 National Environmental Management: Air Quality Act (AQA), 2004

After the publication of a critical policy document (a White Paper on Integrated Pollution and Waste Management) for South Africa in 2000, this new policy represented a paradigm shift in approach and necessitated the introduction of a new approach to air quality management.

The National Environmental Management: Air Quality Act (AQA) was promulgated in 2005 as the updated approach to air pollution control, introducing air quality management (AQM) as the control strategy. The implementation of the National Environment Management: Air Quality Act, Act no 39 of 2004 (NEM:AQA) resulted in the reform of air quality legislation in South Africa and include regulations and standards to monitor and improve ambient air quality in South Africa, which was not the case before the act was signed into commencement on 11 September 2005. The main shift was from the source-based management to holistic and integrated effects-based air quality management (Barnwell, 2009).

This Act focuses on the adverse impacts of air pollution on the ambient environment and sets standards for pollutant levels in ambient air. It further provides a complete list of requirements and legal aspects which pertain to air quality and dust management in South Africa.

2.6.4 Local Context

2.6.4.1 City of Tshwane (CoT)

According to City of Tshwane (CoT) (2008), air quality management involves pollution minimisation, management and prevention, improving air quality in areas where it is poor, and maintaining it where it is good. It is in this context that the Environmental Health Division initiated the development of an Air Quality Management Plan (AQMP) for Tshwane. The purpose of developing an AQMP is to empower the CoT to meet its obligations as outlined in the Air Quality Act. The AQMP will initiate best practices in air quality management and ensure cost-effective and equitable reduction of emissions. This will

improve air quality in Tshwane and reduce environmental and health risks in line with the requirements of the TIEP. The main goals of the AQMP are to:

Achieve and sustain acceptable air quality levels throughout Tshwane; minimise the negative impact of air pollution on people's health and well-being and on the environment; promote the reduction of greenhouse gases in support of the CoT climate change protection programme; and reduce the extent of ozone-depleting substances in line with national and international requirements.

The (CoT) currently maintains seven permanent air-monitoring stations: Bodibeng, Rosslyn, Booyens, Pretoria West, Olievenhoutbosch, Mamelodi and Ekandustria. Four (4) mobile stations have been introduced and all these station are fully operational according to data reported to the South African Air Quality Information System (SAAQIS) (CoT, 2008). These monitoring stations are placed in areas where they monitor ambient levels of priority pollutants, comprising particulate matter (PM), sulphur dioxide (SO₂), ozone (O₃), volatile organic compounds (VOCs), carbon monoxide (CO) and nitrogen oxides (NO_x) from established and non-established sites across the City (Wright *et al.*, 2011).

2.7 AMBIENT AIR QUALITY GUIDELINES AND STANDARDS

2.7.1 International air quality guidelines and standards

The National Ambient Air Quality Standards (NAAQS) uses PM₁₀ and PM_{2.5} concentrations as criteria to evaluate the amount of particulate matter entrained in ambient air owing to the health risk associated with particulate matter equal or smaller than 10 microns in diameter. The criteria is used extensively to measure ambient air quality internationally as well as locally, the standard specifies that PM₁₀ levels may not exceed 120 µg/m³ over an averaging of 24 hours and 50 µg/m³ for an averaging period of one (1) year as shown in Table 2.2 below (DEA, 2009). Similarly, PM_{2.5} levels may not exceed 65 µg/m³ for an averaging of 24 hours and 25 µg/m³ for an average period of 1 year. Internationally, USEPA (2012) set the PM₁₀ limit of 150 µg/m³ for an averaging period of 24 hours and 50 µg/m³ for an averaging period of one (1) year. USEPA (2012) further indicated that PM_{2.5} levels may not exceed 35 µg/m³ for an averaging of 24 hours and 155 µg/m³

for an average period of 1 year. Table 2.1 below summarises states/governments set limit for particulate matter.

Table 2.1: National Ambient Air quality Standards for Particulate Matter (State of Air Report, 2005; DEA, 2009).

Pollutant	PM ₁₀		PM _{2.5}	
	Maximum 24-hour concentration (µg/m ³)	Average annual concentration (µg/m ³)	Maximum 24-hour concentration (µg/m ³)	Average annual concentration (µg/m ³)
DEA	120	50	65	25
SANS limits (SANS 1929:2005)	75	40	-	-
Australia	50	-	25	8
EC	50	30	-	-
World Bank (General Environmental Guidelines)	70	50	-	-
UK	50	40	-	-
US EPA	150	50	35	15
WHO	50	20	-	-

ABBREVIATIONS: EC, European Commission; SANS, South African National Standard; SA standards (AQA); UK, United Kingdom; US EPA, United States Environmental Protection Agency; WHO, World Health Organization; and Department of Environmental Affairs (DEA).

2.7.2 South African air quality guidelines and standards

The National Framework for Air Quality Management in South Africa makes provision for the establishment of air quality objectives for the protection of human health and the environment as a whole (The South African National Standards (SANS) 1929, 2011). Such air quality objectives include limit values, alert thresholds and target values. The proposed guideline criteria for dust deposition are outlined in SANS 1929:2005, Edition 1.1. The target, action and alert threshold in Table 2.2 below are used in the evaluation of dust fallout.

The proposed guideline for “Target” level is set at 300 mg/m²/day annually with no permitted frequency of exceedance. The guidelines state that the “Action Residential” level of 600 mg/m²/day, averaged over 30 days period may be exceeded three (3) times within a year, however, the exceedance should not be in two (2) sequential months. The “Action industrial” level is set at 1 200 mg/m²/day averaged over 30 days period within a year. The permitted frequency of exceedance is similar to “Action residential” level. Areas recording monthly average dust fallout rates that exceed 2 400 mg/m²/day under the “Alert threshold” have no permitted frequency of exceedance. However, the first incidence of dust fallout rate exceedance requires remediation and compulsory report to the relevant authorities (SANS 1929, 2011).

The NEM: AQA resulted in the promulgation of the National Dust Control Regulations (NDCR) in terms of NEM: AQA that came into effect on the first of November, 2013 (DEA, 2013). The regulation stipulates the total amount of dust permissible in ambient air monitored in accordance with American Society for Testing and Materials standard method (ASTM D1739-98, 2004) for measuring dust fallout (settleable particulate matter). The regulation stipulates that the dust fallout for residential areas must be kept below 600 mg/m²/day measured over a 30 day average and between 60 and 1200 mg/m²/day for non-residential areas as shown in Table 2.3.

Table 2.2: Dust standards, target, action and alert thresholds for dust deposition (SANS 1929:2011).

1	2	3	4
Level	Dustfall rate, <i>D</i> (mg/m²/day, 30-d average)	Average period	Permitted frequency of exceeding dustfall rate
Target	300	Annual	
Action residential	600	30 days	Three within any year, no two sequential months
Action industrial	1 200	30 days	Three within any year, not sequential months
Alert threshold	2 400	30 days	None. First incidence of dustfall rate being exceeded requires remediation and

Table 2.3: The National Dust Control Regulations (adapted: DEA, 2013).

Restriction areas	Dustfall rate (<i>D</i>) (mg/m²/day, averaged over 30 days)	Permitted frequency of exceeding dustfall rate
Residential area	$D < 600$	Two within a year, not sequential months.
Non-residential area	$600 < D < 1200$	Two within a year, not sequential months.

CHAPTER 3: EXPERIMENTAL DESIGN AND METHODOLOGY

3.1 STUDY AREA

The study was carried out in the City of Tshwane Metropolitan Municipality (CTMM), also known as Pretoria or Jacaranda City owing to the jacaranda trees that line its streets (see Figure 3.1). The CTMM is South Africa's capital city and houses the Union Buildings, the official seat of the South African government. The city has a population of approximately 2.3 million people (Statistics South Africa, 2011). It is located about 50.0 km north of Johannesburg and extends from Centurion in the south to Temba in the north, covering an area of 6 368 square kilometers (km²) and taking up over a third of Gauteng province. It stretches nearly 121 kilometers (km) from west to east and 108 km from north to south. It is one of South Africa's eight (8) metropolitan municipalities. Tshwane is situated about 1 350 m above sea level.



Figure 3.1: The jacaranda trees along Ceiliers street in Muckleneuk suburb.

The topography of the area consists of hills, ridges and undulating plains. The only topographical feature that might influence the dispersion potential of the metro is the Magaliesberg. This mountain range stretches from the eastern to Rustenburg in the west forming shallow valley within the central part of Pretoria and the Crocodile river regions called the Magalies Moot.

The climate around Tshwane is warm and moderate with a mean daily sunshine factor of 8.7 hours per day. The city is characterized by dry, sunny conditions, with light rains in the summer (December – February) season. Summers are hot with afternoon thunderstorms and winters are short and reasonably mild, with early morning frosts and sunny afternoons. It experiences heavy dust outbreaks and windy conditions during winter (June – August) seasons. Owing to the City's high altitude (approx. 1271), temperatures are fairly mild, with the average maximum daytime temperature of 21⁰C in January and dropping to an average maximum of 11⁰C in July (Olowoyo *et al.*, 2013).

CTMM is dominated by different rock types which are divided into six main groups: granite, dolomite, sedimentary and volcanic, gabbro-norite intrusive and karoo sedimentary rocks. The most dominant geological formations of the Tshwane area are Pretoria Group Andesite and Bushveld Gabbro-Norite, Pretoria Group Shale and Pretoria Group Quartzite (Nkopane and Takalo, 2009).

The dispersion potential of the metropolitan region is predominantly influenced by mesoscale processes. These include thermo-topographically induced circulations, the development and dissipation of surface inversions, and the modification of the low-level wind field and stability regime by urban areas (CTMM, 2008). Northerly to north-westerly winds prevail during much of the year due to the prevalence of the high pressure system. In spite of such winds, the northward shift of the high pressure belt and resultant influence of westerly wave disturbances on the region gives rise to an increase in the frequency of winds from the south to south-westerly sector. Owing to the southward migration of the high pressure belt, the frequency of northerly to easterly winds gets elevated particularly during spring and summer months. Furthermore, there is an influence of the airflow by anticyclonic subsidence and easterly wave systems (CTMM, 2008).

3.1.1 Sampling sites and sampling periods

Sampling was undertaken at five (5) different monitoring sites around residential and commercial areas of the CTMM from May 2012 to May 2013. Three monitoring sites are located within the University of South Africa (UNISA) at the Muckleneuk Campus, the fourth site is at the UNISA Vudec Campus and the last site is within the yard of Sunnyside Primary School. Figure 3.2 below shows the CTMM area and the sampling sites. The Global Position System (GPS) coordinates and the characteristics of all the sites are presented in Table 3.1.

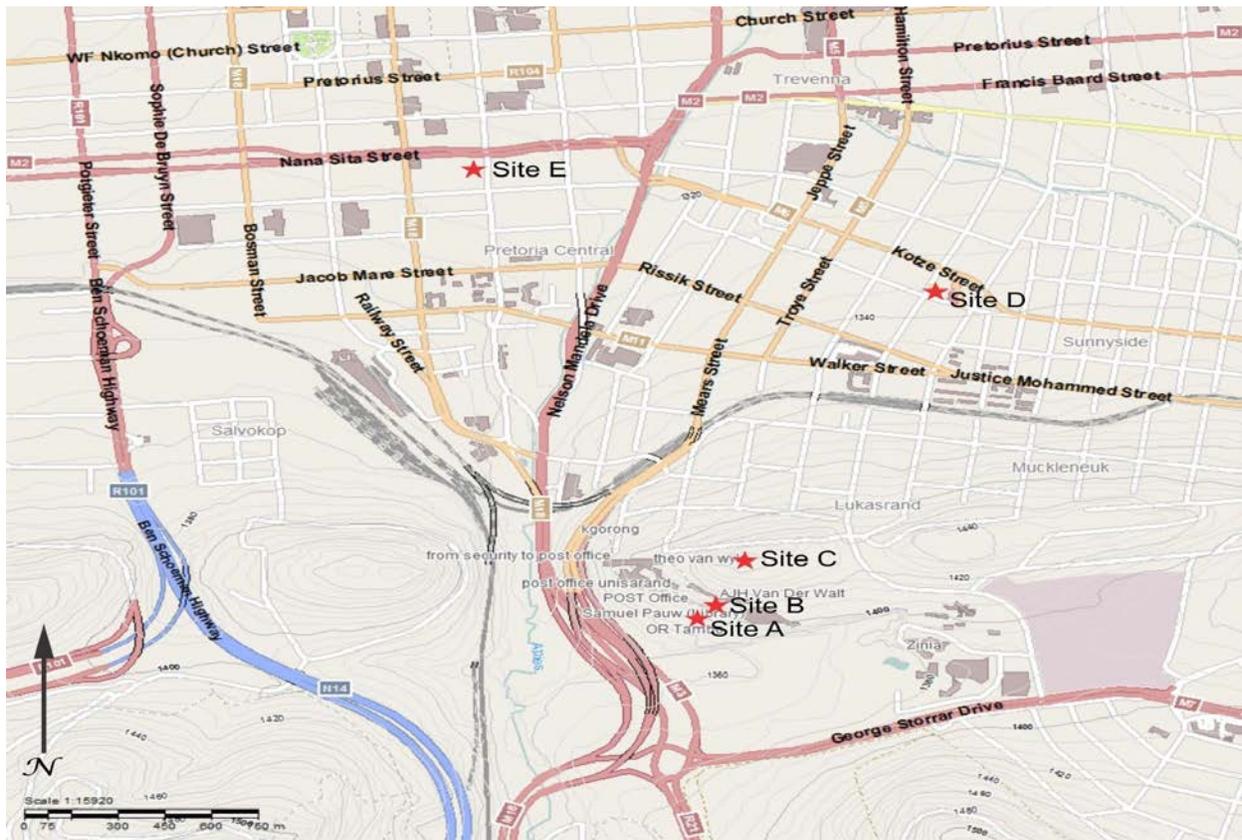


Figure 3.2: City of Tshwane showing the sampling sites of dust fallout rates.

Table 3.1: Location and characteristics of five (5) monitoring sites around the study area (Tshwane).

Site	Study area	Characteristics	GPS		
			Coordinates		
A	Unisa (Muckleneuk campus)	Residential area, bus parking, vegetation, vehicle movement 653 m from fountain circle regional road (R21).	S 25° 05879'	46. E 28° 917703'	11.
B	Unisa (Muckleneuk campus)	Residential area, parking base and vehicular movement.	S 25° 87776'	48. E 28° 89765'	7.
C	Unisa (Muckleneuk campus) Sunnyside	Top of the hill with relatively no anthropogenic activities.	S 25° 06707'	45. E 28° 60161'	11.
D		Residential area, high traffic congestions, commercial activities and few meters from a fuel station.	S 25° 38925'	45. E 28° 27651'	12.
E	Unisa (Vudec campus)	High traffic congestions, residential area, construction and high commercial activities.	S 35° 39554'	45. E 28° 28462'	12.

Site A (UNISA – Muckleneuk Campus)

This site is situated at the southern part of the university and is located near a paved parking lot, vegetation and a few meters from the R21 regional road which is characterized by a high number of vehicles during mornings and afternoon rush hours.

Site B (UNISA – Muckleneuk Campus)

This site is located approximately 25 m from site A, near a bus stop, paved parking area and a beautiful garden.

Site C (UNISA)

The site is located at the peak of the mountain next to Theo van Wyk building and serves as the background site and experience relatively minimal input from anthropogenic sources. The site is characterized primarily by natural sources such as bacteria, fungi and pollen and decaying vegetation.

Site D (Sunnyside Primary School)

The site is located within the school premises and is about 1.4 kilometers south east (SE) from Pretoria central business district (CBD) and approximately one and a half (1.6 km) North of UNISA (Muckleneuk Campus. The school is surrounded by a number of streets (Ceiliers and Leyds streets – from north to south; Rissik and Jorissen streets – east to west) and is also near to the Barclay square shopping center. The area has both paved and unpaved roads which could lead to entrainment of road dust by vehicles.

Site E (UNISA – Vudec Campus)

This sampling site is situated within Pretoria CBD at the corner of Lilian Ngoyi and Nana Sita Street. The activities which characterize this site include high population density, street dust and high traffic congestions during morning and afternoon rush hours.

3.2 SINGLE BUCKET PREPARATION AND COLLECTION

Five (5) single bucket dust fallout monitors were deployed according to the American Society for Testing and Materials Standard Method for collection and analyses of dust fallout (ASTM D1739) (ASTM D1739-98, 2004) and SANS 1929 (2011).

The 5.0 L buckets and their lids were cleaned with a household detergent, rinsed with distilled water and allowed to dry (Loans, 2007). The height of polypropylene buckets was 184.0 mm and the inside diameter of the lip was 236.0 mm. They were half-filled (2.5 L) with distilled water before adding about 10.0 mL of 3.5% of bleach (hypochloride) solution to each bucket to prevent the growth of algae. The buckets were then deployed to different sampling sites and put into the

cradle which was located 2.2 meters above the ground. They were exposed for a period of one calendar month and collected every month (from July 2012 - June 2013) for laboratory analysis. After dust samples were collected, they were filtered using Buchner funnel to determine the mass concentration of dust fallout material after weighing mass of filter paper before and after filtration. The filter papers were preconditioned in the weighing room before use and were manufactured by Munktell filter AB (Grade 389), with 47mm diameter, 84g/m² weight, 20 s/10mL and 8 -12 µm retention rate. They are made of pure cellulose with an alpha cellulose content of almost 100% and an ash content of less than 0.01% (Filtration and Separation Technology, 2015). The suspended material on the walls of the bucket was removed by using the distilled water contained in a wash bottle. Filter papers containing filtered dust fallout material were stored in petri dishes and allowed to dry by evaporation of retained moisture at room temperature. After they were allowed to desiccate, the petri dishes were closed and the settled dust was ready to be analysed.

The dust samples were analysed by a MicroScan Particle Analyser (MSPA), ICP-MS and SEM-EDX (Table 3.2). Thirty (30) samples collected from July to December 2012 were characterized with MSPA and ICP-MS. Further sample characterization was done with SEM-EDX on twenty (20) samples collected between March and June 2013. The MSPA was used to determine the mineralogical composition, size distribution and organic matter. ICP-MS gives valuable information concerning the elemental concentrations. SEM-EDX provides useful information on the morphology, elemental composition and particle density.

Table 3.2: Analytical instruments used for analysis of dust fallout and their objectives.

Analytical Instruments	2012	2013	Objective
MSPA	July-Dec. 2012	Mar – June 2013	Characterization of Mineralogical components and size distribution and organic matter
ICP-MS	July– Dec 2012		Further characterization of elemental concentrations
SEM-EDX	-	Mar – June 2013	Further characterization on the morphology, elemental composition and particle size of dust fallout

3.3 DATA ANALYSIS

3.3.1 MicroScan Analysis

MicroScan particle analyzer (MSPA) is a nondestructive analytical technique used for routine analysis (DustWatch, 2012). The advantage of this method is that the sample is not destroyed, ashed or digested in any way. A method adopted by Loans (2007) was used to calculate the mass concentration of dust fallout. Mass concentration of the sample was calculated by subtracting mass of filter paper from mass of filter paper containing dust filtrate material and multiplied by the number of days (30 or 31 days a month) and the cross sectional area of the inside diameter of the top of the bucket as represented by the Equation below:

$$\text{Mass concentration of dust fallout (mg/m}^2\text{/day)} = \frac{(M_2 - M_1)}{AT} \quad (1)$$

Where,

M_1 = Weight of the filter without sample (mg); M_2 = Weight of the filter with dry dust fallout after filtration (mg); A = the cross-sectional area of the buckets (0.02545m^2); and T = the duration of the sampling period in days (± 30 days)



Figure 3.3: The Buchner Funnel vacuum pump filtration system used in the Department of Chemistry laboratory at UNISA.

Instrumentation

A UOP UB 100j microscope (see Figure 3.4) with a mechanical stage, sample illumination capabilities, fitted 10x eyepiece and objective lenses offering 4 x 10 x 40 magnifications were used. Other specifications include: DCM310 camera with five (5) megapixels; CMOS chip; programme ScopeTek 3.0 and optical 5-50 μm . DCM310 camera works perfectly with any kind of optical microscopes, as biological microscope, metallurgical microscope and stereo - microscope. The images of the observed specimen are genuinely displayed on computer screen.

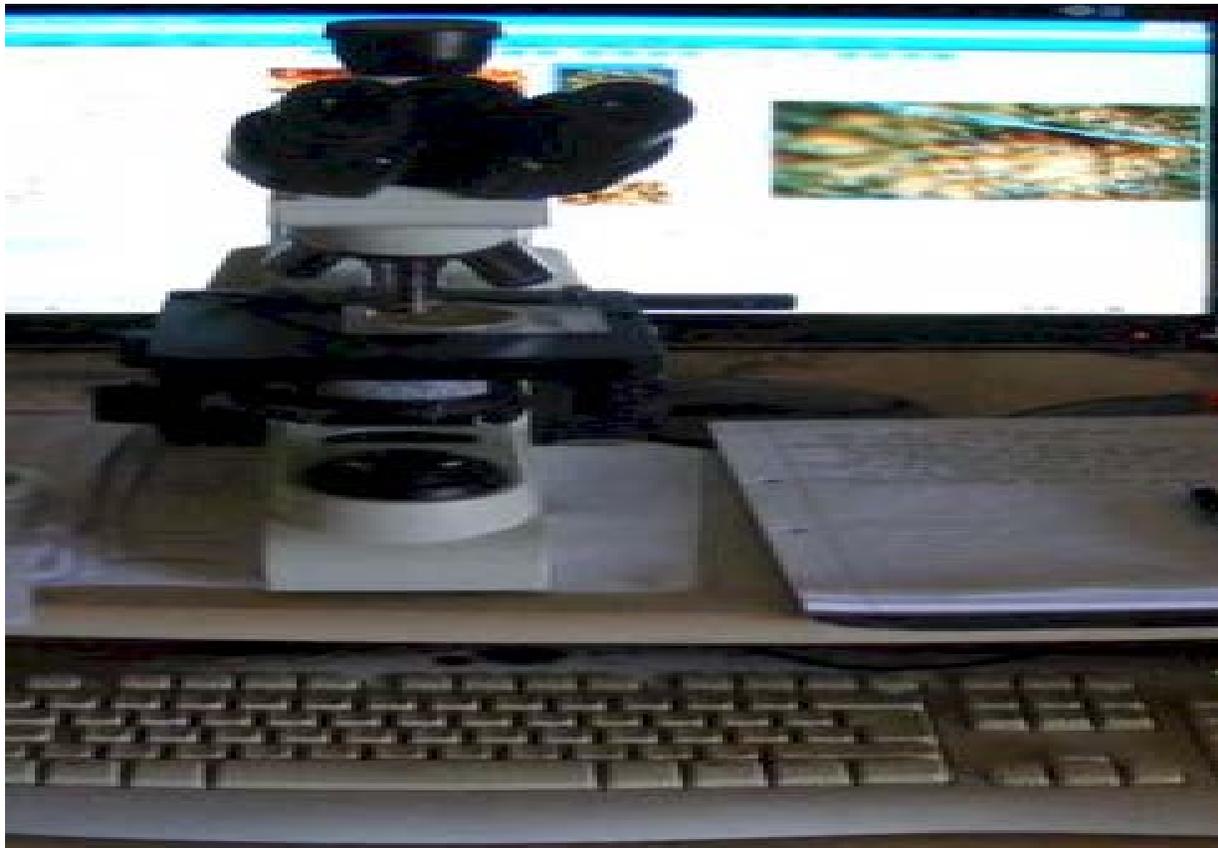


Figure 3.4: UOP UB 100j microscope connected to the computer monitor.

Sample preparation

The Munktell filter papers were weighed before and after sampling with the 0.01 mg precision analytical balance which was preconditioned at a constant humidity (40-45 %) and constant temperature (20-25 °C) for 24 h. The mass concentrations were then computed. All the samples collected from July to December 2012 and March to June 2013 were allowed to dry at room temperature, with the cover lids for petri dishes slightly tilted. The petri dish coverlids were then removed and the lower section of the filter paper loaded with dust was placed on the microscope stage (DustWatch, 2012).

3.3.2 ICP-MS Analysis

Instrumentation and Operating conditions

High Resolution-Inductively Coupled-Mass Spectrometry (HR-ICP-MS) analysis was performed using a Thermo Finnegan Model Element 2 instrument (Bremen, Germany). The radio frequency power was set to 1400 W. Samples were introduced using a SC-FAST flow injection analysis system (ESI, Elemental Scientific, Inc. Omaha, USA) with a peristaltic pump (1 mL/min). The instrument was equipped with a PFA-ST nebulizer, spray chamber (PFA Barrel 35 mm), demountable torch, quartz standard injector and Al sample skimmer and X skimmer cones. The nebulizer argon gas flow rate was adjusted to give a stable signal with maximum intensity. Methane gas was used in the analysis to minimize interference from carbon and to provide enhanced sensitivity. The instrument was calibrated using 0.6 µg/L HNO₃ solutions of multi-element standards. A calibration curve consisting of a series of 5 different concentrations was made from these standards. To check for instrument drift, one of these multi-element standards was analysed after every ten samples.

Principles of operation of ICP-MS

The Thermo Finnegan Element 2 is a double focusing magnetic sector mass spectrometer capable of simultaneous analysis of most elements with a concentration range spanning nine orders of magnitude. Liquid samples aspirated with a nebulizer are ionized in argon plasma for introduction into the mass spectrometer where elemental isotope separation and detection occurs. Magnetic and electric field mass filters separate the sample ions by their mass to charge ratio at an analyzing vacuum of 10⁻⁷ mbar. Only the positively charged ions are focused through the flight tube of the instrument to the detector create a secondary voltage that is used to measure the analyte concentration. The instrument has three (3) resolution settings (low, medium and high) that allow increased separation of isotopes (Schauer *et al.*, 2010).

