UNIVERSITY OF NAIROBI
INSTITUTE OF NUCLEAR SCIENCE & TECHNOLOGY

ASSESSMENT OF HEAVY METALS AND RADIOACTIVITY OF THE SOIL AROUND TITANIUM MINING IN KINONDO AREA, KWALE COUNTY.

Queenter Atieno Osoro

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A thesis submitted in partial fulfilment for the degree of Master of Science in Science at the Institute of Nuclear Science and Technology, University Nuclear of Nairobi.

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DECLARATION

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

Signature ……. Date……13/4/2021……

Queenter Atieno Osoro

S56/71532/2014

Supervisors' Approval

This thesis has been submitted for examination with our knowledge as university supervisors.

Professor Lydia W. Njenga
Department of Chemistry
University of Nairobi.

Signature.....
16-04-2021
Date.....

Professor M. J. Gatari
Institute of Nuclear Science & Technology
University of Nairobi, Kenya.

Signature……
Date……

DEDICATION

I dedicate this thesis to my beloved daughter Zuri Hera and my entire family for their unconditional support throughout this project.

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ABSTRACT

Mining is the process which involves extraction of minerals and geological materials from the earth. This activity may have a detrimental effect on the environment hence impact health of animals and human. The concentrations of the naturally occurring radioactive materials (NORM) in mineral concentrates, products increases during processing of minerals. The main aim of this study was to assess the concentration levels of heavy metal and radioactivity levels of soils in Kinondo area which is 2.86 kms from Ti mining plant in Kwale. A total number of eighty-four (84) samples were collected from twenty-eight sampling points. The points were randomly identified and three samples collected from each point consisting of top soil (0-20 cm), subsoil 1 (20-30 cm) and subsoil 2 (between 30-50 cm). The samples were collected from the three depths since concentration of the heavy metals vary vertically in different soil profiles. Energy Dispersive x-ray fluorescence (EDXRF) was used to analyze the soil samples for heavy metals. The radioactivity levels were determined using the Gamma ray spectrometry, using High Pure Germanium detector. The concentrations of levels of activity of the radionuclides U-238, K-40 and Th-232 in the soil samples were identified and measured. Gamma index, Radium equivalent, external hazard and internal hazard radiological risk parameters were therefore used to assess the radiation hazards for the heavy metal measurements, Ti, Fe, Mn, Zn and Pb were analyzed in the soil samples. The major elements were determined to be Fe (0.5–8.5 %), followed by Ti (0.3–1.5 %). All other elements had concentration values below 0.01%. Ti was determined in all soil samples at a concentration range of 0.3 to 1.5%. The high concentration of Ti may lead to competition with Fe for proteins hence leading to Ti phytotoxicity Mining may lead to elevated levels of Ti and Fe in the soil. The radioactivity levels recorded for the soil samples were used in assessing the radiological risks pose to residents. The levels of radiation were used to measure the radiation hazard that the people living in areas around the mining plant were exposed to. The results from this study will be used as reference to monitor the environmental impact of the titanium mining activities. According to the results of this study, mining activities of titanium do not lead to elevation of the heavy metals levels and radioactivity levels in Kinondo area

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LIST ABBREVIATIONS

AXIL	Analysis of X-rays using Iterative Least square method.
BSS	Basic Safety Standards
CRM	Certified Reference Materials
EDXRF	Energy Dispersive X-ray Analysis
ESIA	Environmental and Social Impact Assessment
GPS	Global Positioning System
HPGe	High purity germanium detectors
IAEA	International Atomic Energy Agency
ICRP	International Commission on Radiological Protection
LDL	Lower Detection Limits
MDA	Minimum Detectable Activity
NORM	Naturally Occurring Radionuclide Materials
UNSCEAR	UN Scientific Committee on Effects of Atomic Radiation

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Ionizing radiations are inevitable feature of life on earth. These radiations naturally exist in the environment and originates from terrestrial and cosmic sources. Since most of the natural exposure is from terrestrial sources, cosmic radiation is not the major source of gamma radiation and X-radiation exposure. The radionuclides that originate from terrestrial which is also referred to as primordial radionuclides, occur in different forms in the environment. Human beings are continuously exposed to radiation through natural radioactivity in the environment (Kannan, et al., 2002). U-238, Th-232 and K-40. These radioactive elements are classified as Naturally Occurring Radioactive Materials (NORM) (Ademola et al.,2014; Sanchez-Gonzarez et al., 2014). The NORM, which forms part of the earth's crust, are widely distributed in different geological ecosystems and formations like rocks, soil and groundwater.

According to WNA, (2018), the public receives an average of 2.4 mSv/yr. from background radiation. This depends on the altitude and geology where people live which ranges from 1 to 10 mSv/yr. The radiation levels may be elevated by human activities such as exploration of minerals and raw materials which may result to contamination of soil, water and hence adverse effects to the plants, animals and human (Bhattacharya et al. 2006). When radionuclides are discharged to the environment, they are transferred to plants by directly being deposited on their surfaces and also by uptake through their roots in the soil. This results to contamination of both ground water and surface water due to off-site mobility. As a result, there is heavy metal build up in the food chain due to ingestion of water and food which are contaminated since they are grown in the soil and affect the human health (Thakur, 2013). Therefore, there has been great concern, by both national and international communities, on the levels of contamination of soil by heavy metals.

To this end, several research studies have been undertaken in different regions to ascertain the levels of heavy metal concentration and their phytotoxic effects in order to prevent the environmental pollution through industrial and mining activities.

In order to assess the radiological impact of mining activities in given location, the baseline concentrations of the environmental matrices of naturally occurring radionuclides before the commencement of the mining activities is determined. An assessment on the radioactivity undertaken near the proposed sites for mining of Titanium in the coastal area of Kenya (Osoro, K.M 2007) reports that the average concentrations of activity levels for 232 Th, 226 Ra, and 40 K are 27.6± 9.1, 20.9 ± 7.6, and 69.5 ± 16.5 $Bqkg^{-1}$, respectively. Another study formulated by Maina, D. N (2008) to provide data of radioactivity from regions Nguluku and Maumba in Kwale district that are identified for the Titanium mining project reported that the activity concentrations of the three major primordial radionuclides Th-232 and U-238 as 72.0 and 50.2 Bq/kg in Maumba and 178 and 162 Bq/kg in Nguluku.

Globally, a study conducted to determine the contamination levels of soil samples collected from an area that surrounds the Dabaoshan Mine, which is in Guangdong Province, China revealed that the pollution of the environmental results from contamination from the following heavy metals; Cd, Zn, Cu, and Pb (Zhou et al., 2007). The study predicted an increase in the potential risk to the environment from the heavy metals Therefore, it is significant to monitor the radiation levels of an area where such anthropogenic activities, such as mining, take place in order to have an effective radiological impact assessment from both human and natural activities. In order to estimate the exposure of human to radionuclides, experimental data and monitoring techniques may be used to estimate the transfer through the environment (Doyi et al., 2015).

1.1.1 IMPACT OF TITANIUM MINING

In the recent past, mining activity as a source of metal has rapidly grown in Kenya. Various metals and industrial minerals are exploited from different areas and include; Ti, Ag, Zn, Cu and Au. Mining as an economic activity has a role in creating employment hence reducing poverty. Apart from the benefits of mining in the economic growth, mining activities are known to have many environmental and health impacts. Metal mining is considered is considered to be one of the largest source of emission of the heavy metals to the environment and is associated with both health and safety hazards (Zhao et al., 2012).

These negative effects include contamination of water, soil by chemicals which emerge from the mining process and majorly results from the operation methods used during mining (Dudka and Adriano, 1997). Strip mining method, for example, results to exposure of the communities living

near mining area to heavy metals from the mineral sands. Heavy metals including Pb, Zn, Cd, Hg, Ti, Cr are usually released in the environment in large quantities through various channels. These channels include wastewater from irrigation, disposal of solid waste products, application of sludge, runoff from industries and continuously accumulate in the environment and atmospheric deposition (Zhao et al., 2012).

According to study by Bian and Zender (2003), mineral dust is determined to have an impact on the climate change. Additionally, the dispersal of waste through air is reported as the main pathway of contamination of environment and the human health. Mining activities are also known to lead to land degradation and hence destruction to the flora and fauna (Bashir et al., 2012). Materials and chemicals that are toxic are channeled into streams and rivers which are used by the towns and villages in the area leading to contamination of t drinking water by heavy metals (Wang et al., 2010). Therefore, heavy metals are considered to be substantial pollutants of the environment (Jaishankar et al., 2014). According to the Environmental and social impact assessment carried out at the Base titanium mining in Kwale, various environmental effects such as loss of natural resources are outlined. (Base resources, 2015).

Base titanium, located in Kwale County, mines titanium sands that produces heavy metals of high grades which include rutile, ilmenite, and zircon. According to studies carried out by Kabata-Pendias A (2010), Ti and Zr can be phytotoxic to plants at high concentrations. The physical, socio-economic and natural environment of Kwale county has been greatly impacted by the development of the mineral sands. There is loss of habitat, fragmentation of the forest due to clearing of the area for access roads (Abuodha and Hayombe, 2006).

The vegetation in the environment is lost around the mining area and hence leading to soil erosion. Therefore, the area may be exposed to environment degradation resulting to poor supply of food to the animals and human beings. Moreover, the process involved in transportation of the dust may lead to increase in concentrations of Fe and Mn in the streams, rivers and agricultural land. Concentrations of the heavy metals may increase to toxic levels leading to contamination of the soil and water and hence adverse effects to organisms in the soil (Šalamún et al., 2015). When the microorganisms are reduced in the soil the fertility decreases due to the interference with the carbon and nitrogen biochemical cycles. Since the metals are assimilated in the soil and also deposited on the leaves, the plants are also contaminated by the heavy metals (Dudka and Adriano 1997; Bech et al., 1997).

1.1.2 MINING AND ENVIRONMENTAL IMPLICATIONS

The process of exploration through mining activities may result to material and physical damage of the environment and populations within the area. Since surface mining involve clearing of extensive areas of land and vegetation, it leads to great impact on both land and vegetation. This consequently affect the lives of the people who depend mainly on the land. (Dudka and Adriano, 1997). These effects occur at various stages of mining, processing and utilization. The effects majorly differ and is dependent on the grade of mining. It also varies with the environmental sensitivity of the site. This includes depletion of water, soil, air and natural vegetation and fauna, degradation of agricultural land, changes in landscape and volatility of rock and soil masses. Mining of rocks and mineral leads to irreversible impacts on soil quality. The damage of the top soil which is normally fertile changes the soil quality within in the areas surrounding the mine that is its properties such as chemical, microbiological and physical (Ghose, 2004) and reduction of nutrients content and organic matter (Akala and Lal, 2001; Panwar, 2001). These effects may result to be long term when they spread past the mining area boundaries (Nartey et al., 2012).

Study carried out by Miller (1999) points out that water resources are affected in terms of the quality and quantity. Mining results to adverse changes in water levels and flow, sediment flow and deposition hence resulting to decrease in the diversity of the aquatic species through deprivation of habitat of the aquatic flora and fauna (Naja et al., 2010). Mining is also reported to lead to modification of the quality of shallow groundwater and the surface water. Research by Ravichandran et al. (2009) reveals a decline in the water quality of Madukkarai limestone mine in terms of exceeded standard limits for parameters of water quality such as the dissolved solids.

Since mining activities involve blasting of rock beds, drilling of blast holes and transportation using heavy vehicles. This results to generation of hefty noise thus causing noise pollution in the area which may have health effects to the inhabitants. The vibrations may also cause undesirable effects which includes geological displacement of the area, decrease of water table, weakening of rock formation which may lead to letdowns of the slopes hence an increase in the likelihood of landslides (Sikka et al., 1984).

In relation to air quality, mining activities such as drilling, quarrying and transportation leads to generation of dust hence leading to pollution of air which is majorly suspended particulate matter (SPM) (Ghose and Majee, 2004). Exposure to the air pollutants have adverse health effects to

human when exposed for long term (Sunyer, 2001). Elevation of dust concentration during quarrying also affects the physiology of plants (Rajwar ,1983)

The health effects and exposures that results from mining can be classified into two categories: immediate impacts which include accidents; and impacts that are accumulative and progressive like acute and chronic effects as either chronic or acute. Moreover, the chemicals and explosives used in mining areas pose health and safety hazards to the environment through exposure to pollutants such as fumes, chemicals and dust. A research carried out by Mishra et al. (2004) reports health related problems as a result of mining. Mines contain a mixture of minerals, the primary substance mined may not be the main health hazard for mine workers. For instance, it is not easy to separate mineral impacts of individual minerals of lead-zinc-copper mine which forms a compound set of occupational exposures (UN,1993). Therefore, health and safety hazards do not, in some cases, originate from the product minerals itself but from materials which are used in the extraction and processing stages that are normally hazardous (Stephens and Ahern, 2001).

1.2 PROBLEM STATEMENT.

Environmental and health effects of mining is becoming a matter of concern to developing countries. In the recent past, there has been a rise in awareness of these effects to the people. According to studies, the main pathways of the heavy metals are reported to be soil, indoor air inhalation and consumption of vegetables produced from the contaminated soil. The amount of uptake of metals by the plants is increased when its levels are elevated in soils. This leads to exposure of human beings to harmful concentration, through the food chain, which results to health effects to the people who live in these areas (Guo et al., 2014).

