Trace Element Analysis of Soil Samples from Mui Basin, Kitui County for Mineral Content Evaluation using Multivariate Statistics

By

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DECLARATION

I declare that his thesis is my original work and has not been presented to any other University for the purposes of an award of any degree.

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This work is dedicated to the Lord God Almighty and to my wonderful family members for their immense support during the entire period of my study.

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ABSTRACT

The importance of minerals for economic development and sustainability of a country cannot be ignored in modern society. However, mineral exploration in deeply weathered environments is often hampered by significant depths, greater than five meters, of weathered or transported material over mineralized bedrock. Nonetheless, mineral exploration in thick vegetation cover can be undertaken by evaluating trace elements levels in underlying soils. In Kenya however, there exists limited studies on geochemical mapping.

The main aim of this study was therefore, to identify selected trace elements in block C of Mui basin, Kitui County on an area of 131 Km^2, identified as Yoonye, Kateiko and Kathonzweni and to use multivariate analyses on the data set to determine mineral content of buried ores. Seven (7) trace elements, namely; copper (Cu), nickel (Ni), zinc (Zn), chromium (Cr), vanadium (V), strontium (Sr) and zirconium (Zr) were studied in fifty (50) soil samples randomly sampled from the three locations between 3rd to 10th March, 2014, following EDXRF analyses. The soil samples were analysed with Shimadzu tube-excited EDX 800HS spectrometer available at Material Research Testing Laboratories in the Ministry of Transport, Infrastructure Housing and Urban Development. Multivariate analysis was done on the results of trace elements concentrations using Principal Component Analysis, Cluster Analysis and Regression Analysis so as to determine the predominant element and inter-elemental associations in the samples analyzed.

In general, the study found the following trace elements variations; that zirconium had the highest concentration (599-2917) mg/kg, and nickel had the lowest concentration ranging from (6.88-35.8) mg/kg in the study area. In addition, the concentrations of copper, zinc, chromium, vanadium and strontium were found to vary between (16.3-85.1) mg/kg, (10.9-161) mg/kg, (38.7-93.3) mg/kg, (293-657) mg/kg, and (70.3-770) mg/kg, respectively. The elevated concentrations of Zr and V in the soil samples were attributed to their significant role as mineral indicators of buried minerals. Additionally, the Pearson correlation coefficient between Cr and V, Ni and V, Ni and Cr were found to be highly correlated; with R values of 0.64, 0.569 and 0.515, respectively. This was linked to the presence of primary minerals pyroxene and biotite in the underlying geological strata.

Moreover, Principal Component Analysis (PCA) qualitatively identified three key clusters which represented the sampling locations, namely; PC1 (87%)-Yoonye, PC2 (11%)-Kateiko and PC3 (1%)-Kathonzweni areas. This explains the difference of three different soil types;

clay, loamy and sandy in the study area. Moreover, the results of the PCA loadings indicate the presence of zircon and coal bearing minerals in Yoonye and Kathonzweni areas, respectively. These sampled locations can therefore be used as the target points for further exploration of these minerals. The method used was in addition, successful in identifying primary minerals pyroxene and biotite in the underlying geological strata.

Finally, the study was able to determine; quartz, orthoclase, kaolinite and albite in these sub-top soil samples insubstantial levels using x-ray diffraction. Quartz in these soils is attributed to the presence of substantial quantities of sands in the study area and therefore presents a sand mining potential.

In conclusion, this study has successfully demonstrated that, multivariate statistical approach to analysis of geochemical data for mineral exploration is effective and useful, especially, in establishing elemental associations and in evaluating possible mineralizations of a given area. The challenge in the wider application of the method used in this study, however, is the geological strata difference which may vary from one location to another and therefore needs to be considered when using this approach. Therefore, the study recommends that the method can be improved by sampling rocks outcrops and bioindicators plants species.

ABBREVIATIONS AND ACRONYMS

AAS- Atomic Absorption Spectroscopy

AES- Atomic Emission Spectroscopy

ASCII-American Standard Code for Information Interchange

AXIL-Analysis of X-Rays using Iterative Least Square Method

EDXRF -Energy Dispersive X-ray Fluorescence spectroscopy

FPT- Fundamental Parameters

IAEA- International Atomic Energy Agency

ICRAF-International Centre for Research in Agroforestry

ICP- Inductively-Coupled Plasma

INAA- Instrumental Neutron Activation Analysis XRF- X-rays Fluorescence Spectroscopy

GPS- Global Positioning System

LLD -Lower Limits of Detection

MoE- Ministry of Energy

WDXRF- wavelength-dispersive spectrometers

PCA- Principal Component Analysis

QAES -Quantitative Analysis of Environmental Samples

QXAS-Quantitative X-Ray Analysis System

UTM-Universal Transverse Mercator

XRD- X-ray Diffraction

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CHAPTER ONE

INTRODUCTION

1.1. Background

The importance of minerals for the economic development and sustainability cannot be ignored in the modern society. Mineral exploration has had a long and fascinating history; beginning with the use of Stone Age tools to the present day sophisticated mining and extractive machineries. However, knowledge of the origin of the bedrock materials has limited discoveries of unknown buried deposits (Tonui and Wolfgang, 2003). In their study, Tonui and Wolfgang, (2003) suggested that the greatest potential for future ore deposits discoveries lies in areas of substantial cover of un-explored mineralized areas. These usually have complex subsurface relationships, which include complex stratigraphy and basin architecture (Tonui and Wolfgang, 2003). In addition, these sediments and underlying bedrocks have been subjected to prolonged periods of diagenesis and weathering. Many of these interrelationships are poorly understood and hence exploration work is tedious, highly expensive and frequently unsuccessful (Woodruff et al., 2009).

1.2. Trace Elements in Mineral Exploration

Mineral exploration through thick vegetation cover can be improved by looking at trace elements levels in underlying rocks. This is because their distribution is influenced primarily by the composition of the parent material (Woodruff et al., 2009). Studies show that geochemistry of soils can play an important role in mineral exploration (Cheng, 2014; Reimann and De Caritat, 2012; Kabata-Pendias and Pendias, 2011).This is attributed to the fact that the trace elements found in soils is the chemical composition transmitted from the parent material, usually called geochemical background (Woodruff et al., 2009). This corresponds to the mineralogical composition of the parent rock whether originally-formed in the case of extrusive igneous rocks or initially deposited in the case of marine sediments, moraines, loess and alluvium, which have sometimes been modified by subsequent mineralization. It is common to find soils which have high levels of nickel and chromium for example, because they developed from parent material containing large amounts of olivine, pyroxenes, chromite, spinels, etc. which are all minerals bearing nickel and chromium elements (Woodruff et al., 2009).

Multivariate analysis has been used to investigate the relationship between elemental composition and mineralogy in soil (Sitko and Zawisha, 2012; Garcia-Gonzalez and Aragoneses, 1992). Garcia-Gonzalez and Aragoneses, (1992) were able to use principal components analysis to study elemental analysis of soil samples in Central Spain where it was shown that phyllosilicates and Fe and Mn-oxides in the ratio of 2: 1 respectively, were the principal trace element carriers in the soils analyzed. In addition, the study noted that Kaolinite did not play a role as a trace element carrier. The study further pointed outthat the principal difference is found between samples rich in clay-kaolinite Al_2O_3 and samples rich in quartz-SiO_2. In the same study, alkaline and alkaline-earth elements: sodium (Na), potassium (K), rubidium (Rb), barium (Ba) and strontium (Sr) showed a similar behavior, being directly related to the contents of illite and feldspars. Cobalt (Co) and lead (Pb) contents were found to be related to the Mn-oxides, while Copper (Cu) and Zinc (Zn) showed a relatively erratic distribution. On the other hand, vanadium content was clearly associated with the Fe-oxides, but other metals: such as chromium (Cr), nickel (Ni) and lanthanum (La), showed distinct associations depending on particle size.

In Kenya, many companies are exploring for mineral potential for economic exploitation. For instance, Panorama Resources Inc has been exploring the Migori greenstone belt for gold mineralization since the year 2009. Titanium deposits in Kwale County were explored by Tiomin Resources while MD Mineral Technologies of Australia is exploring for zircon and rutile deposits in Kilifi. There are substantial trona deposits in Lake Magadi, situated within the Great Rift Valley, are described as one of the largest known deposits in the world (Thornton, 2010). The challenge however, lies in the fact that very few studies have been done on trace elements concentrations in relation to mineral exploration in Kenya.

Previous geochemical studies in national parks and wildlife in Kenya have shown that large variations of trace element content in soils were largely attributed to differences in soil parent materials (Thornton, 2010; Odumo, 2009). It was noted that the influence of parent rock material on elements and minerals distribution tends to decrease with soil development. Studies on distribution of major and trace elements in soils and in grass have been done at Shimba Hills National Reserve in Kenya by Sutton et al., (2002). The authors investigated the influence of soil and vegetation type on the concentrations of sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), manganese (Mn), phosphorous (P), cobalt (Co), copper (Cu), zinc (Zn), molybdenum (Mo), nickel (Ni) and selenium (Se) in soils and grass. They concluded that low concentrations in surface soils for most major and minor elements were

attributed to the geochemical nature of the underlying parent rock materials of sands, sandstone and grits.

Moreover, Mangala and Patel (1996) used x-ray fluorescence to analyze elemental content in geological samples of Kenya Fluorspar Company in Kerio valley. In their findings, the concentration levels of manganese (Mn), copper (Cu), zinc (Zn), zirconium (Zr), niobium (Nb), Lead (Pb) and uranium (U) in fluorite mineral samples were found to be less than 1000μg/g. They further showed that elemental concentration of a few trace elements had an influence on the various colours associated to fluorite minerals. This study recommended further studies to determine possible mineralization in areas that reported high elemental concentrations.

In this study, we demonstrate the potential of mineral exploration by using multivariate analysis of geochemical data following X-rays fluorescence analysis.

1.3. Description of the Study Area

1.3.1. Geographic Location

The Mui basin is located in Kitui County within the eastern part of Kenya. It is bound by UTM coordinates 0406000 & 0418000 eastings and 9900000 & 9800000 northings respectively as shown in Figure 1.1. The basin is located approximately 180 Km North East of Nairobi at an altitude of between 600 and 900 metres above sea-level. It is about 500 Km^2 in size divided into four Blocks; A, B, C and D. Block A covers (Zombe-Kabati, 121.5 Km^2), Block B (Mutito-Itiko, 117.5 Km^2), Block C (Yoonye-Kateiko, 131.5 Km^2) and Block D (Karunga-Sekele, 120.0 Km^2). It is located on Map series Y731, sheet 137/3 and 151/1. Figure1.1 shows the study area- block C of the basin.

Exploration for coal by Kenya's Ministry of Energy (MOE) has been completed where it focused on four blocks, Blocks A, B, C and D, including surface geological mapping, geophysical surveys and exploration drilling. However, geochemical methods were not used during exploration process. Detailed coal quality analyses and resource evaluation with estimated total tonnage of 400,000,000 metric tonnes in block C alone has been established. Seam thicknesses varying from 0.3m to 13m have been identified in 40 of the holes drilled at depths of between 20m to 320m. Tender for concession was awarded to Flenxi Company for subsequent mining following an advertisement in 2010 (MoE, 2011).

Figure 1.1: Location of the Mui basin (MoE, 2011).

1.3.2. Climate, Drainage and Infrastructure of Mui Basin

Mui Basin climate is characterized by hot and dry climate. This is influenced by the cooler climate adjacent to the hills and along rivers. On the other hand, hot climate is experienced in

low lying areas. These regions usual have rainfall twice a year in the months of February, May and December. February and June are main harvesting periods. The months of June to September are usually very dry with no rains. The average rainfall of the study area is about 280mm per year (Mukabana, 2009).

Mui Basin experiences high temperatures throughout the year, ranging from 16ºC to 34ºC. The hottest months are between June-September and January-February; with the mean annual temperature of about 28ºC. As a result of low rainfall level, the area has limited surface water sources resulting into seasonal rivers in the area (Mukabana, 2009).

The drainage pattern is widespread with the area being traversed by many seasonal rivers and streams which become flooded during heavy rainfall but turn into dry sand courses for most parts of the year when there is no rains. The rivers become sandy beds during the dry seasons. The Mui basin is accessible by murram road which branches off Mwingi-Garissa road to the south and traverses the basin all the way to Zombe, the southern end of the basin. It is served by tarmacked road, Mwingi-Garissa highway, good all-weather roads, together with numerous tracks and footpaths. The roads are generally good in dry weather, and only become impassible during heavy rains seasons. There are several drifts constructed to enable free movement especially in the rainy seasons (Mukabana, 2009).

1.3.3. General Geology of Mui Basin

Mui Basin lies in the Mozambique belt of Kenya (Figure 1.2). The periphery of Mui Basin is largely covered by Precambrian crystalline rocks, which mainly consists of gneisses, migmatites, with minor Intrusives (Abuga, 2014). These Precambrian rocks are generally referred to as "Neoproterozoic Mozambique Belt rocks" and generally show a regional structural North-South trend of foliation. Originally this Neoproterozoic Mozambique Belt consisted of sedimentary rocks. These rocks are metamorphosed. One of the noticeable features is the major fault running N-S through Mutito (Figure 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˚ (Abuga, 2014). This activity is presumed to have taken place during the middle Pleistocene period when the Rift Valley was forming, and this is probably when the Mui Sediments were deposited.

The major soil types defining Mui basin area are; sands, clays, silt and a mixture loam. 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 (Abuga, 2014).
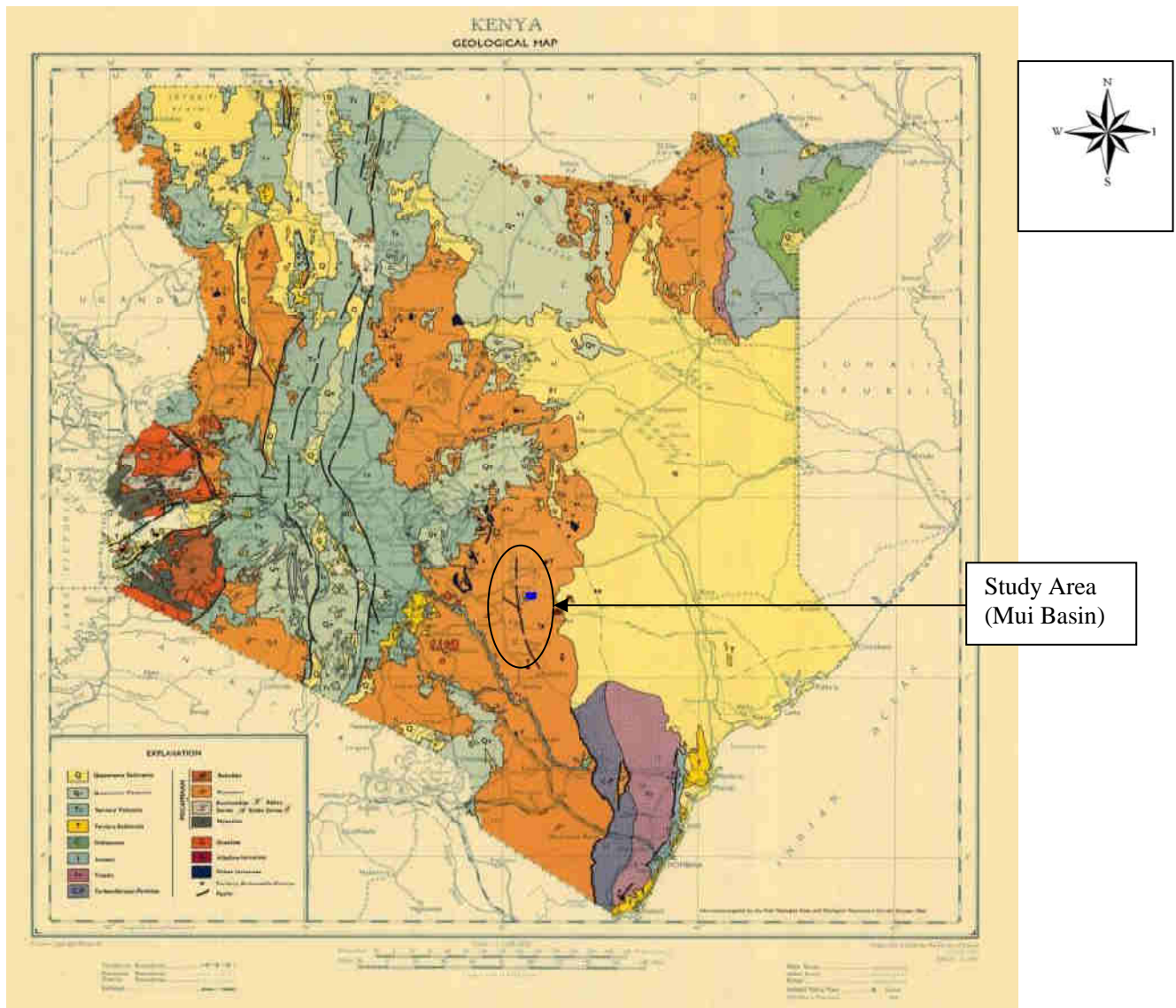
Figure 1.2: The study area superimposed on the geological map of Kenya

Legend	
	Precambrian Basement System
	Mutito fault

It shows in detail, the geology of Kenya and location of the study area in the Precambrian Basement System. Note the prominent Mutito fault (F) stretching through the entire study area (MoE, 2011)

1.4. Problem Statement

Mineral exploration through thick weathered environments is usually a challenging task due to significant depths of the bedrock. This poses major problems while locating buried mineral deposits in various geological strata. In addition, drilling through the overburden is not only costly, but also the rewards of finding the buried ore may be relatively low and uneconomical.

Complexity in characterization of minerals in terms of trace elements content is often another uphill task. This is due to limited knowledge on elevated concentrations of trace elements in soil samples, known as soil geochemical anomalies, which is crucial in improving the reward to risk ratio of finding a buried deposit in a given area. These notwithstanding, there exists very limited credible published data on relationship between soils trace elements and mineralogy for mineral exploration in Kenya.

1.5. Study Objectives

1.5.1. Broad Objectives

To evaluate the potential of mineral deposits in Mui Basin, specifically Block C using geochemical distribution of trace elements in soil samples.

1.5.2. Specific Objectives

i) To identify the trace elements in various soil samples from Mui Basin, Block C.

ii) To determine the concentration levels of trace elements and their distribution in various soil samples from Mui Basin, Block C.

iii) To evaluate the potential of mineral deposits of Mui Basin, Block C soil samples from the results of trace elements using statistical methods.

1.6. Significance and Justification of the Study

It has become a norm for geologists to conduct exploratory drilling through several depths of overburden in trying to explore buried mineral deposits (Kabata-Pendias and Pendias, 2011). Geochemistry is one tool that can be applied to this search. Trace elements in soils are known to provide the necessary data on mineralogical composition. Understanding their levels in soil samples is therefore extremely relevant to exploration of buried mineral deposits as they will help in identifying some minerals. In addition, the knowledge of trace element in soils is very useful in providing information which may be used by other disciplines for purpose of environmental management and in particular in mineral exploration. Furthermore, the data obtained is vital in agricultural management and planning where trace elements plays a critical role in establishing bioavailability of the elements to plants as well as reveal any toxic effect that they might pose to crops grown on these soils.

1.7. Scope and Limitation of the study

This study was limited to a few selected trace elements which were identified as essential in mineral characterization, namely; copper (Cu), nickel (Ni), zinc (Zn), chromium (Cr), vanadium (V), strontium (Sr) and zirconium (Zr) in soil samples collected in block C of Mui basin, Kitui County. Specifically, these elements are also associated to coal mineralization which has been identified in the area of study for exploitation. Moreover, the sampling depth was limited to a few centimeters (10-20cm), below the surface due to the high cost needed in drilling to several meters for sampling, after identifying the possibilities of surface exposure by rock mineral intrusions. The other elements such as; iron (Fe), manganese (Mn), potassium (K), calcium (Ca) among others were also found to be present in all the samples but were not included in the study as they are usually found in high concentrations.

CHAPTER TWO

LITERATURE REVIEW

2.1. Overview

This chapter contains five sections that review the basis of this study. Section 2.2 and 2.3 highlights on the origin and occurrence of trace elements in the earth crust while section 2.4 emphasizes on the relationship between trace elements and soil minerals. In addition, Section 2.5 of this chapter covers various methods used in mineral prospecting and exploration whereas Section 2.6 reviews the applications of multivariate statistics in analyzing geochemical data. Finally, Section 2.7 offers a detailed discussion on various quantitative methods used in X-rays Fluorescence analysis.

2.2. Origin and Occurrence of Trace Elements in the Earth Crust

The earth crust is composed of 95% igneous and metamorphic rocks and 5% sedimentary rocks (Kabata-Pendias and Pendias, 2011). Trace elements occur as constituents of primary minerals in igneous rocks which crystallize from molten magma. They become integrated into these minerals by isomorphously substituting in the crystal lattice for ions of one of the major element at the time of crystallization (Kabata-Pendias and Pendias, 2011). This replacement is controlled by the ionic charge, ionic radius and electro negativity of the major element and of the trace element replacing it.

Sedimentary rocks are more important in characterization of soil parent materials. They are formed by the lithification of sediments comprising rock fragments or resistant primary and secondary minerals such as clays or chemical precipitates including calcium carbonates. The concentration of trace elements in sedimentary rocks depends on the mineralogy and adsorptive properties of the sedimentary material (Kabata-Pendias and Pendias, 2011).