Sample preparation

The Munktell filter papers were weighed before and after sampling with the 0.01 mg precision analytical balance which was preconditioned at a constant humidity (40-45%) and constant

temperature (20-25⁰C) for 24h. To avoid physical contact with the filters, forceps were used to handle and load the filter papers into the analytical balance. The mass concentrations were then computed. All samples were grouped according to their sites (A, B, C, D and E) of collection to form a composite sample.

The Thermo-Finnegan Element 2 ICP-MS Magnetic sector was used for the analysis of dust fallout. A combination of Occupational Safety and Health Administration (OHSA) ID-125G and National Institute for Occupational Safety and Health (NIOSH) 7300 base methods adapted for ICP-MS analysis was used for sample preparation. The chemical analysis was carried out at Biograde laboratory in Elarduspark, Pretoria.

Sample digestion and analysis

Approximately 250.0 mg of dust fallout was weighed on an analytical balance. Sample digestion was facilitated by heating on a hotplate with 5.0 ml of 70% concentrated Nitric acid (HNO₃) until effervescence ceased and subsequently 2.0 ml of 30% hydrogen peroxide (H₂O₂) was added. The solution was quantitatively transferred to 25.0 ml volumetric flasks for analysis.

3.3.3 SEM-EDX Analysis

Instrumentation and operating conditions

Scanning Electron Microscope-Energy Dispersive X- ray (SEM-EDX) is an instrument that is used to determine the size and morphology of the particles and surface elemental composition. The JSM-7600F model is a state-of-the-art thermal Field Emission (FE)-SEM that successfully combines ultra-high resolution imaging with optimized analytical functionality. The analysis was carried out using the SEM-EDX JEOL JSM-7600F equipped with Energy Dispersive X-ray (EDX) microanalysis system at Tshwane University of Technology (TUT) in the Department of Chemical & Metallurgical Engineering (see Figure 3.5). The SEM-EDX JEOL JSM-7600F specifications are listed in Table 3.3 below.

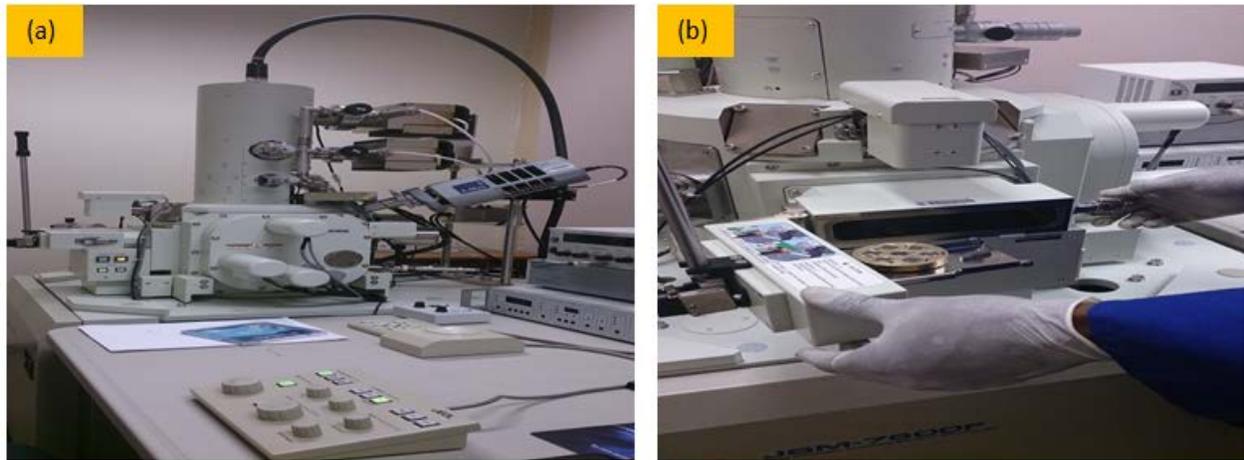


Figure 3.5: (a) Scanning Electron Microscope in the Department of Metallurgical Engineering at TUT (b) Prepared dust samples getting loaded for analysis.

Table 3.3: Specifications of SEM-EDX JEOL JSM-7600F

Resolution	1mm to 10mm
Magnification	25 to 1. 000. 000 X
Probe current	1 to 20 Amp
Acceleration voltage	500V to 30kV
Electron gun	Schotky Field Emission
Specimen stage	X=75mm, y=75mm, z=25mm
EDX	Working distance 8.5 mm
Detectors	In-Lens annular secondary Electron Detector (SED), Backscattered Electron Detector, (BSED) and Electron Backscatter Diffraction (EBSD)
Image processing	Pixel averaging, Frame integration continuous averaging
Image resolution	640 x 480 to 5120 x 3840
Image formation	2D
Working environment	Vacuum 8.7 E-4

The ability to provide detailed information on the morphological and chemical characteristics associated with individual particles has made SEM the method of choice in many studies where bulk analytical methods have insufficient resolution to identify the source(s) effecting ambient air quality (Casuccio *et al.*, 2004). However, Ma *et al.* (2001) as cited by Blanco *et al.* (2003) pointed out that SEM EDX is time consuming and furthermore, the loss of volatile components can hamper its quantitative estimates inaccurate.

In this study, SEM coupled with EDX was used to analyse the physico-chemical properties of dust fallout from March 2013 to June 2013. The other samples collected from July 2012 to December 2012 could not be analysed with SEM-EDX owing to its inaccessibility and high costs. SEM provides magnified image in order to study the size, morphology and the shape of individual dust particles, while EDX determines the elemental fingerprint of dust material. Fruhstorfer and Niessner (1994) used SEM-EDX to carry out chemical identification, classification and size analysis of soot particles in a single step. SEM-EDX was purposefully chosen in this study on the basis of its versatility and non-destructiveness of samples.

Principles of SEM-EDX

A focused electron beam (5kV to 50kV) is scanned over the sample in parallel lines. The electrons interact with the sample, producing an array of secondary effects, such as backscattering, that can be detected and converted into an image. The image can then be digitized and presented to an image analyser, which uses complex algorithms to identify individual particles and record detailed information about their morphology.

According to Casuccio *et al.* (2004), SEM allows a focused electron beam with the sample while under vacuum. The interaction of electron beam with the sample produces various effects that can be monitored with suitable detectors. The resulting signals include secondary and backscattered electrons along with the position of the beam to provide highly detailed spatial and compositional information.

However, this technique has limitations and errors. The single most evident source of error is sample preparation. To avoid it, the primary particles must be well-dispersed in monolayer in the substrate surface, and must be clearly separated from each other.

Sample preparation

Twenty (20) samples of dust fallout collected from March to June 2013 were analysed using SEM-EDX. Approximately one eighth of Munktell filter papers with settled dust were cut and mounted on the aluminium stubs. The samples were coated with a thin layer (10 nm) of Iridium (Ir) using a vacuum-coating Quorum Q150T-ES unit (Figure 3.5 (b)). The unit has the capacity to hold a total of six (6) samples at a time as depicted in (Figure 3.5 (b)). The dust samples were loaded into the SEM-EDX system for analysis.



Figure 3.6: (a) the loading of samples in Quorum system (b) the inside of Quorum (c) The data output of Quorum after coating.

The purpose of coating with Iridium (conductive layer) was to eliminate the charging artifacts and increase the contrast and conductivity of the sample. The samples were then put in the SEM-EDX for analysis. The working conditions were set at focused electrons beam of 30 kV, a beam current of 1–20 Amps, X-ray detection limit of ~0.1% and an 8.5mm working distance of samples away from Si (Li) detector. The electrons interacted with the sample to produce an array of secondary effects, such as backscattering, that can be detected and converted into an image.

The method adopted by Pachauri (2013) was used in the analysis. In each and every analysis of dust fallout by EDX, every element present was measured qualitatively (what is in the dust fallout) and quantitatively (how much of the element). The weight percentage of each element present in the spectrum was identified. On normalization to 100% for C and O the weight percentage of different elements were identified.

3.3.4 Statistical Analysis

The Statistical Package for the Social Sciences (SPSS) package from Windows and Microsoft Office (MS) Excel software were used to perform descriptive data analysis of five (5) composite dust samples by calculating their mean, standard deviation (SD), minimum concentration, maximum concentration, and median (see Table 3.2). Pearson correlation coefficients and one way Analysis of Variance (ANOVA) analysis were also performed on the elemental concentrations and dust fallout concentrations respectively.

3.3.4.1 Pearson Correlation Analysis

The correlation coefficient is a number between -1 and +1. In general, the correlation expresses the degree that, on an average, two variables change correspondingly. If one variable increases when the second one increases, then there is a positive correlation. In this case the correlation coefficient will be closer to 1. If one variable decreases when the other variable increases, then there is a negative correlation and the correlation coefficient will be closer to -1. The P-value is the probability that would have found in the current result if the correlation coefficient were in fact zero (null hypothesis). If this probability is lower than the conventional 5% ($P < 0.05$) the correlation coefficient is called statistically significant.

In this study, this statistical method was employed to analyse the strength of relationships among metal elements in order to identify their sources, strength of relationships among the sites to determine the their same source origin and the influence of meteorological parameters on dust fallout at sampling sites. Various degrees of Pearson correlation are represented by the Table 3.4 below:

Table 3.4: Degree of correlation (r).

Value of r	Degree of correlation
± 1	Perfect correlation
± 0.90 or more	Very high degree of correlation
± 0.75 to ± 0.90	Sufficiently high degree of correlation
± 0.60 to ± 0.75	Moderate degree of correlation
± 0.30 to ± 0.60	Only the possibility of correlation
Less than ± 0.30	Possibly no correlation
0	Absence of correlation

3.3.4.2 One way ANOVA test

In order to analyse significant difference among the average dust fallout concentrations of the monitoring sites, the one-way ANOVA test was performed using MS Excel. ANOVA is a method for testing the null hypothesis that there is no difference between two or more population means (usually at least three) (Heron, 2009). One-way ANOVA is carried out when there is only one qualitative variable which denotes the groups and only one measurement variable (quantitative).

If the null hypothesis is true, then the between-groups variance and the within-groups variance are both estimates of the population variance. On the other hand, if the null hypothesis is not true, the population means are not all equal, then the between-groups will be greater than the population variance, true population variance will be increased by the treatment of differences.

3.3.5 Enrichment Factor Analysis

The Enrichment Factor (EF) is a scientific approach used to characterize the chemical composition of airborne particulate matter. The elemental and the crustal (Si, Al, Ti, or Fe) concentrations in the air are taken into account and their ratio is normalised in the average continental crust (Wedepohl, 1971; Hoffmann *et al.*, 1972; & Zoller *et al.*, 1983). The EF estimates serve the purpose of differentiating between elements emanating from natural or

anthropogenic sources (Zhang *et al.*, 2004). The EF estimates of different elements were determined through comparison of elemental concentrations measured against the concentrations of crustal reference elements in order to identify possible original sources (natural or anthropogenic).

Cong *et al.* (2007) pointed that the estimate values of EFs are fundamentally significant in assessing the degree of anthropogenic influence and differentiating elemental concentrations emanating from man-induced activities and those that are from geogenic origin. There are quite a number of elements that can be used as a standard or reference (e.g. Si, Al, Ti or Fe). In this study, aluminium (Al) was used as a reference element. The choice was made on the basis of its low occurrence variability and presence in the environment in trace amounts (Loska *et al.*, 1997). The EFs for crustal material were calculated according to the following formula adopted from Rashki (2012):

$$EF_{Crust} = [E/R]_{Air} / [E/R]_{Crust} \quad (3.1)$$

Where E is the elemental concentration, R is a reference element (i.e. R represents Al in this dissertation) of crustal material and $[E/R]_{Air}$ is the concentration ratio of E to R in a collected dust fallout sample, and $[E/R]_{Crust}$ is the concentration ratio of E to R in the earth's crust. Si was used as a normalizing crustal element owing to its minor or negligible concentration to anthropogenic sources.

According to Hobbs (2000), the computation of EF values aid in deciding whether a particular element emanates from extraneous sources other than its major sources. When the EF_{crust} estimate of an element is less than 10, it is generally assumed that its origin is from natural sources (Chester *et al.*, 1999; Finlayson-Pitts and Pitts, 2000; Saliba *et al.*, 2007; Torfs and van Grieken, 1997). Conversely, Scheff and Wadden (1997), Gao *et al.* (2002) and Wang *et al.* (2006) as cited by Rashki (2012) pointed out that if the EF_{crust} value is above 10, then the element is considered to be of anthropogenic (man-induced) origin.

Anthropogenic activities have no significant contribution to the ambient elemental concentration mainly when EF_{crust} values are in the range of 1 to 5 (Rashki, 2012). This author further alluded to the fact that EF_{crust} values are directly proportional to anthropogenic source contribution i.e.

when EF_{crust} values increase, anthropogenic source contributions increase. Sutherland (2000) categorized enrichment factors as follows:

$EF < 2 \rightarrow$ depletion to minimal enrichment; $EF = 2-5 \rightarrow$ moderate enrichment; $EF = 5-20 \rightarrow$ significant enrichment; $EF = 20-40 \rightarrow$ very high enrichment and $EF > 40 \rightarrow$ extremely high enrichment.

3.4 QUALITY CONTROL

Table 3.5: Indeterminate errors for single bucket monitoring system (Adapted: Loans, 2007)

Positive errors	Negative errors
Bucket preparation – If too much bleach was added to the water then the excess bleach would come out of solution and form a solid material that would be collected on the filter	Bucket being emptied – When the water and dust was being put into the Buchner funnel to be filtered. Any dust that remained in the bucket was not measured
During the filtering process – The sieve used to keep insects, plant materials and small stones from being added to the precipitant dust samples have approximate apertures of 1mm^2 and any dust that adhered to the insects, plant materials and small stones was not collected on the filter.	During the filtering process – Spillages from the buckets would result in loss of sample.
During changing of buckets - positive error if dust was allowed to enter either the old or new buckets.	During changing of buckets – Negative error if old bucket water was spilt accidentally,
If algae grew in the buckets – Either because too little bleach was put into the bucket or because of unusual weather conditions, such as excessive rain that diluted the bleach to a point where it was not able to prevent the formation of algae. The acidity of the rainfall also affects the formation of algae.	Any dust that remains suspended on the walls of the bucket after its contents were poured into the Buchner funnel, an error would occur if dust was not washed and measured.

Bucket cleaning. Residual dust left in bucket between times that it was used.

Similarly any dust on the insect when it entered the bucket could also be added to 20 the mass of precipitant dust collected.

According to Vallius (2005), measurements differ in terms of their degree of uncertainty owing to the limits of measurement equipment and the people using the equipment. Errors were limited through the application of the following procedure in the dust fallout monitoring: the 5.0 L buckets were prepared in-house in order to prevent the surrounding dust to land on them while they are open. The lids were slightly opened while the buckets were prepared and closed immediately after processing. During the transportation, the buckets were kept in an upright position with the lids tightly fitted on them to prevent spillage. In the field, buckets were changed one at a time and precautionary measures were taken to ensure that dust is not kicked into the buckets.

In the laboratory, buckets were kept tightly closed until they were ready to be processed. Latex gloves were worn to inhibit skin contact with the water in the bucket. Forceps were also utilized to hold filter papers when they were removed from the Buchner funnel after filtration to avoid contact with the skin. After the filtration process, the buckets were washed with soap and distilled water. They were allowed to dry in an upside down position while waiting to be prepared and transferred to the field.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 ANALYSIS OF METEOROLOGICAL DATA

The meteorological data comprising of monthly averaged temperature, humidity, rainfall and wind velocity for Tshwane were obtained from South African weather service (SAWS). The data was divided into two categories according to the sampling points. The data for site A, B and C (situated inside UNISA Muckleneuk campus) was collected from Pretoria-UNISA weather station (S 25° 46' 12", E 28° 12' 0"). For site D (Sunnyside primary school) and E (Vudec UNISA campus), data was collected at Pretoria-Eendracht weather station (S 25° 44' 35.527" , E 28° 11' 3.995") situated at Lerskool Eendracht along 89 Bosman street. The meteorological parameters were arranged according to the four (4) seasons i.e. July and August 2012 (winter season), September and October 2012 (Spring), November and December 2012 (Summer), March and April 2013 (Autumn) and May and June 2013 (Winter) for ten (10) months (July – December 2012 and March – June 2013). Two (2) months (January and February 2013) data was not available because the monitoring instruments were vandalized. Tables 4.1 and 4.2 show the average meteorological parameters i.e. temperature (maximum and minimum), humidity, rainfall and wind velocity around Tshwane study area.

4.1.1 Maximum and minimum temperature (°C) results

Table 4.1 shows the average monthly temperature ranges from a minimum (5.4 - 8.3) to a maximum (20.4 - 23.3) for July and August (winter season) respectively. For November and December (summer season), the average monthly temperature ranges from a minimum (14.5 - 15.7) to a maximum (30.1 - 29.0). On the other hand, May and June 2013 (winter) sampling period recorded average monthly minimum temperature (8.0 - 5.7) and a maximum (22.9 - 21.1). These seasonal variability in temperature is only applicable to site A, B and C.

Table 4.1: Average meteorological parameters recorded during the sampling period at the UNISA weather station.

Season	Period	Temperature*(°C)		Humidity*	Rainfall*	Wind Velocity*
		Max.	Min.	(%)	(mm)	(m/s)
Winter	Jul-12	20.4	5.4	59	0	2.4
	Aug-12	23.3	8.3	48	0	2.2
Spring	Sep-12	25.1	9.8	63	61.6	2.3
	Oct-12	27.6	13.6	67	78	1.2
Summer	Nov-12	30.1	14.5	63	81.4	1.4
	Dec-12	29	15.7	74	143.2	1.6
Autumn	Mar-13	29.3	15.1	77	40.2	1.1
	Apr-13	24.5	11.1	73	70.4	1.8
Winter	May-13	22.9	8	65	0	1.7
	Jun-13	21.1	5.7	63	0.8	2.4

*Monthly average values

Table 4.2 shows the average meteorological parameters at site D and E. the average monthly temperature ranges from a minimum (5.6 - 7.7) to a maximum (22.7 - 24.7) during July and August (winter season) sampling period. During summer sampling period (November and December), the minimum temperature remained constant at 15.9 while the maximum temperature were 30.3 and 25.9.

Table 4.2: Average meteorological parameters recorded during the sampling period at the Pretoria Eendracht weather station.

Season	Period	Temperature*(°C)		Humidity* (%)	Rainfall* (mm)	Wind Velocity* (m/s)
		Max.	Min.			
Winter	Jul-12	22.7	5.6	54	0	0.4
	Aug-12	24.7	7.7	43	0	0.6
Spring	Sep-12	26	11	53	51.6	1.1
	Oct-12	28.3	14.6	56	58.2	1.5
Summer	Nov-12	30.3	15.9	57	122.2	1.5
	Dec-12	29.4	15.9	62	139.6	1.6
Autumn	Mar-13	30.6	16.5	65	16	1.4
	Apr-13	25.9	11.6	62	16.8	0.4
Winter	May-13	23.9	7	60	0	0.2
	Jun-13	22.1	4.3	57	0	0.2

*Monthly average values

4.1.2 Rainfall (mm) results

The total average rainfall (mm) for the entire sampling period at site A, B, and C (UNISA) is recorded in Table 4.1. The winter season recorded no rainfall; spring recorded a mean rainfall of 69.8 mm followed by summer and autumn with rainfall of 112.3 and 55.3 mm respectively. The 2013 winter season recorded 0.4 mm of total mean rainfall.

Winter, spring, summer, autumn and winter 2013 at Pretoria Eendracht weather station recorded the total average rainfall of 0.0, 54.9, 130.9, 16.4 and 0.0 mm respectively (see Table 4.2). Therefore, winter seasons are the ones associated with lesser or no rainfall. It is also evident that summer seasons are characterised by heavy (139.9 mm) rainfalls followed by spring (54.9 mm) season.

4.1.3 Humidity (%) results

Table 4.1 shows the average monthly humidity at the UNISA weather station. The winter season recorded an average of 53.5% of humidity and the summer recorded an average of 68.5%; followed by winter 2013 with an average of 64%. Summer recorded the highest percentage

humidity and this observation could be attributed to the heavy rainfall during summer which causes the air around the atmosphere to be moist and thereby trapping the dust particles. Pretoria Eendracht weather station (Table 4.2) recorded humidity of 48.5, 59.5 and 58.5 % for winter, summer and winter 2013 respectively. It is observed that summer season recorded the highest percentage humidity as compared to winters.

4.1.4 Wind velocity (m/s) results

The average monthly wind velocities from the UNISA weather station are given in Table 4.1(above). The winter, spring, summer, autumn, winter 2013 recorded average wind velocities of 2.3, 1.8, 1.5, 1.5 and 2.1 m/s respectively. It should be noted that both winters (2012 and 2013) recorded the highest wind velocity followed by spring. Summer and autumn recorded the same (1.5 m/s) wind velocities. Pretoria Eendracht weather station (Table 4.2) recorded average wind velocities of 0.5, 1.3, 1.6, 0.9 and 0.2m/s for winter, spring, summer, autumn and winter 2013 respectively. In both winter seasons, relatively higher wind velocities (2.3 and 2.1 m/s) were recorded at the UNISA weather station as compared to 0.5 and 0.2 m/s from the Pretoria Eendracht weather station.

4.1.5 Wind roses results

Wind roses are defined as radial graphs for a specific location that summarises the occurrence of winds by direction and speed (Sekonya, 2009). Different categories of wind velocity are represented by different colours: yellow represents wind velocity of 0.1 to 1.5 m/s, purple represents wind velocity of 1.5 to 3.0 m/s, red represents 3.0 to 5.0m/s, turquoise represents 5.0 to 8.0 m/s, bright green represents 8.0 to 11.0 m/s and blue represents wind velocity of greater than11.0 m/s. The length of each spoke tells the frequency of wind coming from a particular direction. The circle in the center indicates calm winds. Figure 4.1A shows the monthly average wind roses for July and August 2012 (winter season) at the UNISA weather station, also the location of sampling sites A, B and C. About 1% of the total time (24 hours), the wind blows from south (S) at 5.0 to 8.0 m/s, 5% and 8% of the time, the wind blows predominantly from the

south it blew from the S at 3 to 5 and 1.5 to 3 m/s respectively. In the SSE direction, the winds blow 3, 5 and 8 % of 24 hours at 5 to 8, 3 to 5 and 1.5 to 3m/s respectively. Strong winds also blew from W and WNW. Winds are calm at 5.8% of the time. The month of August is characterised strong winds from the S and moderate winds from the NW. Therefore, winter season is characterised by strong to moderately strong winds particularly from S to SSE and NW.

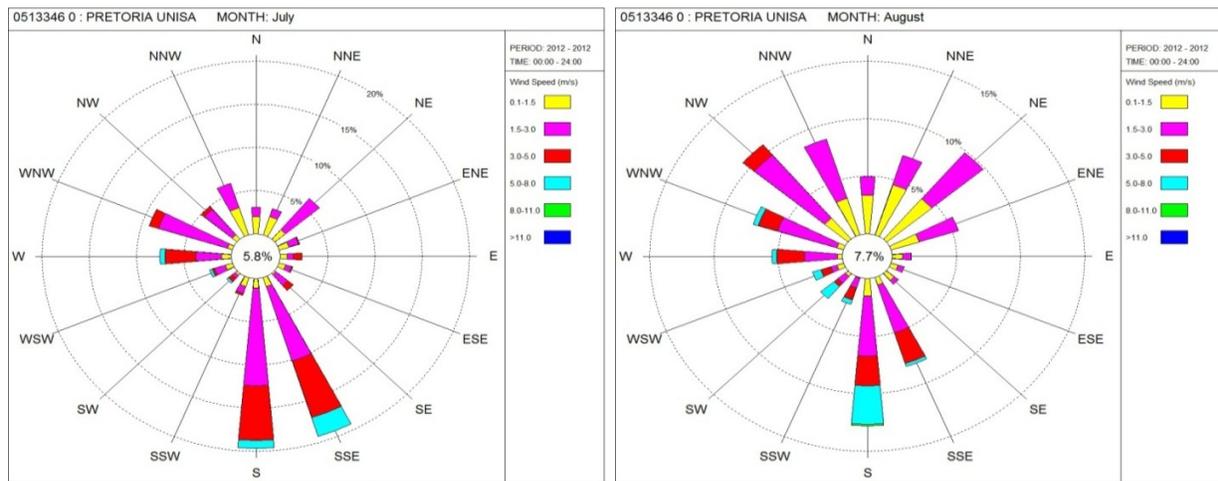


Figure 4.1A: Monthly averaged wind roses for July and August 2012 (winter season) at UNISA (sites A, B and C).

Figure 4.1B shows the monthly average wind roses for November and December 2012 (summer season) at UNISA with the prevailing wind direction in November is from N to NW. About 6% and 5% of the time, winds blow from the N and NNW at 1.5 to 3.0 m/s. strong winds blow 1% of the time from S and SSE at 5.0 to 8.0 m/s. moderate winds of 3.0 to 5.0 m/s prevailed 2 and 4% of the time from E and W direction respectively. Winds were calm 10% of the time. December also showed similar trends as November and 9.9% of the time the winds were calm. Therefore summer is characterised by strong winds blowing from SSE.