As much as environmental impact assessment study has been undertaken and the Titanium mining project in Kwale is in progress, there is need to assess the contamination of soil This is to ensure that the environment is safe and hence crops grown are free of heavy metals which may be toxic in high amounts. According to UNSCEAR (1993), there is limited information and knowledge on the elevated concentrations of heavy metals in the soil that surrounds the area of mining activities and effects of mining on the level of radiation exposure to public resulting from mining activities. This is a reflection of Kenya's status as there is very limited credible data which is published on how mineral exploration in Kenya affect the heavy metals content in soil.

1.3 RESEARCH OBJECTIVES

1.3.1 MAIN OBJECTIVE

The main objective of this study was to determine the radioactivity and heavy metals levels in the soils that surrounds the Titanium mining located in Kinondo area in Kwale County.

1.3.2 SPECIFIC OBJECTIVES

i. To identify the heavy metals in the soil samples collected from Kinondo area.
ii. To determine the levels of concentration of the heavy metals and their distribution in the various soil profiles of the samples collected from Kinondo area.
iii. To determine the radioactivity levels of Th-232, K-40 and U-238 in soil samples and the radiological risk levels posed on the inhabitants of the Kinondo Area.

1.4 SIGNIFICANCE AND JUSTIFICATION

Environmental and strategic impact assessment for titanium mining project, outlines various possible negative effects to the environment that may result from the mining activities This include contamination of the water bodies (surface and ground water) as a result of heavy metals and general deprivation of fertile lands for agriculture (Abuodha et al., 2006). Pollution of soil by high amounts of heavy metals affects the ecosystem and in particular its productivity. This poses a high risk to the animal and health of the people living around the mining area. Exposure to elevated levels of heavy metals may lead to damage of the kidneys, brain and even the developing fetuses (Martin and Griswold, 2009).

Therefore, a good knowledge and understanding of the levels of heavy metals, radioactivity and the spatial variation in the soil is very relevant and essential. This information can be used for environmental management. The knowledge can be used to monitor and evaluate the potential of exposure of the people who reside in the area to elevated levels of radiation. Furthermore, the findings and recommendations from this study will give opportunities for further research on the environmental effect of mining to the people living around the Titanium mining site in Kwale and any toxic effects that it might pose to soil, water and the crops grown on the soil.

Additionally, the data from the radiometric analysis conducted to ascertain and measure the concentration of radionuclides activity in the subsoil will be used by the regulatory body to estimate any radiological hazard and analyze radiological protection and safety measures needed. The study will be used to create awareness to miners, the local population on radiation protection. It will also enable projections on the possible levels of radioactivity and heavy metal concentrations enhancement due to the mining activities hence provide basis for protection of the environment and remediation measures.

Since Kenya is a newly industrialized country, it faces lots of challenges in developing its economy and improving the lives of its citizen without compromising the natural environment. The development activities undertaken should therefore conform, uphold the environmental sustainability and conserve the biodiversity. The vision 2030 gives provision for the country's environmental change through a long-term plan for development. This study therefore contributes to the realization of the country's pillar of health which is part of the big four agenda. The government targets to achieve 100 percent quality health and affordable health care for all citizens. Therefore, the study contributes in protection of the people and maintenance of natural environment to achieve quality health for all the citizens.

1.5 SCOPE

This study was carried out in Kinondo area which surrounds the Base Titanium, Kwale county. The study focused on identifying heavy metals and assess their concentrations in soil samples collected from the area of study. The concentrations of the heavy metals determined in this study include: Fe, Ti, Mn, Zr, Zn and Pb. The radioactivity levels of the following; K-40, Th-231, U-235 were also determined. The study determined the extent of radio-ecological hazards in the area by use of radiological risk parameters; Radium equivalent, external hazard, Gamma index and internal hazard.

CHAPTER TWO

LITERATURE REVIEW

2.1 MINING

Metal mining is an important economic activity that has the potential to contribute to the growth of areas that has the resource. According to Aryee, B (2001), this activity leads to economic growth of the local communities. Consequently, the local inhabitants and the population residing around the towns are directly affected by mining operations. Generally, mineral development is considered very significant for the economic and social growth of countries. Wang, X., (2010) reports that employment can be used to gauge the impact of mining on economy and even on income generation of any country. In addition, it is reported that worldwide, small-scale mining offers income to close to 13 million workers in countries such as Venezuela, Ghana, Tanzania, Brazil, Madagascar and Indonesia. According to G. Walser (2009), mining increases tax incomes for states, improves services and creates employment. It increases demand for goods and services leading to improved economy. For instance, mining industry has filled gaps left by the state in remote areas by promoting sustainable socio-economic development. Industrialized countries like Sweden, Canada, Australia and United States among others highly depend on the mining industry for the development of their economic. Mineral exploitation and extraction generates foreign exchange and income through exports. Metal mining companies create employment, and the government collect tax incomes from mineral production which hence used to fund infrastructure development such as health care, education, electricity supply and roads (ICMM, 2012).

Local communities benefit from mining companies as they provide infrastructure development to areas where they operate. Furthermore, through job creation and economic growth, the companies increase investments at the local, national and regional levels (Aryee, B, 2001)). Metals have varied characteristics hence serve many purposes. They are able to combine in almost any proportion, giving a wide range of alloys which normally have the characteristics of a metal and are hence regarded as metals as well. Alloys have the ability to be shaped through machining, casting and plastic forming. Through heat treatment, alloys can be varied in order to exhibit mechanical properties considered advantageous such as: durability, elasticity and strength. Therefore, metals are important and can be applied in infrastructure and services in the society.

The application areas include energy supply, consumer goods and services, food, water supply, construction, shelter, manufacturing, sewage treatment, health and transport (ICMM, 2012).

Due to the increase of technological needs and human population, demand for metals has also increased. It has been demonstrated by studies that the mining sector is projected to grow and provide the needed metals. Many countries are therefore involved in metal mining as a way to meet their growing demand (Gajigo, 2012). Countries such as Russia, South Africa, Ukraine, Europe, South America, China, New Zealand and Australia are involved in mining of metals such as lead, zinc, silver, iron, titanium, manganese, beryllium and copper among other metals (ICMM, 2012). In Australia, silver metal is mined and produced as a by-product of lead, zinc and copper. Due to its scarcity, malleability and attractive appearance of silver, it is used in jewelry and households' silverware. Australia contributes to about 15 – 20% of global production of zinc and lead and is the dominant producer globally (Weber-Fahr, 2002). Apart from that, lead metal is also mined in countries such as Sweden, United States, Peru, Mexico, South Africa, and Russia among others. Lead extraction is simple due to its widespread occurrence and is normally mined mainly in form of galena which is largely used in batteries for vehicles. Snodgrass (1986) states in the review paper "Lead in South Africa" that lead is used in storage batteries, gasoline additives, cable sheathing, paint pigments and protection against radiation in the nuclear field. In china, due to the increase of electric bikes, there is growing demand for lead to make batteries for e-bikes. Reports show that China is among the world's leading producer of lead as it produced over 1.58 Mt of refined lead in 2003. Mao down (2006) reports that environmental pollution caused by lead is the most challenge with the electric bikes since it is used in manufacturing of the battery.

2.2 ECONOMIC IMPACT OF MINING

In some countries, the mining sector contributes significantly to the national economies. For instance, in 1993, the mining industry in Peru contributed 11% to the country's GDP. In Ghana, Akabzaa and Danimani (2000) reported that mining is the main source of foreign exchange, employment, government revenue, provided both capital and social infrastructure and development of the community and public who live in the areas.

Furthermore, mining companies normally invest in the remote areas by developing infrastructures. As much as studies demonstrate that mining is considered among the risky occupations in the

world with short and long-term impacts such as respiratory conditions and even cancers it has positive effects on the economic development (Stephens and Ahern, 2001).

Mining highly contributes to the development since it is an essential source of wealth. Therefore, the mining industry is the main contributor in the industrial revolution and the infrastructure. Countries known traditionally for mining have dominated the mining division and become the leaders in metal extraction and exploration technology and methods. These countries include; Australia, South Africa, Chile, USA and Canada (Roman, P.A., 2000).

According to evaluation of the contributions of mining to the economy of countries, in Peru for instance, the mining industry contributes about 50% annual export earnings of the county. In 1993 for example, mining contributed to the Peruvian economy ; $240million paid in taxes, $400million which was spent on local purchases and $280 million was spent on the imported goods which translated to over 11% of GDP. Therefore, it is evident that mining has a great implication in development and growth of the economy of countries.

2.3 HEAVY METALS

Heavy metals naturally exist in the environment. Indiscriminate use of heavy metals by human such as in industries, agriculture or mining changes their atmospheric biogeochemical hence causing pollution (Wang et al., 2010). This leads to excessive release of heavy metals such as mercury, chromium, cadmium, lead, copper, iron, which are the environmental pollutants, mainly in areas which have high anthropogenic activities.

The heavy metals are toxic if not absorbed in the body and stored in the soft tissues. Human are exposed to the heavy metals through various routes such as inhalation as dust, vaporization, and ingestion which occur via drink and food.

2.3.1 HEAVY METALS AND MINING

Heavy metals in the soil results for sources like agricultural activities, mining activities and industrialization. Mining operations involves processes such as grinding, concentration of ores, disposal of tailings which leads to pollution of soil by elevating the concentrations of heavy metals

(Adriano, 1986). These adverse effects on the soil and water streams depend on the geochemical characterization of the tailings and the type of mining activities involved. Elevated concentration of heavy metal levels in soil are majorly around the metalliferous mines because of the discharge and dispersion of waste to the agricultural soils, water sources and food crops. The residues, which are usually dispersed, are included in the particulate materials and water after there are disposed (Lottermoser 2007). This eventually find its way to the food chain hence endangering the human health.

Many studies have been undertaken globally on the contamination of the soil, plants and waters by the heavy metals. A regional study carried out by Aliyu et al., (2015) to determine the impacts of mining to the environment considered the radio ecological effects of zinc, copper and barite mining in Nasarawa state, Nigeria, that shares boarders and geological features with plateau states suggested that there is likelihood of certain terrestrial flora and fauna being affected significantly by solid minerals from the mining activities. This is due to the fact that the Plateau states is drained by various fast-flowing watercourses with the source being the Jos Plateau. It has been established that there exists a connection between concentrations of heavy metals and radionuclides. According to an assessment carried out by Maina (2008) on the levels heavy metal concentration in soils that surround the titanium mining in Kwale, coastal Kenya, Fe and Ti were identified as the major elemental constituents, at 1.2% and 1.5% respectively. The assessment revealed that there was a substantial correlation between concentration levels of Ti, Nb, Zr and Fe, with the levels of radioactivity levels of radionuclides in the 232Th and 238U series. Furthermore, a study conducted to assess the impact of tungsten mining on agricultural soils in Rwanda reports that the major constituents of soil are Mn, Fe, Zr and Ti. Traces of toxic metals, Pb, As and W, due to tungsten mining were found in traces with Arsenic levels being determined at levels above the interventional value (50 µg g-1).

According to assessment carried out by Odumo et al. (2009) in Migori, Southwestern Nyanza, Kenya to determine the predominant elements and concentration in the gold mining, the concentrations in soil were determined in the range of: Ti (711 – 13,000 µg g-1); Co (83 - 1,010 µg g-1); Zn (30 – 63,210 µg g-1); Au (14 – 73 µg g-1); Cu (40 -118,533 µg g-1) and Hg (16 – 150 µg g-1). Pb and As were determined in high quantities. The predominant elements in water samples were Cu (29 - 14,976 µg l-1 and Zn (34 - 683 µg l-1). As, Pb and Zn were also detected in higher quantities, with average levels of 3274 µg g-1, 1473 µg g-1 and 587 µg g-1, respectively.

Patel and Mangala (1991) carried out an analysis of carbonatite rock samples collected from Mrima Hill, Kenya, using EDXRF. According to this study, there was reported a significant concentration of rare earth elements such as Ce, Ba and Nb. Concentration ranges of Fe, Ti and Mn were determined at (5 – 30%), (0.3 – 17%) and (1.1 – 9%) respectively. The study identified 232Th, with a mean concentration of 770 μg $g^{-1,}$ as the major source of high environmental radiation in the area.

2.4 EFFECTS OF HEAVY METALS

Some heavy metals are important to living things as trace elements, which are needed in small quantities by the organism for growth and development. The human body requires different minerals in varied amounts. The requirements vary and depend on various factors like sex, state of health, physiological state and age. Trace elements; Fe, Zn, Cu, Mg, Ni, Co, Cr have significant roles in human bodies. On the other hand, Zinc performs a vast role in division of cell and growth since it is essential for synthesis of protein and DNA (Nielsen, 1990).

Although trace elements are necessary for biological activities, they are toxic to the body when in excessive levels. Elevated levels may lead to reduced energy levels and damage the normal functioning of important body organs such as lungs, brain, liver and kidney. The accompanying anions of the titanium are the major source of existing hazards related to titanium. Titanium halogen if ingested, may lead to sickness and vomiting, corrosion of the eye or skin when it contacts the mucus membrane. Apart from this, titanium can cause health effects due to breathing of the particles of the titanium dioxide, which are small and result to lung disease. According to literature sources these metals get to the environment through anthropogenic and natural sources which include activities of industry and mining (Ravichandran S, 2009b).