Sedimentary rocks such as sandstones are composed of minerals that are resistant to weathering and usually have little amounts of trace elements (Morelli et al., 2012). In their study, Morelli et al., (2012) noted that the high amount of trace elements including copper, zinc, chromium, lead, cadmium and manganese occur from shales, which are derived from fine sediments of inorganic and organic origin. In addition, soils formed from the weathering of coarse-grained materials such as sands and sandstones and also from acid igneous rocks including rhyolites and granites tend to contain lower quantities of elements such as Cu, Zn,

and Co than those derived from fine-grained sedimentary rocks such as clays and shales, and from basic igneous rocks. The authors attributed this to their ability to adsorb metal ions.

Weathering processes such as biochemical processes leads to the damage of parent materials and the subsequent transfer of elements from the minerals into solutions (Ashraf et. al., 2015). The nature of chemical weathering changes widely and is governed by numerous variables including parent rock type, topography, climate, time and vegetation. The extent of weathering is a contributing factor on trace metal distribution and mobilization, the influence of mineralogy and geological setting within weathered profiles. Besides, metals including: copper, zinc, chromium, cobalt and manganese which are found in trace concentrations occur mainly in the weathered processes components of igneous rocks such as; augite, hornblende and olivine (Alloway, 2004).

The principal concentration of metals in igneous and sedimentary rocks is given in Table 2.1. Trace metals such as Cu, Zn, Cd, and Pb are often associated with sulfur and sulfides in their modes of occurrence. Under superficial environmental conditions, sulfides are rapidly oxidized and Cu, Zn, Cd, and Pb are released and separated from sulfur at an early stage of mineral weathering (He et al., 2005). At some stage of soil development, they noted that Cu, Zn and Cd tend to concentrate in Mn oxides, whereas Pb was more likely enriched in the oxides and hydroxides of Fe. Trace metals are often presented in the form of carbonates, oxides, sulfides, or salts in most soils (He et al., 2005).

Table 2.1: Trace elements concentrations in rocks (mg/kg) (Alloway, 2004)

Trace elements	Earth's crust	Igneous and Metamorphic rocks	Sedimentary rocks
As	1.5	1-1.5	1-13
Cd	0.1	0.09-0.13	0.02-0.22
Co	20	1-110	0.1-19
Cr	100	4-2980	11-90
Cu	50	13-90	5.5-39
Mn	950	400-1500	460-850
Ni	80	0.5-2000	7-68
Pb	14	3-24	5.7-23
Zn	75	52-100	20-120

The occurrence of minor and trace metals in estuarine sediments associated with the main estuaries of the region in southeast Queensland was investigated by Morelli et al. (2012). The

trace metals included in their study were: vanadium, chromium, molybdenum, cobalt, nickel, copper, zinc, cadmium, lead and arsenic. They were able to note that Zn, V and Cr occurred as the dominant trace elements in the area. In addition, the study pointed out that all trace metals found in the study area were controlled by the presence of Fe and Mn oxides, and by the grain size of the soil. Specifically, fine-grained Fe-rich materials tend to adsorb more trace metals than sandy sediments.

2.3. Dynamics of Trace Elements in Soils

Kabata-Pendias (2007) stated that in soils, trace metals interact with soil minerals and its organic constituents in soils. This is attributed to the fact that soil is an active system with various soil properties. Nevertheless, the fate of metals in the soil environment is dependent on both soil properties and environmental factors (Bolan and Duraisamy, 2003). The dynamics of trace metals in soils depend on the physico-chemical and biological interactions with inorganic and organic soil constituents (Bolan and Duraisamy, 2003). Physico-chemical processes aim at retaining trace metals in soils, largely by adsorption, precipitation and complexation reactions as outlined by Bolan and Duraisamy, (2003). In this study, it was shown that adsorption is the accumulation of matter at the interface between the solid adsorbent and the aqueous phase and includes; ion exchange, formation of surface complexes, precipitation and diffusion into the solid. In many situations, the authors concluded that adsorption is believed to be the precursor for subsequent precipitation and it is difficult to separate the boundary between adsorption and precipitation processes.

Additional studies have indicated that chemical solubility of trace elements during weathering, erosion, and transport processes depends on their specific properties (Fadigas et al., 2004; Kabata-Pendias, 2007). The ratio of concentration of element dissolved in river water to concentration of the upper continental crust (C_x/C_y) shows the elements that are very stable as ($C_x/C_y < 0.001$ for Nb, Ti, Zr). Moreover the most mobile elements are indicated as ($C_x/C_y > 1$ to < 10 for Mo, Sb, As, Se, B, Cd, Re, Pd) (Kabata-Pendias, 2007). It is worth noting that it is these unique elemental properties that determine their behavior in soil as well as their bioavailability.

2.4. Relationship between Trace Elements and Minerals

The original source of trace elements in soils is the underlying parent material (Fadigas et al., 2004). In this parent material, the trace elements present makes up different rocks and geologic units in various proportions. Therefore, total concentration of trace elements in soils under native vegetation is primarily influenced by the type and mineralogical properties of the

parent material, as well as the process by which the soil was formed, and the proportion of mineral constituents in the solid phase (Fadigas et al., 2004).

Studies have demonstrated that soils enriched in trace elements mainly originate from basic igneous rocks, in which the levels of metals are higher compared with other rocks such as granites, gneisses, sandstones and siltstones (Fadigas et al., 2004; Singh and Gilkes, 2006; Palmer et al., 2014). For instance, the association of trace elements with manganese minerals in Australian soils has been investigated by Garcia-Gonzalez and Aragoneses, 1992. The authors found out that in different types of Australian soils birnessite and lithiophorite appear to be the common forms of occurrence of mineralized manganese. It was further noted that the concentration of trace elements in these minerals were quite high particularly cobalt concentration were found to be up to 79% in these minerals.

In addition, Li and Thornton, (2001) investigated soils from historical Pb mining and smelting areas in Derbyshire, England. The study pointed out that carbonate specifically adsorbed and Fe–Mn oxide phases were the largest fractions for Pb in soils contaminated by both mining and smelting. They further noted that most of the Zn was associated with Fe–Mn oxide and the residual fractions. Further work on the relationship between trace elements and mineralization has been done by Singh and Gilkes, (2006). The study demonstrated that goethite and hematite were the only two Fe oxides minerals present in thirty nine (39) soils derived from various parent materials in south-western Australia. They further noted that the elements Co, Cr, Cu, Mn, Ni and Zn were present in substantial levels in the iron oxides, and the dissolution kinetics of these elements indicated that some may be present in the structure of the iron oxides. In addition, it has been demonstrated that the proportion and composition of the clay/organic matter fraction, may also influence the levels of trace elements in soils (Lützow et. al., 2006; Palmer et. al., 2014; Bauer and Velde, 2014).

Table 2.2 shows trace elements found in some major rock forming minerals. The minerals are listed in order of stability during weathering; more easily weathered materials followed by most resistant ones (Smith and Huyck, 1999).

In this study we have determined the levels of trace elements in soil samples from Mui Basin in order to establish a possible relationship between the elements and possible underlying minerals.

Table 2.2: Trace elements of interest commonly found in rock-forming minerals (Smith and Huyck, 1999)

	Elemental content proportion			
Mineral	Y%	0.Y%	0.0Y%	0.00Y% or less
Olivine		Mn, Ni	Co, Cr, Ti	Cu, V, Zn
Pyroxene		K, Mn, Ti	Cr, Ni, V	Ba, Co, Cu, Zn
Plagioclase Feldspar	K		Ba, Mn, Ti	Cu, Ni, Pb, V, Zn
Amphibole		K, Mn, Ti	Cr, Ni,V,Zn	Ba, Co, Cu, Zn
Biotite	Ti	Ba, Mn	Cr, Ni,V,Zn	Co, Cu, Pb
Potassium Feldspar		Ba	Ti	Cu, Ni, Pb,V, Zn
Muscovite		Ba, Ti	Cr, Mn, V	Cu
Quartz				Mg, Mn, Ti,Zn

2.4.1 Trace elements and coal mineralization

The Ministry of Energy has been exploring for coal in the Mui Basin of Kitui County since the year 2000. This has been done by collecting samples from drilled wells and carrying out comprehensive analysis on the samples to determine their composition and to ascertain their quality (MoE, 2004). In general, elements with concentrations of 100 ppm and below in coal are classified as trace elements (Prakash, 2012; Xu et al., 2004). The occurrence of these trace elements in coal samples is linked to the different solid constituents present. This in addition plays a critical role in predicting the element behavior throughout the production process (Prakash, 2012). Prakash (2012) noted that trace elements in coal exist either in the mineral or organic portion. The introduction of these elements into the coalification process is often carried out through interaction between decomposition of the decaying plant matter with solutions entering the mineral (Bhebhe, 2008). In addition, mutual reaction between minerals and selected plants leads to chemical binding with the organic matter which results into increased concentration of trace elements (Xu et al., 2004).

The existence of trace elements may be due to organic or inorganic association to coal (Prakash, 2012). The presence of mineral matter in coal results into inorganic association and may vary based on different coal samples (Bhebhe, 2008). Bhebhe (2008) suggested that organic association often prevails in coals having low ash yields of below five percent weight. It was further noted that these trace elements may be bound to certain organic functional groups such as, carboxylic acid, hydroxyls, amino among others. In general, for most coals, trace elements exist with mineral matter either as distinct minerals or attached to the organic matter of the minerals (Prakash, 2012).Trace elements that are weakly attached can be easily

leached into the environment thereby causing harm to the ecosystem (Prakash, 2012).Moreover, trace elements that are strongly attached to coal are sometimes concentrated in the ash and therefore calls for additional treatment before being released into the environment (Prakash, 2012). Therefore the manner in which these elements occur and their concentration may vary depending with the characteristics of the element (Xu et al., 2004). This further emphasizes the importance of determining their concentrations in all major coal prospecting areas.

2.5. Methods used in Mineral Exploration

The challenge of finding new ore deposits and to define their extent and metal content is of great concern to geologist (Jackson, 2010). This has made the mining companies to ensure that the deposits are economically viable as well giving a guarantee of ore production over a sufficiently long period of time, before considering setting up mining operation. On the other hand, prospecting implies looking for mineral deposits with an aim of mining it at a profit whereas exploration refers to the systematic examination for the occurrence of a mineral deposit (Averill, 2007).

A geologist prospecting an area looks for surface exposure of minerals, by observing irregularities in colour, shape or rock composition. Several methods have been employed to explore about the probable existence of an ore body (Averill, 2007; Xu et al., 2004). Figure 2.1 below shows a general sequence of mineral exploration and exploration activities, described in the following subsequent sections of this report.
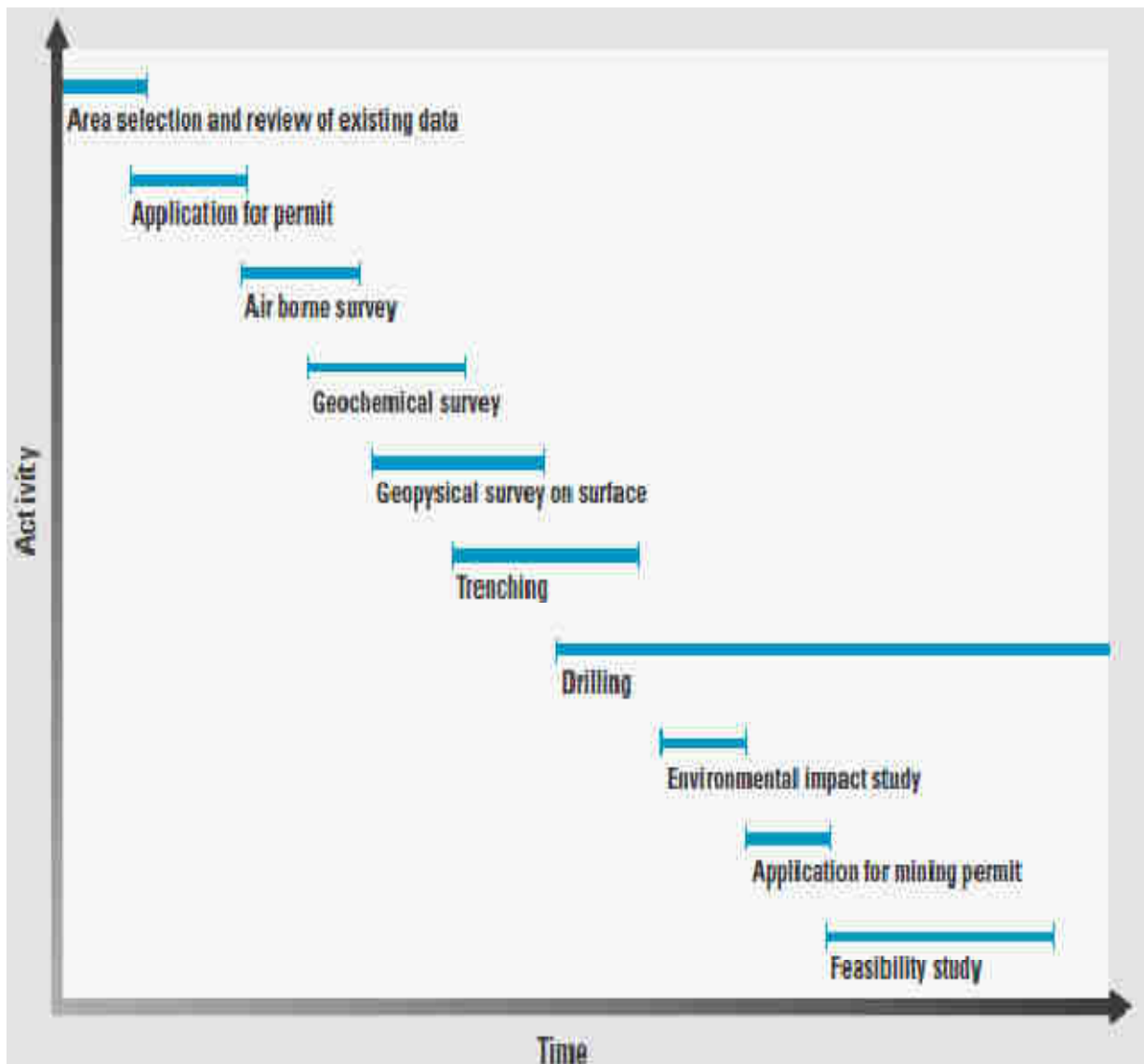
Figure 2.1: Exploration activities in general (Averill, 2007)

2.5.1. Geophysical Methods

There are several geophysical methods used in mineral exploration as shown in Figure 2.2. Airborne geophysical survey is a method which allows large areas to be explored effectively in a span of very few hours (up to 2 hours depending on the area of coverage (Jackson, 2010). Various types of aero-geophysical maps include; magnetometer maps which mainly report the difference in the earth's magnetic field with very high precision. From surface, different geophysical methods are used to explore subsurface formations, based on the physical properties of rock and metal bearing minerals such as magnetism, gravity, electrical conductivity, radioactivity, and sound velocity (Averill, 2007).

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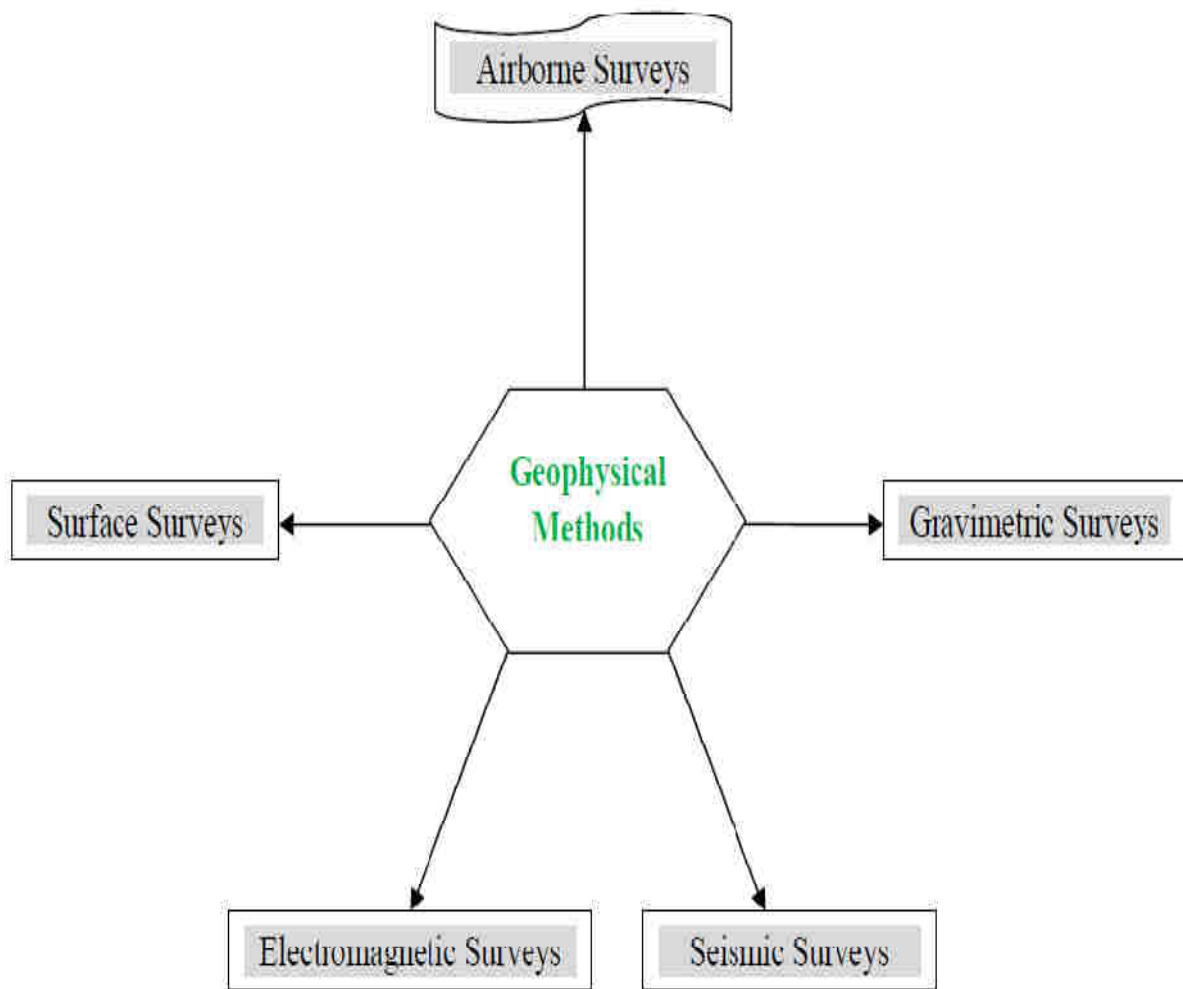
Figure 2.2: Geophysical methods used in mineral prospecting

Geophysical methods have also been employed in relation to mineral exploration in Kenya (Chen et al., 2014; Abuga et al., 2013; Wang'ombe et al., 2014). A combined geological and geophysical survey was undertaken in Kimachia area of Meru County in central Kenya and was able to establish the existence of small scale iron ore deposit that seems to be part of a more extensive iron rich zone (Abuga et al., 2013). The study was able to identify magnetite as the main ore in the geological formations. Gravity surveys revealed a zone of high gravity anomaly aligned in the same direction as hills on the elevated topography. Further, magnetic methods conducted along the same stations used in the gravity survey revealed several zones with high magnetic anomalies coincident with the gravity anomalies characteristic of ferromagnetic rocks some of which have been magnetized over the hilly areas (Abuga et al., 2013).

2.5.2. Geochemical Methods

Geochemical surveying is another mineral exploration method with a main aim of establishing the presence of metals in the earth crust (Schatzel, 2009). This involves various method of mineral exploration that deals with systematic measurement of chemical constituents of a naturally occurring material such as rocks, soils, gossan, glacial debris, vegetation, stream sediment, or water (Schatzel, 2009).The chemical property that are usually monitored is the trace content of specific element or group of elements. This is often done by sampling a wide area then performing analysis of the composition of the sample to identify the regions of interest for further studies (Awadh et al., 2013).

In general, geochemist often collects stream of samples covering an extended area over a specified period of the pre-selected mineral favorable terrain and investigate the average abundance of certain elements in earth materials and its distribution (Awadh et al., 2013). Rapid and accurate analytical methods such as; atomic emission spectroscopy (AES),Inductively-Coupled Plasma (ICP), X-rays Fluorescence Spectroscopy (XRF) and Instrumental Neutron Activation Analysis (INAA) are often used to determine many elements in each sample at the same time which generates a vast amount of data (Sitko, 2009).

Generally, geochemical process for mineral exploration usually entails soil sampling; which involves excavation at given intervals to collect soil samples. The samples are stored in containers, dried and reduced to fine particle which are afterwards screened and analyzed for pathfinder elements. This may results into massive data and may require the use of effective data analysis techniques. Geochemical surveys may also be carried out on rock chips samples of outcrops or rocky debris and in some cases might require chemical analyses of biological materials considered as bioaccumulator of trace elements (Awadh et al., 2013).

Geochemical method has been applied in several studies (Awadh et al., 2013; Schatzel and Stewart, 2003; Schatzel, 2009; Landry et. al., 2014). Schatzel and Stewart (2003) studied the relationship between the source of mineral and sources of rare earth element in rocks and coal from Pennsylvania. However, this study focused mainly on an individual coal bed where several samples across the region were used. The findings pointed out a strong correlation between rare earth element concentrations and silicon concentration in the analyzed coal.

Schatzel (2009) study focused on geochemical methods for identifying sources of quartz and silica dust in underground coal mines. Since the sources of silica dust are thought to be the rock strata immediately above and below the mined coal bed, the study was primarily

concerned with the composition of the rock units and dust and less on the analysis of coal samples. The findings included the identification of a group of cations in the parent rock that were present in similar distributions within the mineral fraction in the dust.

