



University of Nairobi

Institute of Nuclear Science & Technology

**ASSESSMENT OF HEAVY METALS IN SOILS IN BLOCK C, MUI
BASIN KENYA: PRECOAL MINING**

by

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**A thesis submitted in partial fulfillment for the degree of Master of Science in
Nuclear Science of the University of Nairobi**

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DECLARATION

This thesis is my original work and has not been submitted in support of award of any degree or qualification at any other University.

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ABSTRACT

Over the past two decades or so, a rapid growth in the mining industry has been witnessed in Kenya. Some of the minerals being mined include metals, such as; titanium, gold, copper, zinc, and silver, in addition to other industrial minerals ranging from gypsum and talc to gemstones and dolomite, and more recently, the discovered coal deposits in Mui basin. Exploitation and processing of these minerals has diverse effects on the country's varied ecosystems and the general environment, in particular as a source of uncontrolled exposure to heavy metals contamination.

This study, specifically determined; the presence and concentrations of heavy toxic metals and assessed the level of metal pollution in soil samples from block C, Mui basin, in Kitui County, prior to the commencement of coal mining.

Forty (40) randomly sampled soil samples were collected from block C and analysed for heavy metal content using EDXRF facilities, available at the Material Testing and Research Department Laboratories, Ministry of Transport and Infrastructure.

Results of EDXRF analyses of the soil samples showed a mean concentration of; 355 mg/Kg for vanadium, 1637 mg/Kg for manganese, 52657 mg/Kg for iron, 45 mg/Kg for copper, 89 mg/Kg for zinc, 30 mg/Kg for lead and 423 mg/Kg for strontium. Higher concentrations levels of these metals were registered in samples that were obtained from areas where they had extensive human activities. In general, these concentrations compared very well with data from uncontaminated soils in other parts of the world and the world averages.

The elemental data was further subjected to statistical tests; one-way ANOVA to determine whether the heavy metal concentrations levels varied significantly between the various sampling sites and to Pearson's correlation analyses, to test if there was any significant correlation between total metal concentrations in the different soil samples analysed. Factor and Cluster Analysis was done to determine inter-elemental associations in the samples analysed. Factor analysis identified three main factors; Factor 1 which accounted for 37% of the variability, is associated with

lead and copper, Factor 2 account for 32% of the variability and is associated with vanadium, manganese, iron and zinc and while, factor 3 which account for 19% of the variability is associated with strontium. Cluster analysis show that the elements found in these soil samples can be put in two major clusters; cluster 1 with V, Fe, Cu, Mn, Zn and Pb, while the second cluster had only Sr. In addition, Pearson correlation showed strong correlations between V/Fe, V/Zn, V/Pb, Mn/Zn, Zn/Pb, and Cu/Pb. Statistical analysis using ANOVA showed a significant correlation between the experimental and certified values for most of the elements analysed in this study.

Heavy metal pollution was determined from calculation of Enrichment Factor, Pollution Load Index as well as Geo-Accumulation Index. The calculated value of PLI for the soil samples collected was 1.01, an indication that the soil in Mui basin is uncontaminated with the investigated heavy metals. Additionally, geo-accumulation values for Fe, Cu, Zn, Pb and Sr were all below zero which means the soil is uncontaminated with these metals. However, the Igeo value for vanadium and manganese was between 0 and 1 meaning the soil was moderately contaminated with the two elements, normally associated to coal mineralization.

In conclusion, the results of this research has provided a baseline data for heavy metal exposure levels prior to the start of coal mining, which is relevant for future environmental assessment and monitoring programmes useful in formulation of pollution and management regulation policies.

The study recommends similar studies for the entire Mui basin and its environs and be extended to other media such as water and plants to assess heavy metal contamination.

LIST OF ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AMD	Acid Mine Drainage
ANOVA	Analyses of Variance
ASCII	American Standard Code for Information Interchange
ASR	Analysis of Spectral Results
AXIL	Analysis of X-Ray Spectra using Iterative Least Square method
CF	Contamination Factor
CNS	Central Nervous System
CRM-	Certified Reference Material
EDXRF	Energy Dispersive X-ray fluorescence spectroscopy
EF	Enrichment Factor
GIT	Gastrointestinal Tract
IAEA	International Atomic Energy Agency
Igeo	Geo-accumulation
IQ	Intelligent Quotient
LLD	Lower Limits of Detection
MoE-	Ministry of Energy
NEMA	National Environment Management Authority
PLI	Pollution Load Index
PNS	Peripheral nervous system
QAES	Quantitative Analysis of Environmental Samples
RDS	Road deposited sediments
TDS	Total Dissolved Solids
UTM	Universal Transverse Mercator
WDXRF	Wavelength-Dispersive X—ray fluorescence
XRD	X-ray Diffraction
XRF	X-rays Fluorescence Spectroscopy

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CHAPTER 1

INTRODUCTION

1.1 Background Information

Mineral ores are complex chemical compounds in nature. In general, mining of minerals results in the exposure to heavy metal pollution of the environment. Oxides of some of these minerals are soluble and can easily enter the water bodies making them readily available for assimilation by plants and for, their subsequent consumption by humans and animals. Exposure to heavy metals has both chronic and acute health effects, such as; mental lapse, kidney problems, liver problems and problems of the central nervous system, among others (Ademoroti, 1986).

Several studies done in Britain and Wales indicate that 2% of the rivers in Scotland, and 9% in England and Wales failed to meet the set water quality guidelines in terms of ecological and chemical status as a consequence of the past mining activities. These rivers act as a repository of metal discharges including iron, cadmium, zinc and copper emanating from mining activities (Dave *et al*, 2008).

Babajide *et al*. (2006) noted that in most African countries, mining activities are the key contributor to heavy metal pollution in the environment; for example, copper in the Zambia, arsenic in South Africa and Namibia, tin in Zaire and Nigeria, and mercury in Algeria.

Roberts *et al*. (2007) carried out an investigation on the effects of coal mining on the environment. The results showed that, coal mining pollutes the environment with heavy toxic metal such as; mercury, arsenic, lead, selenium, cadmium, nickel, copper and vanadium found within the coal and associated strata.

Other related studies measured heavy metal concentrations in water and bottom sediment, as well as in different parts of the aquatic macrophytes samples obtained from a lake reservoir located near a coal mine in India (Mishra *et al*. 2008). The results obtained indicated that different parts of plant samples collected from near the lake exhibited high

concentrations of copper, cadmium, manganese, lead and mercury due to bioaccumulation. In general, heavy metals were found to be enriched in coal mining sites.

A study conducted on a coal mining project site in northwestern Bangladesh to examine the impact of coal mining processes on the environment, found water and soil samples to be highly contaminated with heavy metals, among other pollutants found (Rashid *et al* 2014).

A similar study was done by Adaikpoh *et al* (2005), attributed the high concentration levels of toxic metals in sediments collected from River Ekulu in Enugu, in Nigeria, to the nearby coal mining activities.

The demand for energy resources due to the rapid growth in population, urbanization, and industrialization has resulted in search for alternative energy sources (Rosen and Dincer, 2001).

Globally, coal is the most abundant fossil fuel and contributes approximately 75 % of the global fuel resources. It contributes to over a third (39%) of total electricity production worldwide. In addition, it is combusted to generate heat and when liquefied to produce diesel fuel and gas. However, effects of coal mining on the ecosystem have profound negative effects despite its economic gains to a country (Rashid *et al.* 2014).

The discovery of large deposits of Coal in Mui basin, Kitui County, Kenya has attracted the interest of many for its economic exploitation as a national revenue resource. The huge deposits in Mui Basin are billed as the ideal alternative energy source at a time when the country seeks affordable and reliable energy source to drive Vision 2030, the economic blueprint that aims to make Kenya a middle income country.

Mui Basin is divided into four blocks; block A, B, C & D. Block C and D are projected to hold over 400 million metric tonnes of coal which can be exploited for the next 50 years and whose value is estimated to be \$34 billion, going by the current market rates. Prospective studies are being conducted in Block A and B to ascertain their full potential (Business Daily, 2012). So far, 40 wells have been drilled and coal seams in 27 wells have been intercepted (Business Daily, 2012). The Ministry of Energy has carried out

tests on samples and established that the coal resource is of good quality, Fig 1.1 (Coal in Kenya, Softkenya.com, 2012). The concession of the coal mining contract has been awarded to a Chinese firm Jung'u group with its subsidiary Fenxi Mining Industry Limited to undertake the actual Coal Mining in block C and D.



Figure 1.1: The field sampling team assessing the coal quality of various coal samples at the MoE offices in Mui basin during the sampling exercise.

The aim of this study was to provide relevant data of the quantities of heavy metal in soil samples from coal deposit areas of Mui basin Kitui County, prior to the commencement of the mining activities. The results were analyzed to determine the extent of heavy metal pollution levels.

1.2 Description of the study area

1.2.1 Geographic location

The Mui basin is located approximately 180 Km North East of Nairobi at an altitude of between 600 and 900 metres above sea-level. The highest area is the periphery of Mutito Hills of over 1000 metres. The area runs from Kyamatu in the south through Makongo hills to the southern parts of the Nuu hills. The western boundary runs from Kyengomo in the south through Inyuu Bridge, Miambani to slightly beyond Mikuyuni market in the north. Mui Basin lies within the Mozambique Belt on the eastern parts of Kenya – east of the Rift Valley. The region cuts through Kitui Central and Mutito districts covering an area that is approximately 500 square kilometres. It is bound by UTM coordinates 0406000 & 0418000 eastings and 9900000 & 9800000 northings, respectively (Fig.1.2).

The basin is divided into four Blocks; A, B, C and D. Block A covers (Zombe-Kabati, 121.5 Km²), Block B (Mutito-Itiko, 117.5 Km²), Block C (Yoonye-Kateiko, 131.5 Km²) and Block D (Karunga-Sekele, 120.0 Km²). The basin partly covers the four map sheets of Migwani 151/1, Nuu 151/2, Kitui 151/3 and Mwitika 151/4 (MoE, 2011).

1.2.2 Description of Mui basin

The Mui basin climatic conditions vary in terms of temperature and rainfall. The region experiences two rainy seasons (bi-modal); short rains between November-February and long rains in the months of March to May. It receives roughly between 710 mm and 760 mm of rainfall annually. The average rainfall in high areas around Mutito ranges between 760 - 1200 mm annually (Mukabana, 2009).

High temperatures are experienced in Kitui county throughout the year, ranging between 14⁰C to 34⁰C; highest are recorded in between January to February and mid- July to September, with means of between 26 to 34⁰C. The lowest mean annual temperature ranges between 13⁰C to 21⁰C. The area is therefore characterized by hot and dry climate which is influenced by the topography of the area with cooler climate near hills and along rivers whereas hotter climate is found in fairly flat areas (Mukabana, 2009).

The major sources of water are bore holes and seasonal rivers that form during the rainy seasons and dry up shortly after the rains. The major rivers are; Ngoo, Kathi, Mui, Ithikwa and Kagowe. These rivers become flooded during the heavy rains and turn into sandy beds in the dry season. The stream pattern in Mui basin is dendritic with the smaller streams draining into the main rivers. The drainage is controlled by the geological structures with majority of the rivers draining to the south.

The natural vegetation for most of the area is characterized by dry bush and thickets composed mainly of acacia trees shrubs similar to those found in most semi-arid areas of Kenya and are sparsely forested. The indigenous vegetation is characterized by trees that are drought resistant and whose distribution is influenced by rainfall amounts, geology and soils, and topography (Mukabana, 2009).

Mui basin is accessed by the tarmacked Thika-Garisa highway and gravel roads which branches off the highway into the basin. There are good all-weather roads, together with numerous tracks and footpaths which are generally good in dry weather, and only become impassible during heavy rains seasons. The basin is well served with electricity by the national grid to schools, dispensaries, market centres and households. Mobile communication services are available by Safaricom, Airtel and YU (Mukabana, 2009).

The population distribution of Mui basin is moderate with people settled mostly near market and shopping centers. The main economic activity is agriculture; farming and livestock keeping. The main crops grown are maize, beans and cassava, while for livestock, they keep cows, goats, sheep and chicken (Mukabana, 2009).

The area lies on the Mozambique belt of Kenya. The periphery of Mui Basin is largely covered by Precambrian crystalline rocks, which mainly consists of gneisses, magnetites, with minor intrusives. The rocks show a regional North-South structural trend of foliation (Ndolo *et al.*, 1997). Hills at the periphery are mostly formed by granitoid gneisses, which are resistant to erosion. One of the noticeable features is the major fault running N-S through Mutito (Fig 1.2) and Ikoo, which traverses the drainage axis of Ikoo river, affecting the drainage system. The fault plane has an eastward dipping of 50° to 80° (Mukabana, 2009).

The Mui basin sediments include; sandstones, mudstones and shales, peat, lignite and coal, basal conglomerates, clays, limestone and gypsum, recent sediments and lateritic soils. The composition of the soil cover varies in the central plain of Mui basin where transport is restricted; the variation in the character of the soil is a reflection of the contrasting nature of the underlying rocks. The alluvial sandy soils include river deposits and outwash from the hills. Sandy soils dominate the western and north-western parts (on sides of the hills) due to outwash from the Mutito fault hills. On the north-east and central parts of the study area, clay soils appear to boarder the sands (deposits on Enziu and Mui rivers) and the silt on the periphery. Clay soils stretch from the north through to the south sand witching silt all through (Mukabana, 2009).

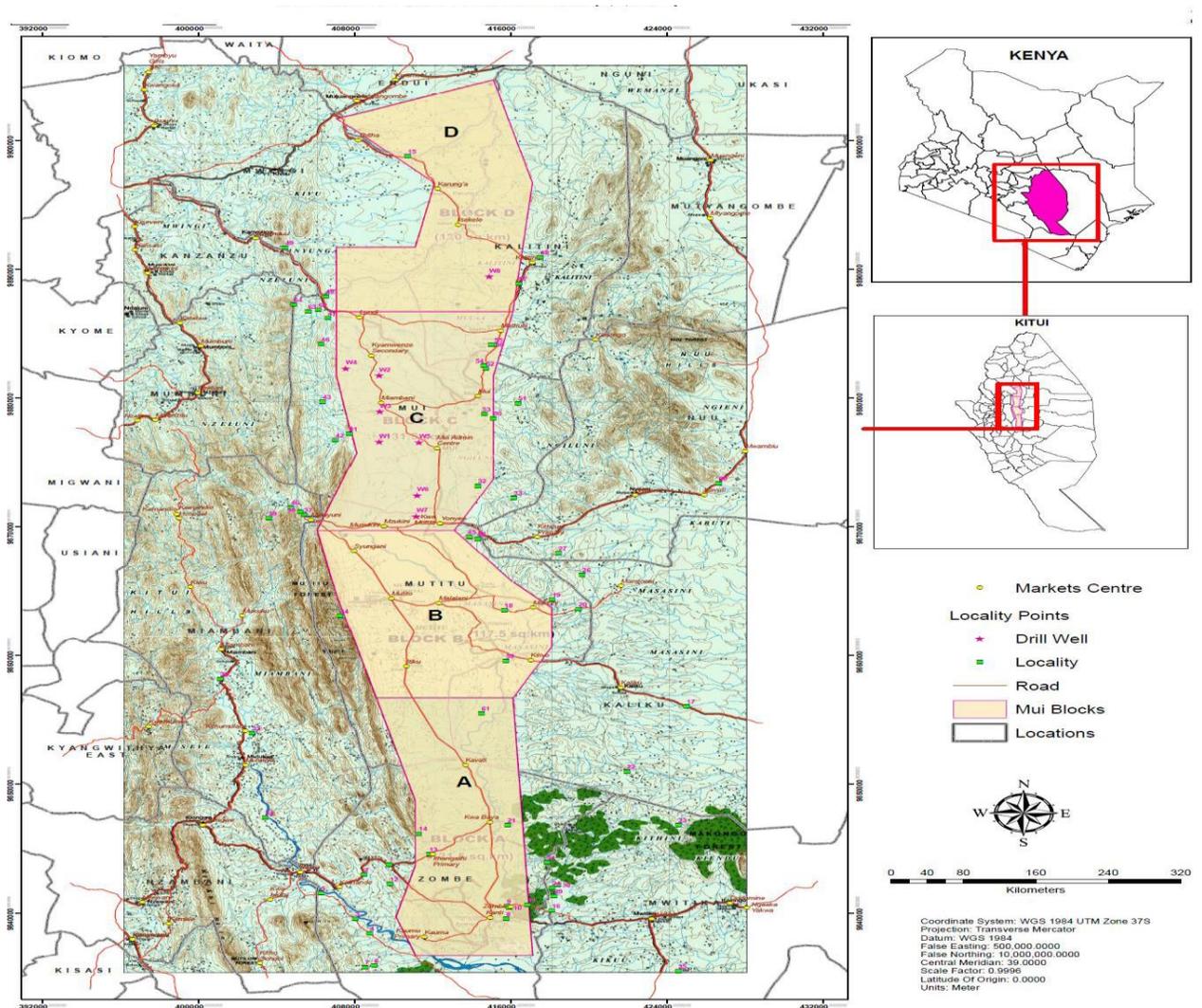


Figure 1.2 Geological map of Mui basin showing the location of study area (MoE, 2011).