Heavy metals get into the body through ingestion of food, air and water. They then bio-accumulate with time. The chain for contamination of the metals is in recurrent order as they move from industries to the atmosphere, soil, water to the food then enter the human body (Krishna AK, 2016). There are several routes through which these heavy metals enter the human body. For instance, lead, manganese, arsenic and cadmium are able to get to the body system through the gastrointestinal route which is by eating of food or drinking of water. Heavy metals are usually disseminated through the blood to tissues in the body (Florea A-M, Busselberg D., 2006).

Heavy metals become toxic by generating free radicals causing oxidative stress, impairment of the biological molecules which include lipids and enzyme. This may also lead to damage of the DNA which results to neurotoxicity and carcinogenesis. The heavy metals are non- biodegradable and persist in \ environment, therefore increased concentrations to harmful levels result to negative effects to animals and plants. (Yahaya et al., 2010)

Lead is mostly redistributed as phosphate salts to the teeth, hair and bone from kidney and liver by the red blood cells. When humans are exposed to elevated levels of lead, it can result to headache, sleeplessness, hallucinations, allergies, psychosis, damage to kidney and brain. Manganese is distributed from the blood system to the lungs and then its vapor diffuses to the membrane of the lungs to the Central nervous system (CNS). The lipid soluble organic salts of manganese are circulated in the intestines and eliminated as fecal waste. On the other hand, soluble inorganic manganese salts are distributed in kidney and plasma and later released as renal waste. Arsenic is accumulated in the lung, heart, muscle, liver, skin and nails through the blood. Exposure to Arsenic may result toxicity which can be acute or chronic such as acute arsenic poisoning hence destruction of gastrointestinal tissue, blood vessels may affect the heart and brain. Arsenicosis an example of chronic arsenic toxicity typically manifests on skin such as pigmentation and keratosis (Martin S, Griswold W., 2009).

Iron produce free radicals when it does not bind to the protein hence affecting its concentration in biological fluids and cells. The free iron radical circulates in the body system leading to corrosive effects on the gastrointestinal tract and also penetrate to the brain, liver and heart. The free iron may lead to disruption of oxidative phosphorylation; this leads to conversion of the ferrous iron to ferric iron which results to release of hydrogen ions that increases metabolic acidity. Additionally, the free iron causes peroxidation of lipid hence causing severe damage to cellular organelles. (Albertsen, 2006). The radicals may lead to the oxidation of DNA and result to damage of the cells, transformation of the malignant tissues leading to diseases (Grazuleviciene et al., 2009). Figure 1 below shows how the heavy metals enter the human body.

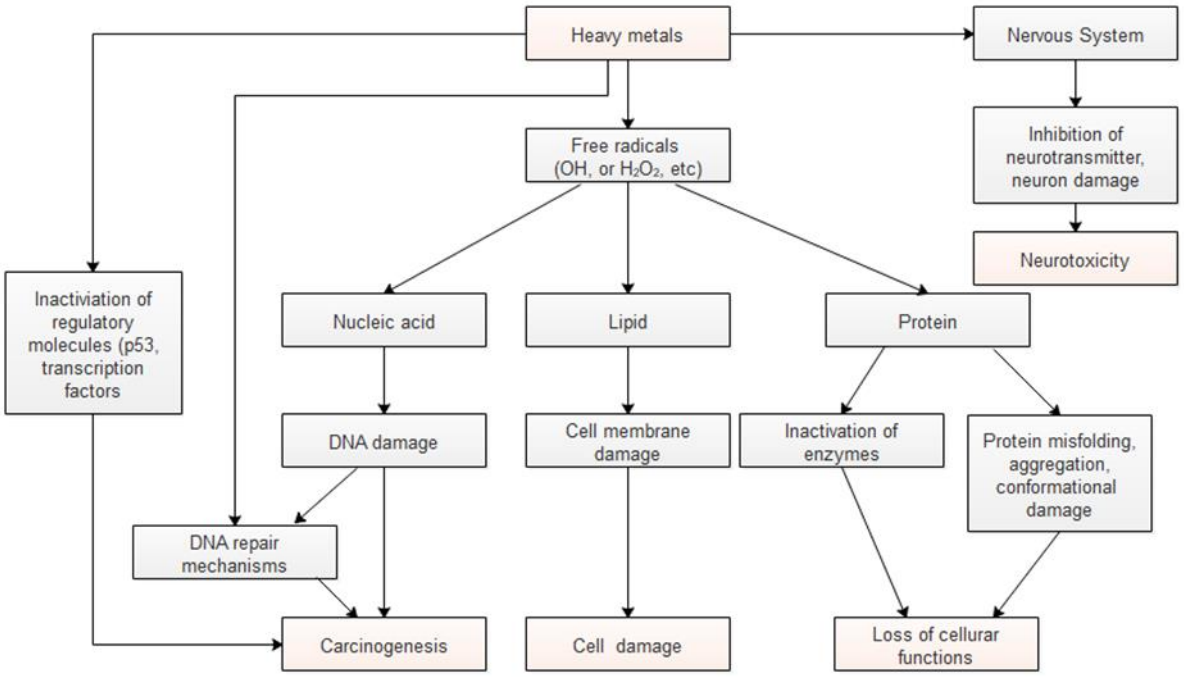

Figure 1: Pathway of heavy metals sources and exposure to humans (IAEA, 2009).

2.5 IMPACTS OF HEAVY METAL CONTAMINATION IN SOIL

In recent years, there have been reports that contamination of soil in both agricultural soils and urban soil is increasing rapidly due to development of various human activities such as mining. Heavy metals when excessively deposited in the soil through human activities may be toxic. This may therefore lead to reduced quality of soil. The rates of generation of heavy metals through human activities are rapid compared to natural sources. The random transfer to environmental locations increases the potential of toxicity. The contamination affects the enzymatic and microbial activities of the soil by inhibiting the microbial activity. Levels of contamination of soil can be determined through the microbial biomass whereby the lower the biomass the higher the contamination level. According to study by Bolan and Duraisamy (2003), the microbial growth may be stimulated by low concentrations leading to an increase in microbial biomass. On the other hand, high concentrations cause a significant decrease in microbial biomass of the soil. Since soil is an active system, heavy metals interact with organic constituents and minerals in the soil and this is dependent on both the biological and physio-chemical interactions the environmental properties of the soil (Kabata–Pendias, 2007).

Additionally, heavy metals are reported to affect the activities of enzymes in the soil. Studies by Chander et al. (1995) reveals that activities of enzymes are reduced significantly by about 10 to 50 times as the heavy metals increase in concentrations. This increased concentration may further exceed levels which can be tolerated by the plants grown on the soil hence leading to poisoning and finally death of the plant. Contamination that results from anthropogenic sources are usually mobile and therefore bioavailable compared to geogenic ones. Major anthropogenic sources are normally from disposal of waste in landfills that are not properly protected and mining tailings.

2.6 TITANIUM

Titanium is a chemical element which exist in the earth's crust therefore known for many years. It is a transition element that belongs to Group 4, with atomic number of 22 and atomic weight of 47.88. The element exists in mineral sources as rutile and ilmenite. According to research by Kabata-Pendias, (2007), the worldwide ranges of Ti in surface soils is recorded to be 0.02 to 2.4% and the mean being 0.33% and about 30 mg L^{-1} Ti in soil solutions. The average worldwide ranges in river water is recorded to range from 0.49 μg L^{-1} (. In the US, the drinking waters is recorded to contain approximately 0.5 to 15 μg L^{-1} (Kabata-Pendias and Pendias, 2011). The concentrations in the air is reported to range between 10 to 100μgm^{-3} with a probability of increasing in industrial regions to ≤1,000 μg m^{-3}. Globally, Ti is recorded to exist with a median value of 7 μg m^{-3} in regions that are far from pollution from anthropogenic releases and about 85 μg m^{-3} in zones prone to pollution (Kabata-Pendias, 2007).

2.7 APPLICATIONS OF TITANIUM COMPOUNDS

Titanium and its compounds have varied applications in the world. For instance, Titanium dioxide nanoparticles (TiO_2NPs) which is estimated to be produced worldwide at 88,000 t per year are used in the plastic, cosmetic, painting and food industries. Some of the properties that makes Ti important and attractive include; strong, resistant to corrosion, low thermal conductivity and its melting point is 1668 °C. Titanium is hardly used in its pure state but very important as an alloying agent with metals such as iron, molybdenum and aluminum. Due to the low density and the capability of the alloys to tolerate high temperatures, they are mainly useful in aircraft, rocketry and spacecraft industries (Du et al., 2012).

Apart from its application in various fields of industries as a metal, Titanium (Ti) element is of benefit to plants. At low concentration, Ti is known to stimulate activities of some enzymes by enhancing chlorophyll which is essential for photosynthesis in the plant. Additionally, it promotes the uptake of nutrient and strengthens the stress tolerance. This results to an increased performance, improved yield and hence good crop quality. The benefits of Ti is high in crops when there is decrease in Fe in the system. In this case, Ti enhance the uptake and utilization of Fe by inducing genes that are related to acquisition of Fe. Ti element can also be used for production of crop (Li et al., 2011). However, high concentration of Ti may lead to competition with Fe for proteins hence leading to Ti phytotoxicity (Wallace et al., 1977). TiO2NPs as a compound of Ti is also used for protection of plants since it plays a photocatalytic role. According to a research by Sun et al. (2014) in Europe, the concentrations of TiO2NPs is reported to be about 0.13 μg kg−1 yr^{-1} but higher values of about 1,200 μg kg^{-1} in areas polluted with sewage.

2.8 RADIOACTIVITY

Radioactivity naturally exist in the environment and characterized by the spontaneous change of the atomic nuclei which is unstable. The change leads to energy release which is normally as ionizing α-, β- and γ radiation. This transition which leads to a stable nuclide can occur directly or in many stages of unstable intermediate stages. The earth consists of primordial radioisotopes that exists in significant amount from the olden days (Gregory, 2013). Most radioactive elements present on earth have since decayed since they have short half-life. The artificial radioactivity is from the human activities such as fission products of heavy nuclei resulting from atomic bombs, nuclear products and particle accelerators.

Depending on the present natural radioactive elements in an area, humans are usually exposed to varied natural radioactivity levels. The radioactivity levels can therefore be used to determine the dose rates of the public and contaminations. Radioactivity assessment can therefore be used in predicting any environmental changes due to industrial activities, nuclear accidents or human activities that lead to exposure. Some of the natural elements and their decay products which contribute largely to the radiation dose that humans receive from environment include; Potassium-40, uranium-238, and thorium-232.These radionuclides occur in rocks or soil and even water bodies hence easily accrued in the food chain and transferred to the human system (Achola et al., 2012).. Radionuclide 238U and its decay products, occur in monazite sands, soils and rocks and

are the major source of natural background radiation. Consequently, there has been great interest to carry out research since the exposure to varied natural radioactivity levels (ICRP, 2007). To this end, various organizations in the world have enhanced the radiation protection standards and guidelines based on the studies and research carried out on natural and occupational exposure to radiation.

2.8.1 EFFECTS OF IONIZING RADIATION ON HEALTH

There is a great concern on the effects of heavy metals to the human health. Therefore, it is very important to understand the various factors such as concentration levels that make them harmful to human. Additionally, there is need to identify the sources and ways through which they are deposited in the environment. Metals are released into the environment through various ways. This include natural and anthropogenic sources which are majorly mining and industrial activities (Martin and Griswold, 2009). These particular metals for instance U-238, Th-232 and K-40 amongst others are acquired by plants from the soils through the process of absorption.

Human beings and animals consume plants as food which results to radiation exposure through the process of ingestion. In a study by Maina (2008) on given foodstuffs and products consumed in Nairobi, K-40 was identified to majorly contribute to annual ingestion dose due to food consumed which range from 0.02 mSv y^{-1} for tea leaves to 0.16 $mSvy^{-1}$ for maize meal .On average ,the infant milk also contribute to 0.05 $mSvy^{-1}$.The damage to tissue and organs by radiation depends on various factors which range from absorbed dose, radiation type and sensitivity of the organs and tissues .For better understanding of the effects of radiation, there is extensive research being carried out to relate the exposure to radiation and effects to health in the long and short term. Radiation effects are categorized as either deterministic; which are health effects that are as a result of extensive cell death or malfunctioning, and stochastic effects; which result from modification of genetic material of some cells or even unit cell but still compatible and cells still survive examples being cancers, heritable disease and leukemia (UNSCEAR, 2012).

According to ICRP (2007), health effects classified as deterministic occur mainly in the doses that range above 100 mGy in that the tissues show functional impairment which are clinically relevant. These effects increase in severity with increase in the dose rate, and may result to death. In a study based on mortality of atomic bomb survivors, the doses are also associated with effects such as stroke, respiratory diseases, heart disease. The effects can also include radiation sickness like skin

burns, diminished organ functioning, hair loss, nausea, and general weakness (EPA, 2012). On the other hand, stochastic effects which include hereditary disorders, cancers are linked to long term exposure to radiation of low level (<100 mSv). The probability of these effects to occur increases with increase in the equivalent dose (ICRP, 2007) The reference levels and dose constraints are as per the IAEA is as shown in the Table 2.