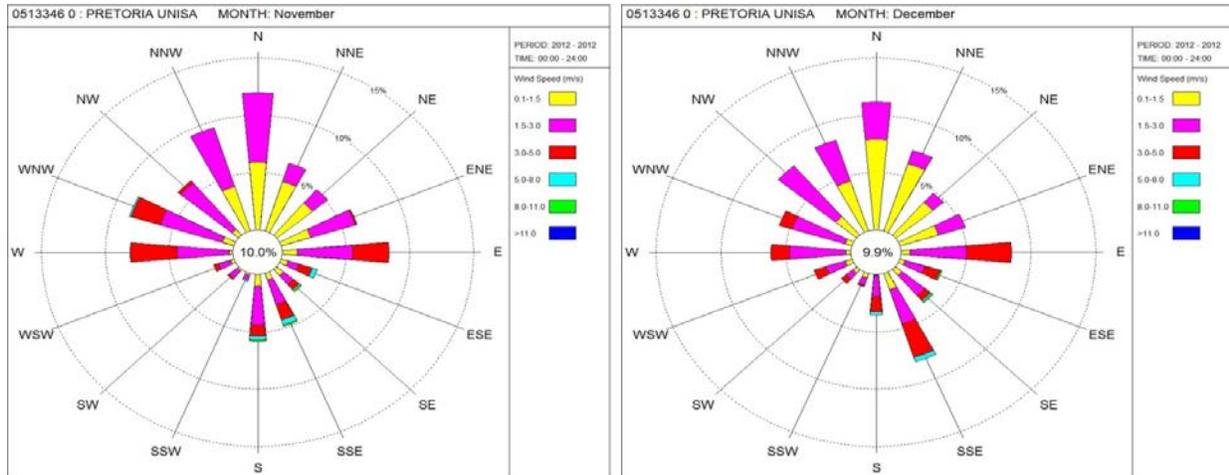


Figure 4.1B: Monthly averaged wind roses for November and December 2012 (summer season) at UNISA (site A, B and C).

Figure 4.1C shows the monthly wind roses for May and June 2013 (winter season) at UNISA. The month of May shows that 14% and 12% of time, winds blow from S and SSE at 1.5 to 3.0m/s and approximately 1% of time, strong winds of 5.0 to 8.0m/s were experienced from SSE and SE direction. 12.4% of time the winds were calm. 1 and 6% of time winds from S and SSE at 1.5 to 3.0 m/s. once again, June shows similar trends as May except that the strong winds are also blowing 1% of time from the S at 5.0 to 8.0m/s. June experienced 10% of calm winds. Therefore, June 2013 is characterised by strong winds coming from S, SSE, SE and W directions.

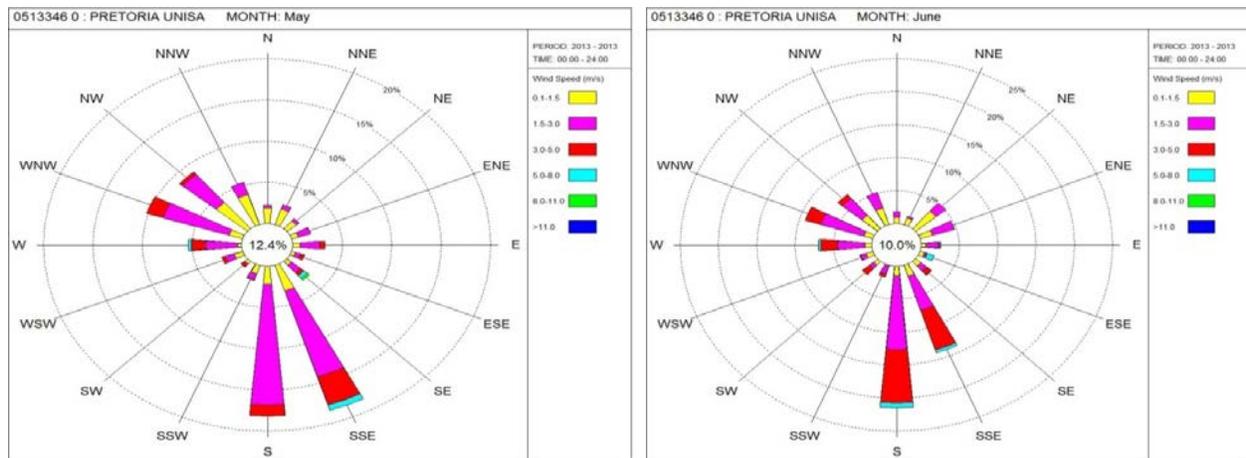


Figure 4.1C: Monthly averaged wind roses for May and June 2013 (winter season) at UNISA (site A, B and C).

Figure 4.1D shows average wind roses for July and August 2012 (winter) at Pretoria Eendracht weather station, also the location of sampling sites D and E. 4 and 3% of total time, winds blow from WSW and E at 1.5 to 3.0 m/s. approximately 1% of time, it blew from W at 3.0 to 5.0 m/s during July. August is characterised by winds blowing 7 and 3% of time from WSW at 1.5 to 3.0 m/s and 3.0 to 5.0 m/s respectively. Furthermore, at 1% winds blow from NE, ENE and W direction at 3.0 to 5.0 m/s. therefore, winter 2012, winds are predominantly from WSW (4th quadrant) mostly at wind velocity of 1.5 to 3.0 m/s and strongly at 3.0 to 5.0 m/s during August. Both July and August experienced calm winds at 52.8 and 45.4% respectively.

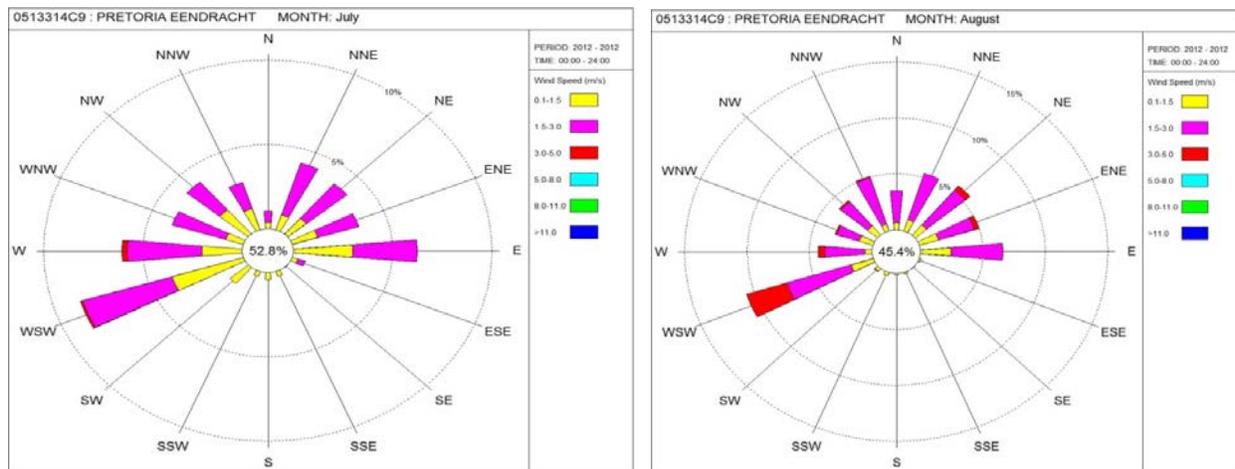


Figure 4.1D: Monthly averaged wind roses for July and August 2012 (winter season) at Pretoria Eendracht (site D and E).

Average monthly wind roses for November and December (summer) at Pretoria Eendracht are shown on Figure 4.1E. during November 2012, the prevailing wind directions are NE, ENE and E. 8, 5 and 12% of time, winds blow from NE, ENE and E at 1.5 to 3.0 m/s. approximately 1% of time, moderately stronger winds blew from NE and ENE at 3.0 to 5.0 m/s and calm winds were experienced at 25.6% of the total time. December 2012 shows similar trends except for moderately stronger winds only from NE at 3.0 to 5.0 m/s. it may be concluded that summer season is characterised by slightly weaker winds blowing from NE, ENE and E (1st quadrant) mostly at 1.5 to 3.0 m/s.

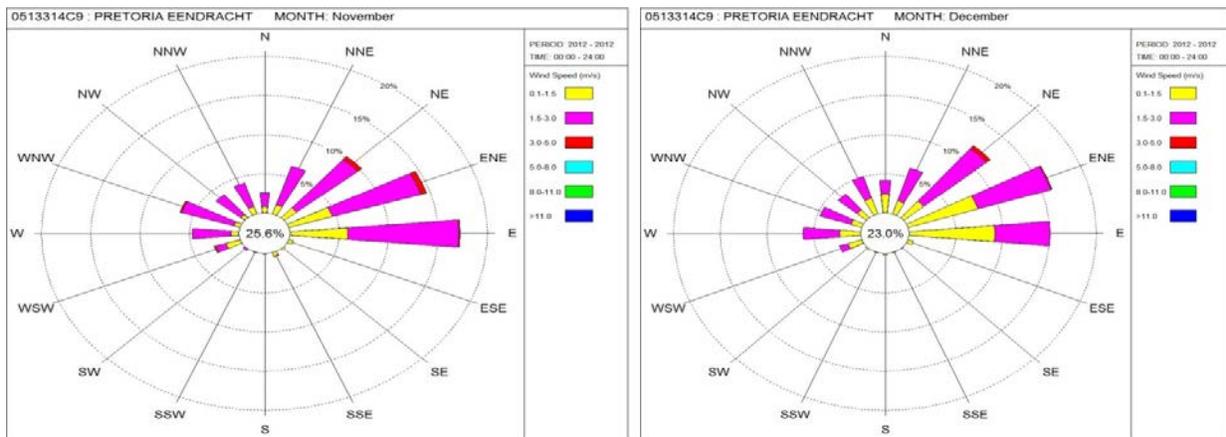


Figure 4.1E: Monthly averaged wind roses for November and December 2012 (summer season) at Pretoria Eendracht (site D and E).

Figure 4.1F shows the averaged wind roses for May and June 2013 at Pretoria Eendracht. Winds are predominantly blown from NNE, NE and ENE on the 1st quadrant. On the second quadrant, winds blow from NW and WNW. Moderately strong winds (1.5 to 3.0 m/s) blew from WNW for 4 and 2% of the total time. It is notable that approximately 1% of time, winds of 3.0 to 5.0 m/s blow from NE. May 2013 experienced 65.2% of calm winds. During June 2013, 5% and 4% of time, winds blew from W and WNW at 1.5 to 3.0 m/s and also 3% and 1% from NE and ENE respectively. Therefore, winter 2013 is characterised by winds blowing from N to E and N to W at 1.5 to 3.0 m/s for the entire season. There are no notable winds from the S to E and S and W. June 2013 experienced 64.7% of calm winds. Both summer 2012 and winter 2013 exhibit almost the same trend in terms of wind direction.

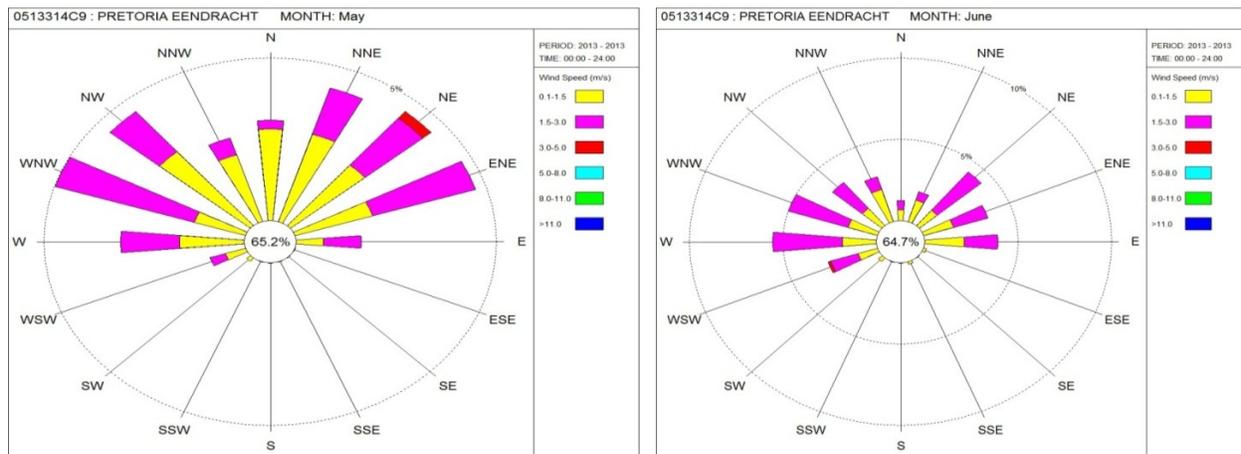


Figure 4.1F: Monthly averaged wind roses for May and June 2013 (winter season) at Pretoria Eendracht (site D and E).

Figure 4.1G shows the annual average wind roses at both UNISA and Pretoria Eendracht sampling sites. UNISA sites experienced stronger winds blowing from S and SSE and lower percentage (9.7 and 11.4%) of calm winds. In contrast, Pretoria Eendracht sites experienced winds blowing predominantly from E, ENE and NE with high percentage of calm winds (40.1% and 48.4%). The UNISA mountainous sampling sites (A, B and C) experienced significantly stronger wind velocities (5.0 to 8.0 m/s) as compared to the low lying Pretoria Eendracht sampling sites (D and E) with moderately low wind velocities (1.5 to 3.0 m/s).

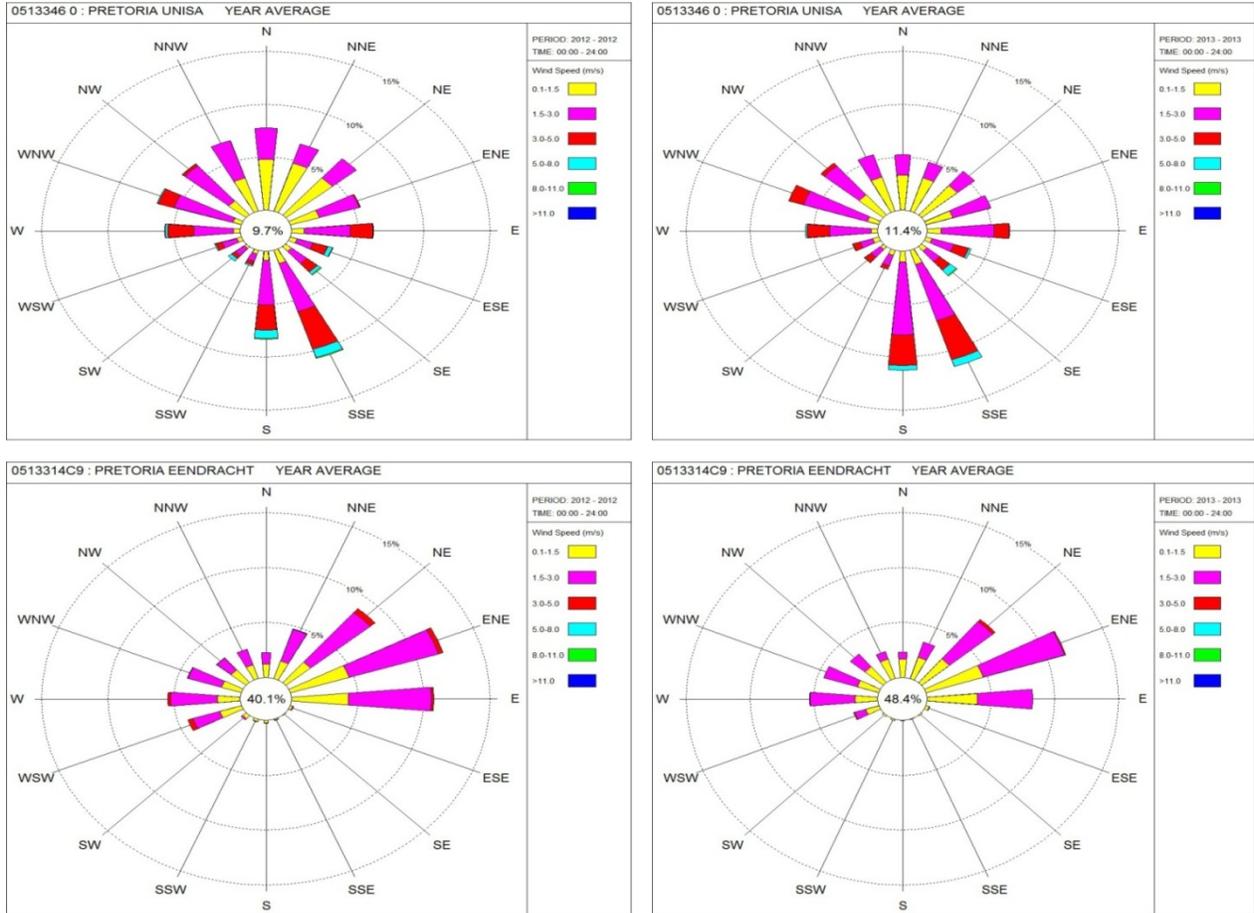


Figure 4.1G: Annual averaged wind roses for July 2012 and June 2013 at UNISA and Pretoria Eendracht sampling sites.

4.2 DUST FALLOUT RATES

4.2.1 Monthly dust fallout rates

The monthly dust fallout rates recorded at sampling sites A, B, C, D and E for July 2012 to June 2013 are presented in Table 4.3.

Table 4.3: Descriptive statistics of dust fallout concentrations at five monitoring sites from July 2012 to June 2013.

	Month	Monitoring Sites				
		Site A	Site B	Site C	Site D	Site E
Dust fallout rates (mg/m²/day)	Jul-12	44.62	77.82	142.43	99.92	94.42
	Aug-12	46.15	44.21	*N/A	201.69	196.60
	Sep-12	94.89	86.19	93.12	147.91	106.42
	Oct-12	289.77	67.76	53.94	85.65	88.81
	Nov-12	20.82	69.18	52.10	41.18	31.67
	Dec-12	204.78	17.03	93.64	101.36	141.23
	Mar-13	200.78	67.05	62.47	58.28	102.16
	Apr-13	80.55	37.19	44.26	45.44	79.11
	May-13	52.52	45.97	38.37	135.42	230.78
	Jun-13	36.54	60.24	30.38	78.71	127.83
Descriptive Statistics	Min	20.82	17.03	30.39	41.17	31.67
	Max	289.77	86.19	142.43	201.68	230.78
	Median	66.53	63.65	53.02	92.78	104.29
	Range	268.94	69.15	142.43	160.51	199.11
	Mean	107.14	57.27	67.86	99.55	119.90
	STD	91.62	20.91	39.87	50.25	57.98

*N/A: not available

The recorded dust fallout rates in July 2012 are 44.62, 142.43, 99.92 and 94.42 mg/m²/day for site A, B, C, D and E respectively. Site C recorded the highest dust fallout rate of 142.43 followed by site D and E with 99.92 and 94.42 mg/m²/day respectively. Site A recorded the lowest dust fallout as compared to the rest of the sites. The higher dust fallout rate at site C may be attributed to the location of the site being at the top of the hill and more exposed to high input from natural material. The higher concentrations at Site D and E may be emanating from vehicle emissions, vehicle entrainment of paved and unpaved roads that are evident at Pretoria CBD and Sunnyside suburb and construction activities for “a re yeng” bus rapid project along Nana Sita street. The possible sources of burning of domestic fuel from townships from west of city centre e.g. coal and paraffin cannot be ruled out. All the sites in July 2012 recorded the dust fallout rates within the SANS 1929 (2005) and DEA (2013) average RESIDENTIAL limit of 600 mg/m²/day.

The dust fallout rates for August 2012 recorded 46.15, 44.21, not available (N/A), 201.69 and 196.60 mg/m²/day for site A, B, C, D and E respectively. Site D recorded the highest dust fallout of 201.69 followed by site E and A with 196.60 and 46.5 mg/m²/day respectively. The contributory sources of dust fallout rates at site D and E may be vehicle emissions, vehicle entrainment of paved and unpaved roads. At site A the sources may also be vehicle emissions (situated close to parking lot and R21 regional road to OR Tambo International airport and N1 to Johannesburg). These roads are characterised by heavy traffic especially during morning and afternoon peak hours. Site B recorded the lowest dust fallout rate. All the sites fell within the SANS 1929 (2011) monthly average dust fallout rate of 600 mg/m²/day. Although these sites did not exceed the SANS 1929 (2011) threshold, the future possibility of exceedance cannot be ruled out. August is characterised by strong winds which have the potential to lift up dust particles from the earth surface and gust them into single bucket units.

September and October mark the spring season. Similarly, just like August, September marks the end of winter and beginning of spring. Therefore, the trend of dust fallout rates in September is the same as the month of August. Site D recorded the highest dust fallout rate of 147.91 mg/m²/day followed by site E and A with 106.42 and 94.89 mg/m²/day respectively. Of great

interest is that the dust fallout rate in September is less compared to August and this observation signifies the transition from one season to the next (from dry and windy periods to dry and cooler periods). The high dust fallout rate at sites D and E in September may be linked to low relative humidity (53%), rainfall (51.6 mm) and wind speed (1.1 m/s). Low humidity and rainfall have great influence on the evaporation process which increases the number of particles in the atmosphere, hence, high dust fallout rates at these sites. The opposite trend is true for site A. the low dust fallout rates at sites B and C are associated with high relative humidity (63%) and rainfall (61.6 mm). these two parameters have great influence on the condensation process which ameliorate particle loading in the atmosphere. The low wind speed (1.1 m/s) at site D and E led to the built-up of high dust fallout rates because it prevents dilution while the high wind speed (2.3 m/s) at site a caused suspension in the atmosphere owing to mobilisation of dust particles from the ground. All the sites in September 2012 recorded the dust fallout rates within the SANS 1929 (2011) and DEA (2013) monthly average RESIDENTIAL limit of 600 mg/m²/day.

The October 2012 recorded the highest dust fallout rate of 289.77 mg/m²/day at site A followed by site E and D with 88.81 and 85.65 mg/m²/day respectively. October marks the end of spring and beginning of summer. The summer season is mainly characterised by heavy rainfalls. The October month recorded the highest dust fallout rate of 289.77 mg/m²/day at site A followed by sites E and D with 88.81 and 85.65 mg/m²/day respectively. It is noted that October 2012 showed the same but opposite trend of dust fallout rates at sites A, D and E. the contributory sources at site A may include amongst others vehicle emissions, routine maintenance of garden which involves tiling of the grounds, burning of vegetation and vehicle entrainment of paved and unpaved roads. Site D and E are characterised by light and heavy vehicles emissions and use of coal and paraffin for cooking, therefore these are the contributors of elevated dust fallout particles. In terms of meteorological parameters, at low temperatures, dust fallout was high at site A. this observation may be attributed to temperature inversions which make the atmosphere to be stable. Surprisingly, at high relative humidity (67%) and rainfall (78.0 mm), site A recorded 289.77 mg/m²/day dust fallout. Site A, D and E recorded within the permissible RESIDENTIAL threshold of 600 for 30 days. The low wind speed (1.2 m/s) led to the built-up of dust fallout at site A while high wind speed (1.5 m/s) led to the suppression dust fallout at site D

and E. All the sites in October 2012 recorded the dust fallout rates within the SANS 1929 (2011) and DEA (2013) monthly average RESIDENTIAL limit of 600 mg/m²/day.

In November 2012, site B recorded the highest dust fallout of 69.18 mg/m²/day followed by site C and D which recorded 52.10 and 41.18 mg/m²/day respectively. The likely contributory sources of dust fallout at site B may be vehicle emissions (idling and movement) and garden maintenance. Fugitive dust such as wind erosion may be the source of emission at site C. site D is a residential area, situated inside the school and next to Gynaecological hospital and playground. Vehicle emissions, vehicle entrainment of paved and unpaved roads, burning of refuse and coal by residents could be the sources of dust. The high dust fallout concentration at site B may be the result of temperature inversions which causes the atmosphere to be stable and vertical movement of pollutants (dust fallout) inhibited. During this period, warm air overlying cooler air acts as a lid and prevents upward movement, which leaves pollutants trapped near the ground (Cossience, 2013). Low humidity (63%) led to the evaporation process which increases the dust fallout rates in the atmosphere and low rainfall contributed to minimum or less wash-out of dust fallout. Furthermore, low wind speed of 1.4 m/s also validates the elevated concentration of dust fallout as it allows build-up of dust fallout and inhibits dilution. Similarly, site C shows the same trend as site B. site A recorded the lowest dust fallout rate of 20.82 out of all the sites. This observation may be attributed to the location of the site. All the sites recorded within the SANS 1929 (2011) and DEA (2013) monthly average RESIDENTIAL target of 600 mg/m²/day.

December 2012 recorded 204.78, 17.03, 93.64, 101.36 and 141.23 mg/m²/day at site A, B, C D and E respectively. Site A recorded the highest concentration and followed by sites E and D respectively. The elevated dust fallout concentration at site A may be due to burning of veld fires and vegetation, vehicle emissions and vehicle entrainment on paved roads. The contributory sources of dust fallout rates at sites D and E are predominantly vehicle emissions, vehicle entrainment of paved and unpaved roads and construction activities. The lowest concentration was recorded at site B which has minimum movement of vehicles, hence, less emission. It is interesting to note that the dust fallout concentrations for site B in both November and December vary significantly. In November 2012, site B recorded the highest of 69.18 mg/m²/day and the lowest of 17.03 mg/m²/day in December 2012. These differences are possibly due to the high

rainfall (143.2 mm) and relative humidity (74.0%) in November and low rainfall (81.4 mm) and relative humidity (63.0%) in December. The reason for low concentration of dust fallout rate during December 2012 could be the result of the relationship between relative humidity and rainfall which has great influence in condensation process that reduce the number of dust fallout particles in the atmosphere. All the sites in December 2012 recorded the dust fallout rates within the SANS 1929 (2011) and DEA (2013) average RESIDENTIAL level of 600 mg/m²/day.