1.3 Statement of the problem

Mineralization is a key factor towards the economic development of a country. However, exploitation of minerals can also have adverse negative effects to the environment and human health, specifically resulting to heavy metal pollution.

Following the discovery of huge deposits of coal in Mui basin Kitui County, a mining and processing company, (Fenxi) is in the process of setting up plants to develop block C and D (Business daily, 2012). The mining process is likely to be a source of uncontrolled exposure to heavy metals contamination when commercial extraction and processing starts.

This study specifically determined; the presence and concentrations of heavy toxic and assessed the level of pollution prior to the start of coal mining.

1.4 Broad Objective

The main purpose of this study was to provide baseline data necessary for future environmental heavy metal soil pollution assessment and monitoring associated with the coal mining of Mui basin.

1.4.1 Specific Objectives

- 1) To identify the toxic heavy elements namely; copper (Cu), zinc (Zn), lead (Pb), vanadium (V), iron(Fe), strontium (Sr) and manganese(Mn) in soil samples from Mui Basin, Block C in the regions; Yoonye, Kateiko and Kathonzweni;
- 2) To determine the concentration levels of seven (7) toxic heavy elements namely copper (Cu), zinc (Zn), lead (Pb), vanadium (V), iron(Fe), strontium and manganese(Mn) in sub- soil samples from selected sites of Mui Coal Deposits, Kitui County, using EDXRF analytical technique;
- 3) To determine the extent and distribution of heavy metal pollution in block C, Mui basin.

1.5 Scope of the study

The study focused on the levels of seven (7) toxic heavy metals namely; vanadium, manganese, iron, copper, zinc, lead and strontium due to their effects on the environment and human health. Due to financial constraints, the study was undertaken specifically on block C where coal deposits have been discovered. The soil samples were collected from near coal wells in three regions (Kathonzweni, Yoonye and Kateiko) in block C of the Mui basin Kitui County.

1.6 Justification and Significance of the Research

Mining activities have previously, been shown to be associated with heavy metal pollution of the environment due to disposal of large amount of tailings (Dudka & Adriano, 1997).

In general, coal mining activities have profound impact on the environment; degradation of soil fertility, contaminated water sources and airborne trace metal contamination.

The results of this research are relevant for future environmental assessment and pollution monitoring.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents a review of selected studies on the effects of mining activities in general and heavy metal contamination in soils, water bodies and in various plant samples in the mining areas.

2.2 Mining and Toxic Heavy Elements Pollution

Studies have shown that, mining results in the exposure to heavy metal pollution in the environment. For instance, a study to investigate heavy metal contamination levels (Zn, Cu, Cd, and Pb) in soils, rice, and vegetables grown near the Dabaoshan mine, south China, indicated concentrations of Zn, Cu, Pb and Cd in paddy soil surpassed the recommended limits for agricultural soil. The metal concentrations in vegetables varied from Zn; 34.7 - 170 mgkg⁻¹, Cu; 5.0 - 14.3 mgkg⁻¹, Cd; 0.45 - 4.1 mgkg⁻¹ and 0.90 - 2.23 mgkg⁻¹ for Pb. The study further showed that the Cd and Pb concentrations in rice grain surpassed the tolerable limits in China (H. Xiangjiang, 2011).

A study done at Apuseni Mountains, a part of the Western Carpathians in Romania, on an exploration exercise evidently found that there was a significant acid mine drainage, in addition to heavy metal contamination in the surface waters. The acid mine drainage (AMD) production was on account of increased pyrite oxidation in ore pits and deposits of ore (Miahela, 2007).

In a similar study, Yoshinori *et al.* (2010) determined the distribution of heavy metals within the major copper producing regions of Zambia, in effort to understand pollution characteristics in each of these areas. Soil samples as well as lake and river sediments were obtained from these areas and analyzed for Cu, Zn, Cr, Co, Hg, Pb, Sr, As, Cd and Ni. Strong regional differences in heavy metal pollution patterns were observed. Using cluster analysis, the heavy metal pollution patterns could be categorized into three key clusters; Copper belt, Kabwe and Lusaka and other areas. The authors further noted that heavy metals emanating from the Copper belt area are transported downstream areas by

the Kafue River. Significant pollution levels were also detected in Lake Itzhi-tezhi and national parks that were heavily contaminated with Cu, probably from exploration activities taking place in the upper sections of the river. However, low to moderate heavy metal contamination was recorded in areas geographically distant from the mines, but the concentrations of Zn and Pb were significantly correlated to the populations of each of the sampled town. These findings indicated that heavy metal contamination in Zambia was on the rise mainly due to mining activities (Yoshinori *et al* 2010).

Ogola *et al*, (2002) studied the impact of gold mining activities in Migori Gold Belt, Kenya, on both the human health and environment. The study revealed that the heavy metal concentrations, especially Pb (6.6 – 510 mg kg⁻¹), As (0.07 – 76 mg kg⁻¹) and Hg (0.47 – 1921 mg kg⁻¹), were beyond the permissible limits. In the stream sediments, values between 0.014 – 1.88 mg kg⁻¹, 0.29 – 347 mg kg⁻¹, and 3.0 – 11076 mg kg⁻¹ were reported for As, Hg and Pb, respectively. The highest metal concentrations were recorded in the sediment samples from Nairobi mine tailings (76.1 mg kg⁻¹ for As), Macalder stream (11076 mg kg⁻¹ for Pb), and Mickey tailings (1921 mg kg⁻¹ for Hg).

Mulwa *et al*, (2012) carried out a heavy metal analysis exercise in soil and limestone samples obtained from the limestone deposit areas in Kitui County, Kenya. The assessment was done in a framework of environmental impact assessment of heavy metal contamination in the region. The results revealed the existence of various heavy metals; tin, manganese, Pb, Cu and Zn at varying degree in both soil and limestone samples. Interestingly, the heavy metal concentration levels were higher in the soil samples than in the limestone, an indication of other sources other than those of limestone.

Babajide I (2006), in his report notes that, in most African countries, mining activities are the single most dominant source of heavy metal pollution in the environment, for instance, arsenic in South Africa and Namibia, mercury in Algeria, copper in Zambia and tin in Zaire and Nigeria. Consequently, it results in excessive deposition of metal-rich mine tailings and metal smelting. The studies were conducted on the occurrence, exposure sources and distribution of metals in Nigeria in all the environmental matrices

(fauna and flora, water, air, and sediment) but with more emphasis on water and suggestions on how to minimize exposure were reported.

He further notes of the various studies on heavy metal contamination of various environmental media for which lead among other metals in the water bodies, atmosphere, vegetation and soils were in high levels that are detrimental to human health. Mercury, cadmium, and chromium were sparsely distributed and that, some recent data had high concentration levels of Cd in dust samples from high traffic and densely populated areas. Heavy metal concentrations in biological species; fish, plants etc. in aquatic environments were also reported to be in high levels.

2.3 Coal Mining and Toxic Heavy Elements Pollution

A lot of studies have been done in Europe on coal mining and its effects to the environment. For instance, Sajadi (2010) analyzed waste waters from various wells located in a nearby a coal mine for heavy metal contamination and acidic content. The studies showed that because of acidic character, the waste water contained elevated heavy metals levels. Similarly, Henton (1981) reported heavy metal contamination in river Ore in Scotland, while Bird (1987) describes pollution of Tawe River in South Wales. In their reports they indicate that, mine drainage is increasingly becoming a challenge in the United Kingdom as water tables rise and acid drainage waters rich in heavy metals impact on the quality of water in the river systems.

A similar but related study was done in Bangladesh where the total heavy metal concentrations in soils from mine drainage and agricultural fields in the vicinity were determined to be heavily contaminated. The concentrations of titanium, manganese, zinc, lead, arsenic, iron, rubidium, strontium and zirconium exceeded the world averages (Bhuiyan *et al*, 2010). Rashid *et al*, 2014 evaluated the environmental impacts of coal mining, particularly in relation to soil and water pollution in Barapukuria, Middle -East coal mining project in northwestern Bangladesh. The soil and water samples were found to contain high levels of heavy metal among other nutrients. This suggests that coal mining activities have profound impact on the surrounding water and soil quality.

Mishra *et al*, (2008) carried out a study on a lake affected by coal mining in India for determination of heavy metals in water, lake sediment and aquatic macrophytes samples from the lake reservoir in three different sites. Five heavy metals; copper, cadmium, manganese, lead and mercury were found in high concentration. Plants samples collected from the lake showed high concentrations levels of copper, cadmium, manganese, lead and mercury due to bioaccumulation.

Roy *et al*, 2014, carried a study on impact of coal mining in the environment, with a special focus on soil, water and air in Asansol-Raniganj Area, India. His study concluded that due to deep coal pit mines, the natural environment had been degraded. The agricultural outputs had been reduced due to the degraded soil fertility of the soil and very low precipitation.

Yu *et al*, (2010) did an evaluation of reclamation effects on the methods used in the coalmine reclamation area in China's Fushun coalmine. The results indicated that the top soils had high levels of heavy metals.

George *et al*, (2010) did a research on effects of coal mining on water resources in South Africa. From his findings, he reported that; acid mine drainage was a major problem in coal mines in South Africa and therefore a significant threat to South Africa's environment.

In India, Bhawna (2012) did a comparative study on concentrations of airborne particulates and trace metals in the coal mining and non-mining areas. A significant difference in metal concentrations was noted between these two areas. The mean metal concentrations within the coal mining areas were determined in the order; Ni < Pb < Cd < Cr < Mn < Zn < Cu < Fe. Mean Cu concentrations varied from 0.06 - 6.32 $\mu\text{g}/\text{m}^3$, Pb; 0.024 - 0.32 $\mu\text{g}/\text{m}^3$, Mn; 0.14 - 1.9 $\mu\text{g}/\text{m}^3$, while Ni ranged from 0.002 - 0.02 $\mu\text{g}/\text{m}^3$. Zinc, Fe, Cr and Cd varied from 0.16 - 2.55 $\mu\text{g}/\text{m}^3$, 1.43 - 28.48 $\mu\text{g}/\text{m}^3$, 0.11 - 0.42 $\mu\text{g}/\text{m}^3$ and 0.03 - 0.07 $\mu\text{g}/\text{m}^3$, respectively. Coal mining and associated activities were identified as the key sources of airborne trace metal contamination.

McKeague and Wolynetz (1980) recorded a lower mean lead concentration value in uncontaminated Canadian soils from regions remote from mining activities to be 20mgkg^{-1} . Slightly higher values (21mgkg^{-1}) were recorded in the Appalachian regions.

In general, the soils background copper concentration is dependent on the parent material as well as the soil-formation processes (Kabata-Pendias and Pendias, 2001). McKeague and Wolynetz (1980), reported the total zinc background level in the Appalachian Region of Canada as 81mgkg^{-1} , a value higher than 64mgkg^{-1} which is the estimated global mean zinc concentration in soils.

Kabata-Pendias and Pendias (2001), reported that the lead concentration in plants grown on uncontaminated sites to range between $0.2 - 10\text{mgkg}^{-1}$, with a mean value of 2mgkg^{-1} per dry weight.

In general, the impact of coal mining processes to the environment affects both underground water as well as surface water; rivers, lakes, streams, etc. in addition. These effects include altered waterways, acid mine drainage, increase in total dissolved solids (TDS) and contamination with heavy metals and other pollutants and toxins contained in coal waste, coal sludge and coal ash. For instance, in underground mining, mine wastes are usually stacked on the surface, thus not only polluting but also altering the flow of local water ways. As rain water flows and percolates through these heaps, the water soluble components are dissolved resulting in an increase in TDS. The occurrence of TDS in water bodies is often an indication of the presence of calcium, bicarbonates, carbonates and sulfates. Although these pollutants don't pose a significant risk to human health, they however make the water unpleasant by altering its taste and quality to an extent that it can no longer be used for domestic purposes.

Acid mine drainage (AMD) can be defined as the outflow of acidic water from active or abandoned mines. It is particularly severe where sulphur-bearing rocks (pyrite; FeS_2) are exposed during coal mining process. Exposure of the pyrite to air and water, leads to formation of dilute sulfuric acid that is washed into the water systems. Although the acidity of the runoff is a problem on its own, it also dissolves metals such as nickel, zinc and manganese, ultimately becoming a part of the water. The resultant acidity and

dissolved metals are directly toxic to aquatic life and render the water unfit for use (Martha K, 2001).

In conclusion, the studies indicate that, mining and in particular coal mining, results in extensive heavy metal pollution of the environment. It is therefore important that the Mui basin coal mining and its subsequent processing is preceded by an assessment of the levels of these environmental hazards for subsequent management of the pollutants in the environment.

2.4 Health Impacts of heavy metals pollution

According to Hendryx & Ahern (2008), each phase of coal mining cycle right from transportation, washing, combustion, to waste disposal, have an impact on human health. For instance, coal ash contains various harmful components that are known to leach out of coal ash disposal sites with adverse effects on environmental and human health.

The bio-toxic effects of heavy metals refer to their detrimental effects. Although each metal exhibits distinct signs of their toxicity, the following have been reported as general effects linked to lead, cadmium, zinc, aluminium, arsenic, copper and mercury poisoning; vomiting and convulsion, gastrointestinal (GI) disorders, depression, tremor, paralysis, stomatitis, hemoglobinuria, ataxia, diarrhea, and pneumonia when volatile vapours and fumes are inhaled (McCluggage, 1991). The magnitude of these effects ranges from carcinogenic, toxic (chronic or acute), neurotoxic, teratogenic or mutagenic (Duruibe, J. O *et al*, (2007).

2.4.1 Toxicity by heavy metals

In human beings and life in general, effects of metal toxicity depend on metal form and dose. For example, some metals such as Cu or Mn are essential only in micro amounts, while other metals are toxic only when they form poisonous soluble compounds. These toxic metals tend to bio-accumulate in the body as well as the food chain. Toxic metals can imitate the action of an essential element in the body, thus affecting various metabolic processes with adverse effects on health.

The toxicity of heavy metals results from their interference with the typical body metabolic processes and biochemistry. Once ingested, in the acid medium of the stomach, these metals are converted to their most stable oxidation states (Cd^{2+} , Pb^{2+} , As^{3+} , As^{2+} , Zn^{2+} , Ag^+ and Hg^{2+}) and combine with proteins, enzymes and other biomolecules forming strong and stable chemical bonds.