Additionally, Landry et. al., (2014) analyzed elemental concentration of selected elements in Southern Cameroon to show patterns of enrichment and depletion which related to localized mineralization conditions or local lithological changes. The geochemical dispersion of the metal elements (especially gold) from their study revealed that high concentrations were recorded in the northern part of the prospect, close to the quartz-tourmaline vein within the quartzite. Their results indicated that the Au and other metal elements probably originated from the quartz-tourmaline veins hosted by surrounding rocks. Their study recommendations included a detailed exploration work including geochemical soil sampling and geophysical survey to be done in the northern part of the Gouap-Nkollo prospect, where anomalous concentrations of Au were observed, for further investigation.

Lastly, Alexander (1997) undertook to investigate the feasibility of surface geochemical techniques applied to exploration for coloured gemstones in the Mangare area, South Eastern Kenya. The study found out gem corundum mineralization in a pegmatite reef lining the boundaries of a major ultramafic body with gneisses. In these samples, anomalous Ni, Co and Cr concentration were reported. Moreover, additional anomalies were identified in the calcareous soils which appeared to have a superior ability to accumulate trace elements in the samples.

2.5.3. Exploratory Drilling

In principle, the data obtained from the geochemical and geophysical surveys of a given area under investigation is used to formulate probable definitions and realizations of the geologic structure that may contain the mineral (Abedi and Norouzi, 2013). In general, the exploratory well is drilled in a location determined by the geologists and geophysicists as potential for mineralization (Abedi and Norouzi, 2013). This is then followed by the samples being collected and examined for their composition and fluid content. The data obtained after analysis of the sample is afterwards used to identify the type of formation versus depth and to check on the presence of hydrocarbon materials within the rock. Finally, cores of the formations are also obtained, preserved, and sent to specialized laboratories for analysis of possible minerals

Abedi and Norouzi (2013) noted that often, the exploratory well provides important data on rock and fluid properties. The study pointed out that detail of these parameters was essential for the development of exploratory program in the field. Moreover, they argued that in most cases the data provided by the exploratory well will be insufficient and therefore additional wells may need to be drilled to provide a better definition of the size and characteristics of the new reservoir. It is worthwhile to note that the results of minerals from the wells explored may be economical or non-economical for development (Abedi and Norouzi, 2013). In view of the fact that exploratory drilling involves drilling through 100 m or more of cover in search for buried mineral deposits, a basic understanding of the origin and distribution of these mineral compounds is clearly essential. Therefore, the present study was motivated by these considerations and explores the use of multivariate analysis on geochemical data to evaluate potential underlying mineral prior to conducting exploratory drilling.

2.6. Statistical Analysis of Geochemical Data

The most widely applied multivariate statistical methods in analysis of geochemical data include principal component analysis (PCA), cluster and factor analysis and different types of regression analysis Figure 2.3 (Reimann et. al., 2002).
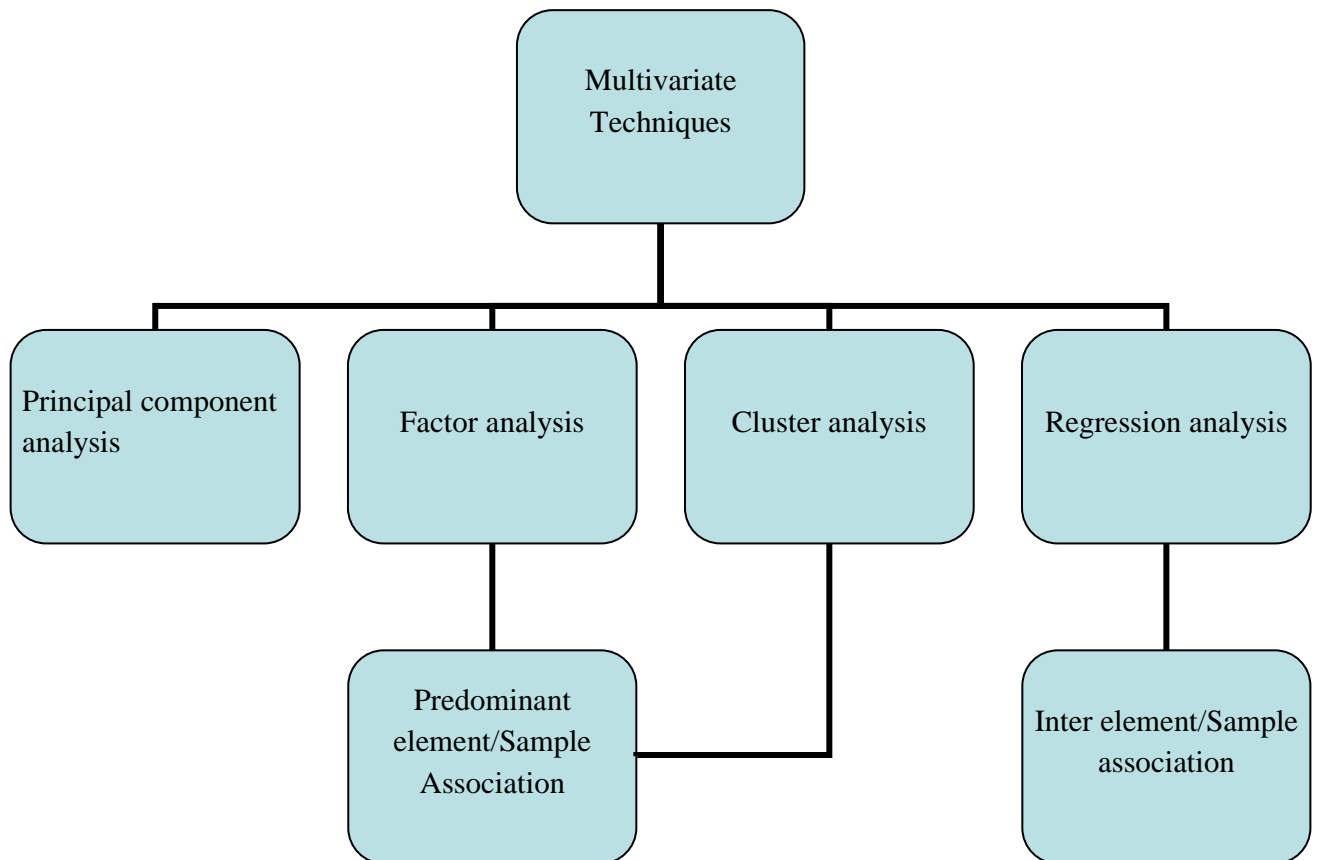
Figure 2.3: Selected Multivariate techniques used in geochemical analysis of data

The most dominant elemental associations in multi-element data can be determined using principal component analysis as well as factor analysis. Sample associations can be identified using cluster analysis while inter-element and inter-sample relationships can be analysed using regression analysis (Reimann et al., 2002). Real data rarely matches the ideal models and therefore methods using multivariate normal distribution are often susceptible when used in geochemical data and this may affect credibility of the results. Therefore it is crucial for one to carefully take into consideration all the factors that may affect the final results before performing multivariate analysis (Reimann et al., 2002).

2.6.1 Principal Component Analysis (PCA)

Principal component analysis (PCA) can be used to perform compression of data, detection of outlier, deciphering and detecting a correlation matrix (Grunfeld, 2005). This is done by transforming a set of correlated variables into uncorrelated variables which are later used as independent factors, P^t.

The principal component analysis implies decomposition of the original 2D matrix X, *i.e.,* representing it as a product of two 2-Dimensional matrices T and P.

$$X = TP^t + E = \sum_{a=1}^{A} t_a P_a^t + E \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.1)$$

Where;

T-the matrix of scores

P-is the matrix of loadings

E-is the matrix of residuals (Figure2.4).
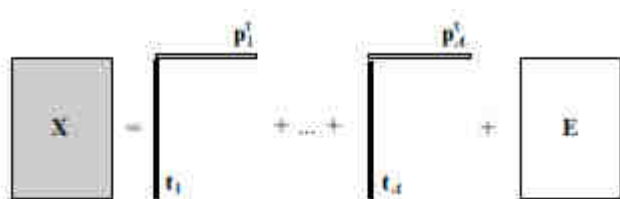
Figure 2.4: Graphical representation of Principal Component Analysis

The numbers of columns, t_a in the matrix **T** and p_a in the matrix **P**, are equal to the effective (chemical) rank of the matrix X. This value is designated by A and is called the number of principal components; naturally, it is smaller than the number of columns in the matrix X (Rodionova and Pomerantsev, 2006).

Principal component analysis also determines a sequence of orthogonal factors which in turn absorb a maximal number of the variance of the data. PCA % stands for the ratio of the total variance extracted by the factor. In summary, the correlation matrix, where the variances of all variables are equal to 1.0 is first done. The total variance in that matrix is equal to the number of variables. As successive factors are extracted, they account for less and less variability. The conclusion on when to stop extraction is primarily affected by when there is only very little and insignificant random variability left (Grunfeld, 2005). For data compression, only the components having the largest variances are retained.

Principal component analysis has been used extensively for various applications related to geochemical analysis (Nude et al., 2012). Firstly, Nude et al. (2012) conducted multivariate analysis on soil geochemical data from Koda Hill – Bulenga in Wa–Lawra gold prospect in Northwest Ghana with the objectives of defining the relationship of gold with other trace elements and to identify pathfinders for gold. Factor analysis reduced the data to three main components, which were related dispersion from parent materials and secondary processes including laterization.

A study by Chen et al., (2014) determined association of trace elements iron oxide phase of red-bed sandstones using a selective leaching scheme. In their finding, principal component analysis of the data obtained from the analysis of the leachates targeted, at dissolution of the Fe oxide phase showed that in addition to Fe oxides, dolomite and chlorite were also being dissolved. Besides, the authors suggested that, since no extraction reagent could be considered totally specific for its target phase, a better approach to extraction tests was to consider the extracts as mixtures of different phases and to use multivariate mathematical procedures based on techniques such as PCA and factor analysis to resolve the mixtures into their component parts. Moreover, Cheng (2009) demonstrated the use of a robust PCA on isometric log-ratio transformation. The method utilized real data set from analysed trace elements and equated the results with both the non-transformed and non-robust versions of PCA. The finding pointed out that the procedure of using isometric log-ratio transformed data and robust PCA gives better results as compared to other methods. The authors therefore recommend that because of the nature of geochemical data, suitable transformation should be performed while using PCA.

Elsewhere, the PCA method has been used in determining the position of intrusive bodies from geochemical data in the Gejiu mineral district in Yunnan, China (Cheng, 2009). The results from the study indicated that PCA enhanced the signal-noise ratio of the component

representing igneous intrusions and reduced the effect of sedimentary rocks. Therefore it made possible the areas delineated as potential areas for new intrusions; such as buried intrusions and therefore provided important leads for tin mineral prospecting. Furthermore, a case study involving the analysis of stream sediment geochemistry data from an area in Yunnan province, South China, applied principal component analysis to compress the information to as well as assist in identification of elemental associations (Cheng, 2009). The author noted that high elemental concentrations were identified in the Ailaoshan metamorphic belt. The study further demonstrated that gold deposits were linked to ultramafic intrusives within the Ailaoshan metamorphic belt.

2.7. Quantitative X-rays Fluorescence Analysis Methods

X-Ray Fluorescence is a widely used nuclear-analytical method for simultaneous elemental analysis in a wide range of samples presented as solids, powders and particulates (Sitko, 2009; West et al., 2012; Angeyo et al., 2012). Elements upto U are routinely determined using energy-dispersive X-ray fluorescence spectrometry (EDXRF). Wavelength-dispersive spectrometers (WDXRF) allows for determination of low-Z elements. (Sitko and Zawisza, 2012). Although the samples can be analyzed without treatment, high quality results can be ensured if appropriate sample preparation is applied (Angeyo et al., 2012).

In quantitative XRF analysis, the measured fluorescent intensities of analytes are converted to concentrations. (Sitko, 2009). However, the measured intensities depend on several parameters including:-

   i)   Analyte concentration
   ii) Sample matrix
   iii) Sample type
   iv) Sample preparation Methods
   v)   Sample sizes
   vi) Measurement conditions

Several methods have been proposed for quantitative XRF analysis (Sitko, 2009). They are categorized into two compensation and matrix correction methods. However, Beckhoff et al. (2006) reported that only one method allows for minimization of the matrix effects; the use of thin samples during the preparations for analysis. For thin samples there is a linear relationship between measured radiation intensity and analyte concentration. In other quantitative methods, the matrix effects are corrected for during analyses by mathematical method (Sitko, 2009).

2.7.1. Compensation Methods

The compensation methods are used to minimize matrix effects resulting from specimens' compositions (Beckhoff et al., 2006). In these methods, sample preparation techniques are used which allows for one or few elements to be determined (Sitko, 2009). In general, compensation methods are less popular and least applied.

2.7.2. Matrix Correction Methods

The absorption, enhancement, sample in-homogeneity and non-uniformity constitute the so-called matrix effects which prohibit the realization of a simple relationship between the fluorescent intensity and the elemental concentration (Beckhoff et al., 2006).

Non-uniformity at the sample surface leads to the boundary absorption phenomena having a special variation and therefore each sample region defines a center of micro absorption. There are various experimental methods used for matrix correction in XRF (Beckhoff et al., 2006; Sitko, 2009; Sitko and Zawisza, 2012). The methods employed include Emission-Transmission method, Fundamental parameters method and Influence coefficients algorithms among others (Angeyo et al., 2012).

2.7.2.1. Emission-Transmission Method

The method is grounded on the transmission measurement of the X-rays emitted by constituent elements of a target located in an adjacent position to the sample. In this method, the change in analyte signal for a homogeneous intermediate thick sample is measured by placing a pure standard element behind the sample (Beckhoff et al., 2006). This technique often applies for intermediate thick samples and has been used in this study for absorption matrix corrections in the sample.

2.7.2.2. Fundamental Parameter Methods

The fundamental parameter methods utilizes a relationship between measured x-ray intensities and analyte concentrations using fundamental physical parameters of X-ray emission process and instrumental as well as sample parameters (Beckhoff et al., 2006). These include; mass absorption coefficients, photoelectric cross sections, photo electric absorption jumps, fluorescence yields, emission line probabilities and energies.

The following assumptions are usually considered while using this technique:-

    a) Monochromatic source of primary radiation;

    b) Homogenous sample;

c) Fixed geometry of sample, source, and detector is maintained;

d) Transparent sample;

Applications of fundamental parameter methods call for two steps;

I. Calibration based on the measurements of pure element samples to calculate the relative intensities for each analyte.

II. Computation for comparison of the theoretical results with the experimental data, for determination of the elements.

Analysis by fundamental parameter method is preferred for transparent samples as discussed by Angeyo et al., (2012). Therefore, geometrical constant, G_o, and relative excitation detection efficiencies, K_i for different elements and for particular excitation source are determined using tabulated data values of fundamental parameters, photo electric efficiency cross sections and fluorescence yields. The efficiency of the detector is determined using data for radiation transmission through; air path, Be window, Au contact, Si(Li) dead layer absorption in the detector dead layer, and for escape peaks and as discussed in detail in several studies (Beckhoff et al., 2006; Sitko, 2009).

In general, application of fundamental parameter method involves two steps namely calibration and analysis of unknown samples. The fundamental parameter method is advantageous asit can be applied to analysis of all sample forms, thick samples, thin films and multilayers. The method is however limited by the assumption that, the intensity of the fluorescence radiation is linearly dependent on its concentration (Beckhoff et al., 2006) and the requirement for homogeneous flat samples. Its application is confined to determination of heavy Z elements.

2.7.2.3. Influence Coefficients Algorithms

Use of influence coefficients can be performed either from theory from measurements. The algorithms used are generally classified into two groups: theoretical and empirical influence coefficients algorithms (Sitko and Zawisza, 2012). The method is capable of quantifying matrix effects individually based on the matrix effect of element j and that of element k on analyte i. The concentration of an element i can then be determined from its characteristic spectral line intensity, corrected for the concentrations of other sample matrix elements by influence coefficients, using the expression shown in equation 2.4.

$$C_i = R_i\left(1 + \sum_j \alpha_{ij} C_j\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2.4)$$

Where:

C_i is the concentration of the analyte, C_j the concentration of other elements in the sample and α_{ij} is the influence coefficient of element *j* for analyte *i*.

Influence coefficients can take into account both absorption and enhancement effects but require more standards than the fundamental parameters method. The algorithms can use a single or more than one coefficient per matrix element (Sitko and Zawisza, 2012). Moreover, the influence coefficients can be constant or can vary with composition of the sample.

In this work we have used matrix correction method using the fundamental parameters method for determining trace elements concentration in the soil samples. In addition, we have used multivariate statistics namely; Principal Component Analysis, Cluster Analysis and Correlation and regression analysis to demonstrate the possibility of using trace elements in predicting underlying minerals for application in prospecting and exploration.

CHAPTER THREE

METHODOLOGY

3.1. Introduction

In this chapter, the procedures used for sampling, sample preparation, EDXRF instrumentation, sample analysis and data evaluation are all described.

3.2. Sampling

A total of fifty (50) soil samples were randomly sampled for this study from block C in the month of 3rd to 10th March 2014 for one week in these sampling locations namely; Yoonye, Kathonzweni and Kateiko. The soil varied from sandy, loamy and clay soils. The sampling sites were identified at locations 5m adjacent to the exploratory wells where drilling for coal exploration had been done by the Ministry of Energy and Petroleum in 2004 (Figure 3.1). Approximately 300g of the top surface soil was collected using an augur at a depth of 20cm below the surface, stored in labeled transparent polythene bag, sealed and transported to the laboratory for analysis of trace element contents. The samples were collected across block C within an area of (100-120) km^2 such that; 21 samples were collected from Yoonye, 17 from Kathonzweni and 12 from Kateiko. The location of each of the sampling point was recorded using a Global Positioning System (GPS) as shown in appendix 1. The samples were labeled as shown in Table 3.1;

Table 3.1: Sampling location and sample codes

Area	Sample code	Number of Samples
Yoonye	S1-S13, S26-S33	21
Kathonzweni	S34-S50	17
Kateiko	S14-S25	12
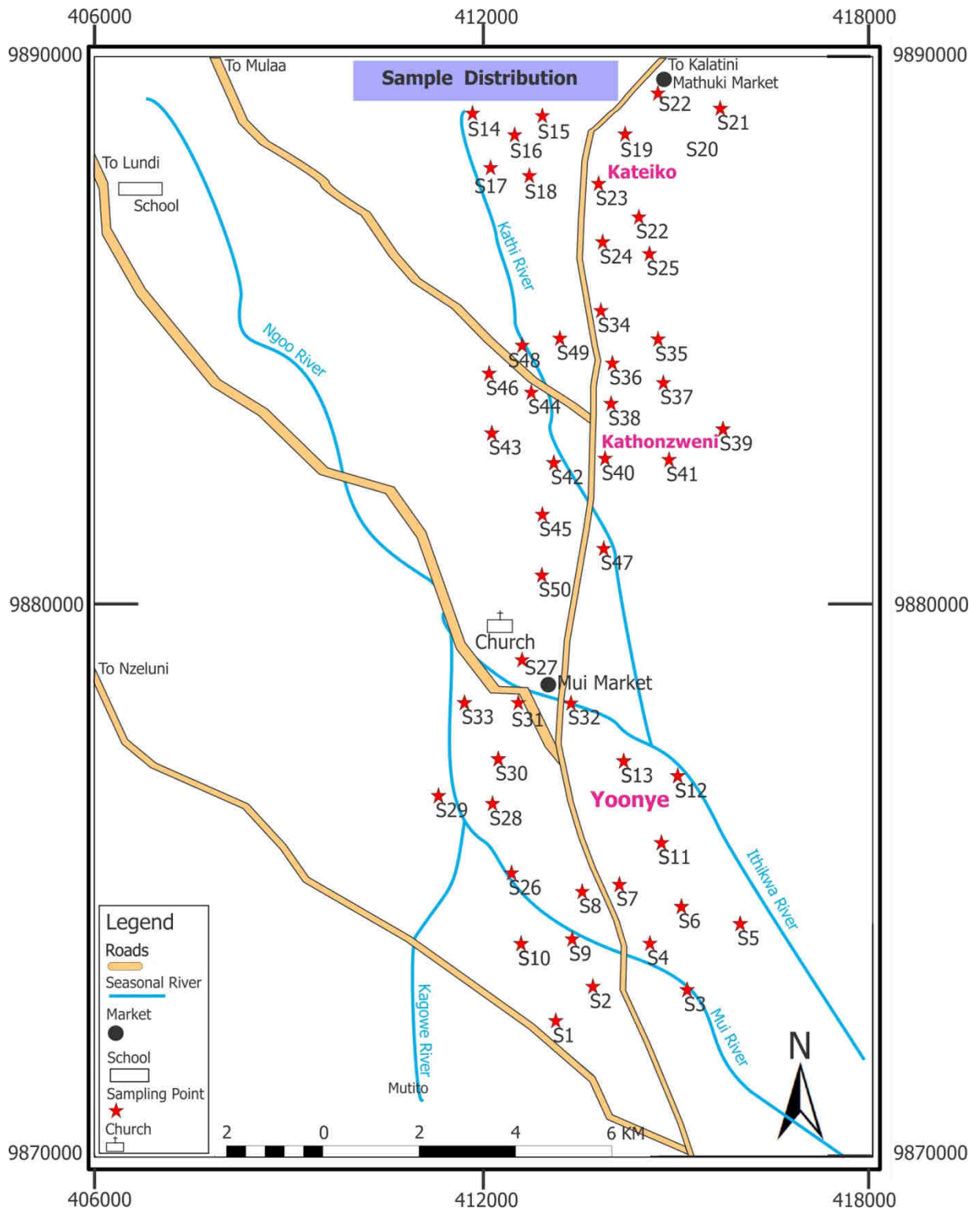
Figure 3.1: Map showing the sampling areas; the stars represent sample points where the samples were collected.