Table 0 : Framework for source related dose constraints and reference levels (IAEA, 2000)

Range for a dose constraint	Category of exposure and type of exposure situation
20 to 100 mSv	Reference level for public exposure in an emergency exposure situation.
1 to 20 mSv per year	Dose constraint for occupational exposure in a planned exposure situation, medical exposure of carriers, for individuals undergoing non-medical human imaging. Workers in an existing exposure situation Public exposure due to radon in dwellings, areas with residual radioactive material.
Not greater than 1 mSv per year	Public exposure in planned exposure situations, specific existing exposure situations, e.g. exposure due to radionuclides in food, drinking water or construction materials.

2.9 MINING AND NATURALLY OCCURING RADIONUCLIDE MATERIALS

There is a great concern about the radiation exposures which results from the extraction and processing of minerals. According to UNSCEAR (1993), there is a rise in the annual worldwide exposure due the extraction and processing of earth minerals, this is estimated to be about 20 mSv y^{-1}. Due to this increase, radiological studies have been carried out globally within the mining regions and areas suspected to be of high background radiation (Ademola, 2014; Sivakumara et al., 2014; Darko et al., 2005; Mustapha et. al., 2007). Such research led to an increase of the awareness and better understanding on the radiological hazards posed by the activities.

In natural environment, the concentration levels of naturally occurring radionuclide materials (NORMs) are very low, and their associated health risks usually considered negligible. Mining activities and industrial processes such as extraction can lead to exposure to the elevated concentrations of NORMS. The liberated, exposed or concentrated NORMs due to anthropogenic activities are referred as technologically enhance naturally occurring radioactive materials (TENORM). The physical, chemical and radiological properties of the TENORMs are altered by being disturbed, processed, thus enhancing their potential for environmental and/or human exposure.

According to (UNSCEAR, 2008) natural background contributes to approximately 80% of the ionizing radiation exposure which is recorded to be 2.4 mSv/y. The radiation results from cosmogenic radionuclides which occur in the atmosphere, cosmic rays and NORM. In order to control exposure of human to the natural sources of ionizing radiation, ICRP recommends dose limits which are implemented by the national regulatory authorities (ICRP, 2017). The levels of NORM in the terrestrial environment depends on many factors like the soil where they originate from, how the rocks are distributed and how they are concentrated and immobilized. Due to geochemical processes such as erosion, that leads to disequilibrium in the U decay series and redistribution and enhancement of NORM, the composition of NORM in the soil doesn't tally with the parent rock (Navas et al., 2011).

Table 1: Average radiation dose from natural sources (UNSCEAR, 2000)

Source effective dose (mSv)	Worldwide average annual (mSv)	Typical range (mSv)
External exposure Cosmic rays Terrestrial gamma rays	 0.4 0.5	 0.3-1.0 0.3-0.6
Internal exposure Inhalation Ingestion	 1.2 0.3	 0.2-1.0 0.2-0.8
Total	2.4	1-10

The average annual effective dose in Kenya is reported to be above the global average (Mustapha et al 1997). According to a study, the average annual dose results from different sources which are contributed to by 0.1 -2.1mSv/y from gamma radiation of terrestrial source; 0.5 to 6.1mSv/y from inhalation of Radon (^{222}Rn) and 0.22-0.75mSv/y and per capita of 0.5 mSv/y from cosmic radiation.

A radioactivity and elemental analysis carried out by Achola et al. (2012) on carbonite rocks from western part of Kenya revealed that the annual external affective dose rates in that area were 5.7mSvy^{-1} compared to the global average, which is 0.46 mSvy^{-1} it is about twelve times the global average. The study showed the ranges of radioactivity levels to be between 14-6560 Bq kg^{-1} with an average of 1396 Bq kg^{-1} for 232Th ;56 to 1454 Bq kg^{-1}with an average of 509 Bq kg^{-1} for ^{40}K; from 2 to 499 Bq kg^{-1}with an average of 179 Bq kg^{-1} for ^{238}U equivalent. The absorbed dose rates outdoors at 1m above the ground was further reported to range between 700-6000nGy h^{-1}, and an overall mean value of 2325nGyh^{-1}. This area was therefore described as being of a high background radiation and the findings agreed with Patel (1991), whose study on carbonatite rocks were linked with availability of natural radionuclides and high background radiation.

A comparative study conducted between underground and surface miners in Ashanti gold mine of Ghana reveals more radiation exposure to the underground miners. According to the study, surface miners was reported to be 0.11 mSv while that of underground miners was recorded as average effective annual dose of 0.56 mSv y^{-1}. The higher dose rate in underground mine was attributed to radon gas that is a product of ^{238}U decay series and normally trapped within the soil and rocks. This gas could therefore easily be found in mines through water and air. The report was also supported through a study undertaken by Lipsztein et al. (2001), which reported that radon gas is the main source of occupational exposure to the coal miners in Brazil. The impact of mining is majorly due to the constant release of waste from mining into the environment which leads to increased levels of radionuclides in air, water and soil, and hence negatively affecting plants and animals (Ademola, 2008).

A research was conducted by Arogunjo et al. (2009) comparing the specific activities of thorium and uranium in soil samples collected from the Jos-Plateau tin mines and soil samples from other countries. This research reveals that the specific activity levels of U and Th in the assessed soils of the Jos Plateau tin mines are higher compared to the averages for the high background natural radiation areas (HBNRAs). According to analysis carried out on the population in the HBNRAs,

radiation has effects on plants, humans and animals (Forster et al., 2002; Aliyu and Ramli, 2015). In global context, assessments have been conducted on environmental and radio ecological impacts of solid mineral mining which reveals the effects of radiation on the environment. Déjeant et al. (2014) carried out an assessment of the levels of radioactivity in Cominak and Somaïr uranium mines in Niger Republic, Salbu et al. (2013) also carried out a study in Kazakhstan and Lind et al. (2013) with the objective to analyze the impacts of uranium mining. According to the studies on the uranium mining areas, the dose received by population which is about 90 % emanates from ^{226}Ra.

Another assessment conducted in Portugal on the effects of mining on the radioactive ores in Viseu and Guarda regions revealed that there are adverse impacts of mining on the population. These effects are reported to be promoted by the use of water for irrigation of vegetables that they grow in some regions in Portugal. The study reports that there are substantial levels of leaked activities in the Iberian rivers such as River Zezere and Mondego which had their spring from a region in Portugal where there were uranium mining and milling. The rivers drain through both active and abandoned uranium mines, making the water radioactive, (Carvalho et al. 2014)

According to review done by researchers on the radiological consequence of tin mining on mine workers in Thailand, Indonesia and Malaysia, mine workers receive a range of annual effective dose estimated at 1–120 mSv which is attributed to external radiation exposure (Ademola, 2008). This estimate was made with consideration of the different pathways of radiological exposure for the mine workers. According to a study by Saat et al. (2014), mining and processing of Tin in Perak, Malaysia, shows that the mining leads to buildup of NORM in aquatic life such as the fish species. In the fish samples studied, activities of NORM were reported to be $^{228}Ra < ^{226}Ra < ^{40}K$. This consistent arrangement is attributed to the concentration of ^{238}U, the parent of ^{226}Ra, which is higher compared to that of ^{232}Th, the parent of ^{228}Ra found in the fish.

A report on research carried out by Aliyu et al. (2015) reveal that extractions and processing of earth minerals (mining and smelting) results to radiation exposure which are relatively low when compared to the overall exposures from other sources. Human activities like mining of coal, result to redistribution and transportation of radioactivity of coal to the surface hence leading to enhanced radioactivity levels which is above background in the environment (Charro and Pena, 2013).

According to the findings, the average annual effective dose globally from the mining activities is estimated to be 20μSv (UN, 1993). An assessment carried out on the Australian mineral mining

plant reveals that members of the public who lived and worked on a property near the mining site were projected to have received a dose which was slightly greater than 1mSv and was attributed to the external irradiation which was from the mining plant.

It was also reported that members of the public who lived at about 1.5-2km away from the mining plant received dose which was attributed to the inhalation of dust from the plant with the highest dose being estimated to be about 2.5mSv /a for five persons (UN, 1993).

2.10 TECHNICAL ASPECTS OF ANALYTICAL METHODS

The following analytical methods were used for elemental quantification and radiological analyses of the samples that were collected for research.

2.10.1 HIGH PURITY GERMANIUM DETECTOR GAMMA RAY INSTRUMENTATION AND ANALYSES

Gamma rays are high - energy photons which are emitted from some stable and excited nuclei. The three major ways in which these photons interact with matter include; Compton scattering, photoelectric effect and pair production. The three processes involve transfer of the photon energy to electron partially or completely. This principle of detection of radiation draws on the detecting the ionization which results from the excitations generated by the movement of the high energy in a given material (Knoll, 2010). Pair production interactions are dominant at high energy (> 5 MeV), photoelectric effects are at low energy, and Compton scattering at the mid-energy range. The observed response of the high purity germanium detector (HPGe), result from all the three interactions, though the main contribution to the full-energy peak is due to all the three interactions.

High resolution gamma ray spectrometry with a HPGe is a form of non-destructive technique which is used to determine the radioactive concentration of the artificial and natural radionuclides that are in environment. The ionizing radiation enters the germanium crystal which is the sensitive volume of the detector. It then interacts with the semiconductor material. Due to the interaction of photons in a HPGe detector within its depletion region, charge carriers is created (also known as electron- hole pairs). Charge carriers are then swept by the effect of the electric field. The total number of the electron-hole pairs generated is comparative to radiation energy to the

semiconductor. Under the influence of an electric field, the electrons and holes travel to the electrodes.

The total number of the collected electrons is converted by a charge sensitive preamplifier to an electric pulse (whose size is proportional to the photon's energy) and is transferred to the detector.. The gamma spectrometer used in this study is available at Institute of Nuclear Science and Technology(INST), University of Nairobi. It consists of a HPGe detector that is cylindrical in shape with a coaxial geometry (5 .74 X 5.79 cm) and 30% relative efficiency. The coaxial geometry inhibits any leakage current that is likely to be produced by the detector at the front surface. Additionally, it provides a planar front surface which has a thin electrical contact that enables the detection of the weakly penetrating low energy radiation (Knoll, 2000). In addition, the detector an active volume of 144 cm^3 and original measured resolution of 1.8 Kev (FWHM) at 1.33 MeV peak of Co-60. During operations, the HPGe detector is cooled to minimize the thermally-induced leakage current, so that superior energy resolution is not impacted by the associated noise (Knoll, 2000).This is achieved by reducing the detector temperature to 77 K. This is done by maintaining it in contact with the liquid nitrogen. The thermally induced leakage current arises because of the small band gap of 0.7 eV.

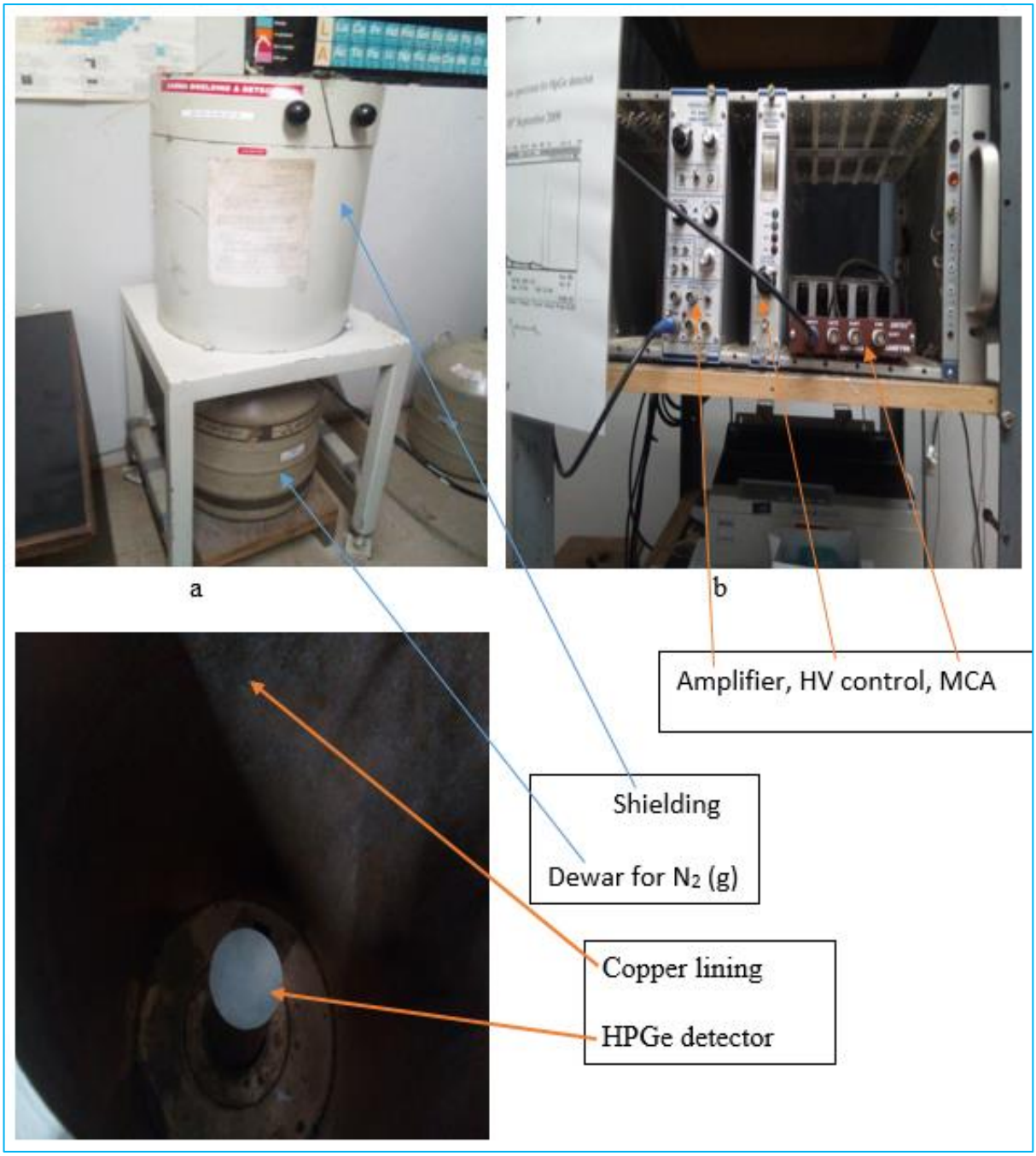

Figure 0: HPGe Gamma Spectrometer Instrumentation, INST UoN.