The dust fallout rates in March 2013 are 200.78, 67.05, 62.47, 58.28 and 102.16 mg/m²/day for sites A, B, C, D and E respectively. Site A recorded the highest dust fallout rate of 200.78 followed by 102.16 and 67.05 mg/m²/day at sites E and B respectively. The lowest dust fallout rate of 58.28 mg/m²/day was recorded at site D. Site A is situated north (N) of National roads (N1) and regional road (R21) which are characterised by heavy traffic congestion in the mornings and afternoons. The winds were blowing from SSE and E at average wind speed of 1.1 m/s. Low wind speeds lead to the build-up of high local pollutant concentrations because it inhibits dilution. Site E is located in a residential area, characterised by heavy traffic congestions which lead to elevated particle loading (dust fallout). Other possible sources such as vehicle entrainment on paved and unpaved roads, burning of coal and paraffin and construction activities may also be the primary contributors, therefore they cannot be ruled out. All the sites recorded the within the SANS 1929 (2011) and DEA (2013) monthly average RESIDENTIAL level of 600 mg/m²/day.

April 2013 recorded the highest dust fallout rates of 80.55 and 79.11 mg/m²/day for sites A and E respectively. A similar trend was observed in April 2013 as in March 2013 for sites A and E. site B recorded the lowest (37.19 mg/m²/day) dust fallout rate out of five (5) sites. The high wind speed (1.8 m/s) at site A may be reason for high dust fallout rate in that it causes dilution in the atmosphere owing to mobilisation of dust particles from the ground. On the same note, the relatively high dust fallout rate at site E could be the result of low wind speed (0.4 m/s) which led to the build-up of local dust fallout concentrations because it allows less mixing and dilution, therefore, enhancing the dust fallout pollution. The sampling sites in April 2013 fell within the SANS 1929 (2011) and DEA (2013) average monthly RESIDENTIAL limit of 600 mg/m²/day.

May 2013 recorded the dust fallout rates of 52.25, 45.97, 38.37, 135.42 and 230.78 mg/m²/day for site A, B, C, D and E respectively. Site D and E recorded the highest fallout rate of 135.42 and 230.78 mg/m²/day respectively. These two sites are situated in densely populated suburb of Sunnyside and Pretoria Central Business District (CBD) respectively which are commonly characterised by high traffic congestions (morning and afternoon peak hours), vehicle entrainment of paved and unpaved roads, burning of coal and paraffin by residents and street vendors particularly during winter periods and frequent construction activities. The above-mentioned activities are possible sources of high dust fallout rates at these sites. There were no rains recorded in May 2013, therefore, low wind speed of 0.2 m/s could be the contributing factor which led to increase of local dust fallout concentrations at these sites. Site C (the background) recorded the lowest dust fallout rate of 38.37 mg/m²/day. It is not surprising that it recorded less concentration of dust fallout owing to its location at the top of the hill where there are relatively minimum or no anthropogenic activities at all. All the sites in May 2013 recorded the dust fallout rates within the SANS 1929 (2011) and DEA (2013) monthly average RESIDENTIAL limit of 600 mg/m²/day.

June 2013 recorded dust fallout of 36.54, 60.24, 30.38, 78.71 and 127.83 mg/m²/day for sites A, B, C, D and E respectively. A similar trend is also observed as in May 2013. Sites D, E and B are the ones that recorded the highest dust fallout rates in descending order. Once again, site C recorded the lowest of 30.38 mg/m²/day. In terms of meteorological parameters, site B recorded the low rainfall of 0.8 mm compared to no rainfall recorded at sites D and E. rainfall acts as a removal mechanism of atmospheric particulates (including dust fallout) and further prevents the generation of dust particles and vice versa. The elevated dust fallout concentrations at site D and E may be the result of vehicle tailpipe emissions, vehicle entrainment of paved and unpaved roads, burning of coal and paraffin by residents and street vendors particularly during winter periods and frequent construction activities. Both May and June 2013 are categorised as winter season, therefore, it is not surprising that they projected similar trends. All the sites in June 2013 recorded dust fallout rates within the SANS 1929 (2011) and DEA (2013) monthly average RESIDENTIAL limit of 600 mg/m²/day.

The monthly mean dust fallout rates at different monitoring sites are shown in Figure 4.2. Site A has the highest dust fallout rate (107.14 mg/m²/day) as compared to other sites with and the lowest dust fallout rate is observed at site B (57.27mg/m²/day). The mean dust fallout rates are in the following decreasing order: Site A > Site E > Site D > Site C > Site B. the highest rate site A could be attributed to the vehicle movement and routine garden services which generate dust. Based on the location of site D and E, it is not surprising that these sites also recorded elevated amount of dust fallout. These could be the result of various residential activities such as burning of refuse, sweeping the yard, and vehicle activities including transport on paved and unpaved road, construction activities. The city of Tshwane recently embarked on the public transport improvement project named “a re yeng” which resulted in extensive construction activities (excavation, drilling etc.) in different parts of the city particularly CBD.

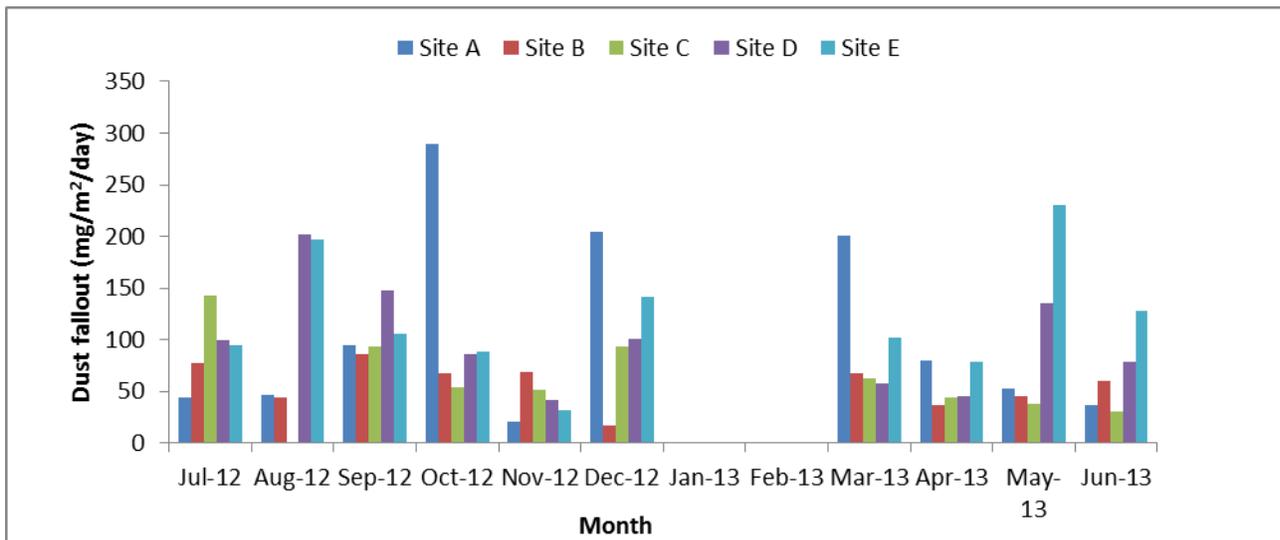


Figure 4.2: Comparison of the monthly dust fallout rates at Unisa (Site A, B and C), Sunnyside (site D) and Tshwane CBD (site E) monitoring sites.

The mean mass concentrations among these sites varied between 57.27 and 119.90 mg/m²/day (Figure 4.2). The highest mean dust fallout rate of 119.90 mg/m²/day was recorded at Tshwane CBD (site E) and the lowest of 57.27 mg/m²/day was recorded at UNISA (site B).

All the five (5) monitoring sites fall within the SANS 1929 (2011) annual average limit of 300.0 mg/m²/day, however, site A (UNISA), site D (Sunnyside) and site E (Tshwane CBD) have

recorded high mass concentrations of 107.14, 99.56 and 119.90 mg/m²/day respectively. This observation could be attributed to the high volumes of traffic and unpaved roads. Sites D and E recorded the most elevated particle loading which could be a result of vehicle tailpipe emissions, unpaved roads and construction activities. Site A, on the other, recorded the highest mass concentration which could be the consequences of vehicle diesel particulates and biomass burning as the site is situated next to the bus shelter and in the vicinity of vegetation. The predicted possible sources will be further analyzed after sample characterization with analytical instruments.

4.2.2 Seasonal average dust fallout rates per site

The seasonal average mass concentrations of dust fallout monitored per sites are shown in Figure 4.3. Months were organized seasonally with winter (July – August), spring (September – October), summer (November – December), autumn (March – April) and winter seasons (May – June) during the 2012 – 2013 sampling period.

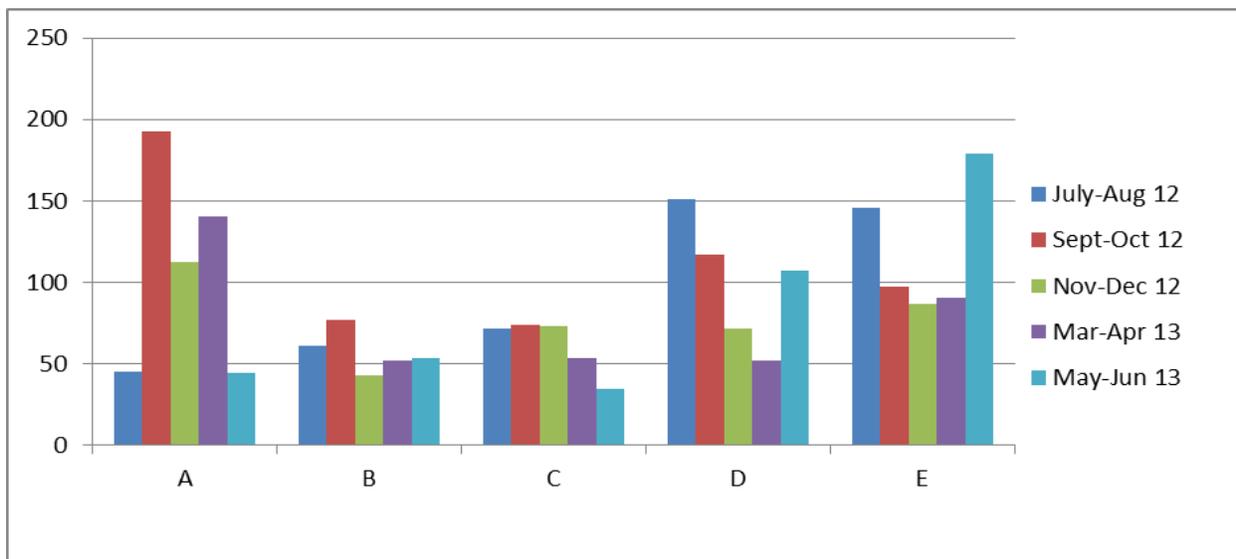


Figure 4.3: Seasonal variations of average dust fallout rates per site.

Winter 2012 recorded the average dust fallout rate of 45.39, 61.02, 71.22, 150.81 and 145.51 mg/m²/day for site A, B, C, D and E respectively. Site D and E dominated with elevated dust fallout rates while the lowest dust fallout rate was recorded at site A during winter. Winter

season at site A experienced average temperature of 21.9°C, no rainfall and average wind speed blowing from S to SSE at 2.3m/s. the lowest dust fallout rate at site A high temperature which causes increase in mixing depth and dilute the concentration of dust fallout in the atmosphere.

The maximum dust fallout rate at site D and E were observed during winter 2012 season. These sites recorded the average temperature of 23.7°C, no rainfall and average wind speed of 0.5 m/s blew from WSW to E. Site D (Sunnyside suburb) and site E (Pretoria CBD) are downwind of Pretoria west which is an industrial area. The wind direction influenced the high dust fallout rates at these two sites. Low wind speed also contributed to the build-up of high local dust fallout concentration which prevents dilution. Sibanda (2009) pointed out that the wind velocities determine the capacity of dust generation, the distance of downwind transport and the rate of dilution of pollutants.

Summer 2012 season recorded 112.80, 43.11, 72.87, 71.27 and 86.45 mg/m²/day for site A, B, C, D and E respectively. Site A and E recorded the highest dust fallout concentrations followed by the lowest recorded at site B. November and December mark the end of Spring and the beginning of Summer season, therefore, relatively high concentrations at site A and E are evident. Summer season is characterised by average heavy rainfall of 112.3 mm, average wind speed of 1.5 m/s blowing from SSE direction. High moisture content due to heavy rainfall suppresses and reduces dust generation and human exposure through inhalation. Site E is further downwind than site A, hence relatively high dust fallout concentration (lower than site A). Rainfall washes out dust fallout particles which have accumulated over time in the atmosphere, particularly during summer season. Furthermore, summer season is characterised by heavy rainfall which keeps the air around the atmosphere humid or moist, thereby, contributing to high percentage humidity.

Winter 2013 recorded 44.53, 53.11, 34.38, 107.07 and 179.31 mg/m²/day for sites A, B, C, d and E respectively. Site D and E recorded the highest dust fallout rate while site C recorded the lowest concentration. Average temperature, rainfall and wind speed and direction at sites D and E are 23°C, no rainfall and 0.2 m/s blowing from WSW to E respectively. Winter 2013 shows similar trends as winter 2012. Winter seasons are characterised by windblown dust being readily

available in the atmosphere and consequently leads to humans being exposed to it through inhalation.

In conclusion, Sekonya (2009) indicated that summer rainfall causes pollutants to be removed through wet deposition while on the other hand; winter seasons experience atmospheric stability through persistent high pressure system, which leads to subsidence by causing clear skies and temperature inversions at night. Environment (2003) as cited by Sekonya (2009) indicated that the air pollutants remain trapped in the lower atmosphere as a result of temperature inversion layer, thereby causing an increased deterioration of air quality.

4.3 MINERALOGICAL ANALYSIS

4.3.1 MicroScan particle analysis

The mineralogical analysis of dust fallout samples at site A shows the major components of both organic and inorganic materials. The inorganic material is comprised of crustal material (i.e. quartz, haematite, feldspar, garnet, aluminium silicates and calcium hydroxide) with quartz being the dominant in all the sampling cycles. The particle loading was found to be high during the dry season (July – August 2012 and March – June 2013). They make up to 60 – 65% mass concentrations as compared to 35% mass concentrations during with season (September – December 2012). No samples were collected from January to February 2013 due to the sampling buckets being removed without permission.

Site A

The major components of the sample include both the organic and inorganic materials. The inorganic material is comprised of crustal material (i.e. quartz, haematite, feldspar, garnet, aluminium silicates and calcium hydroxide) whereby quartz predominates in all sampling cycles. There are traces of mica and organic smoke carbons. Other organics include vegetation fibres, vegetation burn carbon (veld fire) mainly gasses. The particle loading seem to be high during the dry season (March – August). It makes up 60 – 65% mass concentrations (on average) compared to 35% mass concentrations during wet season (September – February). The particle sizes ranges

from 48 – 72 μm during dry season and 76 - 83 μm for wet season. The predominant particle morphology was found to be fine rounded sandy in shape. The sources of pollutants could be biomass burning (veld fires), vehicle exhaust emissions and tyre wear. Of great interest was the high amount of carbon detected which could be linked to industrial sources (mainly light oil fuel and petrol sources) and burning vegetation material, contributing < 2%. This validates the characteristics of site A as it is situated near a parking lot and few meters from R21 road and veld.

Site B

The dominating mineralogical components of the samples in site B are organic and inorganic particulates. Inorganic particulates include quartz, haematite, feldspar and mica while organic particulates are comprised of organic fibre (burnt cellulose), synthetic fibres. The mass concentrations range from 10 – 70% with particle sizes ranging from 50 - 74 μm during the dry season.

During wet season mass concentrations of haematite and quartz are 70% and 65 – 70% respectively. The particle sizes range from 46 - 53 μm during wet season. The differentiating feature of particle size in both seasons is the dust suppression which favours the wet season. The natural sources of pollutants are biomass burning and anthropogenic sources i.e. fossil fuel burning, industrial (large furnace emissions) and agricultural humus (to enhance growth on garden plants). Similarly, as in site A, the morphology of particulates in site B was found to be fine rounded and sandy. This is commonly the feature for quartz particulates.

Site C

The predominant constituents of the samples are categorised into organic and inorganic particulates. Inorganic particulates are composed of quartzite, feldspar, quartz, silicate, haematite and aluminium silicate while the organic components are traces of cellulose, fibrous material, loamy humus topsoil and agricultural material making up to 60 – 65%. The mass concentration ranges from 5 – 50% with worn roadway silicate at 5 – 10%; loamy topsoil at 40% and quartz and feldspar at 50%. Once more quartz was observed to be prevalent and dominant as in previously mentioned sampling periods. In August, the sample collection bucket was removed; hence the results are not recorded.

The particle size ranges from 43 – 73 μm during dry season and 43 – 67 μm during wet season. Some worn roadway (unpaved) silicate material present at 5-10% was observed with traces of cellulose fibres and several cactus origins. The overall mineral composition further shows the traces of copper chloride mineralisation present on some of the particulate individual particles with most of the sample being topsoil and rounded sandy clear quartz. The mineralisation could be remnants of dump material particulates liberated during the recovery operations.

Site D

The major mineralogical components are quartz (rounded sandy), quartzite (worn rounded) feldspar, olivine, haematite, jasper, aluminium silicate and kaolin. The organic particulates are comprised of vegetation burn carbon material and oily smoke carbon. The particle size range from 54 - 64 μm for quartz during dry season and 60 - 62 μm in wet season. The mass percentages of quartz, haematite and aluminium silicate are 40%, 5 – 10%, and 20% respectively. The morphology of particulates in this site is gritty, rounded and sandy. The sources of inorganic particulates are predominantly combustion-related (vehicle tailpipe emissions). We note increased hydrocarbon slightly oily smoke carbon suggesting a light fuel oil (diesel) combustion source. Organic sources include biomass burning.

Site E

The inorganic particulates in this site are comprised of quartz, quartzite, feldspar, copper oxide, haematite, iron oxide, kaolin and aluminium silicate. The organic particles are primarily organic fibre, textile fibres (nylon, propylene and polyester), systematic fibres, organic vegetation smoke, diesel or light fuel oil and carbon smoke. Quartz particle loading range from (30 - 60%), (10-30%), 50% and 20% respectively. Quartz dominate throughout the entire sampling period (July – December 2012), particularly during dry season (highest of 60%) as compared to lowest of 30-35% during wet season. The particle size ranges from 63-74 μm , which signifies coarse mode. The morphological characteristics range from round to broken sandy material

4.3.2 SEM-EDX analysis

Particle size, elemental composition and morphology

In order to have a clear understanding of the morphology, size and elemental concentration, the SEM micrographs and their corresponding EDX-spectra were analysed. Figure 4.4A-T shows the SEM micrographs and EDX-spectra for dust fallout particles collected at five sites around Tshwane. A total of 135 particles were analysed and classified according to their different sizes and types, morphologies and elemental concentrations at 5 sites. These particles have the diameter ranging from 1.0 to 10.0 μm

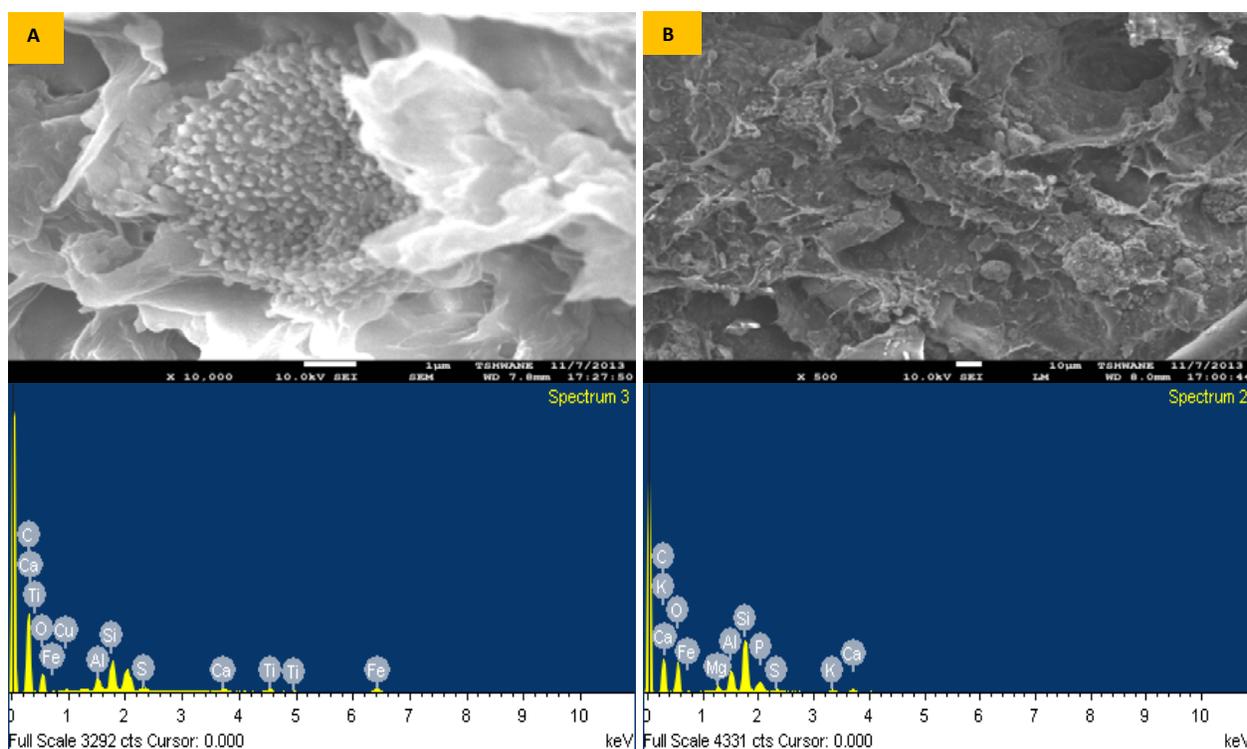


Figure 4.4 A and B: SEM images and EDX spectra of particles ranging from small clustered spherical to large irregular shapes collected at site A in March 2013.

The average elemental compositions of the sample collected during March, obtained through EDX is given in Figure 4.4 A and B above. The EDX-spectrum from particle a magnified 1.0 μm particle (A) shows the elemental weight percentages of Al, Si, S, Ca, Cu, Fe and Ti. This particle shows the dominant peaks of Ca, Ti, Si and Al with minor Fe, Cu and S. The dominance of Ca,

Si and Al signify soil and fly ash as the sources of this particle while Ca may be originating from cement manufacturing plant (Xie *et al.*, 2005) and surface soil. Ti could be linked to ilmenite (FeTiO_3) and rutile (TiO_2) minerals (Miler, 2014). The morphology of particles ranges from small clustered spherical to large irregular shapes.

Figure 4.4 B shows a magnified 10 μm particle and its respective spectrum showing the elemental composition of Al, Si, S, K, Ca, Fe, P and Mg. It also shows dominant peak of Si and minor peaks of Ca, Al, Mg and P. The morphology of this particle was found to be irregular coarse material likely to emanate from geological material based on elemental finger print (Al, Si, Fe, and Mg). Based on the characteristics of the site a, K could be the result of burning of biomass, since it is a tracer of biomass (Kgabi *et al.*, 2008). P could be attributed to garden fertilizers, bird droppings and pet waste while S is mainly traced to the combustion of fossil fuels and released in the form of SO_2 into the atmosphere.

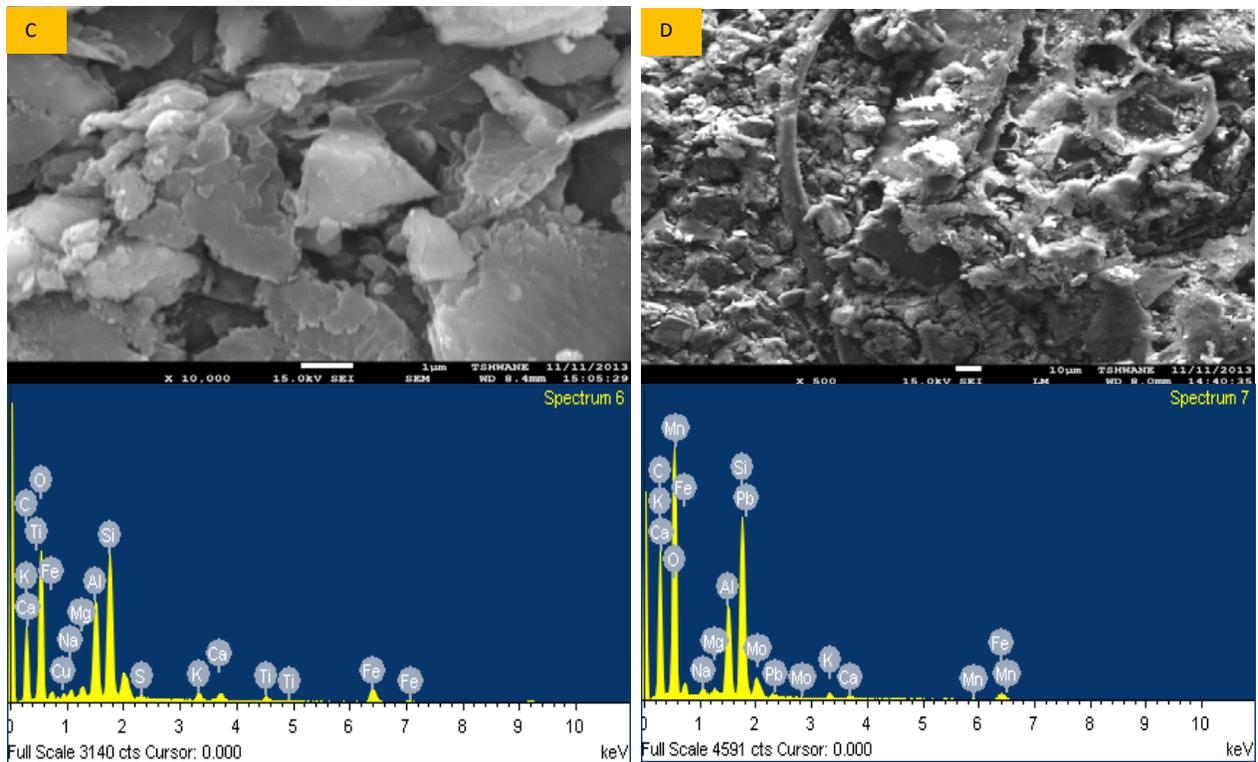


Figure 4.4 C and D: SEM images and EDX spectra with morphology ranging from small oval-like to irregular shapes collected at site A in June 2013.

