

**ATMOSPHERIC CONCENTRATIONS, DRY DEPOSITION
FLUXES AND COMPOSITIONAL ANALYSIS OF
SUSPENDED PARTICULATE MATTER IN NAIROBI,
KENYA**

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**Atmospheric Concentrations, Dry
Deposition Fluxes and Compositional Analysis of Suspended
Particulate Matter
in Nairobi, Kenya**

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Degree of Masters in Environmental Legislation and Management of
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DECLARATION

This thesis is my original work and has not been presented for a degree in any other university

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DEDICATION

This thesis is dedicated to my spouse Leonard and our children Jerome and Mikayla for their encouragement, support and prayers throughout the research period.

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TABLE OF CONTENTS

DECLARATION.....	ii
DEDICATION.....	iii
ACKNOWLEDGEMENT	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF APPENDICES	xii
ACRONYMS AND ABBREVIATION	xiii
ABSTRACT	xvii
CHAPTER ONE	1
INTRODUCTION.....	1
1.1 Background of the Study	1
1.2 Statement of the Problem	3
1.3 Objectives	3
1.3.1 Main objective	3
1.3.2 Specific Objectives	3
1.4 Justification	4

1.5 Scope and Limitations	4
1.6 Conceptual Framework	5
CHAPTER TWO	6
LITERATURE REVIEW.....	6
2.1 Introduction	6
2.1.1 Classes of Air Pollution	6
2.1.2 Air Pollution in Developing Nations	7
2.2 Atmospheric Pollutants	8
2.2.1 Particulate Matter/Settleable Solids.....	8
2.2.2 Heavy Metals	10
2.2.3 Volatile Organic Compounds	12
2.3 Dustflux Monitoring and Analyzing Instruments	13
2.3.1 Monitoring Instruments	13
2.3.2 Analytical Techniques/Instruments	18
CHAPTER THREE	25
MATERIALS AND METHODS	25
3.1 Study Sites	25
3.2 Determination of the Particulate Matter (Pm _{2.5} and Pm ₁₀) Levels	26

3.3 Determining the TDS, TSS & TS in the Dustfall	27
3.3.1 Total Soluble Matter	28
3.3.2 Insoluble Matter	29
3.3.3 Total Solids	30
3.4 Assessment of the Trace Elements in the Deposition	30
3.4.1 Element Concentrations	30
3.4.2 Estimation of Dry Deposition Fluxes	30
3.4.3 Calculation of the Enrichment Factors (EFs)	31
3.5 Assessment of the Organic Compounds in the Dustfall	32
3.6 Quality Control	32
3.7 Further Analysis	32
CHAPTER FOUR.....	34
RESULTS AND DISCUSSION	34
4.1 Particulate Matter	34
4.1.1 Residential Zones.....	34
4.1.2 Industrial Zones	36
4.1.3 Commercial Areas	37
4.1.4 Hourly Mean Concentrations.....	37

4.1.5 Spatial Variations between Different Sites	39
4.1.6 PM Variation in relation to Precipitation and Windspeed	40
4.2 TSS, TDS and the TS in the Dustfall	40
4.3 Heavy Metals and Metalloids in the Dustfall	42
4.3.1 Average Concentrations.....	42
4.3.2 Annual Deposition Fluxes	44
4.3.4 Enrichment Factors	45
4.3.5 Correlation Coefficients.....	47
4.4 Organic Compounds.....	48
CHAPTER FIVE.....	50
CONCLUSIONS AND RECOMMENDATIONS.....	50
5.1 Conclusions	50
5.2 Recommendations	51
REFERENCES.....	52
APPENDICES	63

LIST OF TABLES

Table 3.1: Study Sites and their Descriptions	26
Table 4.1: Average Daily Concentrations of PM _{2.5} And PM ₁₀ at the Sites and WHO Limits	34
Table 4.2: COD Values of PM Concentrations Between the Different Monitoring Sites	39
Table 4.3: Average TDS, TSS and TS at the Study Sites	42
Table 4.4: LODs and Percentage Recovery	42
Table 4.5: Average Concentration of Elements	43
Table 4.6: Comparison of Trace Elements Concentrations with other Studies	44
Table 4.7: Estimated Dry Deposition fluxes	45
Table 4.8: EFs for Heavy Metals and Metalloids in the Sites.....	47
Table 4.9: EFs Compared to Other Studies.....	47
Table 4.10: Correlation Coefficient (r) between Element Concentrations.....	48
Table 4.11: Organic Compounds Detected	48
Table 4.12: Organic Compounds and Their Likely Sources.....	49

LIST OF FIGURES

Figure 1.1: Conceptual Framework	5
Figure 2.1: PMs Translocation through Respiratory Tract	10
Figure 2.2: BS 1747-1:1969.....	14
Figure 2.3: ASTM D1739:82	15
Figure 2.4: Construction Scheme for MDC	16
Figure 2.5: BS 1747-5:1972 Deposit Gauge.....	17
Figure 2.6: SUSTRA Sampler	18
Figure 2.7: Structural Diagram of the EDXR	20
Figure 2.8: Flame AAS	21
Figure 2.9: ETA-AAS	22
Figure 2.10: Schematic of a GC-MS System.....	23
Figure 2.11: ICP-AES	24
Figure 3.1: Map Nairobi County.....	25
Figure 3.2: Flowchart Showing Sample Treatment	28
Figure 4.1: Weekly Averages, Median, and 1st/3rd Quartile Values for PM _{2.5} for the Study Sites	36
Figure 4.2: Weekly Averages, Median, and 1st/3rd Quartile Values for PM ₁₀ at the Study Sites.....	37

Figure 4.3: Hourly PM2.5 Trends38

Figure 4.4: COD Values of Pm Concentrations between the Different Monitoring Sites
.....40

Figure 4.5: TDS, TSS and TS (in mg m-2 day -1) at the Study Sites41

Figure 4.6: EFs for Heavy Metals and Metalloids in the Sites46

LIST OF APPENDICES

Appendix I: Dust Fall Jar Installed at NCPB Depot Industrial Area.....	63
Appendix II: Purple Air Monitor Installed at Embakasi	64
Appendix III: Sample PM Data.....	65
Appendix IV: Calibration Curves for the Trace Elements	74
Appendix V: Chromatograms for the Dustfall Samples	80

ACRONYMS AND ABBREVIATION

AAS	Atomic Absorption Spectrometry
AEEs	Anomalously Enriched Elements
APIS	UK Air Pollution Information System
AQI	Air Quality Index
ASTM	American Society for Testing and Materials
BAMs	Beta Attenuated Mass Monitors
CITEPA	Interprofessional Technical Centre for Studies on Air Pollution
COD	Coefficient of Divergence
CO_xs	Oxides of Carbon
EDXF	Energy –Dispersive X-Ray Fluorescence
EFs	Enrichment Factors
EDC	Endocrine Disrupting Chemicals
ETA	Electro Thermal Atomizers
F_d	Dry Deposition Fluxes

GC-MS	Gas Chromatography-Mass Spectrometry
HCL	Hollow Cathode Lamp
HDPE	High Density Poly Ethylene
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometer
IUPAC	International Union of Pure and Applied Chemistry
KNBS	Kenya National Bureau of Statistics
LCMs	Low-Cost Monitors
LODs	Limit of Detection
LOQ	Limit of Quantification
MDCO	Marble Dust Collector Sampler
NASA	National Aeronautic & Space Administration
NEEs	Non-Enriched Elements
NEMA	National Environment Management Authority
NOxs	Oxides of Nitrogen
OCPs	Organochlorine Pesticides

PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PCDFs	Polychlorinated Dibenzofurans
PCDDF	Polychlorinated Dibenzo-P-Dioxins and Dibenzofurans
PM	Particulate Matter
POPs	Persistent Organic Pollutants
PPM	Parts per Million
SO_xs	Oxides of Sulphur
SUSTRA	Suspended Sediment Trap Sampler
TDS	Total Dissolved Solids
TS	Total Solids
TSS	Total Suspended Solids
US EPA	United States Environmental Protection Agency
VOCs	Volatile Organic Compounds
WDFG	Wedge Dust Flux

WHO World Health Organization

XRF X-Ray Fluorescence

ABSTRACT

Nairobi City is a rapidly growing regional center with divergent land uses, pollutants and pollution sources. Different sizes of particulate matter with varying compositions are released into and dispersed in the air through activities on the earth's surface that generate such materials. Settleable particulate matter of size greater than $10\mu\text{m}$ are readily deposited on the ground and on vegetation. The settleable solids/dustfall and their pollution severity is dependent on their composition. Presence of harmful trace elements like Pb, Cu, and organic compounds in the dustfall pose risks to the environment. This study assessed the composition of dustfall in Nairobi. Purple air PM monitors were used to assess the concentrations of particulate matter ($\text{PM}_{2.5}$ and PM_{10}). The British Standard (BS 1747-1:1969) dustfall jar was used for the collection of dustfall. Atomic Absorption Spectrometer (AAS) was used to determine the concentrations of trace elements (Pb, Cu, Zn, Al, B, Co, Cr) in the dustfall samples. The samples were also screened for presence of organic molecules using a Gas Chromatograph with Mass Spectrometer (GC-MS) detector. The mean $\text{PM}_{2.5}$ and PM_{10} recorded in this study were 20.16 and $24.33 \mu\text{g}/\text{m}^3$, respectively. Four out of the six sites studied recorded $\text{PM}_{2.5}$ levels higher than the WHO daily averages of $15 \mu\text{g}/\text{m}^3$ while only one site recorded PM_{10} higher than WHO of $45 \mu\text{g}/\text{m}^3$. The sites showed wide variations which can be attributed to land use as well as vehicular traffic volumes at the sites. The study found the overall mean deposition rates of Total Solids to be $127\pm 40 \text{ mg m}^{-2}\text{day}^{-1}$ with a range of 69 to 158. The average dry deposition fluxes (Fd) of cobalt, boron, aluminum, zinc, copper and chromium were; 77, 49, 44, 2, 1.4, $0.01 \text{ mg m}^{-2} \text{ yr}^{-1}$, respectively. Industrial and residential/industrial zones recorded higher amounts of dustfall than commercial zones. The study revealed that heavy metal contamination in the dustfall is dependent on human activities and therefore mitigation measures should be designed to control causative activities. Organic molecules such as; tridecane, benzenediamine, salicylic acid, hexadecane, dibutyl phthalate, methy salicylate, aniline, undecane, dibutyl phthalate, trichloromethane, ethanedinitrile, propane, xviiexadecenoic acid and phenol were detected in all samples analysed. Their sources can be attributed to industry related sources and motor-vehicle fuel constituents. The findings of this study indicate that air in Nairobi has pollutants at levels that are harmful to its residents. It is therefore recommended that legislation of, adherence to and enforcement of environmental laws should be done to control air pollution.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Good air quality is desired for sustainable human health and comfort. Air quality can be measured by determining the mass concentrations of pollutants in the atmosphere. The first step in controlling air pollutants is to establish their presence and concentrations in order to rid or limit harmful pollutants as guided by local air quality standards to safeguard human health. In Kenya, air quality management is under the National Environmental Management Authority (NEMA) which oversees matters to do with the environment.

Air pollution as defined by WHO 2011 refers to the contamination of the outdoor or the indoor environment either by a physical, biological or a chemical agent that alters the atmospheric characteristics. It can also be defined as the introduction into the air of substances like solid particles, gases or liquid aerosols at levels that exceed the environment's natural capacity to dilute, dissipate and/or absorb them (Nathanson, 2020). It has become a global concern due to its negative effects on human health, the climate and nature at large. This type of pollution affects the climate because it leads to the release of trace gases and particles that can alter the radiation balance in the atmosphere. The deposition of aerosols and gases in the atmosphere may result in acidification of both the terrestrial and the aquatic ecosystem and this alters the natural ecosystems. Air pollution has however been felt the most in the health sector since the effects are direct whether in short term or long-term exposure. According to WHO 2018, air pollution has become a global health concern that claims around 4.2 million every year.

Air pollution is not a new phenomenon and its impacts were greatly noticed in the nineteenth century as a result of industrial revolution. This occurred mainly in the urban areas of industrialized nations especially in the United States and Europe (Fowler et al., 2020). The 19th Century episodes of air pollution resulted in large numbers of hospitalization and deaths like the 1952 Great Smog of London that led to almost 12000

deaths (Polivka, 2018). This evidently shows that air pollution has deleterious effects on health. According to Stanaway et al., 2018 and WHO 2018, air pollution is among the top-ranking causes of premature deaths. The impacts of air pollution have recently been felt in developing countries which are rapidly industrializing (Mannucci et al., 2017).

There are several industrial activities in the urban centers that have led to an influx of people into these areas especially in the developing countries (Mannucci et al., 2017). This influx has further deteriorated the quality of air by resulting in an increase in indoor pollution in addition to the outdoor pollution linked to the industries (Bruce et al., 2000). It has also resulted in increased vehicular emissions which further aggravates the air pollution problem (Angnunavuri et al., 2019).

The deposition of atmospheric pollutants on land or water bodies occurs over time and it depends on a number of factors. The lifetime of particles in the atmosphere depends on their sizes and their chemical properties. Pollutants will be deposited depending on the prevailing weather conditions. This deposition can either be wet or dry with wet deposition of particles occurring only when there is precipitation. These pollutants are deposited either on vegetation, buildings or even on the soils (Pacyna, 2008).

The quality of air in Nairobi is among the worst in Kenya due to numerous industrial activities in the city as well as emissions from traffic (Kiai et al., 2021, Raje et al., 2018). Because of these activities, the air contains high concentrations of PMs whose composition includes toxic substances like heavy metals (Pb, Cd, Zn etc.), organic molecules among others (Muindi, 2017, Mutua et al., 2021). These particles will eventually get into the food chain whether they are deposited on aquatic or terrestrial lands and can have adverse health effects on both plants and animals. It is also important to note that during the deposition process, such pollutants may damage buildings and corrode metals depending on their composition. Both dry and wet deposition of pollutants on the soil changes the soil pH and this alters the ecological properties of such soils and hence alter the ecosystem.

1.2 Statement of the Problem

Air quality has continued to fall in Kenya because of increase in human population and industrialization. Health complications associated with poor air quality have become rampant in Kenya. Urban areas like Nairobi have witnessed an increase in the release of more pollutants into the ambient air. This is despite the air quality regulations set under Act No. 8 of 1999 (NEMA, 2014) that guide on permissible emission levels for pollutants by various sectors. With more pollutants going into the atmosphere, atmospheric deposition of these settleable solids on terrestrial lands and water bodies has increased. The settleable solids especially in the urban areas contain toxic substances like trace elements and organic molecules that can have serious health impacts on living organisms. More focus by way of research should therefore be directed on determining the constituents of these pollutants so as to help regulating authorities in designing and formulating effective policies and implementation measures to address air quality problems. The purpose of this study was to determine the presence and concentration of heavy metals and organic compounds in settleable solids.

1.3 Objectives

1.3.1 Main Objective

The main objective of this study was to assess the composition of settleable solids, dry deposition fluxes of trace metals, presence of organic compounds and concentrations of atmospheric PM_{2.5}, PM₁₀ in Nairobi, Kenya.

1.3.2 Specific Objectives

- i. To assess the airborne concentrations of particulate matter (PM₁₀ and PM_{2.5}) in Nairobi.
- ii. To determine the rates of deposition of settleable solids in Nairobi.
- iii. To determine the concentrations of trace elements (Pb, Al, Cr, B, Cu Co & Zn) in dust-fall in Nairobi.

- iv. To screen for the presence of organic compounds in dust-fall in Nairobi.

1.4 Justification

A host of health issues ranging from cardiovascular diseases, respiratory complications such as asthma, lung cancer are becoming more prevalent in urban areas in Kenya. These categories of diseases are directly related to poor air quality resulting from increased anthropogenic activities in populated urban centers. It is important to assess the extent of air pollution in spaces occupied by humans and other living organisms so as to come up with the necessary mitigation measures. Several studies have been done on the quality of air in the urban areas however, focus should be directed on identifying the composition of these pollutants so as to provide information on the damage these pollutants have on human health. This study purposed to determine the composition of particulate matter in Nairobi. The findings of this research will provide a reference for action in controlling air pollution and its impacts.

1.5 Scope and Limitations

This study focussed on the quality of air in selected areas within Nairobi County. Concentrations of PM_{2.5} and PM₁₀, and the concentrations, deposition fluxes and enrichment factors of trace elements in the particulates were assessed. Also, screening the particulates for the presence of organic compounds was done.

PM monitors and dustfall jars were placed in areas that were considered to be safe and free from fouling. Air quality data collected from each study site was a representation of the local conditions which were influenced by activities in the surrounding facilities and premises. Due to limited funding, only a few trace elements were targeted for analysis but more elements which are harmful could be present in the dustfall. However, from this study vital information about presence of harmful trace elements and organic molecules was acquired.

1.6 Conceptual Framework

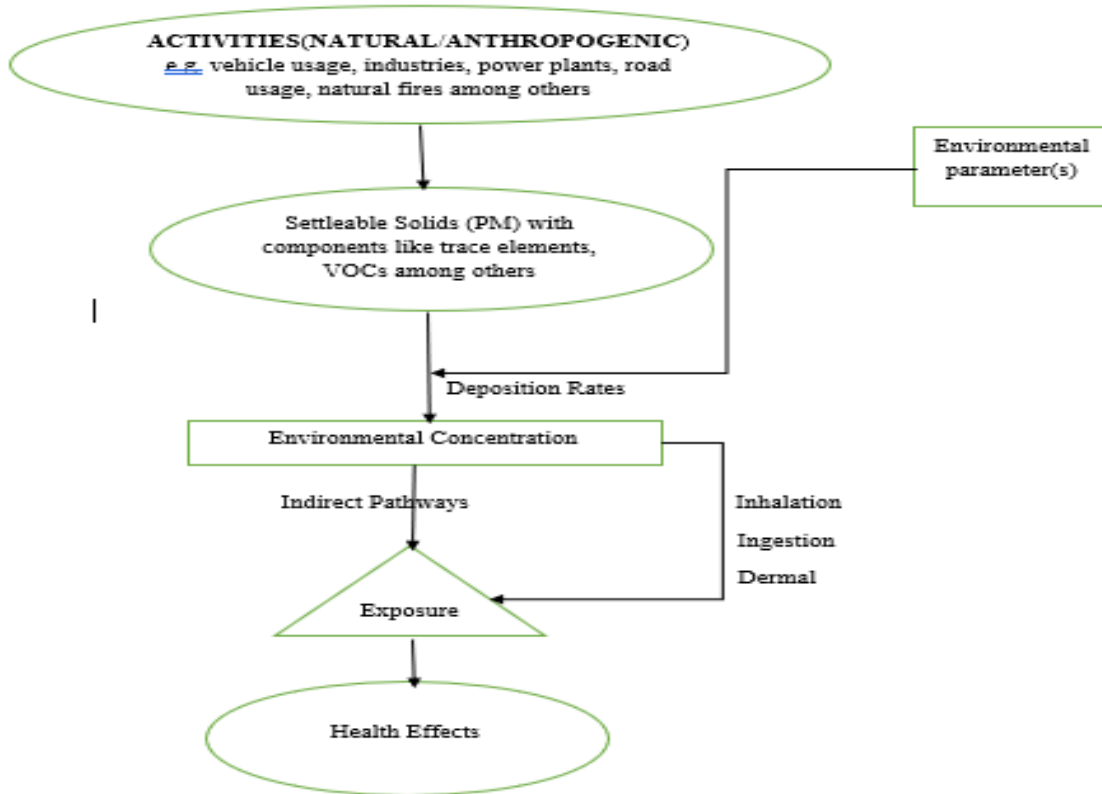


Figure 1.1: Conceptual Framework

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

The air around us is composed of pollutants which can be of solid, liquid and gaseous compounds. The solid and liquid components in the air are referred to as particles and are grouped into different classes depending on their sizes. The sizes will range from $PM_{\leq 0.01\mu m}$ (ultra-fine particles) to PM_{100} (very coarse particles). All these particles have different properties depending on their sources. The gaseous components in the air are composed of pollutants like the SO_{xS} , ammonia, NO_{xS} , O_3 as well as the VOCs. The gaseous components undergo chemical reactions with the solid particles (PM) to form other compounds that have different effects on both the environment and human health at large. The prevailing environmental conditions (e.g., humidity, temperature) will determine how these pollutants undergo complex chemical reactions in the atmosphere (Zhang et al., 2018).

