ANALYSIS OF SELECTED HEAVY METALS AND THEIR CORRELATIONS IN TOMATOES, SOILS, AND COMMONLY USED INORGANIC FERTILIZERS IN KIRINYAGA COUNTY, KENYA

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A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Master of Science in Chemistry of Murang'a University of Technology

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DECLARATION

Student Declaration

I hereby declare that this Thesis is my original work and to the best of my knowledge has not been presented for a degree award in this or any other university. I understand what plagiarism is and I am aware of the University's policy in this regard. I understand that any false claim in respect of this work shall result in disciplinary action in accordance with the University Anti-Plagiarism Policy.

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Supervisors' Approval

The undersigned certify that they have read and hereby recommended for acceptance of Murang'a University of Technology a thesis entitled **"Analysis of Selected Heavy Metals and Their Correlations in Tomatoes, Soils, and Commonly Used Inorganic Fertilizers in Kirinyaga County, Kenya".**

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DEDICATION

I dedicate this Thesis to my parents and to Madam Kabale Dadacha, whose exceptional support, encouragement, and belief in me have been pivotal throughout this journey. I also extend my gratitude to my brothers and sisters for their unwavering support and dedication, which have greatly contributed to this achievement.

I will be forever grateful.

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ABSTRACT

The contamination of Agricultural products by harmful Heavy metals poses a significant global health concern, with potential links to severe public health issues such as cancer and neural impairment. Tomatoes (*Lycopersicon esculentum Mill.),* a dietary staple, can absorb and store both essential micronutrients and potentially harmful heavy metals, particularly in their consumable parts. Due to increased demand and value, many farmers have adopted modern farming methods which include application of Fertilizers, Pesticides, Compost manure, and Irrigation. Yet some of these Agricultural practices such as application of fertilizers and pesticides are known to increase the concentration of heavy metals in the soil. Some of these heavy metals such as Pb and Cd are toxic even at low concentrations while Cu and Cr though essential in the body, are toxic at high levels. This calls for monitoring to make sure that the levels of heavy metals do not exceed the threshold limits recommended by WHO/FAO due to their adverse health effects to human. This study therefore investigated the concentration of cadmium, lead, copper, and chromium in Fertilizers, tomatoes and corresponding soil samples from Kirinyaga County, Kenya. The findings will inform mitigation strategies for farmers and policymakers, promoting sustainable agriculture and food safety. Ultimately, the study supports soil preservation and long-term agricultural viability. A total of 27 tomato samples; 27 soil samples and 7 fertilizer samples were randomly collected from each of the three ecological zones of Kirinyaga County. Known weights of oven dried fertilizer, tomato and soil samples were digested using 4.0 mL of 35% HNO_3 and 6.0 mL of H_2O. The samples were digested using the dry ashing method and elemental analysis was performed using Microwave Plasma-Atomic Emission Spectroscopy (MP-AES). The mean concentrations of heavy metals in soil samples ranged from; cadmium: 0.0100±0.100 to 0.1133±0.0667, lead: 0.0570±0.0566 to 0.667±0.0367, copper: 0.8667±0.273 to 1.9±0.0577 and chromium 0.0670±0.0600 to 1.333±0.040 mg/Kg. The mean concentrations of heavy metals in tomatoes ranged from; cadmium: 0.00367±0.003 to 0.00867±0.01, lead: 0.00133±0.003 to 0.00667±0.02, copper: 0.00667±0.02 to 0.0667±0.003 and chromium: below detection limit to 0.027±0.035 mg/Kg. The mean concentrations of heavy metals in fertilizer samples ranged from; cadmium: 0.2±0.21 to 1.7±0.21, lead: below detection limit to 3.5±0.44, Copper: 0.8±0.18 to 2.1±0.18 and chromium 0.9±0.74 to 5.8±0.74 mg/Kg. The ANOVA results suggested that there was a significant difference ($p = 0.05$) in the levels of heavy metals between soil and tomatoes in all the regions. The correlation analysis between the concentration of metals in soil and tomatoes and the use of the inorganic fertilizer revealed relevance for the fertilizer NPK 27-10-16 + TE EASY GROW. The bioaccumulation index (BI) for cadmium, lead, copper, and chromium ranged from 4-12%, 0.7-4%, 2-5%, and 0.9-3%, respectively, suggesting that their accumulation in tomato fruits is low. The concentrations of the heavy metals in fertilizer, soils and tomatoes were significantly lower than the maximum concentrations set by the WHO/FAO. Although the tomatoes from the region are safe for human consumption regarding Cd, Pb, Cu, and Cr, repeated application of aforementioned fertilizer could put consumers at risk of exposure to these heavy metals. All the other sampled fertilizers were found to be safe for application on agricultural lands. There is a need to monitor the levels of heavy metals regularly to ensure they do not exceed acceptable limits.

TABLE OF CONTENTS

DECLARATION ..... **ii**
DEDICATION ..... **iii**
ACKNOWLEDGEMENT ..... **iv**
ABSTRACT ..... **v**
LIST OF TABLES ..... **ix**
LIST OF FIGURES ..... **x**
ACRONYMS AND ABBREVIATIONS ..... **xi**
CHAPTER ONE: INTRODUCTION **1**
1.1 Background Information 1
1.2 Statement of the Problem 2
1.3 Significance of the Study 3
1.4 Objectives of the Study 3
1.4.1 General Objective 3
1.4.2 Specific Objectives 3
1.5 Null Hypotheses 4
1.6 Scope and Limitations 4
1.7 Contributions of the Thesis 4
1.8 Organization of the Thesis 5
CHAPTER TWO: LITERATURE REVIEW **7**
2.1 Introduction 7
2.2 Pollution by Heavy Metals 7
2.3 Presence of Heavy Metals in Tomatoes 8
2.4 Presence of Heavy Metals in Soil 8
2.5 Uptake of Heavy Metals by Plants 9
2.6 Tomatoes 10
2.7 Tomato Farming in Central Kenya 11
2.8 Heavy Metals 12
2.9 Uses of Heavy Metals 12
2.10 Implications of Heavy Metals on Human Health 14
2.11 Routes of Heavy Metal Exposure to Humans 15
2.12 Sources of Heavy Metal Contaminations 16

2.12.1 Fertilizers 16
2.12.2 Pesticides 17
2.12.3 Bio- Solids and Manures 18
2.12.4 Use of Wastewater for Irrigation 18
2.12.5 Air-borne Sources 18
2.13 Methods of Analysis: Microwave Plasma Atomic Emission Spectroscopy ..19
2.14 Summary 21
CHAPTER THREE: MATERIALS AND METHODS 22
3.1 Introduction 22
3.2 Study Area 22
3.3. Research Design 23
3.4 Collection of Samples 24
3.4.1. Collection of Soil and Tomatoes Samples 24
3.4.2 Collections of Fertilizer Samples 26
3.5. Analysis of Samples 26
3.5.1. Pretreatment of Soil and Tomatoes Samples 26
3.5.2. Pretreatments of Fertilizer Samples 26
3.5.3. Digestion of Samples 26
3.5.4 Elemental Analysis 27
3.5.5 Operating Condition for MP-AES 27
3.6 Statistical Analysis. 28
3.7 Bioaccumulation Index 28
3.8 Summary 29
CHAPTER FOUR: RESULTS AND DISCUSSION 30
4.1 Introduction 30
4.2 Recovery of Selected Metals from Spiked Samples 30
4.3 Concentrations of Selected Metals in Soil Samples 31
4.4 Concentrations of Selected Metals in Tomato Samples 33
4.5 Concentrations of Selected Metals in Commonly used Inorganic Fertilizers ..35
4.6. Bioaccumulation Index 38
4.7 Comparative ANOVA Analysis of Tomato and Soil Samples 39

4.8 Means Plots of Selected Metals in Soil and Tomato Samples 42
4.9 Test of Homogeneity of Variance.....43
4.10 Analysis of Variance for Tomato and Soil Samples 44
4.11 Descriptive Statistics for Selected Metal Concentrations 45
4.12 Means Plot for Metal Concentration in Controlling for Sample Size.....48
4.13 Test of Homogeneity of Variances of Selected Metals across the Three Zones.....49
4.14 Correlation Analysis of Selected Metals in Tomatoes, Soil, and Fertilizer Samples 51
4.14.1 Highland Zones 51
4.14.2 Midland Zones 53
4.14.3 Lowland Zones.....54
4.15. PCA Analysis 57
4.16 Total Variance Explained 57
4.17 Component Matrix 58
4.18 Reliability Statistics 59
4.19 Cluster Analysis 62
4.20 Summary 64
CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS.....65
5.1 Conclusion 65
5.2 Recommendations.....65
5.2.1 Recommendations for Policy 65
5.2.2 Recommendation for Further Work 65
REFERENCES.....67
APPENDICES.....82

LIST OF TABLES

Table 1.1 Maximum Tolerable Limits for Selected Metals in Plants and Soil 2
Table 3.1: Sampling Sites, Sample Type and Number of Samples 25
Table 3.2: Operating Condition for MP-AES 28
Table 4.1: Spike Recoveries for Selected Metals in Tomatoes Samples.....30
Table 4.2: Mean Concentrations of Selected Metals in Soil Samples 31
Table 4.3: Mean Concentrations of Selected Metals in Tomato Samples.....34
Table 4.4: Mean Concentrations of Selected Metals in Fertilizer Samples 36
Table 4.5: Bioaccumulation Index of Selected Metals in Tomato Samples.....38
Table 4.6: Descriptive Statistics for Soil and Tomato Samples 40
Table 4.7: Test of Homogeneity of Variances 44
Table 4.8: Analysis of Variance between Soil and Tomato Samples 45
Table 4.9: Descriptive Statistics for Soil and Tomato Samples in Three Zones 47
Table 4.10: Test of Homogeneity of Variances for Selected Metals across the Three Zones.....50
Table 4.11: Correlations Analysis of Selected Metals in Soil, Tomatoes, and Fertilizer Samples from Highland Zones.....52
Table 4.12: Correlations Analysis Selected Metal Soil, Tomatoes, and Fertilizer Samples from Midland Zones.....55
Table 4.13: Correlations Analysis of Selected Metals in Soil, Tomatoes, and Fertilizer Samples from Lowland Zones 56
Table 4.14: Communalities from PCA Analysis 57
Table 4.15: Total Variance Explained 58
Table 4.16: Component Matrix 59
Table 4.17: Reliability Statistics 60
Table 4.18: Inter-Item Correlation Matrix 60
Table 4.19: Item-Total Statistics 61
Table 4.20: Initial Cluster Centers based on Cluster Analysis on Standardized Concentration of Metals.....62
Table 4.21: Final Cluster Centers Representing the Concluding Stage of a Clustering Analysis.....63

LIST OF FIGURES

Figure 2.1: Tomato Fruits....11
Figure 2.2: Tomato Plant....11
Figure 2.3: Routes of Heavy Metal Exposure....16
Figure 2.4: Working Principle of MP-AES (Vysetti et al., 2014) 20
Figure 3.1: Map of a Kirinyaga County showing the Sampling Sites (QGIS) 23
Figure 4.1: Mean Plots of Selected Metal Concentrations in Soil and Tomato Samples 42
Figure 4.2: Means Plot for Metal Concentration in Controlling for Sample Size 48
Figure 4.3 Screen Plot for Factor Analysis and Principal Component Analysis 58
Figure 4.4 Final Cluster Centers for Unique Z-scores for each Metal Concentrations 63

ACRONYMS AND ABBREVIATIONS

AFAP	African Fertilizer and Agribusiness Partnership
ANOVA	Analysis of Variance
BI	Bioaccumulation index
CAN	Calcium Ammonium Nitrate
DAP	Di-ammonium Phosphate
FAAS	Flame Atomic Absorption Spectrometry
FAO	Food and Agricultural Organization
GAPs	Good Agricultural Practices
HCDA	Horticultural Crops Development Authority
HCLO	Per chloric Acid
HNO_3	Nitric Acid
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
KEBS	Kenya Bureau of Standards
KEPHIS	Kenya Plant Health Inspectorate Service
LED	Light-Emitting Diodes
mg/Kg	Milligram per Kilogram
MP-AES	Microwave Plasma Atomic Emission Spectroscopy
NEMA	National Environment Management Authority
NP	Nitric acid-per chloric acid
NPK	Nitrogen, Phosphorus and Potassium
Ppm	Parts per million
SSP	Single Superphosphate
USD	United States Dollar
WHO	World Health Organization

CHAPTER ONE
INTRODUCTION

1.1 Background Information

Tomato *(Lycopersicon esculentum mill*) is among the most produced and consumed vegetables in the world. Globally, the leading producers of tomatoes are China, USA, Turkey and India (Costa and Heuvelink, 2005). In Africa, Kenya is among the largest producers of tomatoes, and produced 973,304 tons in 2020 (AFA-HCD, 2020). In Kenya, Taita Taveta, Kirinyaga and Kajiado Counties are the leading producers of tomatoes (Sigei *et al*., 2014; AFA-HCD, 2020).

Tomatoes contains several antioxidants including lycopene, β-carotene and quercetin (Beecher 1998). Antioxidants prevent or reduce oxidative damage of cells, proteins and DNA, and thus mitigate against diabetes, cardiovascular diseases, cancers and neurodegenerative diseases (Beecher, 1998; Nguetti *et al*., 2019; Ali *et al*., 2021). Tomatoes are consumed fresh, added to salads, cooked as a vegetable or processed to produce several products including tomato juice, paste, puree, powder and sauce, which are then consumed directly or used as ingredients for other foods (Beecher, 1998).

In 2020, Kirinyaga County produced 64,038 metric tons of tomatoes in valued at about 1.8B Kenya shillings (AFA-HCD, 2020). The bulk of the tomatoes are grown in open fields using the furrow irrigation (Waiganjo *et al*., 2006). Pesticides are extensively used to control diseases (e.g. fungal blights, bacterial and viral wilts) and insect pests such as the African bollworm, thrips and cutworms (Waiganjo *et al*., 2006). In addition, inorganic fertilizers such as di-ammonium phosphate (DAP), calcium ammonium nitrate (CAN) and nitrogen, phosphorus, and potassium (NPK) fertilizers are widely used (Waiganjo *et al*., 2006).

Rivers can become contaminated with heavy metals via agricultural and urban run-offs, disposal of household wastes (Gatere *et al*., 2022). Consumption of food containing heavy metals can cause severe health effects including cancers, growth retardation and mental disorders (Rai *et al*., 2019). Cadmium can cause several adverse effects including kidney dysfunction, sexual disorders, lung and breast cancers and osteoporosis (Rai *et al*., 2019). Lead can have adverse effects on the central

nervous system, cardiovascular diseases, cancers and mental disorders in children (Rai *et al*., 2019). Copper can affect renal and metabolic functions while chromium can cause renal dysfunction and respiratory diseases (Rai *et al*., 2019).

Some of these heavy metals such as Pb and Cd are toxic even at low concentrations while Cu and Cr though essential in the body, are toxic above the recommended levels. The maximum allowable limits of heavy metals have been established by World Health Organization (WHO) as shown in the Table 1.1.

Table 1.1 Maximum Tolerable Limits for Selected Metals in Plants and Soil

	(WHO/FAO, 2021)	
Metals	**Tolerable Limits in mg/Kg**	
	Plants	**Soil**
Cadmium	0.05	0.3
Lead	0.10	10
Copper	5.0	36
Chromium	2.3	65

1.2 Statement of the Problem

The increasing global population and the resulting high demand for food products have stressed the ability to produce enough food over time. Consequently, modern farming methods, including the application of inorganic fertilizers, have been adopted to meet these growing demands. While these fertilizers contain high concentrations of essential micronutrients to maintain soil health, they can also introduce heavy metals into farms and, consequently, into the products. One of the raw materials in the manufacture of inorganic fertilizers is phosphate rocks, which contain heavy metals. Additionally, fertilizers blended with recycled industrial wastes, such as steel mill flue dust and mine tailings, can further contribute to heavy metal contamination in the soil. In Kenya, although the government has implemented robust measures to monitor imported goods for heavy metal levels, there are few or no measures in place to monitor locally produced food. As a result, consumers could be exposed to unknown concentrations of heavy metals, posing potential health risks.

1.3 Significance of the Study

The significance of this study lies in its ability to provide a comprehensive assessment of heavy metal contamination in agricultural lands and to identify associated sources. The results from this research will enable regulatory bodies such as KEPHIS, KEBS, and NEMA to formulate policies that support Kenya's Vision 2030 by ensuring quality agricultural inputs and produce, thereby promoting food security, health, and sustainable development.

The findings will also enhance public awareness of the importance of good agricultural practices (GAPs) and will serve as a foundation for agricultural extension work in Kirinyaga County, guiding and educating farmers on effective fertilizer applications. It also provides farmers, policymakers, and stakeholders with critical information about contamination levels and sources, supporting the development of effective strategies and guidelines to mitigate risks. Ultimately, this research aims to protect human health and the environment, promote sustainable agricultural practices, ensure food safety, preserve soil quality, and support the long-term viability of agricultural systems in the region.

1.4 Objectives of the Study

1.4.1 General Objective

To analyze the levels and correlations of Cd, Pb, Cu and Cr in soil, inorganic fertilizers, and tomatoes grown in Kirinyaga County.

1.4.2 Specific Objectives

i. To determine the concentration of selected heavy metals in tomato and soil samples collected from Kirinyaga County.

ii. To determine the concentration of selected heavy metals in commonly used inorganic fertilizer in tomato production in Kirinyaga County.

iii. To determine the correlations of selected heavy metals in soil, tomatoes and commonly used inorganic fertilizers in Kirinyaga County.

1.5 Null Hypotheses

H_{o1}: There is no significant difference in the concentration of selected heavy metals in tomatoes and soil samples collected from Kirinyaga County.

H_{o2}: There is no significant difference in the concentration of selected heavy metals in inorganic fertilizers used in tomato production in Kirinyaga County.

H_{o3}: There is no significant correlation between the levels of selected heavy metals in soils, inorganic fertilizers, and tomatoes grown in Kirinyaga County.

1.6 Scope and Limitations

The research, conducted in Kirinyaga County, Central Kenya, focused on analyzing Cadmium, Lead, Copper, and Chromium concentrations in fertilizers, soil, and tomatoes. These heavy metals were chosen due to their prevalence in Agriculture and their potential impact on human health and the environment. However, the study did not investigate other potential sources of metal contamination, such as pesticides and wastewater used for irrigation, nor did it consider other heavy metals that could affect soil and crop quality. Additionally, the analysis was limited to specific periods and did not include tomato leaves, stems, or roots. Factors like seasonal variations, farming practices, and soil properties may influence heavy metal levels and were not examined in this research.

1.7 Contributions of the Thesis

The contributions made by this study are highlighted below:

i. This research provides a detailed analysis of selected metal concentrations in soil, tomatoes, and fertilizers from Kirinyaga County, Kenya, enhancing understanding of metal accumulation in the agricultural products.
ii. The study compares the concentrations of heavy metals from the study with permissible limits set by FAO/WHO. This confirms that the levels of selected heavy metals in soil, tomatoes, and fertilizers are below regulatory thresholds, indicating that the agricultural produce in the region meets safety standards.
iii. The study provides recommendations for regular monitoring of heavy metals and suggests further research on additional trace elements and pesticide-related contamination.

iv. A paper containing the results of this study has been published.