3.3. Sample Preparation and Analysis

3.3.1. Sample Preparation

The soil samples were dried for a period of one month to constant weight then grounded to small particles using a grinder. These sample aliquots were further pulverized to yield a particle size of less than 75µm after quartering and sieving through 300 mesh size. Approximately 1.5g of the sample was then weighed using analytical weighing balance and transferred to a clean crucible, onto which was added 0.5g of starch as a binder and the mixture homogenized by mixing. Dilution factors were determined from the weights. Soil pellets weighing approximately 0.3-0.5g were prepared as intermediate thick pellets for each sample using Specac hydraulic press by applying a pressure of 6 tons in 2.5cm diameter steel die. The sample pellets were carefully transferred into a petric dish and labeled for subsequent analysis using the EDX-800HS spectrometer based on Emission Transmission (E-T) method employing the use of a Molybdenum (Mo) target.

3.3.2. EDXRF Instrumentation and Measurements

In this study, the Energy Dispersive X-ray Fluorescence spectrometers series EDX-800HS model CE 212-23701-36; S/N: 2264400090CZ available at the Materials Testing Laboratories in the Ministry of Transport and Communication. The physical dimensions of the instrument were 580 (W) X 750 (D) X 420 (H) mm and weighs approximately 100 kg. The schematic presentation of EDX 800HS instrumentation arrangement is shown in Figure 3.2.
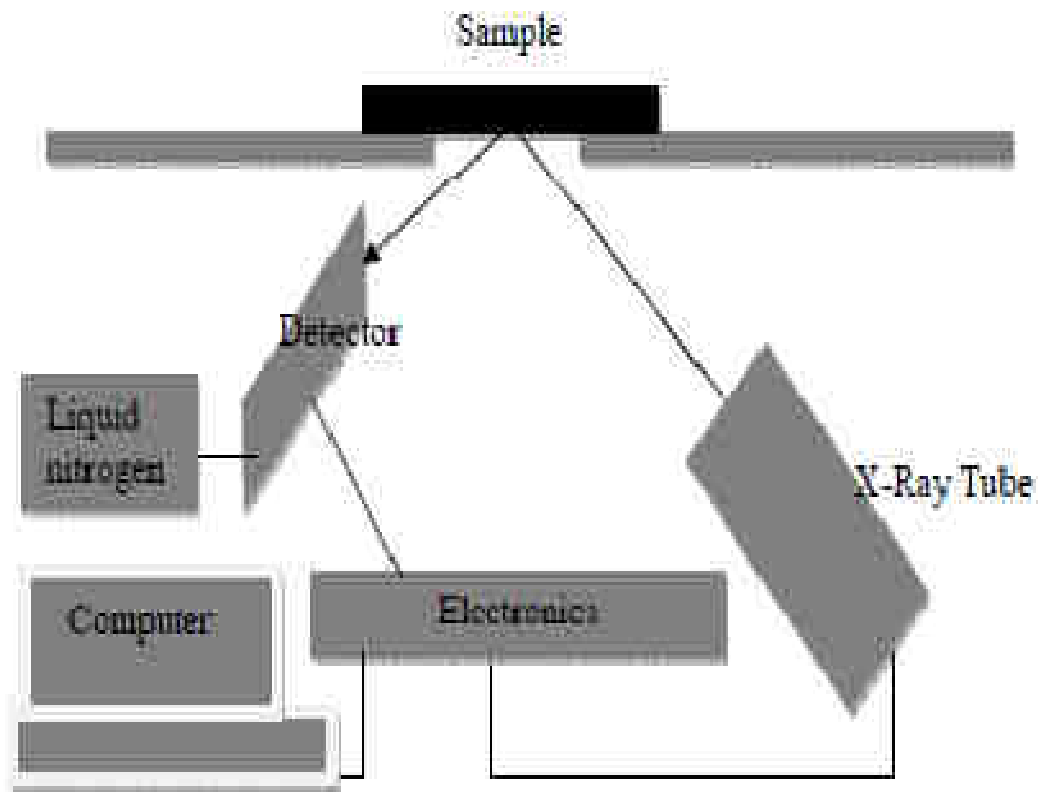
Figure 3.2: Schematic diagram of EDX 800HSinstrumentation arrangement

The instrument consists of the following:

a) X-ray generator unit which consists of the air cooled X-ray tube with Rh target operated at 5-50kV, tube current of 1-1000µA, primary X-ray filters automatically switched between 5 types with an exposure area of 10mm in diameter.

b) Semiconductor Si (Li) detector 10mm^2 mounted at 45^0 take off angle geometric with respect to the sample. The detector is cooled with liquid Nitrogen (LN$_2$) during measurements with approximate consumption of 1litre per day. It is biased with a high

c) Voltage supply at approximate 1000V connected to a preamplifier. The detector measured resolution is 140eV for Mn-Kα at 5.9Kev.

d) A large sample chamber which automatically opens and closes and can accommodate samples of upto 300mm wide and 150mm high.

e) Data processing unit which consists of the following modules: IBM PC/AT compatible computer Hard Disk Drive approximately 20GB, Operating System

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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.

The samples were irradiated for 50 seconds and measurements done in air at dead time of between (20-25%).

The sample exposure area was maintained at 10 mm diameter throughout measurements in this study. The spectral data was collected and quantitative analysis performed 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.

3.3.3. Quantitative Analysis of EDXRF Spectra

The spectral data obtained following sample irradiation by EDX-800HS (as shown in appendix 2) were analyzed using AXIL software obtained from the International Atomic Energy Agency (IAEA) following the steps shown in Figure 3.3.
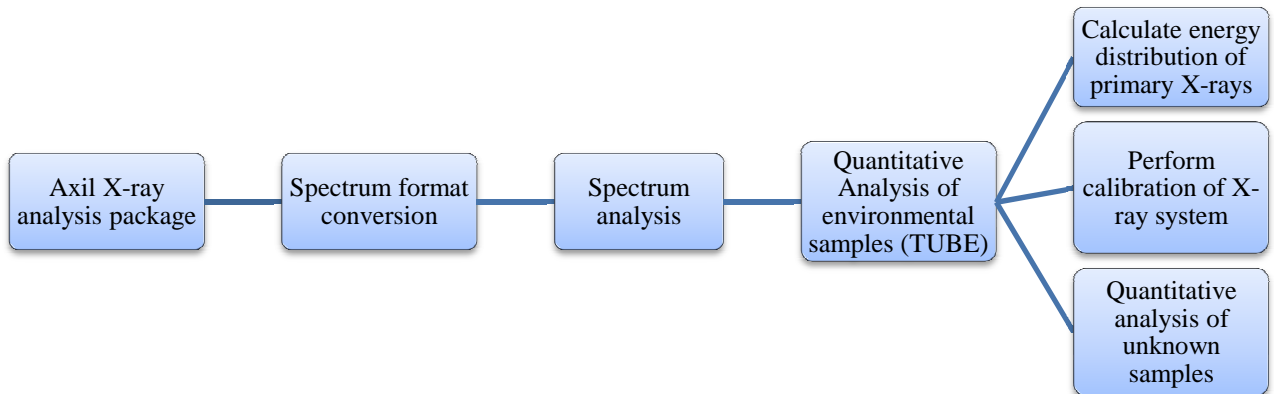
Figure 3.3: Block diagram showing the steps followed in Axil spectral analysis

The Spectrum data was analysed using Quantitative Analysis of Environmental Samples (QAES), after spectra format conversion to the ASCII (American Standard Code for Information Interchange) in AXIL. The QAES, a modular program of the IAEA's QXAS was

calibrated for quantitative analysis. Three sub–routines of the program are available for selection. These are:

i) Quantitative analysis of unknown Samples.
ii) Perform calibration of X-ray system.
iii) Calculate energy distribution of primary X-rays.

The method involves fitting spectrum (*SPE file) with a well-matched mathematical functions by utilizing a non-linear least squares scheme, until the best agreement between the measured and calculated spectrum is achieved after 20 iteration. Typical SPE data is shown in appendix 3.

In the entire spectrum, the chi-squares values were <10 which is a clear indication that the fitted model and the measured spectrum are in agreement. The fitted results report were finally saved as *.ASR (Analysis of Spectra results-appendix 4). The AXIL analysis results obtained were used for quantitative analysis after calibration for use with X-ray tube source of excitation with notable spectra of pure element standards of Iron (Fe), Cobalt (Co), Copper (Cu), Molybdenum (Mo), Zinc (Zn), Lead (Pb), Tin (Sn), Tantalum (Ta), Titanium (Ti) and Tungstein (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 Rh target of 20.70 keV was used. The accuracy of the method was verified by analysis of reference soil standard PTXRF IAEA 09.

Quantitative analysis of unknown samples of spectral data in the *.ASR files were analysed 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. Typical results obtained after quantitative analysis is shown in appendix 5.

3.3.4. Validation of EDXRF Measurements
To assess the validity of the measurements, certified reference materials from IAEA (PTXRF-09) was analysed by the same analytical method where experimental and certified values were compared.

The lower limit of detection (LLD) values for samples prepared in the pellet forms was also obtained from the analysis of PTXRF-09 soil sample. These values were calculated according to the equation 3.2:

$$LLD = 3 \times \frac{C}{P}\sqrt{R_b} \ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

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},

3.4. Multivariate Statistical Analysis

Multivariate data analysis of results on concentration of trace elements in all the samples studied was performed using principal component analysis (PCA) and cluster analysis. PCA was performed using the UNSCRAMBLER 9.7 (CAMO As, Oslo, Norway) software while cluster analysis was done using Origin Lab 9.0 software. The data set containing the sample code and results of trace elements concentration for; Cu, Ni, Zn, Co, Cr, V, Sr and Zr as variables were imported to the UNSCRAMBLER. This was followed by performing normality test where descriptive statistics using histogram was selected and used to investigate whether the data was normally distributed.

The data was then normalized and PCA executed using random cross-validation option. The maximum number of components extracted was equal to the number of variables. The eigenvectors, which comprised of coefficients corresponding to each variable, were used to calculate the principal scores 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.

OriginPro 9.0 software was used to conduct cluster analysis of the result. The data was used as obtained with the entire variable measured in same scale of mg/kg. The data was prepared in Excel as a spreadsheet and imported into OriginPro 9.0. Multivariate cluster analysis was then conducted on the seven trace elements (variables) from 50 soil samples (observations). Hierarchical clustering of the variables using agglomerative method was then performed and the results obtained in the dendrogram.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1. Results of Analysis of Certified Reference Material

A certified reference material from IAEA, (PTXRFIAEA 09)-River clay soil was analyzed to assess the accuracy of the analytical method used in this study. The results obtained were compared to the certified values for the elements of interest and are presented in Table 4.1. Typical EDXRF spectrum of the samples analysed is shown in Figure 4.1.

Table 4.1: Results of Analysis of Certified Reference Material, IAEA PTXRFIAEA 09.

Element	Energy (KeV)	Concentrations in mg/kg (n=3, μ±1δ)		RSD (%)
		Experimental	Certified	
Zirconium	15.7	289 ± 15	302 ± 10	5.3
Strontium	14.1	101 ± 6	106 ± 5	5.8
Zinc	8.6	92.7 ± 1.1	96.1 ± 3.9	1.2
Copper	8	25.0 ± 1.4	20.1 ± 1.1	5.6
Nickel	7.5	26.3 ± 0.7	37.9 ± 1.8	2.7
Chromium	5.4	86.8 ± 2.6	89.6 ± 3.6	3
Vanadium	4.95	79.8±1.9	80.9±2.6	6

Where n=Number of determination, μ= Mean concentration, δ=Standard deviation RSD=Relative Standard Deviation

In general, the relative standard deviations of the experimental values for most elements of interest in the certified reference material were below 10%. The experimental concentrations were within the standard reference certified values except for Ni which had low experimental value (26.3 ± 0.7) mg/kg as compared to the certified value of (37.9 ± 1.8) mg/kg.
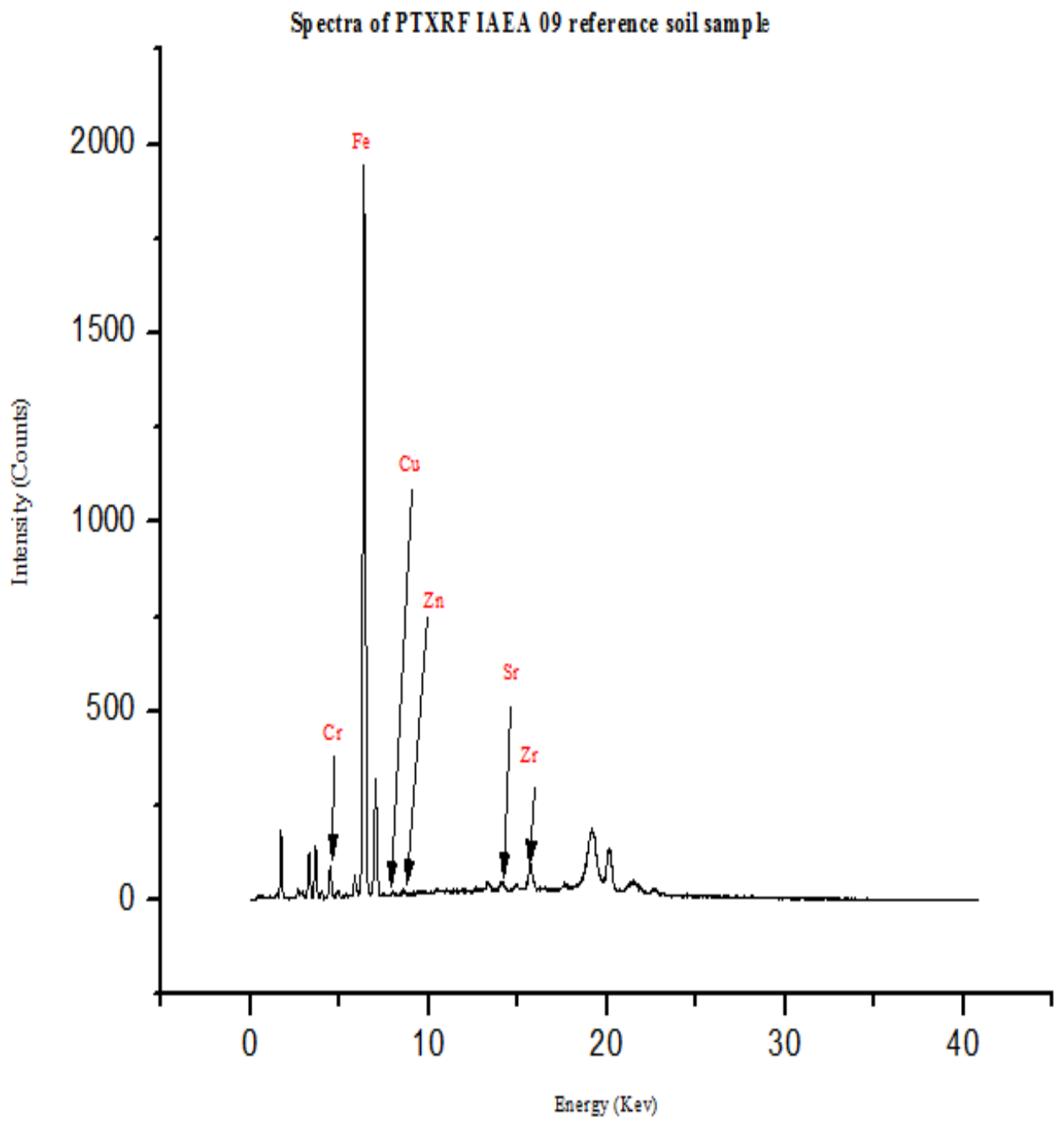
Figure 4.1: Typical spectrum of PTXRF IAEA 09 reference soil sample.

4.2. Results of Detection Limits

The lower limits of detection (LLD) values of the elements of interest analysed in this study after analysis of the samples prepared in the pellet form are presented in Table 4.2.

Table 4.2: Detection limits for soil sample, PTXRF IAEA 09-River clay analysis with EDXRF

Element	Atomic Number	LLD Value (mg/kg)
Vanadium	23	33
Chromium	24	18
Nickel	28	7
Copper	29	6
Zinc	30	6
Strontium	38	3
Zirconium	40	3

In Table 4.2, the detection limit improves with increasing atomic number and varied between (3-33) mg/kg. These values were consistent with those determined in various studies (Kaniu et al., 2011; Mangala and Patel, 1996).

4.3. Distribution of Trace Elements in the Soil Samples

Table 4.3A, 4.3B and 4.3C shows the results of the trace elements analysed namely; vanadium, strontium, zirconium, chromium, nickel, copper and zinc

Table 4.3A: Results of trace element concentration in mg/kg from Yoonye Area (μ±1δ, n=3)

Sample code	V	Cr	Ni	Cu	Zn	Sr	Zr
S1	480±13	68.8±6.9	13.7±4.5	25.2±9.2	26.3±12.2	283±30	2650±487
S2	355±40	52.9±3.3	8.4±1.19	26.3±0.9	22.2±6.7	181±8	1143±170
S3	346±33	54.3±3.0	14.3±3.3	30.4±3.5	14.2±1.6	419±31	2233±344
S4	354±42	46.7±2.0	10.5±5.1	18.0±5.9	10.9±6.0	228±17	2213±135
S5	479±76	74.2±12.8	19.1±1.0	52.7±4.6	76.5±4.5	343±71	1248±237
S6	629±27	93.3±4.7	23.8±7.8	51.6±1.2	102±6	362±66	1313±219
S7	430±67	71.1±10.3	20.0±3.7	36.5±7.9	54.0±10.5	296±34	1044±211
S8	425±64	50.7±9.9	22.6±5.8	57.7±10.9	95.7±3.8	268±37	1070±296
S9	380±73	66.8±11.4	9.8±0.9	32.7±5.0	34.7±10.0	373±26	1383±106
S10	323±88	65.9±12.0	25.1±4.8	30.3±1.9	13.4±10.9	392±150	2917±116
S11	418±91	89.9±11.5	25.7±4.0	73.4±10.4	122±16	336±57	1299±334
S12	393±28	59.3±10.7	8.4±0.35	35.6±4.3	78.3±7.6	282±64	1270±319
S13	535±79	74.0±12.2	14.6±2.7	52.2±7.2	79.3±14.3	282±21	1571±40
S26	568±70	78.0±5.5	13.7±5.3	55.1±7.3	77.9±5.8	295±40	1041±71
S27	349±52	77.9±14.5	11.7±1.7	35.0±8.0	85.7±20.7	249±41	1314±241
S28	528±54	80.0±3.7	6.88±1.17	42.6±7.1	111±3	196±7	1245±79
S29	351±21	54.8±3.0	14.3±1.9	37.0±7.7	69.5±11.3	161±14	833±136
S30	586±78	92.4±12.0	27.4±3.3	46.4±10.0	86.4±6.0	257±61	1408±303
S31	637±88	79.0±6.0	35.8±5.2	43.5±1.1	94.7±3.7	256±40	1504±248
S32	361±92	64.3±14.4	15.9±3.2	33.0±10.1	92.1±5.5	208±33	1149±206
S33	508±48	80.2±2.3	19.9±3.6	54.8±14.4	79.9±10.6	411±48	1750±260
Mean	449±40	70.2±5.1	17.2±2.4	41.4±6.3	68.0±5.6	289±30	1505±190
Maximum	637	93.3	35.8	73.4	122	419	2917
Minimum	323	46.7	6.88	18	10.9	161	833

Table 4.3B: Results of trace element concentration in mg/kg from Kateiko Area (μ±1δ, n=3)

Sample code	Trace elements						
	V	Cr	Ni	Cu	Zn	Sr	Zr
S14	293±57	59.0±12.7	19.8±1.6	39.4±8.1	30.6±3.9	404±92	1065±263
S15	512±50	72.0±10.6	20.6±2.8	54.0±14.5	65.0±18.2	369±26	768±34
S16	445±67	40.4±9.6	17.0±3.0	56.9±15.9	51.9±17.7	770±17	1095±58
S17	605±39	77.6±2.8	28.2±3.0	45.2±18.7	38.0±23.4	295±26	2075±246
S18	453±90	80.7±0.4	26.0±1.9	64.1±1.5	100±4.3	318±50	938±44
S19	340±95	65.9±12.1	11.4±2.1	40.7±5.8	33.0±2.8	415±60	1163±161
S20	640±91	82.0±0.5	24.1±3.8	85.1±4.7	84.0±8.0	450±3	802±14
S21	470±83	75.4±1.6	19.3±2.4	61.9±9.1	90.9±11.0	633±67	1109±134
S22	657±47	79.8±1.4	27.5±2.9	29.5±6.1	21.8±1.9	212±14	2071±180
S23	437±91	63.3±10.1	11.3±2.5	59.1±5.5	128±19.6	183±33	1788±131
S24	413±23	71.2±17.3	17.0±3.8	51.9±1.3	61.5±4.1	431±22	1554±177
S25	422±90	73.0±2.4	17.0±2.1	67.9±6.4	97.9±10.9	224±26	599±13
Mean	**473±73**	**70±5**	**19.9±2.1**	**54.6±5.2**	**67±6.3**	**392±40**	**1252±112**
Maximum	**657**	**82**	**28.2**	**85.1**	**128**	**770**	**2075**
Minimum	**293**	**40.4**	**11.3**	**29.5**	**22.5**	**183**	**599**

Table 4.3C: Results of trace element concentration in mg/kg from Kathonzweni Area (μ±1δ, n=3)

Sample code	Trace element						
	V	Cr	Ni	Cu	Zn	Sr	Zr
S34	537±33	74.3±16.3	17.4±2.5	35.6±11.9	52.4±1.61	434±103	2797±20.8
S35	331±48	54.8±9.3	14.4±2.0	19.1±4.5	29.1±1.5	240±30	2304±505
S36	280±14	49.0±3.3	17.8±2.1	22.0±4.1	26.8±4.7	281±15	1333±82
S37	287±51	51.8±2.5	7.65±1.01	28.5±1.0	25.4±2.4	278±12	1168±92
S38	356±73	63.7±13.6	15.7±2.0	35.4±12.0	27.5±5.1	155±30	2233±403
S39	356±32	75.2±21.5	19.2±3.8	51.7±14.1	51.8±10.4	82.0±16	1265±122
S40	300±20	63.8±4.4	13.0±1.7	57.3±14.7	46.1±6.6	80.2±26	1070±204
S41	369±89	86.3±9.5	24.5±3.6	43.3±8.5	33.1±2.0	442±36	1076±172
S42	605±89	91.1±11.9	25.8±5.7	65.0±14.3	90.3±2.2	497±5	1027±91
S43	289±63	56.3±4.5	13.0±2.1	27.8±8.1	35.3±2.5	108±23	1700±407
S44	343±94	66.7±7.6	12.2±2.5	38.9±3.0	49.4±11.1	70.3±15	1212±190
S45	464±76	67.3±8.3	10.0±1.9	38.2±6.5	70.6±8.5	278±20	1195±128
S46	420±59	65.8±9.4	16.9±2.8	16.4±1.7	13.1±1.4	287±52	1830±111
S47	311±61	61.1±12.8	19.3±2.4	49.5±9.9	62.1±4.3	355±49	778±156
S48	506±36	38.7±7.1	18.7±2.1	63.5±16.1	78.3±1.3	407±55	719±93
S49	306±18	56.9±5.2	9.20±1.51	48.8±3.5	86.3±2.4	267±25	838±47
S50	516±92	69.4±3.5	10.7±2.8	66.6±9.1	161±10.1	202±7	1913±66
Mean	**387±55**	**64.2±7.1**	**15.6±2.2**	**41.6±6.4**	**55.2±5.5**	**262±42**	**1438±130**
Maximum	**605**	**91.1**	**25.8**	**66.6**	**161**	**497**	**2797**
Minimum	**280**	**38.7**	**7.65**	**16.4**	**13.1**	**70.3**	**719**

In general, the results indicate that the mean concentrations of all the trace elements analyzed were uniformly distributed across the sampled areas (Figure 4.2).