2.1.1 Classes of Air Pollution

Air pollutants are classified into two; primary and secondary pollutants. Primary pollutants are those that are emitted at the source while secondary pollutants are those that are produced when the primary pollutants react with each other in the atmosphere. These pollutants will be processed and dispersed depending on the prevailing environmental conditions (Sitaras et al., 2008). Vertical dispersion of these pollutants ranges from 1-2 km but others can have a lifetime that is long enough for them to be displaced in higher altitudes including the stratosphere.

Air pollution is caused by both anthropogenic and natural sources. Natural sources include volcanic activities, dust, wildfires among others. However, the fraction contributed by the natural factors is small hence one can conclusively say that air pollution is mainly caused by anthropogenic activities especially in the urban areas (Manisalidis et al., 2020).

Air pollution can be classified into three levels depending on the scale of study. The levels are; global, regional and local pollution (Ramanathan and Feng, 2009). Local air pollution is felt within the immediate surrounding of the emission source and the pollutants mainly consist of the primary pollutants like suspended PM, CO, NO_x, SO₂, VOCs, metals, PAHs (polycyclic aromatic hydrocarbons compounds), carbon soot among others. Regional extends to larger areas (a few to hundreds km) from pollutant source and it mainly consists of secondary pollutants like O₃, HNO₃, H₂SO₄, NH₄NO₃. The global air pollution however is much wider and may alter the entire ecosystem of the earth. This class contributes to global warming, climate change and may also affect the stratospheric ozone layer. All these classes of air pollution affect human health depending on the properties of the pollutants at each level.

2.1.2 Air Pollution in Developing Nations

Stanaway et al. (2018) established that air pollution is among the major causes of premature deaths. The health risks that result from air pollution in developing countries are more adverse as compared to the developed countries. This is attributed to factors like poverty and poor environmental laws and/or implementation of the laws in such nations. The pollutants are emitted by industries during manufacturing processes or combustion of fossil fuels by the industries since clean energy has not been fully adopted in developing countries. Indoor air pollution is also high because 50% of the population do not have access to clean sources of energy for domestic heating (IEA-IRENA-WHO, 2022).

There are several activities in the urban areas that contribute to air pollution. These include; emissions from vehicles, domestic heating, industrial emissions among others. Some of the components of vehicular emissions are PM, CO, SO₂, NO_x & VOC (e.g., benzene, Polychlorinated Dibenzofurans, Polychlorinated biphenyls) and according to Hoang, (2017), 70 % of air pollution in the urban areas is contributed by vehicles. The number of vehicles in the cities is increasing and so is the number of motorbikes which further contribute to air pollution.

2.2 Atmospheric Pollutants

2.2.1 Particulate Matter/Settleable Solids

The deposition of settleable solids (particulate matter (PM)) is dependent on size with the smaller particles being not easily settleable (Shastri, 2020) while the coarse particles whose $PM \geq 10\mu\text{m}$ go through deposition at a faster rate. The concentration of the PM on the dustfall depends on the rate of emission, dispersion, transport and the rate of removal from the atmosphere.

Settleable solids are composed of Persistent Organic Pollutants (POPs), heavy metals and other pollutants depending on the pollutant source (Sharma et al., 2023) These pollutants can directly affect plants by covering the leaf lamina/blade thus hindering photosynthetic activities or indirectly affect by altering the soil pH thus affecting the physiological functions of the plants when they are absorbed.

2.2.1.1 Deposition of Settleable Solids

Atmospheric deposition is a non-point source of pollutants to both aquatic and the terrestrial lands. Globally, theoretical and experimental studies have been done on dry deposition and the properties of their constituents (Yi et al., 1997a, Shahin et al., 2000, Pryor & Barthelmie 2000). Davidson, (1977) in his study in California established that, large particles accounted for 70% of dry deposition through sedimentation on flat surfaces. Dry deposition occurs through either impaction, sedimentation and even Brownian diffusion (particles $<0.1 \mu\text{m}$ in diameter).

Aside from the environmental factors, deposition of particles on surfaces also depends on; the surface (land characteristics, biological and chemical reactivity), atmospheric properties and the physical characteristics of the particle, i.e., shape, density and size (Hussein et al., 2011). Small particles of $PM_{0.1}$ - $PM_{2.5}$ stay for a long period of time in the atmosphere and they are mainly deposited through wet deposition (if precipitation is present). The deposition of large particles of ($PM_{2.5}$ - PM_{20}) occurs mainly through

impaction and the winds play a big role in this. The main mode of dry deposition of coarse particles is through gravitational sedimentation and such particles do not stay for long in the atmosphere.

2.2.1.2 Impacts of Particulates on Human Health

The health effects of pollutants depend on their properties. Air pollution has been shown to cause serious cardiovascular, respiratory problems and even brain inflammation in case the pollutants reach the brain through circulation (Karl et al., 2009). The effects of exposure to humans also depend on the person exposed. Studies have shown that people with pre-existing respiratory or cardiovascular conditions can have more advanced effects from air pollution than healthy individuals. The length of exposure (chronic or acute) also determines the effects of these pollutants on humans. Age is also another factor with children being more susceptible due to their faster breathing rates than adults. This has been evidently shown with the increasing usage of asthma medication by children (Favarato et al., 2014).

The human respiratory system is directly affected by air pollution with the lungs being the main organ that is directly exposed if the pollutants get into the system during inhalation. According to Hofmann, (2011) the deposition of these PMs along the tract depends on the PM characteristics, deposition mechanisms, fluids dynamics and biological factors like breathing patterns, lung morphology etc. The mode of deposition along the tract is through sedimentation for between PM_1 - PM_5 , inertial impaction for $PM > 1\mu m$, diffusion $PM < 0.5\mu m$, electrostatic interaction and interception. The particles are deposited along the various parts of the respiratory tract. Particles of PM_{10} are mainly deposited along the upper respiratory surface while particles of $PM_{2.5}$ - PM_{10} get deposited on the ciliated surfaces. The fine or ultrafine particles however ($PM < 2.5$) get into the alveoli and may get into the blood capillaries through diffusion. If they get into the blood capillaries, they translocate into the blood stream and may find their way into the various body tissues through blood circulation. Chronic bronchitis, increase in respiratory cancer and respiratory diseases has been linked to air pollution (Manisalidis et al., 2020, WHO, 2006).

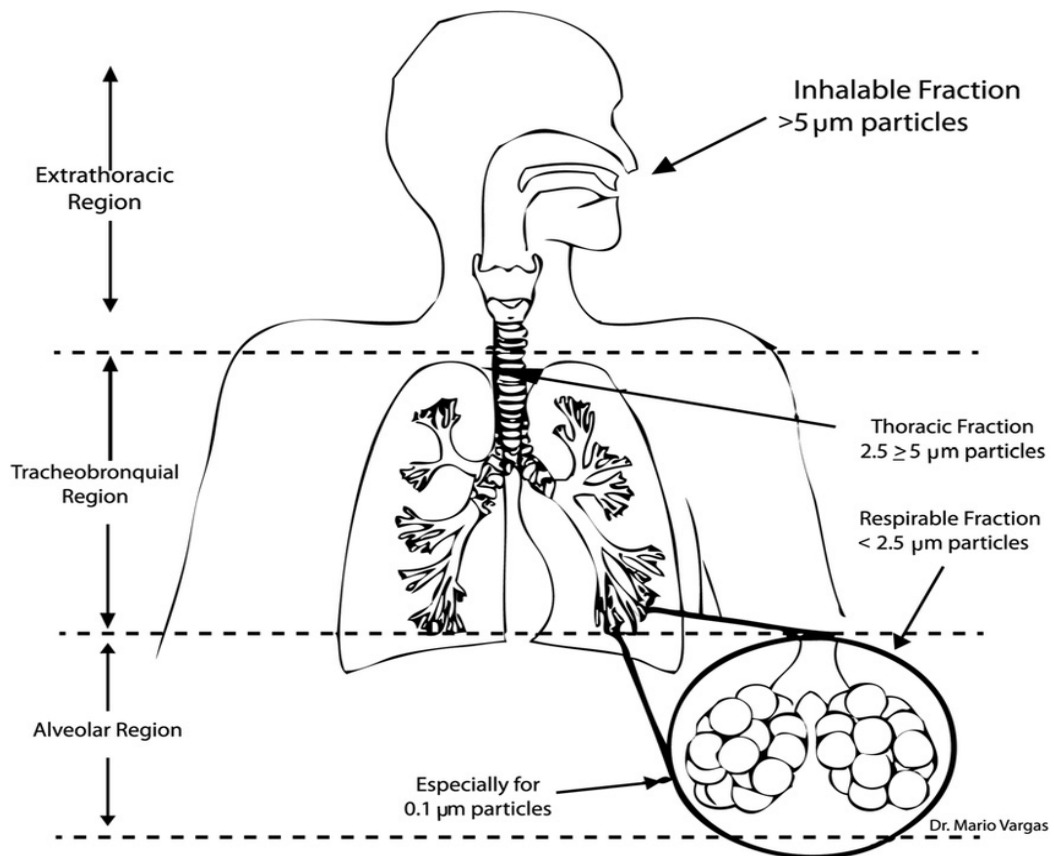


Figure 2.1: PMs Translocation Through Respiratory Tract

Source: (Vargas and Teran et al, 2012)

2.2.2 Heavy Metals

Trace elements as defined by IUPAC, 2014 refers to any element whose average concentration is not more than 100 mg/kg or less than 100 ppm. Heavy metals which are among components of the PM (Duffus, 2002), are very toxic and can have adverse health impacts on living organisms. A big percentage of trace metals are from different anthropogenic activities. Combustion processes, e.g., internal combustion engine, incineration, smelting, and power generation are the major emitters of heavy metals (Galloway et al., 1982). The type of industry or activity determines the type of metals emitted, e.g., Hg is mainly emitted during chemical production of chlorine and in cement processing, steel plants emit both Ni and Cd, ferrous metallurgy industries emit both Zn

and Pb, steel mills and foundry industries emit Cr (CITEPA, 2010). Zn, Cu and Pb are also emitted by car tires, brakes and tire rubber which is also responsible for the emission of Mn, Ni, Cd and Sb.

2.2.2.1 Routes of Exposure to Heavy Metals

Exposure pathways for human beings are inhalation, ingestion and dermal contact (APIS Report, 2011, Osman et al., 2019). Uptake of heavy metals by terrestrial organisms is mainly through food. If such elements are deposited on leaf surfaces or absorbed from the soils by plants, they will get to the animals through the food chain. When humans consume contaminated food, water or sea animals, they get in direct contact with these metals and they can also be exposed through inhalation of contaminated air (Ming-Ho, 2005). Basically, heavy metals contamination follows a cyclic order, i.e., from the industry then to the atmosphere, from atmosphere to the soils or water then to the foods (plants or animals) then finally to humans (Krishna, 2016).

2.2.2.2 Impact of Heavy Metals on Living Organisms

Since heavy metals are elements, they cannot be broken down hence they persist or bio-accumulate in the environment. They can be transported from one environment to another, such as from aquatic to terrestrial and vice versa (APIS Report, 2011). At low concentrations, heavy metals have toxic effects on living organisms with the exception of essential heavy metals (like Zn, Cu among others.) whose concentrations are homeostatically controlled by the organism's body as per the demand. They accumulate in living organisms through direct and/or indirect exposure.

Heavy metals have several effects on both plants and animals. They may inhibit growth in plants when absorbed by the plants from the soils and affect several physiological processes of the plant. In humans, these metals can be carcinogenic, cause respiratory problems, intellectual disability, neurotoxic, cause cardiovascular diseases, behavioral

disorders, damage organs etc. (Azeh et al., 2019, Osman et al., 2019). The effects of these metals on children are more severe compared to adults.

2.2.3 Volatile Organic Compounds

Volatile Organic Compounds (VOCs) as defined by US EPA are compounds of carbon (excluding metallic carbides/carbonates, carbonic acid, carbon II oxide & carbon IV oxide) that have low water solubility and high vapor pressure. A big fraction of these pollutants in the atmosphere are as a result of anthropogenic activities such as vehicular emissions, paint operations, manufacturing industries, printing ink, dry-cleaning, auto refinishing, petroleum handling among others (Srivastava and Mazumdar, 2011). Volcanoes, wetlands, forests, termites, oceans and tundras are some of the natural sources of VOCs which constitute 1150 Tg/yr (Guenther et al., 1995).

VOCs take part in photochemical reactions in the atmosphere together with other primary pollutants like NO_x to form secondary pollutants such as O₃ (Liu et al., 2021). Some of them however have low reactivity and hence their atmospheric lifetimes are long. Such VOCs are referred to as POPs (Persistent Organic Pollutants).

2.2.3.1 Persistent Organic Pollutants (POPs)

Some of the persistent organic pollutants (POPs) are; Polychlorinated biphenyls (PCBs), Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F), Polycyclic aromatic hydrocarbons (PAHs) and Organochlorine pesticides (OCPs) (de Boer et al., 2023). Due to their low reactivity nature POPs accumulate in the atmosphere. They undergo dry deposition through gravitational settling and as they fall, they adsorb or absorb particles in the atmosphere along the way. These POPs combine with other PMs in the atmosphere and over time, they are deposited on either the ground or water surfaces (i.e., aquatic or terrestrial habitats). In case, there is precipitation, they fall off to the ground or water surfaces through wet deposition.

2.2.3.2 Routes of Exposure and Impacts on Human Health

The main pathway to which humans get exposed to POPs is through consumption of contaminated foods especially meat, fish (WHO, Report, 2008). Dermal exposure and inhalation or even consumption of contaminated water are also exposure routes to POPs. POPs bioaccumulate through the food chains and their effects on humans and organisms can be adverse since these substances are very toxic. Some of the POPs can be carcinogenic, mutagenic, teratogenic, neurotoxic, genotoxic while others may cause birth defects (Srivastava and Mazumdar, 2011, WHO, 2020).

2.3 Dustflux Monitoring and Analyzing Instruments

2.3.1 Monitoring Instruments

These are the instruments that are used in measuring the rates at which dust is deposited as well as the direction of the pollutant source. The instruments can also be used to determine the mean concentrations of the atmospheric particles that pass the flux gauge. There are two types of gauges available i.e., the horizontal and the vertical dust flux gauges.

2.3.1.1 Vertical Gauges

The vertical gauge is used in the measurement of the deposition rate of the dust. Examples of the vertical gauges are; the British Standard 1747 deposit gauge, ASTM D1739:82 deposit gauge, Metdust (wind sampler), Nilu dust deposit gauge and the MDCO (Marble dust collector sampler) among others. Some of these instruments are further discussed in detail in the section below.

2.3.1.1.1 British Standard Deposition Gauge (BS 1747-1:1969)

This instrument is used in the collection of particles or dust that fall vertically. The dust collection exercise is done for 30 days (one month). The device uses sedimentation

technique to collect large particles from the air (settle able solids of $PM_{\geq 10}$). The collection bowl is made of HDPE to ensure that only free fall dust particles get collected. The bird guard ensures no bird droppings are collected. Collecting bottle of about 30 cm height and 15 cm diameter are used.

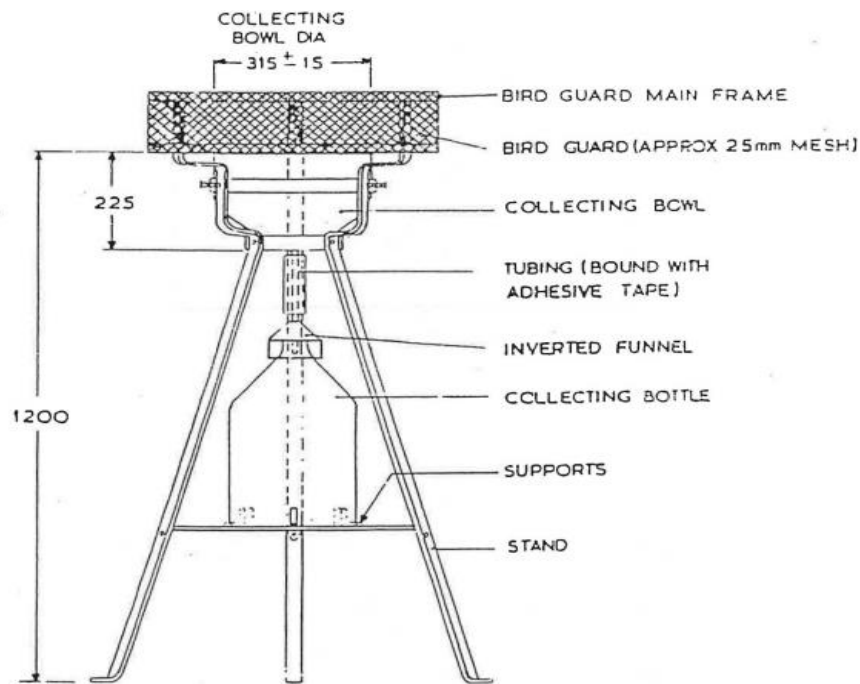


Figure 2.2: BS 1747-1:1969

Source: (BSI, 1969)

2.3.1.1.2 ASTM D1739:82

This consists of a bucket monitor that is deployed in line with the ASTM standards for dust collection and deposition flux analysis. It constitutes a cylindrical container (bucket) that is half filled with deionized water and then exposed for one month. The bucket is

raised by 2 m above the ground and supported by a metal frame. Dust is vertically deposited on the bucket container and it can either be wet or dry deposition.



Figure 2.3: ASTM D1739:82

Source: Kornelius G, 2010

2.3.1.1.3 The Marble Dust Collector Sampler

This device consists of a shallow container that has a layer of glass marbles whose diameter is 1.6 cm. It is specifically designed for geological researches and is often used in desert studies.

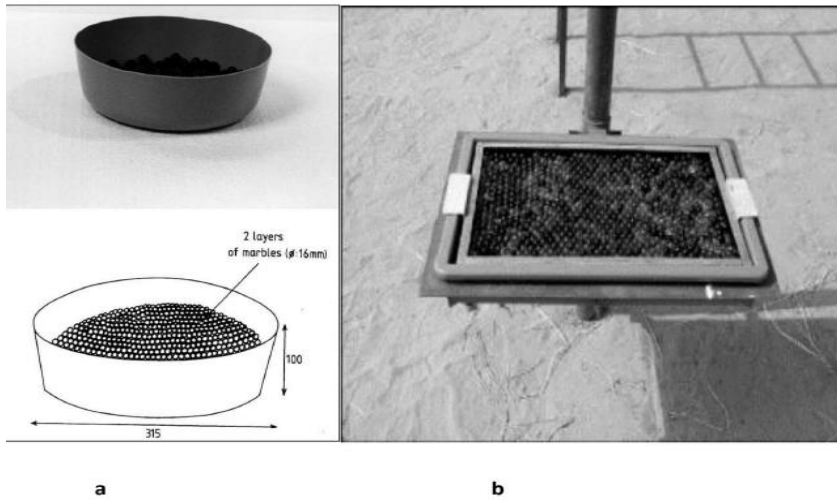


Figure 2.4: Construction Scheme for MDC

Source: Sow et al., 2006

2.3.1.2 Horizontal Gauges

The horizontal gauge is used in determining the direction of the source of deposited material. Examples are; BS 1747 part 5, Dust scan, SUSTR (suspended sediment trap sampler), WDFG (wedge dust flux) among others. Some of these instruments are discussed below;

2.3.2.1.1 British Standard 1747 Part 5 (BS 1747-5:1972)

This gauge consists of 4 vertical tubes and a vertical slot that faces the 4 compass points i.e., N, S, E & W and. Dust collection is done between 28-33 days and the device indicates the direction of the source of emission.