In the ionic forms, metals are most toxic in their most stable oxidation state. For example, Hg^{2+} , Pb^{2+} , Cd^{2+} , As^{3+} and Ag^+ . In such stable states, these ions interact with biomolecules in the body forming very stable bio-toxic compounds. Due to their bio-stabilities, such compounds are very difficult to dissociate during extraction from the body by medical detoxification therapy (Duruibe, J. O *et al*, (2007).

Lead is the most significant toxic of the heavy metals. Its exposure can occur through contaminated water, food, air, dust and consumer products (Ferner, 2001). Teratogenic effect is one of the most detrimental effects of lead toxicity. Lead poisoning also leads to; dysfunctions in the cardiovascular system, reproductive system, kidneys and joints; damage to the peripheral nervous system (PNS) and central nervous system (CNS); and inhibition of the haemoglobin synthesis (Ogwuegbu and Muhanga, 2005). Other effects are neurological disorder, damage to the urinary tract and gastrointestinal tract (GIT), and brain damage. While organic forms of Pb mainly affect the central nervous system, its inorganic forms usually affect the GIT, PNS, CNS and other biosystems, (McCluggage, 1991; Ferner, 2001). In children, Pb leads to the poor development of the grey matter of the brain, thus resulting in poor intelligence quotient (IQ) (Udedi, 2003). Zn and Ca deficiencies enhance lead absorption in the body.

Zinc is an essential micronutrient, but toxic in excessive amounts causing dysfunctions in the body systems that can lead to impaired growth and reproduction (Nolan, 2003). Symptoms of zinc poisoning can easily be mistaken for those of lead causing (McCluggage, 1991). Ingestion of excessive amounts of Zn can lead to gastrointestinal effects like vomiting, diarrhea and abdominal pain. Additionally, long-term intakes of Zn at pharmacological doses (150–2000 mg/day) can lead to hypochromic microcytic anemia, leukopenia and sideroblastic anemia. These effects can be reversible by

discontinuation of zinc therapy. High Zn levels have also been noted to disrupt the homeostasis of other essential elements. For instance, it can lead to copper deficiency by affecting its uptake in the body. In adults, high Zn doses have been associated with subtle effects on Cu and Fe absorption and utilization in the body and distortion of lipoprotein metabolism. However, these effects can be alleviated by reducing the Zn intake (Hendryx, 2008).

Copper is an essential micronutrient (2 mg/ day) that is involved in formation of hemoglobin, bone health, collagen creation, enzyme coding, and myelination of neurons, among others. Its deficiency can lead to osteoporosis in infants and children, anemia, skeletal problems due to defects in connective tissues and low counts of white blood cells. Acute poisoning from ingestion of excessive copper can result in temporary gastrointestinal distress that is accompanied by symptoms like vomiting, abdominal pain, and nausea. Chronic exposure to Cu can damage the kidneys and liver (Hendryx, 2008).

Iron is a very essential trace element in human nutrition and life. It is actually required in every cell of the body. It is a key component in formation of hemoglobin that is required in carrying oxygen in the body. Iron plays a role in stimulating immune function and physical endurance, regulating muscle function, breathing and digestion as well as brain functions. Recommended dietary intake of Fe ranges between 10 - 50mg/day, depending on physiological status, sex, age, and iron bioavailability (FAO/WHO 1998). The average lethal dose of Fe is 200–250 mg/kg of body weight, although deaths have occurred following ingestion of doses as low as 40 mg/kg of body weight. Autopsies have shown hemorrhagic necrosis and sloughing of areas of mucosa in the stomach. Chronic iron overload is mainly due to hemochromatosis; a genetic disorder characterized by enhanced Fe absorption. In adults, iron supplements (0.4–1 mg/kg of body weight per day) can be taken for long periods without any side effects (Blackwell, 1979; Finch et al, 1972).

Vanadium is classified as carcinogenic to humans (Zenz C, 1962). It has multiple effects on human health such as stomach cramps, mild diarrhea and nausea, especially for people under vanadyl sulfate or sodium metavanadate for the experimental treatment of diabetes.

Stomach cramps have also been reported in a study of people taking about 13 mg vanadium/ day. Inhalation of vanadium pentoxide can cause coughs that can last for days.

Chronic exposure to arsenic has been linked to various forms of cancer such as bladder cancer, skin cancer, kidney cancer and lung cancer. Arsenic ingestion has also been associated with diabetes mellitus and cardiovascular diseases. Exposure to lower levels can cause reduced production of white and red blood cells, nausea and vomiting and cardiovascular effects such as damage to blood vessels and peripheral nervous system and abnormal heart rhythm (Hendryx, 2008).

CHAPTER 3

THEORETICAL PRINCIPLES OF METHODOLOGIES

3.1 Principle of Quantitative X-ray fluorescence spectroscopy

X-ray fluorescence spectroscopy has found wide range of applications especially in qualitative and quantitative determination of sample composition, in addition to measuring coating thickness. In this technique, a high energy beam of primary x-rays is used to bombard an atom. If the incidence beam is of sufficient energy, it dislodges and ejects an electron in the inner shell leaving the atom in an excited (unstable) state. Upon ejection of the inner orbital electron, another from a higher energy orbital is transferred to fill the created hole emitting x-rays (fluorescence) characteristic of that specific element. The energy and wavelength of the emitted photon will be the difference between electron binding energies in the two orbitals. Therefore, measuring the energy of the emitted photons enables determination of the element concentrations in the soils sample irradiated with high energy photons (Andrew, Keith, 2013). In general, figure 3.1 shows the typical instrumentation used for EDXRF spectroscopy.

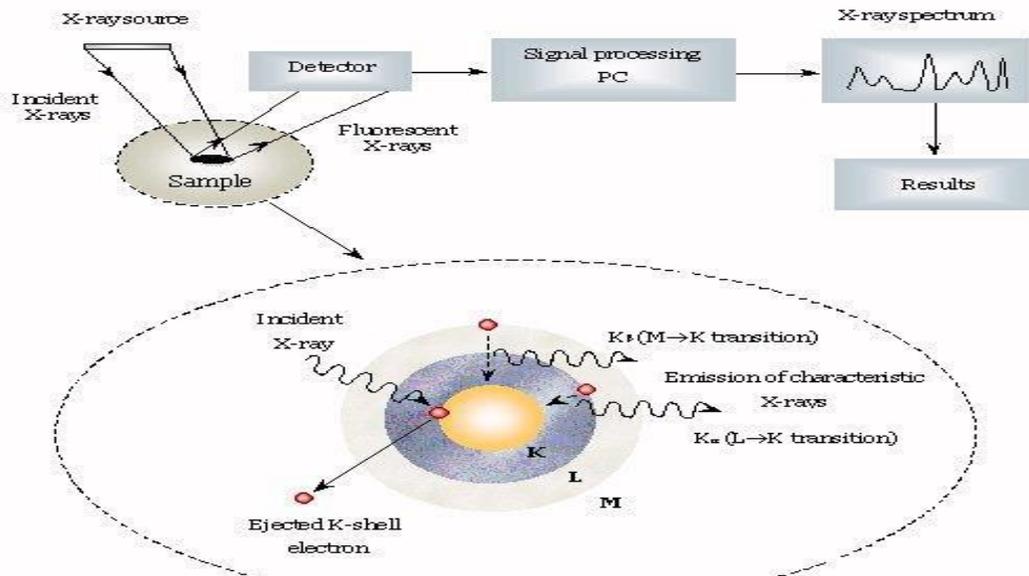


Figure 3.1: The principle of XRF and the typical XRF detection arrangement (Andrew, Keith, 2013).

X-ray spectroscopy is widely used for simultaneous elemental analysis in a wide range of samples presented as solids, powders and particulates (Angeyo *et al*, 2012). Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) can be used to determine the high-Z elements (Na to U). On the other hand, wavelength dispersive spectrometers (WDXRF) enable efficient determination of low-Z elements (Beckhoff, 2006). In practice, the capabilities of a particular XRF instrument and what it is calibrated for, vary between manufacturers. Most instruments are only calibrated for analysis of between 20 - 25 elements and cannot detect light elements. Although the samples can be analyzed without treatment, it necessitates an appropriate sample preparation procedure to achieve high quality results.

In quantitative XRF analysis, the measured fluorescent intensities are converted into the concentration of the analytes. However, the measured intensities depend not only on the concentration of the analyte but also on method of sample preparation, sample type and matrix, thickness and shape of the sample and measurement conditions such as geometrical setup of the spectrometer, irradiated size, flux and spectral distribution of the exciting radiation and the efficiency of detection systems (Beckhoff, 2006).

In general, the detection limits for most XRF measurements varies between 5 to 100 ppm. However, the elemental detection limit is dependent on the x-ray source and the type of detector used in the instrumentation. Ideally, the instrument limit of detection (LOD) should be between 3 to 5 times less than the guideline value that are being used to assess.

Quality control and assurance is crucial in assessing if the accuracy and precision of the data obtained from measurements meet the project's data quality objectives. Standard reference materials containing elements of known concentrations are used for accuracy determination, while precision is the replicability of repeated measurements. The selected reference material should contain all the elements of interest as well as cover the concentration range of interest. Additionally, the selected reference material should be of similar composition as the analyzed samples. In making a decision on the accuracy and suitability of the analytical method and procedure, the experimental values should be within 10 % of the certified value.

XRF analytical technique has been used in a number of studies to determine elemental content in samples and has been found to give accurate results. For instance, Mangala and Patel (1987) used x-ray fluorescence to analyze elemental content in geological samples from Kenya Fluorspar Company in Kerio valley. In their findings, the concentration of copper (Cu), zinc (Zn), niobium (Nb), zirconium (Zr), lead (Pb) manganese (Mn), and uranium (U) in fluorite mineral samples were found to be less than 1000µg/g. They further indicated that elemental concentration of a few trace elements had an influence on the various colors related to fluorite minerals.

A similar study was done by Maina D.M *et al*, (2009) on the distribution of copper and lead levels in soils and *acacia xanthophloea benth* from lake Nakuru National park, Kenya. From their findings, EDXRF and AAS analytical results obtained for IAEA Bowen Kale leaves, certified reference material indicated good agreement between the certified and experimental values. In addition, copper and lead were found to be present among other elements. The data showed good agreement between the two experimental techniques employed, attesting to the accuracy of EDXRF experimental procedure for analysis of samples for heavy metals.

Bosneaga et al. (2009) used EDXRF techniques in evaluating heavy metal pollution status in soils around the Steel and Iron Integrated Works (ISIW) at Galati, Romania. A significant difference was reported between the study area and the control zone that was situated far from industrial and traffic activity. The authors found a decreasing trend in heavy metal concentrations with the distance from the metallurgical works.

Mwendwa (1992) utilized EDXRF for quantitative analysis of elements in various samples from geothermal areas in the rift valley, Kenya. Similarly, in 2012, Mulwa B.M used EDXRF assess heavy metal concentrations in limestone deposits of Kitui county, Kenya.

In conclusion, these studies and others indicate that EDXRF analytical technique is a reliable analytical procedure for analysis of heavy metal levels in soil type matrices.

3.2 Statistical Analysis of Geochemical Data

Factor analysis, cluster analysis, principal component analysis (PCA) and different types of regression analysis are the most commonly used multivariate techniques for studying regional geochemistry (Fig.3.2, Riemann et al., 2001).

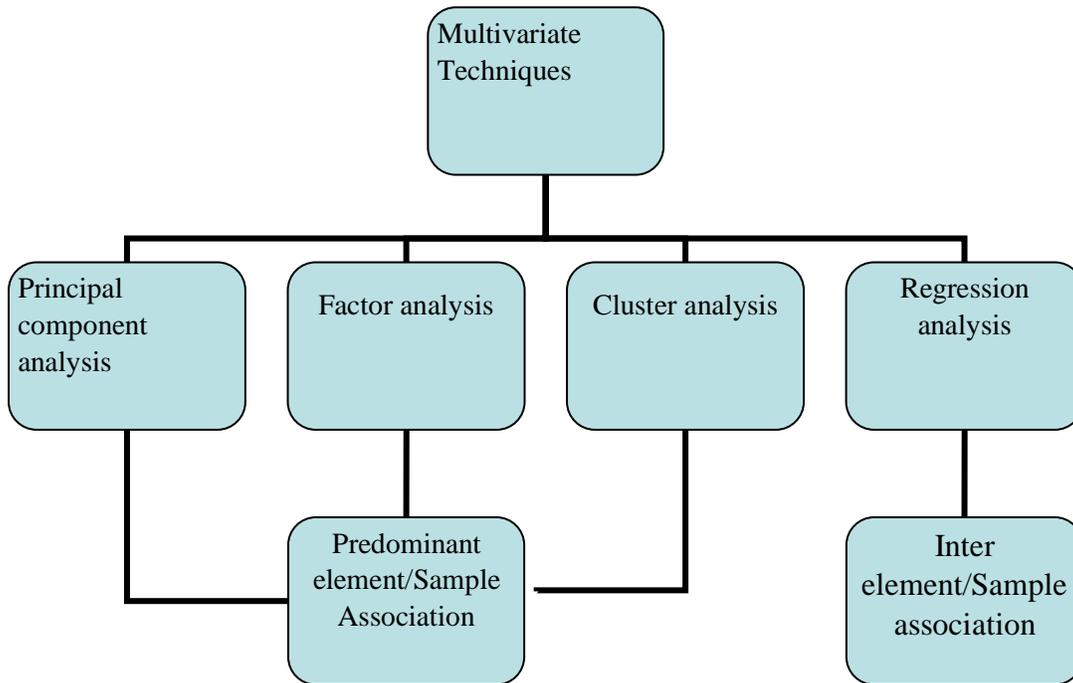


Figure 3.2: Selected Multivariate techniques used in geochemical analysis of data

The predominant element associations or geochemical processes in multi-element data can be identified with factor analysis and principal component analysis. Cluster analysis can be used to detect sample associations while regression analysis for inter-sample and inter-element relationships (Grunfeld, 2005). Real data rarely matches the idealized models of parametric statistics and the data values are often transformed to counteract the effect of outliers. Methods requiring a multivariate normal distribution are especially vulnerable when used with geochemical data and will often deliver unstable and faulty results (Riemann et al., 2001).

3.2.1 Factor Analysis

Factor analysis is a multivariate statistical procedure employed in understanding the dimensionality of a set of variables. Firstly, factor analysis cuts down the number of variables into a smaller set (factors). Secondly, from the larger set of variables, a subset is selected depending on which of the initial variables have the highest correlations with the principal component factors. Thirdly, fundamental dimensions are established between the measured variables and latent constructs. Factor analysis can also create a set of factors that are treated as uncorrelated variables and lastly, it is used to validate the index by showing that the constituent items load on the same factor, while eliminating those that have only one factor.

Factor analysis is used for data reduction and in exploring the fundamental structure of a sizeable set of variables, with an aim of identifying relationships between the variables. It determines trends among sets of variables. The key variables/ indicants are identified, closely reflecting the hypothesized fundamental parameters that assist in validating the derived factors and evaluating if the outcomes are valuable.

When deriving factors, the variables are specified and the correlation matrix is prepared so as to establish the fundamental structure of relationships. For a factor to be retained for interpretation, it should account for the variance of at least one variable. The contribution of each variable to the eigen value is one. Therefore, only the factors with eigen values greater than one are considered significant.

In interpreting factors, factor loadings threshold is ± 0.30 , where loadings of ± 0.40 are considered significant, while loadings greater than ± 0.50 are considered practically significant. Factor loading correlates the variable and the factor, thus the bigger the size of the factor loading, the more significant the loading in interpreting the factor matrix. The squared loading indicates the variable's total variance accounted for by the factor. Therefore, a 0.30 loading denotes that about 10 % of the variance is accounted for by the factor, while a 0.50 loading accounts for 25 % of the variance. For a factor to translate to 50 % explanation, the factor loading must exceed 0.70.