Figure 2: Setup of HPGe gamma spectrometer at INST, UoN

Enclosing the HPGe detector, is a 10 cm thick lead shielding. The shielding minimizes the effect of the external background radiation and cosmic rays on the sample spectral data. In addition, the shielding is lined with a thin film of copper inside to absorb any x-rays that maybe generated from the excitation of lead by background radiation, hence not reaching the detector. The HPGe detector is coupled with a PC containing the operating installed program and for spectral display, multi-channel analyzer, an amplifier and a high voltage power supply.

2.10.2 EDXRF INSTRUMENTATION AND ANALYSES

Energy dispersive x-ray fluorescence (EDXRF) technique has found wide applications in analyses of environmental samples. This is because it is non-destructive ,fast, easy to use and can analyze different kind of samples such as solids, liquids , biological samples and can do multi-element analysis of materials (Tiwari et al., 2001). The apparatus involves X-ray source (about 30-60 kV) represented by an X-ray tube and a liquid nitrogen cooled detector, Si (Li) or NAI detectors. EDXRF is applied in identification and quantification of elements in a sample. The elements contained in the sample are identified from the characteristic x-rays emitted, while quantification is by calculating the intensity of the emitted x-rays. EDXRF spectroscopy has three main components; an excitation source, a detector, and a data processing unit as in figure 3.

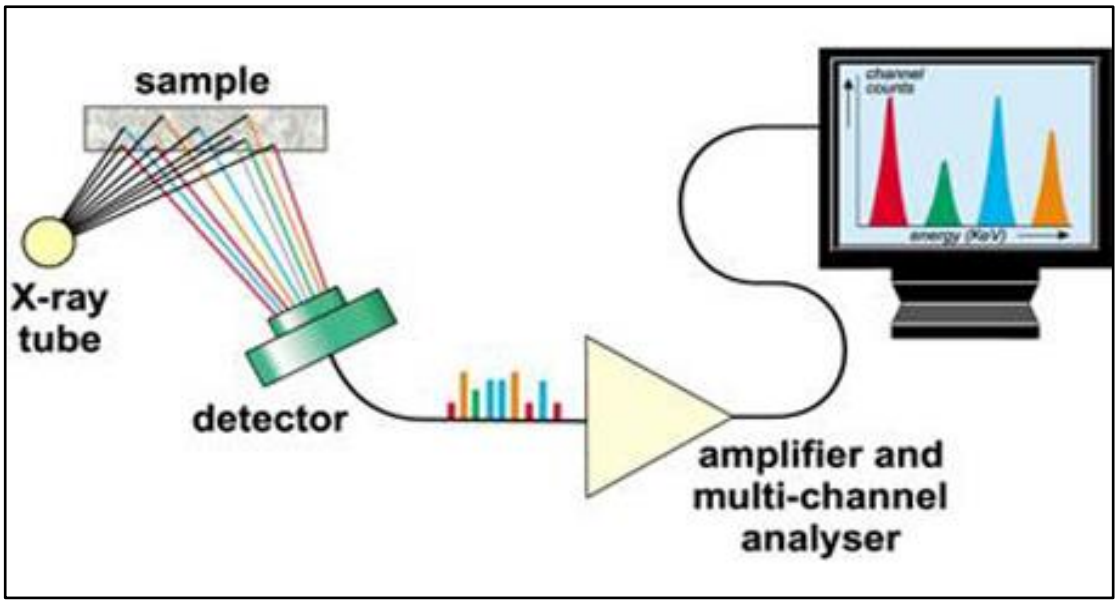

Figure 3: Diagram of a EXDRF (Malvern Panalytical)

In this study, an AMPTEK experimenter's kit EDXRF available at INST, University of Nairobi was used. The spectrometer has an x-ray generator which acts as the excitation source and is operated at 5-50kV, the tube current is 1-1000µ, and SiLi detector 10mm^2 which is mounted at 45^o take off angle with respect to the sample. The equipment was operated at 30 Kev and 80 µA. The instrument consists of a large sample chamber able to accommodate samples of width 300mm and 150mm height and opens and closes automatically. The operating principles of the equipment is that once the x-rays, which originates from an external source like X-ray tube or a radioactive source, are emitted from the cathode, are accelerated towards the silver target. The atoms in the sample material are excited by primary photons in a process known as direct excitation (Angeyo et al., 2012). Due to this interaction, electron is ejected from the inner shells of the atoms that make up the sample hence creating a vacancy.

The photoelectrons exit with a kinetic energy (E-φ) which equals the difference between incident particle (E) and the atomic electron's binding energy (φ). Electron from a higher energy shell fills the vacancy that is left by the ejected electron in the electronic structure of the atom. A characteristic X-ray photon, which is of the same energy as difference in binding energies of the two electron shells, is then released. The characteristic x-rays are unique for each element, hence acting as a fingerprint for a particular element (Knoll, 2000). Detection of characteristic x-rays and

measuring its energy acts as the principle for determination of the element and the specific electronic transition of its origin (Jenkins, 1995)

The emitted characteristic x-rays reflecting different atoms/ elements are transmitted to the SiLi detector, giving an energy spectrum. The intensities of these x-rays forms basis of elemental quantitative analysis. The characteristic X-rays is then transformed by the preamplifier into a low-voltage pulse. The pulse amplitude is converted into a digital signal after being received by the main amplifier. The signal which is digital is shaped, sorted, and then transformed into a pulse counter which has the information of the amplitude. The information is then stored in a multichannel analyzer and formatted to an XRF spectral line (Gürol, A, 2008).

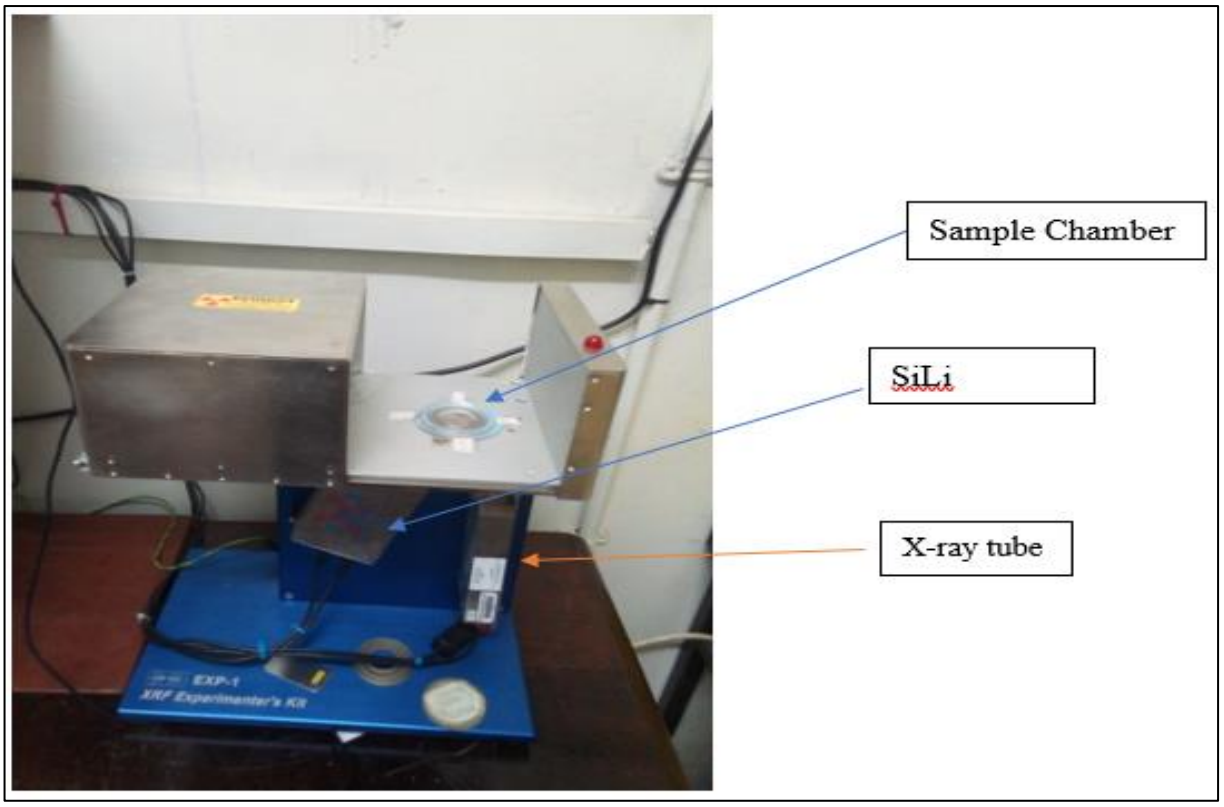

Figure 4: Setup of EDXRF spectrometer at INST, UoN

CHAPTER THREE

MATERIALS AND METHODS

3.0 OVERVIEW

In this chapter, the following are presented; a brief description of the study area, procedures followed for sampling, the materials that are used, detailed procedures for sample preparation, measurement instruments and evaluation of data using various methods.

3.1 DESCRIPTION OF STUDY AREA.

The study was conducted in Kinondo area located in Kwale county which is around -4°10′28″S 39°27′37″E; 30 km southwest of Mombasa in Coastal region of Kenya. This area lies at -4°22′57″S 39°31′59″E; and approximately 2.86km from the Base titanium mining. The mine covers a total of area of 88km^2 and is located about 50km south of Mombasa which is 8km inland from the Indian Ocean. The mining is managed, explored and processed by Base Titanium Limited. The economy of this area is diverse. The community in the region carry out farming activities in small scale and livestock rearing (cattle, sheep and goats). The agricultural activities include farming of coconut, cassava, cashew nut, vegetables such as ‘mchicha’ and okra. The area has forest which host a wide range of both exotic and indigenous tree species such as palm trees. The drainage pattern of this area is good and has rivers and springs. The Mukurumudzi river, a perennial river, is the main source of surface water in the area. It flows from northwest to southeast and drains its water into the Indian ocean. Other smaller rivers and springs are Ramisi, Pemba, Marere and Umba springs. The maps for Kwale county and sampling area is shown in Figure 5 and 6 respectively.