Figure 4.4 C above shows a magnified size 1.0 μm particle and its respective EDX spectrum shows the elemental composition of Ca, K, Mg, Na and metals Cu, Ti and Fe. The EDX spectrum of this particle shows the dominant peak of silica (Si) followed by Cu, Ti and Fe metals. Cu and Fe are likely to originate from combustion of fossil fuel and brakes from automobiles (Bhattacharya, 2013). The morphology ranges from small oval-like to irregular shapes. These types of morphology may be linked to high combustion sources e.g. power plants.

Figure 4.4 D shows a magnified size of a 10.0 μm particle which was collected in June 2013 (dry) with elemental composition of Mn, Pb, Fe, Ca, K, Al, Si, Mo, Mg and Na. The highest peak is that of Mn followed by Si, Al, K, Ca and minor Mo. It has some mixture of crustal (Al, Si, Mg and Fe) and anthropogenic (Mn, Pb and Mo) elements. The morphology ranges from irregular and small oval particles.

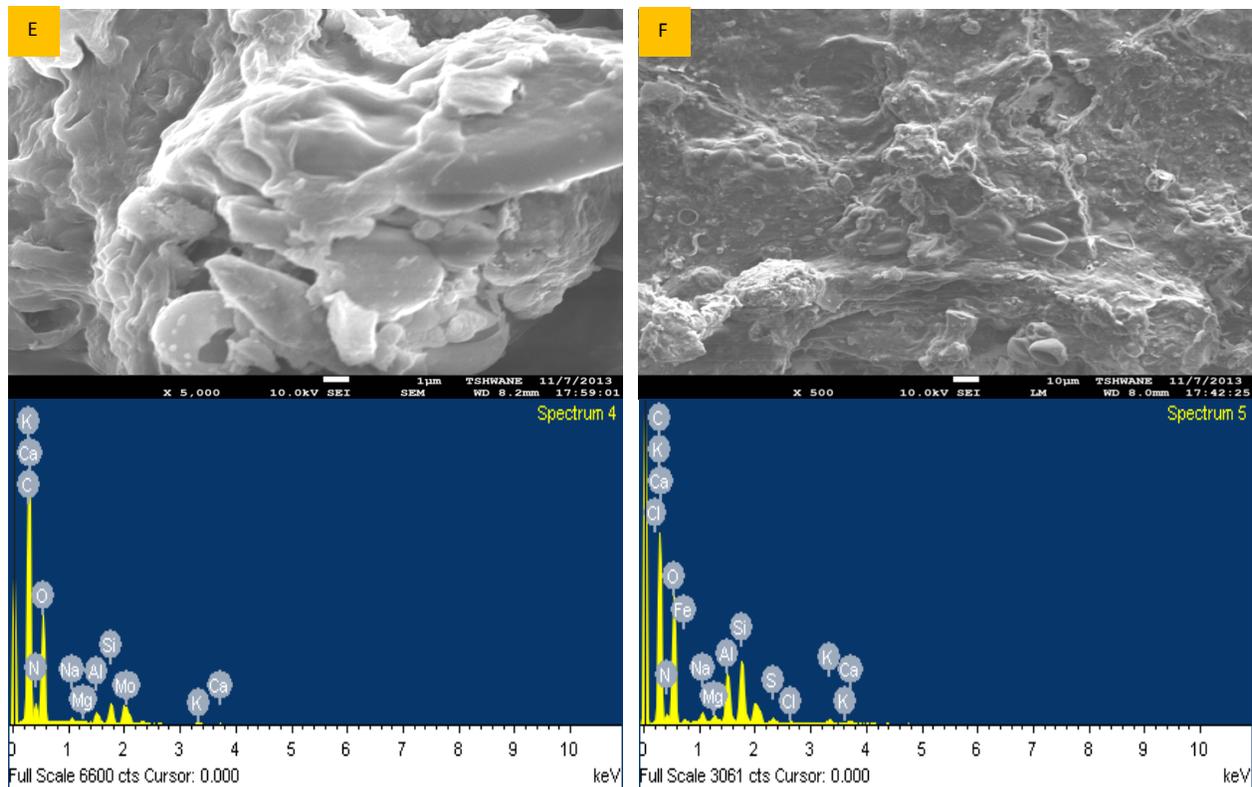


Figure 4.4 E and F: SEM images and EDX spectra of particles ranging from small oval to large irregular shape collected at site B during March 2013 sampling period.

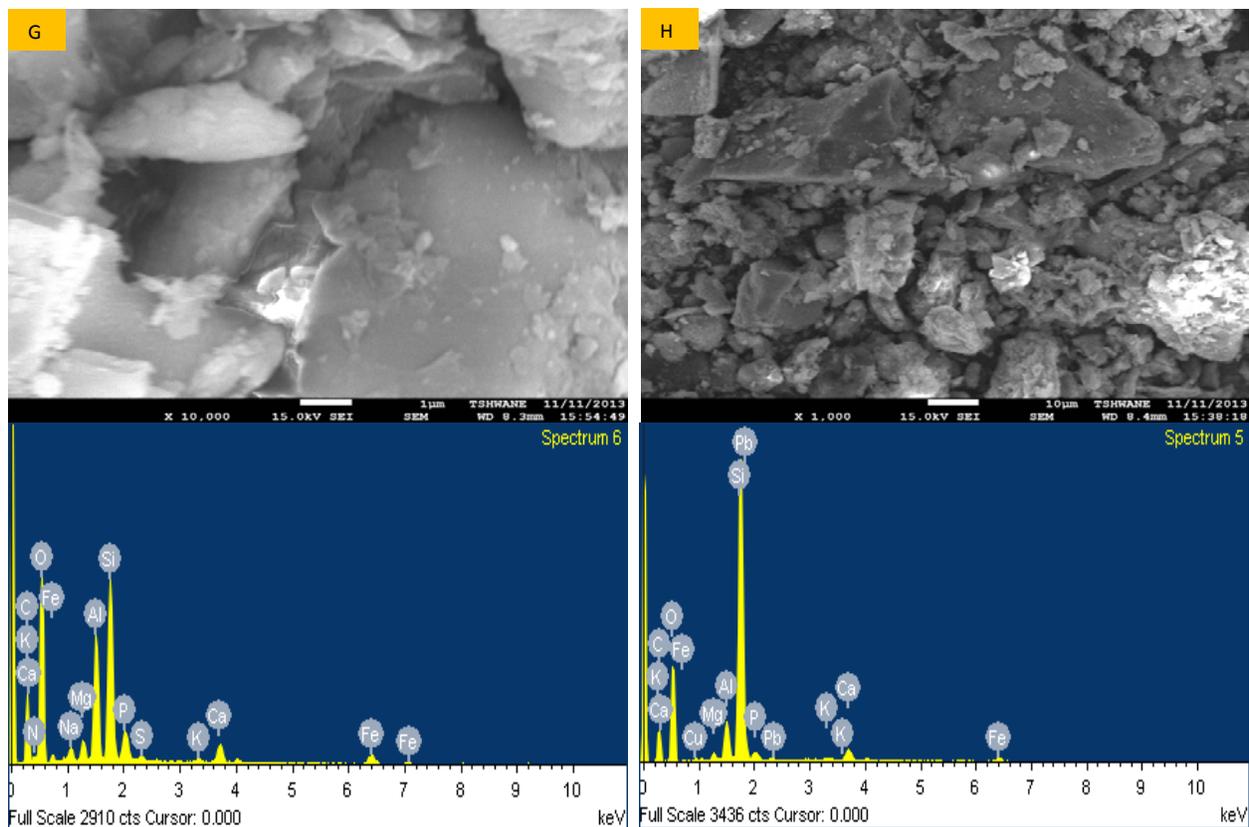


Figure 4.4 G and H: SEM images and EDX spectra of particles with round smooth edges and irregular shaped collected at site B during June 2013 sampling period.

Particle E of 1.0 μm and its EDX spectrum (Figure 4.4 E) were collected at site B during March (wet) season. The particle is composed of Al, Si, Ca, K, Mg, Na, N and Mo. The dominant peaks are those of Ca and K followed by minor peak of Si. The morphology of this particle is irregular with smooth surfaces. Particle F of 10.0 μm and its EDX spectrum (Figure 4.4 F) under the same season showed elemental composition of Al, Si, Ca, K, Mg, Na, N, S, Fe and Cl. Both particle E and F show the same elements with the exception of Fe, S and Cl which are found in particle F of coarse mode. Particle F has tubular and spherical morphology with smooth surfaces.

Particle G (Figure 4.4 G) above of 1.0 μm was collected at site B during the dry season (June 2013). The EDX spectrum for this particle shows the elemental weight percentages of Al, Si, Ca, K, Mg, Na, N, S, P and Fe. The Si has the highest peak with traces of Al, Mg, Ca and Na. the particle exhibit the spherical morphology with rough surfaces. Particle H of 10.0 μm and its

spectrum (Figure 4.4 H) showed the elemental composition of Al, Si, Ca, K, Mg, Fe with Cu and Pb metals. Pb has a dominant peak on the spectrum followed by Si. The morphology is irregular.

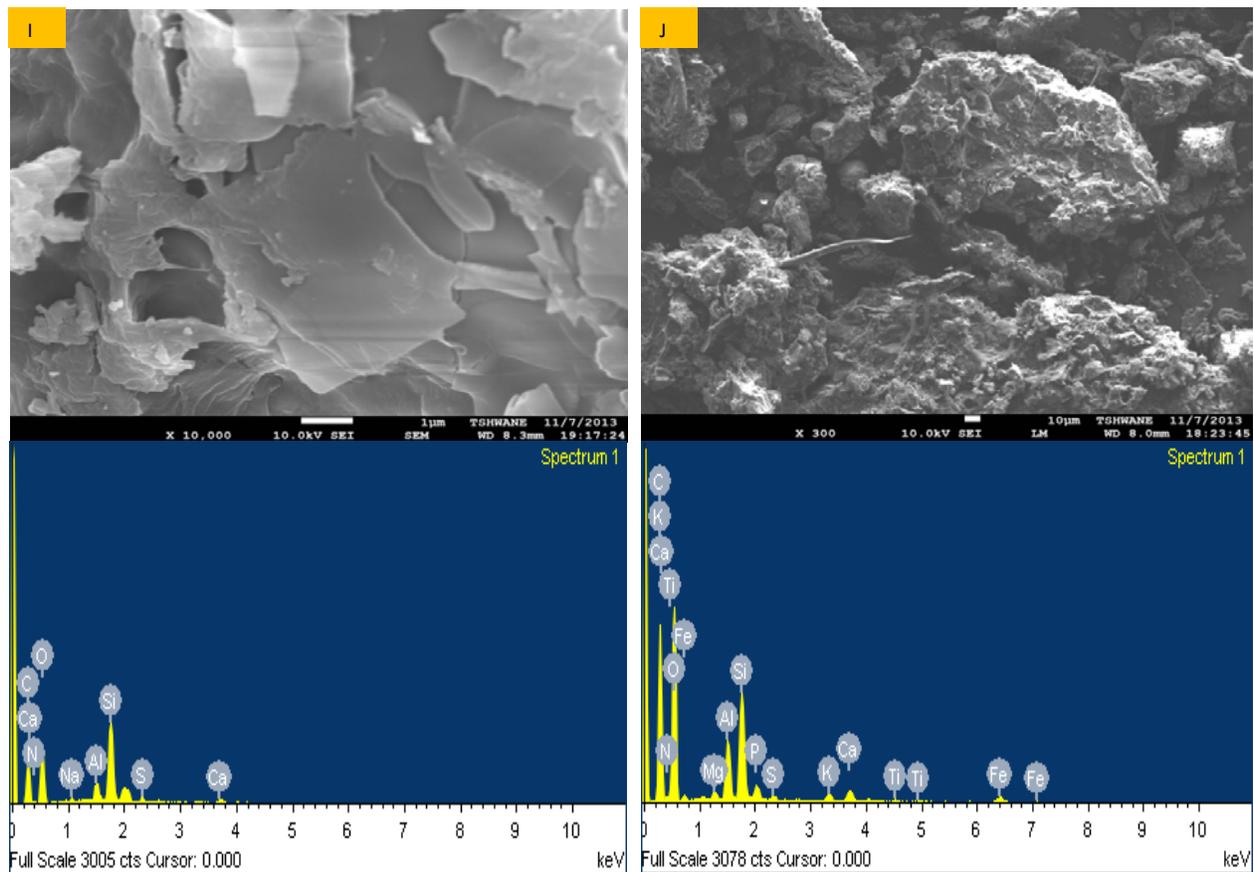


Figure 4.4 I and J: SEM images and EDX spectra of particles with smooth rectangular and grossular-shaped collected at site C during March 2013 sampling period.

Particle I of 1.0 µm and its EDX spectrum (Figure 4.4 I) above were collected at site C during wet season (March 2013). The EDX spectrum on this particle is made up of Ca, N, Na, Al and Si. Si has the dominant peak followed by Ca, S and Al. the morphology ranges from smooth rectangular to irregular. Particle J (Figure 4.4 J) of 10.0 µm (coarse) gave the EDX spectrum with elemental composition of Al, Si, Ca, K, Mg, P, S, Fe and Ti. Si, Ti and Al have the dominant peaks with grossular morphology. These two particles (I and J) gave the same elemental composition with the exception of Na found under the coarse mode (10.0 µm).

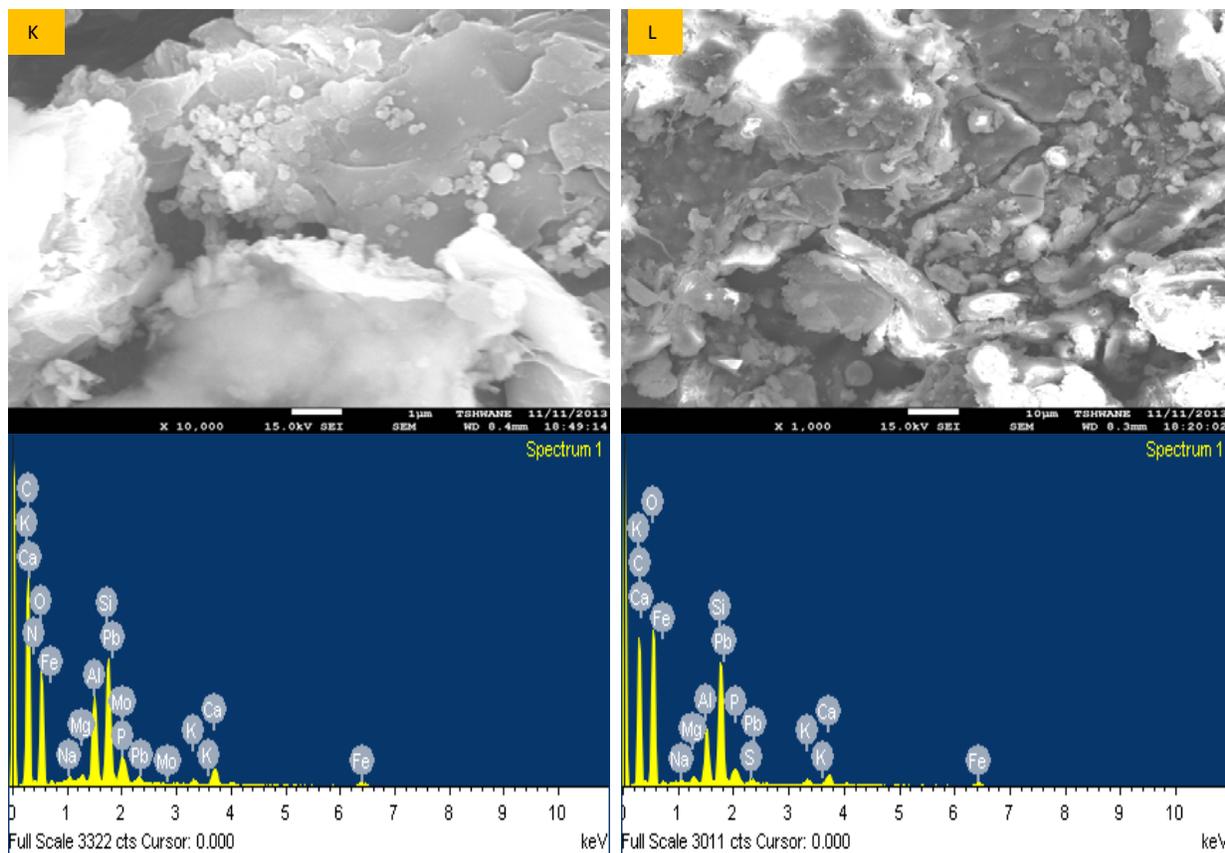


Figure 4.4 K and L: SEM images and EDX spectra of particles with small spherical and irregular shape collected at site C during June 2013 sampling period.

Particle K of 1.0 µm in diameter and its spectrum (Figure 4.4 K) above was collected at site C during the dry season. The EDX spectrum of this particle shows the weight percentages of Al, Si, Ca, K, Na, Mg, P, Pb and Mo. The small spherical particles are evident and irregular in morphology. The EDX spectrum of particle L of 10.0 µm in diameter shows the elemental weight percentages same as particle K with the exception of S, Mo and N. Ca and K have the dominant peaks followed by Si, Pb, Al and Mg. S seems to dominate under coarse fraction (10.0 µm) in particle L while Mo and N dominated under fine fraction (1.0 µm) in particle K.

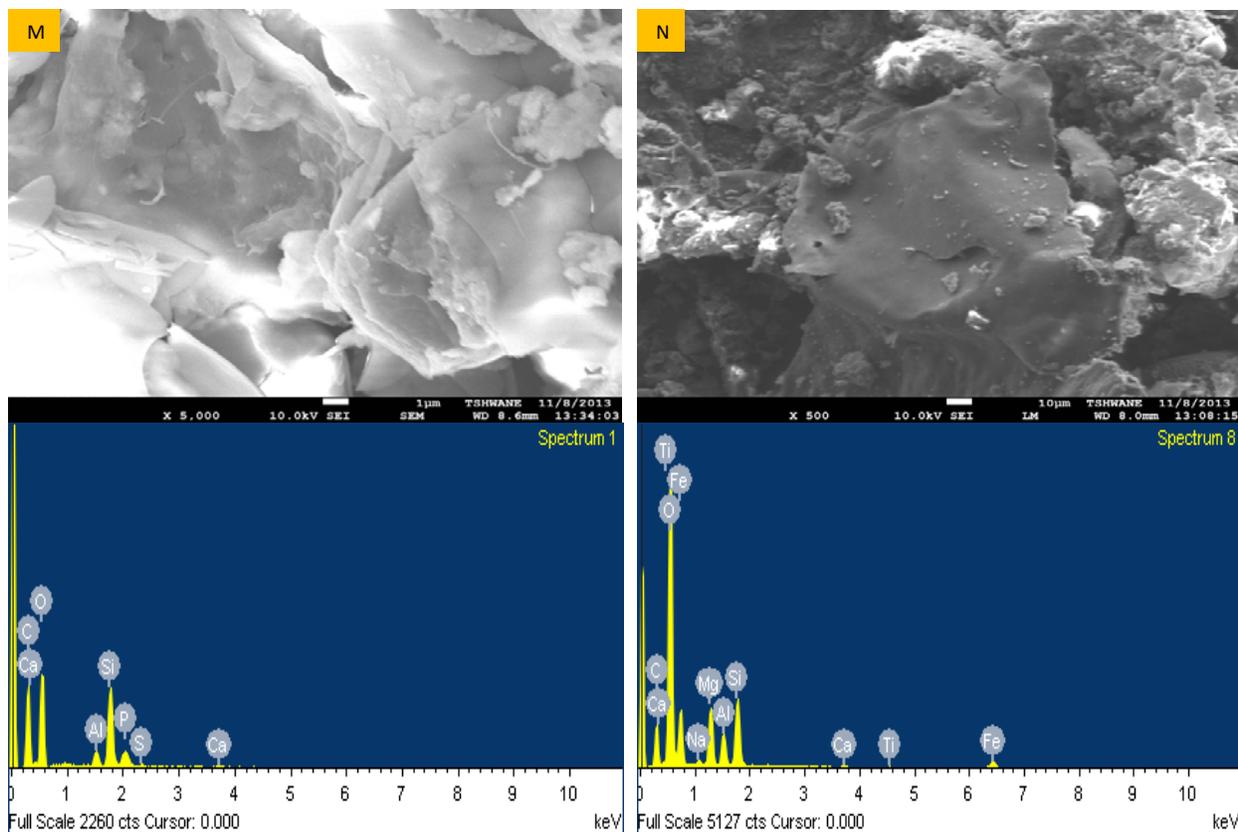


Figure 4.4 M and N: SEM images and EDX spectra of particles with small spherical and irregular shapes collected at site D during March 2013 sampling period.

Particle M of 1.0 μm in diameter and its spectrum (Figure 4.4 M) shown above was collected at site D during the wet season. The EDX spectrum of particle M shows the presence of Ca, Si, Al, P and S. Si has the highest peak followed by Al and P. The EDX spectrum of particle N (Figure 4.4 N) shows the elemental weight percentages of Ca, Ti, Fe, Na, Mg, Al and Si. Ti has the highest peak, followed by Al, Si and Mg. P and S which are non-metals were found under fine (1.0 μm) fraction. Mg and Na (alkali metals) and Ti and Fe (heavy metals) were found under coarse fraction. These particles displayed smooth irregular shape.

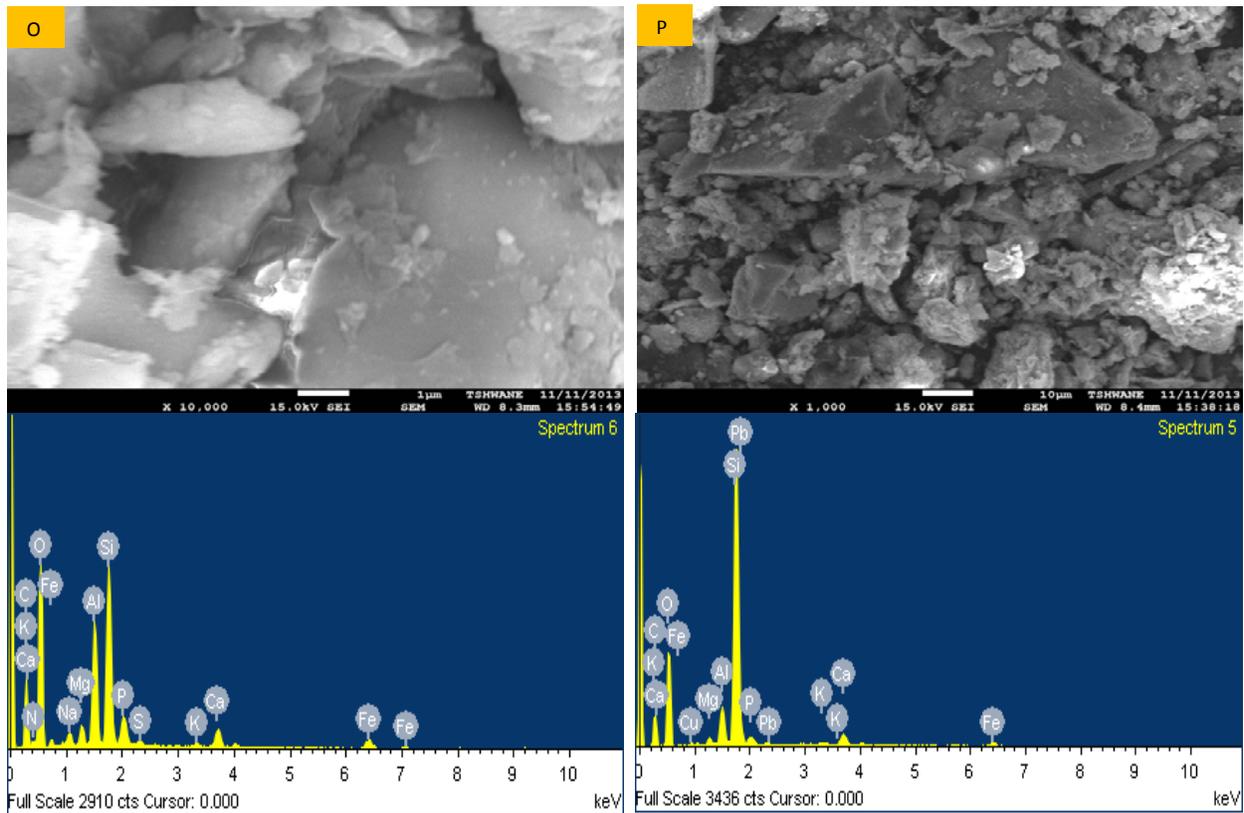


Figure 4.4: O and P: SEM images and EDX spectra of particles with large spheroidal to irregular shape collected at site D during June 2013 sampling period.