1.8 Organization of the Thesis

The content of this research thesis is organized into five chapters as highlighted below:

Chapter one is the Introduction. This chapter provides a comprehensive overview of the research, starting with the background information that contextualizes the study. It outlines the statement of the problem and issues that the research aims to address. The chapter also defines the objectives of the study, including both the general and specific objectives. It highlights the significance of the study, emphasizing its importance. Additionally, the scope and limitations of the research are discussed to clarify the boundaries and constraints of the study.

The second chapter is Literature Review. This chapter examines existing research related to the current study, highlighting what has been done and identifying gaps in the knowledge. It reviews the extent of heavy metal pollution, focusing on its impact on tomatoes, soil, and agricultural practices. Key areas include the presence of heavy metals in tomatoes and soil, uptake mechanisms by plants, and tomato farming in Central Kenya. Additionally, it covers the implications for human health, Sources of contamination, and Methods of Analysis. This review sets the foundation for addressing research gaps and advancing understanding of heavy metal contamination.

Chapter Three is Materials and Methods. This chapter outlines the research design and methodology used to conduct the study. It begins with an introduction to the overall approach and strategy. The chapter then describes the study area, including relevant geographic and environmental details. It details the research design, specifying the methods and procedures employed in the study. The chapter further elaborates on the collection of samples, including the procedures for collecting soil, tomato, and fertilizer samples. It includes sections on the methods sample collection and protocols used for each type of sample. It explains pretreatment processes for soil, tomatoes, and fertilizers, followed by digestion and elemental analysis Techniques.

The methodology section also includes the operating conditions for Microwave Plasma Atomic Emission Spectrometry (MP-AES) used in the analysis. Statistical analysis methods are described, outlining how data were analyzed to derive

meaningful results. Additionally, the chapter introduces the Bioaccumulation Index, explaining its application and relevance to the study. The chapter concludes with a summary that encapsulates the methodology and its significance to the research objectives.

Chapter Four is the Results and Discussion. This chapter presents and interprets the findings of the study. It begins with an introduction to the results, followed by the recovery of heavy metals from spiked samples to ensure accuracy. The chapter then details the concentrations of heavy metals in soil and tomato samples, providing data on Cd, Pb, Cu, and Cr in commonly used inorganic fertilizers. The Bioaccumulation Index is discussed, highlighting its role in assessing heavy metal accumulation. Comparative analyses, including ANOVA, are presented to evaluate differences between tomato and soil samples. Means plots and tests of homogeneity of variance are used to illustrate the distribution and variance of heavy metals.

Further analyses include tests for metal concentration variations by zones, descriptive statistics, and means plots controlling for sample size. Correlation analysis examines relationships between heavy metals in tomatoes, soil, and fertilizers, with separate sections for different zones (Highland, Midland, Lowland). Principal Component Analysis (PCA) and cluster analysis are used to identify patterns and groupings in the data.

Chapter Five is the Conclusion, Recommendations, and Future Work. This chapter summarizes the key findings of the research and provides concluding remarks. It includes recommendations for policy and suggestions for further research to address remaining questions and explore new areas.

CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction

This chapter begins by introducing the problem of heavy metal pollution, both in general and in specific matrices such as soil, fertilizers, and food materials. Literature is cited to explain how pollution processes occur and, more importantly, how heavy metals end up in tomato fruits. The tomato-growing regions in Kenya are discussed, and earlier studies on heavy metal contamination in tomatoes are highlighted. The instruments used in the analysis of heavy metal levels in various matrices are also discussed.

2.2 Pollution by Heavy Metals

Heavy metals contribute to soil pollution, air pollution, and water pollution. Urbanization and Industrialization have made it possible for the transfer of heavy metals by the runoff from industries and homes, which accumulate heavy metals in raw sewage contamination of water bodies such as rivers, seas and oceans. Heavy metals pollutants, enter the food chain through marine life, like fish, and their predators (Briffa *et al.,* 2020). As a result, humans are also affected as they feed on these creatures.

Heavy metals also contribute to air pollution as pollutants enter the atmosphere as droplets or gaseous forms. The particles and droplets fall to the ground as they cannot be transported for long distances. Air pollution is also caused by natural and anthropogenic activities emitting particulate matter. Air pollutants then enter air circulation and cause problems. Heavy metals also contribute to soil pollution. Use of inorganic fertilizers, pesticides, and paints causes deliberate soil pollution (Briffa *et al.,* 2020).

Untreated sewage contains heavy metals, which are more likely to be absorbed by crops when effluents get into contact with irrigation waters. The crops are then consumed by humans, contributing to health risks. On the other hand, non-deliberate pollution occurs when pollutants transfer to land from water bodies through flooding. Heavy metals contaminate soil, thus ruining the ecosystem by entering the food chain.

2.3 Presence of Heavy Metals in Tomatoes

Tomatoes (*Lycopersicon esculentum mill*) are an essential part of the diet and a source of protein and vitamins. Studies by Gebeyehu & Bayissa (2020) have reported the concentration of heavy metals such as Pb, Cd, Cu, Cr, and Zn in fresh tomatoes from different markets worldwide. These studies highlight the widespread contamination of tomatoes with heavy metals, reflecting global environmental pollution issues.

The study conducted by Piscitelli *et al*. (2020) analyzed and evaluated the concentration of heavy metals in soil and tomato fruits, demonstrating a significant transfer of metals from the soil into the plant. In the aforementioned study, Fe and Cr were found in small concentrations, whereas Pb, Zn, and Cu were shown to be higher. Further, Piscitelli *et al.* (2020) reported high levels of zinc metal in the roots and stalks of tomato plants. The study also established that tomatoes grown in contaminated soil have elevated concentrations of heavy metals compared to tomatoes grown in uncontaminated soil due to the high absorption of heavy metals via the roots.

Phosphate fertilizers, such as single superphosphate (SSP) and di-ammonium phosphate (DAP), are commonly used in agriculture to promote plant growth. These fertilizers often contain trace amounts of heavy metals, including cadmium and lead. When applied to tomato crops, these heavy metals can be absorbed by the plants and accumulate in the edible parts (Briffa *et al.,* 2020). For example, the use of SSP and DAP has been linked to increased levels of cadmium and lead in the soil, which in turn leads to higher concentrations of these metals in tomatoes.

2.4 Presence of Heavy Metals in Soil

Soil is a crucial component of both rural and urban environments and is a valuable and indispensable natural resource. Most of the foods we eat grow in the soil, and the water we drink seeps through the soil into ground reservoirs or flows over it to rivers. Activities such as mining, manufacturing, and the use of synthetic products like pesticides, paints, industrial wastes, and fertilizers, as well as the land application of industrial or domestic sludge, result in heavy metal contamination of urban and agricultural soils. Although fertilizers are intended to enhance soil nutrients and promote plant growth, they have been found to contain trace amounts of other elements, mostly heavy metals, which may be toxic to humans and plants (Alloway, 1995).

Bonfires and the burial of metal-containing household wastes in domestic gardens can also lead to significant metal accumulation in soils used for growing food crops. Temporary waste stockpiles can cause significant soil contamination, and the foliar uptake of atmospheric heavy metal emissions has been identified as an important pathway for heavy metal contamination in crops (Salim et al., 1992). Landfilling of municipal solid waste can disperse several metals, including Cd, Pb, Cu, and Zn, into the soil (Alloway, 1995). Prabu (2009) observed that the concentration of heavy metals in soil depends on the clay content because clay-sized particles have many ionic binding sites due to their large surface area. This immobilizes heavy metals, reducing leaching through the soil profile, but can increase soil heavy metal concentrations and lead to soil toxicity.

Higher soil heavy metal content can result in higher levels of uptake by plants. Soil acts as a long-term sink for heavy metals such as Zn, Cu, Pb, Ni, and Cd, which have residence times ranging from hundreds to thousands of years, depending on the element and soil properties (Kaara, 1992). Heavy metals also occur naturally, but rarely at toxic levels. Excessive heavy metal accumulation in soils is toxic to humans and animals, with exposure typically being chronic due to food chain transfer. Metal contamination in agricultural soil is an increasing concern due to food safety issues and the potential health risks associated with the intake of contaminated plants.

2.5 Uptake of Heavy Metals by Plants

Plants grow by absorbing nutrients from the soil, and their ability to do this depends on the soil's nature. Soil contains a combination of sand, silt, clay, and organic matter. The makeup of soil texture and its acidity (pH) determines the extent to which nutrients are available to plants. The path taken by metals to transport into the plant is: soil → roots → stem → leaves. The minerals, dissolved in water, are often accompanied by various organic molecules supplied by root cells. Once in the xylem, water with the dissolved minerals moves up through vessels and tracheids (Kirmani et al., 2011). Minerals enter the root by active transport into the symplast of epidermal cells and move toward and into the stele through the plasmodesmata connecting the cells. Metals usually concentrate in the roots, followed by the twigs and leaves.

A large number of factors control metal accumulation and bioavailability, including soil and climatic conditions, plant genotype, and agronomic management (Kirmani et

al., 2011). Additional sources of these metals for plants are rainfall, atmospheric dust, and plant protection agents, which can be absorbed through the leaf blades. An important source of contamination in vegetable crops is considered to be foliar uptake of atmospheric heavy metal emissions (Salim et al., 1993).

Studies conducted by Kisku et al. (2000) in Kalipur, Bangladesh, on the uptake of Cd, Pb, Ni, and Cu by Brassica oleracea from fields irrigated with industrial effluent indicated widespread contamination from heavy metals, despite the plants showing healthy and robust external morphology. High levels of heavy metal accumulation from soil by common garden vegetables have been reported by many environmental researchers (Boon and Soltanpour, 1992; De Pieri et al., 1997; Xiong, 1998). Therefore, heavy metal contamination of widely consumed plants cannot be underestimated.

Plant uptake is a critical pathway by which bio solids-borne, potentially toxic trace metals can enter the food chain (Chaney, 1990). Plant availability of trace metals differs widely among plant species and organs. Hooda et al. (1997) measured variability in the accumulation of Cu, Ni, Cu, Pb, and Zn in wheat, carrots, and spinach grown on biosolids-amended soils. Cd, Ni, and Zn increased in plants to a greater extent than Pb and Cu compared to their background levels, suggesting that Cd might pose the greatest hazard among the trace metals studied.

2.6 Tomatoes

The tomato is the edible berry of the *Solanum lycopersicum* plant (Kumar *et al.,* 2016).This species originated in western South America, Mexico, and Central America. The word "tomato" comes from the Spanish word "tomate," which in turn originates from the Nahuatl word "tomatl." It is believed that the domestication and cultivation of tomatoes began with the indigenous peoples of Mexico (Onwuka *et al.,* 2019). Tomatoes are a major source of umami flavor and can be eaten in a variety of ways: raw, cooked, and in numerous dishes, sauces, salads, and beverages (Beecher, 1998). Although tomatoes are botanically classified as berries and therefore fruits (Figure 2.1), they are often used as vegetables in culinary contexts. Many varieties of tomato plants are extensively cultivated in temperate regions worldwide, and greenhouses facilitate their year-round production (Onwuka *et al.,* 2019). Typically, tomato plants grow to a height of 1–3 meters (3–10 feet). They are vines with weak

stems that usually require support (Figure 2.2). In their native environment, indeterminate tomato plants are perennials but are grown as annuals in cultivation. Determinate, or bush, plants grow to a specific height and produce a single crop before dying. The size of tomatoes varies depending on the cultivar, ranging from 1–10 cm in width (Beecher, 1998).



Figure 2.1: Tomato Fruits



Figure 2.2: Tomato Plant

2.7 Tomato Farming in Central Kenya

In Kenya, tomatoes are vital source of nutrients and livelihood for most farmers. Tomato farming is one of the main agricultural practice in Kenya, specifically in the country's central region (Ochilo *et al.,* 2019). Some factors that favor growth in the central region are soil fertility, water availability, and cool climatic conditions.

Farming is conducted in small-scale as most of the farmers utilize the traditional method of farming. However, modern farming technologies, such as greenhouse farming, are slowly being adopted by farmers to increase yields and fight diseases (Mwangi *et al.,* 2020). Farmers prefer modern methods as most of them experience challenges such as pests, high costs of production as well as market fluctuation (Mwangi *et al.,* 2020).

According to the article "Technical efficiency in tomato production among smallholder farmers in Kirinyaga County, Kenya," tomato farming in the central region is moderately efficient because of limited access to necessary education, credit, and extension services (Mwangi *et al.,* 2020). The article proposes that by enhancing the availability of information, education, and credit, it is possible to enhance farmers' technical efficiency, which can result in higher productivity and earnings. Additionally, the investigation suggests that exploring crop diversification and other methods of generating income can be beneficial for enhancing the living standards of smallholder farmers in the area. However, more research is required to establish the effectiveness of these measures.

2.8 Heavy Metals

Heavy metals refer to metallic elements that have a density slightly higher than that of water (Gatere *et al.,* 2022). It is a broad term used to describe a group of metals and metalloids with an atomic density greater than 4 g/cm^3, or at least five times greater than water (Poot *et al.,* 2007). Today, there have been concerns due to the presence of heavy metals in foods we consume. The phenomena have exposed human beings to various health risks throughout the world. In Kenya, like in any other country, tomatoes are highly used for cooking for their nutritional content. Kenya is among the top producers of tomatoes in the continent (Mwangi *et al.,* 2020). The preliminary studies on heavy metals in tomatoes and the health risks associated with their consumption. As a result, there is need to examine the levels of heavy metals in tomatoes which are consequently contaminated through the soil and fertilizers.

2.9 Uses of Heavy Metals

Cadmium (Cd) is used in various fields, albeit with caution due to its toxicity. In agriculture, it is often found as an impurity in phosphate fertilizers. Industrially, cadmium is a key component in nickel-cadmium (Ni-Cd) batteries, known for their

durability (Hussain *et al.,* 2022). It is also used in electroplating to provide corrosion-resistant coatings for steel and iron, particularly in aerospace and military applications. Cadmium sulfide (CdS) and cadmium selenide (CdSe) pigments are used for their bright colors in plastics, ceramics, and glass. Cadmium telluride (CdTe) is utilized in thin-film solar cells for efficient energy conversion. Additionally, cadmium alloys are used in low melting point applications like soldering and automatic sprinkler systems (Muzolf-Panek *et al.,* 2017. In the nuclear industry, cadmium control rods regulate fission processes, and cadmium-based quantum dots enhance color performance in LED screens. Despite these uses, cadmium's application is strictly regulated due to its environmental and health risks.

Lead (Pb) has diverse applications across various sectors, despite concerns regarding its toxicity and environmental impact. In agricultural practice application of lead-containing pesticides is common, which can unintentionally introduce lead into soils (Poot *et al.,* 2007). Industrially, lead-acid batteries are a prominent application, used in vehicles, backup power systems, and various electronic devices for their reliability and low cost. Lead is also utilized in the production of lead-based solders, providing a low-melting point material for joining electronic components. Lead-based pigments, such as lead chromate and lead carbonate, are valued for their brightness and durability in paints and coatings, although their use has decreased due to health and environmental concerns (Tchounwou *et al.,* 2012). Additionally, lead is employed in radiation shielding and as a soundproofing material in construction. Despite its versatility, the use of lead is heavily regulated due to its known health hazards, and efforts are ongoing to reduce its usage and find safer alternatives across industries.

Copper (Cu) holds pivotal roles across agriculture, industry, and other diverse applications (Tchounwou *et al.,* 2012). In agriculture, copper-based fungicides such as copper sulfate and copper oxychloride effectively combat fungal diseases like downy mildew and bacterial blight in crops such as grapes and tomatoes. Furthermore, copper fertilizers, including copper sulfate and copper oxide, rectify soil deficiencies, ensuring optimal plant health and growth (Poot *et al.,* 2007). In Industry, copper's high electrical conductivity makes it indispensable in electrical wiring, with examples including power distribution systems and electronic devices. Its durability and corrosion resistance find application in construction materials like copper roofing and

plumbing fixtures, enhancing the longevity and reliability of structures. Additionally, copper's antimicrobial properties are harnessed in various surfaces and alloys, such as copper alloys used in hospital surfaces and HVAC systems, to inhibit the growth of harmful bacteria and viruses. Moreover, copper's historical significance in coinage, exemplified by coins like the US penny, and its use in art, seen in sculptures and architectural features, showcase its enduring cultural value. Lastly, copper's role in water treatment, through copper ionization systems in swimming pools and reservoirs, highlights its importance in ensuring safe and clean water supplies ((Poot *et al.,* 2007).

Chromium has diverse applications and are integral to agricultural productivity and industrial advancements. For instance, Chromium (III), or trivalent chromium (Cr^{3+}), is the form of chromium that acts as a micronutrient to enhance plant growth and is included in slow-release formulations to improve nutrient efficiency (Muzolf-Panek *et al.,* 2017). Industrially, chromium is vital in producing stainless steel, providing corrosion resistance and strength, and is used in alloys to enhance mechanical properties. It serves as a catalyst (Cr_2O_3) in chemical production and is essential in manufacturing pigments for paints and dyes. Chromium salts, particularly chromium sulfate ($Cr_2 (SO_4)_3$), are also crucial in leather tanning, imparting durability and suppleness to leather products (Hussain *et al.,* 2022). Thus, chromium's diverse applications are integral to agricultural productivity and industrial advancements.

2.10 Implications of Heavy Metals on Human Health

Urbanization and industrialization growth have increased exposure to heavy metals in recent years. Human body can withstand some amounts of heavy metals in normal situations. However, continuous exposure to large concentrations of heavy metals can pose health risks. For instance, continuous exposure to cadmium causes severe pulmonary and gastrointestinal irritation. Direct exposure to cadmium also causes pulmonary adenocarcinomas and proliferative lesions (Tchounwou *et al.,* 2012).

Furthermore, lead exposure contributes to poisoning for both children and adults. Lead also intoxicates several organs in the body, including the kidney, liver, reproductive system, and central nervous system. Lead exposure continues to be a major problem, especially for children and pregnant women. Heavy metal is a concern for pregnant women, it exposes them to health hazards and transfers to the developing fetus

(Tchounwou *et al.,* 2012). Evidence shows that prenatal exposure to lead traces reduces birth weight and premature delivery.

Copper (Cu) toxicity can result from excessive intake, leading to symptoms such as nausea, vomiting, and liver damage. Wilson's disease, a genetic disorder, causes copper accumulation in organs, resulting in severe health issues like liver damage and neurological symptoms. For instance, excessive copper intake from contaminated food or supplements can lead to acute gastrointestinal distress, as seen in cases of accidental ingestion of copper sulfate (Tchounwou *et al.,* 2012).