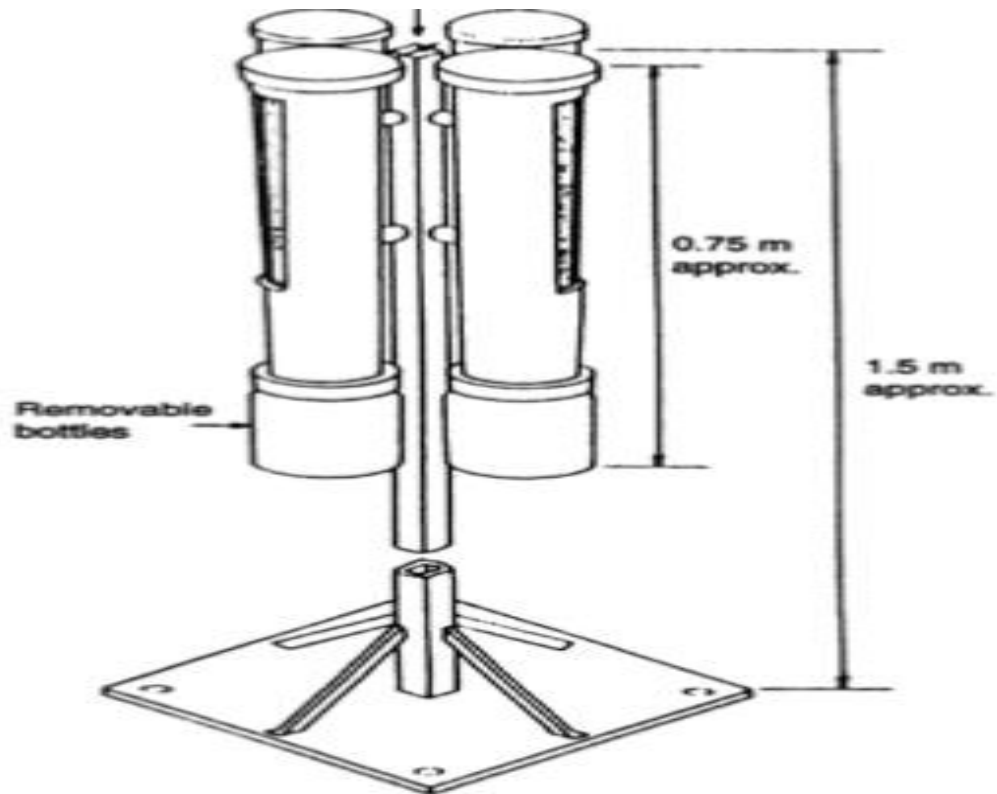


Figure 2.5: BS 1747-5:1972 Deposit Gauge

2.3.2.1.2 SUSTRA

This device was developed by Janssen et al, (1991). It collects all types of sediments. It has a horizontal metal tube with a diameter of 5 cm where the dust enters through. At its top is a wind vane that helps in indicating the source of emission of the material that is deposited in it.

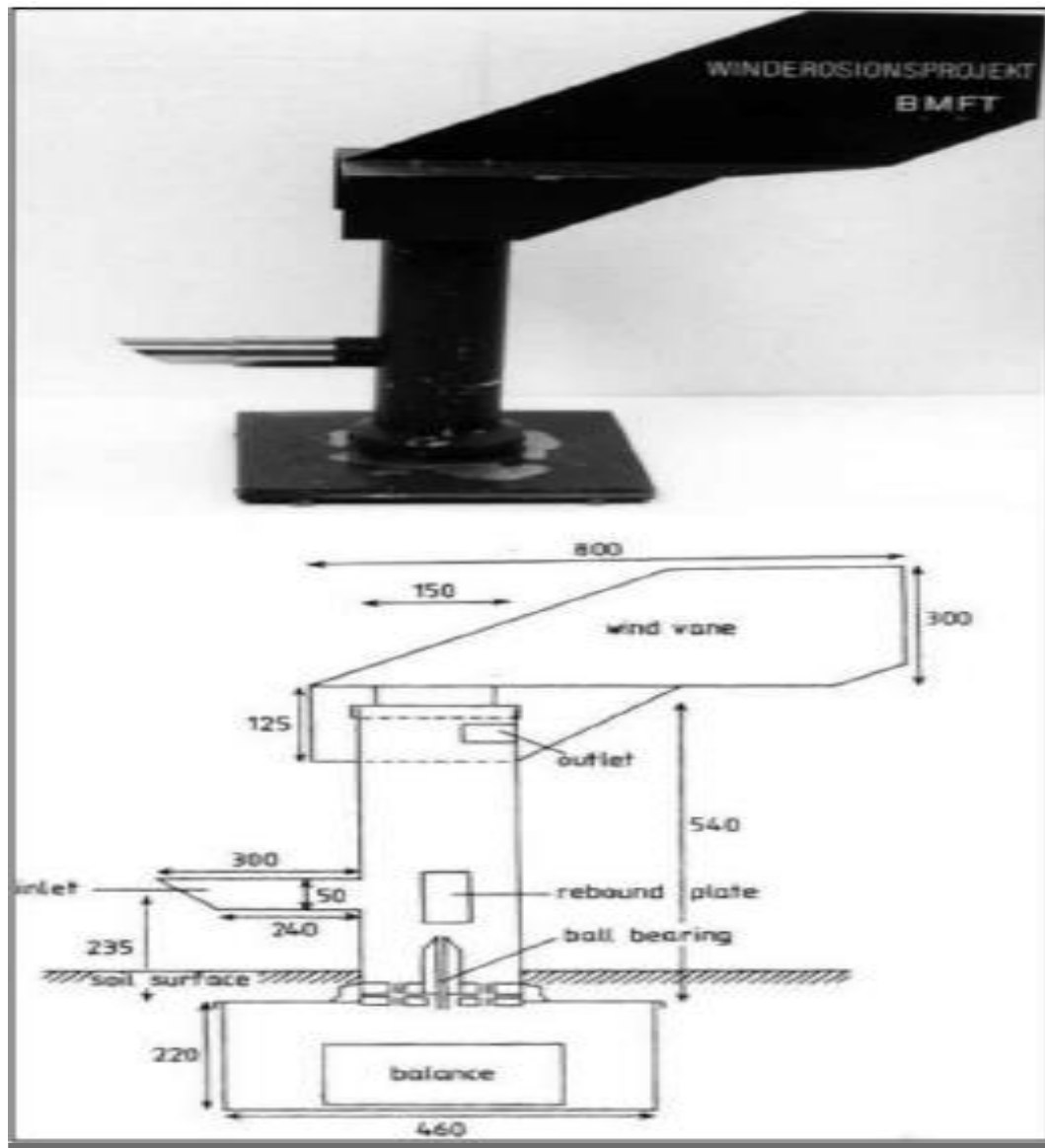


Figure 2.6: SUSTRASampler

2.3.2 Analytical Techniques/Instruments

There are various techniques that can be used to analyze these trace elements and organic molecules i.e., both their presence as well as their concentrations (Bulska and Ruszczyńska, 2017). Determination of pollutants and trace elements in complex matrices

normally require extensive sample extraction and/or preparation before instrumental analysis.

2.3.2.1 Energy –Dispersive X-Ray Fluorescence

Energy –Dispersive X-Ray Fluorescence is a non-destructive, multi-element technique that is very accurate. It can measure several samples while still meeting the requirements for every sample (Wakisaka et al., 1996). This instrument can simultaneously detect several elements and can be used on different sample types (liquid, powder, gas). The EDXF consists of a computer (PC), a control circuit, light path subsystem and a power supply (Yao M. et al., 2015). The X-Ray tube is supplied with high voltage power for it to release or emit a primary X-ray for irradiating the sample. This stimulates the sample to emit X-Ray Fluorescence (XRF) received by X-Ray Fluorescence detector. The detector then classifies the received photons as per energy and also tallies the number of photons corresponding to different energy levels. The detector then sends this information to the computer (PC) which completes the quantitative and qualitative analyses. Qualitative analysis identifies the elements present in the sample and this forms the basis for quantitative analysis. Quantitative analysis on the other hand determines the concentration or levels of each element present (elemental content). Some experiments done using this spectrometer showed 92 % accuracy levels but when done repeatedly, the accuracy went up to 98 % (Yao M et al., 2015).

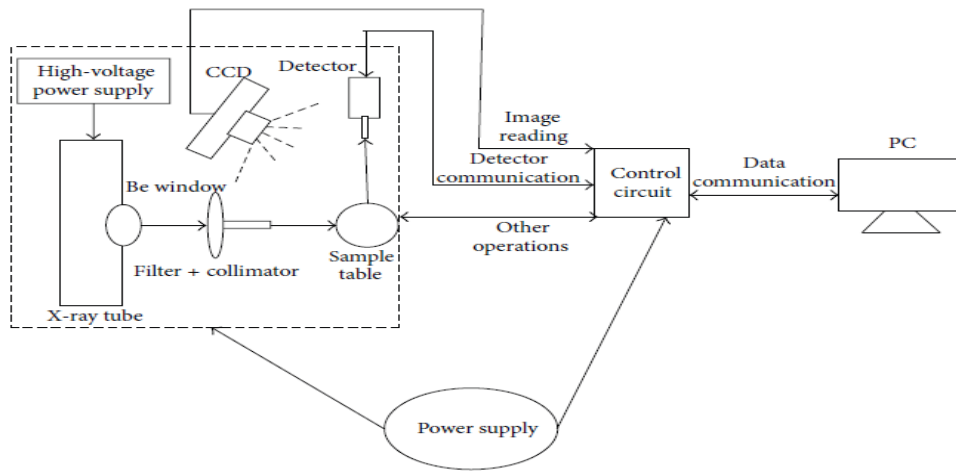


Figure 2.7: Structural Diagram of the EDXR

2.3.2.2 Atomic Absorption Spectrometry

Atomic Absorption Spectrometry is an elemental analysis method that can be used in determining metals in various samples. AAS can also be used in determining the quantity or levels of a specific element in a given sample. It uses the principle that ions and/or atoms can absorb light at a specific wavelength and when this wavelength of light is availed, the atom absorbs this light and hence the electrons in that atom move to an excited state (from the ground state). The quantity or amount of light that is absorbed is then measured so as to calculate the element concentration in the sample. The Beer Lambert Law is used in calculating the concentration and is given by Equation 2. 1 below.

$$A = \epsilon * c * l \dots\dots\dots\text{Equation 2.1}$$

where;

A is the absorbance (measured by the AAS)

ϵ is the molar absorption coefficient (absorptivity of the sample at a particular wavelength)

c is the determined concentration of the element,

l is the path length through the flame.

AAS consists of a hollow cathode lamp (HCL) that can emit specific wavelengths that is absorbable only by the analyte; an atom cell (flames or electro thermal atomizers/ETA) for converting samples to gaseous atoms; detection system for isolating and quantifying target wavelengths and lastly a computer system for data processing. For accuracy and optimum precision, samples are often converted into aqueous solutions and this also helps in minimizing interference. AAS with flames as atom cells are easy to use but their efficiency is low. ETA-AAS are more sensitive and are therefore more efficient compared to the flame AAS. ETA-AAS can also analyze small volumes (about 20 microliters per measurement) (Butcher, 2005). ETA-AAS however has more interferences compared to the flame AAS and this affects the accuracy of the results (Butcher, 2005).

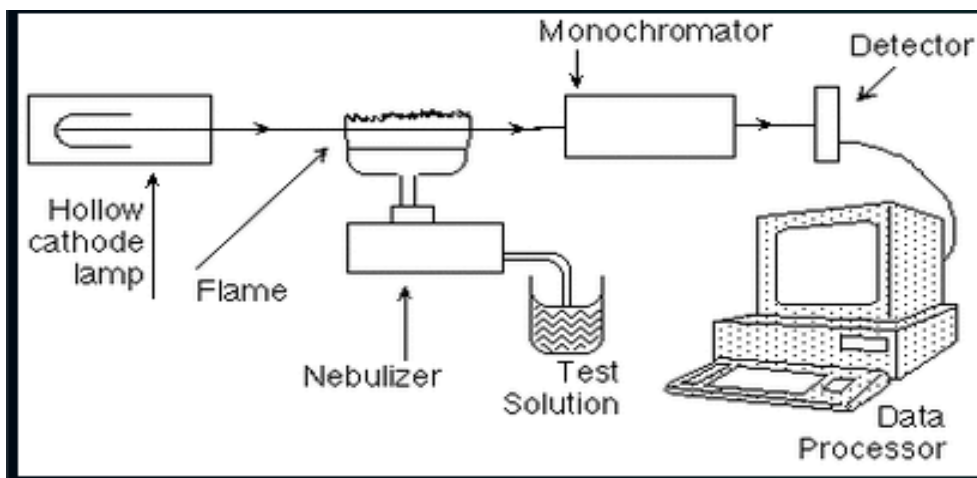


Figure 2.8: Flame AAS

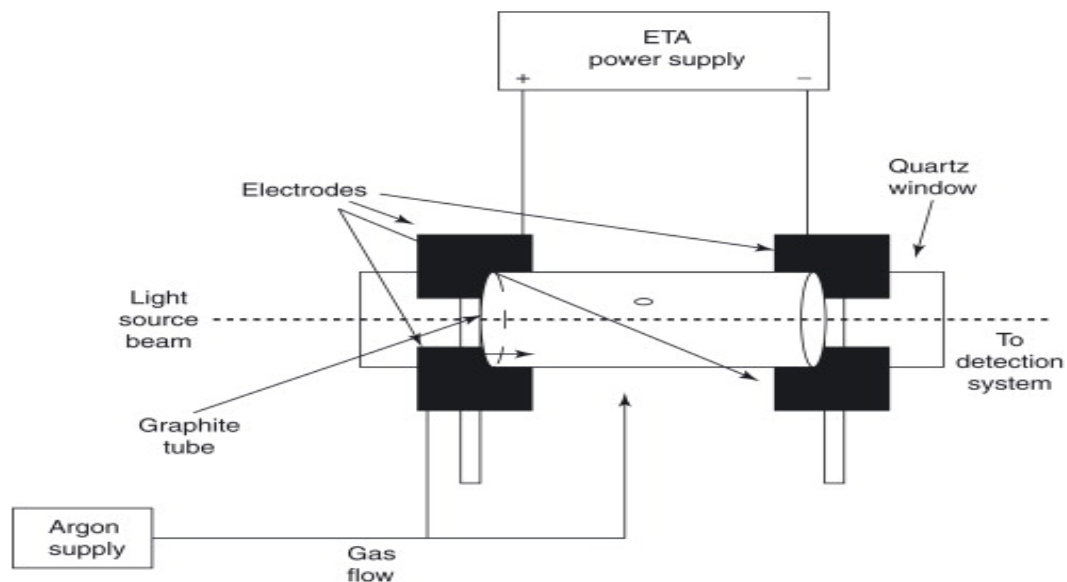


Figure 2.9: ETA-AAS

Source: Butcher, 2005

2.3.2.3 Gas Chromatography-Mass Spectrometry

The Gas Chromatography-Mass Spectrometry can be used to analyze, solid and gaseous samples. GC analyses small volatile and semi-volatile organic molecules and when combined with MS, trace levels of unknown contaminants can be analyzed. GC can also analyze complex mixtures that contain hundreds of compounds. The analysis process starts with the GC and it involves effective vaporization of the sample into gaseous state after which it is separated into its various constituents. This separation is done with the use of a capillary column which has a stationary (solid or liquid) coating (Medeiros, 2018). The compounds or constituents are driven through the stationary phase using an inert mobile phase (e.g., helium). As these constituents are driven through the stationary phase, each compound elutes from the column at different times depending on its polarity and boiling point. The time at which each compound or component elutes from the column is referred to its retention time.

Once these components leave the Chromatography column, they are fragmented and ionized by mass spectrometer (MS) using chemical or electron ionization sources (Medeiros, 2018). The fragments and ionized molecules are then accelerated through the MS mass analyzer (can be an ion trap or a quadrupole) and this is the point where the separation of ions occur depending on their mass to charge (M/Z) ratios. The last step involves the detection and analysis of ions. Peak areas are proportional to the corresponding compound's quantity. In case of a complex sample, several different peaks will be produced in the GS with each peak generating a specific mass spectrum that is used to identify the specific compound.

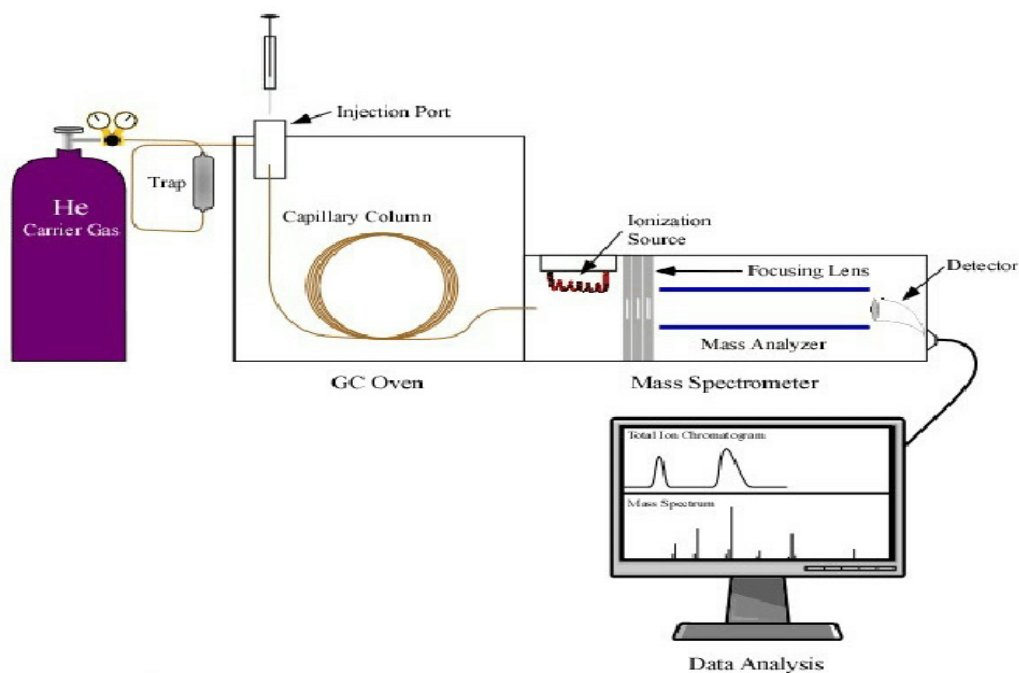


Figure 2.10: Schematic of a GC-MS System

Source: Gaojin et al., 2012

2.3.2 4 Inductively Coupled Plasma-Atomic Emission Spectrometer

This is another instrument that can be used to detect metals in solutions. The process involves injection of a liquid sample into an argon gas plasma in a strong magnetic field.

This will excite the elements in the injected sample and the electrons will emit energy that correspond to a given wavelength when returning to their ground state. Optical spectrometry is used to measure the emitted light. However, this instrument is often faced with both spectral and physical interference and at the same time, it is not sensitive to some elements. This lowers the accuracy of the results obtained.

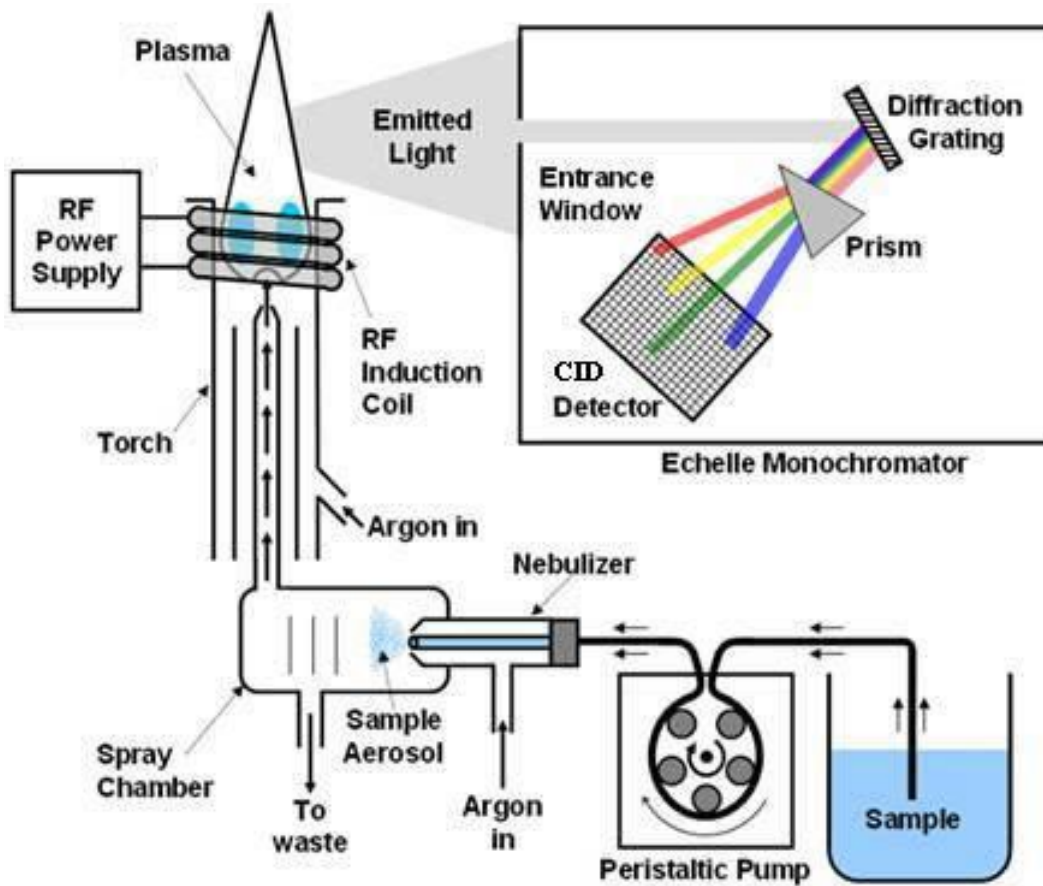


Figure 2.11: ICP-AES

Source: Nakach, 2016

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Sites

Nairobi (01°17'11"S 36°49'02"E) is the capital city of Kenya and is the largest urban center in the country. It hosts a population of over 4.3 million people (KNBS, 2019). The city is classified as a subtropical highland climate and its average annual temperature ranges from as low as 16.5 °C to 20.5 °C with an average annual humidity of 72% and an annual precipitation of 745 millimeters.