Particle O of 1.0 µm in diameter and its spectrum (Figure 4.4 O) below was collected at site D during the dry season. It shows the EDX spectrum with elemental weight percentages of Al, Si, Ca, K, Na, Mg, P and S. Al and Si dominate in this particle with traces of Ca, K, Mg, Na and P. the morphology of this particle ranges from large spheroidal to irregular. The coarse mode (10.0 µm) shows the EDX spectrum (Figure 4.4 P) of Al, Si, Ca, K, Mg, P, Cu and Pb. Si and Pb have the highest peaks. This particle has a mixture of crustal (Si) and anthropogenic (Pb) elements. The morphology of this particle is agglomerate. Si is associated with quartz (SiO₂) form crystal source while Pb could be linked to vehicle tailpipe emissions (as this site is characterised by high traffic congestions).

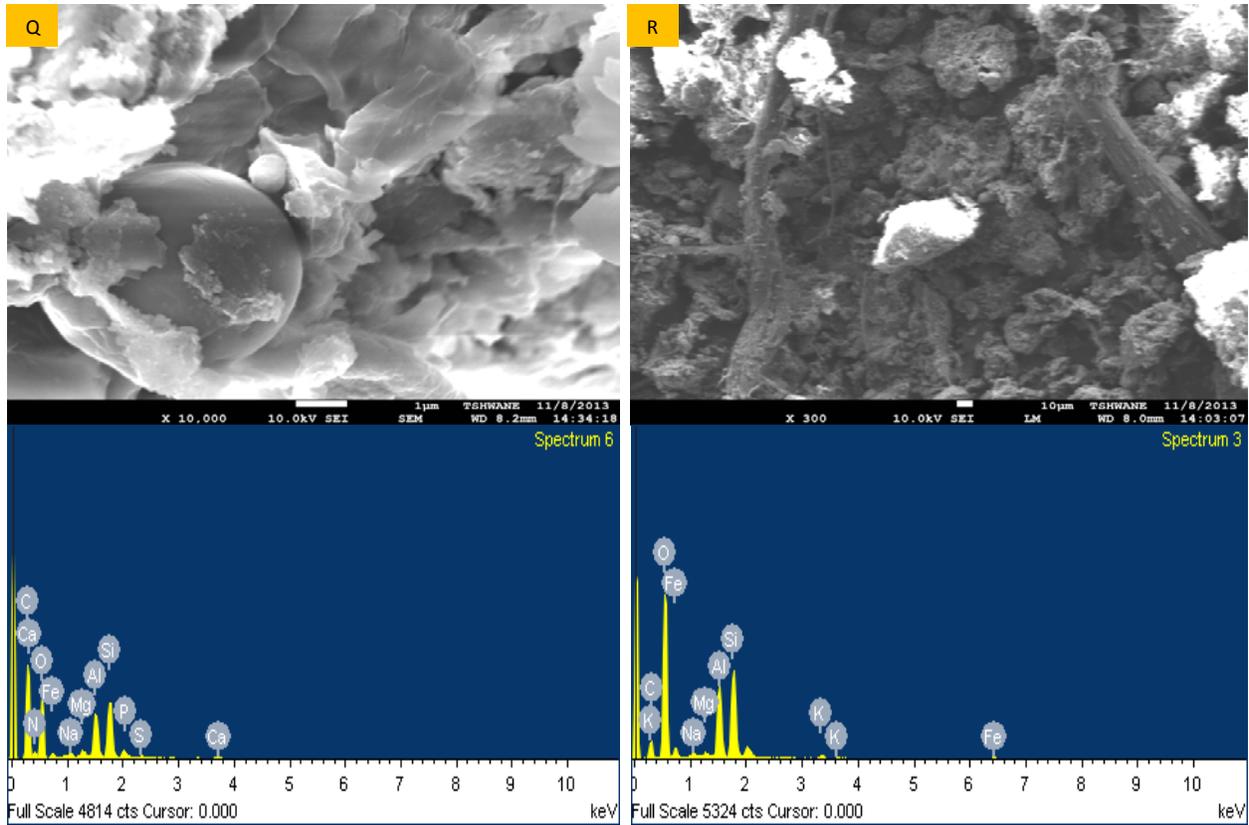


Figure 4.4: Q and R: SEM images and EDX spectra of particles with large spheroidal and irregular shape collected at site E during March 2013 sampling period.

Figure 4.4 shows the SEM photomicrographs of and their respective EDX spectra of particle Q of 1.0 μm (Figure 4.4 Q) and particle R of 10.0 μm diameters (Figure 4.4 R). These particles were collected at site E during the wet season. Particle Q gave the EDX spectrum showing the elemental weight percentages of Ca, Fe, N, Al, Si, Na, Mg, P and S. The EDX spectrum of particle R showed the presence of K, Fe, Na, Mg, Al and Si. Particle Q shows the dominant peak of Ca followed by Si and traces of Na, P, Mg and Al while particle R has a dominant peak Si followed by Al and minor peaks of Mg, Na, K and Fe. The observed morphology of particle Q is big spheroidal with smooth surface and a small round particle on top of the big one while that of particle R shows an irregular shiny particles.

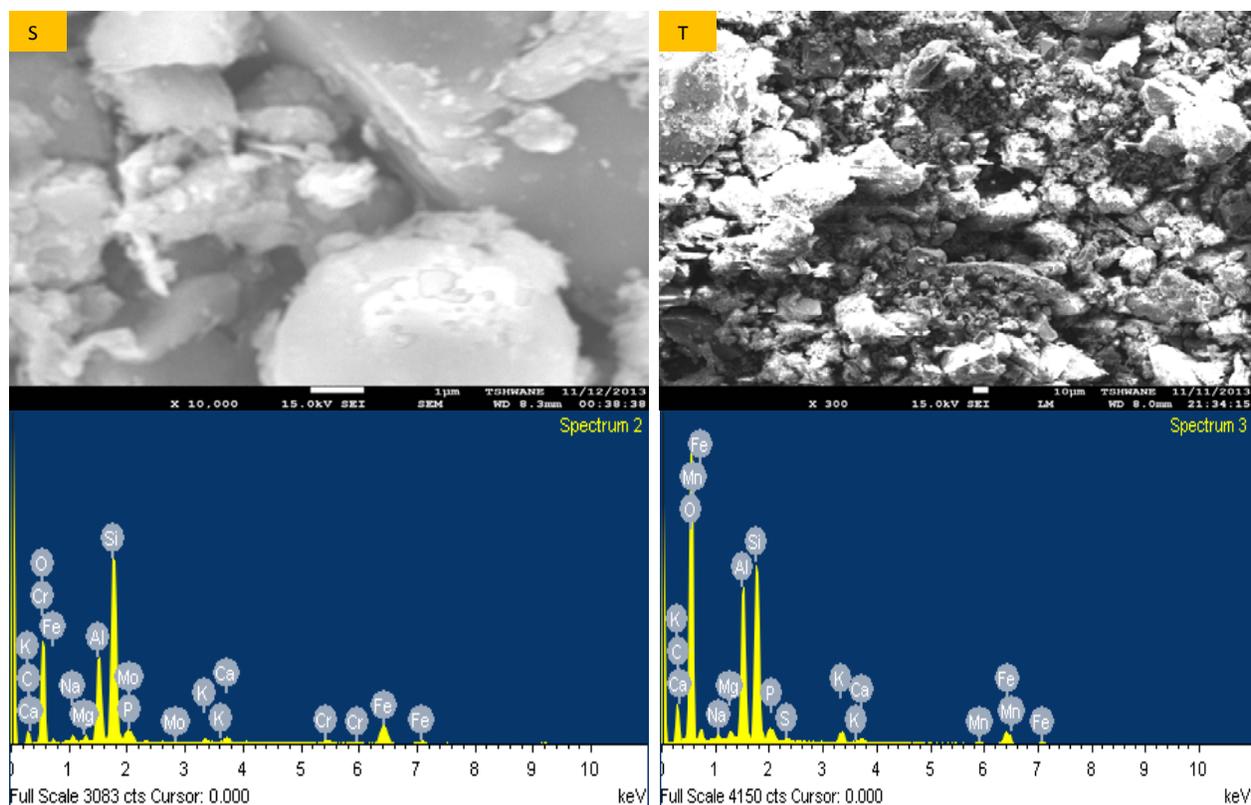


Figure 4.4: S and T: SEM images and EDX spectra of particles with spheroidal rough surfaces and small irregular shapes collected at site E during June 2013 sampling period.

Particle S (Figure 4.4 S) of 1.0 µm diameter with the EDX spectrum showing elemental weight percentages of Al, Si, Ca, K, Na, Mg, P, Fe, Cr and Mo was collected during the dry season. Particle T (Figure 4.4 T) of 10.0 µm diameter showed EDX spectrum of Al, Si, Ca, K, Na, Mg, K, Mn and Fe during the wet season. Particle S has the dominant peaks of Si, Al and a trace of Fe, Mo and P. Si has the most dominant peak than the rest of the elements. This has been a trend throughout the entire particles which were analysed. The morphology is spheroidal with rough surfaces. There is also the presence of Cr in traces amounts and may occur in the form oxides of Cr₂O₃ and CrO₃ and its origin is mostly anthropogenic. Cr may be linked to the burning of natural gas, oil or coal. Particle T has the dominant peaks of Al, Si and Mn with minor peaks of Mg, K, Ca and P. It has irregular morphology. Al and Si are associated with aluminosilicates particle which are derived mainly from crustal source. Mn in urban areas could be linked to mobile sources such as vehicles and stationary sources such as industry. It may further be linked to cosmetics, paints, fertilizers and fireworks (ATSDR, 2012).

Types of individual particles and their origin

A total of 135 particles were analysed using the method adopted by Pachauri (2013). In each and every analysis of dust fallout by EDX, every element present was measured both qualitatively and quantitatively. The weight percentage of each element present in the spectrum was identified. On normalization to 100% for C and O the weight percentage of different elements were identified. The EDX spectra of individual particles yielded weight percentages of 18 elements, i.e. C, O, Al, Si, S, K, Ca, Fe, P, Mg, Mo, N, Na, Pb, Cu, Cl, Ti and Zn. According to the criteria used by Okada and Kai (2004), Li and Shao (2010), and Li *et al.* (2010), the identified particles were classified into seven (7) types and twenty (20) sub-types (see Table 4.4 below). Seven (7) major elements i.e. Si, Fe, Ca, Cu, N, Ti and P were used in the classification process of particles. $P(X_i)$ is defined as follows:

$$P(X_i) = X_i / (Si + Fe + Ca + Cu + N + Ti + P) \times 100\% \quad (4.1)$$

($i = 1, 2, 3, 4, 5, 6, 7, 8, 9$),

Where, $P(X_i)$ represents weight ratio of element X_i , such as Si, Fe, Ca, Cu, N, Ti and P. A particle with element X_i which has the highest weight percentage is chosen and classified into X_i -rich type. If the weight ratio of the element X_i is greater or equal to 65%, the particle will be considered as the X_i -dominant sub-type. If the weight ratio of the element X_i is less than 65%, the element X_j with the second highest relative weight percentage is used, and then the particle is classified as X_i - X_j sub-type.

The percentage abundance of mineral types were computed and are: Si-rich (74%), Fe-rich (4.0%), Ca-rich (4.0%), N-rich (9.0%), Cu-rich (3.0%), Ti-rich (1.0%), P-rich (1.0%) and others (such as Al, K & P) (1.0%). Table 4.4 below summarises the types, sub-types, number of particles per sampling site and percentage abundance of the above-mentioned particles.

Table 4.4: Type of 135 analysed dust and their elemental composition particles collected in Tshwane within the radius range of 1.0 – 10.0 µm evaluated by EDX.

Mineral type	Sub-type	Averaged major elements (wt. %)	Number of Particles/site					Abundance (%)
			A	B	C	D	E	
Si-rich	Si-dominant	Si(27); Al(5)	4	10	5	7	5	23
	Si+Al	Si(18); Al(6)	7	2	12	7	8	27
	Si+Fe	Si(21); Fe(6)	4	3	1	5	10	17
	Si+ Ca	Si(9); Ca(5)	1	0	0	0	0	1
	Si+Cu	Si(14); Cu(9)	0	0	0	1	0	1
	Si+N	Si(14);N(6)	0	1	3	0	1	4
	Si+P	Si(6);P(5)	1	0	0	0	0	1
Fe-rich	Fe-dominant	Fe(35); Al(4)	1	0	0	2	0	2
	Fe+Si	Fe(20); Si(13)	0	0	0	2	1	2
Ca-rich	Ca-dominant	Ca(2); Al(0)	0	0	1	0	0	1
	Ca+Si	Ca(5); Si(4)	0	0	1	1	0	1
	Ca+N	Ca(19); N(14)	0	0	1	0	0	1
	Ca+Mg	Ca(12); Mg(9)	1	0	0	0	0	1
	Ca+P	Ca(21); P(11)	1	0	0	0	0	1
Cu-rich	Cu+Si	Cu(13); Si(12); Al(5)	0	0	0	3	0	2
N-rich	N-dominant	N(12); Si(7)	2	2	2	1	1	6
	N+Si	N(8); Si(5)	1	1	0	1	0	2
	N+P	N(7);P(4)	0	1	0	0	0	1
Ti-rich	Ti-dominant	Ti(36); Si(5)	1	0	0	0	0	1
P-rich	P+N	P(6);(5)	0	0	1	0	0	1
Others			0	0	0	0	0	4
TOTAL								100%

Si-rich particles (74.0%)

Table 4.4 above shows the six sub-types of mineral particles containing Si in association with Al (second most abundant element), N, Fe, Ca, P and Cu. Si-dominant particles (23%) were determined by Si weight ratio, P(Si) of greater than 65%. These particles are primarily made of quartz or silica. Site B recorded the highest number of particles (10) followed by site D (7) and the lowest were recorded at site A (4) (see Table 4.4). According to Pachauri *et al.* (2013), these

particles form a large part of the earth's crust and also a major component of the sandstone and granite. Naturally, these types of particles are soil or crustal related (Genga *et al.*, 2012). Pachauri *et al.* (2013) further added that they are also anthropogenically related to building construction and demolition; manufacturing of building materials such as cement, glass, ceramics etc..

“Si+Al” particles (27) are the most abundant in this category before Si-dominant. These particles fall under alumina-silicate group and their primary source is crustal origin through windblown dust. The “Si+Fe” particles recorded 4.0, 3.0, 1.0, 5.0 and 10.0% at site A, B, C, D and E respectively. Based on the location and characteristics of these sites, the likely source of these particles is traffic-related. The “Si+Ca” particle (1.0) was collected only at site A. the likely source could be the loose soil during the garden maintenance and re-suspended road dust. “Si+N” particles were collected at site B, C and E, with site B recording the highest and site C and E the lowest. They are in abundance of approximately 4.0% of the total particles. Silicon nitrite is a structural ceramic which is applied in the manufacturing of automotive engine parts. It is also applied to automotive components including turbocharger rotors and glow plugs (Okada, 2007). “Si+Cu” particles (1.0%) were collected at site D (characterised by high traffic congestions). Cu is related to traffic and Si is associated with earth's crust. This particle is of crustal origin and its abundance is 1.0%. “Si+P” were collected at site A. based on the characteristics of site A, the source of P could be linked to the use of fertilizers and compost for the maintenance of garden.

N-rich particle (9.0%)

These particles are in abundance of 9.0% of total particles. The particles are predominantly N with some contributions from Si and P. “N-dominant” particles dominated at site A, B and C at 2.0% and D and E at 1.0%. Approximately 1.0% of “N + Si” particles were detected at site A, B and D. Both N and P are deposited in H₂O and soil in different forms. N is deposited as NH₃ which evaporates from animal manure and as NO_x coming from combustion of fossil fuels, i.e. power plants and transportation. P is deposited as dust, falling leaves and bird faeces (European Environment Agency (EEA) Report No 7, 2005). It could also be linked to phosphate minerals such as apatite and monazite (Miler, 2014).

Fe-rich particles (4.0%)

These particles are in abundance of 4.0% of total particles. They are composed of Fe as the dominating element in association with Si. The “Fe-dominant” recorded 1.0% and 2.0% at site A and D respectively. The “Fe+Si” particle recorded 2.0% and 1.0% at site D and E respectively. According to Genga *et al.* (2012), the origin/source of these particles could both be crustal and anthropogenic. The processes which could be anthropogenic include industrial, abrasion of metallic materials and traffic-related. The contributory source of Fe is likely to be traffic related as these sites as they are characterised by high traffic congestions, however, crustal origin, particularly at site A cannot be ruled out. Xie *et al.* (2009) further attributed the sources to be fossil fuel combustion or steel manufacturing. Site D and E being residential areas, combustion of fossil fuel for space warming and cooking, particularly during winter is likely.

Ca-rich particles (4.0%)

These particles are in abundance of 4.0% of total particles and are probably limestone (CaCO_3). They are dominated by Ca with some contributions of Si, N, Mg and P. The “Ca-dominant” particle collected at site C, could be the result of higher plants as sources where it serves as a structural component (Likens *et al.*, 1998) and the type of soil around the sampling area. “Ca + Si” particles were collected at site C and D and therefore could be linked to the type of soil. Limestone is widely distributed as a crustal mineral and is found in soil dust and road dust (Xie *et al.*, 2005). Although, Ca may be of crustal origin, its link to anthropogenic sources is inevitable (Olowoyo *et al.*, 2013). The “Ca+Mg” and “Ca+P” particles were both collected at site A. Mg occurs naturally as alkali-earth metal found mostly in fossil fuels and P may be associated with minerals such as apatite and monazite (Miler, 2014). Therefore, both the natural/geogenic and anthropogenic sources are the possible sources at this site.

Cu-rich particles (3.0%)

These particles are in in the abundance of 3.0% of total particles. They are composed primarily of Cu with traces of Si within the sampling area (site D); the main source of Cu is likely to be combustion of fossil fuel and brakes from automobiles (Bhattacharya, 2013). Naturally, Cu may originate from windblown dust, decaying vegetation and forest fires (ATSDR, 2004).

Ti-rich particles (1.0%)

These particles are of the crustal origin and makes 1.0% of total particles. Ti dominates in association with Si. These particles are found in site A and they are derived primarily from the earth's crust, soil/road dust and anthropogenic activities such as construction and vehicle tailpipe emissions. Ti could be linked to ilmenite and rutile minerals (Miler, 2014). Though Ti may be from geogenic sources, Titania nanoparticles (nano-TiO₂) have wide spectrum of application in pigments, coatings, sunscreen, cosmetic additives, and widely for the photocatalytic degradation of various pollutants in water, air and soil media. (Luo *et al.*, 2011)

P-rich particles (1.0%)

These particles are in the abundance of 1.0% of total particles. They were collected at site C (characterised by relatively less or no anthropogenic activities). “P+N” particles, similar to “N+P”, were deposited as dust, falling leaves and bird faeces (EEA Report No 7, 2005). It could also be linked to phosphate minerals such as apatite and monazite (Miler, 2014).

4.4 CHEMICAL ANALYSIS

4.4.1 ICP-MS analysis

Elemental Composition of dust

The concentrations of all elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mn, Mo, Na, Ni, P, Pb, S, Ti, V and Zn) in dust fallout samples around some parts of central Tshwane are summarised in Table 4.5 and their corresponding statistical data in Table 4.5 as obtained from ICP-MS analysis.

Table 4.5: Concentrations of elements ($\mu\text{g}/\text{m}^3$) (Mean \pm SD) ($n = 3$) in dust fallout

Elements	Site A	Site B	Site C	Site D	Site E
Al	2330.8 \pm 2.3	1911.1 \pm 11.1	2593.6 \pm 5.8	4009 \pm 3.8	3786.6 \pm 3.5
As	1.6 \pm 0.2	1.1 \pm 0.3	2.2 \pm 0.4	2.6 \pm 0.3	2.0 \pm 0.4
Ca	7454.2 \pm 4.0	1777.2 \pm 8.3	4718.8 \pm 2.9	4427.4 \pm 3.6	5967.6 \pm 3.9
Cd	0.4 \pm 0.3	0.2 \pm 0.2	0.6 \pm 0.4	0.4 \pm 0.2	0.3 \pm 0.1
Co	6.2 \pm 0.2	2.9 \pm 0.4	5.3 \pm 0.4	12.3 \pm 0.5	14.7 \pm 0.4
Cr	25.6 \pm 0.3	17.0 \pm 0.3	23.3 \pm 0.2	44.3 \pm 4.6	42.3 \pm 0.3
Cu	273.6 \pm 0.4	169.9 \pm 0.9	612.7 \pm 54.2	101.1 \pm 1.2	255.5 \pm 0.4
Fe	5890.8 \pm 1.5	4383 \pm 3.0	5440.4 \pm 2.9	9165.6 \pm 4.8	9169.6 \pm 8.3
Mn	439.2 \pm 2.7	203.2 \pm 0.9	293.8 \pm 4.5	715.7 \pm 2.1	741.5 \pm 1.7
Mo	1.2 \pm 0.4	0.7 \pm 0.3	0.9 \pm 0.3	1.4 \pm 0.3	2.2 \pm 0.4
Na	249.3 \pm 1.3	246.1 \pm 0.6	247.2 \pm 1.5	258 \pm 2.8	251.5 \pm 2.7
Ni	20.2 \pm 1.9	7.9 \pm 0.5	12.5 \pm 0.4	21.9 \pm 0.6	20.5 \pm 0.2
P	449.8 \pm 0.4	560.7 \pm 2.0	751.1 \pm 0.9	671.4 \pm 0.3	502.2 \pm 1.8
Pb	47.1 \pm 0.7	33.4 \pm 0.6	38.0 \pm 2.1	85.2 \pm 0.7	101.3 \pm 2.3
S	572.3 \pm 1.9	462.7 \pm 3.5	523.8 \pm 3.1	735 \pm 2.7	540.5 \pm 0.3
Ti	39.2 \pm 2.9	30.0 \pm 0.5	36.6 \pm 2.8	54.8 \pm 1.4	50.5 \pm 1.3
V	12.3 \pm 0.5	9.9 \pm 0.6	13.6 \pm 0.3	22.3 \pm 1.0	20.3 \pm 0.8
Zn	163.4 \pm 2.5	101.7 \pm 1.5	140.3 \pm 1.0	293.0 \pm 1.4	281.0 \pm 1.4

The elemental mean concentrations within the study area decreased in the following order: Fe > Ca > Al > P > S > Mn > Cu > Na > Zn > Pb > Ti > Cr > Ni > V > Co > As > Mo > Cd.

The mean concentration of at site A, B, C, D and E recorded 1.6, 1.1, 2.2, 2.6 and 2.0 $\mu\text{g}/\text{m}^3$ respectively. Site D recorded the highest concentration followed by site C and E respectively. The overall mean concentration for study period is 1.9 $\mu\text{g}/\text{m}^3$. As is a hypertoxic element which

is emitted during combustion of fossil fuels (Ozaki *et al.*, 2004), therefore, the elevated concentrations at site D and E may be attributed to such. As is naturally occurring mineral found predominantly in the environment, therefore, its concentrations may be attributed to natural phenomena such as windblown dust and weathering of As-containing minerals and ores (ATSDR, 2015).

National Institute for Occupational Safety and Health (NIOSH) (2007) recommends a Recommended Exposure Limit (REL) of 0.002 mg/m^3 ($2.0 \text{ }\mu\text{g/m}^3$) of As per 15 minutes and Occupational Safety & Health Administration.

(OSHA, 2015) recommends a PEL of 0.010 mg/m^3 ($10.0 \text{ }\mu\text{g/m}^3$). Arsenic (As) is classified as a carcinogen by NIOSH (2007). Children are at a risk of exposure to Arsenic (As) owing to pica and mouthing and play activities. It causes gastrointestinal effects more often after ingestion, and less often after inhalation or dermal absorption (ATSDR, 2015). Site C and D exceeded the recommended limit set by NIOSH and site A, B and E are within the limit. All sites are within the OSHA (2015) limit of $10.0 \text{ }\mu\text{g/m}^3$.

The mean concentration of iron (Fe) in all monitoring sites ranged from 4383.0 to $9169.6 \text{ }\mu\text{g/m}^3$. Considering all sites, site E recorded the highest concentration of $9175 \text{ }\mu\text{g/m}^3$, followed by site D ($9165.0 \text{ }\mu\text{g/m}^3$), site A ($5891.0 \text{ }\mu\text{g/m}^3$), site C ($5437.0 \text{ }\mu\text{g/m}^3$) and site B ($4385 \text{ }\mu\text{g/m}^3$) respectively. The elevated concentration of Fe at sites D and E could be attributed to anthropogenic sources such as high level of traffic congestions during morning and afternoon peak hours. According to Adachi & Tainosho (2004), the concentration could further be the result of brake lining material in the form of brake dust. These findings are consistent with the findings by Thakur (2003) and Olowoyo *et al.* (2013). Surprisingly, site C recorded moderately high concentration, even though there are no notable activities. However this could be the consequences of natural processes i.e. weathering, wind-blown dust and erosion. Site A and B concentrations could be attributed to the rusting of automobile parts.

Calcium (Ca) concentrations ranged from 7454 to $1784 \text{ }\mu\text{g/m}^3$ with a mean concentration of $4870 \text{ }\mu\text{g/m}^3$. Site A recorded the highest concentration of $7454 \text{ }\mu\text{g/m}^3$ while site B recorded the lowest concentration of $1784 \text{ }\mu\text{g/m}^3$. The highest concentration at site A could be result of higher plants as sources where Ca serves as a structural component (Likens *et al.*, 1998) and the type of

soil around the monitoring area. Ca is also associated with crustal element and therefore the link to its anthropogenic source is inevitable (Olowoyo *et al.*, 2013). The concentrations of Ca in different monitoring sites are in the following decreasing order: Site A > site E > site C site D > site B.

The lowest element detected was cadmium with the mean concentration varying between 0.4, 0.2 and 0.6 $\mu\text{g}/\text{m}^3$ at sites A, B and C respectively. Sites D and E recorded 0.3 and 0.4 $\mu\text{g}/\text{m}^3$ respectively. Sites A and D recorded the same (0.4 $\mu\text{g}/\text{m}^3$) concentration values. These observations suggest the same source contribution. All the sampling sites exceeded the United States Environmental Protection Agency (USEPA) (2012) and (DEA, 2009) annual standard limit of 0.005 $\mu\text{g}/\text{m}^3$.