Mean concentration of trace elements in Block C of Mui Basin

	V	Cr	Ni	Cu	Zn	Sr	Zr
Yoonye	449	70.2	17.2	41.4	68.0	289	1505
Kateiko	473	70	19.9	54.6	67	392	1252
Kathonzweni	387	64.2	15.6	41.6	55.2	262	1438
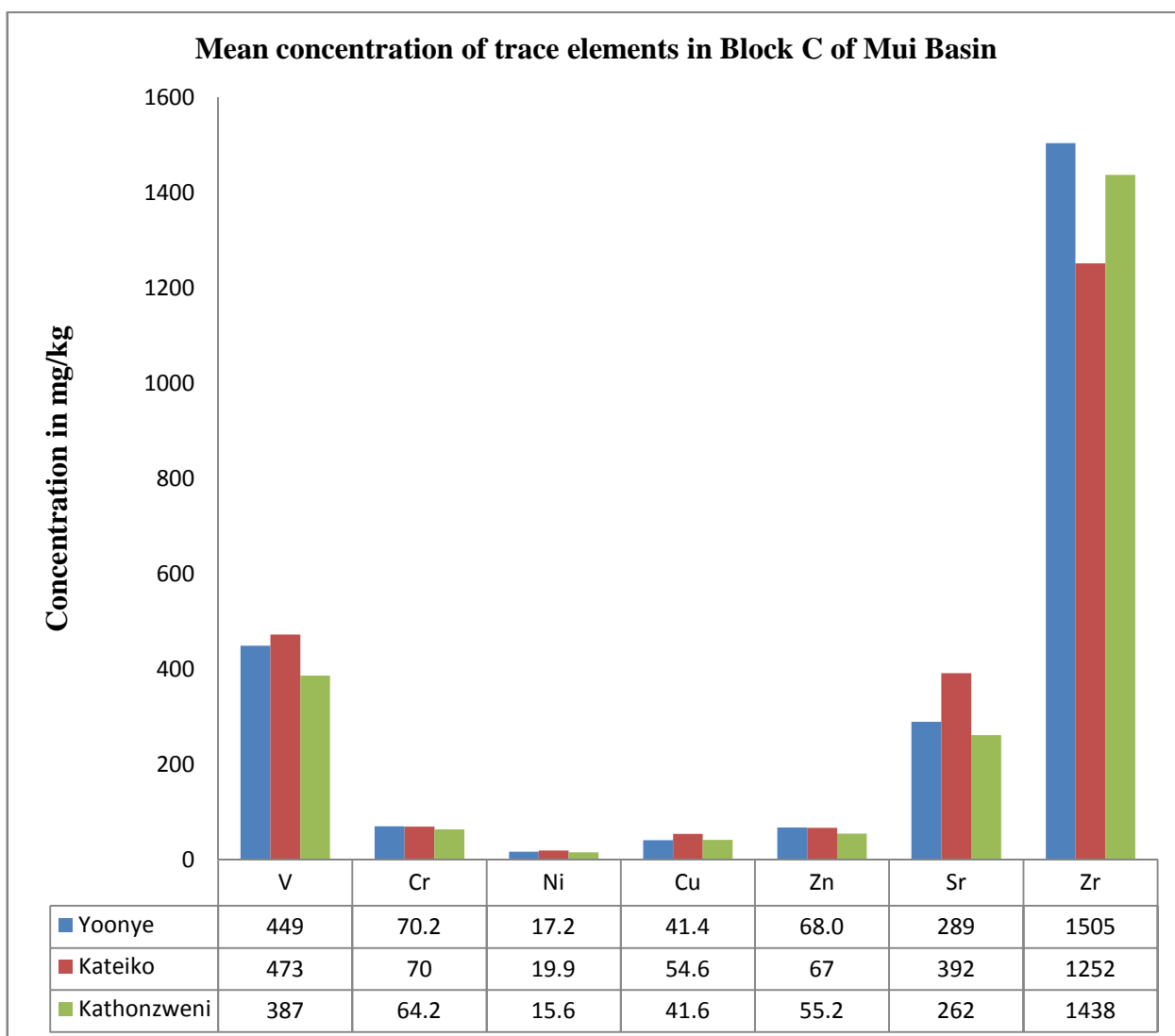
Figure 4.2: A bar graph of the mean trace elements concentration values in block C of Mui Basin

Zirconium was found in all the samples analysed to vary from 599 to 2917 mg/kg (Table 4.3A, 4.3B and 4.3C). The least Zr value was recorded in sample S25, from Kateiko area with a concentration of 599 mg/kg (Table 4.3B, Figure 4.3); sample S10, from Yoonye area reported the highest value of Zr (2917±116 mg/kg) as indicated in Table 6A.

In general, the mean Zr concentrations were found to be 1505 mg/kg for samples from Yoonye, 1438 mg/kg for Kathonzweni and 1252 mg/kg for Kateiko samples (Figure 4.3). These values were above the average worldwide reported value of Zr (330-850 mg/kg) in heavy loams soils (Kabata-Pendias, 2010). Since zirconium in the soils originates from the parent rocks, it implies that these samples may have been derived from Zr-rich rocks and is a likely indication of their association with zircon mineral sands in the study area.

Zirconium (Zr) concentration in soil samples from block C, Mui basin

	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min
		Yoonye			Kateiko			Kathonzweni	
Zr	2917	1505	833	2075	1252	599	2797	1438	719
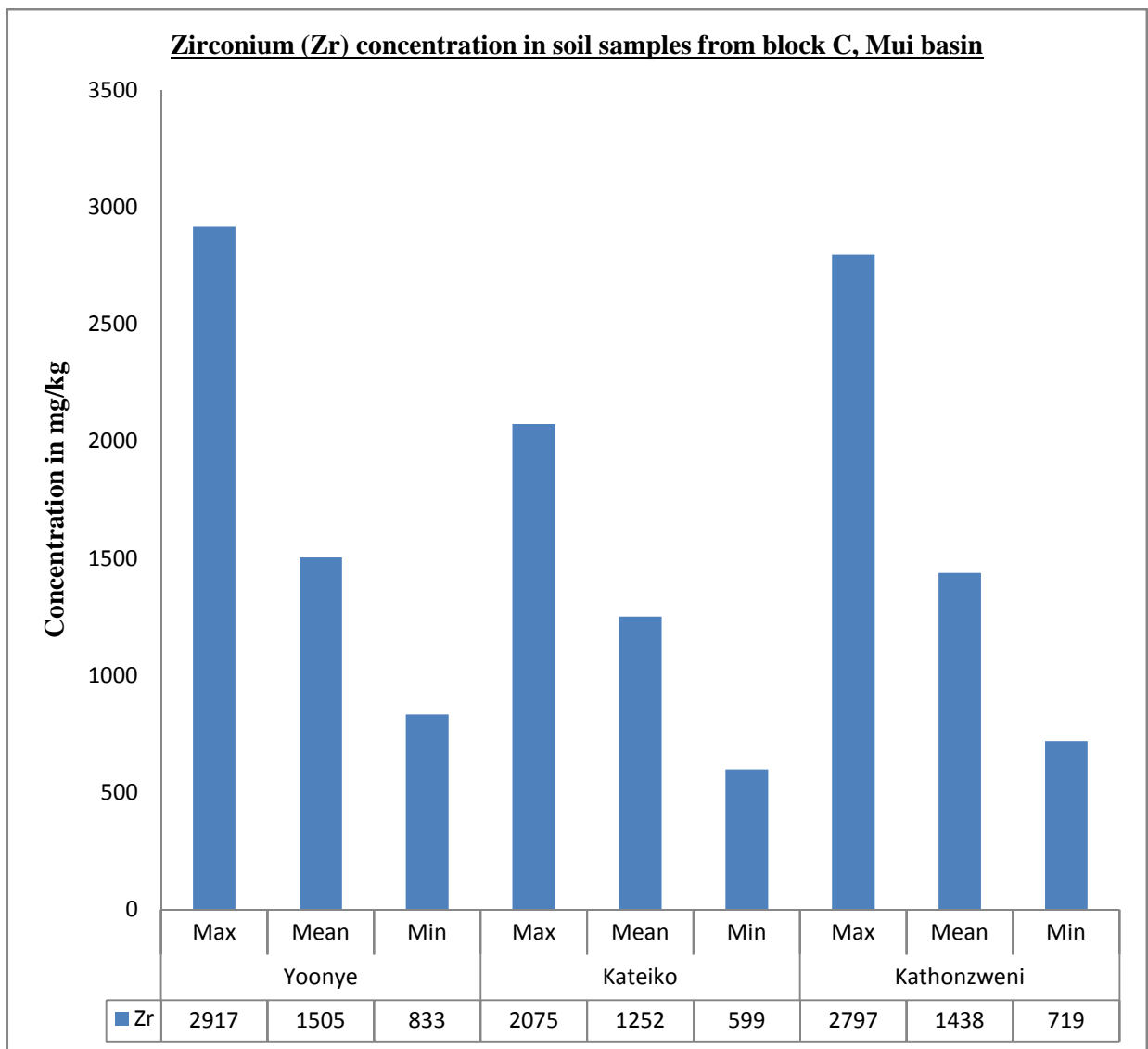
Figure 4.3: Zirconium concentration in soil samples from block C of Mui basin

On the other hand, nickel levels were the lowest and ranged between 6.88 and 35.8 mg/kg, in all samples analysed in this study (Table 4.3A, 4.3B and 4.3C and Figure 4.4).

Nickel (Ni) concentration in soil samples from block C, Mui basin

	Yoonye			Kateiko			Kathonzweni		
	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min
Ni	35.8	17.2	6.88	28.2	19.9	11.3	25.8	15.6	7.65
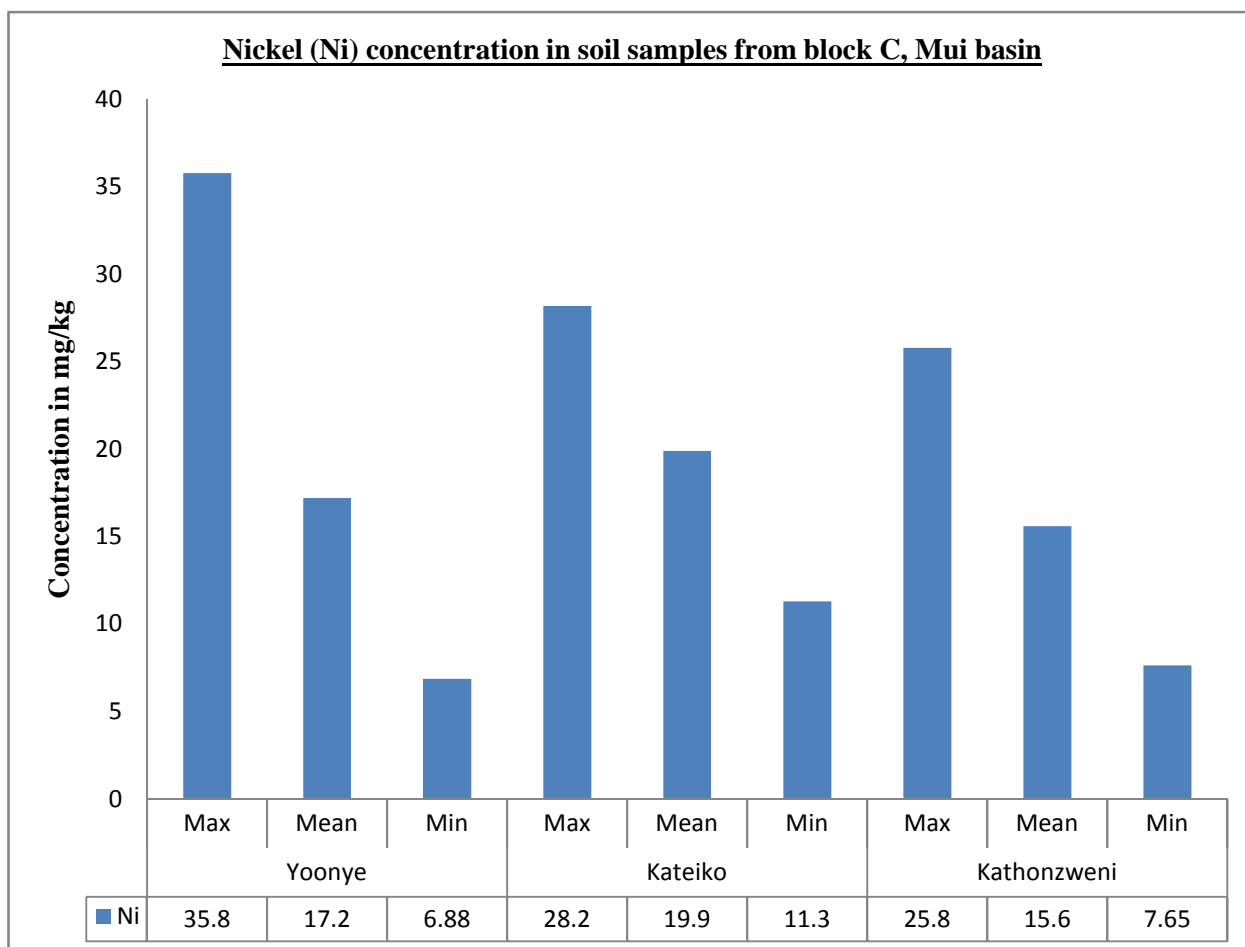
Figure 4.4: Concentration of Nickel in block C of Mui basin

Moreover, the results show that there was insignificant statistical variation between the means of Ni concentration in the regions studied; 15.6 mg/kg, 17.2 mg/kg and 19.9 mg/kg for Kathonzweni, Yoonye and Kateiko, respectively (Figure 4.4). These values were however within the worldwide average concentrations range of 13–37 mg/kg (Kabata-Pendias, 2010). In general, nickel levels in soils heavily rely on the composition of the parent material. Therefore, low levels of Ni concentration in surface soils indicate that there are no anthropogenic activities and unlikely presence of underlying Ni-rich mineral.

Vanadium (V) levels in the samples were found to be between 280-657 mg/kg (Table 4.3A, 4.3B and 4.3C and Figure 4.5).

Vanadium (V) concentration in soil samples from block C, Mui basin								
Max	Mean	Min	Max	Mean	Min	Max	Mean	Min
Yoonye			Kateiko			Kathonzweni		
V 637	449	323	657	473	293	605	387	280
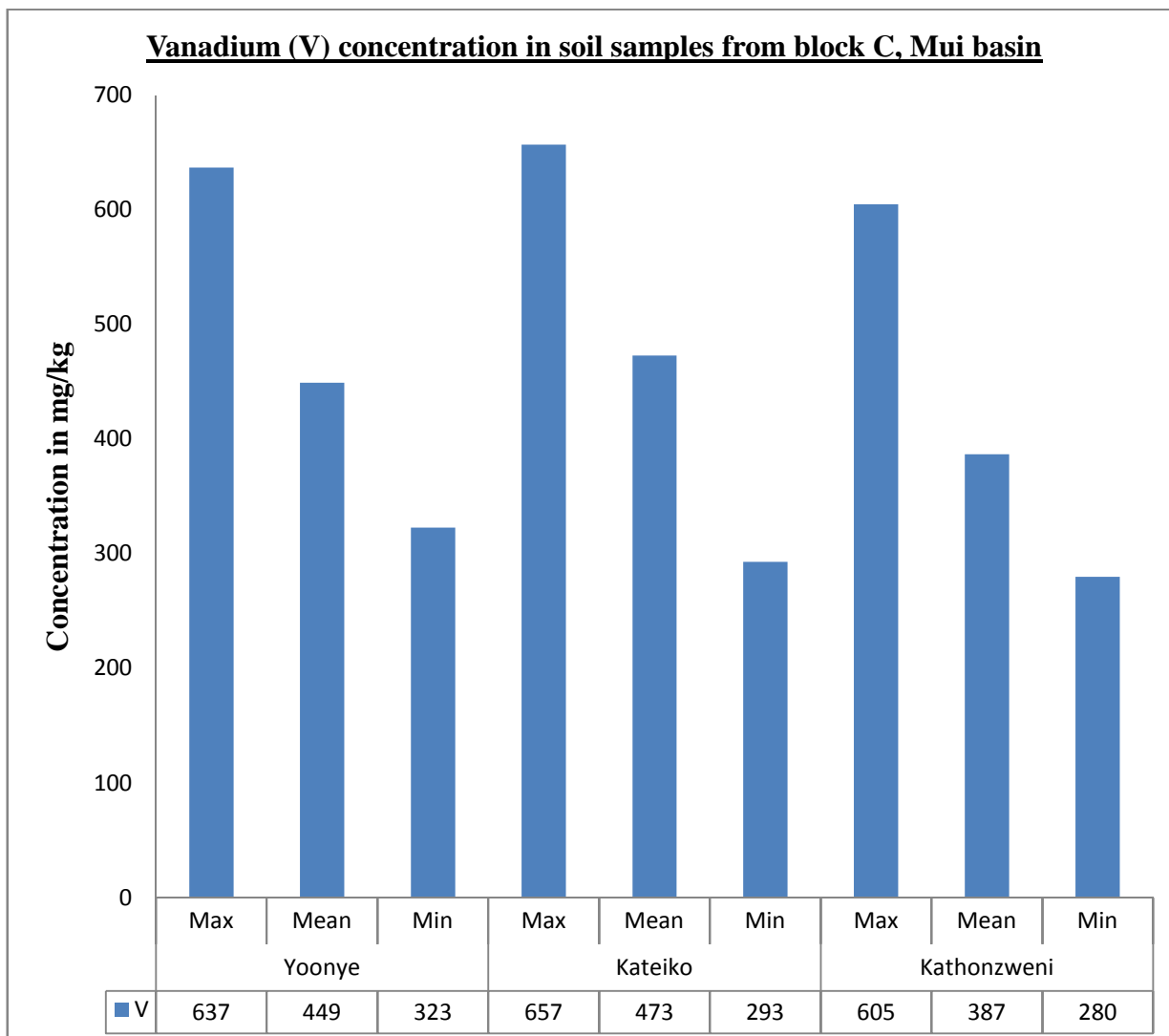
Figure 4.5: Vanadium concentration in soil samples from block C of Mui Basin

However sample S22, S31 and S42 had higher vanadium levels (605-657) mg/kg greater than worldwide averages of up to 500 mg/kg (Kabata-Pendias, 2010). Furthermore, Vanadium concentration levels are closely related to the parent rock types (Som and Joshi, 2002). Its elevated concentration in samples from Kateiko and Yoonye areas can therefore be attributed to presence of V-rich mineral in the underlying sub soil (Cances et al., 2005). In addition, a study by Seredin (2007) established high concentration of vanadium in various bituminous sediment and coal samples. In that study, the average vanadium level in coal was estimated at 58 mg/kg. It is of interest to note that Kateiko area is one of the regions in Kitui County where drill tests for coal have been completed and have successfully yielded the presence of coal (MoE, 2011). Vanadium is a possible pathfinder for coal mineralization.