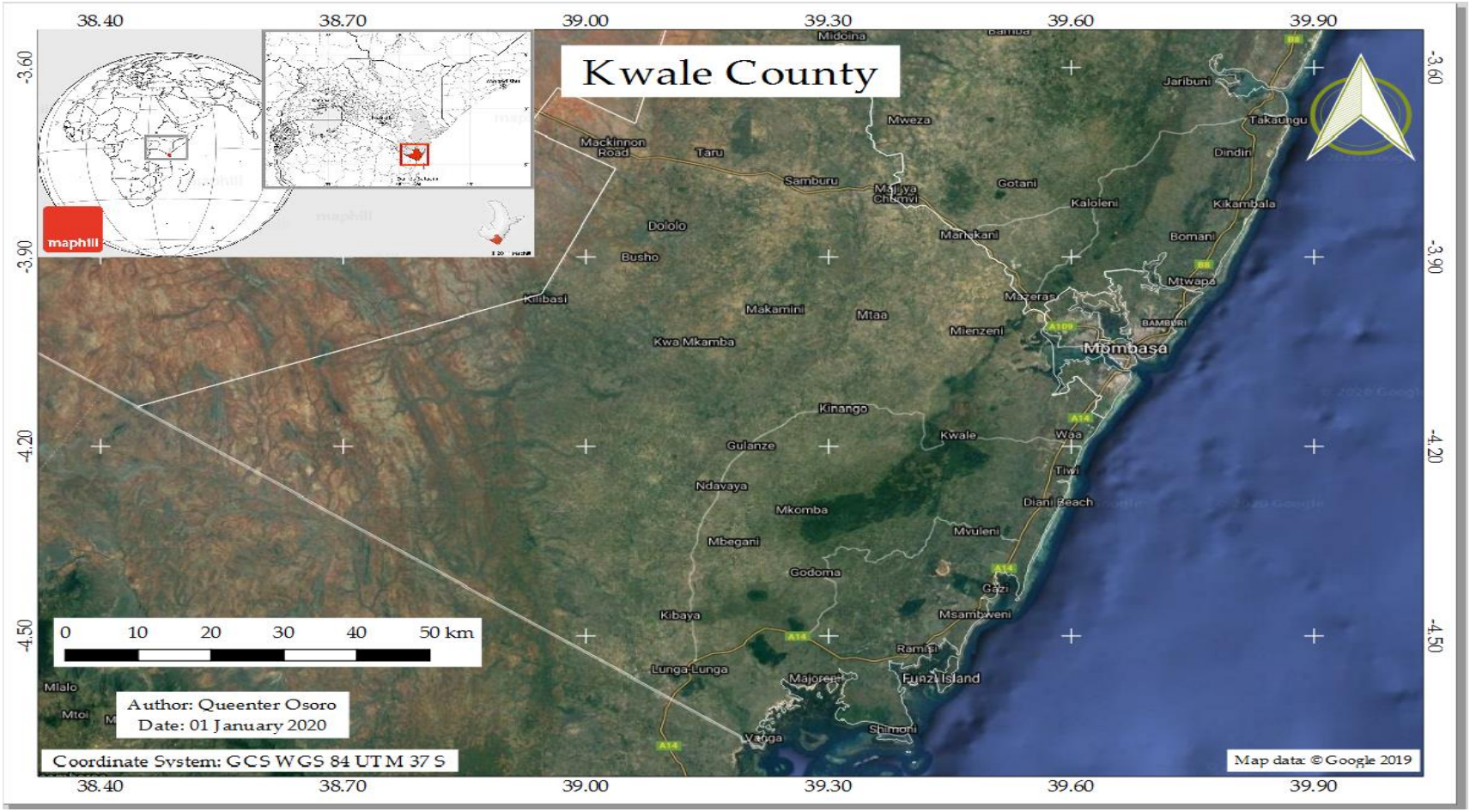

Figure 5: A map of Kwale County

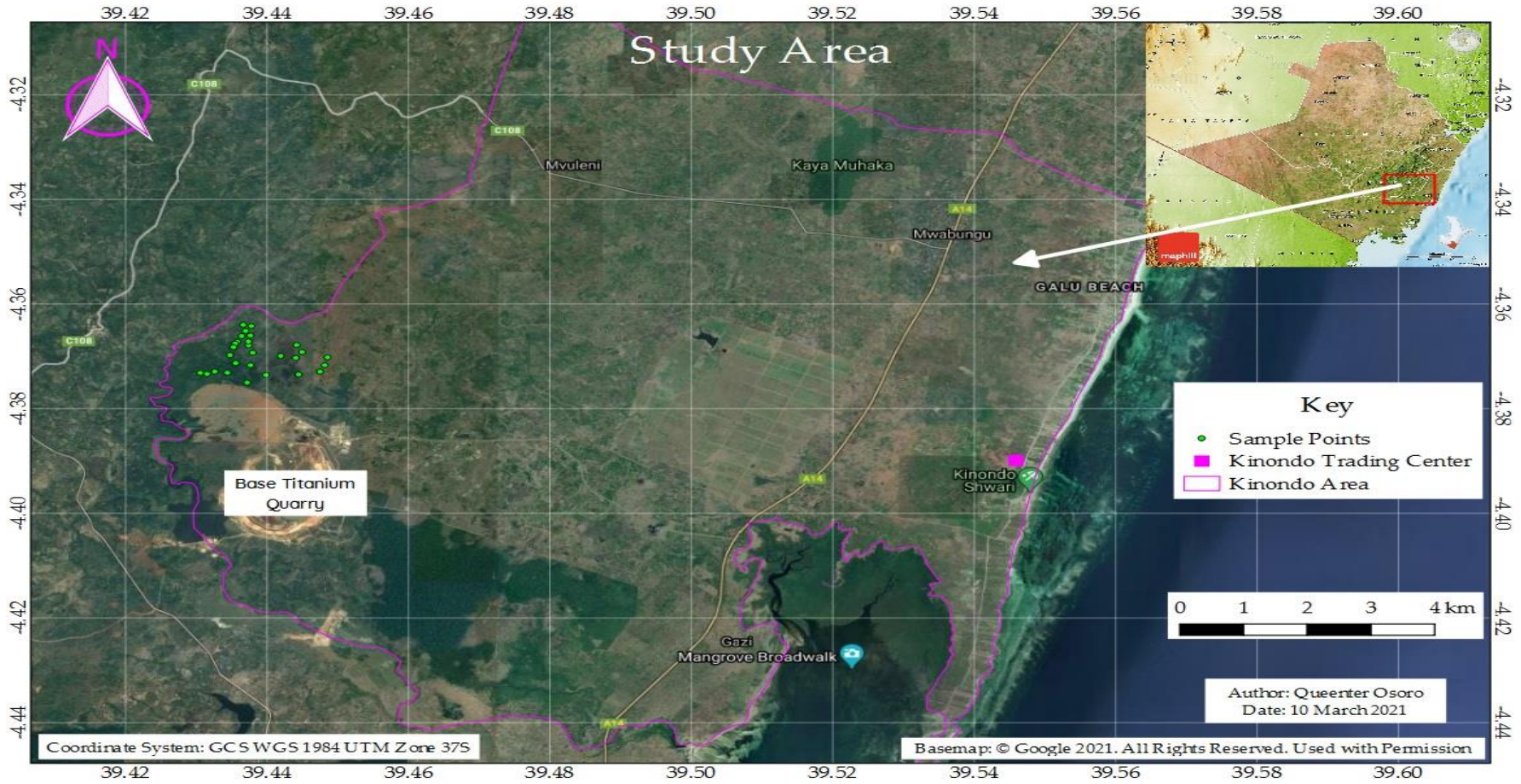

Figure 6: Map showing the sampling points

3.2 SAMPLE COLLECTION

In this study, 28 sampling points were randomly identified in the sampling site which is approximately 2.86 km from the mining area. The area was cleared from trees, large stones, or roots. The geographical location for the sampling sites was recorded using a Global Position System (GPS) gadget, later used for mapping purposes. The top humus and vegetation were cleared from the sampling sites. Three (3) samples were collected from each of the sampling points , as shown in Figure 7 below, using a clean auger, to ensure minimum contamination, at a depth of about 0 - 20 cm a (top soil sample), 20- 30 cm (subsoil 1) and 30- 50cm (subsoil 2) making a total of 84 samples. The representative samples weighing approximately 1 kg were kept in well-sealed and labelled zip lock polythene bags, to minimize radiation exposure level during transportation. The labeled bags were then transported to the Institute of Nuclear Science and Technology (INST) analytical laboratory, University of Nairobi, for preparation and analyses. The locations of the Global Positioning System (GPS) l for the sampling points were recorded in table 2 below.

Table 2: Measurements of GPS location readings at sampling points

SAMPLE CODE	SOUTHINGS	EASTINGS	ELEVATION
S1	04'22.192'S	039'26.517'E	125m
S2	04'22.066'S	039'26.653'E	135m
S3	04'22.147'S	039'26.699'E	136m
S4	04'22.214'S	039'26.645'E	136m
S5	04'22.404'S	039'26.669'E	138m
S6	04'22.372'S	039'26.851'E	121m
S7	04'22.208'S	039'26.914'E	121m
S8	04'22.298'S	039'26.890'E	108m
S9	04'22.411'S	039'26.392'E	132m
S10	04'22.498'S	039'26.232'E	118m
S11	04'22.298'S	039'26.261'E	126m
S12	04'22.155'S	039'26.280'E	94m
S13	04'22.070'S	039'26.245'E	89m
S14	04'22.027'S	039'26.243'E	77m
S15	04'21.958'S	039'26.260'E	92m

SAMPLE CODE	SOUTHINGS	EASTINGS	ELEVATION
S16	04'21.849'S	039'26.269'E	98m
S17	04'21.835'S	039'26.199'E	95m
S18	04'21.905'S	039'26.219'E	100m
S19	04'21.964'S	039'26.186'E	99m
S20	04'22.029'S	039'26.151'E	100m
S21	04'22.050'S	039'26.131'E	77m
S22	04'22.091'S	039'26.117'E	88m
S23	04'22.182'S	039'26.087'E	114m
S24	04'22.273'S	039'26.135'E	123m
S25	04'22.384'S	039'26.064'E	128m
S26	04'22.371'S	039'25.958'E	131m
S27	04'22.398'S	039'25.892'E	105m
S28	04'22.386'S	039'25.834'E	133m

Figure 7: Collection of samples in the field sample point S9 (04'22.411'S .039'26.392'E)

3.3 SAMPLE PREPARATIONS FOR EDXRF ANALYSIS

In the preparations for the analysis using EDXRF, the samples were covered in order to prevent cross contamination and dried in the sun for 30 days. This was done to remove all the moisture content and achieve constant weight. The soil samples were then sieved by use of a 2 mm sieve to remove any stones, leaves, twigs or any other large particles. It was then put in a tight plastic bag to avoid contamination. In order to ensure no difference in weight, the samples were put in the oven to dry at 103℃ for 48 hours. The samples were then crushed using a mortar and a pestle. The procedure of coning and quartering was then carried out on the dry samples in order to attain a representative aliquot of 25 g of each of the soil sample. The samples were further pulverized using an electric mortar and pestle to reduce particle size to less than 75 µm in order to pass through a 60-100 µm sieve (IAEA, 1997). A hydraulic pellet press was then used palletization. Approximately 0.4 g of the sample was weighed then uniformly spread in a die. The die, cups, pestle and mortar were thoroughly cleaned before a new sample was prepared to avoid contamination. The die was then placed in the hydraulic pellet press and a pressure of 2-3 KPa making a pellet. The pellets of a diameter approximately 2.5 cm and 0.4 grams were made in triplicates, weighed and stored in a well labelled Petri dish.

3.4 SAMPLE PREPARATIONS FOR RADIOACTIVITY MEASUREMENTS

For the purpose of measurement of the radioactivity by use of a high-purity germanium (HPGe) gamma-ray detector, approximately 300g of the pulverized samples were sealed tightly in a 250 ml plastic containers for one month. The process allowed the gaseous radon (half-life 3.8 days) and her short-lived decay daughters (^{214}Bi and ^{214}Pb) achieve equilibrium with the long lived ^{226}Ra in the sample (Mustapha et al., 2007). Prior to measurement of the sample, an empty container under similar conditions was used to record the environmental gamma background radiation. This value was then deducted from the gamma-ray spectra of the samples measured to correct the net peak areas for the counts for accurate calculation of radioactivity levels (Tzortzis et al., 2003). The samples were analyzed in the shielded detector and measurements taken for about 12 hours. This involved measurements of the concentrations and gamma-ray photo-peaks which are emitted by the specific radionuclides of the Thorium and Uranium series.

3.5 SAMPLE ANALYSIS.

In this study, two analytical methods were used. EDXRF spectrometer was used to carry out the content elemental analyses of the samples. The radiometric measurements were undertaken by use of the high-purity germanium (HPGe) gamma-ray detector.

3.5.1 EDXRF ANALYSIS

For each pellet, three measurements were made. The sample pellets were irradiated for a live time of 200 seconds in order to acquire the spectrum of interest. The tube current was optimized at 80 μA while the voltage was set at 30kV. A multi element target with same matrix and characteristics as the sample pellet with a diameter of 2.5 cm made up of a mixture of high purity compounds of titanium, niobium zinc, manganese, and bromine, was used. Sample with multi-element target at the top was irradiated for 50 s, and then the target was irradiated alone for 50 s for absorption correction. The energy of the characteristic x-rays of the elements cover the energy of calibration of the multi-channel analyzer. The spectral data was collected and stored using a PC based MCA. The data deconvolution was done by use of AXIL (Analysis of X-rays using Iterative Least-squares method) a modular program of the IAEA's QXAS program. 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 that are present in the sample (Vekemans et al., 1994).

3.5.2 RADIOACTIVITY MEASUREMENTS

The soil samples upon attaining secular equilibrium were analyzed for radioactivity levels using HPGe detector for a period of 30,000 seconds. A similar procedure and geometry was applied for the standard reference material RGK-1, RGTH-1 and RGU-1 from IAEA, containing ^{40}K, ^{234}Th and ^{238}U, respectively. In addition, background radiation level was obtained using distilled water. The detector was operated at 1000 V and a positive polarity. The acquired spectral data was analyzed using Ortec Maestro program that was installed in a PC for spectral intensities. Using the intensities of the radionuclides of interest in the standard reference materials, and to correct for the background radiation, the levels of the radioactivity of radionuclides in unknown samples were determined by use of comparison method.

Using the obtained radioactivity levels, radiological risks were assessed using different radiation hazard indices as presented in the results and discussion section. To obtain radioactivity levels of the radionuclides, comparison method formula was used (equation 1), using results attained from both the samples certified reference materials.

$$\frac{\mathrm{AsMs}}{\mathrm{Is}} = \frac{\mathrm{ArMr}}{\mathrm{Ir}}$$ ……. Equation 1 (Mohanty et al., 2004)

Where;

M_s= the mass of the sample,

M_r = the mass of the reference material

I_s = the intensity of the sample

I_r = the intensity of the reference

A_s = the activity of the sample

A_r = the activity of the reference material.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 OVERVIEW

In this chapter, the results of this study are presented and discussed. First, the accuracy of the analytical techniques used is determined by use of a standard reference material from the International Atomic Energy Agency (IAEA). The elemental analysis results of the collected 84 soil samples are then presented and discussed. The concentration levels of Ti, Mn, Fe, Pb, Zr, and Zn are presented and discussed. The results are then analyzed for possible trends and compared to results from similar studies conducted in the region as well as other mining areas across the world. Additionally, the concentrations of activity of K-40 U-238 and Th-232 in the soil samples are also discussed. From the reported activities, radiation hazards are assessed based on different radiation indices.