(NIOSH) (2007) considers Cd a carcinogen (cancer-causing). Cd in urban environments is likely to emanate from combustion of fossil fuels in thermal power stations. Exposure to Cd through inhalation may lead to kidney and lung infection, moreover, other effects such as reproductive toxicity, hepatic effects, haematological effects and immunological effects are possible (Agency for Toxic Substances and Disease Registry (ATSDR, 2012).

The mean concentration of chromium (Cr) ranged from 17.0 $\mu\text{g}/\text{m}^3$ with site B recording the lowest concentration and site D recording the highest concentration of 44.3 $\mu\text{g}/\text{m}^3$ throughout the study period (July – December 2012). Sites A, B and C are situated in a suburban area which is characterized by low levels of anthropogenic activities. The low concentrations of Cr in these sites could be attributed to the nature of soil, rocks or plants as it occurs naturally in combination with other elements (ATSDR, 2012). However, the contribution of anthropogenic activities cannot be ruled out. Sites D and E which are urban areas characterized by high traffic congestions and other commercial activities recorded almost two times higher concentrations (44.3 and 42.3 $\mu\text{g}/\text{m}^3$) than sites A, B and C. All sampling sites were within World Health Organisation (WHO) (2000) annual guideline of 2000 $\mu\text{g}/\text{m}^3$.

According to ATSDR (2012), suburban air generally contains lower concentrations of chromium (Cr) (0.001 $\mu\text{g}/\text{m}^3$) than urban air (0.03 $\mu\text{g}/\text{m}^3$). Cr at sites D and E could be attributed to the burning of natural gas, oil and coal. Excessive build-up of Cr in human bodies may trigger lung cancer and stomach cancer (Shi *et al.*, 2011).

The concentration cobalt (Co) ranged from 2.9 at site B to 14.7 $\mu\text{g}/\text{m}^3$ at site E with a mean concentration of 8.8 $\mu\text{g}/\text{m}^3$. The highest concentration at site E could be attributed to vehicular tailpipe emissions and industrial activities. However, the contribution of natural activities i.e. windblown dust cannot be fully negated. The lowest concentration at site B could be attributed to the low levels of traffic. All sampling sites fall within the set limit of 50.0 $\mu\text{g}/\text{m}^3$ (0.05 mg/m^3) by NIOSH (2007) and 100 $\mu\text{g}/\text{m}^3$ (0.1 mg/m^3) by OSHA (2015).

Although Co is an essential element required for good health by humans (source of vitamin B₁₂) (ATSDR, 2012), anthropogenic activities such as coal fired power plants, vehicle emissions, industrial activities, incinerators etc. have contributed to its elevated levels. The groups that are more susceptible to cobalt toxicity are children, adults and the elderly. However children and the elderly are at high risk due to their weak immune system. Humans are exposed to cobalt through inhalation (dust) and touching soil (dermal contact). According ATSDR (2012), cobalt causes asthma, pneumonia and wheezing through inhalation of 0.005mg of Co/m³ (5.0 $\mu\text{g}/\text{m}^3$). And further allergies and skin rashes through dermal contact.

The concentration of copper (Cu) ranged from 101.1 at site D to 612.7 $\mu\text{g}/\text{m}^3$ at site E with a mean concentration of 282.6 $\mu\text{g}/\text{m}^3$. The high concentration at site C could be attributed to natural sources e.g. decaying of vegetation. Site A recorded the second highest concentration which could be explained in terms of natural activities based on the location (down the hill, in the vicinity of vegetation and next to the parking bay). Anthropogenically, it could be the result of the corrosion of metallic parts of cars derived from engine wear, thrust burning, brushing and bearing metals (Olowoyo *et al.*, 2013). All sampling sites recorded concentration below set limit of 1.0 mg/m^3 (1000 $\mu\text{g}/\text{m}^3$) by NIOSH (2007) and OSHA (2015).

Cu is an essential element for all animals including man at low concentrations (ATSDR, 2012). Elevated concentrations of Cu render it toxic. Humans are exposed to Cu through ingestion, inhalation and contact. Symptoms of high level intake include nausea, vomiting, stomach cramps or diarrhea and death may result (ATSDR, 2012).

The mean concentration of zinc (Zn) was found to be 163.4, 101.7, 140.3, 293.0 and 281.0 $\mu\text{g}/\text{m}^3$ at sites A, B, C, D and E respectively. It is evident that sites D and E (urban sites) have recorded high concentrations as compared to their suburban counterparts (site A, B and C). The high

concentration of zinc at sites D and E could be attributed to vehicle tailpipe emissions due to high traffic congestions particularly during peak hours in the mornings and afternoons. Alahmr *et al.* (2012) substantiated that vehicle combustion contribute to elevated concentrations of Zn in urban areas. These findings are consistent with the results from sites D and E in this study.

Zn exists naturally and it is found in the soil, air, water and foodstuffs (ATSDR, 2012). The deficiency of Zn may lead to loss of appetite and decreased immune-function and further causes birth defects to mothers who do not have it in correct proportion. There is no recommended limit as per the health regulatory bodies such as WHO (2000), NIOSH (2007) or OSHA (2015).

The mean concentrations of aluminium (Al) are 2330.8, 1911.1, 2593.6, 4009.0 and 3786.6 $\mu\text{g}/\text{m}^3$ at sites A, B, C, D and E respectively. Once again, the urban sites seem to dominate with the highest concentration at site D followed by site E. the elevated levels of Al in these sites may be attributed to both natural and anthropogenic activities. Naturally, it exists as a major constituent of atmospheric particulates originating from natural soil erosion, volcanic eruptions (WHO, 1997) and weathering process of rocks (Alahmr *et al.*, 2012). Anthropogenically, it may emanate from construction activities and production of metal alloys where is used as a structural component in certain materials; furthermore, it could come from wearing of cooking utensils and food packaging (WHO, 1997). OSHA (2015) recommends the exposure limit of $15\text{mg}/\text{m}^3$ ($15000 \mu\text{g}/\text{m}^3$) and NIOSH (2007) recommends $10.0 \text{ mg}/\text{m}^3$ ($10000 \mu\text{g}/\text{m}^3$) of total dust (ATSDR, 2008). Both OSHA (2015) and NIOSH (2007) recommend $5.0 \text{ mg}/\text{m}^3$ ($5000 \mu\text{g}/\text{m}^3$) of respirable dust. It is evident from that all sampling sites recorded below the set limits. High concentrations of Al could cause brain and bone disease especially in children with kidney disease. (ATSDR, 2008).

The mean concentrations of manganese (Mn) at sites A, B, C, D and E were found to be 439.2, 201.2, 293.8, 715.7 and 741.5 $\mu\text{g}/\text{m}^3$ respectively. The highest mean concentrations of Mn were observed at site D and E. Site A recorded the third highest concentration. The anthropogenic sources of Mn in these sites could be the result of combustion activities of fossil fuels in automobiles and industry. Other sources could be fertilizers used in gardens, paints, cosmetics and fireworks (ATSDR, 2012). Mn is naturally present in rocks, soil, water and food, therefore, it could emanate from windblown dust. Mn is essential for growth, development and

maintenance of health (Edusei, 2012), however, anthropogenic activities have led to its elevated concentrations. NIOSH recommends 1.0 mg/m^3 ($1000 \text{ }\mu\text{g/m}^3$) exposure limit and OSHA (2015) recommends an exposure limit of 5.0 mg/m^3 ($5000 \text{ }\mu\text{g/m}^3$). All the sampling sites recorded below the set limits. High concentration of Mn is toxic and may lead to various adverse effects in the respiratory tract and in the brains (Edusei, 2012; ATSDR, 2012).

Molybdenum (Mo) has been found in the dust fallout at different sampling sites in the range: Site A ($1.2 \text{ }\mu\text{g/m}^3$), B ($0.7 \text{ }\mu\text{g/m}^3$), C ($0.9 \text{ }\mu\text{g/m}^3$), D ($1.4 \text{ }\mu\text{g/m}^3$) and E ($2.2 \text{ }\mu\text{g/m}^3$). Sites D and E recorded the highest concentrations and followed by site A. The concentrations of these sites may be linked to vehicle tailpipe emissions and coal combustion (Morabito *et al.*, 2014). Mo is an essential trace metal for virtually all living things, particularly, persons with sulfite sensitivity, asthmatic and those intolerant to intravenous sulfur-containing amino acids (Utah Department of Health, 2013). Its inhalation (powder), ingestion or contact may lead to eyes, nose, throat irritation, liver and kidney damage (NIOSH, 2007). OSHA (2015) recommends permissible exposure limit of 5.0 mg/m^3 ($5000 \text{ }\mu\text{g/m}^3$) and NIOSH (2007) recommends time-weighted average of 5.0 mg/m^3 ($5000 \text{ }\mu\text{g/m}^3$). In all sampling sites, Mo was found to be within the set limits.

The concentration of sodium (Na) at sites A, B, C, D and E were found to be 249.3, 246.1, 247.2, 258.0 and $251.5 \text{ }\mu\text{g/m}^3$. Sites D and E recorded the highest mean concentration followed by site A. the lowest concentrations were recorded at sites B and C. Na is naturally found in coal as an alkali metal (Zhang *et al.*, 2001). Gaseous Na is released into the atmosphere as NaCl gas during the initial combustion of coal and further undergoes transformation into aluminosilicates with an increase in combustion temperature (Li *et al.*, 2015). It is evident in this study that the combustion of coal is the source of Na. Na is an essential nutrient necessary for maintenance of plasma volume, acid-base balance, transmission of impulses and normal cell function (WHO, 2007; Brown *et al.*, 2009). Naturally, it is the main component of table salt and further found in foods such as milk, meat and shellfish (Alburto *et al.*, 2013). High Na intake may lead to high blood pressure and other related non-communicable diseases.

The mean concentrations of phosphorus (P) at sites A, B, C, D and E are 449.4, 561.2, 751.1, 671.4 and 503.6 $\mu\text{g}/\text{m}^3$ respectively. The overall mean concentration for the entire study at these sites is 587.3 $\mu\text{g}/\text{m}^3$. The concentrations ranged from 449.4 $\mu\text{g}/\text{m}^3$ at site A to 751.1 $\mu\text{g}/\text{m}^3$ at site C. Site C recorded the highest concentration of P and being a suburban area, P may be attributed to the use of compost and fertilizers in the gardens and furthermore, it could emanate from pets waste. Site D (urban) recorded the second highest concentration which could be the result of municipal sewage system, landfilling of incinerated solid waste or direct landfilling (Kalmykova *et al.*, 2012). Hogan (2013) further pointed out that phosphorus at suburban and urban areas could be from lawn and garden fertilizers, leaky sanitary sewer or septic tanks and pet waste. Both NIOSH (2007) and OSHA (2015) recommend a time-weighted average (TWA) exposure limit of 0.1 mg/m^3 (100 $\mu\text{g}/\text{m}^3$). All the sampling sites highly exceeded the exposure limit in the following descending order: Sites C > D > B > E > A. According to NIOSH (2007), the modes of exposure to P are inhalation, ingestion and dermal contact. The symptoms include eye irritation, skins, abdominal pain, nausea, respiratory tract etc. children are more susceptible due to their weak immune system while the elderly's immune system has deteriorated.

The mean concentration of nickel (Ni) at sites A, B, C, D and E were found to be 20.2, 7.9, 12.5, 21.9 and 20.5 $\mu\text{g}/\text{m}^3$. Ni concentrations ranged from 7.9 at site B to 21.9 at site D. the mean concentration for the entire study is found to be 16.6 $\mu\text{g}/\text{m}^3$. According to IPCS (1991) as cited by Tiwari *et al.* (2008), Ni may originate from the combustion of oil and incineration of waste which contribute to more than 70% of total Ni to the atmosphere from anthropogenic sources followed by refining process with 17%. Based on the location of site D (high traffic congestions, commercial and residential activities), the likely contributor of Ni is oil combustion and incineration of waste. Both NIOSH (2007) and OSHA (2015) recommend the time-weighted average (TWA) of 0.015 mg/m^3 (50.0 $\mu\text{g}/\text{m}^3$) and TWA of 1.0 mg/m^3 (1000.0 $\mu\text{g}/\text{m}^3$) respectively. The exposure of humans to Ni happens through inhalation, oral and dermal routes. All the sampling sites recorded concentrations within the set guideline by NIOSH (2007) and OSHA (2015). According ATSDR (2005), exposure to Ni through inhalation of dust showed severe health effects such as chronic bronchitis, reduced lung function and cancer of lung and nasal sinus. The International Agency for Research on Cancer (IARC) (1990) has found that some Ni compounds are carcinogenic to humans, particularly metallic Ni (ATSDR, 2005).

The mean concentration of lead (Pb) were found to be 47.1, 33.4, 38.0, 85.2 and 101.3 $\mu\text{g}/\text{m}^3$ at sites A, B, C, D and E respectively. Sites D and E recorded concentrations which are two times higher than sites B and C. Site A recorded the third highest concentration. The concentration ranged from 33.4 $\mu\text{g}/\text{m}^3$ at site B to 101.3 $\mu\text{g}/\text{m}^3$ at site E. elevated concentrations of Pb at sites D and E may be associated with vehicle exhaust emissions as these sites are characterised by high traffic congestions. Tüzen (2013) further indicated that Pb may come from combustion of gasoline that contains tetraethyl lead as anti-knock agent. It may also be from burning of coal, oil and waste (ATSDR, 2007). Owing to the demolitions and renovations that took place during the sampling period at Tshwane, Pd may come from paint containing Pb (ATSDR, 2007).

According to WHO (1989), humans are exposed Pb through contamination of food and dust, as well as through inhalation. OSHA (2015) and NIOSH (2007) recommend TWA of 0.050 mg/m^3 (50.0 $\mu\text{g}/\text{m}^3$). all sites are within the set guideline by NIOSH (2007) and OSHA (2015) except for sites D and E. WHO (2000), USEPA (2012) and DEA (2009) recommend a maximum Pb guideline value in ambient air of 0.5 $\mu\text{g}/\text{m}^3$ and in all the sampling sites; the set guidelines has been exceeded tremendously. The smaller particles of inhaled Pb (generated by vehicle exhaust emissions) are almost (> 90%) completely absorbed after deposition in the lower respiratory tract (WHO, 1995). Pb exposure causes small increases in blood pressure in middle-aged and elderly people. It further damages brain and kidneys in adults and children (ATSDR, 2007). Moreover, elevated exposure levels, particularly, in pregnant women may cause miscarriage and consequently death.

The mean concentrations of vanadium (V) at sites A, B, C, D and E were found to be 12.3, 9.9, 13.6, 22.3 and 20.3 $\mu\text{g}/\text{m}^3$ respectively. The recorded mean concentration for the entire study is 15.6 $\mu\text{g}/\text{m}^3$. The elevated concentrations at Site D (23.3 $\mu\text{g}/\text{m}^3$) and site E (20.3 $\mu\text{g}/\text{m}^3$) may be attributed to point sources such as oil refineries and power plants where vanadium-rich fuel oil and coal are utilized (ATSDR, 2012). Mkoma *et al.* (2010) further substantiated that V could be attributed to oil burning residuals and cigarette smoking. According to ATSDR (2012), approximately 0.0004 mg of V is released in the smoke of one cigarette. NIOSH (2007) recommends a Recommended Exposure Limit (REL) of 0.050 mg/m^3 (50.0 $\mu\text{g}/\text{m}^3$) of V per 15 minutes (this applies to V compounds except V metal and carbide) and OSHA (2015)

recommends a PEL of $0.5\text{mg}/\text{m}^3$ ($500\ \mu\text{g}/\text{m}^3$) of vanadium pentoxide (V_2O_5). Although V is acceptable in small amounts in food and other supplements, anthropogenic activities have contributed to its elevated concentrations, rendering it harmful. Children elicit similar effects to exposure to toxic levels of V as the adults (ATSDR, 2012). It is considered a carcinogen by IARC (1990) and also causes nausea, mild diarrhea and stomach cramps.

Sulphur (S) recorded mean concentrations of 572.3, 462.7, 523.8, 735.0 and $540.5\ \mu\text{g}/\text{m}^3$ at sites A, B, C, D and E respectively. The overall mean concentration of S is $566.9\ \mu\text{g}/\text{m}^3$. The mean concentrations ranged from $462.7\ \mu\text{g}/\text{m}^3$ (site B) to $735.0\ \mu\text{g}/\text{m}^3$ (site D). The highest concentration at site D may be attributed to coal-fired power plant (Rooiwal power plant) situated at the west side from site D and E; and north site of site A. Parashar *et al.* (2001) as cited by Alahmr *et al.* (2012), generally alluded that S compounds are predominantly released into the atmosphere as a result of fossil fuel combustion. There are no known set guidelines for the regulations of S. The elevated concentrations at site A may also be linked to fossil fuel combustion such as oil and diesel.

The mean concentrations of arsenic (As) at sites A, B, C, D and E recorded 1.6, 1.1, 2.2, 2.6 and $2.0\ \mu\text{g}/\text{m}^3$ respectively. Site D ($2.6\ \mu\text{g}/\text{m}^3$) recorded the highest concentration followed by site C ($2.2\ \mu\text{g}/\text{m}^3$) and E ($2.0\ \mu\text{g}/\text{m}^3$) respectively. The overall mean concentration for the entire duration of study is $1.9\ \mu\text{g}/\text{m}^3$. As is a hyper toxic element which is emitted during combustion of fossil fuels (Ozaki *et al.* (2004), therefore, the elevated concentrations at sites D and E may be attributed as such. As is also a naturally occurring mineral found predominantly in the environment (ATSDR, 2015), therefore, its concentration at site C may be linked to natural phenomena such as windblown dust and weathering of arsenic-containing minerals and ores.

NIOSH (2007) recommends a REL of $0.002\ \text{mg}/\text{m}^3$ ($2.0\ \mu\text{g}/\text{m}^3$) of As per 15 minutes and OSHA (2015) recommends a PEL of $0.010\ \text{mg}/\text{m}^3$ ($10.0\ \mu\text{g}/\text{m}^3$). All sites recorded within the set guideline by NIOSH (2007) and OSHA (2015) except for Sites C and D which exceeded the set guideline by NIOSH (2007). It is classified as a carcinogen by NIOSH (2007). Children are vulnerable to a higher exposure to As owing to pica or mouthing and playing activities. Arsenic exposure causes gastrointestinal effects more often after ingestion, and less often after inhalation or dermal absorption (ATSDR, 2015).

The mean concentrations of titanium (Ti) at sites A, B, C, D and E have recorded 39.2, 30.0, 36.6, 54.8 and 50.5 $\mu\text{g}/\text{m}^3$ respectively. The overall mean concentration for the whole study is 42.2 $\mu\text{g}/\text{m}^3$. The concentrations ranged from 30.0 $\mu\text{g}/\text{m}^3$ at site B to 54.8 $\mu\text{g}/\text{m}^3$ at site D. The elevated concentrations of Ti at sites D and E may be explained in terms of vehicle brake pads and tyres which are a consequence of high traffic congestions.

Table 4.6 summarises the mean, minimum, maximum, standard deviation and median concentrations of 18 elements in 30 dust fallout samples collected from 5 monitoring sites around the study area (Tshwane). The results of the total mean concentrations of individual elements from five monitoring sites showed that iron (Fe) recorded the highest concentration compared to other elements with a mean concentration of 6810.58 $\mu\text{g}/\text{m}^3$ and cadmium (Cd) recorded the lowest concentration of 0.28 $\mu\text{g}/\text{m}^3$. The mean concentrations of the elemental species were found to be in the decreasing trend as follows: Fe > Ca > Al > Mg > P > S > Mn > K > Cu > Na > Zn > Pb > Cr > Ni > V > Co > Mo > Cd.

Table 4.6: Descriptive statistics of concentrations of 18 elements which were measured at the study area (Tshwane) from July 2012 to June 2013.

Element	Descriptive statistics					
	*n	Mean	Median	Std. dev.	Min	Max
Al	5	2926.2	2593.6	923.08	1911.1	4009
As	5	1.9	2	0.57	1.1	2.6
Ca	5	4869.04	4718.8	2101.61	1777.2	7454.2
Cd	5	0.38	0.4	0.15	0.2	0.6
Co	5	8.28	6.2	5	2.9	14.7
Cr	5	30.5	25.6	12.12	17	44.3
Cu	5	282.56	255.5	197.12	101.1	612.7
Fe	5	6809.88	5890.8	2220.79	4383	9169.6
Mn	5	478.68	439.2	243.35	203.2	741.5
Mo	5	1.28	1.2	0.58	0.7	2.2
Na	5	250.42	249.3	4.71	246.1	258
Ni	5	16.6	20.2	6.1	7.9	21.9
P	5	587.04	560.7	123.25	449.8	751.1
Pb	5	61	47.1	30.39	33.4	101.3
S	5	566.86	540.5	102.1	462.7	735
Ti	5	42.22	39.2	10.21	30	54.8
V	5	15.68	13.6	5.35	9.9	22.3
Zn	5	195.88	163.4	86.16	101.7	293

*n=Sampling sites

4.5 STATISTICAL ANALYSIS

4.5.1 Pearson correlation coefficient analysis

Relationships between sites (A, B and C) and meteorological parameters

Pearson correlation coefficients for dust fallout rates at sites A, B and C and meteorological parameters in Tshwane are summarised in Table 4.7. The correlation matrix shows a moderate degree of correlation between minimum temperature and wind velocity with dust fallout at site A. Both minimum temperature and wind velocity showed a moderate correlation (r) of 0.653 and 0.652 with dust fallout rate at site A at 0.05 (5.0%) significant level respectively. This implies that these meteorological parameters have direct positive on the dust fallout rate at site A. At 0.05 (5%) significant level, maximum temperature showed a very high degree of correlation ($r = 0.979$) with minimum temperature. Maximum temperature also showed a sufficient degree of correlation ($r = 0.773$) with rainfall and a sufficiently negative correlation ($r = -0.835$) with wind velocity at 0.01 significant level. Furthermore, sufficient positive correlation between minimum temperature with rainfall ($r = 0.827$) and wind velocity (0.855) at 0.01 (1%) significant level.

Table 4.7: Correlation matrix of dust fallout at site D and E with meteorological parameters.

	Site A	Site B	Site C	Temperature (Max.)	Temperature (Min.)	Humidity	Rainfall	Wind velocity
Site A	1							
Site B	-.117	1						
Site C	.149	.323	1					
Temperature (Max.)	.562	-.119	-.015	1				
Temperature (Min.)	.653*	-.245	.006	.979**	1			
Humidity	.566	-.237	.242	.539	.631	1		
Rainfall	.560	-.353	.242	.773**	.827**	.580	1	
Wind velocity	-.652*	.158	.139	-.835**	-.855**	-.625	-.512	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Temperature (Min) = Minimum temperature

Temperature (Max) = Maximum temperature

Table 4.8: Correlation matrix of dust fallout at site D and E with meteorological parameters.

	Site D	Site E	Temperature (Max.)	Temperature (Min.)	Humidity	Rainfall	Wind velocity
Site D	1						
Site E	.745*	1					
Temperature (Max.)	-.419	-.453	1				
Temperature (Min.)	-.444	-.486	.987**	1			
Humidity	-.748*	-.253	.422	.459	1		
Rainfall	-.286	-.413	.715*	.728*	.235	1	
Wind velocity	-.255	-.464	.915**	.912**	.221	.800**	1

*. Correlation is significant at the 0.05 level (2-tailed).

** . Correlation is significant at the 0.01 level (2-tailed).

Relationships between sites (D and E) and meteorological parameters

Table 4.8 shows the correlation matrix of sites D and E with meteorological parameters. Site D is moderately correlated with site E and negatively with humidity with r-values of 0.745 and 0.748 at 0.05 significant levels respectively. Surprisingly, site E is not correlated to any of the meteorological parameters. This observation could be explained in terms of environmental factors or extraneous variables which are beyond the scope of this study. Maximum temperature is very highly correlated with minimum temperature and wind velocity with r-values of 0.987 and 0.915 at 0.01 significant levels. On the other hand, maximum temperature is moderately correlated with rainfall ($r = 0.715$) at 0.05 significant level. Minimum temperature is moderately correlated to rainfall (0.728) 0.05 significant level and very highly correlated to wind velocity (0.912) at 0.01 significant level. A sufficiently high degree of correlation is observed between rainfall and wind velocity ($r = 0.800$) at 0.01 significant level.

It interesting to note that wind velocity is negatively correlated with minimum temperature and rainfall at sites A, B and C. on the other hand, an inverse trend is evident at sites D and E.

Relationships amongst the elements

Table 4.9 shows the correlation matrix which was developed to investigate the inter-elemental relationships and identify the possible sources of pollution. The elements are significantly correlated with one another at the level of 0.05 (Al to Co, Mn and Pb with $r = 0.951, 0.942$ and 0.935 respectively. These elements show a very high degree of correlation ($r = \pm 0.90$ or more). Ca does not show any correlation with any element (absence of correlation), Cd/Mn, Co/Mo, Co/V, Cr/Ni, Mg/Ni, Mn/Mo, Mn/Ni, Mn/V, Mo/Pb, Na/S, Ni/Zn, Pb/V with r-values $0.936, 0.909, 0.954, 0.888, 0.951, 0.922, 0.925, 0.935, 0.918, 0.949, 0.890$ and 0.944 respectively. All these elements show a high degree of correlation ($r = \pm 0.90$ or more) with the exception of Cr/Ni and Ni/Zn which showed a sufficiently high degree of correlation ($r = \pm 0.70$ to 0.90).