In general, samples from Kateiko had a mean vanadium concentration of 473 mg/kg. Sample S22, recorded the highest concentration 657±47 mg/kg (Table 4.3B). However low concentration value of 280 mg/kg was in sample S36 from Kathonzweni area (Table 4.3C). In general, vanadium minerals do not independently exist and in most case exists in compounds such as vanadinite and roscoelite (Kabata-Pendias, 2010). Due to this, most of the V-containing minerals are of secondary origin mostly associated with primary minerals such as pyroxenes, hornblende, biotite, and magnetite. Smith and Huyck (1999) indicated that these primary mineral occurs in low concentration levels of order 0.01% in agreement with the findings of this study.

This study has revealed that copper (Cu) concentrations in all the samples analysed varied from 16.3 to 85.1 mg/kg (Table 4.3A, 4.3B and 4.3C). This was within the world wide average reported values of between 14 and 109 mg/kg (Kabata-Pendias, 2010) and was in agreement with local study reported by Mulwa et al. (2012) for Mwanyani area of Kitui County for analysed copper levels. However, samples from Kathonzweni region posted low concentration levels of Cu with sample S46 recording the lowest concentration value of 16.4±1.7 mg/kg (Table 4.3C) and higher concentrations values of 85.1±4.7 mg/were reported in sample S20 from Kateiko kg (Table 4.3B). It was observed that higher concentrations of copper were reported in loamy soils. In general, there was no clear pattern among the samples between clay, loamy and sandy soils.

A study by Kabata-Pendias (2010) noted that copper has a common characteristic of being accumulated in the top horizons. This phenomenon was attributed to bioaccumulation as well as anthropogenic sources of copper. Therefore any elevated values reported on the surface soil may act as an indicator of the underlying mineral. In addition, studies reveals that Cu has a tendency to be adsorbed by soil organic matter, carbonates, clay minerals, and oxyhydroxides of Mn and Fe, and therefore may be a good indicator for predicting mineral content in both surface and sub soil layers of the strata (Kabata-Pendias, 2010).

Figure 4.6 shows that the results of zinc concentration varied between (10.9-161) mg/kg.

Zinc (Zn) concentration in soil samples from block C, Mui basin

	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min
		Yoonye			Kateiko			Kathonzweni	
■ Zn	122	68.0	10.9	128	67	22.5	161	55.2	13.1
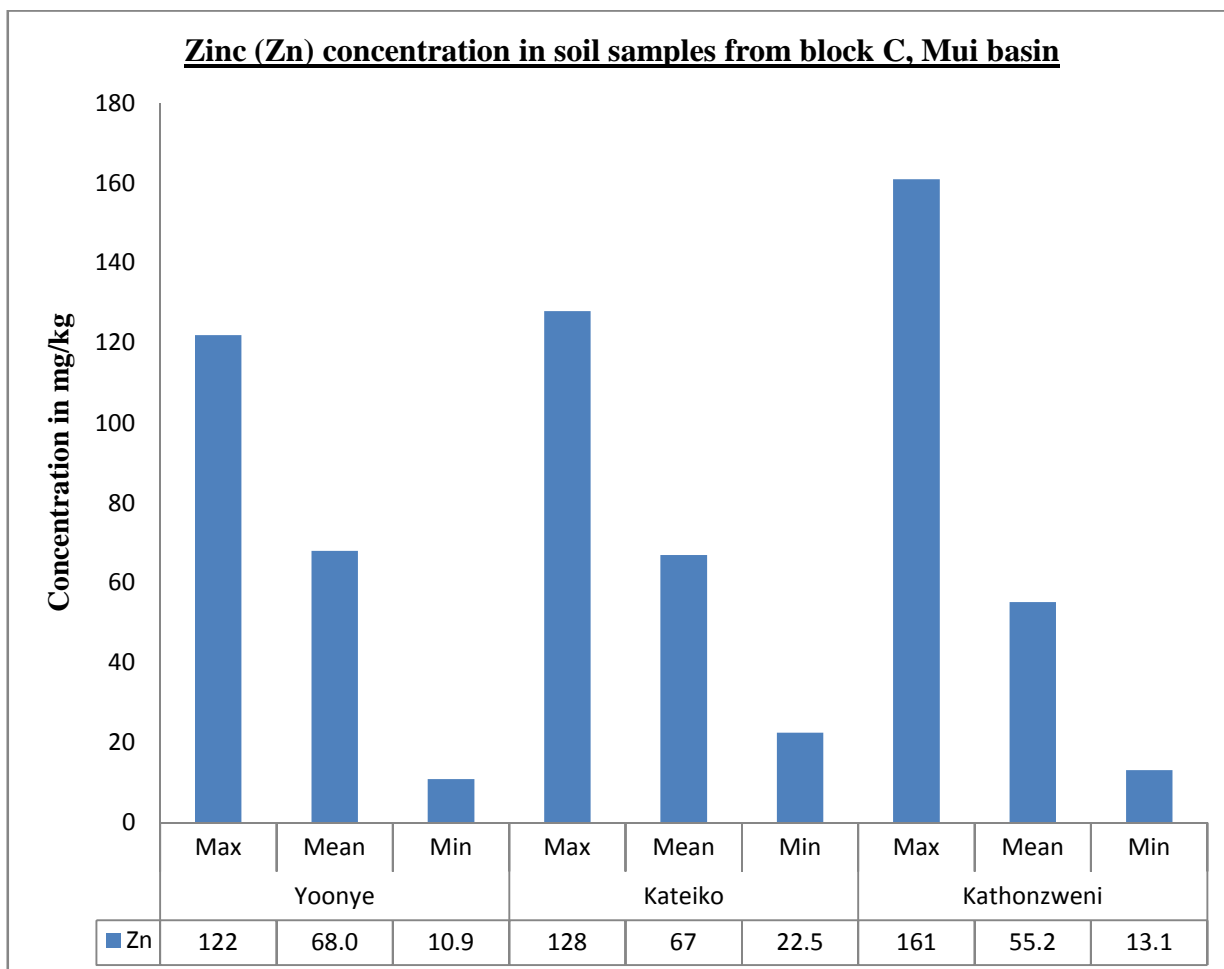
Figure 4.6: Concentration of Zinc in the study Area

It was observed that some samples recorded Zn concentrations that were above the worldwide values of between 60-89 mg/kg (Kabata-Pendias, 2011). Samples included S6, S11, S23, S28 and S50 had values that were above world averages of 100 mg/kg with S50 having the highest value of 161mg/kg (Table 4.3C). In addition, sample S4, S10, S14, S22 and S46 reported Zn concentrations that were below 60 mg/kg. In general, the results indicate that Zn was evenly distributed in the samples with concentration spanning from high, moderate to low values. Related independent studies however indicate that Zn is very mobile during weathering processes as well as readily soluble, specifically in the presence of sulfur anions (Cheng et al., 2009, Alloway, 2004). Alloway (2004) pointed out that the factors controlling the mobility of zinc in soils similar to Cu, but Zn existed in more readily soluble forms.

Strontium contents of the soil samples revealed that its values ranged between 70.3-770 mg/kg (Figure. 4.7, Table 4.3A, 4.3B and 4.3C). This indicates that the highest value of 770±17, reported in sample S16, from Kateiko was above the worldwide reported average range of

260-370 mg/kg (Kabata-Pendias, 2011). The high concentration of Sr reported in the study can be linked to the presence of clay minerals since they have a tendency to absorb strontium and therefore majority of argillaceous sediments are enriched with this element (Dolníček et al., 2010).

Strontium (Sr) concentration in soil samples from block C, Mui basin

	Yoonye			Kateiko			Kathonzweni		
	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min
Sr	419	289	161	770	392	183	497	262	70.3
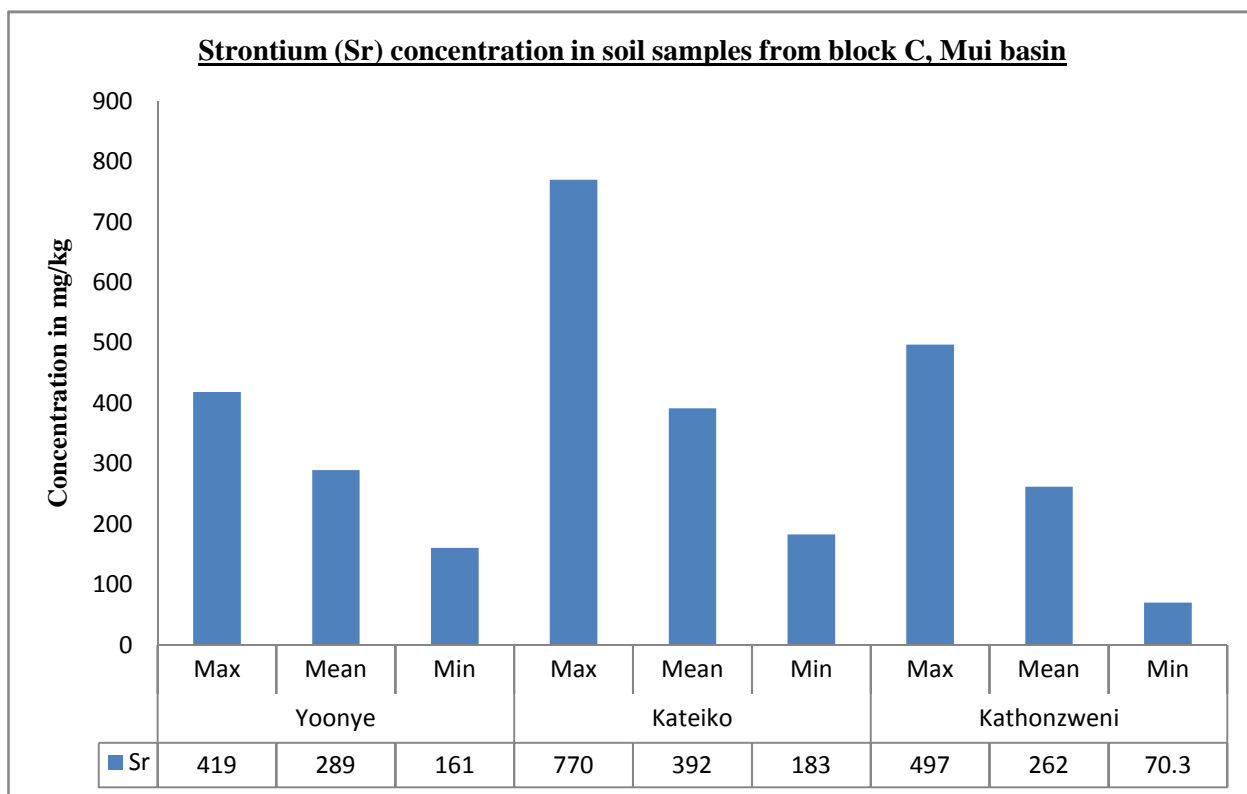
Figure 4.7: Concentration of Strontium in soil samples from block C of Mui basin

Lastly, this study indicates that the mean concentration of chromium was found to be highest in samples from Yoonye (70.2 mg/kg) as presented in Figure 4.8. It was however slightly the same for most samples in the other areas studied which reported mean values of 64.2 and 70 mg/kg for Kathonzweni and Kateiko areas respectively (Figure 4.8). In general, the concentration of Cr was found to vary from 38.7 mg/kg to 93.3 mg/kg. Moreover, chromium concentration was found to be slightly above the mean worldwide reported values of 60 mg/kg (Kabata-Pendias, 2011). The results are in agreement with those by Salvador-Blanes et al. (2006) who stressed on the effect of geological origin of weathered bedrocks on the distribution of chromium in soil profiles. Accordingly, Cr contents of weathered bedrocks were higher in topsoil samples may be linked to the presence of weathered bedrock in the underlying ores.

Chromium (Cr) concentration in soil samples from block C, Mui basin

	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min
		Yoonye			Kateiko			Kathonzweni	
Cr	93.3	70.2	46.7	82	70	40.4	91.1	64.2	38.7
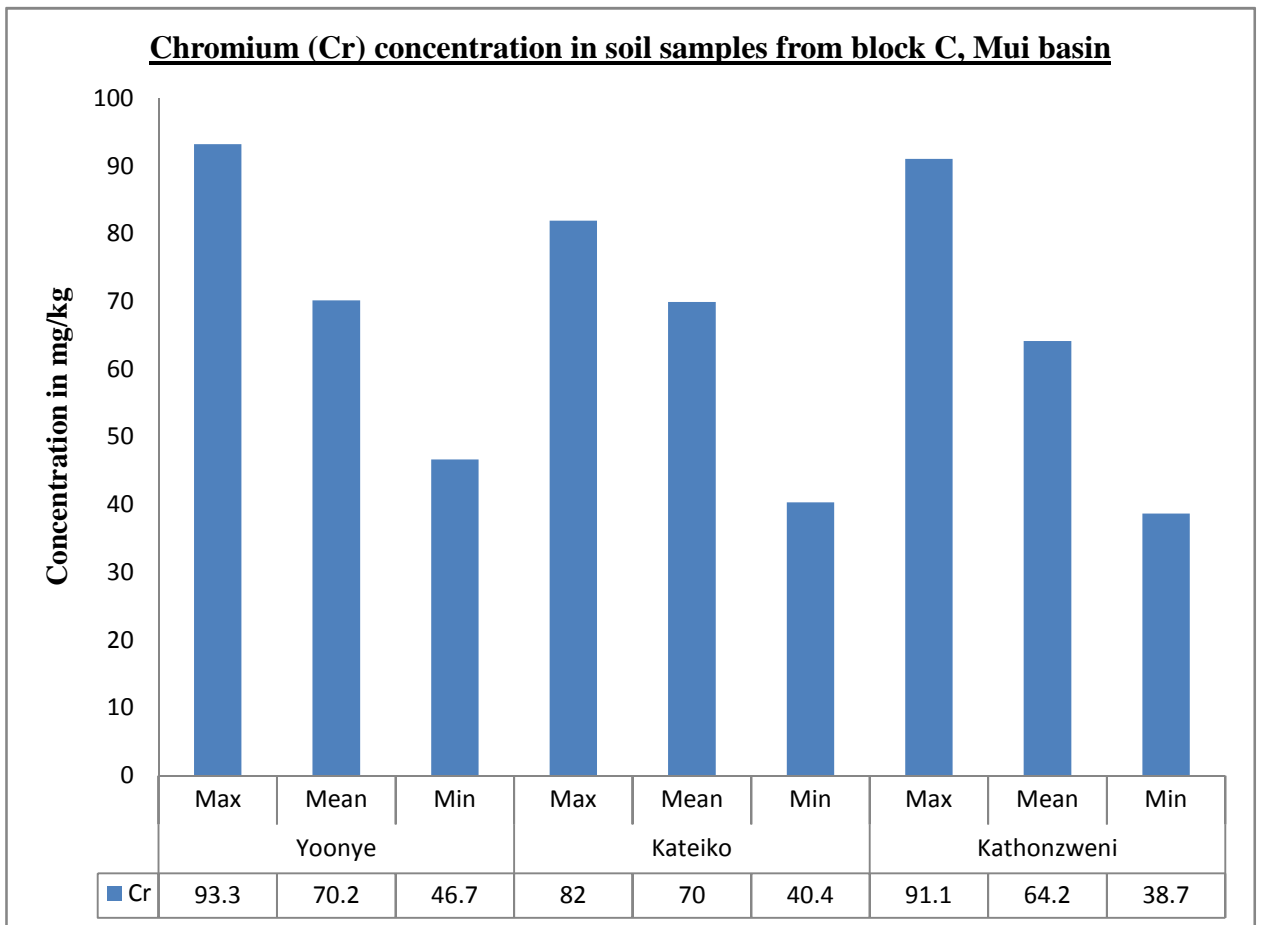
Figure 4.8: Chromium concentration in soil samples from block C of Mui basin

4.4. Results of Multiple Correlation between Trace Elements

Table 4.4 shows the results of multiple correlations between the elements V, Cr, Cu, Zn, Ni, Sr and Zr.

Table 4.4: Multiple correlations results of Trace Elements in the study area

	V	Cr	Ni	Cu	Zn	Sr	Zr
V	1	**0.64**	**0.569**	**0.449**	**0.453**	0.22	0.082
Cr	**0.64**	1	**0.515**	**0.38**	**0.385**	0.048	0.015
Ni	**0.569**	**0.515**	1	**0.332**	0.109	**0.286**	0.011
Cu	**0.449**	**0.38**	**0.332**	1	**0.731**	**0.294**	**-0.474**
Zn	**0.453**	**0.385**	0.109	**0.731**	1	0	**-0.354**
Sr	0.22	0.048	**0.286**	**0.294**	0	1	-0.076
Zr	0.082	0.015	0.011	**-0.474**	**-0.354**	-0.076	1

N/B Values in bold represent significant values at the level of significance alpha=0.050 (two-tailed test)

The R values for Cr/V, Ni/V, Ni/Cr and Cu/Zn were found to be highly correlated at 0.64, 0.569, 0.515 and 0.731 respectively (Table 4.4 and Figure 4.9). This relationship is a result of lithologic association due to similarity in their small ionic sizes and positive oxidation states for metals. In addition, it is linked to the presence of primary minerals pyroxene and biotite in the underlying geological strata (Smith and Huyck, 1999). The inverse relationship between Zr , Cu and Zn indicates that enrichment of Cu and Zn in the soils was accompanied by depletion in Zr.
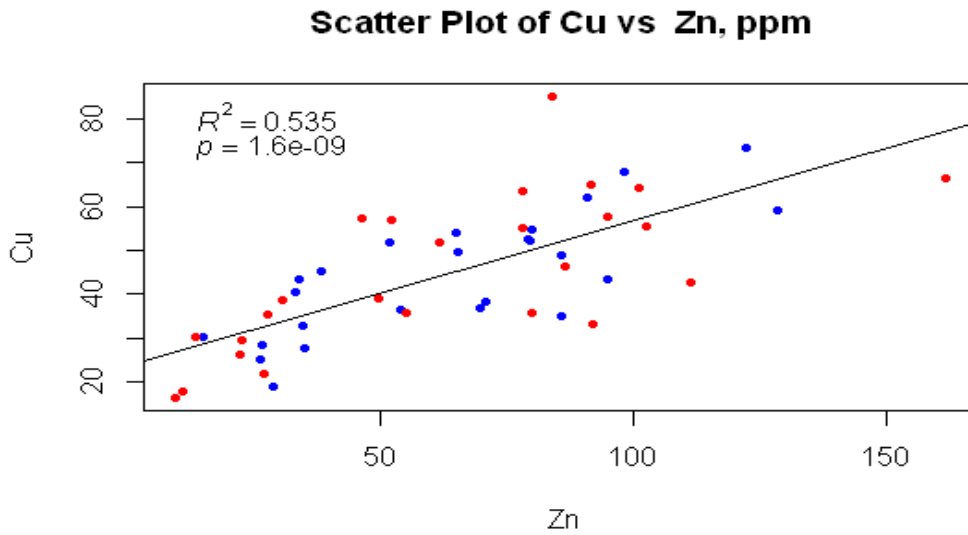
Figure 4.9: Scatter Plot of Cu against Zn: R=0.731

Scatter plots of Sr against all the measured elements showed that there exist no linear correlations with the other elements (Table 4.4 and Figure 4.10). However, Zr plotted against V, Cr, and Ni had slightly positive linear correlation (Table 4.4).
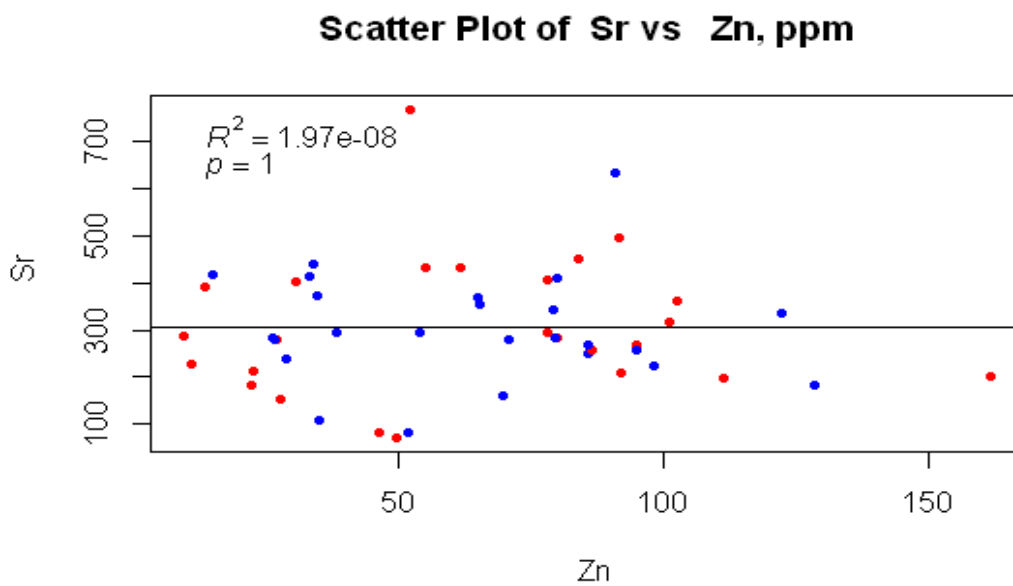
Figure 4.10: Scatter Plot of Sr against Zn: no linear correlation with Sr.