Chromium (Cr) poses significant health risks, particularly in its hexavalent form Cr (VI), which is highly toxic. Exposure to Cr (VI) can result in respiratory problems and skin irritation. For example, workers in chrome plating facilities may develop allergic dermatitis from prolonged exposure to chromium salts. Additionally, chromium salts used in leather tanning can trigger allergic reactions in sensitive individuals. While dietary chromium is generally safe, excessive supplementation or exposure to contaminated sources can lead to health concerns. For instance, ingestion of contaminated food products with high levels of chromium can result in adverse health effects, such as gastrointestinal issues and skin rashes (Jaishankar *et al,* 2014).

2.11 Routes of Heavy Metal Exposure to Humans

Mainly exposure to heavy metal comes from two sources: Anthropogenic and natural sources (Jin *et al.,* 2019). Anthropogenic sources include mining, industrial, and agricultural activities, while on the other hand, natural sources of heavy metals include the weathering of metal-bearing rocks and volcanic eruptions. Figure 2.3, illustrates the pathway of heavy metal exposure (Abdel-Rahman, 2021).

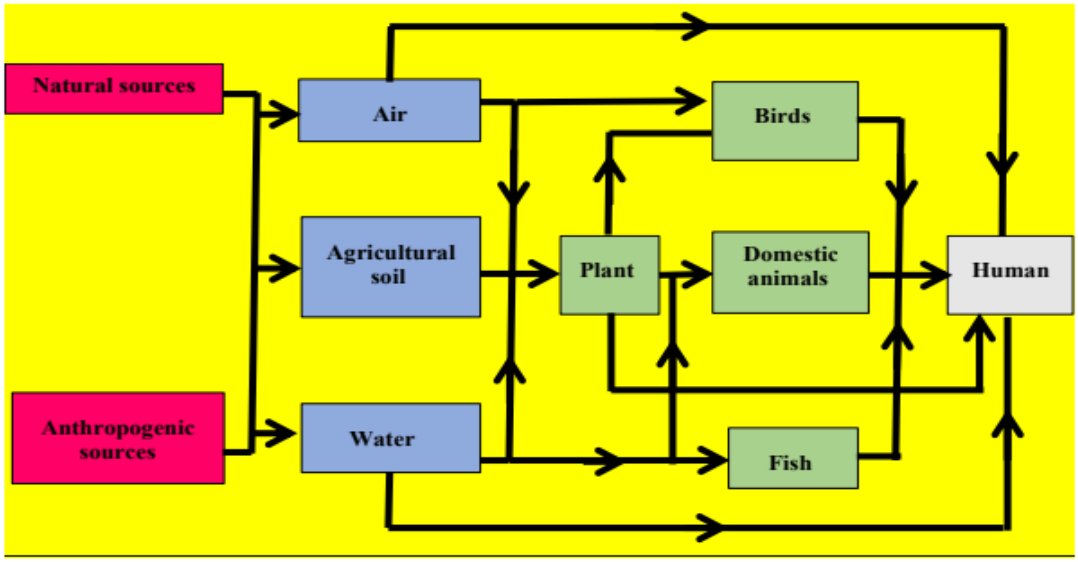


Figure 2.3: Routes of Heavy Metal Exposure

2.12 Sources of Heavy Metal Contaminations

2.12.1 Fertilizers

Agriculture is the primary human activity that had a significant contributions to the heavy metal contamination (Gomez Rodriguez *et al.,* 1981). Plants require macronutrients and micronutrients, such as Cu, Mn, Fe, and Zn to grow and complete their life cycle. However, some soils may be deficient in these, leading to poor plant growth. As a result, farmers often apply the fertilizers containing these nutrients either as an addition or as a foliar spray. Fertilizers, commonly used in agriculture to enhance plant growth and yield, can be significant sources of heavy metal contamination (Yargholi, & Azarneshan, 2014). This contamination often occurs due to the presence of heavy metals in the raw materials used for fertilizer production or through the addition of industrial by-products containing heavy metals.

Heavy metals such as cadmium, lead, and arsenic can be present in fertilizers derived from phosphate rock, as these metals are naturally trapped in the rock during formation (Yargholi, & Azarneshan, 2014). Additionally, some fertilizers may contain sewage sludge or industrial waste as ingredients, which can introduce heavy metals into the soil when applied. Copper and chromium, although not as frequently discussed as other heavy metals, can pose significant risks to environmental and human health. Copper, for instance, is commonly used in agricultural fungicides and pesticides, and

its presence in fertilizers can contribute to soil and water contamination. Chromium, often found in industrial waste products, can also seep into fertilizers, especially those derived from recycled materials, thereby elevating the risk of contamination.

Improper application of fertilizers, such as overuse or inappropriate timing, can exacerbate heavy metal contamination in soil and water bodies (Gomez Rodriguez *et al.,* 1981). As plants absorb nutrients from the soil, they can also take up heavy metals, leading to bioaccumulation in the food chain and potential health risks for humans and wildlife (Yargholi, & Azarneshan, 2014). Effective management practices, including regular testing of soil and careful selection of fertilizers, are essential to minimize heavy metal contamination from fertilizers and safeguard environmental and human health (Yargholi, & Azarneshan, 2014).

2.12.2 Pesticides

In the past, a significant number of commonly used pesticides in agriculture and horticulture contained high levels of metals, such as Cu, Pb, Cd, Zn, Cr and Mn (Alengebawy *et al.,* 2021). These metals were often intentionally added to pesticides for various purposes, such as enhancing their efficacy or extending their shelf life. For instance, copper-containing fungicides like Bordeaux mixture and copper oxychloride were widely utilized for their potent insecticidal and fungicidal properties (Gouda *et al.,* 2018). Additionally, lead arsenate was historically employed as a pesticide to control pests in orchards and vineyards.

The incorporation of heavy metals into pesticides, while providing benefits in pest control, also posed significant environmental and health risks. As these pesticides were applied to crops, the heavy metals could leach into the soil, water bodies, and surrounding ecosystems, leading to contamination. Moreover, the persistence of these metals in the environment could result in long-term accumulation, exacerbating the risks to human health and the ecosystem (Gouda *et al.,* 2018).

Pesticide contamination tends to be more localized than that caused by fertilizers and is often restricted to specific crops or sites (Gouda *et al.,* 2018). Nevertheless, it has the potential to cause considerable problems, especially when these sites are repurposed for agricultural or non-agricultural uses. The persistence of these metals in

the soil can lead to long-term environmental and health risks, necessitating careful management and remediation strategies to mitigate their impact.

2.12.3 Bio- Solids and Manures

The consequence of using a variety of bio solids, including municipal sewage sludge, manures from animals, and composts in farms is the buildup of heavy metals in the soil (Usman *et al.,* 2012). Bio solids and animal manures are regarded as valuable to the soil and consequently to the plants and therefore frequently utilized in farms to nourish plant growth (Bolan *et al.,* 2004). If animal manures from diets containing high levels of heavy metals are repeatedly used on small areas of land, they can cause a significant buildup of these metals in the soil over time (Bolan *et al.,* 2004).

Bio solids, also known as sewage sludge, are mostly organic solid substances created through wastewater treatment processes that can be beneficially recycled. The heavy metals that are typically present in bio solids are cadmium, lead, copper, zinc and Chromium where their concentrations are influenced by the industrial treatment processes.

2.12.4 Use of Wastewater for Irrigation

The industrial and municipal wastewater application and related effluents to land has been used for many years and is now common in many regions worldwide (Sumner, 2000). Around the world, a huge number of arable lands are irrigated with wastewater. According to Raschid-Sally *et al.,* (2007) agricultural activities that rely on wastewater for irrigation provide approximately a half of the vegetable supply to the urban areas. Farmers are typically more concerned with maximizing their yields and profits than with environmental benefits or risks. Even though the metal concentrations in wastewater effluents are usually low, long-term irrigation of land with such water can ultimately result in heavy metal buildup in the soil.

2.12.5 Air-borne Sources

Heavy metals can infiltrate the atmosphere from various sources, presenting a significant environmental concern. Emissions from industrial stacks or ducts, carrying gas or vapor streams, represent a primary origin of airborne heavy metal contamination (Wauna & Okieimen, 2011). Additionally, particulate matter from storage areas or waste piles can contribute to the dissemination of metals into the air.

Metals are typically emitted in particulate form, coexisting with gases during release. For instance, during processes involving high temperatures, certain metals, such as lead, can undergo volatilization and transform into oxides. Without proper maintenance of a reducing atmosphere, these oxides can subsequently condense into fine particulates (Obernberger *et al.,* 2006). This is common in industries such as smelting and refining, where metals like arsenic, cadmium, and mercury can also become airborne. Another significant source of airborne heavy metal contamination is vehicular emissions. Exhaust from cars, particularly those using leaded gasoline, has historically been a major contributor to atmospheric lead levels. Although the use of leaded gasoline has been largely phased out, vehicles still emit other heavy metals, such as zinc, copper, and chromium, from tire wear, brake linings, and lubricants (Obernberger *et al.,* 2006).

The dispersion of heavy metals through airborne pathways poses significant risks to environmental and human health. Once airborne, these contaminants can travel over long distances before settling onto soil, water bodies, and vegetation (Obernberger *et al.,* 2006). For example, Lead particles from industrial emissions can settle in residential areas, leading to chronic exposure through inhalation and ingestion, especially in children. Inhalation of contaminated air and subsequent deposition can lead to bioaccumulation in ecosystems, threatening biodiversity and human well-being.

2.13 Methods of Analysis: Microwave Plasma Atomic Emission Spectroscopy

There are various methods for analysis of heavy metals, including Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Flame Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Microwave Plasma Atomic Emission Spectroscopy (MP-AES). However, for this particular study, MP-AES was used due to its extra sensitivity and low cost of operation. MP-AES uses very cheap consumables such as hollow cathode lamps since it is an atomic emission technique (Balaram, 2020).

Microwave Plasma Atomic Emission Spectrometry is a fast sequential multi-element analytical instrument that uses a microwave excitation assembly to generate a concentrated axial magnetic field surrounding a conventional torch (Vysetti, 2014). This configuration effectively focuses and confines the microwave energy,

creating a steroidal plasma with a cooler central channel. The conventional sample introduction system will allow for the stable introduction of liquid samples.

The emission intensities of different elements depend on factors such as sample flow rate, flow of the gas and microwave power. To achieve higher plasma stability and maximum emission intensity, nebulizer gas flow, observation height, optimization of plasma gas flow and other operating parameters is crucial. 2.11.2 Principles of MP-AES.

It operates based on the principles of Atomic Emission Spectroscopy (Vysetti *et al.,* 2014). It shares similar principles with other emission techniques. The intensity of each emitted line directly corresponds with the concentration of a specific element. The technique involves several steps, including sample introduction into a high-temperature plasma source, formation of the atom, excitation and emission of atoms, measurement of emitted light intensity at a specific wavelength of interest, and computation of concentration by comparing it to a known concentration.

Liquid and gas samples can be directly injected, while solid samples need sample preparation to have it in solution form. Solid samples are converted into aerosols and directed into the central channel of the plasma. Figure 2.4, provides a schematic diagram illustrating the working principle of MP-AES (Vysetti *et al.,* 2014).

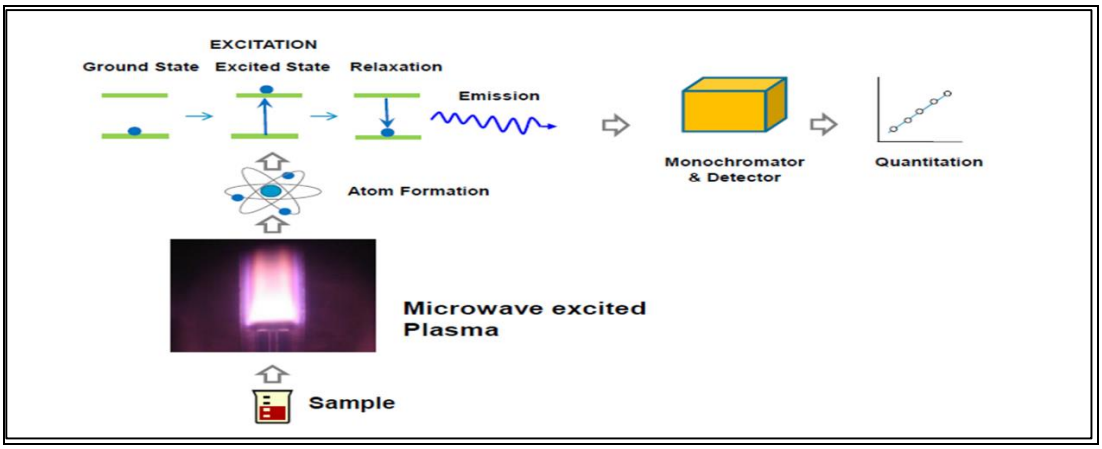


Figure 2.4: Working Principle of MP-AES (Vysetti et al., 2014)

2.14 Summary

The literature review in this chapter comprehensively examines the heavy metal pollution, focusing on its impact on soil and food materials, particularly tomatoes. It elucidates the various sources and pathways of heavy metal contamination, attributing significant roles to urbanization, industrial activities, and agricultural practices like the application of fertilizers and pesticides. The chapter discusses the contamination levels of heavy metals such as Pb, Cd, Cu, and Cr in tomatoes, referencing studies that demonstrate the substantial transfer of these metals from soil to plants. Additionally, it explores the health implications of heavy metal exposure, highlighting the risks posed by ingestion through contaminated food and environmental exposure. The review emphasizes the urgent need for rigorous monitoring and management of heavy metal levels in agriculture to safeguard food safety and public health.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Introduction

Initially, this chapter addresses issues related to sampling, including the sampling sites, research design, and sample collection. Secondly, the chapter considers methods for analyzing the samples, which include sample pretreatment, sample digestion, and elemental analysis. Finally, this section discusses the statistical methods and software used to analyze the data.

3.2 Study Area

Kirinyaga County is located in the central region of Kenya about 120 km from Nairobi. The County lies between 0.6591° S and 37.3827° E and covers an area of 1478.1 km^2 of which 801.7 km^2 is under agricultural production (KNBS, 2019). As shown in Figure 3.1, the county is divided into five sub-counties i.e. Kirinyaga Central, Kirinyaga East, Kirinyaga West, Mwea East and Mwea West (MoALFC, 2021). In 2019, the County had a population of 610411 persons with a projected annual growth of 1.5 % (KNBS, 2019).

Kirinyaga County has three ecological zones, namely, the lowland, the midland and the highland zones (Jaetzold *et al*., 2010). The lowland zone lies between 1158-2000 m above the sea level and covers most of Mwea East and Mwea West sub-counties (Jaetzold *et al*., 2010; MoALFC, 2021). The midland zone lies between 2000-3400 m above the sea level and covers the lower regions of Kirinyaga Central, Kirinyaga East, Kirinyaga West sub-counties (Jaetzold *et al*., 2010; MoALFC, 2021). The highland zone covers the upper regions of Kirinyaga Central, Kirinyaga East, Kirinyaga West sub-counties and the forested regions of Mount Kenya (MoALFC, 2021). Kirinyaga experiences bimodal annual rainfall with long rains falling between the months of March and May and short rains falling between the months of October and December (Jaetzold *et al*., 2010). Rainfall increases with altitude and ranges from 800-2200 mm per annum (Jaetzold *et al*., 2010). The annual average temperature in the study area ranges from 9.7-21.6ºC (Waiganjo *et al*., 2006). The major rivers that support farming in the study area include Thiba, Nyamindi, Tana, Ragati, and Rwamuthambi rivers (Jaetzold *et al*., 2010).

The area consists primarily of the volcanic bedrock of Mt. Kenya with some isolated areas having rocks of the basement System (Jaetzold *et al*., 2010). Fertile volcanic soils are found in the midland and highland zones of the study area (Jaetzold *et al*., 2010). Dark grey to black cotton soils predominate in the lowland zone (Jaetzold *et al*., 2010). Major crops in the study area include tomatoes, beans, maize, bananas, coffee and tea (Jaetzold *et al*., 2010; MoALFC, 2021). In addition, rice and horticultural crops are grown under irrigation in the lowland zone (MoALFC, 2021).

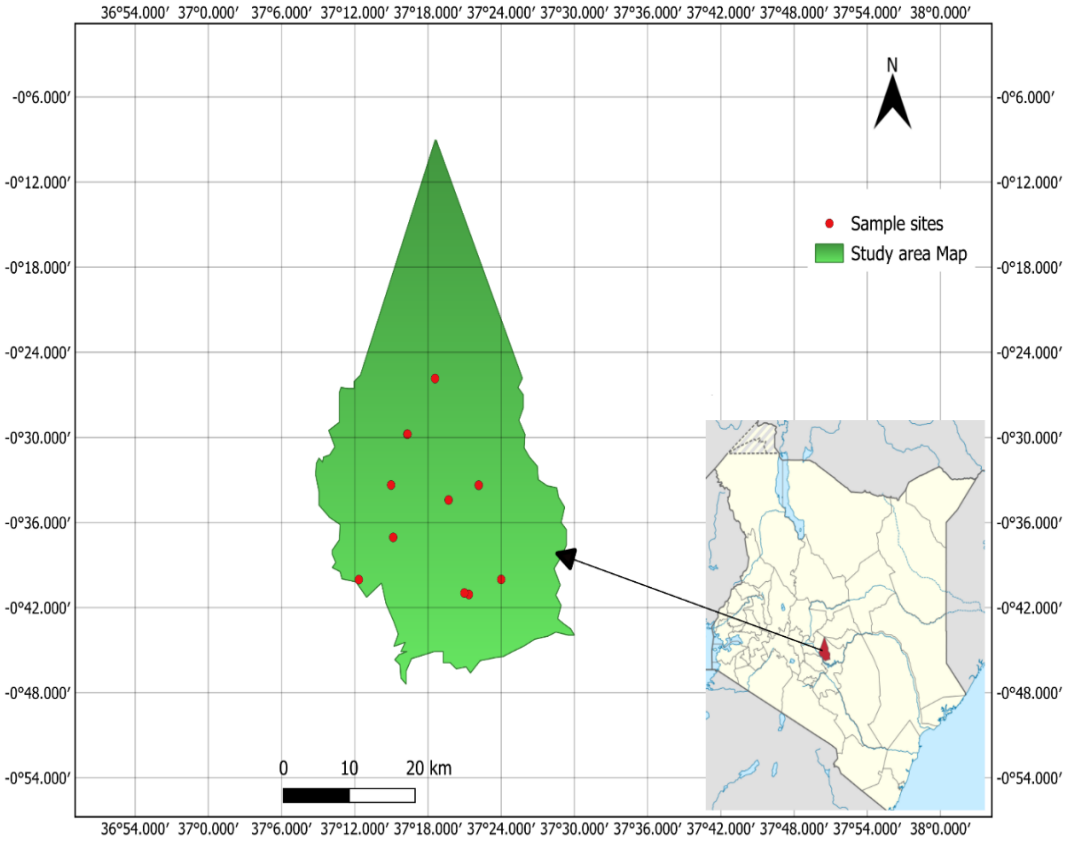


Figure 3.1: Map of a Kirinyaga County showing the Sampling Sites (QGIS)

3.3. Research Design

The experimental design involved determining the concentration of heavy metals in Soil, Tomato, and commonly used inorganic Fertilizer samples from three distinct ecological zones within Kirinyaga County: the highland zone, middle land zone, and lowland zone. Samples were randomly collected from various farms in each ecological zone to ensure representativeness. In the highland zone, samples were obtained from prominent tomato-producing areas, including Kerugoya, Baricho, and Kimunye. The middle land zone included regions such as Sagana, Kagio, and Mururi. In the lowland

zone, characterized by warmer temperatures conducive to extensive tomato cultivation, samples were obtained from Wang'uru, Kiriko, and Thiba. Samples of commonly used inorganic fertilizers were obtained from Agro Vets shops from each of the three ecological zones based on information given by farmers. Upon pretreatment and digestion, the samples were analyzed using Microwave Plasma-Atomic Emission Spectroscopy (MP-AES) to determine their concentrations.