Factor analysis has been used in various studies to determine heavy metal levels in sediments. For instance, Kumar *et al.* (2013) did a statistical analysis of heavy metal (Mn, Ni, Cr, Zn and Cu) concentrations in sediments in order to determine the interrelationship between different parameters as well as in identifying probable source component in an effort to discuss pollution status. In his study, he reported enrichment of the heavy metals which he explained using distinct chemical behavior as is evident with the occurrence of clay, silt in the mangrove environments. The study illustrated the effectiveness of factor analysis (multivariate statistical techniques) in analyses and interpretation of large complex data sets to get better understanding about the heavy metal concentrations and design of monitoring network.

Einax *et al* (1994-2002), in their numerous works considered factor analysis as one of the chemo-metrics methods. The authors were able to demonstrate the possibilities of factor analysis to detect spatial and temporal structures in data sets, and chemo-metrics as a state of the art method in environmental analysis and studies.

Factor analyses methods have been applied in different aspects of environmental studies; atmosphere, hydrosphere, and pedosphere (Simeonov & Tsakovsky, 2000-2003). The studies have played an important role not only in a local aspect where they allow quick response in finding solutions and decision making, but also in a broader sense as a useful environmetrical methodology.

Okuhara et al (2002) suggested applying factor analysis method on ecological data. Observation data was analyzed with and without the outliers, having environmental conditions as the explanatory variables and population of firefly as the explained variable. The authors further incorporated probabilistic neural networks in the proposed model in order to obtain an unknown nonlinear mapping from the environmental conditions (explanatory variable) to the population of firefly (explained variable). This proposed model was able to solve the inverse problem, that is, estimate the effect of the explanatory variables on the explained variable. Furthermore, the authors showed that the model could propose an appropriate strategy for the controllable explanatory variables.

Based on these studies, we can conclude that factor analysis has been successfully used in various fields of environmental studies.

3.3 Sediment pollution indices

To assess the degree of metal contamination in sediments, three parameters can be applied; pollution load index (PLI), enrichment factor (EF) and geo-accumulation index (I-geo).

3.3.1 Pollution load index

Pollution load index (PLI) is used to determine the extent of metal pollution in soils and sediments. This method was proposed by Tomlinson *et al*, (1980), and uses the following equation;

$$PLI = \frac{CF_1 \times CF_2 \times \dots \times CF_x}{n} \dots \dots \dots 3.1$$

where, n is the number of metals and CF_x is the ratio of metal concentration to the respective background value (contamination factor).

Table 3.1: PLI value indicators

PLI Value	Indication
< 1	No pollution
> 1	Significant pollution

Source: Chakravarty and Patgiri(2009)

3.3.2 Enrichment factor (EF)

Enrichment factor (EF) is used to determine the level of contamination, in addition to understanding the distribution patterns of various elements in soil and sediments. It is determined as follows;

$$EF = \frac{\left(\frac{C_n}{C_{Fe}}\right)_{sample}}{\left(\frac{C_n}{C_{Fe}}\right)_{background}} \dots\dots\dots 3.2$$

where, C_n is the elemental concentration; C_{Fe} is the concentration of iron.

In determining EF-values, iron is the most popular normalizing/ reference element. Other commonly used reference elements are aluminium and manganese (Kamaruzzaman, 2009; Kamaruzzaman *et al.*, 2008 and Nyangababo, 2005). In this study, iron was used as the reference element. The level of heavy metal enrichment was determined using the criteria shown in table 3.2.

Table 3.2: EF value Indicators (2005)

EF Value	Significance
<1	Background concentration
1-2	Depletion to minimal enrichment
2-5	Moderate enrichment
5-20	Significant enrichment
20-40	Very high enrichment
>40	Extremely high enrichment

3.3.3 Geo-Accumulation Index (Igeo)

The Geo accumulation index (Igeo) is used for determining the accumulation of heavy metals in sediments (Muller, 1969). It is mathematically expressed as:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \dots\dots\dots 3.3$$

where, C_n is the elemental concentration and B_n is the geological background. The factor of 1.5 accounts for any possible variation in geological background value due to lithologic effect. The Igeo values are rated as shown in table 3.3.

Table 3.3: Geo-Accumulation Index values (Muller, 1969).

Igeo class	Igeo value	RDS quality
0	$I_{geo} \leq 0$	uncontaminated
1	$0 < I_{geo} < 1$	uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	moderately contaminated
3	$2 < I_{geo} < 3$	moderately to heavily contaminated
4	$3 < I_{geo} < 4$	heavily contaminated
5	$4 < I_{geo} < 5$	heavily to extremely contaminated
6	$5 < I_{geo}$	extremely contaminated

Sediment pollution indices have been used in a number of studies to determine heavy metal pollution in soils. Likuku A.S et al (2013) did an assessment of heavy metal (Zn, Cu, Pb, Fe, Ni, Mn and Co) enrichment and level of contamination around the copper-nickel mine in Botswana. The degree of heavy metal pollution was determined using geo-accumulation index, enrichment factors, pollution load index and modified degree of contamination. To assess the enrichment factors, the author used soils samples collected far from the site of concern to represent uncontaminated background concentrations and compared it with the actual Fe content in earth material sources from literature. The latter method was found to be the most relevant. Similarly, Ololade (2014) carried out an assessment of heavy metal pollution in soils within auto-mechanic workshops using geo-accumulation indexes and enrichment and contamination factors.

Shuanxi Fan (2014) assessed the spatial distribution and pollution with heavy metals in roadside soils along Xi'an-Baoji highway in northwest China by determining the pollution load indices. The evaluated results with the pollution level index (PLI),

contamination degree (CD) and contamination factor (CF) were in good agreement proving the reliability of these methods.

Heavy metal pollution of Ni, Zn, Cu, Pb, Mo and As in soils around the open mine, ore enrichment combine and tailing dumps of the zinc, copper and molybdenum combine was assessed by comparing with the control site. According to PLI, CF, CD and I-geo values, the distribution pattern of trace metals in the soil profile showed that the pollution degree in the soils around the open mine and the ore enrichment was higher than that in the soils around the tailing dumps (Ghazaryan et al 2015).

In conclusion, these studies demonstrate the use of pollution load indices as an appropriate method of determining heavy metal contamination in sediments.

CHAPTER 4

MATERIALS AND METHODS

4.1 Introduction

In this chapter, the following topics are discussed; the sampling technique used, sample preparation, measurement instrument and sample analysis for elemental content with EDXRF.

4.2. Sampling

A total of forty (40) soil samples were randomly collected from block C, of Mui basin between 19th to 23rd September, 2013 near the coal wells and others away from the wells at a depth of 10-15 cm. A research assistant from the Ministry of Energy assisted to identify the coal wells during sampling. The samples each weighing approximately 0.5 kg were packed in polyethylene bags and labelled X1-X40, then transported to the Institute of Nuclear Science and Technology, University of Nairobi. The samples were distributed across block C such that; 16 samples were collected from Kathonzweni, 18 from Yoonye and 6 from Kateiko. The location of each of the sampling point was recorded using a GPS (Fig 4.1, Appendix A). Table 4.1 shows the samples collected from each region.

Table 4.1: Sampling Locations and Sample Coding

Sampled site location	Number of samples	Sample codes
Kathonzweni	16	X1-X16
Yoonye	18	X17-X34
Kateiko	6	X35-X40

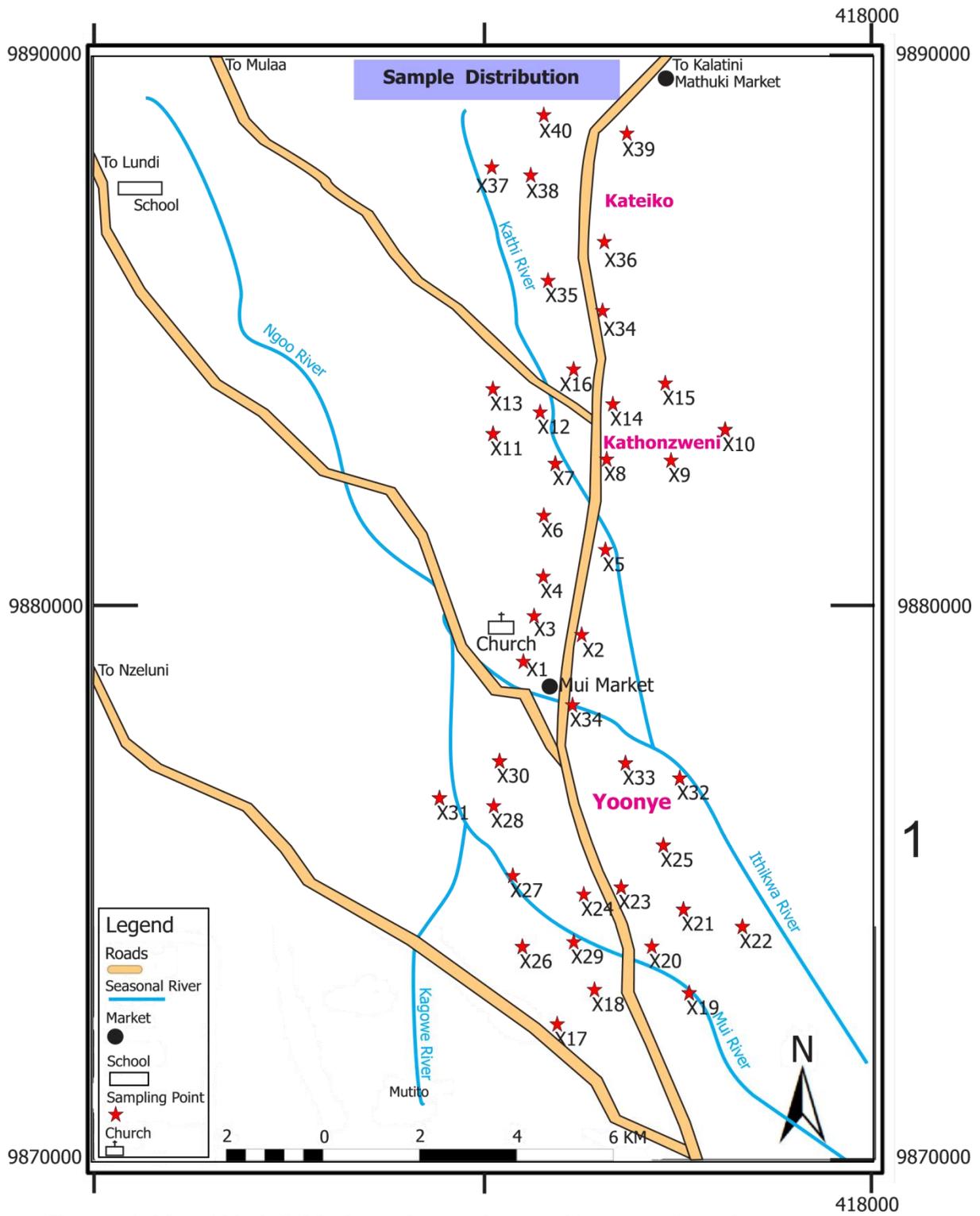


Figure 4.1: Map of block C, Mui basin showing the spatial locations of sampling points.



Figure 4.2: Field soil sampling in block C, Mui basin

4.3 Sample Preparation and Quantitative X-ray fluorescence analysis

The soil samples were dried to constant weight and pulverized into fine powder before being sieved to obtain a powdered matrix of particle $< 75 \mu\text{m}$. Approximately 1.0-2.0 g of the sample was then weighed using analytical weighing balance and transferred to a clean crucible, onto which 0.3-0.4 g of starch was added as a binder. Three pellets of mass between 0.3-0.4 g each were prepared from each sample using special hydraulic press by applying a pressure of 6 tons in 2.5 cm diameter steel die. Three pellets were prepared from each sample, weighed and transferred into a Petri dish, then labeled for subsequent analysis using the EDX-800HS spectrometer based on Emission Transmission (E-T) method using a Molybdenum (Mo) target.

The samples were analysed using an ED-XRF system available at Material Testing and Research Department, Ministry of Transport and Infrastructure. Each pellet was irradiated for 50 seconds live time using molybdenum based X-ray tube. The resultant spectra were collected on the multi-channel analyser in the pulse height analysis mode

and then stored on a suitable memory device (USB -drive) for quantitative analysis using Quantitative X-ray Analysis Software (QXAS). Prior to quantitative analysis, spectral deconvolution was done using AXIL (Analysis of X-ray Spectra by Iterative Least-squares fitting) software. This involved spectrum format conversion from CSV to SPE format and spectrum fitting and finally, qualitative analysis.

4.4. EDXRF Instrumentation and measurements

In this study, the spectral data measurements were taken using an Energy Dispersive X-ray Fluorescence spectrometers series EDX-800HS model CE 212-23701-36; S/N: 2264400090CZ, available at the Material Testing and Research Laboratory, Ministry of Transport and Infrastructure.

The EDXRF spectrometer weighs 100Kg and its physical dimensions were 580 (W) X 750 (D) X 420 (H) mm. It consists of the following modules:

- 1) A large sample chamber which automatically opens and closes and can accommodate samples of up to 300mm wide and 150mm high with optional sample turrets for continuous automatic sample measurements.
- 2) X-ray generator unit which consists of the air cooled X-ray tube with molybdenum target operated at 5-50kV, tube current of 1-1000 μ A, primary X-ray filters automatically switched between 5 types with an exposure area of 10mm in diameter for manual setting, 1, 3, 5 and 10mm diameter are available for automatic settings.
- 3) Semiconductor Si (Li) detector 10mm² mounted at 45⁰ take off angle geometric with respect to the sample. The detector is cooled with liquid Nitrogen (LN₂) during measurements with approximate consumption of 1litre per day. It is biased with a high voltage supply at approximate 1000V connected to a preamplifier. The detector measured resolution is 140eV to Mn-K α for Mn-K α at 5.9Kev.
- 4) Data processing unit which consists of the following modules: IBM PC/AT compatible computer HDD approximately 20GB, Operating System windows XP/Windows 7 and pre-installed factory produced software for qualitative and quantitative

measurements and incorporated algorithm for matrix correlation using Fundamental Parameters (FP) method analysis and calibration curve method of analyses.

Measurements were done in air at dead time less than 25% and were automatically current and voltage adjusted during acquisition. Samples were each irradiated for 50 seconds.

The sample exposure area was maintained at 10 mm diameter throughout measurements in this study. The spectral data was collected and quantitatively analyzed using AXIL (Analysis of X-ray spectra by Iterative Least-squares fitting) software. The program enables for calculation of background subtraction by fitting a polynomial function to the actual spectrum and determines net peak areas of the elements of interest present in the sample.

4.5 Quantitative EDXRF Analysis

The spectral data (Appendix B) obtained following sample irradiation by EDX-800HS were analyzed using QXAS software obtained from the International Atomic Energy Agency (IAEA) after conversion to the ASII format for input (Fig. 4.3).

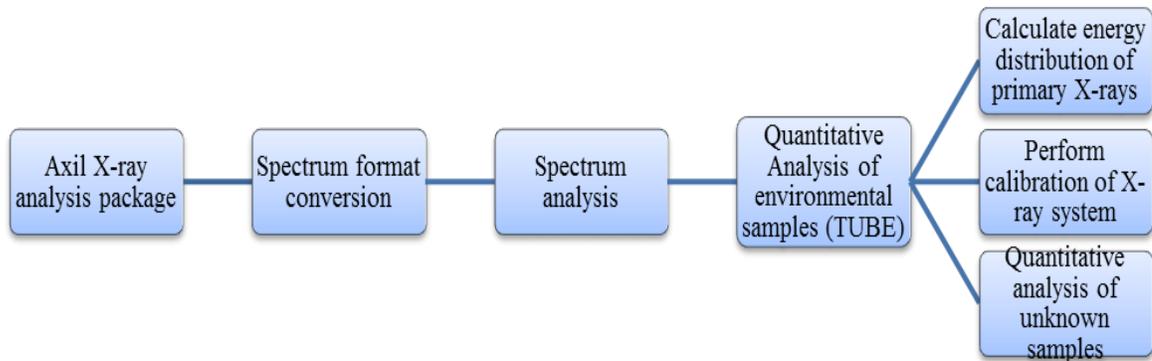


Figure 4.3: Block diagram showing the steps followed in Axil spectral analysis

The spectral data was analyzed by Quantitative Analysis of Environmental Samples (QAES), a modular program of the IAEA's QXAS, was calibrated for quantitative analysis.