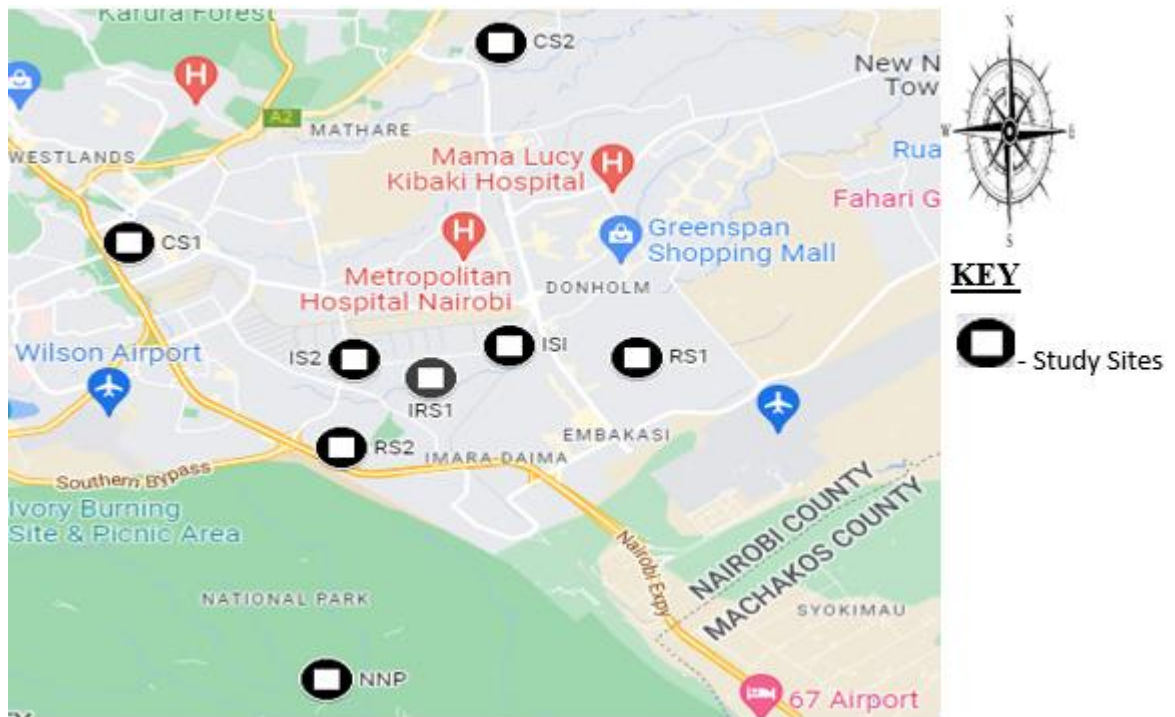


Figure 3.1: Map Nairobi County

The city is zoned into residential, industrial, commercial zones and a national park. Air pollutant sources are therefore related to human activities carried out in a specific area

which could be restricted by zoning laws. Some of these are vehicular traffic, open waste burning, road constructions, use of solid fuels, industrial, manufacturing processes and dust from local soils. In order to have a good picture of the composition of settleable solids in Nairobi, site selection was done to include the diversity of anthropogenic activities in the city since air pollution is highly dependent on anthropogenic activities. The study areas were categorized into three zones based on the activities taking place at the specific areas, namely; Residential areas, Industrial areas and Commercial areas (Table 3.1).

Table 3.1: Study Sites and their Descriptions

Site Code	Study location	Description	Co-ordinates
IS1	NCPB	Industrial area	-1.3052, 36.8824
IS2	Bins (industrial)	Industrial area	-1.3078, 36.8575
IRS1	Mukuru	Industrial/Residential	-1.3118, 36.8698
CS1	CBD	Commercial	-1.2843, 36.8211
CS2	Premier foods	Commercial	-1.2437, 36.8812
RS1	Embakasi	Residential	-1.3076, 36.903
RS2	Eagle Plains	Residential	-1.3259, 36.8552
NNP	Nairobi National Park	Park	-1.3729, 36.8530

* NCPB-National Cereals and Produce Board depot *CBD-Central Business District

3.2 Determination of the Particulate Matter (Pm_{2.5} and Pm₁₀) Levels

PM_{2.5} and PM₁₀ was monitored over a cumulative period of six months. The air quality monitors were mounted at all the sites at a mean height of 3 meters above ground to avoid bias from ground level sources. The PM levels, temperature and humidity were monitored and recorded at intervals of two minutes. Wind and precipitation from the sites were obtained from NASA, 2022. The monitors were pre-calibrated through co-location with a BAM reference monitor and data corrected accordingly. The R² and RMSE were used to assess performance of the LCMS.

Raw data was first cleaned and corrected using regression equation developed using the BAM reference and the LCMs monitors. The data was then subjected through statistical analysis. The average values, minimums, maximums, standard deviations and T-tests

were calculated using excel. Influence of meteorological parameters on PM concentration was investigated by estimating the spearman’s coefficient (r). The spatial variabilities of the pollutant concentrations at the different sites were also done so as to determine their distribution characteristics. Coefficients of Divergence (COD) between data sets of PM concentrations from different sites were calculated using Equation 3.1.

$$COD_{ab} = \sqrt{\frac{1}{n} \sum_{i=1}^n \left[\frac{C_{ia} - C_{ib}}{C_{ia} + C_{ib}} \right]^2} \dots\dots\dots \text{Equation 3.1}$$

Where;

C_{ia} and C_{ib} are the PM concentrations simultaneously recorded at site a and b respectively.

n is the number of observations recorded.

COD which is ≤ 0.2 represent homogeneity between the sites while that which is greater than 0.2 represent heterogeneity between the sites (Krudysz et al, 2009, Pinto et al 2004).

3.3 Determining the TDS, TSS & TS in the Dustfall

Three sampling sites were selected for dustfall collection (i.e., IS1, IRS1 and CS1). Purposive sampling was employed while selecting these sites with considerations being given to the practicality of mounting the dust collector as well as security and freedom from fouling of the set up. A vertical deposition gauge ((BS 1774) was used to collect the dustfall in all the sampling sites. Each of the three dustfall sampling sites had a PM sampler co-located with it. Dustfall collection was carried out for a period of thirty days in order to allow for sufficient quantities of dust to be acquired through sedimentation. Deionized water was used as the holding medium for the collected dustfall in the collecting bottle of the BS sampler. Figure 3.2 is a flow chart summarizing sample treatments for total solids, heavy metals and volatile organic compounds analyses.

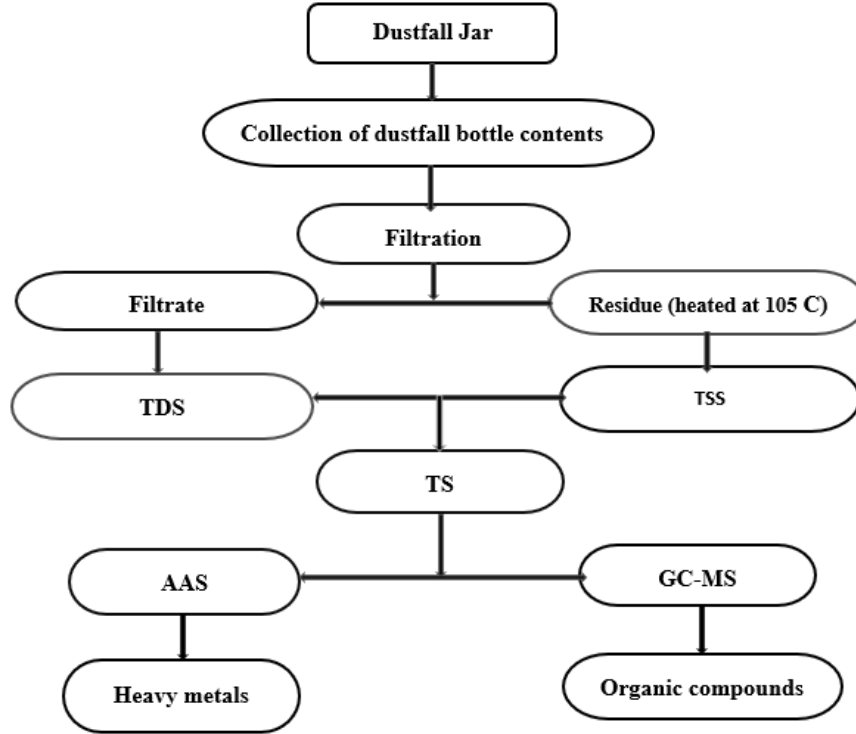


Figure 3.2: Flowchart Showing Sample Treatment

3.3.1 Total Soluble Matter

The total dissolved solids (TDS) in the sample were determined by filtering 50 mL of the sample into a beaker. The filtrate was then concentrated into less than 50 mL on a hot plate after which it was transferred into a pre-weighted evaporating dish then oven-dried at 105 °C for two hours. Finally, it was cooled in a desiccator then weighed repeatedly until a constant weight was attained. The concentration of the dissolved matter in (mg/m² /day) was then calculated using Equation 3.2, (Latiff & Rozali, 1999).

$$C_{TDS} = \left[(M_2 - M_1) \left(\frac{V_1}{V_2} \right) - 18.5 \right] / AT \dots\dots\dots \text{Equation 3.2}$$

Where;

M_1 is the weight of evaporating dish without the dissolved solids (mg),

M_2 is the weight of dissolved matter with the weight of the evaporating dish (mg)

V_1 is the volume of all the solution (mL),

V_2 is the volume of water which evaporated (mL),

A is the surface area of the funnel (m²),

T is the length of the sampling period in days

18.5 is the factor for dissolved solids from 10 mL 0.02 N CuSO₄.5H₂O (BSI, 1969)

3.3.2 Insoluble Matter

For the Total Suspended Solids (TSS), the residue plus filter were oven dried at 105 °C for a period of 2 hours. It was then let to cool on a desiccator before being weighed repeatedly until a constant weight was attained. The concentration of the insoluble matter was determined using Equation 3.3 stated by Norela et al, (2009) which is based on the different filter weights (i.e., before and after use), number of days and the diameter of the separating funnel.

$$C_{TSS} = (M_4 - M_3)/AT \dots\dots\dots\text{Equation 3.3}$$

Where;

M_3 is the weight of the filter with no sample in mg,

M_4 is the weight of the filter paper with dry insoluble solids after filtration in mg,

A is the surface area of the funnel (m²)

T is the sampling period(days).

3.3.3 Total Solids

The Total Solids (TS) in the sample were determined by summing the TDS and TSS according to Equation 3.4.

$$C_{TS} = C_{TDS} + C_{TSS} \dots\dots\dots \text{Equation 3.4}$$

3.4 Assessment of the Trace Elements in the Deposition

The samples collected by the BS Sampler from the sites were analyzed to determine the presence and concentration of targeted trace elements which were; Zinc, Lead, Chromium, Copper, Cobalt, Boron and Aluminum.

3.4.1 Element Concentrations

The concentrations of Zn, Cd, Pb Cr, Cu, As, Co B, and Al were determined using an atomic absorption spectrophotometer (AA500 Spectrophotometer from Pg instruments, UK). The sample was digested using conc HNO₃ until it was ready for analysis using the AAS. Calibration for each element was done using standard solutions. LODs and LOQs for each element were determined from the calibration curves.

3.4.2 Estimation of Dry Deposition Fluxes

In order to estimate the dry deposition fluxes (F_d) in the particulate matter, Equation 3.5 was used.

$$F_d = CV_d \dots\dots\dots \text{Equation 3.5}$$

where;

C is the atmospheric concentration of the element of interest,

V_d is the elemental dry settling velocity.

It is worth noting that V_d changes with the size of the particle, climatic as well as the physical conditions of the troposphere (Herut et al., 2001). The mean values used in this study are similar to those used by Duce et al., (1991) and they range from 0.1 cm s^{-1} which is that of a sub micrometer particulate whose components are the atmospheric pollutants including Pb (Duce et al., 1991). Similar range of V_d values (0.1 cm s^{-1} to 1 cm s^{-1}) were also adopted by other research studies (Pereira et al, 2007; Migon et al, 1997)

3.4.3 Calculation of the Enrichment Factors (EFs)

Many factors contribute to the presence of trace metal and other pollutants in particulate matter or aerosols. Some are anthropogenic (e.g., fossil fuel, smelting of ores etc.) while others are natural (e.g., volcanic activities, the earth’s crust among others). Enrichment factors (EFs) are used to assess and determine the type of source of the heavy metal present in the particulate matter. The source element indicator used for earth’s crust or natural sources is usually Al or Fe while Zn and Pb are often used as the source indicator elements for vehicles and industrial sources. Equation 3.6 (Rahn 1976), was used when calculating EF.

$$EF_{crust} = \left(\frac{C_{xp}}{C_{Fep}}\right) / \left(\frac{C_{xc}}{C_{Fec}}\right) \dots\dots\dots \text{Equation 3.6}$$

Where;

C_{xp} and C_{Fep} are the concentrations of trace metal x and Al/Fe in the particulate respectively

C_{xc} and C_{Fec} are their concentrations in the crustal material.

An EF value which is less than 10 is usually taken to indicate that a trace element present in a particulate has a significant crustal source and these are often referred to as non-enriched elements (NEEs). On the other hand, an EF greater than 10 is normally taken as an indication that a significant fraction of the trace metal is from a non-crustal source which is often referred to as anomalously enriched elements (AEE). It is however

important to note that, when the air has sufficient crustal material AEEs can change character and hence behave like NEEs.

3.5 Assessment of the Organic Compounds in the Dustfall

The samples collected by the BS Sampler from the sites were also screened for the presence of volatile organic compounds. From each of the samples, two 50 mLs were prepared by using an organic solvent (Dichloromethane, DCM) to dissolve organic compounds in the sample in order to facilitate the determination of presence of organic molecules by means of GC-MS. 100 mL of the organic solvent was used to separate organic molecules from the sample by shaking the mixture in a separating funnel for 10 minutes. The step was repeated three times on the same 50 mL sample. During the actual sample analysis, error correction test was carried out by subjecting the organic solvent (blank) through the GC-MS. Lastly, two test runs for each sample was done to determine presence of organic molecules and the findings obtained.

3.6 Quality Control

Measures were taken in order to ensure that the results obtained were reliable by avoiding any interferences both in the field and the laboratory. All the samples were prepared and analyzed in triplicates. All the collecting and analyzing apparatus were placed in a 20% HNO₃ bath so as to eliminate any inorganic substances. They were then rinsed with distilled water before drying. The Whatman filters were also oven dried at 105 °C followed by cooling in a desiccator before use.

For the organic molecules, cleaning of all the apparatus was done through ultrasonic cleaning then incinerated at 450 °C for a period of 4 hrs.

3.7 Further Analysis

Various statistical analyses were done in order to determine how the concentrations of pollutants is distributed. Correlation coefficient and significance was done using one way

ANOVA in order to establish the variations in the average concentrations of the heavy metals, total dust-fall, dissolved matter and undissolved solids in the sample. Excel tools were used in the analysis and presentation of results in graphical form such as charts, bars and line graphs.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Particulate Matter

The daily mean concentrations of PM pollutants in Nairobi from January to June, 2022 are summarized Table 4.1.

Table 4.1: Average Daily Concentrations of PM_{2.5} and PM₁₀ at the Sites and WHO Limits

Site Code	Pollutant	Mean±SD (µg/m ³)	Min (µg/m ³)	Max (µg/m ³)	WHO (µg/m ³)	Daily limit
IS1	PM2.5	19.92.67±9.89	5.94	39.42		15
	PM10	27.29±10.28	7.58	48.6		45
IRS1	PM2.5	42.18±13.44	27.62	99.1		15
	PM10	49.32±12.73	33.49	103.36		45
RS1	PM2.5	21.70±4.09	13.67	32.72		15
	PM10	29.53±3.55	22.13	37.38		45
CS1	PM2.5	15.66±9.22	5.23	36.22		15
	PM10	17.74±11.24	5.7	40.86		45
IS2	PM2.5	22.24±5.80	12	30.4		15
	PM10	-	-	-		45
CS2	PM2.5	20.0±4.04	13.3	26.8		15
	PM10	23.12±5.17	14.8	31.5		45
RS2	PM2.5	10.04±2.56	5.5	14.3		15
	PM10	12.04±3.07	6.6	18.2		45
NNP	PM2.5	9.53±2.76	5	13.3		15
	PM10	11.27±3.19	6	15.6		45

4.1.1 Residential Zones

IRS1 recorded the highest average PM concentrations than any other site with PM_{2.5} of 42.18±13.44 µg/m³ and PM₁₀ 49.32±12.73 µg/m³. IRS1 is an informal settlement with unpaved roads hence dust is continuously being released into the atmosphere. Also, there is no proper solid waste management systems in the area and so open burning of waste is common and this generates smoke in addition to that from charcoal and firewood used by

residents as fuel. All these contribute to the high PM levels in the atmosphere. The area is surrounded by chemical, textile and wood processing industries which continuously release pollutants into the air. All these activities contribute to the high pollutant concentrations in the area and leading to both PM_{2.5} and PM₁₀ of concentrations above that recommended by the WHO.

On the other hand, RS1 though being a formal settlement area is still a developing estate with significant construction activities with diesel engine trucks ferrying construction material being common. Dust from the poor roads, emissions from the trucks and smoke from solid fuels like charcoal contributed to the high PM levels which recorded an average of 21.70 ± 4.09 and 29.53 ± 3.55 PM_{2.5} & PM₁₀ respectively, with PM_{2.5} being above the WHO daily limits. However, RS2 being a completely developed residential place with well-developed social amenities, the main source of air pollution in this area is emissions from vehicles within the estate. The recorded daily average PM_{2.5} and PM₁₀ concentration in this site was found to be 10.04 ± 2.56 and 12.04 ± 3.07 ($\mu\text{g}/\text{m}^3$) during the study period. The weekly averages, quartiles and medians of PM_{2.5} and PM₁₀ in the study sites is further shown on Figure 4.1 and Figure 4.2, respectively.