3.4 Collection of Samples

3.4.1. Collection of Soil and Tomatoes Samples

Samples of soils and tomatoes were collected from twenty-seven farms in the three ecological zones of Kirinyaga County. As shown in Table 3.1, samples were collected at nine farms in the highland zone at Kimunye, Kerugoya and Baricho areas. In the midland zone samples were collected at nine farms at Sagana, Kagio and Mururi areas. In the lowland zone, samples were collected at nine farms at Wang'uru, Kiriiko and Thiba areas. Three of samples of tomatoes and three soil samples were collected at each sampling area.

Table 3.1: Sampling Sites, Sample Type and Number of Samples

Regions	**Location**	**Type of samples**	**Number of samples**
Highland zone	Kimunye	Tomatoes	3
		Soil	3
	Kerugoya	Tomatoes	3
		Soil	3
	Baricho	Tomatoes	3
		Soil	3
Midland zone	Sagana	Tomatoes	3
		Soil	3
	Kagio	Tomatoes	3
		Soil	3
	Mururi	Tomatoes	3
		Soil	3
Lowland zones	Wang'uru	Tomatoes	3
		Soil	3
	Kiriko	Tomatoes	3
		Soil	3
	Thiba	Tomatoes	3
		Soil	3
Total			54

Two Kilograms of tomatoes were collected from each sampling site. The tomatoes were randomly selected, wrapped in pre-cleaned aluminum foil, placed in polythene bags, and transported to the chemistry department laboratory at Murang'a University of Technology. Soil samples were simultaneously collected at a depth of 2.5 to 15 cm at each sampling point using a stainless steel soil auger. The soil samples were placed in pre-cleaned polyethylene bags and transported to the laboratory.

3.4.2 Collections of Fertilizer Samples

To obtain the fertilizer samples that farmers applied, farmers were requested to establish contact with the Agro Vet shops from where the fertilizer was purchased. Approximately 1/4 Kg of the commonly used inorganic fertilizer samples were purchased in all three ecological zones. In total, 7 different fertilizer samples were collected from all the three zones. Subsequently, the collected samples were packed and transported to the laboratory for further analysis.

3.5. Analysis of Samples

3.5.1. Pretreatment of Soil and Tomatoes Samples

Tomato samples were thoroughly washed with distilled water to remove any adhering dirt, sliced into small pieces using a stainless steel knife and air-dried for 24 h to remove moisture (Esther *et al.,* 2016). The dried samples were then placed in a Memmert oven for 24 h at 105°C, cooled and ground into powder using a mortar and pestle. The powder was then sieved using a 150-mesh sieve (Anugrahwati *et al*., 2020). Large particles and other detritus materials were removed from soil samples. The samples were then air-dried for 24 h, oven dried for 24 h at 105°C, ground into powder with a mortar and pestle and sieved using a 150-mesh sieve (Anugrahwa *et al.,* 2020).

3.5.2. Pretreatments of Fertilizer Samples

Pretreatment of fertilizer sample was done following the procedures described by Modaihsh *et al.,* 2004. The samples were air-dried, then placed in a Memmert oven for 24 hours at 105°C. After cooling, the samples were ground into a fine powder using a mortar and pestle. The powdered samples were then sieved through a 150-mesh sieve mm mesh to remove any larger particles or debris. The sieved samples were stored in airtight containers to prevent contamination and degradation before the analytical procedures were performed.

3.5.3. Digestion of Samples

The dry ashing method described in the literature by Anugrahwati and co-workers was used to digest all the samples (Anugrahwati *et al.,* 2020). 2.0 g of each powdered sample was placed in a beaker then 6.0 mL of H_2O and 4.0 mL of 35% HNO_3 were added to the beaker. The beaker was then heated on a hotplate at 100-120^oC to dryness. The resultant sample was heated in a muffle furnace for 1 h at 500^oC, cooled down

and quantitatively transferred to a 100 mL volumetric flask. The volumetric flask was topped with a solution of 2% of HNO_3 and the mixture shaken thoroughly to homogenize and filtered using Whatman filter paper No. 42 and a 0.22-micron syringe filter.

3.5.4 Elemental Analysis

A microwave plasma atomic emission spectrometer (Agilent-4210) was used to measure heavy metal levels in tomato samples. Three duplicates of each standard, blank, and sample were analyzed. Heavy metal content was determined using a four-point calibration curve of a multi-element standard in emission mode. The method was validated for precision and accuracy. The device was calibrated for various parameters before the experiments were conducted.

A pre-digested samples was spiked with 5 mg/Kg, prepared by serial dilution of a 1000 mg/Kg stock standard solution, ensuring quality assurance (Yue *et al*., 2022). The same digestion process was then simultaneously applied to both non-spiked and spiked samples. The levels of the heavy metals in each type of sample were determined by MP-AES, and the percentage recovery was calculated using the following equation.

$$\%\ Recovery = \left(\frac{Concentration\ in\ spiked\ samples - Concentration\ in\ non{-}spiked\ samples}{Amount\ added}\right) x100$$

3.5.5 Operating Condition for MP-AES

The operating conditions for microwave plasma atomic emission spectroscopy (MP-AES) are detailed in Table 3.2. Key parameters include background correction set to auto (Except for Cd and Mo), OneNeb series 2 nebulizer with a 0.5 L/min flow rate, and specific settings for read, rinse, stabilization, and uptake times. The system uses orange/green sample tubing, operates at a pump speed of 15 rpm, and employs a double-pass spray chamber. Total run time for the analysis is 5 minutes.

Table 3.2: Operating Condition for MP-AES

Parameters	Settings
Background correction	Auto (Except Cd and Mo: off-peak right)
Replicates	3
Nebulizer	OneNeb series 2, with nitrogen humidifier
Nebulizer flow (L/min)	0.5
Viewing position	0
Read time (s) Rinse time (s)	3 (Except Pb, 5s and Cd, 10s) 30
Stabilization time (s)	15
Uptake time (s)	120
Sample tubing	Orange/green
Pumps speed (rpm)	15
Calibration fit	Linear/Rational
Spray chamber	Double-pass
Drain tubing	Blue
Total run time (min)	5

3.6 Statistical Analysis.

A Microsoft Excel spreadsheet and IBM statistical software, version 25.1 of the Statistical Package for Social Sciences (SPSS), were used to conduct all of the statistical tests. Microsoft Excel was used to calculate the means, standard deviation, and relative standard deviation, among other descriptive statistics. Multivariate statistical analysis was used to examine the differences in heavy metal concentrations found in fertilizer, tomato and soil samples taken different zones. In order to ascertain the coherence and divergence of the data, the Pearson correlation analysis was used to examine the correlation between variables.

3.7 Bioaccumulation Index

The bioaccumulation index (BI) was used to determine the ability of the tomato fruits to bioaccumulation the target metals from the soil (Trebolazabala *et al*., 2017; Vukelić *et al*., 2021). The BI was defined as the percentage of metal concentration in tomato

fruits to that of the metal in cultivation soil (Trebolazabala *et al*., 2017; Vukelić *et al*., 2021).

$$\text{BI} = \frac{Concentration\ of\ metal\ in\ tomato\ fruit}{Concentration\ of\ metal\ in\ soil} \text{ X } 100$$

3.8 Summary

The chapter outlines the methodology used in this research to achieve the intended objective. It first addresses sampling issues, detailing the sampling sites, research design, and sample collection process. The study was conducted in Kirinyaga County, Kenya, covering three ecological zones: Lowland, Midland, and Highland, each characterized by distinct agricultural activities and climatic conditions. Samples were collected from 27 farms and included soil, tomatoes, and fertilizers. The pretreatment processes including washing, drying, and crushing were done before digestion using a dry ashing method. The experimental design involved determining heavy metal concentrations using Microwave Plasma-Atomic Emission Spectroscopy (MPAES). Elemental analysis was then performed using MP-AES, with strict calibration and quality assurance measures in place.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This section deals with the data obtained from the analytical instruments used to analyze the soil, tomatoes, and inorganic fertilizer samples. This is followed by the interpretations of the data in line with the three objectives of the study. These interpretations or discussions of the results form the basis for the conclusions ahead. Results and discussions concerning Objective One, which was to determine the concentrations of selected heavy metals in soil and tomato samples in Kirinyaga County, are captured in Sections 4.3 and 4.4. For Objective Two, which was to determine the concentrations of selected heavy metals in inorganic fertilizer samples, the results and discussions are captured in Section 4.5. Finally, Objective Three, which was to determine the correlations of selected heavy metals in soil, tomatoes, and inorganic fertilizers in Kirinyaga County, is captured in Sections 4.14.

4.2 Recovery of Selected Metals from Spiked Samples

Matrix spiking was used to evaluate the performance of the MP-AES analytical method for analysis of the selected heavy metals. The percent recoveries of the metals from the spiked samples are shown in Table 4.1. The percent recoveries ranged from 99.4-100.1%. The obtained recoveries are within the acceptable range of 80-120% for metals (Harvey, 2000). Thus, matrix effects were minimal and the metals were quantified using the standard calibration method (Trancoso *et al*., 2003).

Table 4.1: Spike Recoveries for Selected Metals in Tomatoes Samples

Heavy Metals	***Conc. in Non-Spiked sample (mg/Kg)**	**Added amount (mg/Kg)**	****Conc. in spiked sample (mg/Kg)**	**Percentage recovery (%)**
Cd	0.0085	5.000	5.009	100.1
Pb	0.0141	5.000	5.011	99.40
Cu	0.0390	5.000	5.020	99.60
Cr	0.0110	5.000	5.010	99.90

*Average Value; **Mean of Triplicate; % Mean Value of Triplicate.

4.3 Concentrations of Selected Metals in Soil Samples

The mean concentration of heavy metals in soil samples from each sampling area are shown in Table 4.2. The concentrations of cadmium in the highland zone (Kerugoya, Kimunye and Baricho areas) ranged from 0.0533-0.0570 mg/Kg. The mean concentrations of cadmium in the midland zone (Sagana, Kagio and Mururi areas) ranged from 0.0933-0.1133 mg/Kg. The mean concentrations of cadmium in the lowland zone (Wang'uru, Kiriko and Thiba areas) ranged from 0.0100-0.0800 mg/Kg. The mean concentrations of cadmium in all areas were below the 0.3000 mg/Kg maximum tolerable limit for cadmium in soil established by WHO/FAO, 2021). However the midland levels of cadmium is higher because there is more agricultural activities happening than in the highland and the lowland zones. Tea farming (Monocroping) is dominant in the highland zones whereas in the lowland zone mostly rice farming is dominates (Monocroping) but in the middle is mixed farming is done. Cadmium is a non-essential heavy metal that is naturally present in all soils with background concentrations of 0.1000-1.000 mg/Kg (Smolders and Mertens, 2013). Anthropogenic sources of cadmium in soils include phosphate fertilizers, sewage sludge and atmospheric deposition (Smolders and Mertens, 2013).

Table 4.2: Mean Concentrations of Selected Metals in Soil Samples

Sampling Area	**Mean Concentration (mg/Kg)**			
	Cd	**Pb**	**Cu**	**Cr**
Kerugoya	0.0567±0.033	0.0570±0.057	1.167±0.067	0.9667±0.088
Kimunye	0.0533±0.033	0.1400±0.042	1.500±0.115	1.200±0.058
Baricho	0.0570±0.033	0.1533±0.042	1.100±0.058	0.7667±0.080
Sagana	0.1133±0.067	0.2100±0.001	1.267±0.120	0.8333±0.115
Kagio	0.0933±0.145	0.1150±0.012	0.8667±0.273	0.8400±0.163
Mururi	0.1000±0.100	0.3433±0.030	1.667±0.176	1.333±0.040
Wang'uru	0.0567±0.033	0.6670±0.0367	1.833±0.088	0.8000±0.170
Kiriko	0.0100±0.100	0.2900±0.046	1.467±0.033	0.0670±0.060
Thiba	0.0800±0.057	0.3100±0.057	1.900±0.058	0.7833±0.060
Mean ± SE	0.0689±0.067	0.2060±0.0358	1.419±0.109	0.8433±0.092
RSD (%)	45.33	50.24	24.50	41.85

RSD, Relative Standard Deviation; SE, Standard Error.

The mean concentrations of lead in the highland, midland and lowland zones ranged from 0.0570-0.1530, 0.1150-0.3433 and 0.2900-0.6670 mg/Kg, respectively. The mean concentrations of lead in the three agro-ecological zones were below the 10 mg/Kg maximum tolerable limit for lead in soil established by WHO/FAO, 2021. The global background concentrations of lead in soils is estimated to be 17.00 mg/Kg (Nriagu, 1978). The mean concentrations of lead in soils from the study area are therefore considerably lower than the mean concentrations in uncontaminated soils worldwide. This indicate that the amount of naturally occurring lead in the soils in very low. In addition, the soils in the study area are not contaminated with lead from anthropogenic sources such as sewage sludge, mining and smelting of lead, insecticides, lead-based paints, car batteries and leaded gasoline (Steinnes, 2013).

The mean concentrations of copper in the highland, midland and lowland zones ranged from 1.100-1.500, 0.8667-1.667 and 1.467-1.900 mg/Kg, respectively. The mean concentrations of copper in the three ecological zones were significantly lower than the 36 mg/Kg maximum tolerable limit for copper in soil established by WHO/FAO, 2021. The mean concentrations of copper are also lower than the background concentrations of copper (2-50 mg/Kg) in unpolluted soils (Oorts, 2013). This suggest that soils in the study area are generally not contaminated with copper from anthropogenic sources such as fertilizers, sewage sludge and pesticides (Oorts, 2013).

The mean concentrations of chromium in the highland, midland and lowland zones ranged from 0.7667-1.200, 0.8333-1.333 and 0.0670-0.8000 mg/Kg, respectively. The mean concentrations of chromium in the three ecological zones were significantly lower than the 65 mg/Kg maximum tolerable limit for chromium in soil established by WHO/FAO, 2021. The concentrations of chromium in unpolluted soils are usually between 0.5 to 250 mg/Kg with average values of between 40 and 70 mg/Kg (Gonnelli and Renella. 2013). The concentrations of chromium in soils in the study area suggests that the soils are not polluted with chromium from anthropogenic sources. The differences in the concentrations of chromium in the study area can be attributed to geological variations. High concentrations of chromium are found in mafic and ultramafic rocks while low concentrations are found in sedimentary rocks (Gonnelli and Renella. 2013). The spatial variations in the concentration of the heavy metals in soils can be attributed to the different types of soils in the study area. Soils in the

highland and midland zones are the well-drained ando-humic nitisols, with humic andosols and humic nitisols, respectively (Jaetzold *et al*., 2010). Soils in the lowland zone are the pellic vertisols and verto-eutric nitisols, with mollic nitisols (Jaetzold *et al*., 2010).

4.4 Concentrations of Selected Metals in Tomato Samples

The mean concentrations of cadmium, lead, copper and chromium in tomatoes obtained in the study area are shown in Table 4.3. The mean concentrations of cadmium in the highland zone ranged from 0.0053±0.008 to 0.0067±0.008 mg/Kg while concentrations in the midland zone ranged from 0.0037±0.003 to 0.0060±0.010 mg/Kg. The concentrations in the lowland zone ranged from 0.0040±0.005 to 0.0087±0.01 mg/Kg. The mean concentrations of cadmium in all areas were below the 0.05 mg/Kg maximum tolerable limit for cadmium in tomatoes established by WHO/FAO, 2021. Although the concentrations of cadmium in tomatoes are significantly lower than the maximum allowable concentration, there is need for vigilance because cadmium is highly toxic, bioaccumulate in living organisms and has a long biological half-life (25–30 years) in living organisms (Sankhla & Kumar, 2019; Genchi *et al*., 2020). Thus, cadmium can have several chronic effects including testicular damage, renal and hepatic dysfunction, *osteomalacia*, cancers and damage to the adrenals and hemopoietic system (Genchi *et al*., 2020).

The mean concentrations of lead in the highland, midland and lowland zones ranged from 0.0013±0.003 to 0.0060±0.041, 0.0037±0.003 to 0.0063±0.01 and 0.0020±0.01 to 0.0067±0.02 mg/Kg, respectively. These concentrations are significantly lower than the 0.10 mg/Kg maximum tolerable limit for lead in tomatoes established by WHO/FAO, 2021. Nevertheless, lead is highly toxic and bioaccumulate in tissues leading to adverse chronic effects including disorders of the central nervous system, neurological effects (e.g. developmental delays and nerve damage in adults) and cardiovascular diseases (Li *et al*., 2020).

The mean concentrations of copper in the highland, midland and lowland zones ranged from 0.0330±0.006 to 0.0467±0.003, 0.0367±0.003 to 0.0433±0.003 and 0.0533±0.003 to 0.0667±0.003 mg/Kg, respectively. These concentrations are significantly lower than the 5.0 mg/Kg maximum tolerable limit for copper in tomatoes established by WHO/FAO, 2021 listed in Table 1. The copper levels in this

study are considerably lower than those reported in vegetables from peri-urban and rural communities. For instance, a study on vegetable contamination in peri-urban communities reported much higher Cu levels, often exceeding the recommended limits (Tomno et al., 2020). This suggests that tomatoes from the highland, midland, and lowland zones of Kirinyaga County are less contaminated and safer for consumption concerning Cu levels. The lower Cu concentrations found in this study could be attributed to differences in agricultural practices, such as the types of fertilizers and pesticides used, and environmental factors that affect metal uptake by plants. Copper, being an essential micronutrient, is vital for the health of all living organisms (Liu et al., 2023). It is present in several enzymes and proteins crucial for maintaining a healthy central nervous system and preventing neurological diseases like aceruloplasminemia, amyotrophic lateral sclerosis, and Wilson disease (Desai and Kaler, 2008).