4.1 VALIDATION OF THE EDXRF METHOD USING SRM MATERIALS

In this study, EDXRF spectrometer was used for elemental content determination in the soil samples. To validate the analytical procedure, standard reference material, IAEA-PTXRF-09, was used and data presented in table 3. The standard reference material was prepared and then analyzed using a similar procedure employed for the samples. The reference material is a clay sediment sample that contains a varied range of elements, and of similar matrix as the analyzed samples. The elements contained in the reference ranges from potassium (Z = 20) to lead (Z = 72), hence it could be used to test the calibration curve for both K- lines and L- lines. The elements were present at varying concentrations ranging from 2.97 % for iron to below detectable levels (<10 ppm) for elements like mercury. However, all elements of interest for this particular study were above the minimum detectable levels. The experimental values obtained for different elements were determined within the certified range. Therefore, the method could confidently be used in the analyses of the soil samples. The obtained experimental results were compared with the certified values as presented in table 3 below.

Table 3: Analyses of Standard Reference Material, IAEA-PTXRF-09

Element	Experimental Values (ppm)	Certified range (ppm)
K	18700 ± 1800	17800 – 21200
Ca	12900 ± 1100	12300 – 15300
Fe	30100 ± 1000	28700 – 30700
Mn	1042 ± 87	940 – 1060
Ti	4326 ± 333	4100 – 4500
Zr	291 ± 9.7	281 – 322
Zn	101 ± 10	88 – 103
Pb	39 ± 7.6	33 – 40

The results of the standard reference material were further used in calculation of the lower limits of detection of the analytical tool using equation 2 below,

$LDL=3\times(C\sqrt{Nb})/Np$ ……equation 2

Np = the Net peak area for the element

C = the concentration of the element (mg kg^{-1})

Nb = the net background area under the element peak.

The values of the lower limits of detection (LLD) of the elements analyzed in the samples from the pellets prepared for this study were then presented in the table 4 below.

Table 4: Detection limits for soil sample, PTXRF IAEA 09-River clay

Element	Atomic number	Lower limits of Detection(ppm)
K	19	390
Ca	20	220
Ti	22	90
Mn	25	50
Fe	26	40
Zn	30	15
Zr	40	10
Pb	82	8

According to the reported detection limits, these calculated values improved exponentially with an increase in atomic number of the elements. Comparable values and trend were obtained by (Adede, 2015) as shown in the table 5 below.

Table 5: Detection limits for soil sample, PTXRF IAEA 09-River clay

Element	Atomic number	Lower limits of Detection (Mg/kg)
Vanadium	23	33
Chromium	24	18
Nickel	28	7
Copper	29	6
Zinc	30	6
Strontium	38	3
Zirconium	40	3

4.2 ELEMENTAL CONTENT DISTRIBUTIONS

In this subsection, the EDXRF analyses results for samples collected are reported and discussed. The results are presented as the mean concentration of the prepared triplicates per sample as well as that of the sampling profile. In general, the major elemental constituents were found to be Fe (0.5 – 8.5 %), followed by Ti (0.3 – 1.5 %). Other constituents like Zn and Pb had concentration values below 0.1%.

Titanium

Titanium was determined to be one of the major constituents as it was present in all the 84 soil samples that were analyzed at a concentration range of 0.3 – 1.5 %. Figure 8 presents the Ti distribution amongst the three sampling profiles; top soil from (0 – 15 cm), middle soil from (15 – 30 cm) and bottom profile (> 30 cm). The concentration range in the sampling profiles were recorded at Bottom (0.3-1.45%), Middle (0.3-1.4%), Top (0.3-1.5%). Relatively higher mean concentration was reported in the middle profile at 1.03 ± 0.26 %, as compared to the top and bottom profile at 0.94 ± 0.27 % and 0.92 ± 0.25 % respectively. This could be attributed to the response to water as an agent of transport of the heavy metals from the soil surface causing

depletion. However, no significant statistical difference was reported between the three soil profiles as shown in the Appendix 7 as the concentration was within similar range.

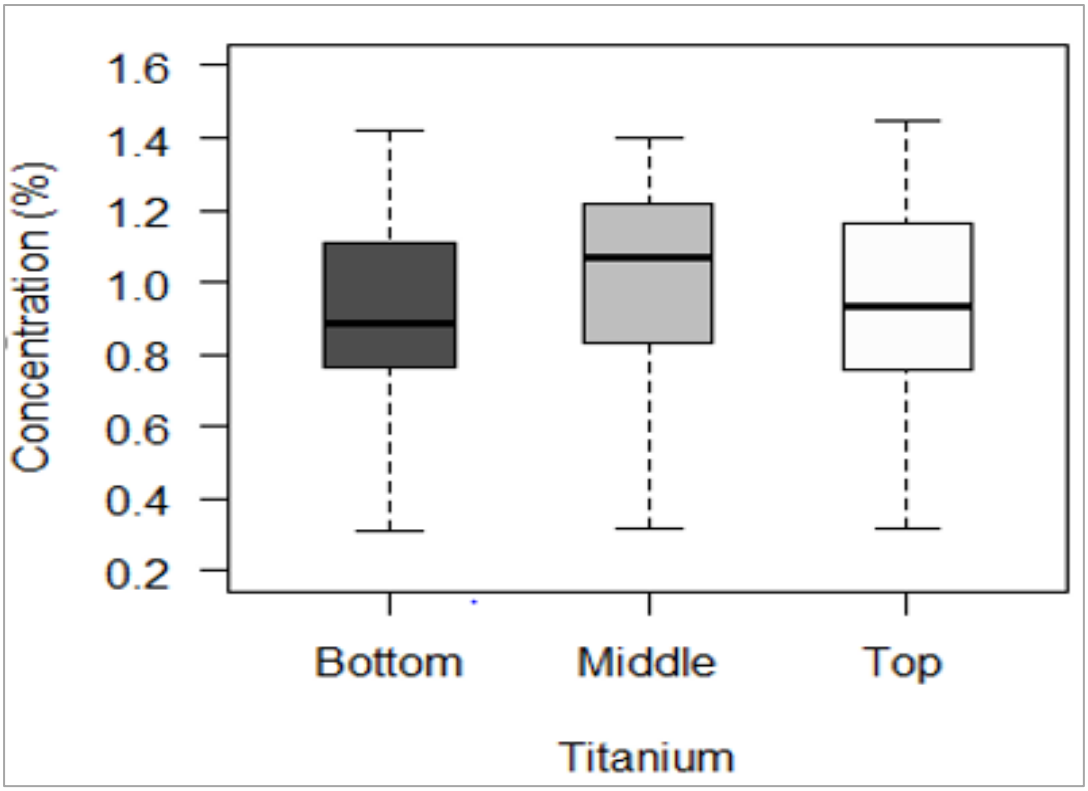

Figure 8: Ti content distribution in the three soil sampling profiles

The results from this study can be compared to those that were reported by Maina et al., (2016), in a research carried out to attain the background concentrations of metal in the vicinity of titanium mine, prior to commencement of mining activities. The study determined the Ti concentrations range to be from 0.47 to 2.8 %. According to an assessment carried out on concentration levels of heavy metal in soils collected from the area surrounding the titanium mining site located in Kwale, coastal Kenya (Maina, 2008), Fe and Ti were identified as the major elemental constituents, at 1.2% and 1.5% respectively. The elemental concentration distribution patterns revealed a significant correlation between concentration levels of Ti, Nb, Zr and Fe, with the radioactivity levels of radionuclides that are in 232-Th and 238-U series. The mean concentrations of Ti were determined at a range of 0.47 to 2.8 %. Similar concentration range was reported by Mulwa et al. (2012), in a limestone mine that lies in the Mozambique belt, a mineral rich region in the East African coast. The reported concentrations are however

lower than those reported in a study conducted in Mrima Hill Coastal Kenya, where a concentration range of 1 – 9 % was reported (Mangala, 1987). Additionally, research conducted by Matoka. Charles et al. (2014) on the bioaccumulation of heavy metal as an indicator of pollution to the environment and health risks in Mombasa municipal determined concentrations of Ti, at 0.15 mg/L in water.

A correlation analysis was conducted between Ti concentrations and those of other elements, as well as between different soil profiles. Ti was found to moderately correlate with Zr and Pb concentrations, and weakly with the rest of the elements determined in this study. The weak correlation between the elements may be attributed to the difference in the parent source. Similar observations were made for different soil profiles as presented in figure 9 and figure 10.

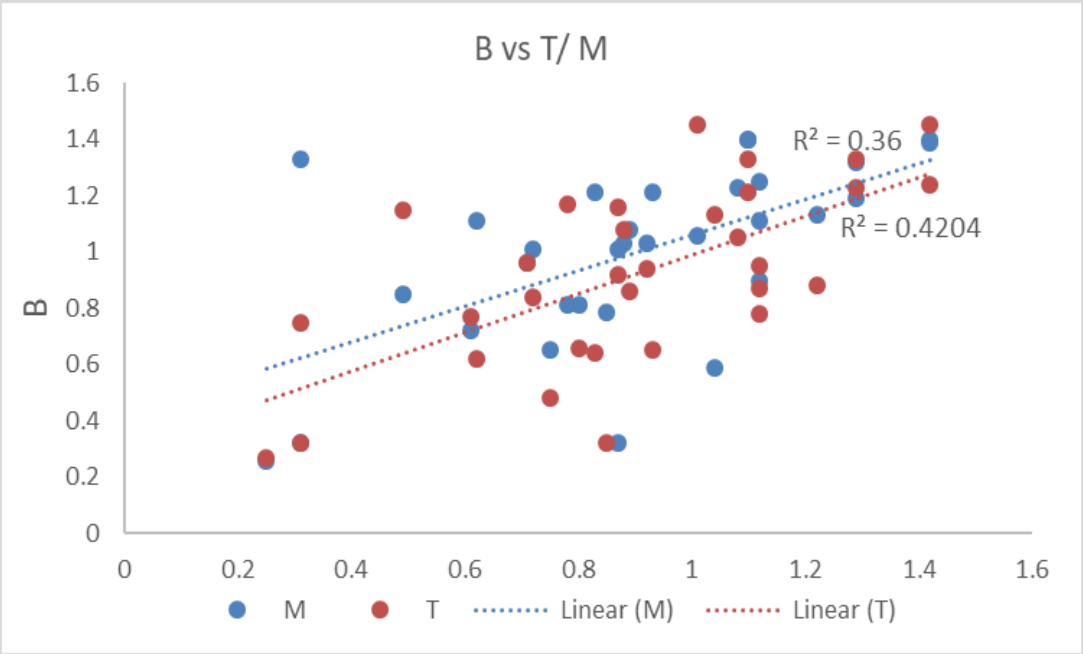

Figure 9: Correlation between different soil profiles B vs T/M of Ti

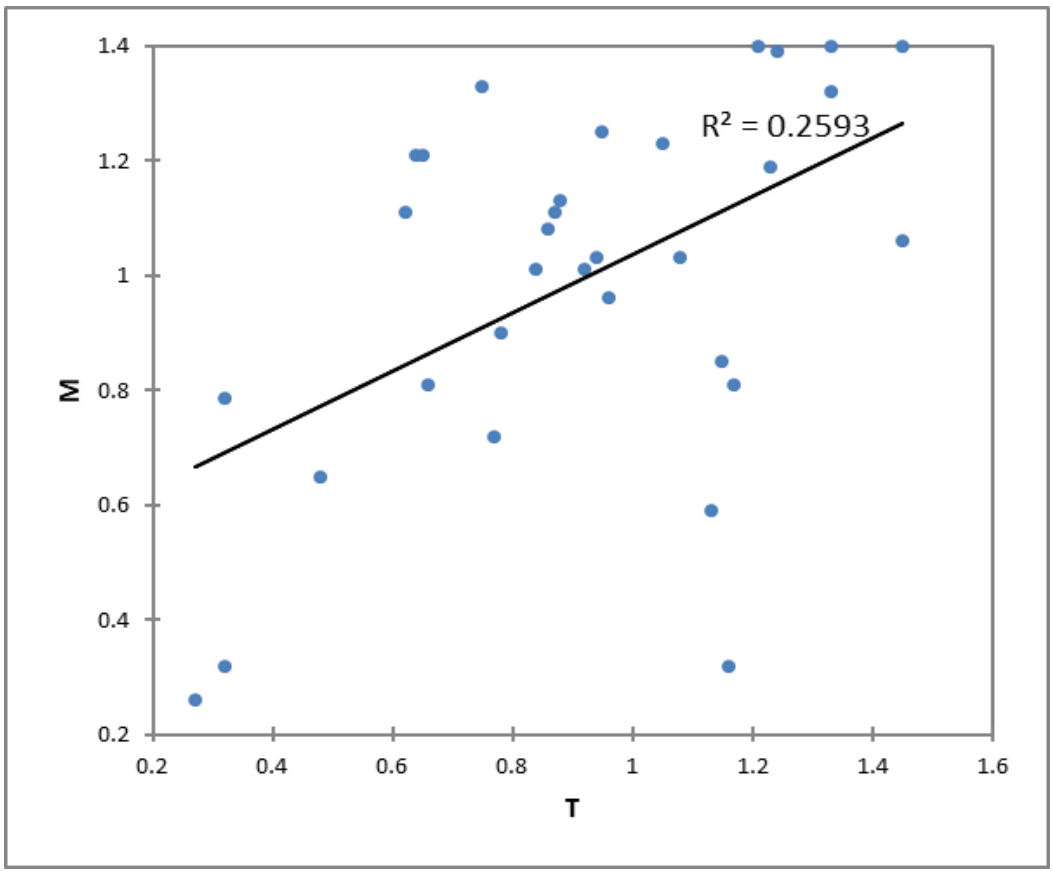

Figure 10: Correlation between different soil profiles T/M of Ti

The positive correlation presented in figure 10 among the soil profiles could be because the Titanium element in the soil samples is from geological processes and therefore has a parent material. The distribution of elements that have parent material shows no variation in concentration in relation to the depth (M. B. Ogundiran et al., 2009).