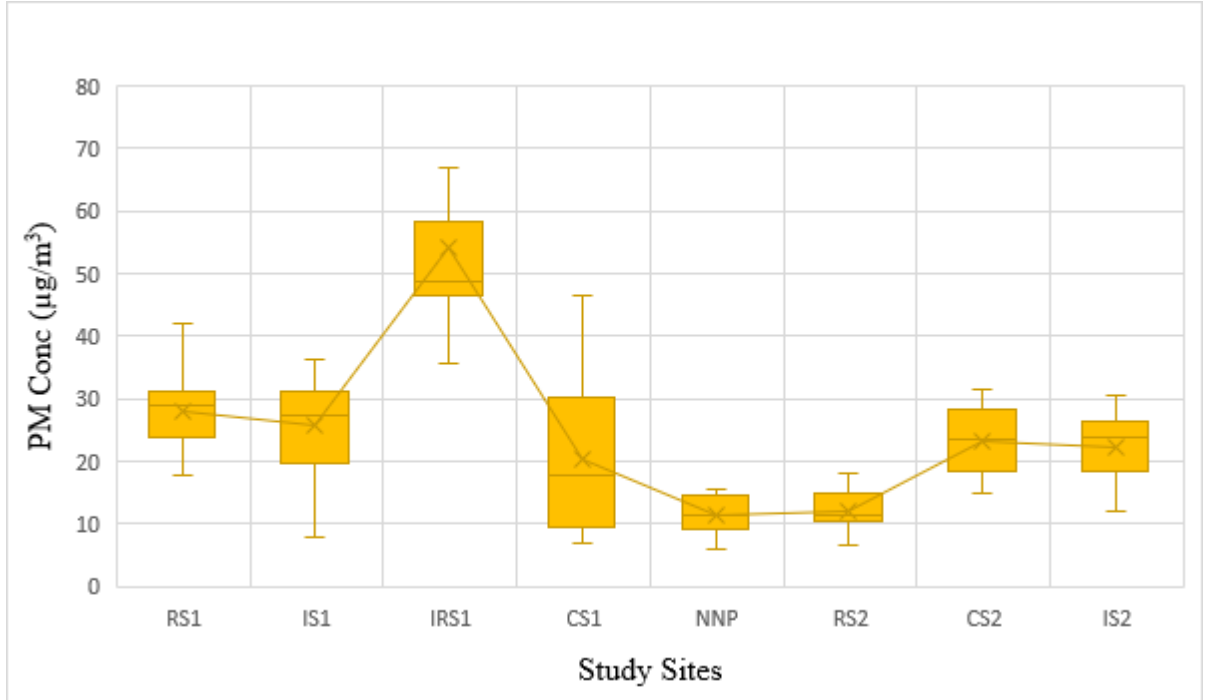


Figure 4.1: Weekly Averages, Median, and 1st/3rd Quartile Values for PM_{2.5} for the Study Sites

4.1.2 Industrial Zones

IS1 registered a mean of 19.92 ± 7.74 and 27.29 ± 10.28 $\mu\text{g}/\text{m}^3$ (PM_{2.5} and PM₁₀, respectively) during the study period. This site is surrounded by plastic manufacturing companies, flour milling industries, textile industries and construction activities which continuously emit pollutants to the atmosphere. Traffic from diesel trucks ferrying goods to and from nearby industries and fuel depots is heavy contributing further to the high PM concentrations.

IS2 on the other hand is on the edge of an informal settlement and is often faced with traffic from garbage trucks accessing the dump site within the area. Pollutant concentration from this site had a PM_{2.5} mean of 22.24 ± 5.80 ($\mu\text{g}/\text{m}^3$) which is above WHO limits. Both IS1 and IS2 are close to a common busy road to town which further contribute to the high PM levels.

4.1.3 Commercial Areas

The average PM concentrations for the sites under this category (CS1 and CS2) were 15.66 ± 9.22 and $17.74 \pm 11.24 \mu\text{g}/\text{m}^3$ for $\text{PM}_{2.5}$ and 20.0 ± 4.04 & $23.12 \pm 5.17 \mu\text{g}/\text{m}^3$ for PM_{10} respectively. Generally, both areas are characterized by vehicular traffic and office buildings yet $\text{PM}_{2.5}$ pollutant concentrations are still above the WHO daily.

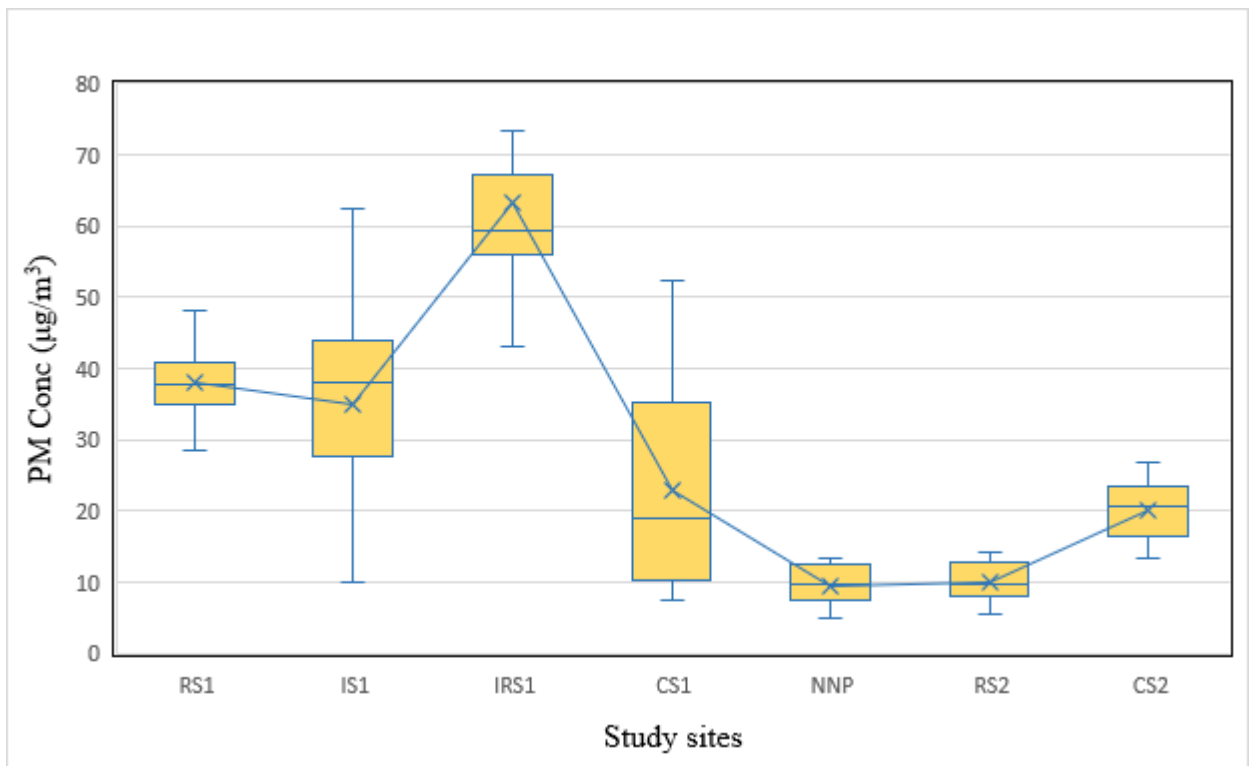


Figure 4.2: Weekly Averages, Median, and 1st/3rd Quartile Values for PM_{10} at the Study Sites

4.1.4 Hourly Mean Concentrations

Figure 4.3 shows the average hourly PM concentrations for a typical day at the IS1, RS1, IRS1 and the CS1. In RS1, the peak PM concentrations occur between 4am to 6am in the morning and at around 5pm in the evening. At the IS1, peak PM concentrations were

recorded between 5am-7am in the morning and from 5pm to 8pm in the evening. The CS1 has a similar peak PM concentration to both RS1 and the IS1 however, the values recorded at the CS1 are much lower in comparison to the two sites. From all these sites, the peak PM concentrations occurred at a time when vehicular traffic is high and therefore, these concentrations are linked to the vehicular emissions and traffic. PM concentration trend in IRS1 is quite different with low PM concentrations recorded only at around 8am. It was also noted that PM concentrations were lower during the night than during the day in all the sites except for IRS1. Emissions from the industries surrounding IRS1 occur even during the night since the industries are operational at all times hence PM levels are always high regardless of the time.

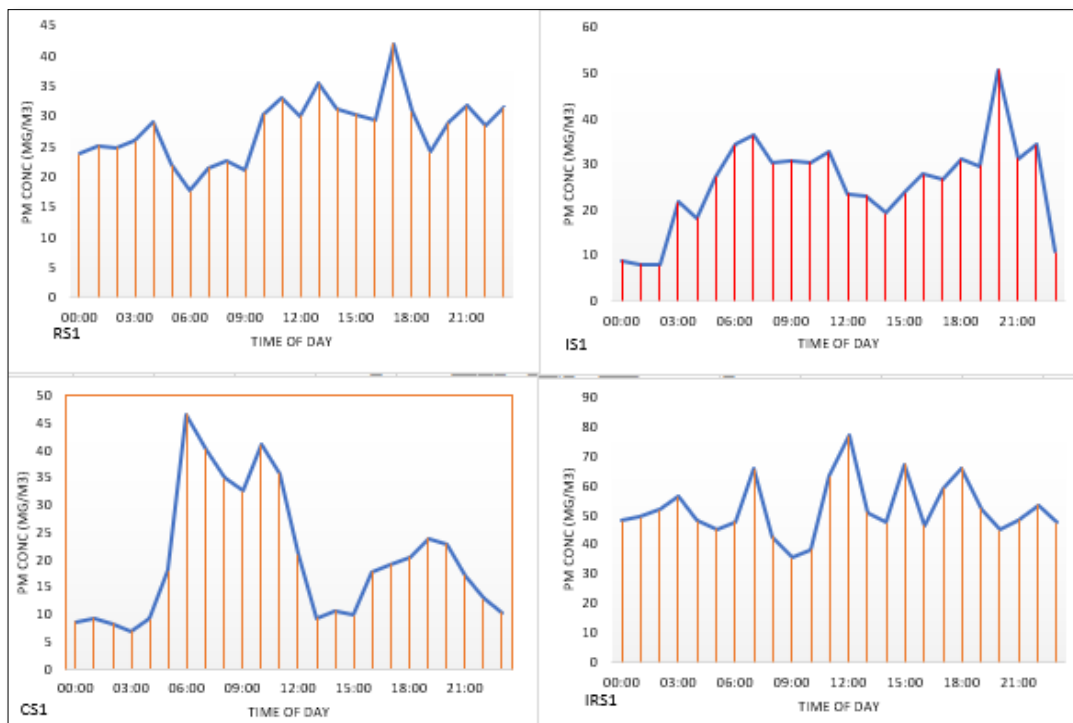


Figure 4.3: Hourly PM_{2.5} Trends

4.1.5 Spatial Variations between Different Sites

The coefficients of divergence between the study sites were calculated using Equation 3.1 under section 3.2 and results are as shown in Table 4.2. The COD values between the sites IS1/RS1, IRS1/RS1, RS1/IS2, CS1/CS2, NNP/RS2 are in the region of 0.2 while the COD values for IS1/NNP, IRS1/RS2 and IRS1/CS2 are higher than 0.5.

Table 4.2: COD Values of PM Concentrations between the Different Monitoring Sites

Sites	IS1	IRS1	RS1	CS1	IS2	CS2	RS2	NNP
IS1		0.37	0.26	0.24	0.43	0.51	0.7	0.71
IRS1			0.25	0.51	0.43	0.5	0.7	0.72
RS1				0.37	0.2	0.27	0.54	0.56
CS1					0.23	0.12	0.34	0.38
IS2						0.18	0.4	0.43
CS2							0.33	0.37
RS2								0.07

The pairs of sites with low COD values have homogenous PM distributions which suggests that sources of pollutants to such sites could be similar. On the other hand, high COD values between pairs of sites have heterogeneous PM distributions and concentrations hence their sources are different.

It is noted from the results in Table 4.2 that to a large extent, the PM concentrations and distributions are similar between sites of similar category while there is a clear difference with those of different land usage. However, some differences were noted in some sites like RS1 and RS2 which have a COD value of 0.54 despite both of them being residential areas. The reason for this is that, whereas RS2 is an already developed estate with less pollutants being emitted, RS1 is still developing and has activities like construction that emit pollutants into the atmosphere.

4.1.6 PM Variation in Relation to Precipitation and Windspeed

The correlation coefficients (r) for wind speed and Precipitation with PM were calculated. The (r)s obtained for both meteorological parameters against PM were low for sites IS1, CS1 and IRS1 indicating that the impact that these factors had on the pollutant concentration was insignificant. However, for the site RS1 r for PM vs wind was -0.53 while PM vs precipitation was 0.67. At RS1, PM concentration is inversely related to wind speed while it is directly related to precipitation. The (r)s obtained for temperature and humidity with the PMs in all the sites were low and this indicates that the impact that these factors had on the pollutant concentration was also insignificant. Figure 4.4 illustrates the relationships between PM_{2.5} with wind speed and precipitation.



Figure 4.4: COD Values of Pm Concentrations Between the Different Monitoring Sites

4.2 TSS, TDS and the TS in the Dustfall

The site-specific TS, TDS and TSS are presented in Figure 4.5. It was observed that, IRS1 recorded the highest TSS of $147.6 \text{ mg m}^{-2}\text{day}^{-1}$ followed by IS1 with $122.8 \text{ mg m}^{-2}\text{day}^{-1}$ then lastly CS1 with $60.3 \text{ mg m}^{-2}\text{day}^{-1}$. IS1 recorded the highest TDS of $29 \text{ mg m}^{-2}\text{day}^{-1}$.

followed by IRS1 with $11 \text{ mg m}^{-2}\text{day}^{-1}$ while CS1 recorded the lowest TDS of $9 \text{ mg m}^{-2}\text{day}^{-1}$. Levels of TS in descending order was $\text{IRS1} > \text{IS1} > \text{CS1}$. Results of One-way ANOVA showed that there no significant differences between the concentrations of TSS, TDS and TS at the different sampling areas ($P > 0.05$).

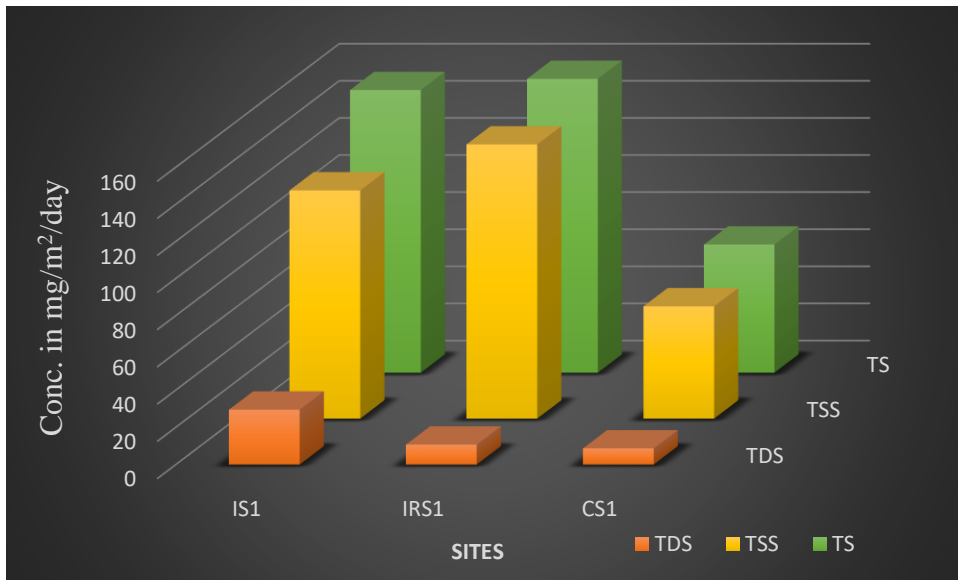


Figure 4.5: TDS, TSS and TS (in $\text{mg m}^{-2} \text{day}^{-1}$) at the Study Sites

The high concentrations recorded at IRS1 was due to its location next to unpaved roads and continuous construction activities as compared to the other sites, although its rates are closer to those of IS1 which also has significant industrial activities. These activities continuously generate particulate matter in form of dust or smoke which are deposited in the atmosphere. Conversely, the low concentrations recorded at CS1 might have been due to the limited activities in the area with the only source being from vehicular traffic.

The overall averages for this study were; TDS; $16 \pm 9 \text{ mg m}^{-2}\text{day}^{-1}$, TSS; $110.3 \pm 37 \text{ mg m}^{-2}\text{day}^{-1}$ and TS; $126.3 \pm 40 \text{ mg m}^{-2}\text{day}^{-1}$. The study findings compare with those reported by Alahmr et al, 2012 and Latiff & Rozali 1999 although higher levels were reported by Norela et al 2005 and Norela et al 2009. The TS for CS1 ($69.3 \text{ mg m}^{-2}\text{day}^{-1}$) was however

lower than all corresponding values from previous studies under comparison as shown by Table 4.3.

Table 4.3: Average TDS, TSS and TS at the Study Sites

Reference	Zone	TSS ($\text{mg m}^{-2} \text{ day}^{-1}$)	TDS ($\text{mg m}^{-2} \text{ day}^{-1}$)	TS ($\text{mg m}^{-2} \text{ day}^{-1}$)
Norela et al., 2009	Residential	37.08±13.53	216.11 ±35.45	253.95±7.54
Latiff & Rozali, 1999	Industrial	63.85 ± 42.02	74.45± 62.76	139.39±87.88
Norela et al,2005	Power station	213.86±114.81	226.69±171.50	440.54± 9.07
Alahmr et al, 2012	Semi urban	53.08 ± 34.64	78.41 ± 37.31	131.50±71.95
This study	Urban	110.3±37	16±9	126.3±40

4.3 Heavy Metals and Metalloids in the Dustfall

4.3.1 Average Concentrations

The analytical procedure was validated using the percentage recovery and the detection limit determination for each element. The data is presented in Table 4.4. The concentrations of As and Cd in all the samples were below their LOQ of 0.0262 and 0.0225 ppm, respectively, hence were not further analyzed statistically.

Table 4.4: LODs and Percentage Recovery

Heavy metal/ metalloid	Percentage Recovery	Detection limit (ppm)
Zinc	89.44	0.0014
Lead	99.91	0.0099
Chromium	99.98	0.0170
Copper	99.50	0.0049
Cobalt	74.68	3.5644
Boron	81.53	0.9816
Aluminum	85.78	0.0023

The average concentrations of the elements (in $\mu\text{g m}^{-3}$) recorded in samples from the various sites are summarized in Table 4.5. The average elemental concentrations in descending order are; Co>B>Al>Zn>Cu>Pb>Cr.

Table 4.5: Average Concentration of Elements

Element	IRS1 ($\mu\text{g m}^{-3}$)	IS1 ($\mu\text{g m}^{-3}$)	CS1 ($\mu\text{g m}^{-3}$)	Range ($\mu\text{g m}^{-3}$)	Mean concentration ($\mu\text{g m}^{-3}$)
Zn	30.77±0.15	140.34±0.58	25.13±0.15	115.21	65.41±53.03
Pb	11.50±0.10	10.01±0.01	10.87±0.12	1.49	10.79±0.61
Cr	0.45±0.02	0.44±0.02	0.42±0.06	0.03	0.44±0.01
Co	1814.32±0.02	3072.33±195.21	2407.13±0.15	1258.01	2431.26±513.86
B	2038.70±0.20	1685.56±132.09	959.83±0.06	1078.87	1561.36±449.12
Al	1281.60±0.10	1597.65±495.92	1184.37±0.15	413.28	1354.54±176.43
Cu	68.17±0.06	21.09±1.75	45.43±0.06	47.08	44.90±19.22

The concentrations of Cobalt, Boron and Aluminium were high compared to all the other elements. Burning of fossil fuels is a major source of Cobalt in the atmosphere. Boron is also used as a fuel additive although some cleaning compounds and agrochemicals also contribute to its presence in the atmosphere. Aluminium's crustal composition is high and that is why its main source in the atmosphere is soil derived particles meaning that in a dust prone area, its concentrations will be high. This explains why the concentration of these three elements was high in these study sites because all these activities take place in the sites therefore continuously generating these pollutants

It is important to note that, even the elements whose concentrations were low are associated with vehicular emissions and other industrial manufacturing processes.

The findings of this study compare with other previous studies as summarized in Table 4.6. Although some of those studies reported lower concentrations for some of the elements, others recorded higher values. The reason for such variations is due to differences in land use and prevalent activities in each study site.