Table 4.3: Mean Concentrations of Selected Metals in Tomato Samples

Sampling Area	Metal Concentrations (mg/Kg)			
	Cd	**Pb**	**Cu**	**Cr**
Kerugoya	0.0067±0.008	0.0015±0.003	0.0333±0.006	0.0270±0.001
Kimunye	0.0060±0.020	0.0060±0.041	0.0467±0.003	0.0120±0.001
Baricho	0.0053±0.008	0.0013±0.003	0.0330±0.006	0.0270±0.035
Sagana	0.0060±0.010	0.0063±0.010	0.0267±0.003	0.0170±0.006
Kagio	0.0037±0.003	0.0040±0.005	0.0367±0.003	0.0110±0.006
Mururi	0.0050±0.015	0.0037±0.003	0.0433±0.003	0.0130±0.001
Wang'uru	0.0067±0.010	0.0067±0.020	0.0533±0.006	ND
Kiriko	0.0040±0.005	0.0020±0.010	0.0667±0.003	0.0140±0.000
Thiba	0.0087±0.010	0.0063±0.010	0.0533±0.003	0.0120±0.003
Mean ± SE	0.0058±0.099	0.0042±0.011	0.0448±0.004	0.0186±0.006
RSD (%)	26.29	52.45	25.27	39.00

ND, Not Detected; RSD, Relative Standard Deviation; SE, Standard Error

The mean concentrations of chromium in the highland and midland zones ranged from 0.0120±0.001 to 0.0270±0.035 and 0.0110±0.006 to 0.0170±0.006 mg/Kg, respectively. Chromium was not detected in samples obtained in Wang'uru area. The

mean concentrations of chromium in samples obtained from Kiriko and Thiba areas were 0.0140±0.000 and 0.0120±0.003 mg/Kg, respectively. The concentrations of chromium are significantly lower than the maximum allowable limit of 2.3 mg/Kg set by the WHO/FAO, 2021. Chromium exists in two oxidation states, the trivalent chromium (III) and the hexavalent chromium (VI), which is highly toxic (Genchi *et al*., 2021). Chromium (III) is essential for humans in trace amounts for metabolism of glucose, proteins and lipids (Genchi *et al*., 2021). However, in larger concentrations chromium have several adverse effects including and cardiovascular, gastrointestinal, hepatic and renal damage (Genchi *et al*., 2021). Gebeyehu & Bayissa (2020) have reported the presence of Pb, Cd, Cu and Cr in fresh tomatoes. Briffa *et al.,* 2020 demonstrated clearly that heavy metals specifically Cd and Pb present in the tomato fruits originate from contaminated fertilizers applied in the crops.

4.5 Concentrations of Selected Metals in Commonly used Inorganic Fertilizers

The concentrations of the selected heavy metals in inorganic fertilizers commonly used during production of tomatoes in Kirinyaga County are given in Table 4.4. The mean concentrations cadmium in the samples ranged from 0.2±0.21 to 1.7±0.21 mg/Kg. The NPK 27-10 -16 + TE EASY GROW and NPK 22-21-17 Murphy Foliar Feeds had the lowest cadmium concentrations of 0.2±0.21 mg/Kg. Among the NPK fertilizers, NPK 23-23-0 had the highest cadmium concentration of 1.2±0.21mg/Kg. The mean concentration of cadmium in DAP 18-46-0 was 1.7±0.21 mg/Kg. The concentrations of cadmium in these fertilizers are comparable to those obtained in a previous study that assessed the quality of fertilizers in the Kenya (Sanabria *et al*. 2018). The mean concentration of cadmium in NPK 23-23-0, DAP 18-46-0 and NPK 10-26-10 Mavuno were 0.46, 2.90 and 0.12 mg/Kg, respectively (Sanabria *et al*., 2018). In addition, the mean concentration in NPK 17-17-17, NPK 27-10-16 + TE Easy Grow, NPK 22-21-17 Murphy Foliar Feeds and NPK 15-5-35 + MgO + TE Agrigrow were, respectively, 0.23, 0.55, 0.24 and 0.11 mg/Kg (Sanabria *et al*., 2018). The concentrations of cadmium in the aforementioned fertilizers were significantly lower than the maximum permissible limits of 15.0 mg/Kg established for fertilizers by the Kenya Bureau of Standards (Lopez *et al.,* 2008).

Table 4.4: Mean Concentrations of Selected Metals in Fertilizer Samples

Fertilizer Types	**Cd**	**Pb**	**Cu**	**Cr**
NPK 23 23 0	1.2±0.21	2.1±0.44	1.9±0.18	5.8±0.74
DAP 18 46 0	1.7±0.21	3.5±0.44	2.1±0.18	3.3±0.74
NPK 10 26 10 Mavuno	0.8±0.21	2.3±0.44	1.2±0.18	0.9±0.74
NPK 17 17 17	0.8±0.21	2.1±0.44	1.8±0.18	0.9±0.74
NPK 27 10 16 + TE Easy Grow	0.2±0.21	ND	1.2±0.18	1.1±0.74
NPK 22 21 17 Murphy Foliar Feeds	0.2±0.21	1.1±0.44	0.8±0.18	1.4±0.74
NPK 15 5 35 + MgO + Te Agrigrow	0.3±0.21	0.4±0.44	1.2±0.18	4.4±0.74
Mean±SE	0.7±0.21	1.9±0.44	1.5±0.18	2.5±0.74
RSD%	16.09	15.65	32.64	17.69

ND, Not Detected; RSD, Relative Standard Deviation; SE, Standard Error

The concentration of cadmium in phosphates fertilizers depends on the concentration of cadmium in phosphate rock deposits used in their manufacture. Igneous phosphate rock deposits contain low concentrations (<1-4 mg/Kg) of cadmium (Carne *et al.,* 2014). Major igneous phosphate rock deposits are found in South Africa, Russia and Brazil (Roberts, 2014). Sedimentary phosphate rock deposits contain higher concentrations (< 1-150 mg/Kg) of cadmium and are found in several countries including China, Morocco and USA (Roberts, 2014). Most NPK fertilizers used in the Kenya in 2022 (92%) and 2023 (97%) were imported from Russia while DAP was sourced from Morocco (57% in 2022 and 26% in 2023) and Saudi Arabia (43% in 2022 and 74% in 2023) (Ortiz et al., 2019). The low concentration of cadmium in NPK fertilizers is therefore consistent with the low concentration (<1-2 mg/Kg) of cadmium in Russian phosphate deposits (Carne *et al.,* 2014).

The concentration of lead in the fertilizers ranged from ND-3.5±0.44 mg/Kg. The concentration of lead in NPK 27-10-16 + TE Easy Grow was below the detection limit. The concentration of lead in NPK 15-5-35 + MgO + Te Agrigrow, NPK 22-21-17 Murphy Foliar Feeds and NPK 17-17- 17 were 0.4±0.44, 1.1±0.44 and 2.1±0.44 mg/Kg, respectively. Relatively higher concentration of lead was found in NPK 23-23-0 (2.1±0.44 mg/Kg) and DAP 18-46-0 (3.5±0.44 mg/Kg). The concentrations of lead in all samples were lower than the maximum permissible limits of 30.0 mg/Kg established by the Kenya Bureau of Standards (Lopez et al., 2008).

The concentrations of copper in the samples ranged from 0.8±0.18 to 2.1±0.18 mg/Kg. NPK 10-26-10 Mavuno had the lowest concentration (0.8±0.21mg/Kg) while DAP 18-46-0 had the highest concentration (3.5±0.44 mg/Kg) of copper levels. The European Union has set the maximum permissible concentration of copper in inorganic macronutrient fertilizers (in which copper has not been intentionally added to correct a soil micronutrient deficiency) at 600 mg/Kg dry matter (EU, 2023). The concentration of copper in the samples are therefore two orders of magnitude lower that the European Union limit.

The concentrations of chromium ranged from 0.9±0.74 to 5.8±0.74 mg/Kg. The lowest concentration of 0.9±0.74 mg/Kg was recorded for NPK 10-26-10 Mavuno and NPK 17-17-17 while the highest concentration (5.8±0.74 mg/Kg) was obtained for NPK 23-23-0 fertilizer. The concentrations of chromium in all samples were lower

than the maximum permissible limits of 500.0 mg/Kg established by the Kenya Bureau of Standards (Lopez *et al*., 2008). In a study by Singh *et al.* (2010), chromium levels in vegetables irrigated with wastewater were significantly higher, often exceeding safe limits. This discrepancy is due to contamination sources; while the current study focuses on fertilizers, Singh et al. highlighted industrial effluents and untreated wastewater as major contributors to heavy metal accumulation in crops. The lower Cr levels in fertilizers from the current study suggest minimal contamination from agricultural inputs compared to the broader environmental contamination described in the literature. Muchuweti et al. (2006) also reported elevated levels of heavy metals, including chromium, in vegetables irrigated with mixtures of wastewater and sewage sludge, often exceeding safe limits. This underscores the risks of using contaminated water in agriculture. In contrast, the present study's findings indicate that fertilizers used in Kirinyaga County are relatively free from excessive Cr contamination, suggesting safer agricultural practices regarding fertilizer application.

4.6. Bioaccumulation Index

The bioaccumulation Index (BI) values obtained in the study are shown in Table 4.5. The BI for Cadmium, Lead, Copper and Chromium ranged from 4-12, 0.7-4, 2-5 and 0.9-3%, respectively. The BI values for these metals are very low suggesting that their accumulation in tomato fruits is low (Rodriguez-Iruretagoiena *et al*., 2015).

Table 4.5: Bioaccumulation Index of Selected Metals in Tomato Samples

Tomato sampling Areas	**Bioaccumulation Index**			
	Cd	**Pb**	**Cu**	**Cr**
Kerugoya	12	3.0	3.0	3.0
Kimunye	11	4.0	3.0	1.0
Baricho	9.0	0.9	3.0	3.0
Sagana	5.0	3.0	2.0	2.0
Kagio	4.0	3.0	4.0	1.0
Mururi	5.0	1.0	2.0	0.9
Wang'uru	12	0.9	3.0	*
Kiriko	4.0	0.7	5.0	20
Thiba	11	2.0	3.0	2.0

* Soil/Tomato ratio was not computed, one of the value is below the Detection Limit.

The uptake of heavy metals by tomato fruits is influenced by several factors including the rate of absorption of heavy metals by the roots and the efficiency of their translocation from the roots to the aerial parts (stems, leaves and fruits) of tomatoes (Eid *et al*., 2021). The rate of absorption of heavy metals by roots depends on among other factors the bioavailability of the heavy metals in the soil. The bioavailability of metals in soils depends on several factors including the pH, redox potential, clay content and organic matter content of the soil (Rieuwerts *et al*., 1998). Translocation of the metals from the roots to aerial parts depends on several factors including the nature of the metal, the plant species and its physiology (Eid *et al*., 2021).

4.7 Comparative ANOVA Analysis of Tomato and Soil Samples

Table 4.6 presents descriptive statistics for soil and tomato samples, highlighting significant differences in their concentrations. The data includes Mean values, Standard errors, Standard deviations, Sample variances, Ranges, Minimum and Maximum values, and 95% confidence levels for Cadmium, Lead, Copper, and Chromium. Soil samples consistently show higher concentrations of these metals compared to tomato samples, reflecting the differential accumulation of these elements in different matrices. The provided statistics offer a detailed overview of the variability and distribution of metal concentrations within the sampled population.

Table 4.6: Descriptive Statistics for Soil and Tomato Samples

Metal	Sample Type	N	Mean	Standard Error	Standard Deviation	Sample Variance	Range	Minimum	Maximum	Confidence Level (95%)
Cd	Soil	9	0.0689	0.0104	0.0313	0.0009	0.1033	0.0100	0.1133	0.0240
	Tomato	9	0.0058	0.0005	0.0015	2.3110	0.0050	0.0037	0.0087	0.0012
	Total	18	0.0747	0.0109	0.0328	2.3120	0.1083	0.0137	0.1220	0.0252
Pb	Soil	9	0.2540	0.0608	0.1824	0.0333	0.6100	0.0570	0.6670	0.1402
	Tomato	9	0.0042	0.0007	0.0022	4.8680	0.0053	0.0013	0.0067	0.0017
	Total	18	0.2582	0.0615	0.1846	4.9010	0.6153	0.0583	0.6737	0.1419
Cu	Soil	9	1.4190	0.1159	0.3476	0.1208	1.0330	0.8667	1.9000	0.2672
	Tomato	9	0.0448	0.0038	0.0114	0.0001	0.0337	0.0330	0.0667	0.0087
	Total	18	1.4630	0.1197	0.3590	0.1210	1.0670	0.8997	1.9670	0.2759
Cr	Soil	9	0.8433	0.1176	0.3529	0.1245	1.2660	0.0670	1.3330	0.2713
	Tomato	9	0.0148	0.0028	0.0083	6.9440	0.0270	0.0000	0.0270	0.0064
	Total	18	0.8581	0.1204	0.3612	7.0690	1.2930	0.0670	1.3600	0.2777

The mean Cd concentration in soil stands notably higher (0.0689mg/Kg) with a standard deviation of 0.0313 as compared with the mean concentration in tomato samples of 0.0058 mg/Kg with a standard deviation of 0.001519. These findings illustrate a considerable disparity in Cd levels between soil and tomato samples. When considering the combined dataset encompassing both soil and tomato samples, the overall mean Cd concentration averages at 0.0747 mg/Kg with a standard deviation of 0.0328, indicating a variation in Cd concentrations when considering both samples.

The analysis of Pb concentrations in soil and tomato samples reveals distinct mean values and deviations. In soil samples, the mean Pb concentration measures notably higher at 0.2540 mg/Kg with a Standard deviation of 0.1824. Conversely, in tomato samples, the mean Pb concentration is substantially lower, recording 0.0042 mg/Kg with a standard deviation of 0.0022. The combined total analysis across both soil and tomato samples yields an overall mean Pb concentration of 0.2582 mg/Kg with a standard deviation of 0.1846. These observations underscore significant variations in Pb concentrations between soil and tomato samples.

Determination of Cu concentrations across soil and tomato samples reveals distinctive mean values and variations. In soil samples, the mean Cu concentration is notably higher at 1.419 mg/Kg with a standard deviation of 0.3476. Conversely, in tomato samples, the mean Cu concentration is substantially lower, recording 0.0448 mg/Kg with a standard deviation of 0.0113 as shown in Table 4.6. Evaluating the combined dataset encompassing both soil and tomato samples, the overall mean Cu concentration averages at 1.4630 mg/Kg with a standard deviation of 0.359. These findings highlight significant differences in Cu levels between soil and tomato samples.

Analyzing Cr concentrations in soil and tomato samples reveals notable differences in mean values and deviations. In soil samples, the mean Cr concentration stands at 0.8433 mg/Kg with a standard deviation of 0.3529, while in tomato samples, the mean Cr concentration is substantially lower, recording 0.0148mg/Kg with a standard deviation of 0.0083. The combined total analysis across both soil and tomato samples yields an overall mean Cr concentration of 0.8581 mg/Kg with a standard deviation of 0.3612. These findings underscore considerable variations in Cr concentrations between soil and tomato samples.

4.8 Means Plots of Selected Metals in Soil and Tomato Samples

A mean plot in Figure 4.1 has been used to show the difference between the average levels of each of the four selected heavy metals in soil and tomato samples. The mean plot effectively illustrates the distribution of heavy metals in soil and tomato samples. From the plot it is evident that the means for Cd, Pb, Cu and Cr are higher in soil samples compared to the tomato samples as shown in the plot.

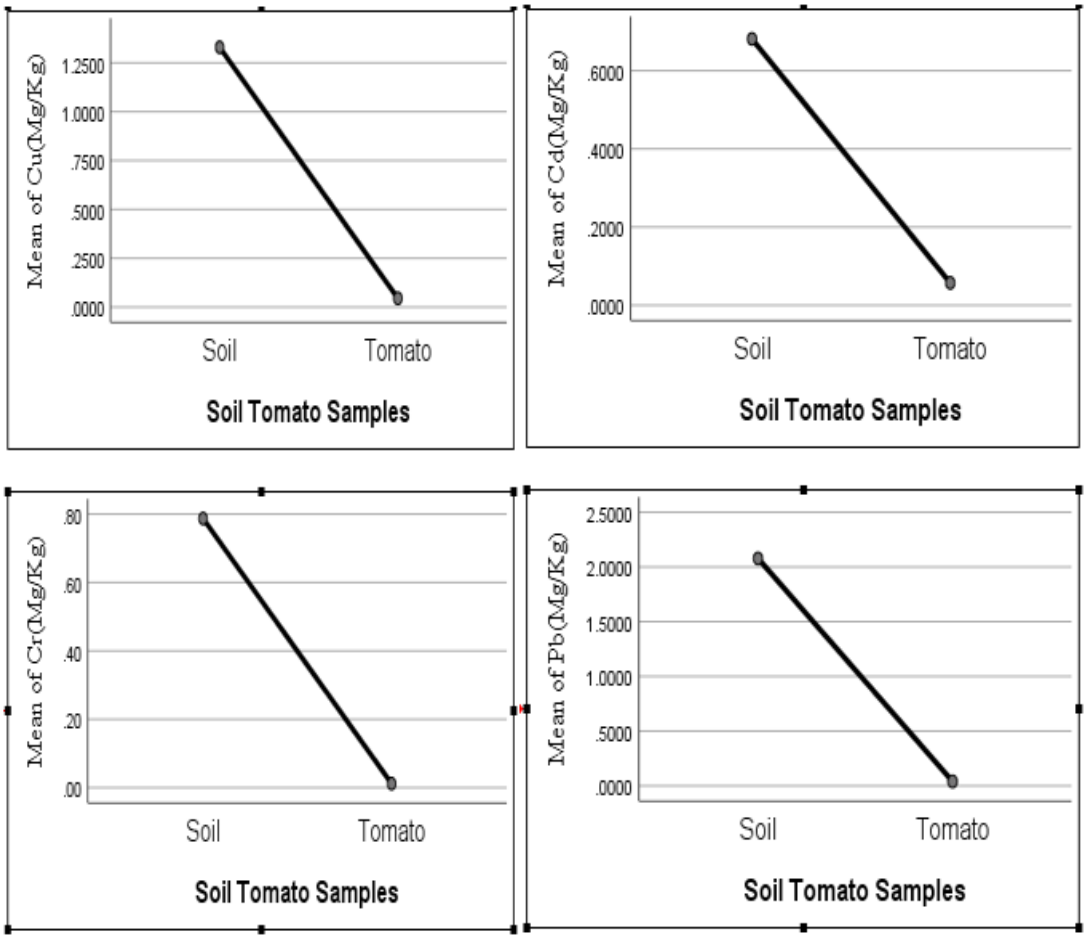


Figure 4.1: Mean Plots of Selected Metal Concentrations in Soil and Tomato Samples

The levels of heavy metals in all selected elements were found to be higher in soil samples compared to tomato samples. This suggests that while plant do absorb some heavy metals from the soil, their uptake is limited. Several factors could contribute to the limited uptake of heavy metals by tomatoes. First, heavy metal availability to plants can be influenced by soil pH and composition, with certain soil conditions causing heavy metals to form compounds that are less bioavailable (Latif *et al.,* 2018).

Additionally, different plant species and varieties have varying abilities to absorb and accumulate heavy metals. The use of organic matter and other soil amendments can also reduce the bioavailability of heavy metals, limiting their absorption by plants (Genchi *et al*., 2021). Furthermore, plants can release organic compounds through their roots that bind heavy metals, making them less available for absorption (Esther, *et al*., 2016).