Three sub-routines of the program are available for selection of:

- (a) Calculation of energy distribution of primary X-rays for calibration of the system
- (b) Elemental calibration of X-ray system for generalization analyses
- (c) Quantitative analysis of unknown Samples.

The method used for elemental spectral intensities calculation involves fitting spectrum (*.SPE file) with a well-matched mathematical function by utilizing a non-linear least squares scheme, until the best agreement between the measured and calculated spectrum is achieved after several iterations, normally 20. During the entire spectrum fitting, the chi-squares values were <10 which is a clear indication that the fitted model and the measured spectrum are in agreement. The fitted spectral results were converted to *.ASR (Analysis of Spectra Results), and used for quantitative analysis (QAES) after calibration for use with X-ray tube source of excitation with notable spectra of pure element standards of copper (Cu), iron (Fe), molybdenum (Mo), cobalt (Co), zinc (Zn), lead (Pb), tin (Sn), tantalum (Ta), titanium (Ti) and tungsten (W). This was done so as to enable calculation of energy distribution of the primary X-rays in which the average energy of excitation using molybdenum target of 20 keV was used. The accuracy of the method was verified by analysis of standard reference soil PTXRF IAEA 09.

Quantitative analysis of unknown samples spectral data in the *.ASR files were analyzed using the fundamental parameter algorithm modular program of QAES software. Molybdenum thick target sample was used for sample absorption matrix correction after irradiation for 50 seconds when positioned on top of the sample and irradiated when alone according to the procedure described for Emission-Transmission method (Andrew R, Keith, 2013).

4.6 Validation of measurements

To assess the validity of the measurements, certified reference materials from IAEA (PTXRF-09) was analyzed by the same method where experimental and certified values were compared. The lower limits of detection (LLD) values for solid samples prepared in the pellet forms was also obtained from the analysis of PTXRF-09 soil sample. These values were calculated using below equation:

$$LLD = 3 \times \frac{C}{P} \sqrt{R_b} \dots\dots\dots 4.1$$

Where;

R_b is the background area of the element,

P is the peak area of the element,

C is the concentration of the element in mg kg⁻¹,

4.7 Statistical analyses of data

The obtained data was analyzed using Microsoft Excel to get mean and standard deviation of the mean. Multivariate data analysis was performed using factor analysis and cluster analysis by using software IBM SPSS, version 20. The data set containing the sample codes and results of trace elements concentration for; V, Cu, Pb, Zn, Fe, Sr and Mn as variables were imported to the IBM SPSS, version 20 software.

The eigenvectors, which comprised of coefficients corresponding to each variable, were used to calculate the principal scores (factors) and indicated the relative weight of each variable in the component. The results of the score, loadings, influence and explained variance plots were displayed and used for analysis of the data. One way ANOVA (analyses of variance) was used to determine whether the mean heavy metal concentrations varied significantly between different sampling points. The data was further subjected to Pearson's correlation analyses to test if there was a significant correlation between total metal concentrations in the different soil samples. Tables and bar graphs were used to present the results.

4.8 Criteria for assessment of heavy metal pollution levels.

The extent of pollution was determined by calculating the pollution indices namely, enrichment factors, geo-accumulation index and pollution load index.

The extent of pollution PLI was used to assess the level heavy metals contamination. It was determined by applying the method based on pollution load index described earlier. A PLI value > 1 indicates there is pollution whereas PLI value < 1 indicates minimal or no pollution (Chakravarty and Patgiri, 2009; Seshan et al., 2010).

The degree of contamination (EF) was used to evaluate the level of metal contamination and to understand the distribution of the elements of anthropogenic origin in soil/sediments.

The Geo accumulation index (I_{geo}) was used for determining the accumulation of heavy metals in sediments (Muller, 1969).

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Introduction

In this chapter, results of the study are presented and discussed for assessment of heavy metal soil pollution.

5.2 Evaluation of the analytical method

The accuracy of the analytical procedure used was evaluated by analysis of Certified Reference Material from IAEA, (PTXRF IAEA 09-River clay soil) and the results presented in table 5.1 and a typical spectrum in figure 5.1.

Table 5.1: Results of Analysis of Certified Reference Material (PTXRF IAEA 09-River clay)

Element	Experimental values(mg/Kg) Mean±1SD , n=3	Certified values (mg/Kg)	Standard Deviation (Percentage Error)
Mn	1065±80	940-1060	7.5%
Fe	29750±1550	28700-30700	5.2%
Cu	37.3±7.8	18.05-22.15	21%
Zn	76.0±6.4	88.37-103.83	8.4%
Sr	94.4±9.7	97.6-114.4	10.3%
Pb	60.9±2.0	60±1.8	3.2%
V	36.0±3.3	33±4	9.2%

From the results of analyses of the CRM using EDXRF spectroscopy in Table 5.1, it is observed that concentrations values for most elements were within one relative standard deviation (10%) of the certified values except for copper, where a slightly higher concentration than the reported was recorded. However, statistical analysis using ANOVA showed that there was no significant difference ($p > 0.05$) between the experimental and certified values, for most of the elements analyzed in this study. Figure 5.1 shows a typical EDXRF spectrum of PTXRF IAEA 09 sample after irradiation for 50 seconds.

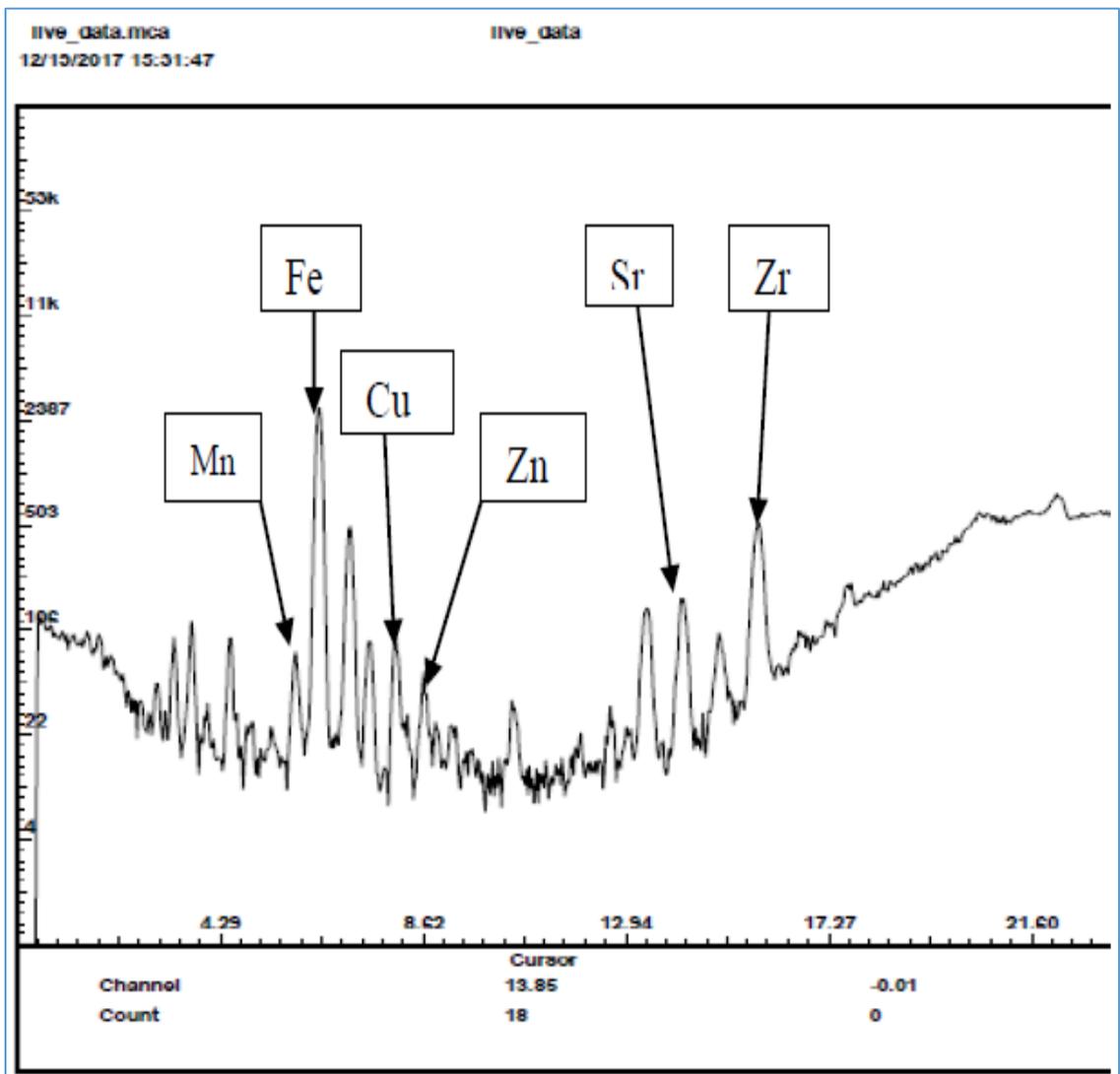


Figure 5.1: Spectra of PTXRF IAEA 09 reference soil sample

5.3 Detection limits

The detection limits were determined using EDXRF, for the elements of interest in the CRM samples prepared in the pellet form (Table 5.2).

Table 5.2: Results of Elemental Detection Limits- PTXRF IAEA 09-River Clay

Element	Atomic Number	LLD Value (mg/Kg)
Vanadium	23	33
Manganese	25	24
Iron	26	15
Copper	29	9
Zinc	30	6
Strontium	38	3
Lead	82	5

From the results in Table 5.2, it can be concluded that the detection limit improves with increasing atomic number and varied in the range of (3-33). These results are consistent with values determined in various studies (Kaniu *et al*, 2011; Mangala and Patel, 1996) mg/kg.

5.4 Heavy metal pollution in soil samples

The EDXRF results obtained from the forty (40) soil samples from the three regions Kathonzwani, Yoonye and Kateiko are presented in the Table 5.3a, 5.3b, 5.3c and in figure 5.2, 5.3, 5.4, 5.6, 5.7 and 5.8.

**Table 5.3a: Results of Heavy Metal Distribution in Block C, Mui basin: Kathonzwani area. (X±1SD)
mg/Kg; n=3.**

Sample	V	Mn	Fe	Cu	Zn	Pb	Sr
X1	280±28	2068±206	66625±883	< 9	80.0±24.0	8.0±3.0	235±18
X2	120±24	1390±207	52083±7375	19.0±2.0	46.0±9.0	21.0±8.0	313±51
X3	271±43	1775±245	58541±8620	45.0±16.1	89.0±27.0	30.0±4.0	371±43
X4	103±18	1743±327	57062±5709	< 9	67.0±25.6	5.4±2.0	478±76
X5	626±108	2037±88	54312±2916	32.0±11.5	108±19	19.0±3.0	462±74
X6	393±42	2888±225	41250±4537	92.0±7.0	200±23	50.0±4.0	1033±109
X7	2083±180	3629±342	97708±8662	97.0±8.0	314±17	67.0±8.0	317±32
X8	549±93	1963±548	34375±6718	69.0±27.0	108±18	53.0±18.0	651±126
X9	419±126	1477±205	47500±4659	51.0±14.0	50.5±17.0	47.0 ±18.0	572±61
X10	298±75	990±114	26917±3212	31.0±3.0	< 6	19.0±4.0	239±45
X11	169±17	1126±172	47500±7748	24.0±4.0	< 6	24.0±5.0	573±86
X12	115±34	929±192	46188±4618	22.0±2.0	< 6	18.0±6.0	486±102
X13	151±30	1128±125	49542±4309	28.0±6.0	45.0±14.6	20.0±3.0	593±129
X14	< 33	667±125	56062±5209	< 9	< 6	15.0±3.0	393±35
X15	55.0±18.0	958±19	53167±7324	< 9	< 6	< 5	700±12
X16	481±74	762±180	47792±6462	56.0±12.0	< 6	36.0±6.0	336±52
Mean	383±50	1595±143	52288±4183	96.0±16.0	80.0±13.0	27.0±4.0	484±62
Max	2083	3629	97708	97.0	314	67.0	1033
Min	55.0	667	26916	19.0	45.0	8.0	235

**Table 5.3b cont.: Results of Heavy Metal Distribution in block C, Mui basin: Yoonye area.(X±1SD)
mg/Kg; n=3**

Sample	V	Mn	Fe	Cu	Zn	Pb	Sr
X17	474±85	1913±210	63250±4075	56.0±18.0	164±22	28.0±3.0	418±64
X18	< 33	925±100	36500±2387	< 9	< 6	< 5	572±42
X19	143 ±46	1617±138	92208±3833	52.0±3.0	< 6	33.0±3.0	464±66
X20	45.0±10.0	855±92	26125±3625	40.0±6.0	42.0±7.0	38.0±5.0	238±26
X21	59.0±6.0	1466±100	43917±6036	21.0±5.0	48.6±27.0	19.0±4.0	465±89
X22	830±183	1379±118	69937±4550	88.0±14.0	174±22	38.0±8.0	276±26
X23	311±105	1929±217	65250±7569	48.9±7.0	87.0±14.0	26.0±3.0	425±81
X24	500±426	2338±247	548123±203	52.0±67.0	138±112	27.0±27.0	347±86
X25	91.0±24.0	2538±298	61917±7251	13.0±2.0	102±14	10.0±2.0	248±24
X26	213±81	1466±113	46250±3939	32.0±3.0	70.0±5.0	20.0±4.0	250±24
X27	643±148	2571±406	60000±8063	57.0±7.0	123±25	30.6±7.4	272±26
X28	473±84	2400±249	52167±6242	43.0±6.0	1367±234	26.0±4.0	312±24
X29	562±88	1542±64	42667±5788	81.0±10.0	139±17	58.0±9.0	471±17
X30	245±93	1775±122	34625±2250	71.0±7.5	107±12	45.0±4.0	545±36
X31	127±31	688±12	25708±1233	36.0±5.0	76.0±16.0	35.0±4.0	365±16
X32	393±53	7789±94	56708±4835	53.0±6.0	75.0±5.0	35.0±5.3	246±25
X33	580±67	598±96	71208±4441	66.3±14.0	87.0±15.0	36.0±3.0	98.0±19.0
X34	884±87	920±156	84042±9076	67.0±6.0	92.0±16.0	43.0±3.0	103±25
Mean	368±55	1538±154	53132±4250	48.0±7.0	96.0±14.0	30.0±5.0	340±51
Max	884	2570	92208	88.0	174	58.0	572
Min	45.0	598	25708	13.0	42.0	10.0	98.0

**Table 5.3c Cont... Results of Heavy Metal Distribution in block C, Mui basin: Kateiko area. (X±1SD)
mg/Kg; n=3 Block C**