Table 4.6: Comparison of Trace Elements Concentrations with other Studies

Reference	Zone	Zn	Pb	Cr	Cu	Co	B	Al
Al momani, 2003	Rural(μgm^{-3})	6.52± 7.84	2.57 ± 2.33	0.40	*	*	*	382.00
Joshi & Balasubramanian, 2010	Industrial (μgm^{-3})	1127.00	90.25	213.80	*	*	*	13.80
Cheng & You, 2010	Urban (μgm^{-3})	64.20	1710.00	0.40	*	*	*	769.30
Alahmr et al., 2012	Semi-urban (μgm^{-3})	47.93± 26.10	4.10 ±1.20	0.52 ± 0.31	*	*	*	17.17 13.86
Pereira et al., 2007	Urban (μgm^{-3})	3.95± 1.26	*	*	121 ± 91.90	*	*	*
Mohamed et al., 2013	Industrial (μgm^{-3})	235.00	22.33		3.80	*	*	*
This study	Urban (μgm^{-3})	65.41± 53.03	10.79± 0.61	0.44± 0.01	44.90± 19.22	2431.26± 513.86	1561.36± 449.12	1354.54 176.43

*No data

4.3.2 Annual Deposition Fluxes

Annual deposition fluxes (F_d) for the elements at the various sites was calculated and results are summarized in Table 4.7. No statistically significant difference was observed between the total elemental fluxes. It was observed that, Co, B and Al recorded the highest deposition fluxes in all the sampling sites. The F_d for other elements in descending order are; Zn > Cu > Pb > Cr. The high deposition fluxes of some elements as compared to others is due to their high rate of emission into the atmosphere. For instance, the rate at which fossil fuels are burned either by the manufacturing industries or diesel engines in these areas are high. Therefore, these pollutants (especially Co, B & Al) released into the atmosphere at fast rates leading to their high deposition rates.

Table 4.7: Estimated Dry Deposition Fluxes

Sampling Site		Zn	Pb	Cr	Cu	Co	B	Al
IS1	Mean ($\mu\text{g m}^{-3}$)	140.34	10.01	0.44	21.09	3072.33	1685.56	1597.65
	Fd(mg m⁻² yr⁻¹)	4.41	0.33	0.01	0.64	98.11	52.17	53.80
CS1	Mean ($\mu\text{g m}^{-3}$)	25.13	10.87	0.42	45.43	2407.13	959.83	1184.37
	Fd(mg m⁻² yr⁻¹)	0.79	0.34	0.01	1.43	75.82	30.23	37.31
IRS1	Mean ($\mu\text{g m}^{-3}$)	30.77	11.50	0.45	68.17	1814.32	2038.70	1281.60
	Fd(mg m⁻² yr⁻¹)	0.97	0.36	0.01	2.15	57.15	64.22	40.37

The elemental settling velocity (V_d) used in this study is that adopted by Duce et al., (1991). As explained in Section 3.4.2, 0.1 cm s^{-1} is the average V_d of a sub-micrometer particulate or aerosol whose components are atmospheric pollutants. This is the V_d range that has been adopted by many studies including Pereira et al., (2007) and Migon et al., (1997). However, it is important to note that, F_d calculations can vary depending on the magnitude of the V_d uncertainties. This is despite the fact that, elemental aerosol size does not change much.

The results obtained compare well with other studies. Closer values were observed between this study and that of; Cheng et al., (2021), Mamun et al., (2020), in the deposition rates of Zn, Cu and Pb though Pb for Mamun et al., (2020) was slightly higher ($10.4 \text{ mg m}^{-2} \text{ yr}^{-1}$). The values of Al, B, and Co were however high in this study. Others studies like Lim, Jeong-Hee H et al, 2006, Pereira et al., (2012), reported high deposition rates of up to 10 times that of this study (Zn-120, Pb-16, Cu-26; Cu-73). Land use type in the sampling sites for these specific studies could probably be the main reason for such variations.

4.3.4 Enrichment Factors

In order to determine the extent of anthropogenic contribution to the concentrations of the individual metals or elements, the EFs of each element were calculated and the results summarized in Table 4.8 and Figure 4.6. Equation 3.6 was used in these calculations. In

this study, the reference metal used was Al due to its higher correlation factor with the other elements under study.

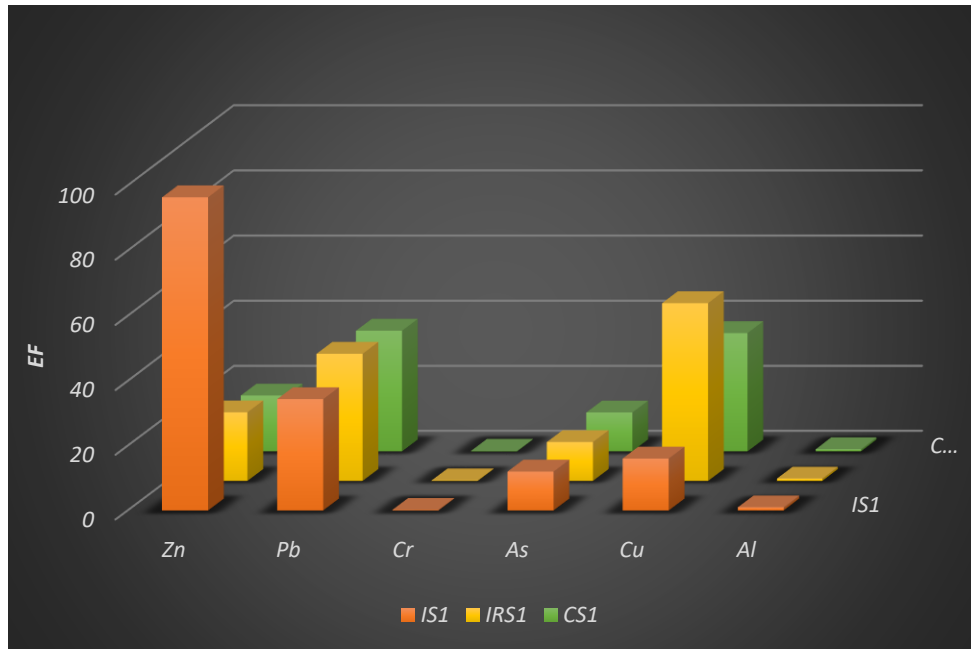


Figure 4.6: EFs for Heavy Metals and Metalloids in the Sites

The EF values of the metals obtained from the sampling sites were above 10 with the exception of Al and Cr. B and Co recorded high values of 4714 and 7478, respectively and this indicates strong anthropogenic sources. IRS1 and IC1 are surrounded with industries which use fossil fuels in their manufacturing. In the process, they release pollutants whose constituents include Co and B contributing to their high EFs. The two sites are also surrounded by agrochemical industries which emit B as one of its pollutants into the atmosphere. Boron's other source is from the emissions from the vehicles since it is an additive to petroleum fuels.

Table 4.8: EFs for Heavy Metals and Metalloids in the Sites

	Zn	Pb	Cr	Cu	Co	B	Al
IS1	96.39	34.42	0.20	16.06	6004.25	7982.07	1.00
IRS1	21.21	39.24	0.21	54.78	3497.49	9825.14	1.00
CS1	17.28	37.18	0.21	36.47	4640.23	4625.58	1.00
Average	44.96	36.95	0.208	35.770	4713.99	7477.60	1.00

Although the concentration of Al in the samples was high, its EF value is low since it was used as a reference element in both the crustal and the sample composition. The poor roads in the sites continuously generate dust which contribute to its high concentrations in the study sites. Emissions from the heavy traffic in all the sites added to the pollutants in the atmosphere and this explains the high EFs of elements like Al, Pb, Zn and Cu in the sample. Comparison of EF values from previous studies with this study is summarized in Table 4.9. As can be observed from the table, EFs from this study are closer to those of Lim, Jeong-Hee et al., (2006) but are however way higher than that reported by the others.

Table 4.9: EFs Compared to Other Studies

Authors	Zn	Pb	Cr	Cu	Co	B	Al
Pereira et al., 2007	8.70	*	*	19.00	*	*	*
Lim, Jeong-Hee H et al., 2006	31.00	22.00	1.00	52.00	*	*	*
Mohamed et al., 2013	8.70	4.30	*	3.50	*	*	*
Eliat et al., 1997	*	21.50	*	*	*	*	4.00
This study	44.96	36.95	0.21	35.77	4713.99	7477.60	0.81

4.3.5 Correlation Coefficients

The correlation coefficients (r) of the average concentrations of the elements in the dustfall samples was done so as to predict if the pollutants had a common source. The results are shown in Table 4.10. The elements that are highly correlated might have had similar pollutant source.

Table 4.10: Correlation Coefficient (r) Between Element Concentrations

	Zn	Pb	Cr	Cu	Co	B	Al
Zn	1						
Pb	-0.7740	1					
Cr	-0.6937	0.9930	1				
Cu	-0.8577	0.9894	0.9653	1			
Co	0.8697	-0.9857	-0.9588	-0.9997	1		
B	0.2085	0.4580	0.5598	0.3239	-0.3015	1	
Al	0.9913	-0.6839	-0.5929	-0.7826	0.7971	0.3354	1

Many of the elements registered strong positive correlations indicating that they could have a common source. Others however showed strong negative correlation indicating diversity of their sources.

4.4 Organic Compounds

The organic compounds detected in the samples from the three sampling sites are shown in Table 4.11

Table 4.11: Organic Compounds Detected

IS1	Chemical Formula	IRS1	Chemical Formula	CS1	Chemical Formula
Trichloromethane	CHCl ₃	Tridecane	C ₁₃ H ₂₈	Aniline	C ₆ H ₇ N
Ethanedinitrile	CH ₃ CN	Benzenediamine	C ₆ H ₈ N ₂	Undecane	C ₁₁ H ₂₄
Propane	C ₃ H ₈	Salicylic Acid	C ₇ H ₆ O ₃	Dibutyl phthalate	C ₁₆ H ₂₂ O ₄
Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	Hexadecane	C ₁₆ H ₃₄	- 2ethylhexyl	C ₉ H ₁₈ O ₂
Phenol	C ₆ H ₅ OH	Dibutyl phthalate	C ₁₆ H ₂₂ O ₄		
		Methy Salicylate	C ₈ H ₈ O ₃		

The exposure routes for most of these compounds are; inhalation, dermal exposure as well as ingestion. The compounds detected from the different sites are linked to the site-specific activities with IS1 and IRS1 having almost similar industrial activities. Table 4.12 is a summary of the organic compounds as well as their likely sources.

Table 4.12: Organic Compounds and Their Likely Sources

Organic compound	Probable Sources
Trichloromethane	Plastic manufacturing, agrochemical chemicals, drug manufacturers floor polishes, adhesives/gum, drugs, disinfectant manufacturers
Propane	Petroleum evaporative processes, natural gas from internal combustion vehicles
Hexadecanoic acid-	Pulp and paper industries, cooking emission
Phenol	Plastic manufacturers, petroleum industries, agrochemicals synthetic/nylon manufacturers, drug manufacturers, disinfectants
Ethanedinitrile	Internal combustion engine, gas welding, steel producing and agrochemicals
Tridecane	Fuel, lubricant & solvent additive, paper processing industries, rubber industry
Benzenediamine	Dye manufacturers, some plastic manufacturers(aramid)
Salicylic acid	Pharmaceutical industries
Hexadecane-	Textile & leather manufacturing industries, diesel fuel additives
Dibutyl phthalate	Plastic manufacturing industries
Methy salicylate	Drug manufacturing industries, food industries
Aniline	Agrochemicals, rubber industries, petroleum, dyes, vanishes
Undecane	Fuel additive, lubricants and greases, adhesives

Many of the detected organic molecules are endocrine disrupting chemicals (EDCs). Nearly all of them are respiratory tract, eye and skin irritants over short-term exposure while others like tridecane and propane are asphyxiant. Some of the long-term effects of most of them are organ damage (liver, kidney, reproductive etc.) and eventually death while others like hexadecanoic acid have not been linked to any serious health complications. Additionally, others like trichloromethane are both carcinogenic and teratogenic among other effects.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study aimed to investigate the composition of settleable solids, dry deposition fluxes of particulate trace metals, presence of organic compounds atmospheric concentrations of trace elements at three different sites in Nairobi, i.e., Industrial (IS1), Industrial/residential (IRS1) and Commercial (CS1). The study also investigated the concentrations of atmospheric PM_{2.5}, PM₁₀ in eight sites in Nairobi (Industrial (IS1, IS2, IRS1), Commercial (CS1, CS2) and Residential (RS1, RS2) and a national park (NNP). The following conclusions were drawn from the study:

- 1 It was established that the concentrations of PM_{2.5} in six sites were above the WHO limits while only one site IRS1 recorded PM₁₀ above WHO daily limits during the study period. Industrial area and its environs have high levels of PM concentrations leading to adverse exposure and high risk of respiratory illnesses among people who spent most of their time in the area. As found out from the study, zones with little or no industrial activities have relatively safer air with less PM pollution.
- 2 The site with the highest TS was found to be IRS1(149 mg m⁻²day⁻¹) followed by, IS1(126 mg m⁻²day⁻¹) then lastly CS1 (61 mg m⁻²day⁻¹). The high concentrations in IRS1 and ISI are linked to the emissions from industrial, construction, heavy vehicular traffic and household activities. CS1 however recorded lower concentrations because its only major source of pollutants is vehicle traffic. One way ANOVA showed that there was no significant difference in their concentrations between the different sampling sites.
- 3 The area that recorded the highest concentration of trace elements was IRS1 then IS1 then lastly CS1. The order of element concentration in decreasing amounts is Co>B>Al>Zn>Cu>Pb>Cr. The Flux densities for the targeted trace elements are significant leading to adverse exposure over long periods of time. Such depositions

were found to be dependent of human activities like combustion of fossil fuels with additives and from plastic and paint manufacturing processes.

- 4 The study also established that the dustfall in Nairobi contains organic compounds such as; tridecane, benzenediamine, salicylic acid, hexadecane, dibutyl phthalate, methyl salicylate, aniline, undecane, dibutyl phthalate, trichloromethane, ethanedinitrile, propane, hexadecanoic acid and phenol. All these organic compounds are emitted from industries and motor-vehicle fuel constituents. These molecules are harmful to living organisms as endocrine disrupting chemicals, carcinogens and asphyxiants.

5,2 Recommendations

- 1 More research within the entire Nairobi region should be done on the sources and composition of particulates as well as their concentrations. Mitigation measures to alleviate poor air quality should be designed with focus on specific areas because of the diversity in the nature of pollution.
- 2 Local authorities (NEMA) should develop policies for site continuous air quality monitoring tools. Dissemination of air quality reports to the public should be done continuously to facilitate precautionary measures like wearing masks when in areas prone to pollution.
- 3 Environmental Authorities and other relevant stakeholders should ensure compliance and adherence to existing laws and legislation for controlling air pollution. Reward and Penalty schemes could be designed for compliant and non-compliant entities respectively in a fair and transparent manner.
- 4 Epidemiological studies should be done so as to identify the health problems related to air pollution. Health data on infections related to the respiratory and cardiovascular systems should be examined. This should be done especially in the severely affected areas so as to establish the link between the specific pollutants and the exposed individuals.

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APPENDICES

Appendix I: Dustfall Jar Installed at NCPB Depot Industrial Area



Appendix II: Purple air Monitor Installed at Embakasi



Appendix III: Sample PM Data

UTCDateTime	current temperature	current humidity	current dewpoint	pressure	pm1_0_	pm2_5_at	pm10_0_at
2022/04/01T00:00:07z	70	65	58	839.23	20.7	30.98	38.21
2022/04/01T00:02:06z	71	66	59	839.32	16.98	25.42	31.12
2022/04/01T00:04:06z	70	66	58	839.22	19.42	29.84	39.93
2022/04/01T00:06:06z	70	66	58	839.25	19.12	28.4	37.86
2022/04/01T00:08:06z	70	66	58	839.29	16.91	26.5	31.07
2022/04/01T00:10:07z	71	66	59	839.29	23.21	34.82	47.66
2022/04/01T00:12:07z	70	66	58	839.31	19.88	29.6	35.74
2022/04/01T00:14:07z	70	66	58	839.35	17.68	24.91	29.37
2022/04/01T00:16:07z	70	66	58	839.3	22.96	33.58	42.63
2022/04/01T00:18:07z	70	65	57	839.25	20.04	28.36	34.61
2022/04/01T00:20:07z	70	66	58	839.26	15.41	23.11	28.11
2022/04/01T00:22:07z	71	66	59	839.3	18.91	26.32	31.54
2022/04/01T00:24:07z	70	66	58	839.37	21.75	31.64	37.18
2022/04/01T00:26:07z	70	66	58	839.4	26.65	39.05	50.82
2022/04/01T00:28:07z	70	66	58	839.36	33.04	47.74	63
2022/04/01T00:30:10z	66	66	54	836.06	24.67	35.38	48.21
2022/04/01T00:32:10z	70	66	58	839.33	21.05	29.88	37.98
2022/04/01T00:34:10z	70	66	58	839.37	16.64	23.98	28.14
2022/04/01T00:36:10z	70	66	58	839.39	13.89	19.3	22.02
2022/04/01T00:38:10z	70	66	58	839.34	14.09	19.14	23.43
2022/04/01T00:40:10z	70	66	58	839.35	14.95	20.95	24.41
2022/04/01T00:42:10z	70	66	58	839.34	20.6	27.25	33.82
2022/04/01T00:44:10z	70	66	58	839.4	18.95	26.58	32.39
2022/04/01T00:46:10z	70	66	58	839.34	14.12	19.66	22.75
2022/04/01T00:48:10z	70	66	58	839.39	15.53	21.95	25.84
2022/04/01T00:50:12z	70	66	58	839.39	20.02	29.44	37.95
2022/04/01T00:52:12z	70	66	58	839.32	22.05	32.5	40.91
2022/04/01T00:54:12z	70	66	58	839.32	17.19	25.23	31.23
2022/04/01T00:56:12z	70	66	58	839.28	22.16	31.29	35.48
2022/04/01T00:58:12z	68	66	56	837.46	21.83	32.88	43.21

2022/04/01T01:00:12z	70	66	58	839.38	19.36	26.37	30.63
2022/04/01T01:02:12z	70	66	58	839.41	16.14	22.07	29.45
2022/04/01T01:04:12z	70	66	58	839.39	14.46	20.14	25.86
2022/04/01T01:06:12z	70	66	58	839.47	13.19	17.61	20.63
2022/04/01T01:08:12z	70	66	58	839.43	16.86	23.09	29.16
2022/04/01T01:10:14z	70	66	58	839.44	19.7	28.55	34.08
2022/04/01T01:12:14z	70	66	58	839.47	17.4	24.67	27.48
2022/04/01T01:14:14z	70	66	58	839.43	16.89	23	27.37
2022/04/01T01:16:14z	70	66	58	839.44	16.75	21.93	24.65
2022/04/01T01:18:14z	70	66	58	839.42	16.68	23.18	28.36
2022/04/01T01:20:14z	69	66	57	838.48	20.6	29.26	39.5
2022/04/01T01:22:14z	70	66	58	839.38	23.36	33.75	45.75
2022/04/01T01:24:14z	70	66	58	839.47	17.61	24	28.34
2022/04/01T01:26:14z	70	66	58	839.48	16.41	22.81	29.64
2022/04/01T01:28:14z	70	67	58	839.43	19.53	25.51	29.64
2022/04/01T01:30:15z	70	67	58	839.47	15.95	22.7	30.52

2022/04/01T01:32:15z	70	66	58	839.45	14.83	20.69	23.53
2022/04/01T01:34:15z	70	66	58	839.46	13.29	17.68	21.48
2022/04/01T01:36:15z	70	66	58	839.48	13.85	20.07	24.61
2022/04/01T01:38:15z	70	66	58	839.4	20.51	30.51	39.36
2022/04/01T01:40:15z	70	66	58	839.4	23.52	34.64	44.95
2022/04/01T01:42:15z	70	66	58	839.38	15.6	21.28	27.02
2022/04/01T01:44:15z	70	66	58	839.42	15.18	22.46	26.38
2022/04/01T01:46:15z	70	66	58	839.44	16.53	23.89	29.07
2022/04/01T01:48:15z	70	66	58	839.46	16.49	23.86	28.39
2022/04/01T01:50:17z	70	66	58	839.44	18.03	26.26	30.56
2022/04/01T01:52:17z	70	66	58	839.46	19.88	28.07	35.84
2022/04/01T01:54:17z	70	66	58	839.46	22.55	32.12	39.09