4.9 Test of Homogeneity of Variance

The Table 4.7 displays the outcomes of the test of homogeneity of variances for various metals (Cd, Pb, Cu, Cr) measured in milligrams per kilogram (mg/Kg). The statistics calculated using different methods (based on mean, median, median with adjusted degrees of freedom, and trimmed mean) offer insights into the variability among different groups.

For the Cd,Levene Statistic ranges between 8.207 and 16.30 with corresponding p-values between 0.001 and 0.021. This suggests significant differences in variances among groups when considering Cd concentrations. The Levene Statistic for the Pb levels varies from 10.616 to 26.026 with associated p-values from 0.000 to 0.012. These results indicate substantial differences in variances across groups concerning Pb concentrations. For the Cu concentrations the Levene's statistics range from 16.727 to 21.976 with p-values between 0.000 and 0.003. These outcomes suggest notable disparities in variances among groups regarding Cu concentrations. Finally Levene Statistic for Chromium concentrations varies from 3.168 to 3.774 with p-values between 0.070 and 0.113. These statistics imply marginal differences in variances among groups for Cr concentrations, where some methods indicate less significant disparities compared to others. The results suggest significant differences in variances among groups for Cd, Pb, and Cu concentrations. However, for Cr concentrations, the differences in variances appear less pronounced.

Table 4.7: Test of Homogeneity of Variances

Test of Homogeneity of Variances					
		Levene Statistic	**df1**	**df2**	**Sig.**
Cd	Based on Mean	15.971	1	16	0.001
	Based on Median	8.207	1	16	0.011
	Based on Median and with adjusted df	8.207	1	8.034	0.021
	Based on Trimmed mean	16.300	1	16	0.001
Pb	Based on Mean	26.026	1	16	0.000
	Based on Median	10.616	1	16	0.005
	Based on Median and with adjusted df	10.616	1	8.004	0.012
	Based on Trimmed mean	24.663	1	16	0.000
Cu	Based on Mean	21.976	1	16	0.000
	Based on Median	16.727	1	16	0.001
	Based on Median and with adjusted df	16.727	1	8.015	0.003
	Based on Trimmed mean	21.591	1	16	0.000
Cr	Based on Mean	3.774	1	16	0.070
	Based on Median	3.168	1	16	0.094
	Based on Median and with adjusted df	3.168	1	8.023	0.113
	Based on Trimmed mean	3.464	1	16	0.081

4.10 Analysis of Variance for Tomato and Soil Samples

The provided ANOVA results in Table 4.8 showcase the variance components and statistical significance across different metals (Cd, Pb, Cu and Cr) in mg/Kg. For each metal, the analysis partitions the total variance between-group and within-group variability. Notably, the between-group variance (Reflecting differences among group means) and within-group variance (Representing variability within each group) are compared. The F-statistic measures the ratio of these variances. In all cases (Cd, Pb,

Cu and Cr), the F-statistic is substantial, indicating a significant difference between at least two group means for each metal. The associated p-values of (0.000) confirm the statistical significance, suggesting that there are significant differences among the groups for Cd, Pb, Cu, and Cr concentrations.

Table 4.8: Analysis of Variance between Soil and Tomato Samples

		Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
Cd	Between Groups	1.755	1	1.755	37.607	0.000
	Within Groups	0.747	16	0.047		
	Total	2.501	17			
Pb	Between Groups	18.686	1	18.686	43.522	0.000
	Within Groups	6.869	16	0.429		
	Total	25.555	17			
Cu	Between Groups	7.428	1	7.428	104.277	0.000
	Within Groups	1.140	16	0.071		
	Total	8.568	17			
Cr	Between Groups	2.706	1	2.706	59.327	0.000
	Within Groups	0.730	16	0.046		
	Total	3.436	17			

4.11 Descriptive Statistics for Selected Metal Concentrations

The descriptive statistics outline mean concentrations in Cd, Pb, Cu, and Cr in mg/Kg across three regions: Highland, Lowland, and Midland, and overall totals as shown in Table 4.9. From the analysis**,** Midland zones exhibits the highest Cd mean (0.0536mg/Kg), while lowland shows the highest Pb mean (0.2137mg/Kg). Lowland records the highest Cu mean (0.8956mg/Kg), and Highland demonstrates the highest Cr mean (0.5182 mg/Kg). Standard deviations indicate notable variations within each

region for all metals. Overall mean concentrations for Cd, Pb, Cu, and Cr are 0.1121, 0.3873, 2.195, and 1.287 mg/Kg, respectively. These statistics highlight regional differences and trends in metal concentrations.

Table 4.9: Descriptive Statistics for Soil and Tomato Samples in Three Zones

Metals	Zones	N	Mean	Standard Error	Standard Deviation	Variance	Range	Minimum	Maximum	Confidence Level (95%)
Cd	Highland	6	0.0308	0.0111	0.0272	0.0007	0.0517	0.0053	0.0570	0.0286
	Midland	6	0.0536	0.0219	0.0537	0.0029	0.1090	0.0037	0.1133	0.0564
	Lowland	6	0.0277	0.0132	0.0324	0.0011	0.0760	0.0040	0.0800	0.0340
	Total	18	0.1121	0.0463	0.1134	0.0047	0.2373	0.0130	0.2503	0.1190
Pb	Highland	6	0.0599	0.0288	0.0706	0.0049	0.1519	0.0013	0.1533	0.0740
	Midland	6	0.1137	0.0571	0.1398	0.0195	0.3396	0.0037	0.3433	0.1467
	Lowland	6	0.2137	0.1082	0.2650	0.0703	0.6650	0.0020	0.6670	0.2782
	Total	18	0.3873	0.1941	0.4754	0.0948	1.1570	0.0070	1.1636	0.4990
Cu	Highland	6	0.6467	0.2779	0.6808	0.4634	1.4670	0.0330	1.5000	0.7144
	Midland	6	0.6529	0.2934	0.7186	0.5164	1.6303	0.0367	1.6670	0.7542
	Lowland	6	0.8956	0.3795	0.9295	0.8640	1.8470	0.0533	1.9000	0.9754
	Total	18	2.1950	0.9508	2.3290	1.8440	4.9440	0.1230	5.0670	2.4440
Cr	Highland	6	0.5182	0.2209	0.5412	0.2929	1.1880	0.0120	1.2000	0.5679
	Midland	6	0.5079	0.2331	0.5709	0.3259	1.3220	0.0110	1.3330	0.5992
	Lowland	6	0.2794	0.1623	0.3975	0.1580	0.8000	0.0000	0.8000	0.4172
	Total	18	1.2870	0.6163	1.5100	0.7768	3.3100	0.0230	3.3330	1.5840

4.12 Means Plot for Metal Concentration in Controlling for Sample Size

The figure 4.2 shows the mean plots of soil and tomato samples based on the ecological zones. The mean plot effectively illustrates the distribution of the selected heavy metals in the three ecological zones.

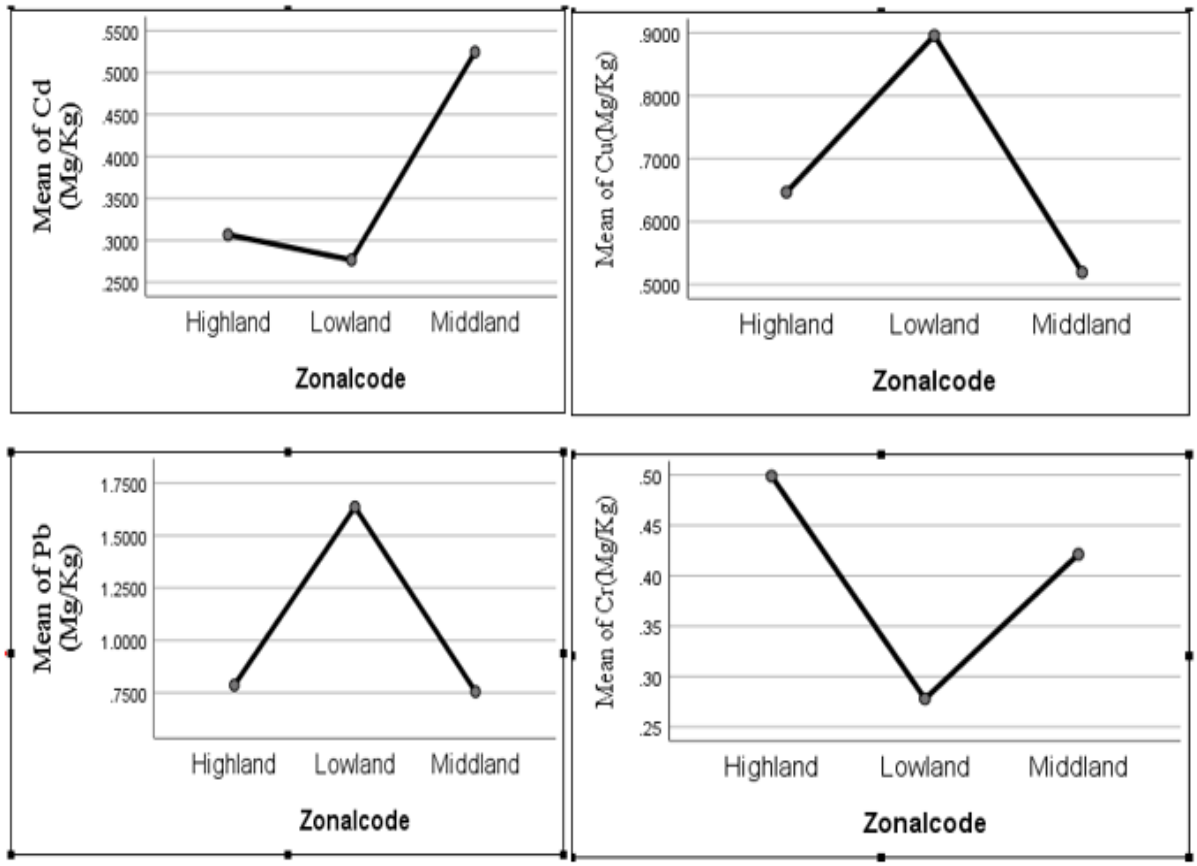


Figure 4.2: Means Plot for Metal Concentration in Controlling for Sample Size

Midland exhibits the highest mean for Cd, succeeded by Highland and Lowlands, in descending order. Conversely, Pb showcases higher mean values in Lowlands, followed by Highlands and then the Midlands, respectively. Cu demonstrates higher mean values in Lowlands, followed by Highlands and then the Midlands. For Cr, the Highland zone records the highest mean values, with the Lowlands showing the lowest value recorded and Midlands displaying intermediate mean values.

4.13 Test of Homogeneity of Variances of Selected Metals across the Three Zones

The evaluation of variances homogeneity for the levels of selected heavy metals across the three ecological zones was conducted using Levene's statistics. The Levene's statistics were calculated based on mean, median, median with adjusted degrees of freedom, and Trimmed mean, as detailed in Table 4.10.

Table 4.10: Test of Homogeneity of Variances for Selected Metals across the Three Zones

Test of Homogeneity of Variances					
		Levene Statistic	**df1**	**df2**	**Sig.**
Cd	Based on Mean	6.667×10^{31}	8	9	0.000
	Based on Median	6.667×10^{31}	8	9	0.000
	Based on Median and with adjusted df	6.667×10^{31}	8	2.016	0.000
	Based on Trimmed mean	7.433×10^{30}	8	9	0.000
Pb	Based on Mean	6.155×10^{31}	8	9	0.000
	Based on Median	6.155×10^{31}	8	9	0.000
	Based on Median and with adjusted df	6.155×10^{31}	8	1.471	0.000
	Based on Trimmed mean	4.460×10^{30}	8	9	0.000
Cu	Based on Mean	1.177×10^{31}	8	9	0.000
	Based on Median	1.177×10^{31}	8	9	0.000
	Based on Median and with adjusted df	1.177×10^{31}	8	4.446	0.000
	Based on Trimmed mean	3.175×10^{30}	8	9	0.000
Cr	Based on Mean	2.666×10^{31}	8	9	0.000
	Based on Median	2.666×10^{31}	8	9	0.000
	Based on Median and with adjusted df	2.666×10^{31}	8	5.016	0.000
	Based on Trimmed mean	7.414×10^{30}	8	9	0.000

The homogeneity of variances test, employing Levene's statistic, revealed significant disparities ($p < 0.05$) among the variances of Cd, Pb, Cu, and Cr concentrations across different ecological zones. This yielded a Levene's statistic value of 0.00, indicating substantial variations in the variances of heavy metal concentrations across the sampled locations. These results reveal substantial deviations from the assumption of

equal variances among the tested groups for all the studied elements, indicating that the variances are significantly distinct from each other within the analyzed groups.

4.14 Correlation Analysis of Selected Metals in Tomatoes, Soil, and Fertilizer Samples

4.14.1 Highland Zones

The correlation analysis between metal concentrations in Fertilizer, Soil, and Tomato samples was conducted. The analysis was performed at a significance level of P =0.05, as shown in Table 4.11.

Table 4.11: Correlations Analysis of Selected Metals in Soil, Tomatoes, and Fertilizer Samples from Highland Zones

Sampling Areas	NPK 23 23 0		DAP 18 46 0		NPK 10 26 10 MAVUNO		NPK 17 17 17		NPK 27 10 16 EASY GROW		NPK 22 21 17		NPK 15 5 35 Agrigrow	
	Corr	**Sig.**	**Corr**	**Sig.**	**Corr**	**Sig.**	**Corr**	**Sig.**	**Corr**	**Sig.**	**Corr**	**Sig.**	**Corr**	**Sig.**
Ker.T	0.464	0.536	-0.142	0.858	-0.501	0.499	-0.104	0.896	0.995*	0.005	0.318	0.682	0.601	0.399
Kim.T	-0.134	0.866	-0.356	0.644	-0.16	0.84	0.349	0.651	0.73	0.27	0.003	0.997	0.015	0.985
Bar.T	0.464	0.536	-0.109	0.891	-0.477	0.523	-0.084	0.916	0.996*	0.004	0.349	0.651	0.613	0.387
Ker.S	0.501	0.499	-0.012	0.988	-0.391	0.609	-0.009	0.991	0.988*	0.012	0.436	0.564	0.633	0.367
Kim.S	0.485	0.515	0.012	0.988	-0.341	0.659	0.046	0.954	0.979*	0.021	0.454	0.546	0.611	0.389
Bar. S	0.393	0.607	-0.023	0.977	-0.284	0.716	0.134	0.866	0.956*	0.044	0.412	0.588	0.521	0.479

* Correlation is significant at $p \leq 0.05$

Ker. T= Kerugoya Tomato Sample *Ker. S= Kerugoya Soil samples*

Bar. T= Baricho Tomato Sample *Bar. S= Baricho Soil Samples*

Kim. T= Kimunye Tomato Samples *Kim. S= Kimunye Soil Samples*

The correlation analysis between metal concentrations highlights the relevance of only one fertilizer among the seven sampled, based on correlations with metals in various regions. For instance, the Tomato Samples from Kerugoya and Baricho, exhibits a correlation coefficient of 0.995 and 0.996 with a significance level of p=0.005 and p=0.004 respectively. This suggests relevance for the fertilizer NPK 27 10 16 + TE EASY GROW. The corresponding Soil Samples from Kerugoya and Baricho show the relevance of the same fertilizer (NPK 27 10 16 + TE EASY GROW) with correlation coefficient of 0.988* and .956* with significant level of p=0.012 and p=0.044 respectively. These findings emphasize the specific fertilizers that exhibit significant correlations with metals across distinct regions and provide valuable insights into potential associations in agricultural contexts. Piscitelli *et al*. (2020) analyzed and evaluated the concentration of heavy metals in soil and tomato fruits, demonstrating a significant transfer of metals from the soil into the plant. In the aforementioned study, Fe and Cr were found in small concentrations, whereas Pb, Cr, and Cu were shown to be higher. Further, Piscitelli *et al.* (2020) reported high levels of chromium metal in the roots and stalks of tomato plants. This was linked to soil contamination. The soil samples from Kagio and Mururi show the relevance of fertilizer NPK 27 10 16 + TE EASY GROW from the seven sampled. The correlation coefficient for these two areas was found to be 0.987* and 0.959* with significant level of p=0.013 and 0.041 respectively as shown in Table 4.12

4.14.2 Midland Zones

In the Midland zones, the correlation analysis was performed at a significance level of P=0.05, as shown in Table 4.12. The correlation analysis between metal concentrations highlights the relevance of certain fertilizers among the seven sampled. For instance, soil samples from Kagio and Mururi exhibit significant correlations with NPK 27 10 16 EASY GROW fertilizer. The correlation coefficients for these areas are 0.987 and 0.959 with significance levels of p=0.013 and p=0.041 respectively. This suggests that NPK 27 10 16 EASY GROW is particularly relevant for these locations. In Sagana, soil samples also show a strong positive correlation of 0.944 with this fertilizer, though it is not statistically significant (p=0.056).

Conversely, tomato samples from all areas in the Midland zone show no significant correlations with any of the fertilizers, as all recorded a p values greater than 0.05. This suggests that while soil samples may reflect the influence of fertilizers, this effect does not appear to extend to the tomato samples in the same areas.

4.14.3 Lowland Zones

In the Lowland zones, the correlation analysis was performed at a significance level of P=0.05, as shown in Table 4.13. The analysis indicates varying levels of correlation between fertilizers and metal concentrations in soil and tomato samples from different areas. For instance, the soil samples from Wanguru and Kiriko show moderate positive correlations with NPK 27 10 16 EASY GROW fertilizer, with coefficients of 0.732 and 0.549 respectively. However, these correlations are not statistically significant with p values of 0.268 and 0.451 respectively. The Thiba soil samples also show a positive correlation (0.831) with the same fertilizer, but it is not statistically significant (p=0.169).

Tomato samples in the Lowland zones generally do not show significant correlations with any fertilizers, as evidenced by the high p values. For example, the Kiriko tomato samples have a non-significant correlation (0.750) with NPK 27 10 16 EASY GROW, with a p value of 0.250. Overall, the correlation analysis in both Midland and Lowland zones provides insights into the associations between specific fertilizers and metal concentrations in soils and tomatoes. The significant correlations observed in some soil samples suggest potential areas of focus for optimizing fertilizer use to mitigate heavy metal contamination.