Moreover, the following elements correlate significantly at level 0.01 (Al/Cd, Al/Cr, Al/Fe, Al/V, Al/Zn, Cd/Co, Cd/Cr, Cd/Fe, Cd/Pb, Cd/V, Cd/Zn, Co/Cr, Co/Fe, Co/Mn, Co/Pb, Co/Zn, Cr/Fe, Cr/Mn, Cr/Pb, Cr/V, Cr/Zn, Fe/Mn, Fe/Pb, Fe/V, Fe/Zn, Mn/Pb, Mn/Zn, Pb/Zn and V/Zn with $r = 0.961, 0.976, 0.981, 0.988, 0.980, 0.960, 0.961, 0.969, 0.966, 0.973, 0.963, 0.989, 0.987, 0.980, 0.997, 0.977, 0.999, 0.992, 0.976, 0.972, 0.998, 0.988, 0.976, 0.979, 0.998, 0.971, 0.989,$

0.964 and 0.975 respectively. There is absolutely no correlation between Ca, Cu, K, P and S with other elements. The high (r) values may suggest common anthropogenic sources. The significant correlations between Pb/Fe ($r = 0.976$, $p = 0.01$) and Zn/Pb ($r = 0.964$, $p = 0.01$) are consistent with the findings by Olowoyo *et al.* (2013), Mn/Cr ($r = 0.992$, $p = 0.01$) correlates with the findings by Addo *et al.* (2012), Ni/Cr ($r = 0.888$, $p = 0.05$) and Mn/Fe ($r = 0.988$, $p = 0.01$) are consistently with the findings by Kendal *et al.* (2011).

Table 4.9: Correlation matrix among the 17 elements detected through ICP-MS.

	Al	As	Ca	Cd	Co	Cr	Cu	Fe	Mn	Mo	Na	Ni	P	Pb	S	Ti	V	Zn
Al	1																	
As	.950*	1																
Ca	0.271	0.386	1															
Cd	.961**	0.826	0.142	1														
Co	.951*	0.848	0.396	.960**	1													
Cr	.976**	.902*	0.402	.961**	.989**	1												
Cu	-0.314	-0.073	0.162	-0.515	-0.397	-0.4	1											
Fe	.981**	.902*	0.368	.969**	.987**	.999**	-0.413	1										
Mn	.942*	0.86	0.472	.936*	.982**	.992**	-0.452	.988**	1									
Mo	0.757	0.6	0.502	0.833	.909*	0.877	-0.599	0.869	.922*	1								
Na	0.81	0.771	0.144	0.79	0.706	0.793	-0.601	0.803	0.79	0.616	1							
Ni	0.811	0.815	0.716	0.743	0.85	.888*	-0.342	0.875	.925*	0.846	0.765	1						
P	0.163	0.329	-0.416	0.001	-0.126	-0.051	0.506	-0.032	-0.166	-0.521	0.104	-0.234	1					
Pb	.935*	0.809	0.348	.966**	.997**	.976**	-0.439	.976**	.971**	.918*	0.685	0.815	-0.159	1				
S	0.731	0.791	0.283	0.63	0.584	0.699	-0.375	0.703	0.695	0.462	.949*	0.77	0.226	0.54	1			
Ti	.947*	.932*	0.545	.882*	.942*	.975**	-0.308	.969**	.976**	0.834	0.808	.955*	-0.032	.913*	0.779	1		
V	.998**	.930*	0.225	.973**	.954*	.972**	-0.334	.979**	.935*	0.76	0.792	0.78	0.157	.944*	0.694	.928*	1	
Zn	.980**	.909*	0.376	.963**	.977**	.998**	-0.426	.998**	.989**	0.862	0.832	.890*	-0.026	.964**	0.741	.976**	.975**	1

4.5.2 One-way ANOVA Analysis

Table 4.10: Single-factor ANOVA test for differences in dust fallout of the sampling sites.

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	31821.94	4	7955.48	2.44	0.061	2.58
Within Groups	146786.13	45	3261.91			
Total	178608.067	49				

The F value of 2.44 is less than the critical value of 2.58, and the P-value of 0.061 is greater than the alpha level 0.05. Therefore there is no significant difference in the average dust fallout among monitoring sites.

4.6 ENRICHMENT FACTOR ANALYSIS

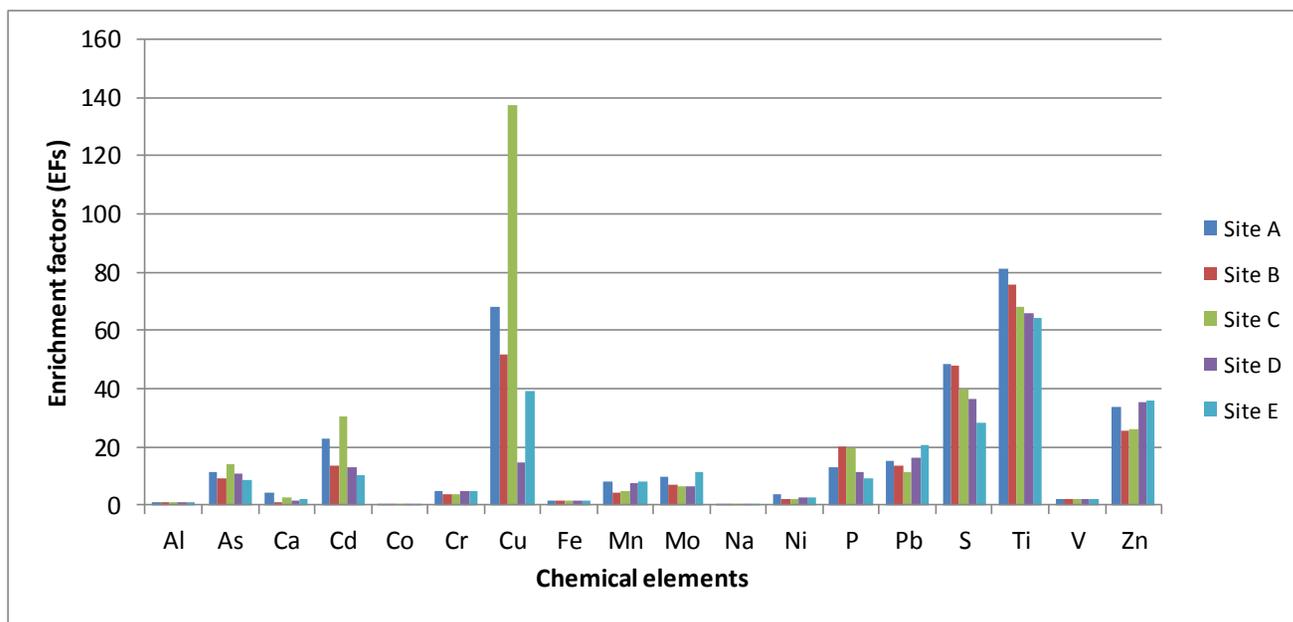


Figure 4.5: Enrichment factors of 18 elements in dust fallout samples around Tshwane.

Table 4.11: Enrichment factor of elemental deposits at the 5 sampling sites around Tshwane.

Sites	Enrichment factors (Efs)				
	<2	2 to 5	5 to 20	20 to 40	>40
A	Al, Co, Fe, Na and V	Ca, Cr, Ni,	As, Mn, Mo, P, Pb	Cd and Zn	Cu, S and Ti
B	Al, Ca, Co, Fe, Na, Ni and V	Cr and Mn	As, Cd, Mo, P and Pb	Zn	Cu, S and Ti
C	Al, Co, Fe, Na and V	Ca, Cr, Mn and Ni	As, Mo, P and Pb	Cd, S and Zn	Cu and Ti
D	Al, Ca, Co, Fe and Na	Cr, Ni and V	As, Cd, Cu, Mn, Mo, P and Pb,	S and Zn	Ti
E	Al, Co, Fe, Na and V	Ca, Cr and Ni	As, Cd, Mn, Mo and P	Cu, Pb, S and Zn	Ti
Comments	Depletion to minimal enrichment	Moderate enrichment	Significant enrichment	Very high enrichment	Extremely high enrichment

Figure 4.5 and Table 4.11 above summarises the calculated EF values of elements which were obtained through ICP-MS analysis. For the purpose of this study the calculated elemental EFs will be discussed according to the sampling sites which they were found. EF values signify the degree of enrichment. According to Sutherland (2000), the EF values which are < 2 shows that the degree of enrichment is depletion and minimal; between 2 to 5 signifies moderate enrichment; 5 to 20 signifies significant enrichment; 20 to 40 signifies very high enrichment and finally > 40 signifies extremely high enrichment. Generally, the EF_{crust} values increases with increasing non-crustal source contribution (Rashki, 2012). He further alluded to the fact that EF_{crust} values > 10 implies that the element is of anthropogenic origin. For the purpose of this study, only elements with $EF > 10$ will be discussed.

Site A

The EF values of As, Mn, Mo, P and Pb are significantly enriched. Based on site A characteristics, As may be attributed to the use herbicides and pesticides to destroy weeds and pests (Cao *et al.*, 2011). P may be linked to fertilizers applied to the soil around the sampling area for plants nourishment. Pb on the other hand may be associated with vehicle tailpipe emissions, tire abrasion and brake linings (Cao *et al.*, 2011). Tüzen (2003) as cited by Olowoyo *et al.* (2013) further pointed that Pb may originate from combustion of gasoline that contains tetraethyl lead as anti-knock agent. Mn could be linked to steel production, alloy manufacturing and in gasoline as an additive to enhance octane rating (Moja & Mnisi, 2013). Mo is used as an alloying agent in the manufacture of stainless steel and in high-speed components and is added to cast iron for hardness control (Morrison *et al.*, 2006). Sabbioni and Bignoli (1980); Reddy and Hasfurther (1989); Morrison and Spangler (1992); Zhang and Reardon (2003) as cited by Smedley (2014) indicated that Mo can be distributed in the environment through fossil-fuel combustion, leaching from fly ash, mobilization from mine and quarry wastes and fertilizer applications.

Site B

Site B is situated few meters from site A and both sites have recorded the significant enrichment of As, Mo, P, and Pb ($EF = 5$ to 20) except for Mn (site A) and Cd (site B). The EF values for

common elements in both sites indicate the same anthropogenic source. The element Zn is highly enriched (EF = 20 to 40) just as is the case in site A. Both sites are extremely enriched with Cu, S and Ti suggesting the same source origin.

Site C

The EF values of As, Mo, P and Pb are 14.0, 6.7, 19.8 and 11.2 respectively. These elements are significantly enriched and show the same pattern as sites A and B with the exception of Mn and Cd respectively. The EF values are in the decreasing order: P > As > P > Pb. P is linked to fertilizers as this site is characterised by vicinity to vegetation while As is associated with pesticides and herbicides (Cao *et al.*, 2011). The elements Cd, S and Zn were significantly enriched same as site A except for S. It could be attributed to oil combustion and industrial thermal processes particularly to polluted urban areas (Makra *et al.*, 1999). Tshwane is no exception to industrial activities especially at the western part of the city. Cd, S and Zn are highly enriched with EF value of 30.5, 40.0 and 26.2 respectively. Their EF values in decreasing order: S > Cd > Zn. According to Makra *et al.* (1999), in polluted areas, the source of S is oil combustion and industrial thermal processes. At site C, the source contributor for S could be linked to veld fires, cement and steel industries which are situated at the western site of the city. Al Momani (2003) alluded that local emissions and long range transport are considered to be source of enriched elements. Cd may be emitted from coal, oil combustion and pyrometallurgical non-ferrous metal production such as Pb, Cu-Ni and Zn-Cd (Tiwari *et al.*, 2008). Nriagu (1989) as cited by Al Momani (2003) indicated that metal smelting and fuel combustion are usually the source of non-crustal volatile metals such as Cd, Zn and Pb in the atmosphere.

Site D

The EF values of As, Cd, Cu, Mn, Mo, P and Pb are 10.7, 13.1, 14.7, 7.6, 6.7, 11.4 and 16.3. The EF values are in decreasing order: Pb > Cu > Cd > P > As > Mn > Mo. Pb emanates from vehicle exhaust emissions, brake linings, tyre wears and engine lubricants such as oil and gasoline. Except As and P, the rest of the elements may be linked to vehicle emissions. Site D is characterised heavy traffic congestions; therefore, Cu is likely to come from the corrosion of metallic parts of cars derived from engine wear, thrust burning, brushing and bearing metals

(Olowoyo *et al.*, 2013). Zn and S have the EF values of 35.5 and 36.3 respectively. Their sources could be attributed to the use of car brakes, building materials and vehicle tailpipe emissions around the city of Tshwane. Ti on the other hand is extremely enriched with EF value of 66.0. The likely possible sources of Ti (in the form of titanium dioxide (TiO₂)) are building concrete and ceramics during the manufacturing of tiles (Burton, 2011). As alluded earlier, Site D is situated in a residential area where traffic congestions and building constructions (e.g. demolition, renovations and paintings) take place. It stands to reason on elevated EF value (66.0) of Ti. As may be originating from industrial activities such as copper production, use of low quality coals, smelter and pesticides (Loska, 2002).

Site E

Site E is characterised by high traffic congestions, residential area, construction and commercial activities. The EF values of As, Cd, Mn, Mo and P are 8.7, 10.4, 8.3, 11.2 and 9.1 respectively. These elements fall under the significantly enriched category (EF = 5 to 20) (see Table 4.11 above). Site D and E show the similar trend of significantly enrichment except for Cu and Pb, Which are enriched in site D only. The EF values are in decreasing order: Mo > Cd > P > As > Mn > Mn. Cu (39.3) and Zn (36.0) are highly enriched and their anthropogenic sources include vehicle exhaust emissions and engine lubricants. Lai *et al.* (2007) as cited by Alahmr *et al.* (2012) further substantiated that the accumulation of Zn and Cu on urban surfaces emanate from vehicle exhaust emissions, oil lubricants, automobile parts, corrosion of building materials and atmospheric deposition. The EFs (20 to 40) trend is in the order: Zn > Cu > S > Pb. Ti shows a similar trend as noted in site D with EF > 40 which signifies extremely high enrichment. Ti enrichment may be linked to building demolitions, renovations and paintings (as an additive to the paint pigments). Tshwane went through enormous building demolition, constructions and renovations including road constructions along Nana Sita Street (formerly Skinner Street).

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The SEM-EDX and MicroScan analysis were performed in order to characterise the size, morphology and elemental composition of dust fallout samples. Various particle sizes, numbers, morphology and elemental composition were found at different sites.

The results from the MicroScan analysis showed the prevalence of sandy rounded-shaped quartz (SiO_2) particles across all sites. A mixture of quartz, quartzite, feldspar calcite and haematite and traces of metal oxides were evident at all sites. However, sites A, B and C dominated the abundance of these minerals. On the other hand, sites D and E showed fine and rounded quartz and quartzite with various trace metal oxides. The particle sizes ranged from 31 to 40 μm the mineral. The morphological characteristics ranged from round to broken sandy material.

The results of SEM-EDX showed the weight percentages of Si, Al, Ca, Cu, N, Mg, Ti and P were obtained using the EDX spectra of individual particles. A total of 135 particles were present in high number fractions (~97%) and size ranged from 1.0 to 10.0 μm . Silicates (Si-rich particles) made up 74.0% of total particles; Fe-rich particles comprised of 4.0%; Ca-rich particles, Ti-rich particles, N-rich particles, Cu-rich particles and P-rich particles were comprised of 4.0, 1.0, 9.0, 3.0 and 1.0% respectively. The particles of sites D and E showed mostly spherical/oval, triangular and irregular morphology. Spherical particles are mostly associated with high combustion activities. The particle sizes ranged from 1.0 to 7.0 μm at these sites. Based on the size distribution of these particles, they fall under fine to ultra-fine mode. The particles from sites A, B and C showed irregular to rectangular morphology, with size ranging from 1.0 to >10. These particles fall within the coarse mode. Elements such as P, S, Ti, Mg, K and Cu were found at site A and B (UNISA-Muckleneuk campus) while heavy metals such as Cu and Ti; alkali metals (Na and K) and alkaline-earth metals (Ca) were found at sites D and E. Inhalation, ingestion and/contact with these elements is detrimental to human health. Fine particles are able to penetrate through the lungs into the alveoli where they can cause chronic

respiratory disease. The groups that are susceptible to the adverse health effects caused by inhalation or ingestion of dust fallout are children and the elderly.

The ICP-MS was used to determine the elemental composition of dust fallout and the mean concentration of the elements of concern ranged from 1.1 - 2.6 for As, 0.2 - 0.6 for Cd, 17.0 - 21.9 for Ni, 449.8751.1 for Pb, 9.9 - 22.3 for V and 101.7 - 293.0 $\mu\text{g}/\text{m}^3$ for Zn. Pearson correlation matrix showed strong positive correlation amongst the elements which signifies common source origin.

The matrix further showed the relationship between the meteorological parameters and dust fallout at sampling sites. Dust fallout rate at site D showed moderate degree of correlation with temperature. Wind velocity and rainfall showed sufficiently high degree of correlation. Site D and E showed positive moderate degree of correlation. This implies that these two sites are influenced by the same source contributors to dust fallout. Humidity showed a negative moderate correlation. It is therefore imperative to take into cognisance the meteorological parameters when conducting a dust fallout studies as they have direct influence on the loading.

One-way ANOVA was performed to analyse the significant difference among the dust fallout rates at different sampling sites. The results indicated that there are no significant differences among the sites

The EF analysis was performed to identify the origin of elements i.e. crustal or anthropogenic. It was discovered that elements such as As, Cd, Cu, Mo, Mn, P, Pb, S and Ti were enriched, meaning they are of anthropogenic origin. The degree of enrichment ranged from significantly enriched to extremely enriched. It can therefore, be concluded that the main contributors of these elements around Tshwane are high traffic congestions (morning and afternoon peak hours), vehicle entrainment of paved and unpaved roads, burning of coal and paraffin by residents and street vendors particularly during winter periods and frequent construction activities. The elements such as Cd exceeded the set limit 0.005 $\mu\text{g}/\text{m}^3$ by OSHA (2015) and NIOSH (2007); Pb exceeded the set standard of 0.5 $\mu\text{g}/\text{m}^3$ set by OSHA (2015), NIOSH (2007), WHO (2000), USEPA (2012) and DEA (2013). The rest of the elements fell within the set guidelines by various regulatory national and international bodies.

Generally, site D (150.81 mg/m²/day) and E (145.51 mg/m²/day) recorded the highest dust fallout rates followed by sites B, C and A during winter 2012 and site D (107.07 mg/m²/day) and site E (179.31 mg/m²/day) during winter 2013 seasons. There were no rainfalls recorded during this period and wind speed of 0.2 to 0.7 m/s blew from WSW to E. These parameters lead to the built-up of dust fallout and inhibit their dilution; hence, high dust fallout at these sites during winter is evident. Although all the sampling sites recorded the concentrations within the SANS 1929 (2011) and DEA (2013) average RESIDENTIAL limit of 600 mg/m²/day, the future accumulation and exceedances cannot be ruled out owing to the increasing developments in urban areas. Summer 2012 (wet) recorded the lowest dust fallout concentrations at site D (71.27 mg/m²/day) and E (86.45 mg/m²/day) as compared to winter 2012 (dry) season. High rainfalls (112.3 mm) and an average speed of 1.5 m/s blew from SSE direction. Heavy rainfalls during this period caused the air to be humid and moist, thereby, suppressing the dust upliftment from the ground and washing out particles from the atmosphere.

5.2 Recommendations

The study recommends that based on the variation in particle size distribution and morphology during the different seasons of the year, it is critical that seasonal variation is considered when characterising dust fallout. Furthermore, a thorough and comprehensive analysis of dust fallout using both techniques (SEM-EDX and MicroScan analysis) is necessary in order to characterise the morphology, size and chemical composition in different seasons of the year. An analytical technique such as XRD for the analysis of minerals can add value in establishing accurate types and percentage of different minerals.

CHAPTER 6: REFERENCES

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APPENDICES

APPENDIX A: Ethical approval to conduct the study.

Ref. Nr.: 2012/CAES/018

To the student:
Mr MM Sebaiwa
Department of Environmental Science
College of Agriculture and Environmental Sciences

Student nr: 33810524

Dear Mr Sebaiwa

Request for Ethical approval for the following research project:

Characterisation of airborne particulates around Tshwane

The application for ethical clearance in respect of the above mentioned research has been reviewed by the Research Ethics Review Committee of the College of Agriculture and Environmental Sciences, Unisa. Ethics clearance for the above mentioned project (Ref. Nr.: 2012/CAES/018) is **granted** after careful consideration of all submitted documentation to the CAES Ethics committee.

Please be advised that the committee needs to be informed should any part of the research methodology as outlined in the Ethics application (Ref. Nr.: 2012/CAES/018), change in any way. Should this be the case, a memo should be submitted to the Ethics Committee in which the changes are identified and fully explained.

We trust that sampling, data gathering and processing of the relevant data will be undertaken in a manner that is respectful of the rights and integrity of all participants, as stipulated in the UNISA Research Ethics Policy.

The Ethics Committee wishes you all the best with this research undertaking.

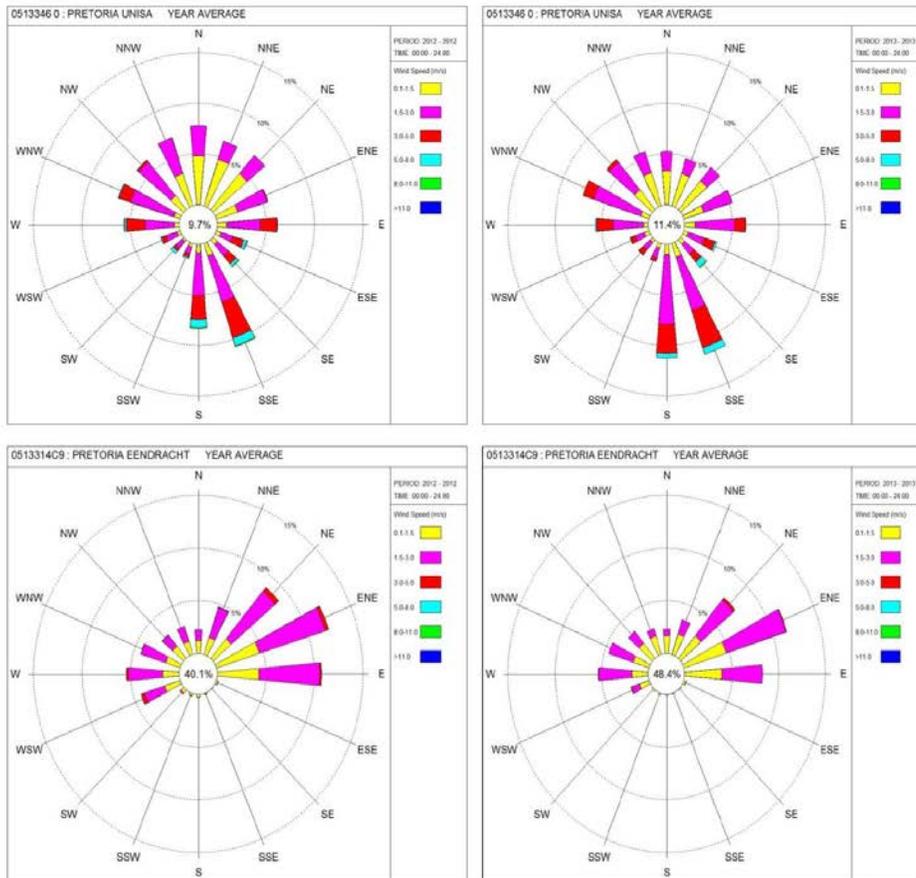
The Ethics Committee wishes you all the best with this research undertaking.
Kind regards,



Prof E Kempen, CAES Ethics Review Committee Chair



APPENDIX B: Annual wind roses for UNISA and EENDRACHT (2012-2013) weather station.



APPENDIX C: Elemental analysis of five combined dust samples.

DUSTWATCH CC

Company registration Number: 2008/134744/23
| P.O. BOX 1810 Sun Valley 7985 Republic of South Africa |
| Tel: 021 785 6999 | Fax: 0866 181 421 | Cell: 082 875 0209 |
| info@dustwatch.com | www.dustwatch.com |
Members: Gerry F. Kuhn and Christopher Loans

Willem Wepener
P.O. Box 4593
Rietvalleirand
Pretoria East
0174
0123455244
Biograde.cc@gmail.com

RE: Elemental Analysis of Five samples

Please do the analysis on the five samples for elemental analysis.

Please use the names shown on the containers, Site A, Site B, Site C, Site D, and Site E respectively to name the analysis results.

The total masses of the five combined samples are shown below.

SAMPLE	PARTICULATE MASS (MG)
Total A	378.9
Total B	276.56
Total C	332.32
Total D	517.43
Total E	503.26

Thanks for the time.



Gerry F. Kuhn
(FMVS, MSAIOH, Grad
SE)



Chris Loans
(BSc Chemical
Engineer, Pr Eng)

Doc Number: 0713050906: Date: 05-Jul-13

1

APPENDIX D: Turn it in originality report.

Turnitin Originality Report
MSc Environmental Science dissertation by M Sebaiwa
From DRAFT SUBMISSIONS (DES 2015 SUBMISSIONS)

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APPENDIX E: Conference proceeding and draft manuscript.

Title of the oral manuscript : Characterization of Dust Fallout with a MicroScan Particle Analyzer and a SEM - EDX.

Authors names : Shadung J. Moja and Marks M. Sebaiwa

Conference details : Proceedings of 4th International Conference on Earth Science & Climate Change. 16-18 June 2015.

Journal name : Journal of Earth Science & Climate Change. Open Access. June. Volume 6, Issue 5. ISSN: 2157-7617

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