2022/04/01T01:56:17z	70	66	58	839.4	25.75	37.27	48.98
2022/04/01T01:58:17z	70	66	58	839.4	19.67	26.88	32.68
2022/04/01T02:00:17z	70	66	58	839.37	15.12	21.07	25.49
2022/04/01T02:02:17z	70	66	58	839.35	15.41	22.58	27.97
2022/04/01T02:04:17z	70	66	58	839.28	17.11	23.91	28.09
2022/04/01T02:06:17z	71	66	59	839.35	25.91	37.76	49.53
2022/04/01T02:08:17z	70	66	58	839.36	33.74	49.88	66.81
2022/04/01T02:10:19z	70	66	58	839.34	23.38	32.28	41.03
2022/04/01T02:12:19z	70	66	58	839.3	23.12	33.28	41.81
2022/04/01T02:14:19z	71	66	59	839.36	31	45.46	59.34
2022/04/01T02:16:19z	70	65	58	839.33	40.6	60.98	76.28
2022/04/01T02:18:19z	70	66	58	839.35	31.19	46.07	60.67
2022/04/01T02:20:19z	70	66	58	839.34	30.19	44.49	58.95
2022/04/01T02:22:19z	70	66	58	839.4	23.53	33.58	45.25
2022/04/01T02:24:19z	70	66	58	839.41	27.06	39.25	50.38
2022/04/01T02:26:19z	70	66	58	839.5	29.93	43.88	57.2
2022/04/01T02:28:19z	70	66	58	839.49	30.05	42.57	55.71
2022/04/01T02:30:21z	70	66	58	839.49	22.44	30.29	42.17
2022/04/01T02:32:21z	70	66	58	839.54	21.98	30.79	37.88
2022/04/01T02:34:21z	70	66	58	839.59	21.41	29.78	35.61
2022/04/01T02:36:21z	70	66	58	839.53	24.09	34.42	42.16
2022/04/01T02:38:21z	70	66	58	839.52	24.04	33.84	43.96
2022/04/01T02:40:21z	70	66	58	839.55	21.15	29.2	34.17
2022/04/01T02:42:21z	70	66	58	839.62	21.16	28.11	34.14
2022/04/01T02:44:21z	70	66	58	839.64	24.04	33.71	40.78
2022/04/01T02:46:21z	70	66	58	839.76	19.68	27.38	35.12
2022/04/01T02:48:21z	70	66	58	839.73	22.75	30.32	37.04

2022/04/01T02:50:23z	70	66	58	839.74	26.17	37.15	47.56
2022/04/01T02:52:23z	70	66	58	839.79	28.91	41.18	53.88
2022/04/01T02:54:23z	70	66	58	839.9	31.07	43.53	57.21
2022/04/01T02:56:23z	70	66	58	839.87	24.22	34.02	42.19
2022/04/01T02:58:23z	69	66	57	838.96	23.58	32.41	39.59
2022/04/01T03:00:23z	70	66	58	839.87	23.17	31.24	35.85
2022/04/01T03:02:23z	70	66	58	839.88	22.23	31.09	38.05
2022/04/01T03:04:23z	70	66	58	839.9	21.92	30.6	38.68

2022/04/01T03:06:23z	70	66	58	839.89	23.96	33.91	39.44
2022/04/01T03:08:23z	70	67	58	839.96	21.11	28.8	36.75
2022/04/01T03:10:24z	70	66	58	839.92	23.85	32.56	43.33
2022/04/01T03:12:24z	70	67	58	839.93	23.63	33.19	42.42
2022/04/01T03:14:24z	70	67	58	839.97	20.64	29.07	36.21
2022/04/01T03:16:24z	70	66	58	839.98	19.84	27.85	32.65
2022/04/01T03:18:24z	70	66	58	840.02	27.42	37.65	45.82
2022/04/01T03:20:24z	70	66	58	840.02	31.08	45.05	59.05
2022/04/01T03:22:24z	70	66	58	840.02	30.47	42.33	54.49
2022/04/01T03:24:24z	70	66	58	840.01	34.48	48.5	63.4
2022/04/01T03:26:24z	70	66	58	840.02	27.28	38.76	51.2
2022/04/01T03:28:24z	70	66	58	840.11	23.75	32.56	39.88
2022/04/01T03:30:25z	70	66	58	840.08	28.05	39.05	48.55
2022/04/01T03:32:25z	70	66	58	840.12	28.48	39.19	50.64
2022/04/01T03:34:25z	70	67	58	840.15	25.02	35.25	44.53
2022/04/01T03:36:25z	70	66	58	840.13	24.96	35.65	45.2
2022/04/01T03:38:25z	70	66	58	840.24	26.67	36.91	47.93

2022/04/01T03:40:25z	70	67	58	840.26	26.45	36.28	46.05
2022/04/01T03:42:25z	70	67	58	840.29	23.73	32.56	42.16
2022/04/01T03:44:25z	70	67	58	840.31	26.13	36.3	46.83
2022/04/01T03:46:25z	70	66	58	840.34	25.89	36.6	45.82
2022/04/01T03:48:25z	70	67	58	840.43	27.24	37.66	48.81
2022/04/01T03:50:27z	70	66	58	840.4	27.44	37.51	44.92
2022/04/01T03:52:27z	70	66	58	840.43	29.74	42.26	56.52
2022/04/01T03:54:27z	70	66	58	840.45	27.96	40.46	52.7
2022/04/01T03:56:27z	70	66	58	840.45	30.43	43.24	54.44
2022/04/01T03:58:27z	70	66	58	840.47	32.74	45.18	57.63
2022/04/01T04:00:27z	70	66	58	840.55	27.83	39.66	49
2022/04/01T04:02:27z	70	66	58	840.61	30.19	42.35	56.06
2022/04/01T04:04:27z	70	66	58	840.62	24.8	34.39	45.76
2022/04/01T04:06:27z	70	66	58	840.7	26.3	36.39	47.98
2022/04/01T04:08:27z	70	66	58	840.62	30.73	42.68	55.36
2022/04/01T04:10:28z	70	66	58	840.73	28.21	40.39	52.37
2022/04/01T04:12:28z	70	66	58	840.75	27.84	37.86	49.14
2022/04/01T04:14:28z	70	66	58	840.77	29.66	41.08	52.45
2022/04/01T04:16:28z	70	66	58	840.81	26.78	37.95	48.25
2022/04/01T04:18:28z	70	66	58	840.87	31.38	42.72	55.52
2022/04/01T04:20:28z	70	66	58	840.93	31.33	43.53	57.82
2022/04/01T04:22:28z	70	66	58	840.95	26.8	36.04	46.61
2022/04/01T04:24:28z	70	66	58	840.96	21.02	29.64	37.93
2022/04/01T04:26:28z	69	65	57	840.1	23.09	31.55	38.95
2022/04/01T04:28:28z	70	66	58	841.13	22.26	30.71	34.41
2022/04/01T04:30:30z	70	65	58	841.09	26.23	35.95	47.72
2022/04/01T04:32:30z	70	66	58	841.09	20.84	28.47	35.95

2022/04/01T04:34:30z	67	65	54	838.9	22.45	31.36	38.74
2022/04/01T04:36:30z	70	65	57	841.21	26.06	36.22	48.13
2022/04/01T04:38:30z	70	65	57	841.15	23.27	33.12	39.61

2022/04/01T04:40:30z	71	65	58	841.1	23.82	33.58	43.12
2022/04/01T04:42:30z	71	65	58	841.11	29.63	42.56	55.49
2022/04/01T04:44:30z	71	65	58	841.09	30.89	43.16	54.57
2022/04/01T04:47:31z	71	65	58	840.99	26.85	37.26	46.39
2022/04/01T04:48:31z	71	64	58	841.03	26.22	36.22	47.56
2022/04/01T04:50:32z	71	64	58	841.05	25.74	35.98	45.11
2022/04/01T04:52:31z	71	64	58	841.16	25.05	35.11	44.8
2022/04/01T04:54:31z	71	63	58	841.09	20.94	28.89	33.89
2022/04/01T04:56:32z	71	64	58	841.14	18.44	25.05	29.08
2022/04/01T04:58:32z	71	63	58	841.12	21.12	29.86	36.45
2022/04/01T05:00:32z	71	63	58	841.11	21.85	30.09	38.35
2022/04/01T05:02:32z	71	63	58	841.17	30.24	42.26	55.72
2022/04/01T05:04:32z	72	63	58	841.18	21.31	29.58	36.1
2022/04/01T05:06:32z	71	63	57	841.16	25.75	36.75	47.69
2022/04/01T05:08:32z	72	63	58	841.18	38.63	52.91	68.5
2022/04/01T05:10:32z	72	62	58	841.26	26.75	38.46	50.14
2022/04/01T05:12:32z	72	62	58	841.24	22.93	32.59	41.52
2022/04/01T05:14:32z	72	61	58	841.2	20.21	26.82	31.44
2022/04/01T05:16:33z	72	61	58	841.19	16.58	22.92	25.1
2022/04/01T05:18:33z	72	61	58	841.24	22.09	30.28	38.07
2022/04/01T05:20:33z	72	61	58	841.27	26.09	37.56	47.05
2022/04/01T05:22:33z	72	61	58	841.27	23.96	33.43	41.91

2022/04/01T05:24:33z	72	61	57	841.4	19	26.7	31.26
2022/04/01T05:26:33z	72	61	58	841.39	20.82	29.38	37.3
2022/04/01T05:28:33z	72	61	58	841.32	32.83	44.36	56.05
2022/04/01T05:30:33z	73	61	58	841.34	24.3	32.97	41.26
2022/04/01T05:32:33z	73	60	58	841.32	23.36	33.1	43.48
2022/04/01T05:34:33z	73	60	58	841.31	30.39	41.34	54.14
2022/04/01T05:36:33z	73	60	58	841.37	22.26	31	37.64
2022/04/01T05:38:33z	73	59	58	841.44	27.2	37.83	48.87
2022/04/01T05:40:34z	73	59	58	841.39	21.78	29.17	37.98
2022/04/01T05:42:34z	74	59	58	841.46	22.94	30.83	40.56
2022/04/01T05:44:34z	74	59	58	841.41	24.02	33.11	41.22
2022/04/01T05:46:34z	74	58	58	841.37	20.41	28.04	37
2022/04/01T05:48:34z	74	57	58	841.47	22.31	30.64	36.42
2022/04/01T05:50:34z	74	56	57	841.48	23.07	31.47	40.29
2022/04/01T05:52:35z	74	56	57	841.52	21.39	28.75	32.98
2022/04/01T05:54:35z	74	55	57	841.47	26.85	36.92	46.15
2022/04/01T05:56:36z	75	55	58	841.5	21.88	30.11	37.63
2022/04/01T05:58:37z	75	55	58	841.47	20.21	27.13	35.74
2022/04/01T06:00:37z	75	55	58	841.49	25.57	34.87	42.98
2022/04/01T06:02:37z	75	55	58	841.49	27.43	38.71	48.93
2022/04/01T06:04:37z	75	55	57	841.46	23.86	30.89	34.2
2022/04/01T06:06:37z	75	55	57	841.44	24.67	34.39	42.74
2022/04/01T06:08:38z	75	55	57	841.43	23.91	33.11	41.23
2022/04/01T06:10:38z	76	55	58	841.41	21.46	29.23	34.35
2022/04/01T06:12:38z	76	54	58	841.48	22.06	29.98	38.81

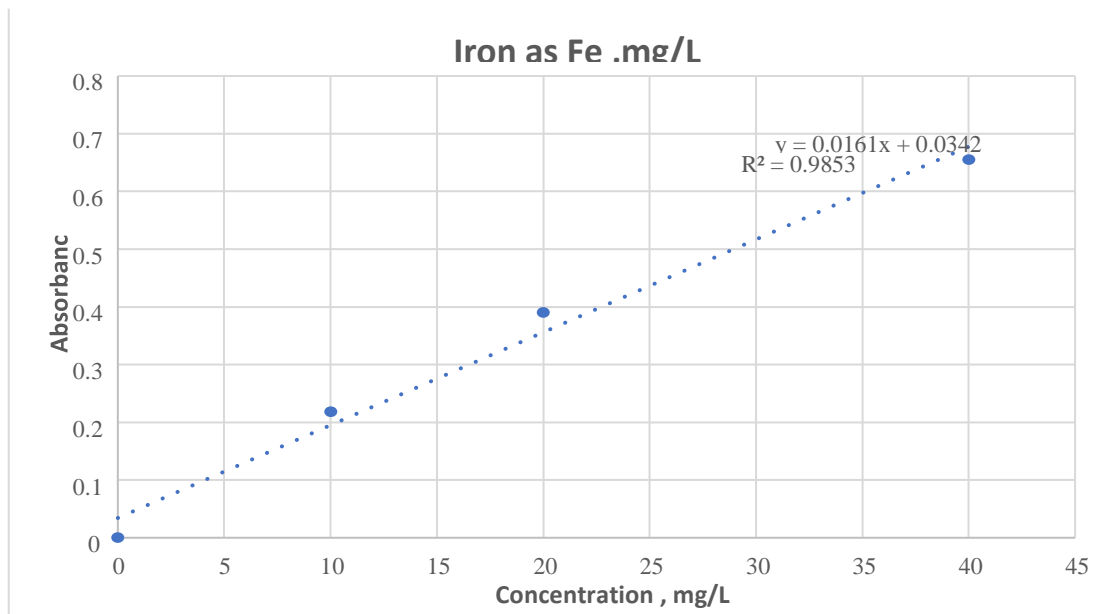
2022/04/01T06:14:39z	75	53	57	841.46	19.07	25.93	31.6
2022/04/01T06:16:39z	76	53	58	841.44	17.54	22.79	25.71
2022/04/01T06:18:39z	76	54	58	841.51	18.15	23.51	29.09
2022/04/01T06:20:41z	76	53	58	841.5	19.66	26.05	29.78
2022/04/01T06:22:41z	76	53	57	841.57	26.18	37.31	45.53
2022/04/01T06:24:42z	76	53	58	841.62	24.09	33.72	37.6
2022/04/01T06:26:42z	76	53	57	841.63	23.12	31.2	35.88
2022/04/01T06:28:42z	76	53	57	841.61	18.6	23.85	28.32
2022/04/01T06:30:42z	75	53	57	841.62	17.03	23.12	25.6
2022/04/01T06:32:42z	76	53	58	841.69	18.64	25.14	32.09
2022/04/01T06:34:42z	76	53	57	841.65	17.89	23.91	28.54
2022/04/01T06:36:43z	77	53	58	841.68	24.7	33.8	40.1
2022/04/01T06:38:43z	77	52	58	841.68	21.46	28.41	32.25
2022/04/01T06:40:43z	77	52	58	841.67	19.42	26.78	32
2022/04/01T06:42:43z	77	51	57	841.67	14.87	20.94	28.17
2022/04/01T06:44:43z	77	51	57	841.76	20.66	30.39	41.46
2022/04/01T06:46:43z	77	50	57	841.73	21.96	30.26	37.81
2022/04/01T06:48:43z	78	50	58	841.77	27.89	37.13	47.44
2022/04/01T06:50:43z	78	50	57	841.67	20.37	27.98	34.81
2022/04/01T06:52:43z	78	50	58	841.77	17.93	24.54	29.88
2022/04/01T06:54:43z	78	50	58	841.7	21.18	29.16	39.37
2022/04/01T06:56:45z	78	50	58	841.66	21.46	28.85	33.66
2022/04/01T06:58:46z	78	50	58	841.69	19.85	26.64	33.19
2022/04/01T07:00:46z	78	50	57	841.69	21.67	28.2	30.44
2022/04/01T07:02:46z	77	49	56	841.65	22.91	30.98	36.46
2022/04/01T07:04:46z	78	49	57	841.7	16.38	21.91	25.53
2022/04/01T07:06:46z	78	49	57	841.62	19.86	26.22	31.93

2022/04/01T07:08:46z	78	49	57	841.63	18.65	25.56	33.29
2022/04/01T07:10:46z	78	49	57	841.64	21.42	28.56	35.96
2022/04/01T07:12:46z	79	48	58	841.57	22.11	29.05	38.64
2022/04/01T07:14:46z	79	48	57	841.61	22.62	30.38	36.83
2022/04/01T07:16:47z	79	48	57	841.51	18.05	24.02	30.15
2022/04/01T07:18:47z	74	47	52	837.34	17.2	25.51	30.64
2022/04/01T07:20:47z	79	47	57	841.57	21.74	28.97	34.52
2022/04/01T07:22:47z	79	47	57	841.58	20.66	28.97	36.07
2022/04/01T07:24:47z	79	47	57	841.55	17.22	23.52	28.38
2022/04/01T07:26:47z	79	47	57	841.48	24.22	33.58	43.4
2022/04/01T07:28:47z	79	46	56	841.52	21.4	27.48	31.64
2022/04/01T07:30:47z	79	46	57	841.46	24.61	31.96	36.23
2022/04/01T07:32:47z	79	46	56	841.44	20.82	26.4	32.64
2022/04/01T07:34:47z	79	46	56	841.5	22.12	28.09	33.77
2022/04/01T07:36:48z	80	46	57	841.51	22.42	31.62	42.28
2022/04/01T07:38:48z	79	46	56	841.42	21.75	28.98	35.41
2022/04/01T07:40:48z	79	46	56	841.42	22.82	31.16	37.76
2022/04/01T07:42:48z	79	47	57	841.41	23.44	31.91	39.05
2022/04/01T07:44:48z	79	47	57	841.45	28.96	40.82	53.96
2022/04/01T07:46:48z	79	47	57	841.42	24.53	33.84	41.79

Appendix IV: Calibration Curves for the Trace Elements

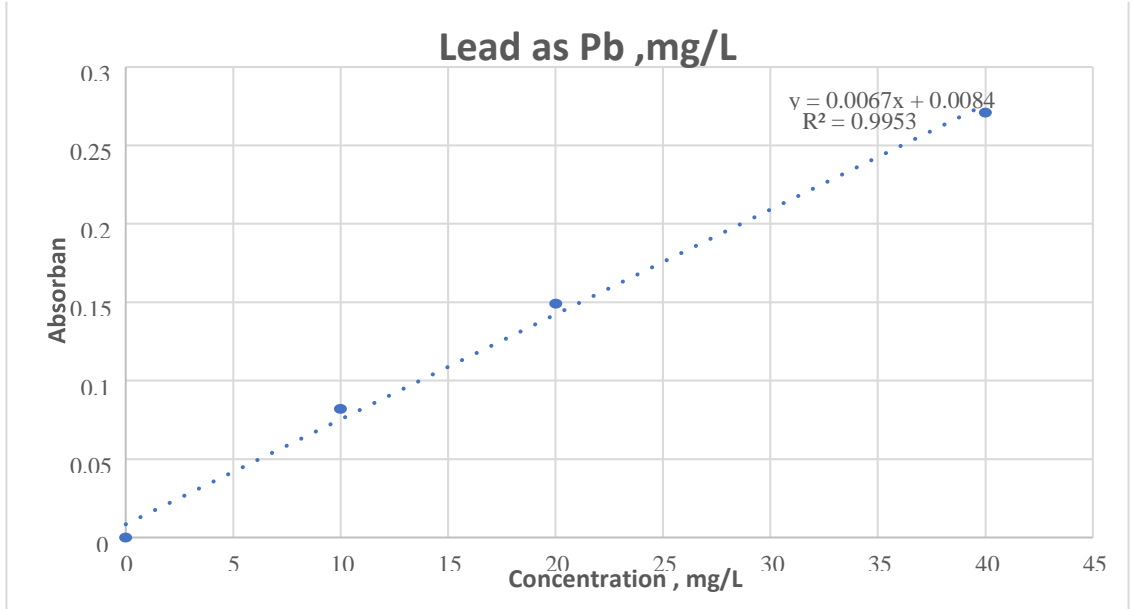
Calibration Curve.Fe.55. Xls Acq. Date-Time: 29/06/2022.12.16PM

Varian SpectrAA-5



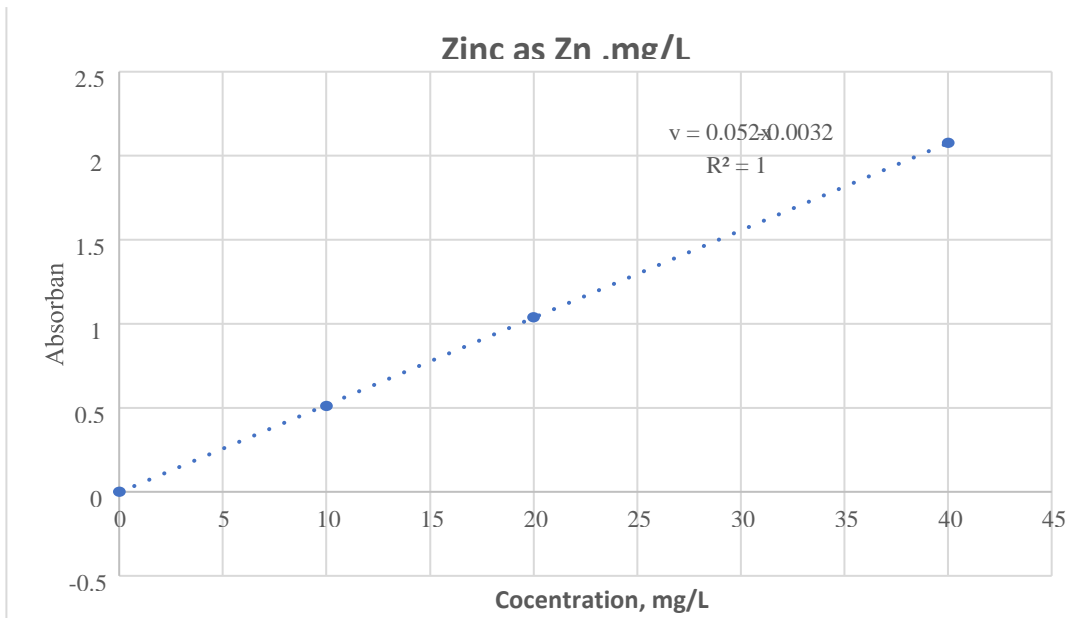
Calibration Curve.Pb.208. Xls Acq. Date-Time: 29/06/2022.12.16PM