Sample	V	Mn	Fe	Cu	Zn	Pb	Sr
X35	42.0±4.0	1850±35	42313±1325	60.0±36.0	601±21	40.0±3.	543±41
X36	360±28	3450±159	60188±3094	52.0±6.0	127±12	37.0±6.0	692±54
X37	87.0±13.0	2225±247	47250±1060	57.0±6.0	101±22	42.0±8.0	692±118
X38	743±71	3071±534	76708±8292	67.0±8.0	143±9	32.0±4.0	409±56
X39	155±56	857±149	38250±5480	35.0±8.0	60.0±9.1	36.0±7.0	318±26
X40	60.0±7.0	820±130	17667±1986	47.0±8.0	66.0±7.0	31.0±7.0	411±66
Mean	241±34	2045±245	47062±4235	54.0±8.0	93.0±14.0	36.0±6.0	510±66
Max	742.5	3450	76708	66.0	143	42.0	692
Min	42.0	820	17667	35.0	60.0	31.0	318

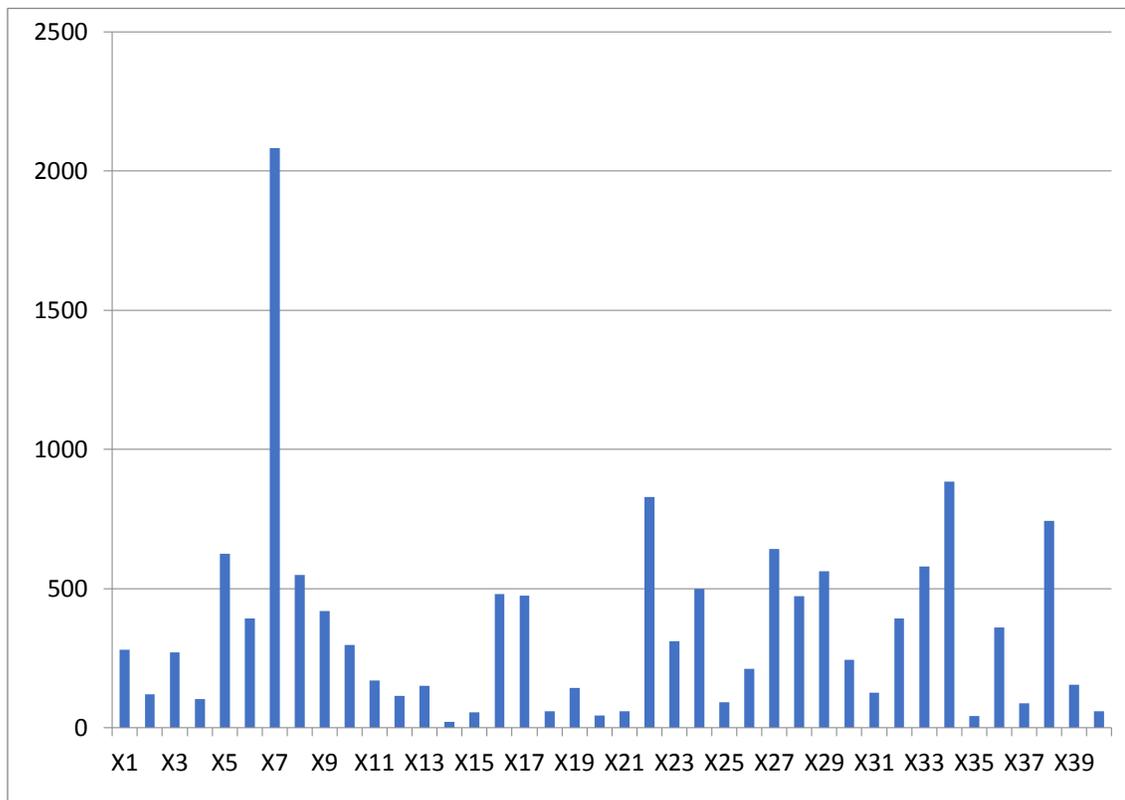


Figure: 5.2: Variation of concentration levels (mg/Kg) of vanadium in block C, Mui basin.

The mean concentration for Vanadium for all samples collected and analyzed from block C was 355 mgkg⁻¹. Soil samples collected from Kathonzweni region registered the highest mean with 383 mgkg⁻¹, Yoonye with 368 mgkg⁻¹. The concentration of vanadium ranged from 41.5 to 2083 mgkg⁻¹ with 355 mgkg⁻¹ and Kateiko 241 mgkg⁻¹. Vanadium is widely distributed in the earth's crust at an average concentration of 100 mgkg⁻¹ (Byerrum, 1991). Krishna and Govil (2007) reported vanadium concentrations with a range of 141.9 to 380.6 mgkg⁻¹ in uncontaminated soils in India. Kabata-Pendias and Pendias (1992), Haluschak *et al.* (1998) and McGrath *et al.*, (2001) reported values of 115 mgkg⁻¹, 455 mgkg⁻¹ and 250 mgkg⁻¹, respectively, of vanadium in uncontaminated soils. On the other hand, Molathegi (2005) reported values as high as 5340 mgkg⁻¹ vanadium in South Africa. The concentration of vanadium in an area is mainly associated with the parent rock type (Som *et al.*, 2002). The high concentration of vanadium in Kathonzweni can be associated to presence of V-rich mineral in the underlying sub soil (Cances *et al.*, 2005). In addition, it is also found concentrated in several bituminous sediments and coals (Seredin, (2007). Mui basin and specifically block C and D have been found to contain huge coal seams (MoE, 2011) and therefore the high concentration of vanadium can be attributed to the coal mineralization.

The mean concentration values for Manganese was 1595 mgkg⁻¹ in Kathonzweni, 1539 mgkg⁻¹ in Yoonye and 2290 mgkg⁻¹ in Kateiko with an overall average concentration for the region as 1637 mgkg⁻¹. It is evenly distributed in Kathonzweni and Yoonye. However, unlike vanadium, manganese registered a higher concentration in Kateiko than in Kathonzweni and Yoonye. The permissible range for the concentration of manganese in soils is 200 to 9,000 mgkg⁻¹ (Eddy *et al.*, 2004). The soils analyzed in this study had a mean metal concentration ranging from 598 to 3629 mgkg⁻¹. Studies carried out by Kabata-Pendias and Pendias (1992) and Haluschak *et al.*, (1998) on uncontaminated soils reported manganese values within the ranges similar to those of this study. McGrath *et al.*, (2001), Kimani (2007) and Awokunmi *et al.* (2010) reported lower levels than those of this study.

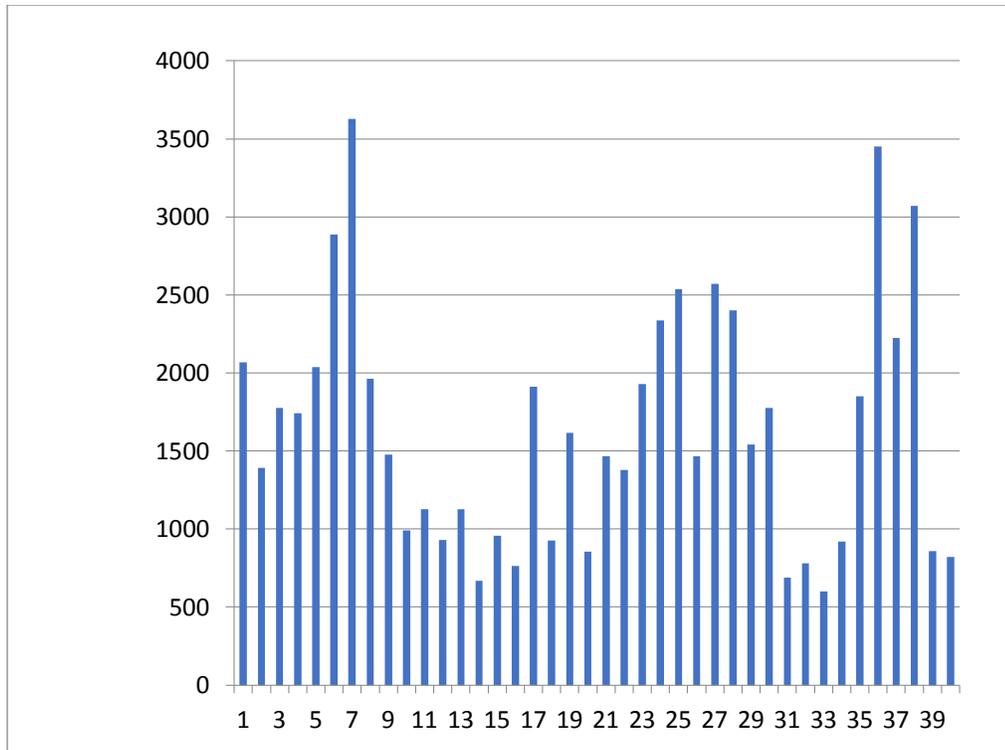


Figure 5.3: Variation of concentration levels (mg/Kg) of manganese in block C, Mui basin.

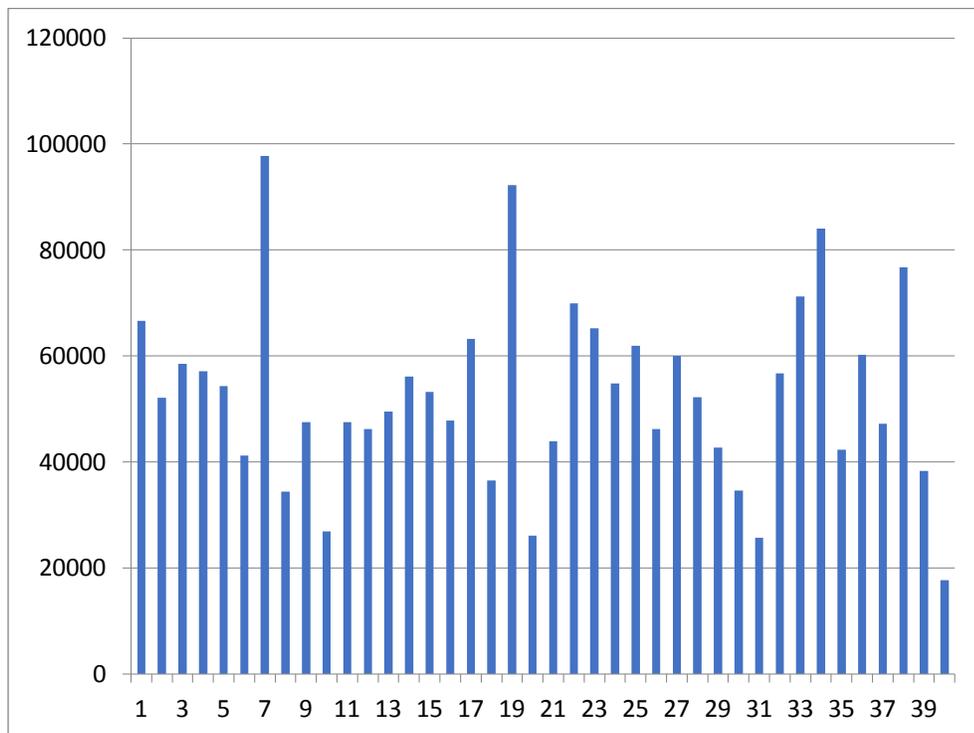


Figure 5.4: Variation of concentration levels (mg/Kg) of iron in block C, Mui basin.

Similarly, the concentration level of Iron showed similar trends as those of vanadium and manganese. In Kathonzwani, the mean concentration for iron was 52288 mgkg⁻¹, 54849 mgkg⁻¹ in Yoonye and 47062 mgkg⁻¹ for Kateiko, which all averaged to 52657 mgkg⁻¹ for the three regions. Awokunmi *et al.* (2010) reported values between 1100 to 10,920 mgkg⁻¹ while McGrath *et al.* (2001) reported an iron metal content of 80000 mgkg⁻¹ and Kimani (2007) reported a mean concentration of 57100 mgkg⁻¹ on uncontaminated soil. These values are within the same range as the ones obtained in this study (17666 mgkg⁻¹ to 97708 mgkg⁻¹). Other studies have however reported lower values than those reported in this study. Akubugwo *et al.* (2012) reported an iron metal content in the soils to range between 74 – 226 mgkg⁻¹. Similarly, Tsafe *et al.* (2012) reported a value of 195.25 mgkg⁻¹ in the soils studied.

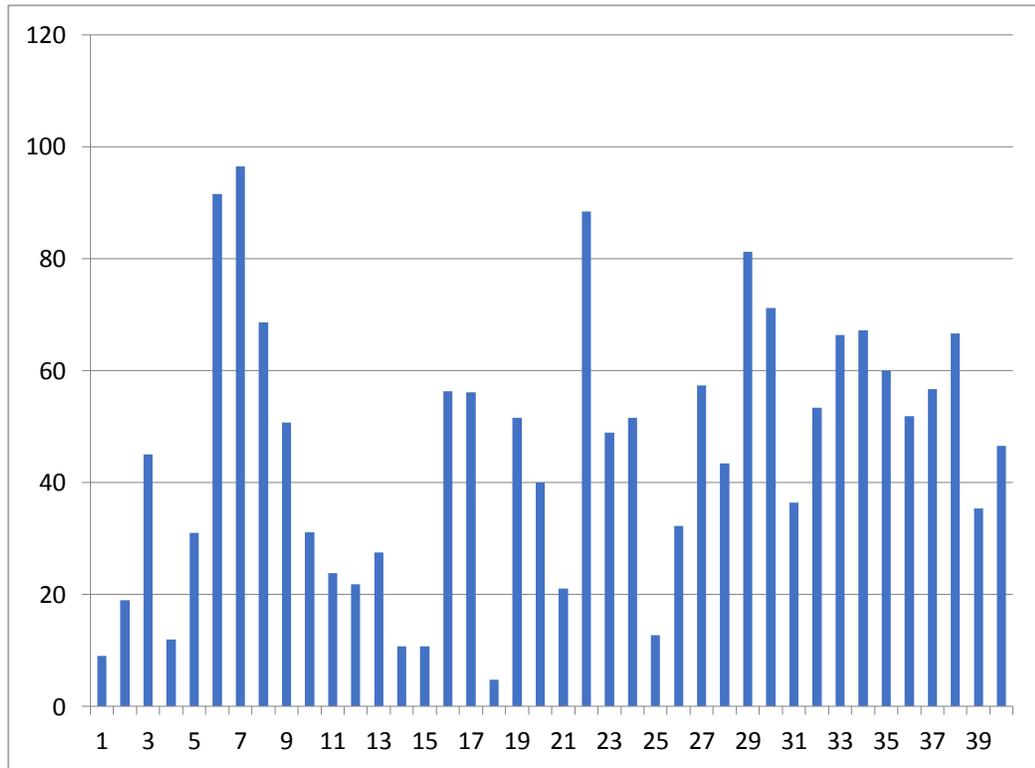


Figure 5.5: Variation of concentration levels (mg/Kg) of copper in block C, Mui basin.

Copper had the lowest mean concentration in soil sample collected from Kathonzwani (37.8 mgkg⁻¹). However, the mean concentration of copper in soil samples from Yoonye and Kateiko averaged 49.1 mgkg⁻¹ and 52.8 mgkg⁻¹ respectively. The mean copper

concentrations in the soil samples in this study ranged between 4.8 - 96.5 mgkg⁻¹. Values reported in literature elsewhere for uncontaminated soils indicate that, the results obtained in this study compare well. For instance, Kabata-Pendias and Pendias (1992) reported soils with higher limits of 140 mgkg⁻¹, Haluschak *et al.*, (1998) 68 mgkg⁻¹, McGrath *et al.* (2001) 100 mgkg⁻¹ and EPA, (1995) 750 mgkg⁻¹. Others like Awokunmi *et al.* (2010) reported higher levels of copper from 95 to 6726 mgkg⁻¹ in soils collected from several dumpsites in Nigeria.

The overall concentration of copper for the block C region was 45.2 mgkg⁻¹ and is within the world average values of between 14 and 109 mgkg⁻¹ (Kabata-Pendias, 2010). This is also in agreement with Cu values reported by Mulwa *et al.*, (2012) for Mwanyani area in Kitui County. Groenenberg *et al* (2010) reports that, copper accumulates in the top horizons. This is attributed to bioaccumulation as well as its anthropogenic sources.