Table 4.12: Correlations Analysis Selected Metal Soil, Tomatoes, and Fertilizer Samples from Midland Zones

Sampling Areas	NPK 23 23 0		DAP 18 46 0		NPK 10 26 10 MAVUNO		NPK 17 17 17		NPK 27 10 16 EASY GROW		NPK 22 21 17 Murphy Foliar Feeds		NPK 15 5 35 Agrigrow	
	Corr	Sig.	Corr	Sig.	Corr	Sig.	Corr	Sig.	Corr	Sig.	Corr	Sig.	Corr	Sig.
Sag.T	0.081	0.919	-0.247	0.753	-0.24	0.76	0.25	0.75	0.856	0.144	0.16	0.84	0.23	0.77
Kag. T	-0.061	0.939	-0.317	0.683	-0.183	0.817	0.322	0.678	0.776	0.224	0.06	0.94	0.088	0.912
Mur.T	-0.063	0.937	-0.346	0.654	-0.219	0.781	0.289	0.711	0.783	0.217	0.036	0.964	0.092	0.908
Sag. S	0.341	0.659	-0.058	0.942	-0.273	0.727	0.16	0.84	0.944	0.056	0.375	0.625	0.473	0.527
Kag.S	0.598	0.402	0.068	0.932	-0.397	0.603	-0.058	0.942	0.987*	0.013	0.509	0.491	0.717	0.283
Mur.S	0.483	0.517	0.073	0.927	-0.26	0.74	0.123	0.877	0.959*	0.041	0.502	0.498	0.597	0.403

* Correlation is significant at $p \leq 0.05$

Sag. T=Sagana Tomato Samples
Kag. T=Kagio Tomato Samples
Mur. T=Mururi Tomato Samples
Sag. S= Sagana Soil Samples
Kag. S= Kagio Soil Samples
Mur.S= Mururi Soil Samples

Table 4.13: Correlations Analysis of Selected Metals in Soil, Tomatoes, and Fertilizer Samples from Lowland Zones

Sampling Areas	NPK 23 23 0		DAP 18 46 0		NPK 10 26 10 MAVUNO		NPK 17 17 17		NPK 27 10 16 EASY GROW		NPK 22 21 17 Murphy Foliar Feeds		NPK 15 5 35 Agrigrow	
	Corr	Sig.	Corr	Sig.	Corr	Sig.	Corr	Sig.	Corr	Sig.	Corr	Sig.	Corr	Sig.
Wang. T	-0.392	0.608	-0.458	0.542	-0.039	0.961	0.459	0.541	0.522	0.478	-0.185	0.815	-0.255	0.745
Kir. T	-0.114	0.886	-0.367	0.633	-0.195	0.805	0.315	0.685	0.75	0.25	0.002	0.998	0.04	0.96
Thib. T	-0.19	0.81	-0.412	0.588	-0.177	0.823	0.336	0.664	0.701	0.299	-0.062	0.938	-0.036	0.964
Wang. S	0.079	0.921	0.013	0.987	0.089	0.911	0.534	0.466	0.732	0.268	0.348	0.652	0.168	0.832
Kir. S	-0.294	0.706	-0.29	0.71	0.079	0.921	0.565	0.435	0.549	0.451	-0.016	0.984	-0.181	0.819
Thib. S	0.089	0.911	-0.162	0.838	-0.14	0.86	0.342	0.658	0.831	0.169	0.229	0.771	0.221	0.779

* Correlation is significant at $p \leq 0.05$

Wang. T= Wanguru Tomato Sample *Wang.S= Wanguru Soil*

Kir. T= Kiriko Tomato Sample *Kir.S= Kiriko Soil Sample*

Thib. T= Thiaba Tomato Sample *Thib.S = Thiba Soil Sample*

The correlation analysis between metal concentrations in the lowland zones does not show the relevance of any of the seven fertilizers sampled. This could be due to the variations in Soil composition, Environmental conditions, or Agricultural practices specific to the lowland zones, which may not result in significant correlations between fertilizer usage and metal concentrations.

4.15. PCA Analysis

The initial communalities for all variables were 1.000, which represents the total variance in each variable before the extraction. Following the PCA extraction, the communalities reduced, indicating the variance explained by the underlying factors as shown in Table 4.14. The extracted communalities after PCA were Cd (0.769), Pb (0.790), Cu (0.918), and Cr (0.839). These values indicate the proportion of variance in each variable retained or explained by the extracted factors after the analysis.

Table 4.14: Communalities from PCA Analysis

Communalities		
	Initial	**Extraction**
Cd	1.000	0.769
Pb	1.000	0.790
Cu	1.000	0.918
Cr	1.000	0.839
Extraction Method: Principal Component Analysis		

4.16 Total Variance Explained

In this analysis, four components were initially generated. The table show the detail eigenvalues for each component. The first component had an eigenvalue of 3.316, explaining 82.903% of the total variance. The cumulative variance explained by the first component and the subsequent components demonstrates that the first component alone covers 82.903% of the variance as shown in Table 4.15 and Figure 4.3. The second, third, and fourth components had eigenvalues of 0.541, 0.134, and 0.009, respectively. Collectively, they explained an additional 13.516%, 3.353%, and 0.228% of the variance, leading to a cumulative variance explained of 96.419%, 99.772%, and

100%, respectively. This indicates that the first component holds the most substantial information among the components extracted.

Table 4.15: Total Variance Explained

Total Variance Explained						
	Initial Eigenvalues			**Extraction Sums of Squared Loadings**		
Component	**Total**	**% of Variance**	**Cumulative %**	**Total**	**% of Variance**	**Cumulative %**
1	3.316	82.903	82.903	3.316	82.903	82.903
2	0.541	13.516	96.419			
3	0.134	3.353	99.772			
4	0.009	0.228	100.000			
Extraction Method: Principal Component Analysis						

Screen plot

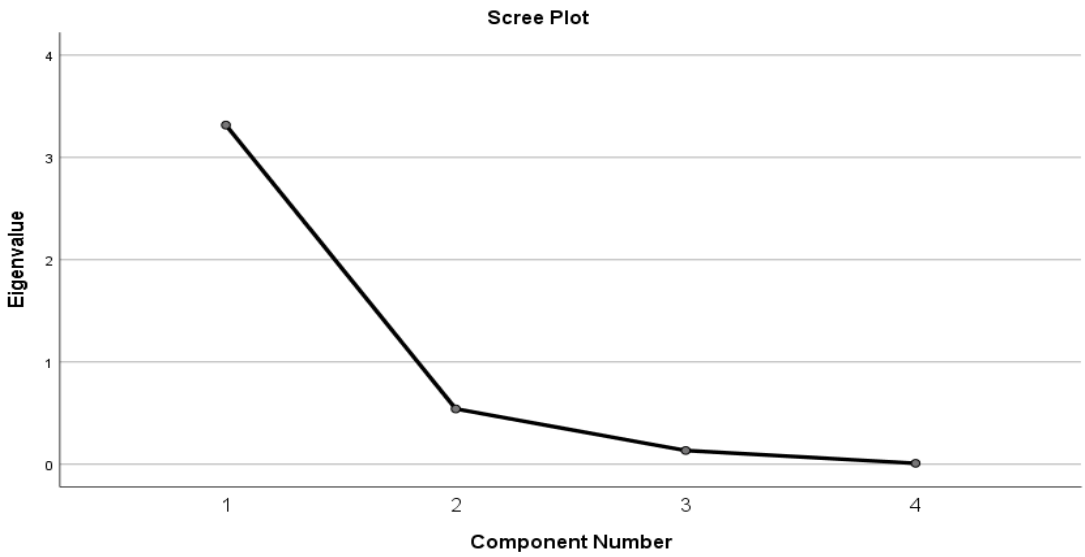


Figure 4.3 Screen Plot for Factor Analysis and Principal Component Analysis

4.17 Component Matrix

The "Component Matrix" resulting from the Principal Component Analysis (PCA) displays the relationship between the original variables (Cu, Cr, Pb, and Cd) and the

principal component(s) extracted. In this case, one principal component was derived. The values in the matrix represent the correlations or loadings between each variable and the single principal component. For this single component, the correlation values are as follows: Cu: 0.958, Cr: 0.916, Pb: 0.889, Cd: 0.877.

These correlation values indicate the strength and direction of the relationship between each original variable and the principal component. Higher values closer to 1 suggest a stronger association between the variable and the principal component as shown in Table 4.16. These loadings imply that all variables have substantial positive correlations with the extracted component, with Cu and Cr having the highest correlations. Only one component was extracted.

Table 4.16: Component Matrix

Component Matrix[a]	
	Component
	1
Cu	0.958
Cr	0.916
Pb	0.889
Cd	0.877
Extraction Method: Principal Component Analysis	
a. 1 components extracted	

4.18 Reliability Statistics

The reliability statistics were calculated for a scale consisting of four items. The Cronbach's Alpha, a measure of internal consistency, was found to be 0.852, suggesting a good level of reliability among these items as shown in Table 4.17. Moreover, when the Alpha was calculated based on standardized items, it showed an even higher value of 0.931, indicating a strong internal consistency within the scale. These results affirm the reliability of the measurement instrument in assessing the construct or variables under consideration.

Table 4.17: Reliability Statistics

Reliability Statistics		
Cronbach's Alpha	**Cronbach's Alpha Based on Standardized Items**	**N of Items**
0.852	0.931	4

The inter-item correlation matrix shows the correlations among four different variables: Cd, Pb, Cu, and Cr. Each variable's correlation with itself is perfectly correlated (1.000), as expected. Examining the correlations between variables, there are significant positive associations observed between Cd and Pb with a correlation coefficient of 0.617. Moreover, Pb and Cu exhibit a strong positive correlation of 0.960. Additionally, Cu and Cr show a substantial positive association of 0.809 as shown in Table 4.18. The variables Cd and Cr also demonstrate a robust positive correlation of 0.873. These correlation values signify varying degrees of relationships between the different metal concentrations, indicating potential associations or commonalities among these elements in the dataset.

Table 4.18: Inter-Item Correlation Matrix

Inter-Item Correlation Matrix				
	Cd	**Pb**	**Cu**	**Cr**
Cd	1.000	0.617	0.713	0.873
Pb	0.617	1.000	0.960	0.652
Cu	0.713	0.960	1.000	0.809
Cr	0.873	0.652	0.809	1.000

The Item-Total Statistics in Table 4.19, provides insights into the relationship between individual items and the overall scale in a measurement. For Cd, removing this item would result in a slight decrease in the scale mean (From 2.145 to 2.145), and the scale variance would also decrease if the item were deleted. The corrected item-total correlation for Cd stands at 0.732, indicating a moderately strong relationship between this item and the total scale score. The squared multiple correlation is 0.811, signifying that Cd shares approximately 81.1% of variance with the total scale. Moreover, the

Cronbach's Alpha if Cd is deleted decreases to 0.852, indicating its contribution to the reliability of the scale.

For Pb, eliminating this item would lead to a decrease in the scale mean from 1.455 to 1.456 and a reduction in the scale variance if deleted. The corrected item-total correlation for Pb is notably high at 0.844, suggesting a strong relationship with the total scale score. The squared multiple correlation, standing at 0.973, indicates that Pb shares around 97.3% of variance with the total scale. The Cronbach's Alpha if Pb is deleted is 0.878, indicating its significance in contributing to the scale's reliability. Regarding Cu, eliminating this item would result in a decrease in the scale mean from 1.827 to 1.827 and a decrease in the scale variance if deleted. The corrected item-total correlation for Cu is notably high at 0.976, indicating a very strong relationship with the total scale score. The squared multiple correlation, at 0.984, suggests that Cu shares approximately 98.4% of variance with the total scale.

The Cronbach's Alpha if Cu is deleted is 0.695, suggesting its substantial contribution to the scale's reliability. Lastly, for Cr, removing this item would result in a slight decrease in the scale mean from 2.115 to 2.115 and a decrease in the scale variance if deleted. The corrected item-total correlation for Cr is 0.781, indicating a moderately strong relationship with the total scale score. The squared multiple correlation, at 0.936, suggests that Cr shares approximately 93.6% of variance with the total scale. The Cronbach's Alpha, if Cr is deleted, is 0.826, indicating its contribution to the scale's reliability.

Table 4.19: Item-Total Statistics

Item-Total Statistics					
Metals	**Scale Mean if Item deleted**	**Scale Variance if Item deleted**	**Corrected Item-total Correlation**	**Squared Multiple Correlation**	**Cronbach's Alpha if Item deleted**
Cd	2.145444	5.116	0.732	0.811	0.852
Pb	1.455796	2.059	0.844	0.973	0.878
Cu	1.827481	3.454	0.976	0.984	0.695
Cr	2.115389	4.795	0.781	0.936	0.826

4.19 Cluster Analysis

The initial cluster centers represent the starting points in a clustering analysis aimed at grouping data points based on standardized concentrations of Cd, Pb, Cu, and Cr in milligrams per kilogram (mg/Kg). Four distinct clusters, labeled as Cluster 1 through Cluster 4, are characterized by their unique z-scores for each metal concentration. In the initial configuration, Cluster 1 demonstrates moderate positive values across all four metals, indicating a moderate presence of these substances.

Cluster 2 stands out with predominantly negative values for Cd, Pb, Cu, and Cr concentrations, suggesting a notably lower presence of these metals compared to the other cluster as shown in Table 4.20. Cluster 3 displays a combination of both negative and positive z-scores for all variables, leaning more toward the negative side compared to the other clusters. Meanwhile, Cluster 4 exhibits moderately high positive values for Cd, Pb, and Cu, suggesting presence of these metals, whereas Cr shows a relatively lower positive z-score in this cluster.

Table 4.20: Initial Cluster Centers based on Cluster Analysis on Standardized Concentration of Metals

Initial Cluster Centers				
	Cluster			
	1	**2**	**3**	**4**
Zscore: Cd	0.51465	-0.85839	-0.70197	1.99197
Zscore: Pb	2.12692	-0.84735	1.50162	0.84913
Zscore: Cu	1.61439	-0.87410	1.09791	0.81619
Zscore: Cr	0.89129	-0.86600	-0.73995	0.96544

In the final configuration, Cluster 1 displays moderately positive values for Cd and Cr, along with notably high positive values for Pb and Cu, indicating a relatively higher presence of these metals within this cluster compared to the other groups. Cluster 2 exhibits a mixture of negative z-scores for all four metals, suggesting a relatively lower presence of Cd, Pb, Cu, and Cr concentrations compared to the other clusters as shown in Table 4.21 and Figure 4.4.

Cluster 3 demonstrates a combination of negative and positive z-scores for all variables, leaning more toward the positive side for Cd, Pb, Cu, and Cr compared to the other clusters. Cluster 4 showcases moderate positive values for Cd, Pb, Cu, and Cr, suggesting a moderate presence of these metals compared to the other clusters as shown in Table 4.21 and Figure 4.4. These final cluster centers represent the optimized groupings achieved after the clustering algorithm's iterations, aiming to establish distinct clusters based on the concentrations of the specified metals.

Table 4.21: Final Cluster Centers Representing the Concluding Stage of a Clustering Analysis

Final Cluster Centers				
	Cluster			
	1	**2**	**3**	**4**
Zscore: Cd	0.81880	-0.81397	-0.70197	1.06502
Zscore: Pb	1.89583	-0.83100	1.50162	0.36429
Zscore: Cu	1.66134	-0.90488	1.09791	0.62056
Zscore: Cr	0.87276	-0.86246	-0.73995	1.12610

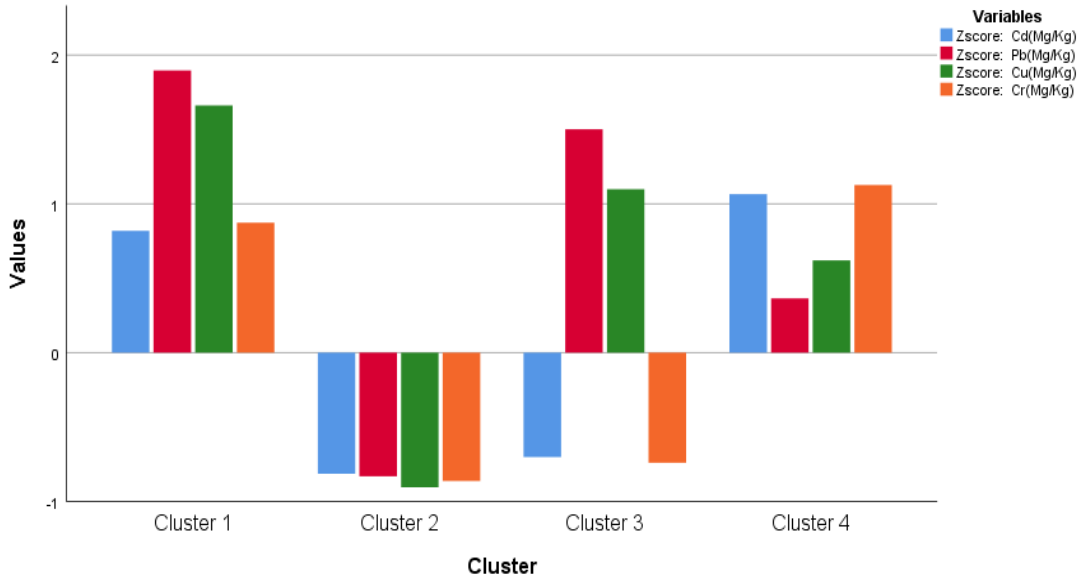


Figure 4.4 Final Cluster Centers for Unique Z-scores for each Metal Concentrations

4.20 Summary

Chapter Four of This thesis presents the results and discussion of the study on heavy metal contamination in tomatoes, soil, and fertilizers in Kirinyaga County, Kenya. The chapter begins by detailing the recovery rates of heavy metals from spiked samples, ensuring the accuracy of the analytical methods used. It then reports the concentrations of heavy metals, specifically Cadmium, Lead, Copper, and Chromium, found in soil samples, followed by those detected in tomato samples. The study further examines the presence of these heavy metals in commonly used inorganic fertilizers.

A significant part of the chapter is dedicated to the bioaccumulation index, illustrating the extent to which tomatoes absorb heavy metals from the soil. Comparative ANOVA analysis highlights the differences in heavy metal concentrations between soil and tomato samples. Mean plots provide a visual representation of these concentrations, and tests of homogeneity of variance ensure the consistency of the data. The chapter also includes a detailed analysis of variance (ANOVA) for both tomato and soil samples, with additional analysis controlling for sample size by geographical zones.

Descriptive statistics offer a summary of metal concentrations across different zones, accompanied by means plots and homogeneity tests to validate the findings. Correlation analysis investigates the relationships between heavy metals in tomatoes, soil, and fertilizer samples across highland, midland, and lowland zones. Principal component analysis (PCA) explains the total variance and identify key components influencing heavy metal presence. The reliability of the data is confirmed through reliability statistics, and cluster analysis is conducted to categorize samples based on heavy metal concentrations. Overall, this chapter provides a comprehensive analysis of heavy metal contamination in the study area, highlighting significant findings.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, the levels of selected heavy metals in soil, tomatoes and fertilizer samples obtained from Kirinyaga County, Kenya, were analyzed. The results from the study showed that:

The soil and tomato samples from all three ecological zones were found to contain Cd, Pb, Cu, and Cr, except for tomatoes sampled from Wang'uru which did not contain Cr.

The selected inorganic fertilizer samples from all three ecological zones were found to contain Cd, Pb, Cu, and Cr, except NPK 27-10-16 + TE Easy Grow, which did not contain Pb.

All the fertilizers sampled were found to have no significant correlations with the soil and tomato samples from all three ecological zones except NPK 27-10-16 Easy Grow which had a significant correlation with the soil and tomato from the highland and midland zones.