Varian SpectrAA-5



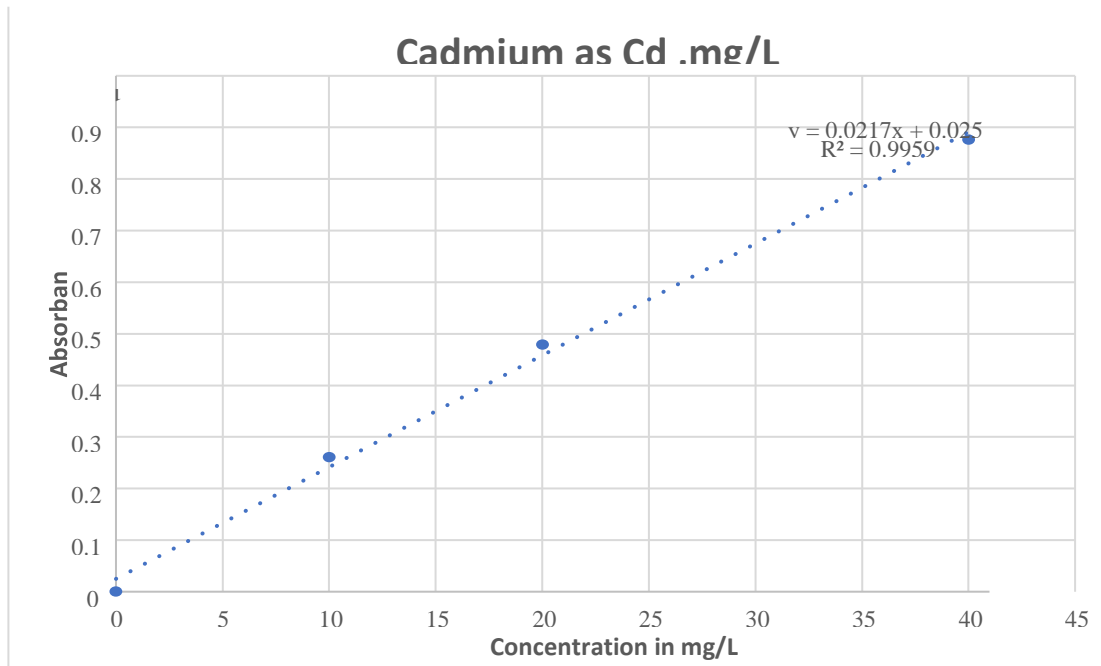
Calibration Curve.Zn.66. Xls Acq. Date-Time: 29/06/2022.12.16PM

Varian SpectraAA-5



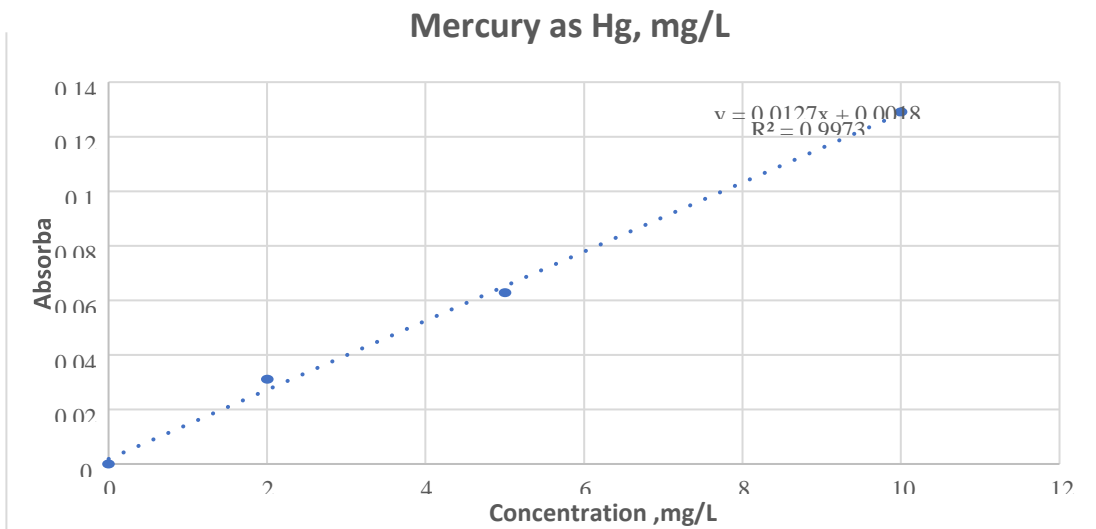
Calibration Curve.Cd.111. Xls Acq. Date-Time: 29/06/2022.12.16PM

Varian SpectrAA-5



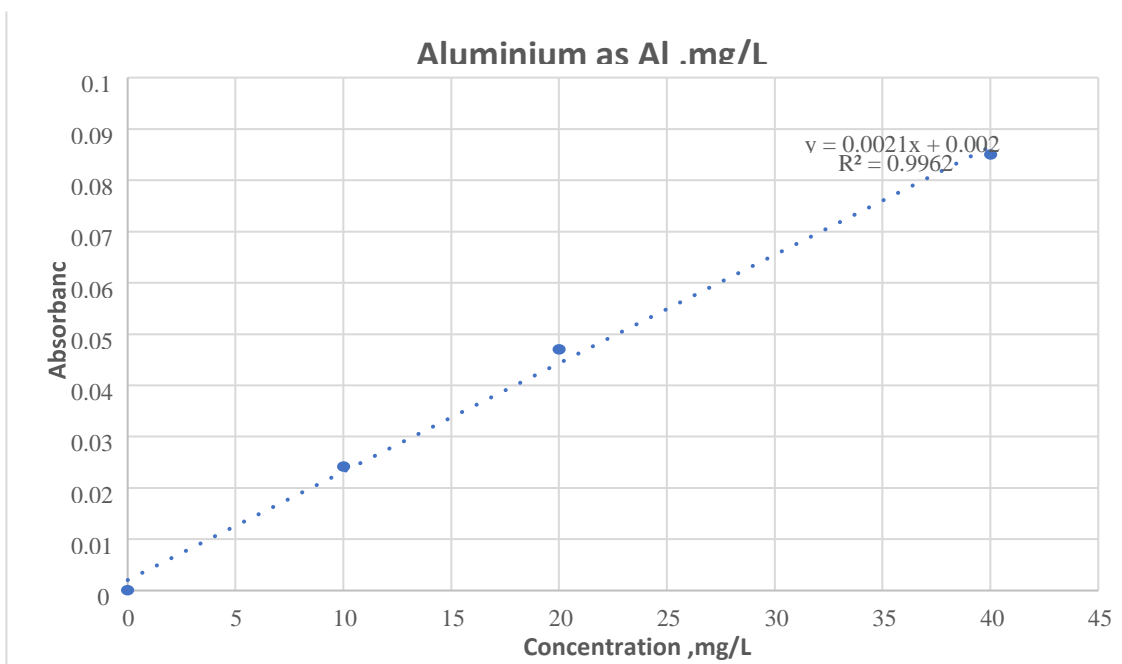
Calibration Curve.Hg.201. Xls Acq. Date-Time: 29/06/2022.12.16PM

Varian SpectrAA-5



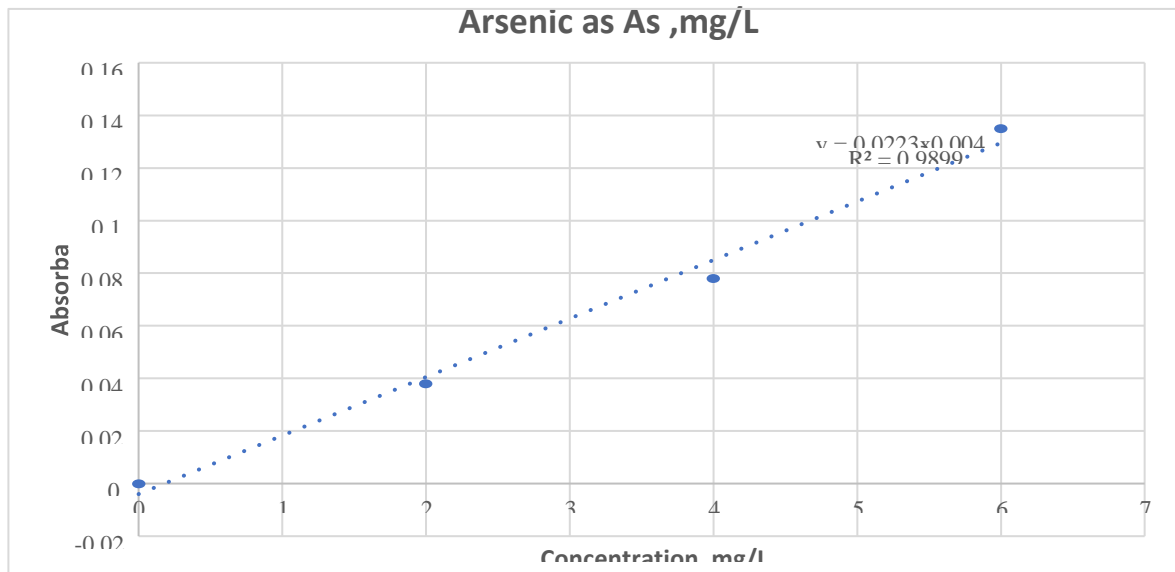
Calibration Curve.A1.27. Xls Acq. Date-Time: 29/06/2022.12.16PM

Varian SpectrAA-5



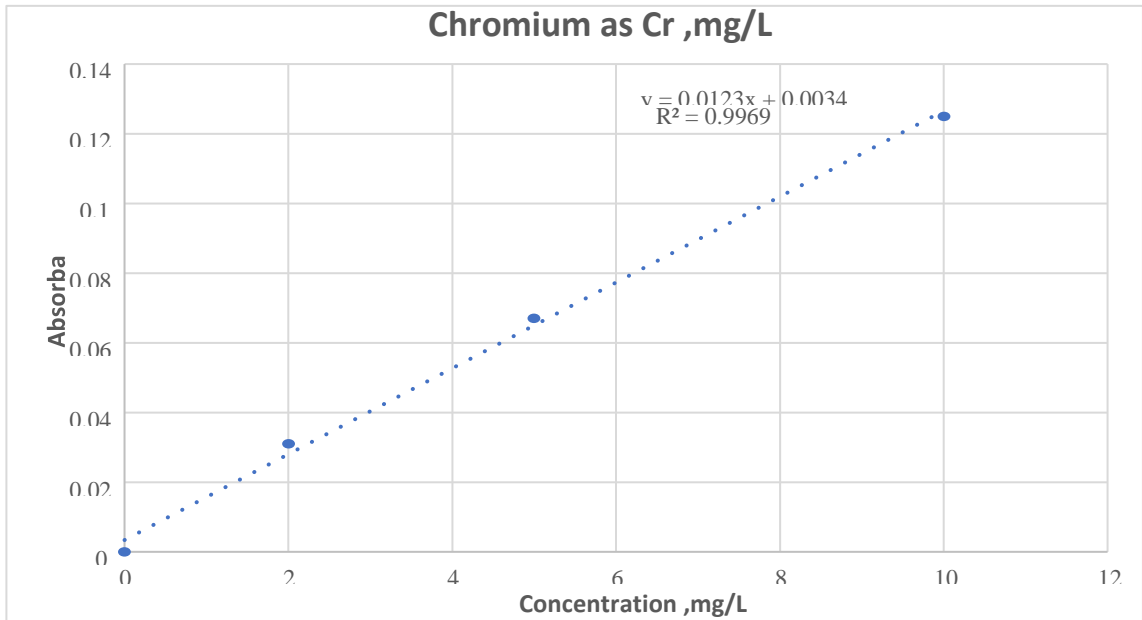
Calibration Curve.As.72. Xls Acq. Date-Time: 29/06/2022.12.16PM

Varian SpectrAA-5



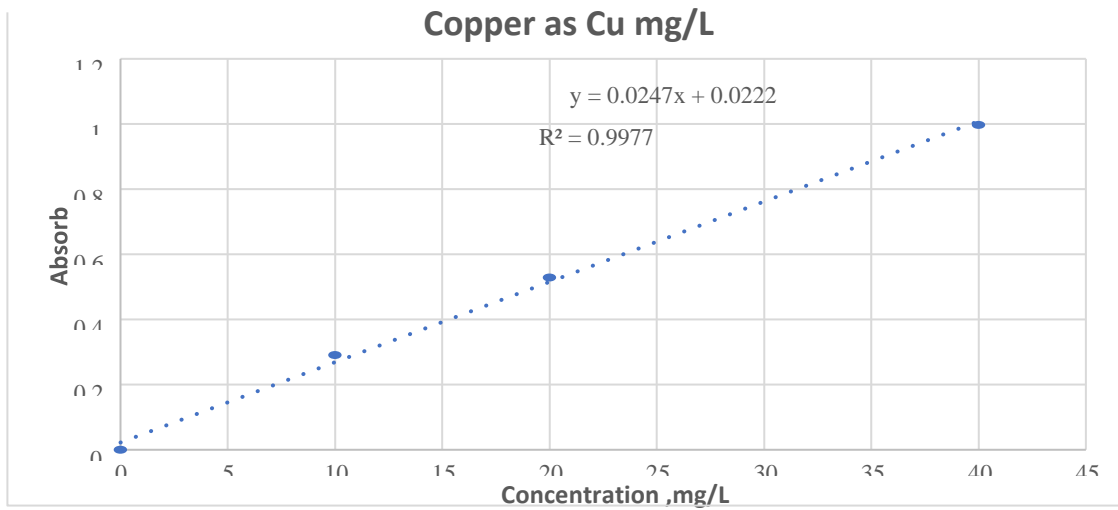
Calibration Curve.Cr.72. Xls Acq. Date-Time: 29/06/2022.12.16PM

Varian SpectrAA-5

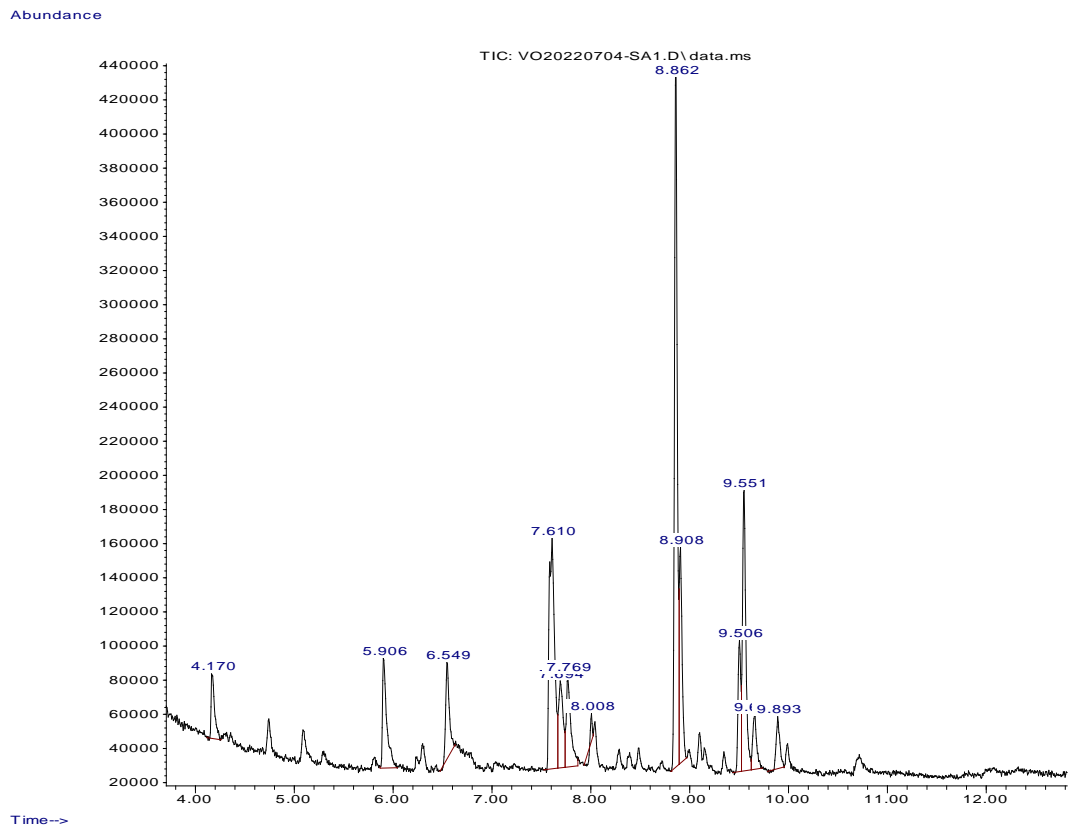


Calibration Curve.Cu.65. Xls Acq. Date-Time: 29/06/2022.12.16PM

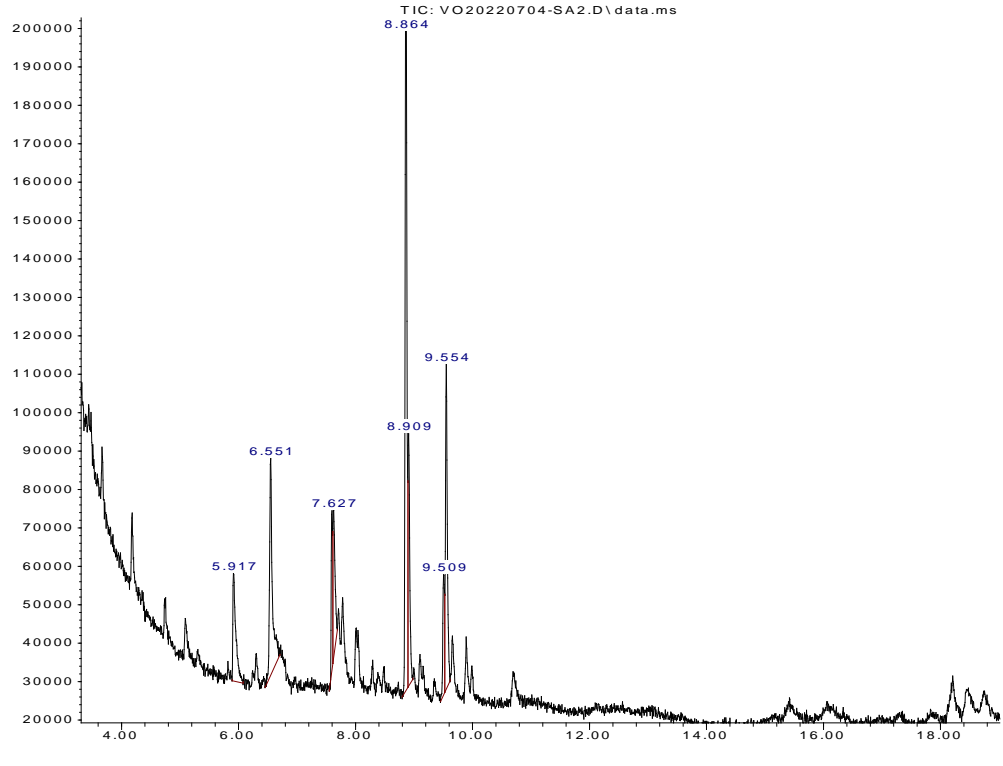
Varian SpectrAA-5



Appendix V: Chromatograms for the Dustfall Samples



Abundance



Abundance