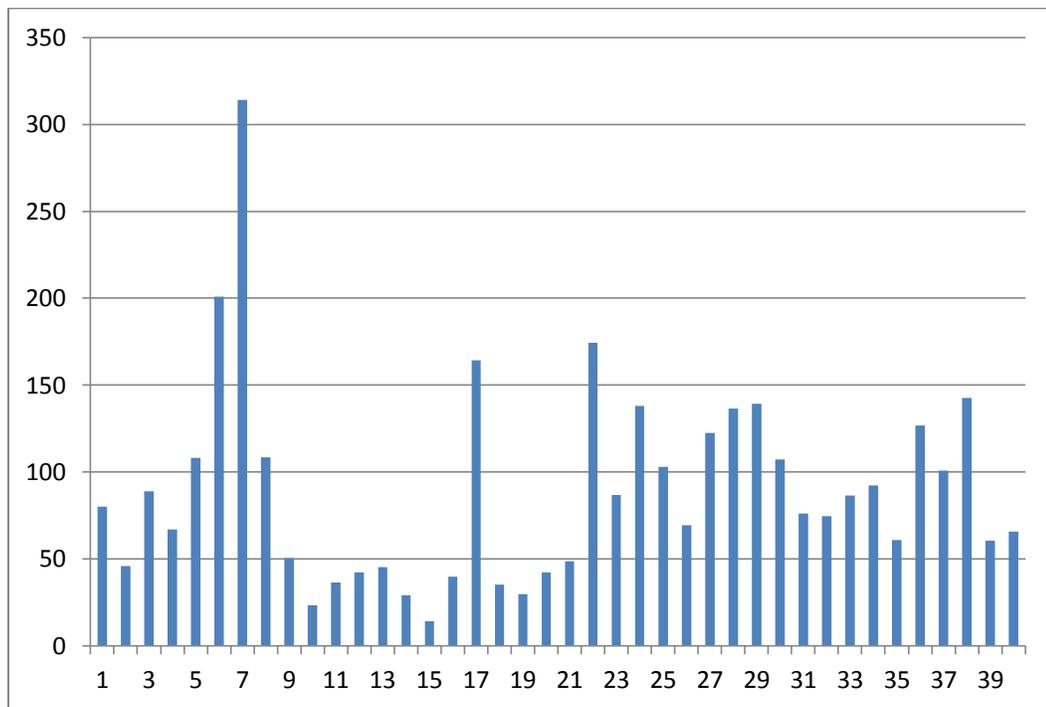


Figure 5.6: Variation of concentration levels (mgkg⁻³) of zinc in block C, Mui basin.

Similar trends for vanadium, manganese and iron are shown for zinc levels as evenly distributed in the region with a mean value of 80.8 mgkg⁻¹ in Kathonzweni, 95.9 mgkg⁻¹ in Yoonye and 92.8 mgkg⁻¹ in Kateiko, and an average of 89.4 mgkg⁻¹ for the whole

region. Except for some samples (X6,X7 from Kathonzweni, X17, X22, X24, X27, X28, X29 from Yoonye and X36, X38 from Kateiko whose concentration levels are above the worldwide averages of between 60- 89 mgkg⁻¹ (Kabata-Pendias, 2011). The normal range of zinc in soils is estimated at 10 – 300 mgkg⁻¹ (Eddy *et al.*, 2004). The concentration of zinc in soils in this study was within values ranging between 14 mgkg⁻¹ to 314 mgkg⁻¹. These results are in agreement with those of several studies done in different countries for uncontaminated soils. Kabata Pendias and Pendias (1992) reports 300 mgkg⁻¹, Haluschak *et al.*, (1998) 230 mgkg⁻¹, McGrath *et al.* (2001) 200 mgkg⁻¹, and Kimani (2007) 200 mgkg⁻¹, Cheng *et al.*, (2009) notes that, zinc is mobile during weathering processes and its easily soluble compounds are readily precipitated by reactions with carbonates, or it is absorbed by minerals and organic compounds, specifically in the presence of sulfur. The factors controlling the mobility of Zn in soils are very similar to those listed for Cu, but Zn appears to occur in more readily soluble forms (Alloway, 2004). Cluster analysis (Table 5.9.3) indicates that trace elements Cu and Zn form a cluster and were strongly correlated with regression value of R=0.714(Table 5.6).

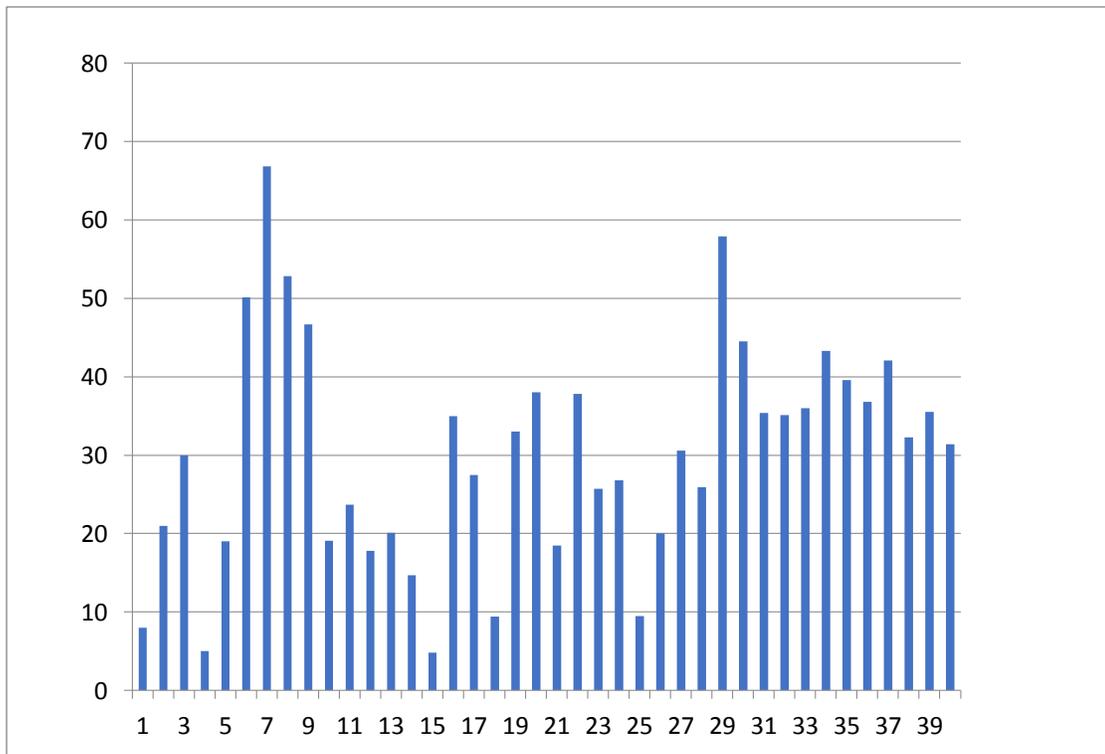


Figure 5.7: Variation of concentration levels (mgkg⁻³) of lead in block C, Mui basin.

Lead mean concentration ranged from 27.2 mgkg⁻¹ in Kathonzweni, 31.1 mgkg⁻¹ in Yoonye and 36.4 mgkg⁻¹ in Kateiko and average mean concentration 30.2 mgkg⁻³ for the whole area indicating an even distribution in the region. In this study, a mean level of lead ranges from 4.8 to 66.8 mgkg⁻¹ and is in agreement with other studies done on uncontaminated soils. Premarathna *et al.* (2011) reported a range of 15 to 311 mgkg⁻¹ ; Kabata-Pendias and Pendias (1992) reported 189 mgkg⁻¹, Haluschak *et al.* (1998) 55 mgkg⁻¹ for uncontaminated soils. However, Awokunmi *et al.* (2010) reported very high levels of lead from soils collected from various dumpsites (contaminated soil) to range ranging between 3500-6860 mgkg⁻¹. Aluko *et al.* (2003) also reported high values of Pb in soil ranging from 1345 -1690 mgkg⁻¹ on contaminated soil.

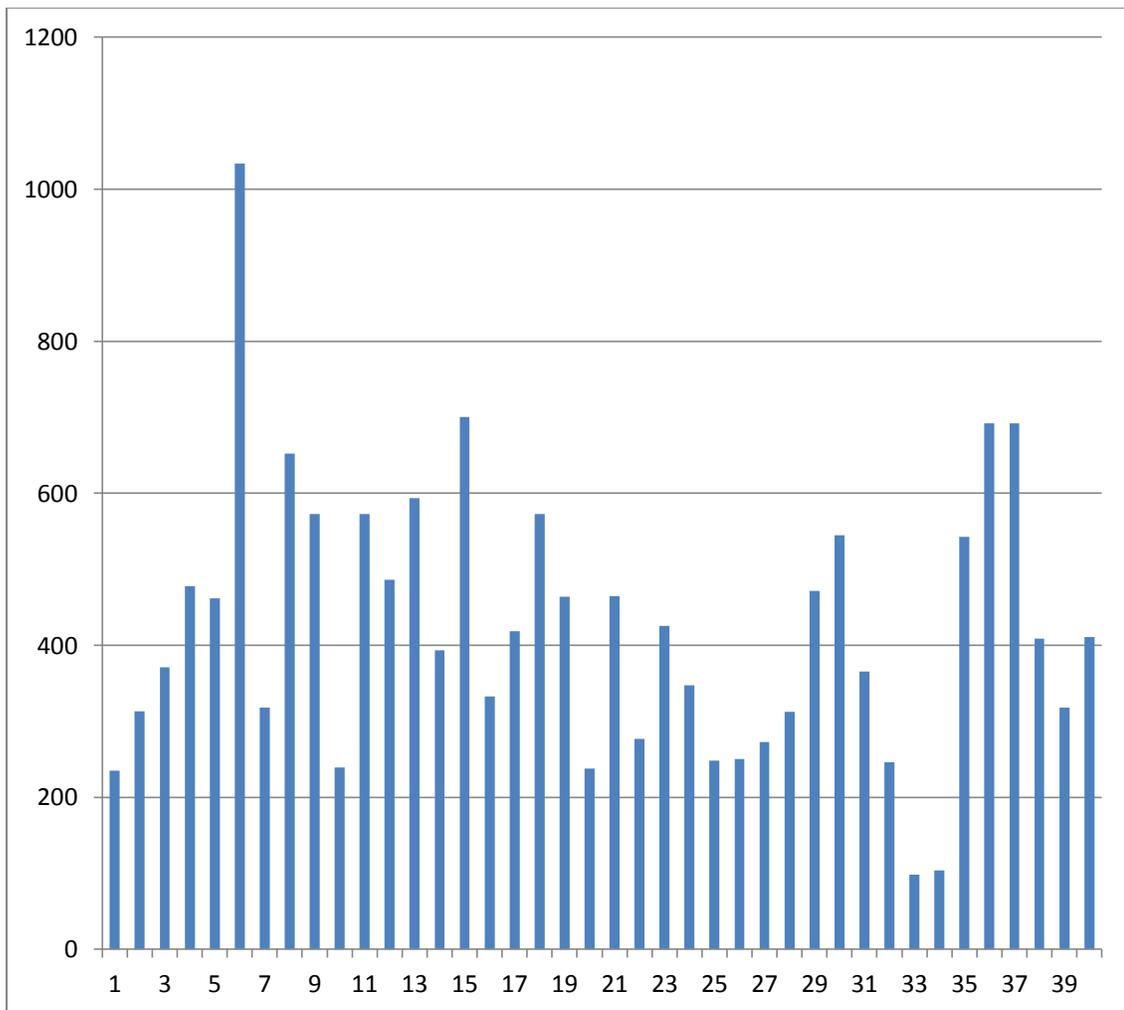


Figure 5.8: Variation of concentration levels (mgkg⁻³) of strontium in block C, Mui basin.

In general, strontium concentration values averaged at 423 mgkg⁻¹ in the region. In Kathonzweni, the mean concentration was 485mgkg⁻¹, while in Yoonye the mean concentration was 340 mgkg⁻¹ and the highest mean concentration was from Kateiko was 509 mgkg⁻¹. The worldwide reported range of strontium in uncontaminated soils is 260-370 mgkg⁻¹ (Kabata-Pendias, 2011). The high concentration levels of Sr reported in the study can be linked to the clay minerals, since they have a tendency to absorb strontium, and thus most argillaceous sediments are enriched with strontium (Dolníček et al., 2010).

The results in table 5.4 and 5.5 indicate the distribution of the elements V, Mn, Fe, Cu, Zn, Pb, and Sr in Mui basin and fro uncontaminated soils from other parts of the world.

Table 5.4: Descriptive statistics of soil heavy metals, (mgkg⁻¹) in block C, Mui basin.

Element	V	Mn	Fe	Cu	Zn	Pb	Sr
Average	355	1637	52657	45.15	89.40	30.18	423
Min	21.0	598	17666	4.8	14.1	4.8	98.0
Max	2083	3629	97708	96.5	314	66.8	1033

Table 5.5: Comparison of the mean concentration of the studied metals in soil samples from Mui basin, Waithaka, Dandora, European soils, world averages and the Romanian guide (World averages, Njagi, 2009).

Element	Mui basin (mg/Kg)	World averages (mg/Kg)	European soils (mg/Kg)	Romanian guide (mg/Kg)	Waithaka (mg/Kg)	Dandora/Korogoch (mg/Kg)
Mn	1637	850	650	900	2400	4366
Fe	52657	48700	35100	-	57100	45800
Cu	45.0	45.0	13.0	20.0	BDL	105
Zn	89.0	95.0	52.0	100	133	462
Sr	423	375	89.0	-	BDL	-
Pb	30.0	20.0	-	-	34.5	264
V	355	135	60.4	50.0		

From the Table 5.5, it can be observed that the concentration levels of most metals were either within the World averages, the Romanian guide, the European uncontaminated soils and or soils obtained from Waithaka which could be used as background values. However, vanadium and manganese registered higher values. This can be attributed to the coal mineral for vanadium and the clay soil which is rich in manganese in the area.

The results of correlation between various metals are presented in Table 5.6. The concentrations of several metals were strongly correlated with each other; for example, V/Fe, V/Zn, V/Pb, Mn/Zn, Cu/Zn, Cu/Pb, Zn/Pb at 0.589, 0.804, 0.575, 0.733, 0.714, 0.893, and 0.575 respectively. This indicate a strong link between them probably the origin which could be the rock type in the study area.

Table 5.6: Matrix (Pearson correlation coefficient)

	V	Mn	Fe	Cu	Zn	Pb	Sr
V	1.00	0.479	0.589	0.663	0.804	0.575	0.236
Mn	0.479	1.00	0.413	0.383	0.733	0.270	0.283
Fe	0.589	0.413	1.00	0.259	0.423	0.080	0.270
Cu	0.663	0.383	0.259	1.00	0.714	0.893	0.075
Zn	0.804	0.733	0.423	0.714	1.00	0.575	0.047
Pb	0.575	0.270	0.080	0.893	0.575	1.00	0.120
Sr	-0.236	0.283	-0.270	0.075	0.047	0.120	1.00

The severity of pollution contamination was determined with the use of pollution load index (Table 5.7).

Table 5.7: Contamination factors (CF) for the studied elements

Element	V	Mn	Fe	Cu	Zn	Pb	Sr
Average for sample	355	1637	52657	45	89	30	423
Background values	135	850	48700	45	95	20	375
CF	2.63	1.93	1.08	1.0	0.94	1.50	1.13

Results of the CF values for most of the metals such as Mn, Fe, Pb, Cu, and Sr in the study area are low (<2) (Table (5.7)). But, CF value for V was higher than 2 which could be attributed to the influence of external discrete sources like agricultural runoff and other anthropogenic inputs. The calculated value for PLI for the soil samples collected was unity.1.01, almost a unit. This is an indication that the soil in Mui basin is not contaminated (Chakravarty and Patgiri, 2009).