4.5. Principal Components Analysis (PCA)

The principal components are linear combinations of the original variables that account for the variance in the data. (Figure 4.11) shows the PCA scores plot for the fifty soil samples used in this study..
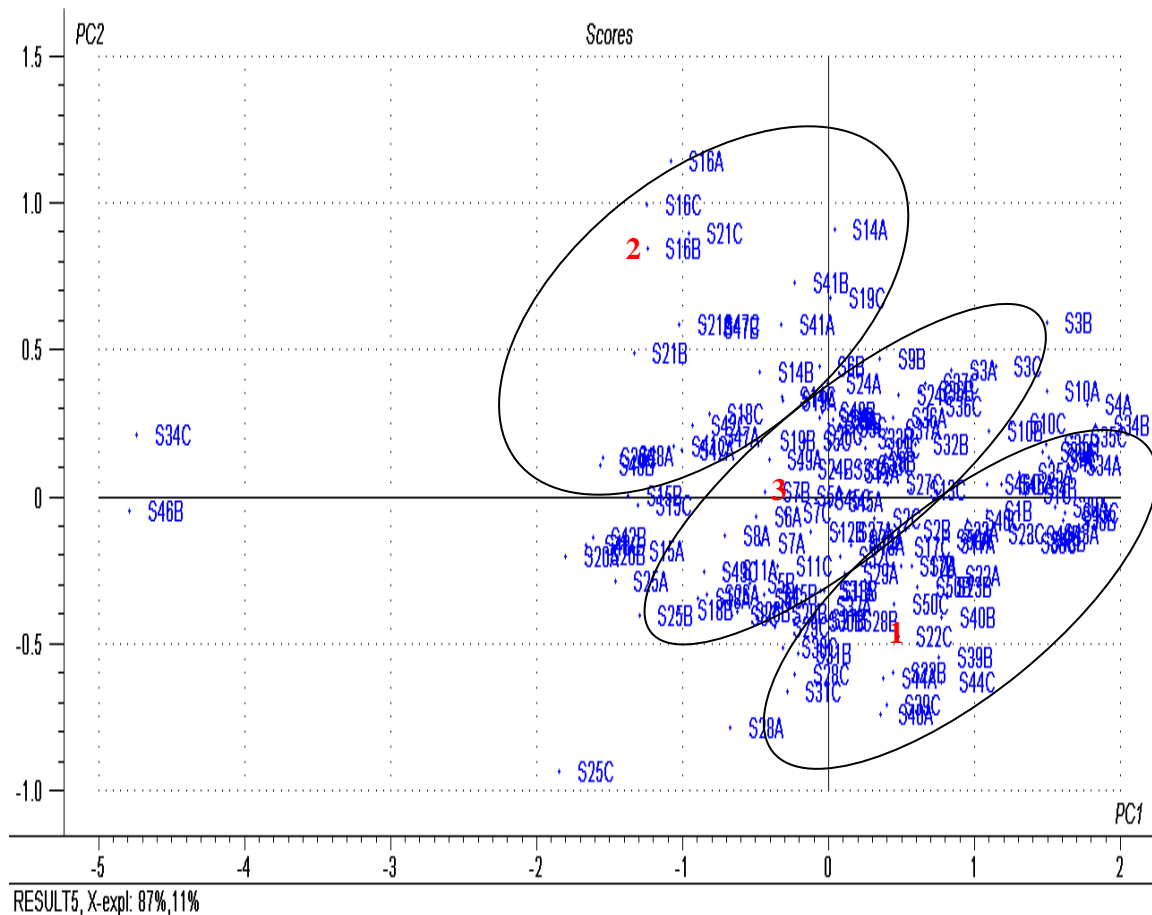
Figure 4.11: Score Plot for the first and second components (PC1 against PC2)

The results of the score plot indicates that samples can be characterized identifiable to the origin; from Yoonye, Kateiko and Kathonzweni areas as shown by three distinct clusters represented by regions 1, 2 and 3 respectively in the score plot shown in Figure 4.11 above.

Eigenvalues were generated for the 7 trace elements to help in data reduction. The eigenvalues of the correlation matrix equals the variances extracted by the principal components. Results of the eigenvalues from the principal components analysis (PCA) are shown in Table 4.5 where the variances of the new factors extracted and the proportions of the total variance extracted are listed.

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Table 4.5: Eigenvalues of the seven trace elements

Component Number	Eigenvalues	Proportion	Percent (%)	Cumulative (%)
PC1	6.09	6.09	87	87
PC2	0.77	6.86	11	98
PC3	0.07	6.93	1	99
PC4	0	6.93	0	99
PC5	0	6.93	0	99
PC6	0	6.93	0	99
PC7	0	6.93	0	99

In extracting factors, several solutions are examined with more or fewer factors and one that makes the best sense is chosen. In this study, all factors extracting variances greater than 0.77 eigenvalue were chosen and these conform to the outcome of the Scree Test (Figure 4.12) which extracted three factors. The Scree Test which is a graphical technique suggested by Cattell (1966) proposed plotting eigenvalues against principal components and to determine the region where the smooth curve levels off.

Principal Components Analysis results of the measured trace elements revealed two main components (Table 4.5 and Figure 4.12) which together extracted 98% of the total variance.
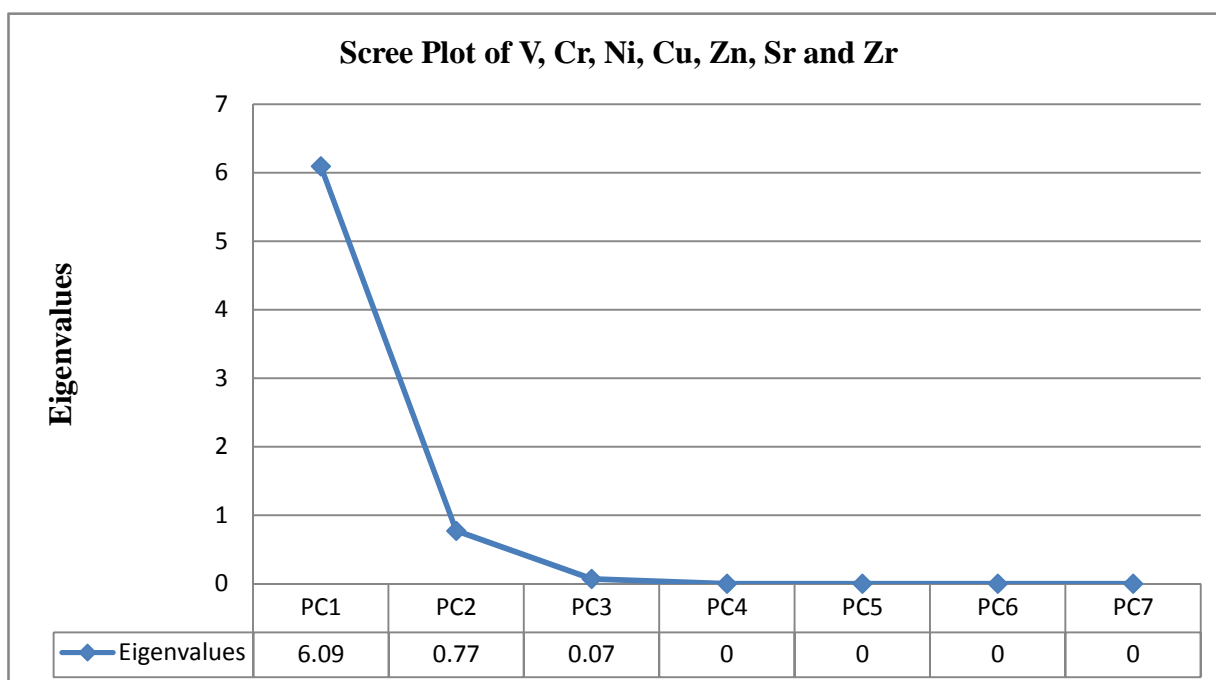
Figure 4.12: Scree Plot of the measured 7 elements. (Eigenvalues plotted against Components).

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The results indicates that most of the data information (variance of 98 %) was explained using only the first two principal components; PC1, 87% of the variance; PC2 accounted for 11% while the remaining 1% of the variance was explained by PC3.

The loadings plot of trace elements concentration for the fifty soil samples shown in Figure 4.13 is interpreted in terms of the three main PCs identified.
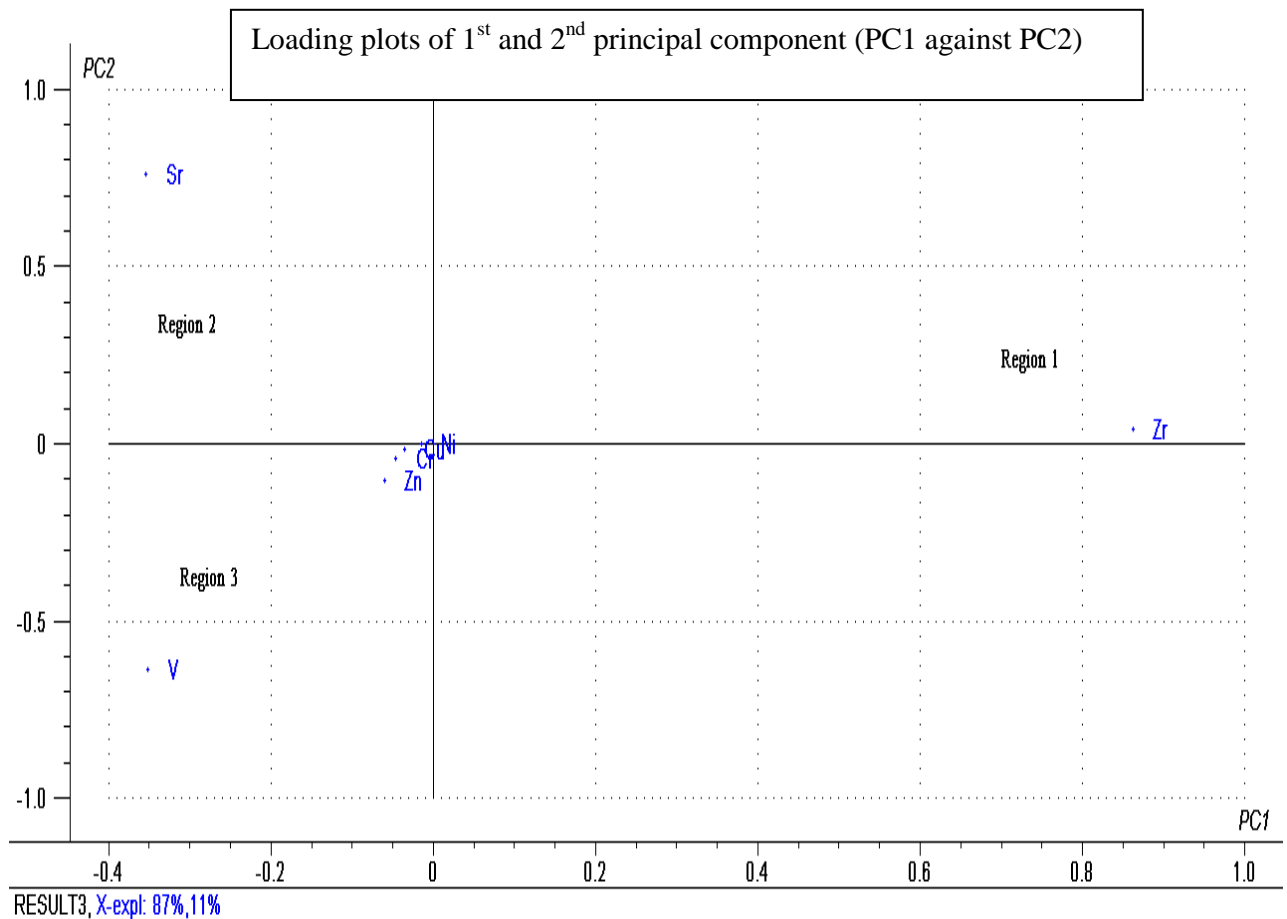
Figure 4.13: Loadings Plot for the first and second components (PC1 against PC2)

Figure 4.13 shows the loadings of the first three principal components; PC1 which accounted for 87 % of the total variance presented large positive loading from Zr (0.86). This can be linked to the underlying Zr-rich mineral such as zircon and baddeleyite. PC2 extracted 11% and had positive loading from Sr. This can be related to the underlying mafic rocks and igneous compact rocks such as basalts, and dolerites as suggested by Dolníček et al. (2010). PC3 explained 1% of the variance and recorded negative loading for V (-0.53). This is associated to bituminous sediments and coals due to their elevated concentration (Seredin, 2007).

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Figure 4.14 shows that the correlation loading plot of the element Zn, Cr, Ni and Cu are correlated and tends to form a cluster related to region 3. Due this correlation, mineral deposits having Cu and Zn as part of their constituent plays a role in predicting mineral content in the sub-soil.
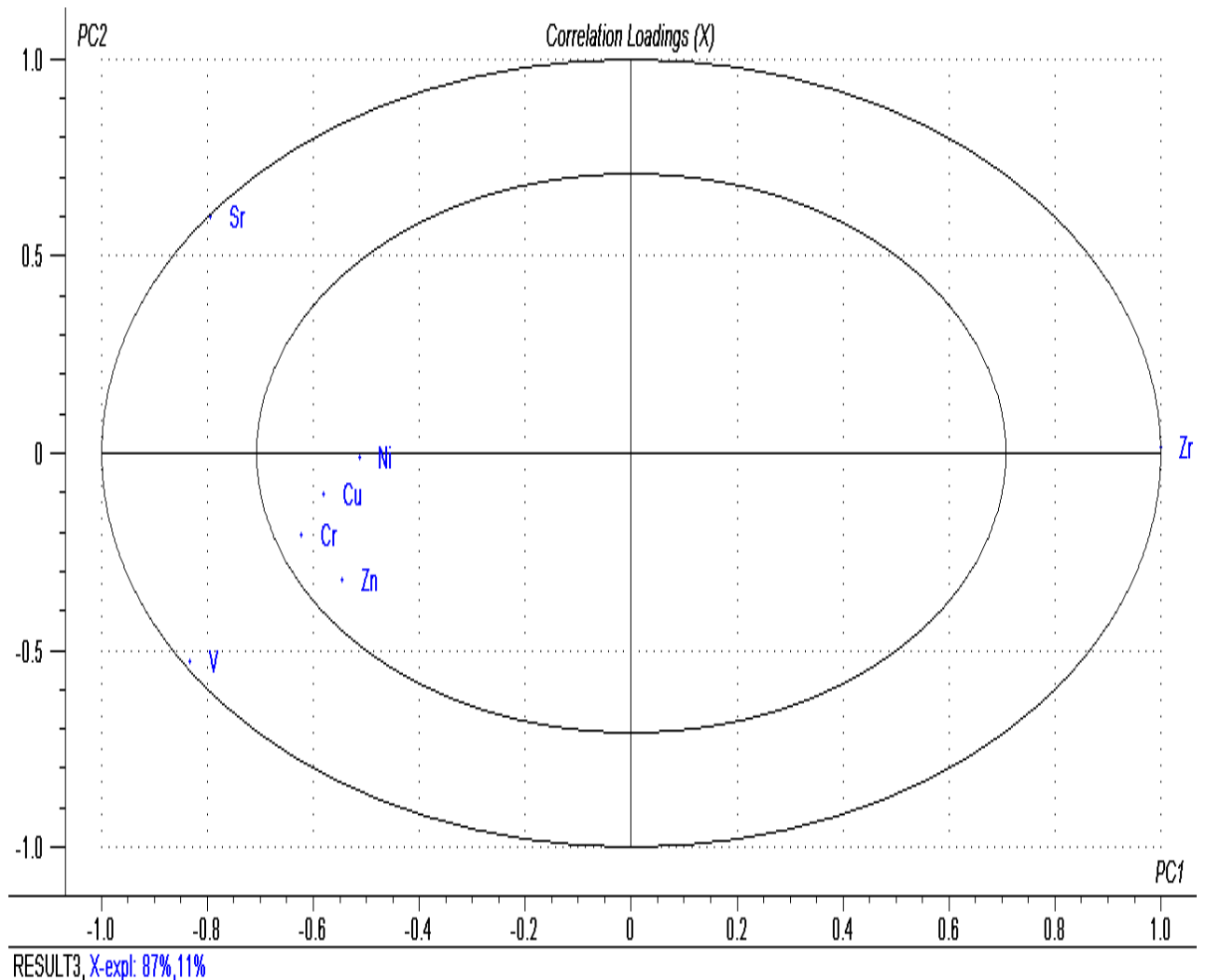
Figure 4.14: Correlation loadings Plot for the first and second components

4.6. Clusters of Elements

The resultant dendrogram from the hierarchical cluster analysis of the seven trace elements was examined at a cut-off point of 0.6 linkage distance to produce three clusters represented by red, green and blue (Figure 4.15)
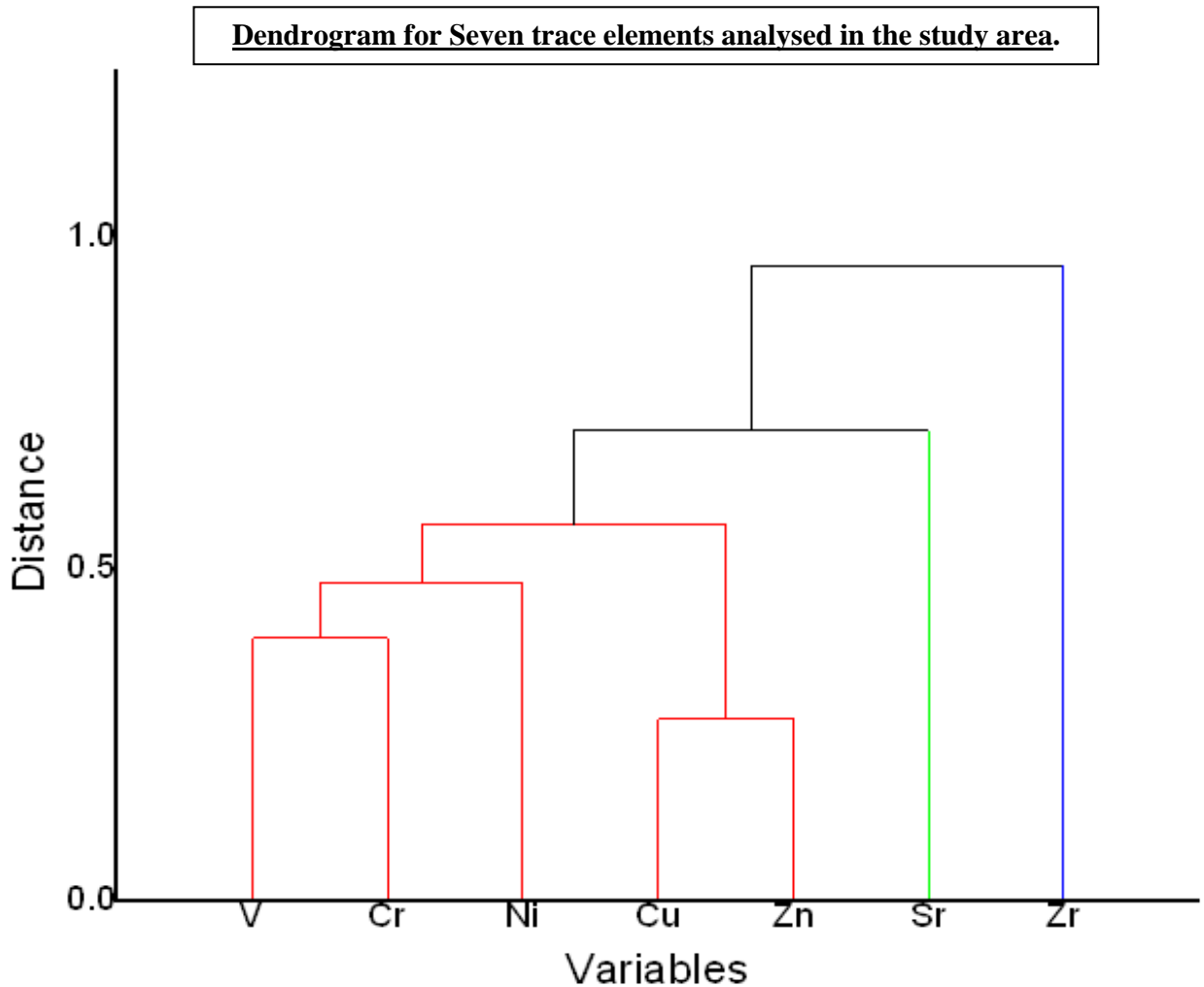
Figure 4.15: Dendrogram of seven trace elements showing three clusters

Cluster 1 which groups Vanadium is made up of Cr, Ni, Cu and Zn as pathfinders for Vanadium rich mineral. The most suitable pathfinders for Vanadium mineral in the study area are Cr and Ni because from the dendrogram the two elements formed closer cluster to vanadium. These results indicate that vanadium cluster consisted of three sub-clusters which joined at a distance of 0.6 (Figure 4.15). The first sub-cluster (V, Cr) joined to the second sub-cluster of Ni at a distance of 0.5. The third sub-cluster of Cu and Zn formed at a linkage distance of 0.3.

Cluster 2 which groups strontium is formed at a distance of 0.7 and the third cluster of Zirconium group formed at a distance of 0.9.