The mean concentration of the heavy metals from all the ecological zones of Kirinyaga County was compared with the permissible limits set by the standard regulatory bodies. The levels of the heavy metals in all the samples were found to be below the permissible limits set by FAO/WHO.

5.2 Recommendations

5.2.1 Recommendations for Policy

There is a need to monitor the levels of heavy metals in soil and tomatoes regularly to ensure they do not exceed the acceptable limits. The government should monitor the levels of heavy metals in inorganic fertilizers in the market.

5.2.2 Recommendation for Further Work

This study covered only four elements. More trace elements, in addition to those considered in this study, should be analyzed to provide comprehensive data on the metal profile in the area. Tomato contamination with heavy metals could also likely to

occur from the pesticides and sprays that farmers usually apply on the farms. Therefore, similar studies should also be done without washing the tomato samples.

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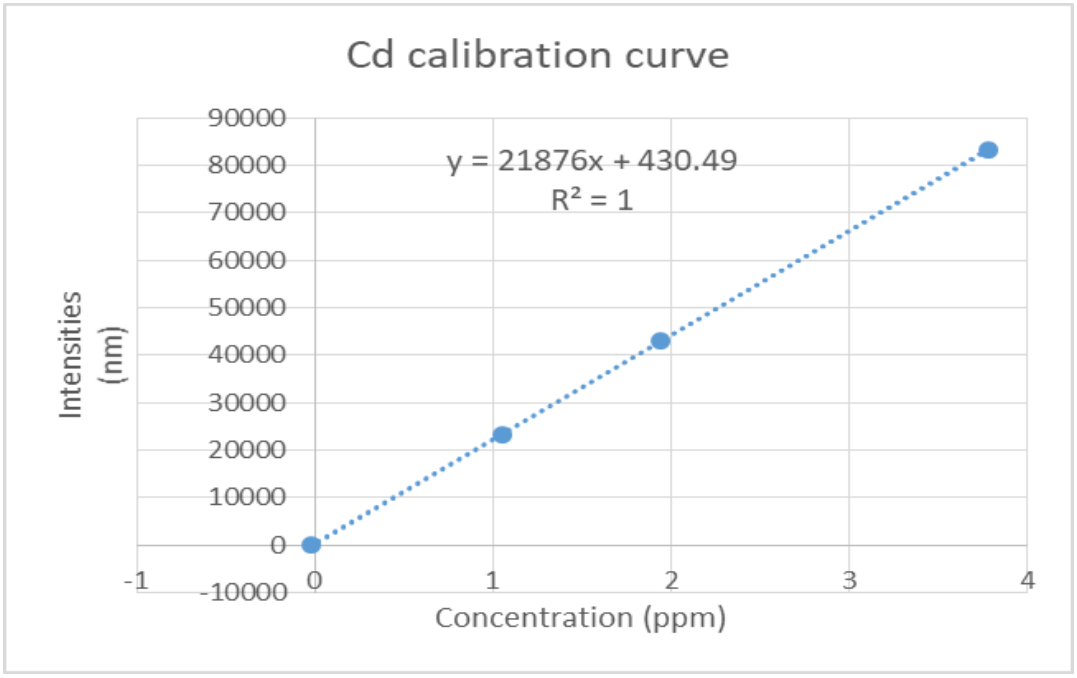
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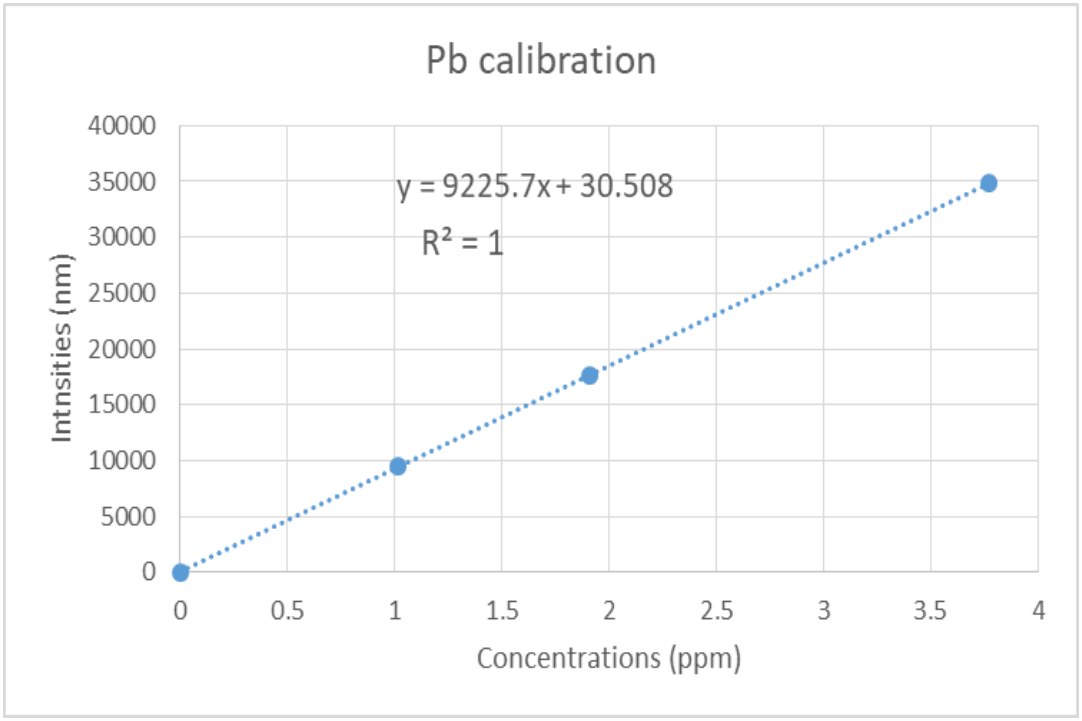
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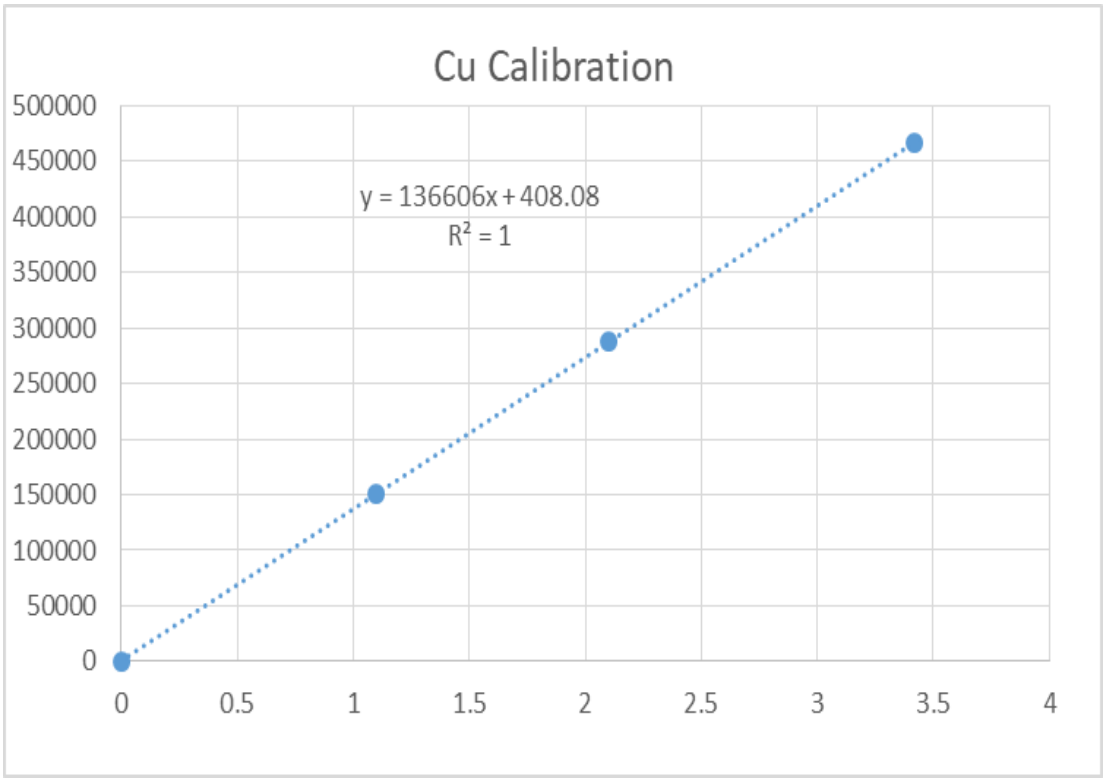
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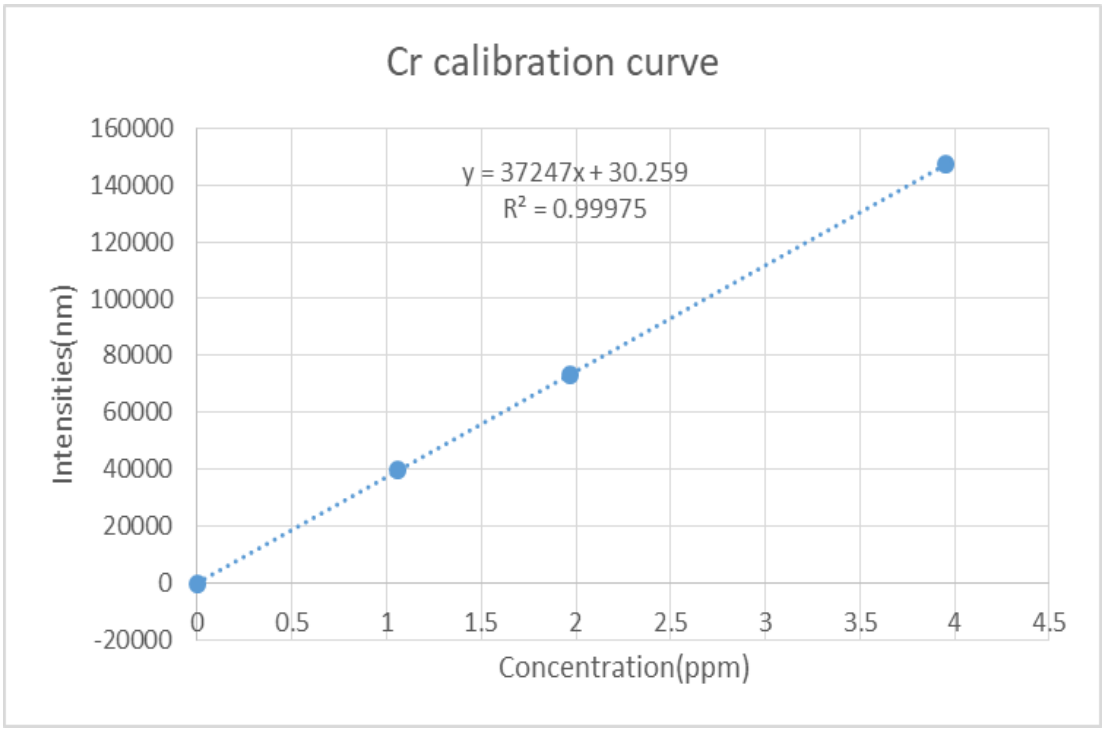
APPENDICES

Appendix 1: Calibration Curves

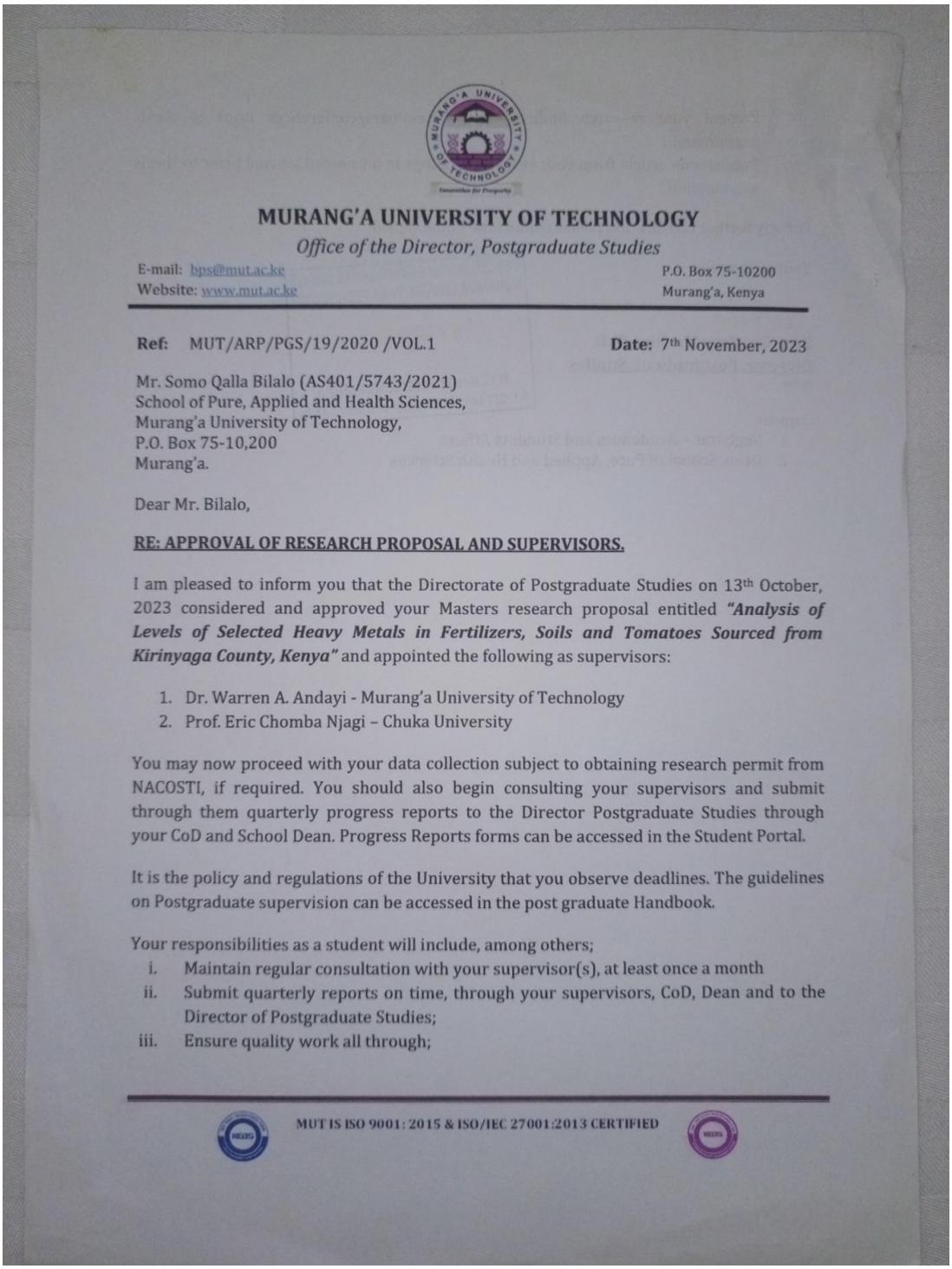





Cu Calibration
y = 136606x + 408.08
R² = 1
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
0
0.5
1
1.5
2
2.5
3
3.5
4


Cr calibration curve
y = 37247x + 30.259
R² = 0.99975
Intensities(nm)
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Concentration(ppm)

Appendix 2: MUT Research Authorization Letter



MURANG'A UNIVERSITY OF TECHNOLOGY

Office of the Director, Postgraduate Studies

E-mail: bps@mut.ac.ke
Website: www.mut.ac.ke

P.O. Box 75-10200
Murang'a, Kenya

Ref: MUT/ARP/PGS/19/2020 /VOL.1

Date: 7th November, 2023

Mr. Somo Qalla Bilalo (AS401/5743/2021)
School of Pure, Applied and Health Sciences,
Murang'a University of Technology,
P.O. Box 75-10,200
Murang'a.

Dear Mr. Bilalo,

RE: APPROVAL OF RESEARCH PROPOSAL AND SUPERVISORS.

I am pleased to inform you that the Directorate of Postgraduate Studies on 13th October, 2023 considered and approved your Masters research proposal entitled ***"Analysis of Levels of Selected Heavy Metals in Fertilizers, Soils and Tomatoes Sourced from Kirinyaga County, Kenya"*** and appointed the following as supervisors:

1. Dr. Warren A. Andayi - Murang'a University of Technology
2. Prof. Eric Chomba Njagi – Chuka University

You may now proceed with your data collection subject to obtaining research permit from NACOSTI, if required. You should also begin consulting your supervisors and submit through them quarterly progress reports to the Director Postgraduate Studies through your CoD and School Dean. Progress Reports forms can be accessed in the Student Portal.

It is the policy and regulations of the University that you observe deadlines. The guidelines on Postgraduate supervision can be accessed in the post graduate Handbook.

Your responsibilities as a student will include, among others;

i. Maintain regular consultation with your supervisor(s), at least once a month
ii. Submit quarterly reports on time, through your supervisors, CoD, Dean and to the Director of Postgraduate Studies;
iii. Ensure quality work all through;

MUT IS ISO 9001: 2015 & ISO/IEC 27001:2013 CERTIFIED

iv. Present your research findings at 2-3 seminars/conferences prior to thesis examination.

v. Publish one article from your research findings in a refereed journal prior to thesis examination.

For any further clarification please contact the undersigned.

Yours Sincerely,

Prof. Geoffrey Muchiri, PhD
Director, Postgraduate Studies
GM/PIM

DIRECTORATE OF POSTGRADUATE STUDIES
MURANG'A UNIVERSITY OF TECHNOLOGY
07 NOV 2023
P. O. Box 75 - 10200, MURANG'A
Tel: 0771463515, Email: info@mut.ac.ke

Copy to:
1. Registrar – Academics and Students Affairs
2. Dean, School of Pure, Applied and Health Sciences

Appendix 3: NACOSTI Research Permit

REPUBLIC OF KENYA

NATIONAL COMMISSION FOR SCIENCE,TECHNOLOGY & INNOVATION

Ref No: **578726**

Date of Issue: **23/November/2023**

RESEARCH LICENSE



This is to Certify that Mr.. Somo Qalla Bilalo of Murang'a University of Technology, has been licensed to conduct research as per the provision of the Science, Technology and Innovation Act, 2013 (Rev.2014) in on the topic: ANALYSIS OF LEVELS OF SELECTED HEAVY METALS IN FERTILIZERS, SOILS AND TOMATOES SOURCED FROM KIRINYAGA COUNTY, KENYA for the period ending : 23/November/2024.

License No: **NACOSTI/P/23/31500**

578726

Applicant Identification Number

Director General
NATIONAL COMMISSION FOR SCIENCE,TECHNOLOGY & INNOVATION

Verification QR Code

NOTE: This is a computer generated License. To verify the authenticity of this document, Scan the QR Code using QR scanner application.

See overleaf for conditions

Appendix 4: Publication

The following paper has been published from this thesis results:

Bilalo, S. Q., Andayi, A. A., Njagi, E. C., & Ptoton, B. M. (2024). Concentrations of Selected Heavy Metals in Soil and Tomatoes (Lycopersicon Esculenta Mill.) Grown in Kirinyaga County, Kenya.