Table 5.8: Enrichment Factor (EF)

Element	V	Mn	Fe	Cu	Zn	Pb	Sr
Average for sample	355	1637	52657	45	89	30	423
Background values	135	850	48700	45	95	20	375
C _n /Fe (sample)	0.0073	0.034	1.08	0.00093	0.00184	0.00062	0.0087
C _n /Fe (background)	0.0028	0.017	1	0.00092	0.00195	0.00041	0.0077
Enrichment factor (EF)	2.632	1.93	1.08	1.0033	0.94103	1.51	1.13

From the results obtained, EF values for zinc was less than one. Copper and iron had an EF value approximately one, while strontium, lead, manganese had EF values ranging between one and two (EF; 1-2) which meant depletion to minimal enrichment for the elements. Vanadium had an EF value between two and five (EF; 2-5) meaning the soil was moderately enriched with vanadium.

Table 5.9: Geo-accumulation values for the studied elements

Element	V	Mn	Fe	Cu	Zn	Pb	Sr
Average for sample	355	1637	52657	45.15	89.39	30.18	423
Background values	135	850	48700	45	95	20	375
Igeo values	0.1088	0.1369	-0.3836	-0.5964	-0.6570	-0.1423	-0.3821

The geo- accumulation values for Fe, Cu, Zn, Pb and Sr were all below zero ($I_{geo} < 0$) which means the soil is uncontaminated with these elements. However for vanadium and manganese the Igeo values were between zero and one ($0 < I_{geo} < 1$) meaning the soil was uncontaminated to moderately contaminated with the two elements to some extent.

Factor analysis was conducted to determine the metals clusters for variability within the study area. Kaiser stopping criterion (i.e., all factors with eigen values greater than 1) was used to decide the number of factors to extract as shown in Table 6.0. Based on the extraction criteria, Table 6.0 shows the factors that were extracted.

Table 6.0: Total Variance Explained

Component	Initial Eigenvalues			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.704	52.917	52.917	2.595	37.070	37.070
2	1.399	19.981	72.898	2.269	32.413	69.483
3	1.080	15.431	88.329	1.319	18.846	88.329
4	.417	5.961	94.290			
5	.217	3.105	97.395			
6	.123	1.761	99.156			
7	.059	.844	100.000			

From the section of “Rotation Sums of Squared Loadings,” it can be observed that only 3 factors met the cut-off criterion for extraction of factors. Factor 1 accounted for 37% of the variability, factor 2 for 32% of the variability while factor 3 accounts for 19% of the variability in all the 7 factors displayed in Table 6.0.

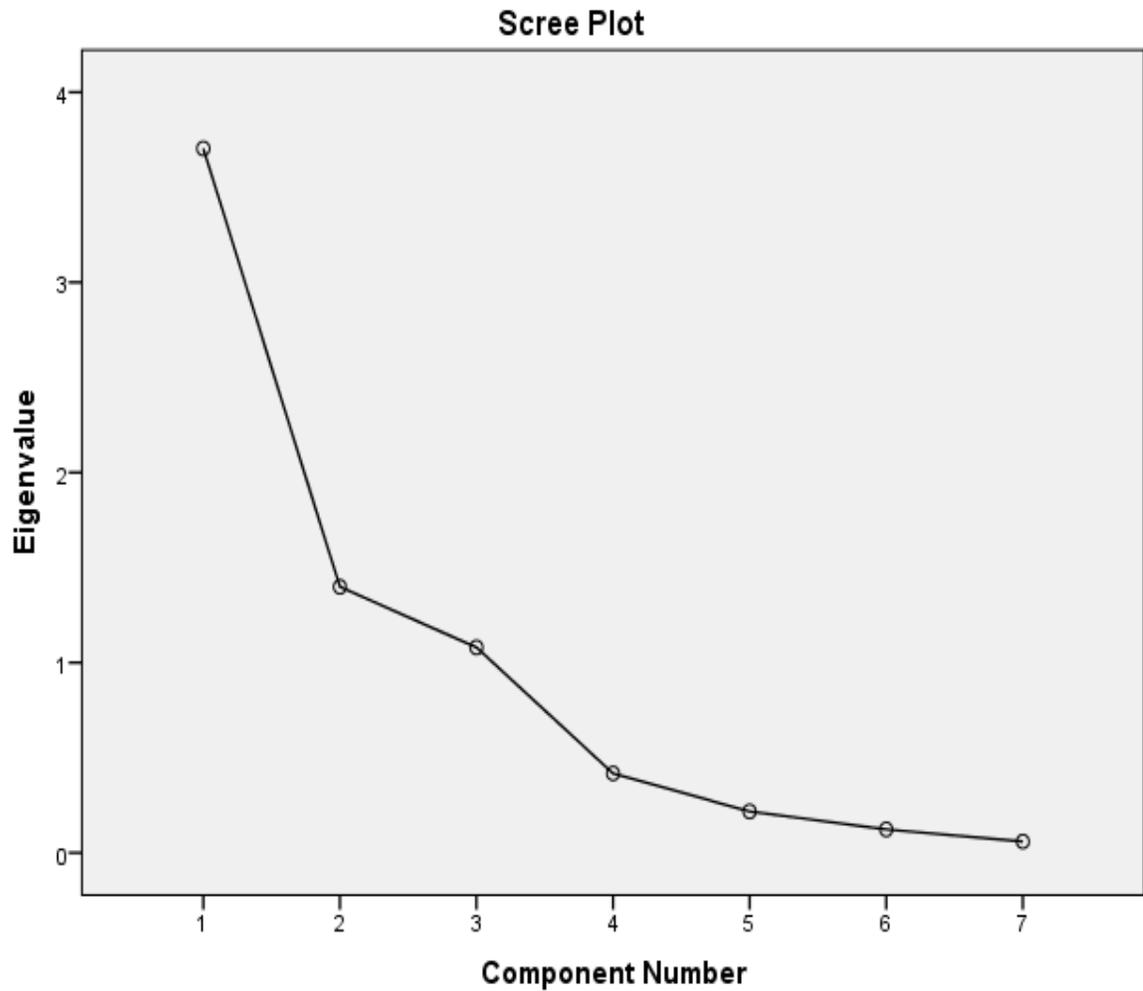


Figure 5.9: The curve shows the variability caused by all the 7 factors

From the fig (5.9), it can be observed that the curve levels out after the first three factors; Factor 1 account for 37.07% of the variability and is associated with lead and copper, factor 2 accounts for 32.413% of the variability and is associated with vanadium, manganese, iron and zinc while factor 3 accounts for 18.84% of the variability and is associated with strontium. This leads us to a conclusion that the 7 metals under study can be grouped into three categories. The results of the scree plot are in agreement with the Kaiser criterion.

Table 6.1:Rotated Component Matrix

Element	Component		
	1	2	3
V	0.618	.640	-.291
Mn	0.193	.816	.430
Fe	0.022	.806	-.375
Cu	0.931	.241	.037
Zn	0.615	.695	.106
Pb	0.964	.042	.079
Sr	0.040	-.039	.944

From the table (6.1), the following can be observed; copper and lead are grouped on factor one implying that sections that had high levels of copper were also likely to have high levels of lead, vanadium, magnesium, iron and zinc are grouped in on factor 2 which suggest their common origin, probably the rock type and that the presence of any of them could also predict presence of the other three. Only strontium grouped in on factor 3, implying that the metal did not have any association with other metals in the study area.

The study adopted k-means cluster analysis to establish various possible groupings that characterized the 7 elements under study as shown in the Table 5.9.3.

Table 6.2:Final Cluster Centers

Element	Cluster	
	1	2
V	592	242
Mn	2112	1409
Fe	71352	43656
Cu	55	40
Zn	124	73
Pb	32	29
Sr	333.21	466.90

The cluster centers show that the 7 elements can be put in two major clusters. According to the table, the first cluster incorporated 6 elements (V, Mn, Fe, Cu, Zn, Pb,) while the second cluster had only Sr.

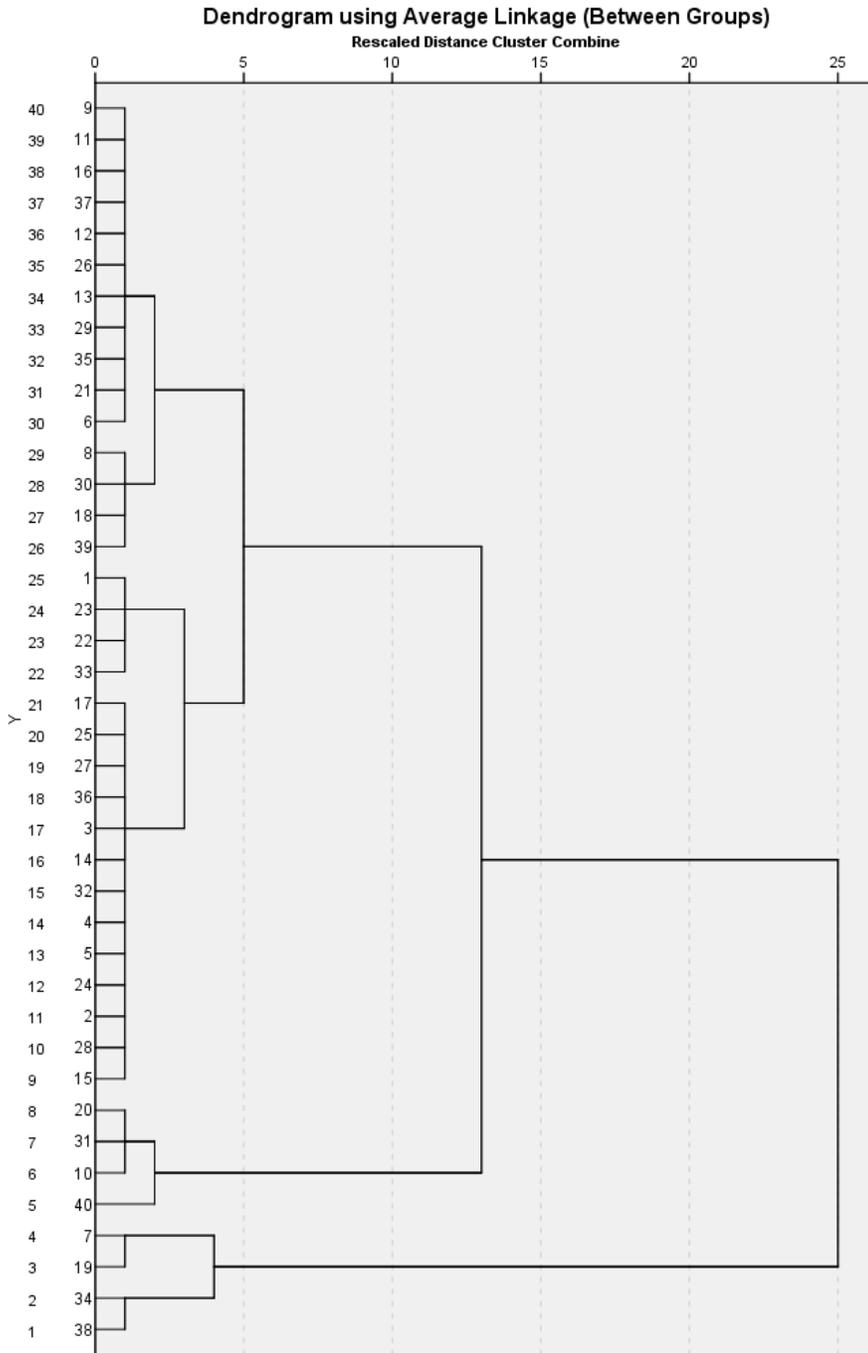


Figure 6.0: Shows various clusters within the 40 Samples

The clustering was performed by the use of Ward's method of linkage, squared Euclidean distance as similarity measure, z-transform of the raw data and Sneath's index for determination of cluster significance. The dendrogram identifies two main clusters, one big cluster with three sub-clusters with samples from the three regions of block C. This cluster could be associated with the elements V, Mn, Fe, Cu, Zn, Pb. The second as is seen from the dendrogram is characterized by the biggest Euclidean distance to the other clusters (high significance of clustering). This cluster could be associated with strontium metal which has no close association with the other six elements. The results of the dendrogram is consistent with the results obtained using the K-means cluster Analysis. The two clusters reflect in a way the sources of the heavy metals which can be associated with the type of soils in the regions and the anthropogenic activities which is mainly agriculture in the area.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

From the results of this study, the following conclusions have been drawn;

- (i) EDXRF results proved existence of vanadium, manganese, iron, copper, zinc, lead and strontium in the soil samples collected from various sites of block C of Mui basin.
- (ii) The concentration of the metals studied was within the world averages, the Romanian guide for uncontaminated soils and similar to those in literature found elsewhere for uncontaminated soils (Table 5.5).
- (iii) From the results obtained, the EF values, the Igeo values and the value of PLI indicate that the soils in Mui basin are not contaminated with heavy metals which can be harmful to environment and subsequently to human beings and animals. However, intensive human activities, especially mining, could lead to heavy metal pollution contamination of the soils hence adversely affect human health and animals in the near future when mining commences.
- (iv) Factor analysis indicated that, 88% of the total variance was explained by the three factors (1, 2 & 3), while Cluster analysis showed that six of the studied elements had a similar source.

6.2 Recommendations

- i) A similar study is highly recommended for the entire Mui basin and its environs. This should be extended to cover heavy metal levels in plants and water sources such as wells and bore holes.
- ii) Research on heavy metal levels should be carried out on coal samples and be compared with the results of this study.

- iii) The Government of Kenya, through the National Environmental Management Authority (NEMA) and the Ministry of Energy and Petroleum (MoEP) to ensure a regular heavy metal level monitoring in Mui basin and the environs especially when Coal mining commences. This would ensure that the enhanced heavy metal level do not put the workers and the public at risk and to provide mitigation measures where and when heavy metal levels are found be a threat to human health.

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APPENDICES

Appendix A: GPS Sample Coordinates

Sample Number	GPS Coordinates	Altitude (m)	Location
X1	0412035 9875912	700	
X2	0400046 9877153	708	
X3	0409917 9877261	727	
X4	0410549 9883734	751	
X5	0411767 9874605	688	
X6	0412009 9872311		Kathonzweni
X7	0411632 9872552	682	
X8	0412242 9872324	678	
X9	0412201 9872306	678	
X10	0414037 9878741	700	
X11	0414028 9878767	698	
X12	0414594 9879621	695	
X13	0413014 9873803	650	
X14	0414275 9879280	689	
X15	0413998 9879651	690	
X16	0414003 9871634	689	

Cont. Appendix A

Sample Number	GPS Coordinates	Altitude (m)	Location
X17	0413999 9879692	692	
X18	0414727 9880525	725	
X19	0412197 9879811	727	
X20	0410112 9881053	725	
X21	0413969 9883135	723	
X22	0410959 9878334	705	
X23	0410955 9878380	703	
X24	0410666 9878310	701	
X25	0412501 9877256	699	
X26	0412626 9877291	699	Kateiko
X27	0412176 9875697	702	
X28	0412433 9875023	695	
X29	0412425 9878334	705	
X30	0413236 9871079	677	
X31	0413255 9871713	678	
X32	0413173 9872110	679	
X33	0413146 9872309	680	
X34	0412669 9871685	678	

Cont.: Appendix A

Sample Number	GPS Coordinates	Altitude (m)	Location
X35	0412172 9870964	678	
X36	0412572 9870325	679	
X37	0411937 9870491	692	
X38	0409998 9879503	724	Yoonye
X39	0410438 9879503	714	
X40	0412944 9879679	688	