4.7. Mineralogical Analysis of Samples using X-ray Diffraction (XRD).

A few selected soil samples (S1, S19 and S39) from the three study areas of Yoonye, Kateiko and Kathonzweni respectively were subjected to X-ray Diffraction (XRD) analysis to determine their mineralogical composition. The results of mineralogical composition are presented in the X-ray diffractograms in Figure 4.16 and Table 4.6

The results revealed that the soil samples composed mainly of quartz, orthoclase, kaolinite and albite. Quartz is the predominant primary mineral occurring in the sandy soil samples analysed. The area accordingly has the potential for sand mining.

Table 4.6: XRD results of Soil minerals for the samples.

Sample code	Area	Mineral composition in percentage (%)						
		Albite	Anorthite	Dickite	Hornblende	Kaolinite	Orthoclase	Quartz
S1	Yoonye	0	24.6	0	0	1.5	6.8	67.1
S19	Kateiko	32.4	0	0	3.5	1.4	12.3	50.5
S39	Kathwonzweni	14.9	0	6	0	0	7.5	71.7
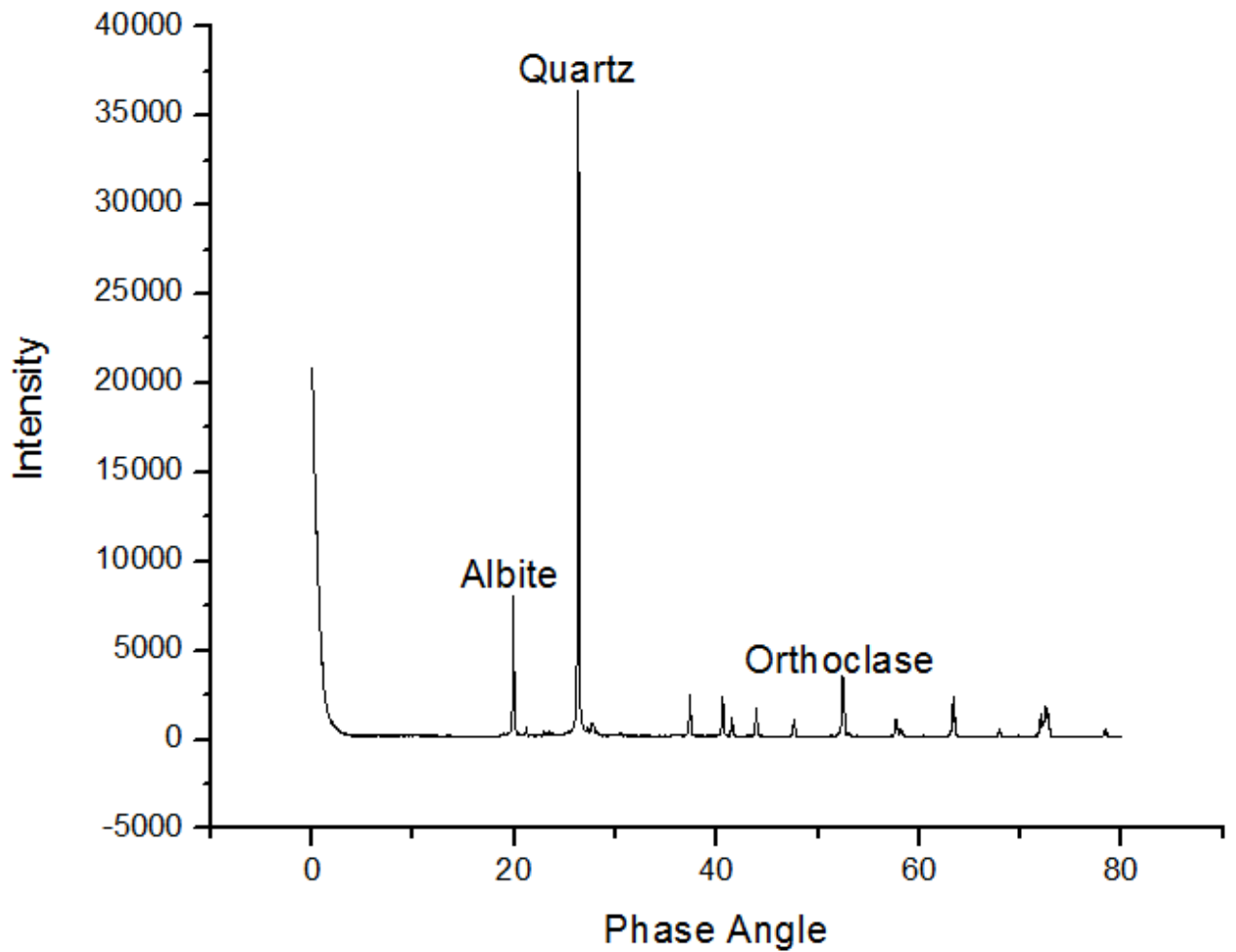
Figure 4.16: X-ray diffractogram of sample S19 from Kateiko area

In addition, the major elements Ca, Al, Si in the mineral samples were revealed; For instance anorthite, a calcium-rich mineral with a chemical formula of $CaAl_2Si_2O_8$, albite $NaAlSi_3O_8$, Kaolinite$Al_2Si_2O_5(OH)_4$, which supports the fact that trace elements were not utilized to characterize the minerals using XRD analysis.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The study was able to successfully identify in substantial levels Cu, Ni, Zn, Cr, V, Sr and Zr as some of the trace elements in the soil sample from Mui basin. In addition, it was observed that Zr reported the highest concentrations (599- 2917) mg/kg while Ni had the lowest concentration of (6.88-35.7) mg/kg. Moreover, Principal Component Analysis was able to qualitatively identify three key components, which represented the origin of the sampling location namely; Kathonzweni, Yoonye and Kateiko areas based on the results of elemental concentrations. Furthermore, the possibilities to evaluate the possible underlying rocks and mineral contents have been proved. This is as a result of the findings which pointed out to a likelihood of zircon and coal bearing minerals being found in Yoonye and Kathonzweni areas respectively based on the levels of Zr and V determined in these areas. These sampled locations can therefore be used as the target points for exploration of these minerals through increasing on sampling depth as well as including plant bioaccumulator species as bioindicators.

The soil samples analysed by XRD technique showed the minerals quartz, orthoclase, kaolinite and albite to be present in substantial levels in sub soil. The persistency of quartz in these soils is attributed to the presence of sand in the area and therefore presents a sand mining potential of the area. The model proposed in this study therefore presents a justification of drilling through tens to hundreds of meters of buried deposit in a given area for underlying mineral exploration as it offers decisive data on possible minerals available in an area.

In general, this study has successfully demonstrated that, multivariate statistical approach to analysis of geochemical data for mineral exploration is effective and useful, especially, in finding elemental associations, determining principal components and thereby identifying and predicting possible mineralization in a given area. The challenge in the wider application of the method used in this study, however, is the geological strata difference which may vary from one location to another and therefore needs to be considered when using this approach.

5.2. Recommendations

1) Further work be carried out in these areas to improve the method proposed by profiling the trace elements level in varying depths.

2) The study method can be improved by sampling rocks outcrops and bioindicators plants species.

3) Based on successful demonstration by the study on the possibility of Zircon minerals being found in the area, further work be carried out to explore the potential of zircon mineral in the area.

4) The study can be extended to cover a wider region in Mui basin and other parts of the country for validation of the method.

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APPENDICES

Appendix 1: GPS sampling location

Location	Sample ID	Eastings	Northings
Yoonye			
	S1	411937	9870149
	S2	412571	9870325
	S3	412172	9870964
	S4	412669	9871685
	S5	413146	9872309
	S6	413173	9872110
	S7	413255	9871713
	S8	413236	9871079
	S9	412425	9873609
	S10	412433	9875023
	S11	412176	9875697
	S12	412626	9877291
	S13	412501	9877256
	S26	413999	9879692
	S27	414403	9879634
	S28	413998	9879651
	S29	413014	9873803
	S30	414594	9879621
	S31	414028	9878767
	S32	414037	9878742
	S33	412201	9872306
Kateiko			
	S14	410966	9878310
	S15	410955	9878380
	S16	410959	9878334
	S17	419998	9879503
	S18	410438	9879787
	S19	412934	9879679
	S20	412895	9879704
	S21	414243	9880162
	S22	413969	9883132
	S23	410112	9881053
	S24	412197	9879811
	S25	414727	9880525

Kathonzweni

	S34	412242	9872324
	S35	411632	9872552
	S36	412009	9872311
	S37	411767	9874605
	S38	412035	9875912
	S39	409946	9877261
	S40	409917	9877261
	S41	412446	9881234
	S42	410549	9883734
	S43	412035	9875912
	S44	409946	9877261
	S45	412626	9877291
	S46	412433	9875023
	S47	410955	9878380
	S48	412895	9879704
	S49	410438	9879787
	S50	410112	9881053

Appendix 2: Typical Spectra for soil sample S1A obtained from EDXRF

Sample : S1A   Group : solid_air   Date : 2014-05-27 17:10:01
Operator: A   Comment : Solid sample (without cell) / Air   01/01
[cps/uA] Na-U
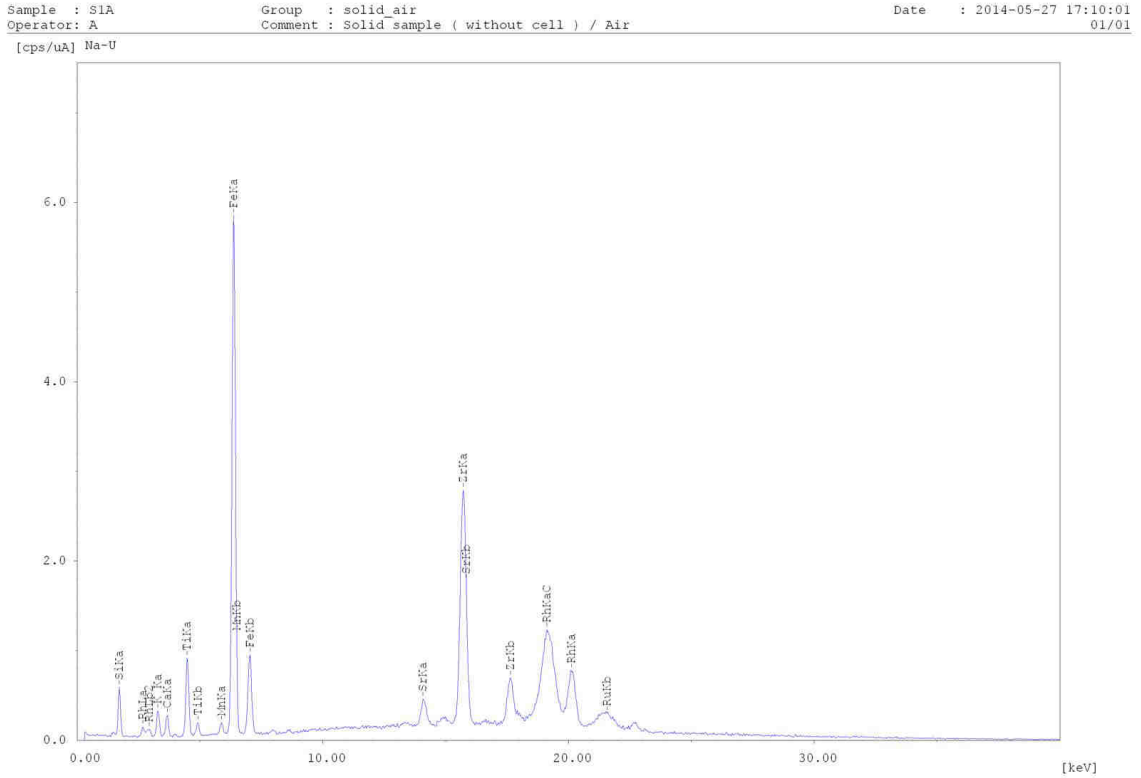
Appendix 3: Typical *SPE data for soil sample S1A obtained from AXIL

$MEAS_TIM:
   50   50
$DATE_MEA:
20-06-2014 10:10:45
$DATA:
  20   1200

66	69	62	65	76	74	56	76	65	66
54	75	62	60	62	64	69	64	59	69
60	60	62	56	60	69	46	67	48	58
60	63	59	50	61	62	58	61	51	55
51	53	39	51	51	52	53	42	46	58
51	62	49	53	60	55	55	65	55	49
46	59	92	141	176	244	254	237	176	130
90	62	58	49	47	43	38	45	41	42
44	40	41	38	28	31	31	35	42	31
42	43	38	35	37	54	43	40	38	38
42	27	42	44	36	44	36	33	38	44
47	59	63	71	71	66	74	56	58	58
53	58	68	58	60	67	60	69	52	66
47	42	32	33	33	35	29	38	47	51
63	74	94	141	129	151	132	119	83	60
51	39	40	29	34	36	47	63	57	66
92	88	114	125	125	103	87	63	43	39
36	32	24	33	38	31	29	39	40	49
44	51	39	38	36	26	32	29	34	29
33	36	26	36	32	38	36	41	62	113
122	213	260	319	374	375	314	298	199	131
95	56	36	40	32	36	42	32	32	43
51	39	64	74	80	82	85	76	74	61
40	42	31	47	31	38	25	40	37	33
31	30	36	37	38	36	43	26	42	38
37	40	35	38	44	41	36	51	47	38
42	30	32	39	39	47	37	42	42	58

63

60 63 83 67 90 85 71 74 60 40
34 42 40 44 38 39 36 47 66 72
110 192 315 554 781 1155 1583 1983 2086 2376
1998 1791 1400 1037 727 447 229 170 101 72
53 49 46 56 42 41 40 45 32 43
44 44 57 80 81 112 149 216 236 300
329 379 385 362 288 232 182 135 102 76
58 52 42 41 36 31 29 38 38 47
41 39 44 38 33 40 42 56 45 36
38 37 34 45 31 42 37 37 40 42
40 46 42 53 45 56 42 60 45 39
72 49 48 53 51 50 42 41 44 42
38 36 36 33 44 42 40 41 36 47
36 35 39 36 42 45 49 44 56 47
45 53 51 62 40 42 44 44 42 40
44 47 44 38 40 42 53 42 49 61
45 44 56 55 42 42 49 40 36 65
44 50 42 62 42 56 43 51 36 51
45 38 44 48 49 56 47 53 51 57
66 50 50 49 49 60 51 38 66 53
56 53 48 60 53 53 58 58 54 47
44 53 56 62 56 42 49 67 49 59
45 47 53 51 53 56 53 55 53 62
51 54 60 53 56 72 60 69 57 62
75 62 52 56 65 58 63 58 64 55
55 68 51 72 51 64 58 65 65 59
60 53 61 62 66 65 53 70 65 69
65 72 67 58 76 62 62 60 55 66
57 60 56 68 62 56 60 55 57 65
51 56 55 67 49 67 69 53 55 62
63 61 61 57 65 64 68 64 67 65
58 61 64 64 67 51 61 69 71 57
60 69 58 55 58 58 66 56 65 61
61 67 64 62 67 70 65 53 87 69
60 76 62 60 60 62 59 67 63 70
74 56 56 60 68 65 78 72 71 63
62 73 60 65 67 71 64 76 60 68
71 73 86 83 73 76 92 89 85 99
79 83 81 85 63 76 76 77 71 69
70 70 74 74 78 60 69 71 76 65
63 60 88 73 75 81 92 121 104 125
139 152 172 168 210 188 175 175 179 163
155 144 122 111 97 99 109 78 85 85
74 85 66 85 75 74 81 74 67 74
85 69 76 85 72 76 78 97 83 95
105 98 114 105 94 110 112 103 90 100
96 97 110 86 76 96 85 84 86 75
95 78 80 89 83 79 91 89 92 81
99 112 143 172 214 270 300 359 481 582
691 744 874 993 1056 1071 1115 1150 1075 1023
855 817 667 595 462 399 301 253 202 159
133 119 102 98 98 88 93 95 83 83
83 87 83 100 96 89 103 75 89 78
91 107 103 99 104 92 108 101 96 100
103 100 105 103 110 101 115 114 97 111
105 121 113 128 117 120 121 113 123 118
134 148 154 160 206 244 319 389 542 677
833 1081 1338 1619 1963 2175 2480 2795 2920 3188
3290 3281 3234 3143 2909 2729 2444 2165 1815 1542
1320 1082 878 710 594 471 351 314 261 222
164 137 158 146 155 136 115 137 106 127
123 107 111 117 116 111 111 100 96 92
95 108 112 92 108 116 88 109 103 112
124 103 123 119 123 125 131 134 139 143
145 150 159 164 159 170 187 201 219 236
247 247 271 274 278 328 341 372 377 400
385 415 453 471 430 457 464 484 465 507
494 465 503 479 471 520 516 523 574 568
584 650 684 768 781 811 875 885 858 860
822 779 757 729 644 543 489 453 371 357
306 289 258 283 276 267 303 314 287 285
299 319 347 325 323 346 343 341 344 303

```
287    272    265    260    214    220    185    158    152    138
103    102    89     75     82     76     59     60     64     63
56     63     59     69     58     78     79     72     78     67
72     69     65     67     76     65     75     75     67     75
80     75     67     78     81     90     94     87     92     99
90     110    94     94     96     134    118    102    119    117
132    116    112    137    141    131    121    122    132    107
115    114    108    106    110    113    102    113    100    92
93     85     89     89     90     84     85     73     78     75
76     64     61     85     62     67     73     58     56     53
54     58     62     58     39     50     42     43     46     53
46     51     53     58     45     48     53     68     59     78
70     72     76     70     76     69     74     74     71     64
66     71     58     65     49     50     42     54     32     36
43     40     53     41     40     40     47     41     39     45
51     35     41     51     39     36     41     43     36     38
24     29     36     29     24     29     40     42     31     30
33     33     36     32     44     35     28     36     31     47
31     39     31     38     33     36     37     36     30     30
43
```

Appendix 4: Typical *ASR data for sample S1A obtained from AXIL

```
$MEAS_TIM:
    50      50
$DATE_MEA:
20-06-2014  10:10:05
$PEAKS:
    36
11   1          1.041           -9.       10.       .32
12   1          1.254          -21.        9.       .31
13   1          1.487           46.       13.       .88
14   1          1.740          744.       30.       .67
15   1          2.013            0.       11.       .26
16   1          2.307          -22.       10.       .87
17   1          2.622           61.       14.      5.81
18   1          2.957           94.       17.       .85
19   1          3.313          429.       26.       .62
20   1          3.691          364.       24.       .38
22   1          4.509         1526.       48.       .22
23   1          4.950           29.       23.       .58
24   1          5.412           -8.       15.       .26
25   1          5.895          228.       24.       .27
26   1          6.399        11941.      109.       .98
27   1          6.925           94.       29.      1.72
28   1          7.472            3.       19.       .71
29   1          8.041           69.       24.       .63
30   1          8.631           71.       22.       .34
32   1          9.875            7.       25.       .49
33   1         10.532            1.       46.       .26
34   1         11.208           -9.       28.       .29
37   1         13.375           98.       35.       .18
38   1         14.142          907.       49.       .21
39   1         14.932          212.       43.       .29
40   1         15.746         8941.      113.       .70
41   1         16.583           94.       47.       .40
42   1         17.443          -47.       63.       .44
47   1         22.103            0.        1.      45.38
48   1         23.108            0.        1.      30.00
51   2          3.604          -27.       14.       .52
56   2          4.464           37.       26.       .34
58   2          4.838          -14.       17.       .48
69   2          7.180            4.       21.      1.34
77   2          9.167           11.       19.       .57
82   2         10.542          -11.       38.       .26
```

Appendix 5: Typical Results of soil sample S1A obtained from AXIL

$ANALYSIS_RESULTS:
20-06-2014 10:33:56

S1A   [A0= 18823] WEIGHT [g/cm^2]:   .1014

EL	E [KEV]	INT [C/S]	S	T	CONC [FRAC]	ERROR
K	3.312	7.653	4.46E+06	0.0018	8.77E-03	8.15E-04
Ca	3.690	5.837	5.43E+06	0.0028	3.61E-03	3.83E-04
Ti	4.508	32.367	5.30E+06	0.0063	9.21E-03	6.47E-04
V	4.949	1.102	3.08E+06	0.0089	3.80E-04	1.57E-04
Cr	5.411	0.306	3.84E+06	0.0127	5.90E-05	5.47E-04
Mn	5.895	3.980	4.70E+06	0.0180	4.55E-04	6.12E-05
Fe	6.400	243.490	5.35E+06	0.0248	1.78E-02	1.16E-03
Co	6.925	2.469	6.24E+06	0.0311	1.23E-04	3.06E-05
Ni	7.472	0.449	7.01E+06	0.0418	1.48E-05	6.72E-04
Cu	8.041	1.245	7.75E+06	0.0556	2.80E-05	9.80E-06
Zn	8.631	0.980	4.31E+06	0.0728	3.02E-05	2.06E-05
As	10.532	0.918	1.04E+07	0.1507	5.68E-06	3.03E-05
Pb	10.540	0.878	3.31E+06	0.2714	9.45E-06	1.06E-05
Rb	13.375	1.347	2.04E+06	0.3199	1.99E-05	2.16E-05
Sr	14.142	18.204	1.87E+06	0.3722	2.55E-04	2.15E-05
Y	14.933	5.694	1.29E+07	0.4276	1.01E-05	1.68E-06
Zr	15.746	182.469	1.47E+06	0.4820	2.51E-03	1.66E-04

When analyzing the same sample with CU II. TARGETS please consider:
Absorption intercept: A0= 17187
   Absorption slope: A1= -2.820

RESIDUAL MATRIX characterised by:
 Absorption intercept: A0= 13692
   Absorption slope: A1= -2.820

 Residual matrix most probably of: INORGANIC ORIGIN and composed of Residual Matrix
containing not responding HEAVY ELEMENTS!
              CHECK THE ANALYSIS!