Iron

Fe was found to be the major constituent in this study. A concentration range of 5.0 – 8.5 % was recorded, with an overall mean of 2.5 ± 1.6 %. An increasing trend in Fe concentrations with depth was noted. For instance, while a mean concentration of 2.72 ± 1.72 % was reported in the bottom profile, the other sampling profiles recorded 2.56 ± 1.67 % at the middle profile and 1.21 ± 0.12% in the top profile. This could be because the source of Iron in the soil is of geogenic origin. According to Borûvka et al., (2005), the levels of concentration of metals which are of geogenic origin increases with an increase in depth. The distribution is shown in Figure 11.

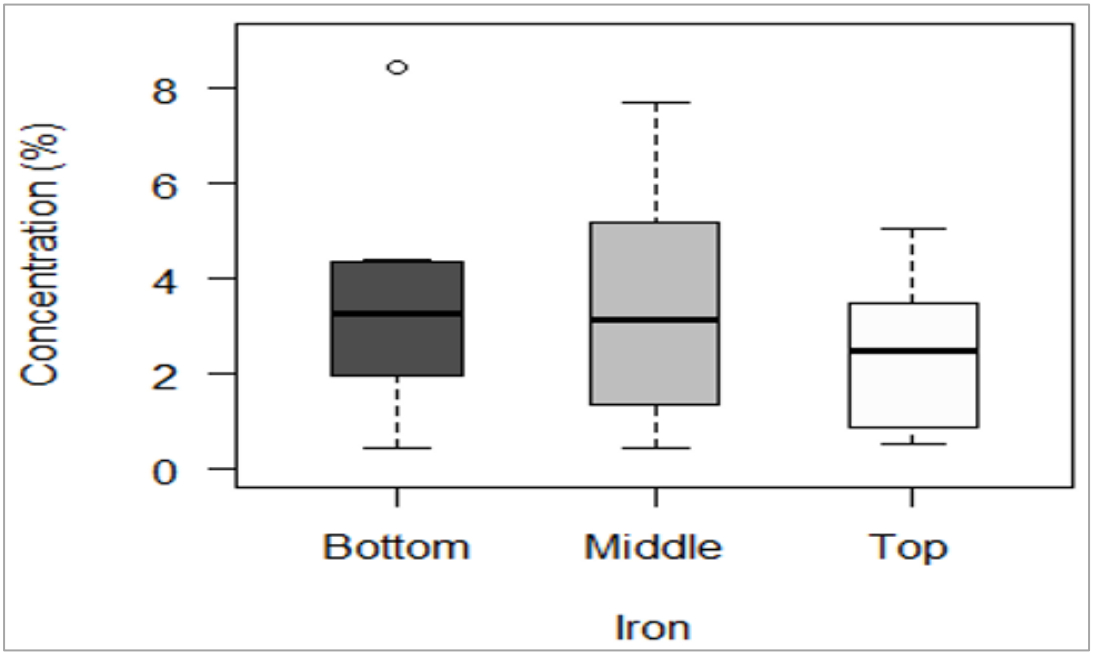

Figure 11:Iron content distribution in the three soil sampling profiles

The Fe content recorded were marginally higher compared to those reported by Maina et al. (2016), at a range of 0.89 to 3.1 % and a mean of 1.57 %, but lower than values reported by Mangala (1991) at range of 5 – 3 %. These two studies were conducted in the same study region but different locality. Comparable to the results of Maina et al. (2016), Fe was found to strongly correlate with Mn and Zn. The observation from this study could be explained by the fact that the elements originated from a similar contamination parent source (Li et al., 2011).

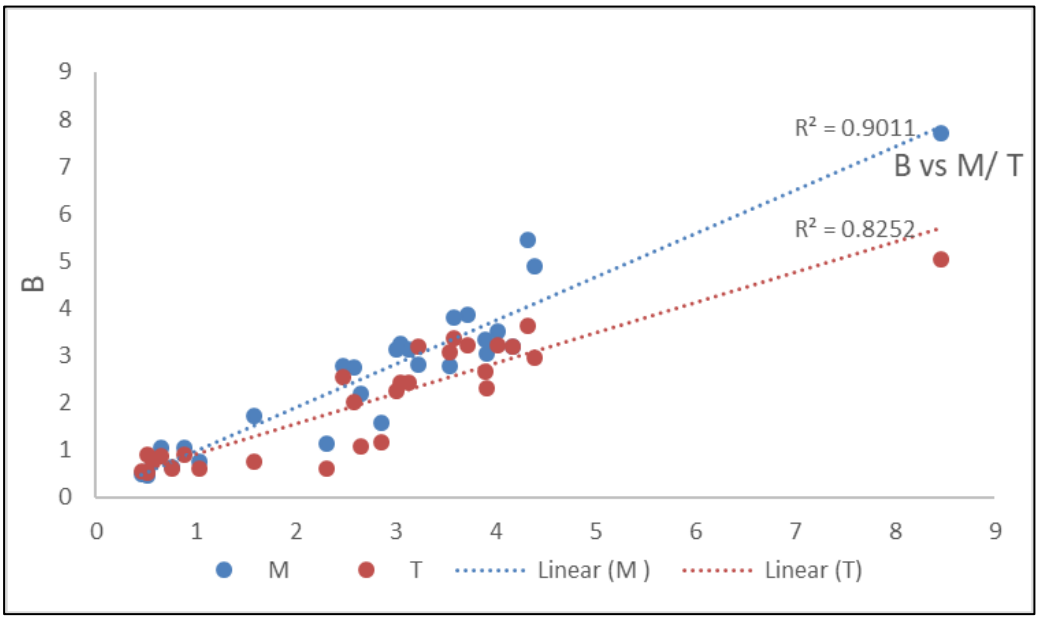

Figure 12: Correlation between the sampling depths Fe

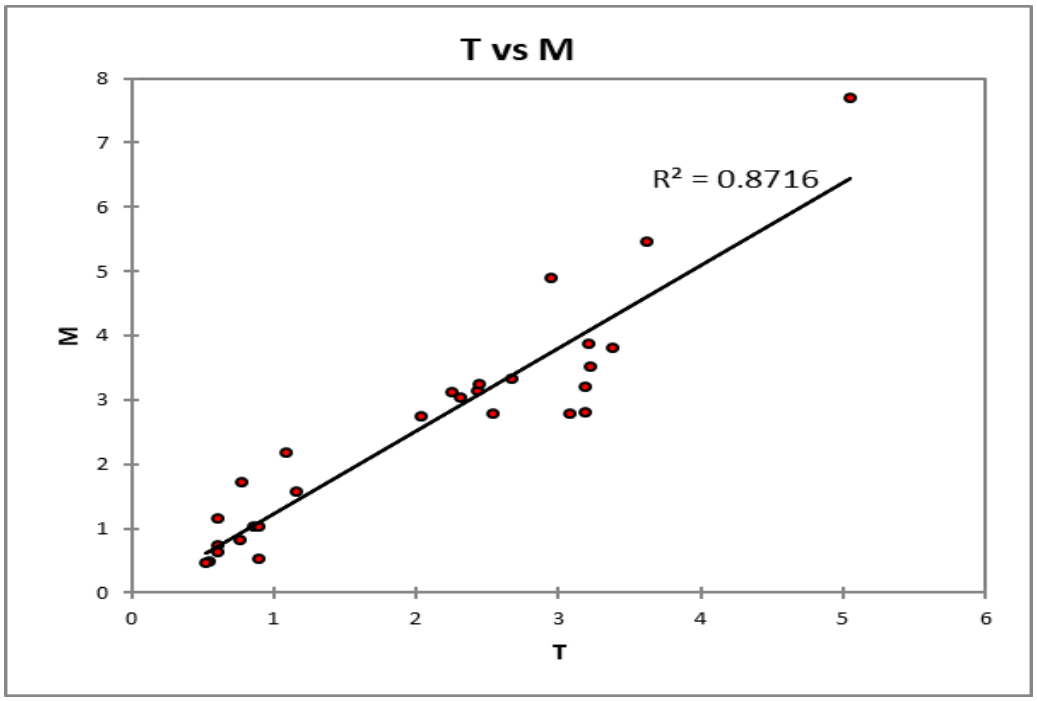

Figure 13: Correlation between the sampling depths T vs M of Fe

A strong correlation was also observed between different sampling depths as shown in Figure 13. This could be due to the fact that the element is of anthropogenic origin.

Therefore, the top layers of the soil are enriched with the iron metal from deposition due to the human activities.

Manganese

Figure 14 represents the mean Mn concentration in the study area. The concentrations ranged between 0.01-0.31%, with the highest mean being reported at the top profile at 0.1145 ± 0.0615 % as compared to the middle and bottom profile at 0.0742 ± 0.0611 % and 0.0529 ± 0.0422 % respectively. A significant difference was noted between the topsoil and subsoil, which could be attributed to surface contamination. The concentration values reported in this assessment can be compared to the ones reported by Mulwa (2011), in a limestone mining area sharing similar geological structure, at a mean of 0.0722 ± 0.0235%. In a Similar study, Maina et al. (2016) determined Mn concentrations at comparable levels of between 0.025 – 0.25 %, and a mean of 0.0822 %.

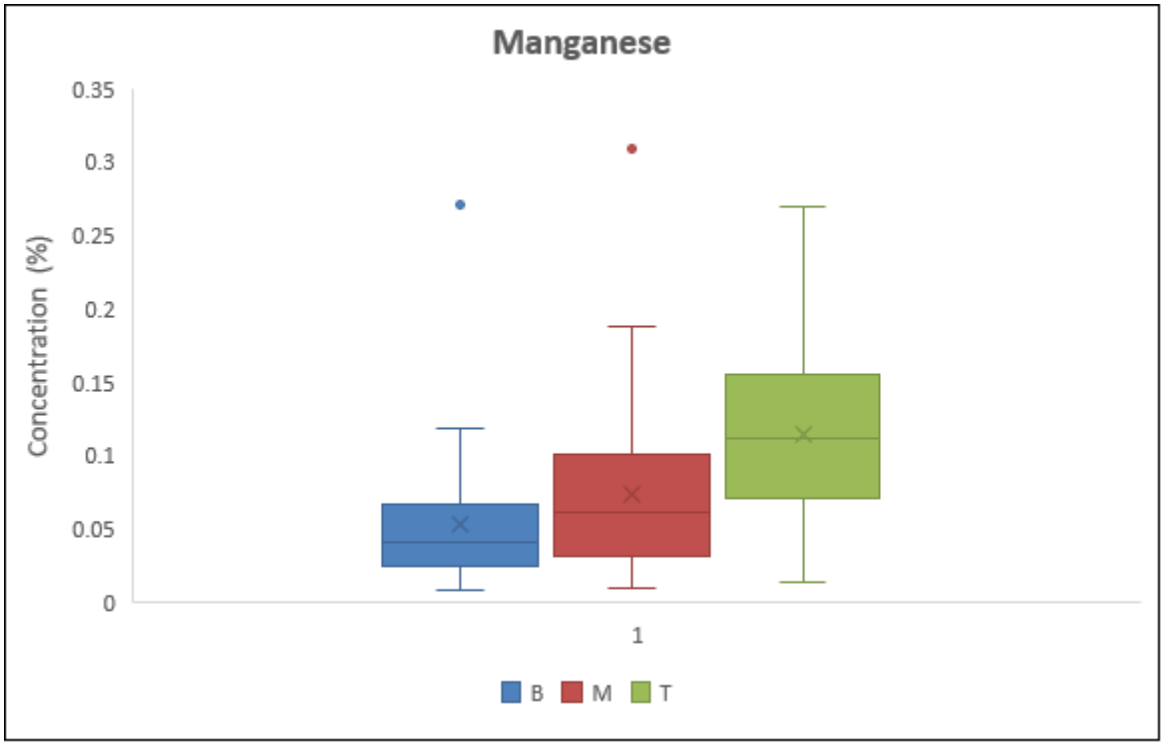

Figure 14: Mn content distribution in the three soil sampling profiles

A significant difference in concentration values was reported between the top profile and the middle and bottom profile. However, a moderate correlation was observed between the three profiles. Similarly, Mn was found to moderately correlate with other

metals. The correlation with other metals could be attributed to the fact that they are from similar parent source.

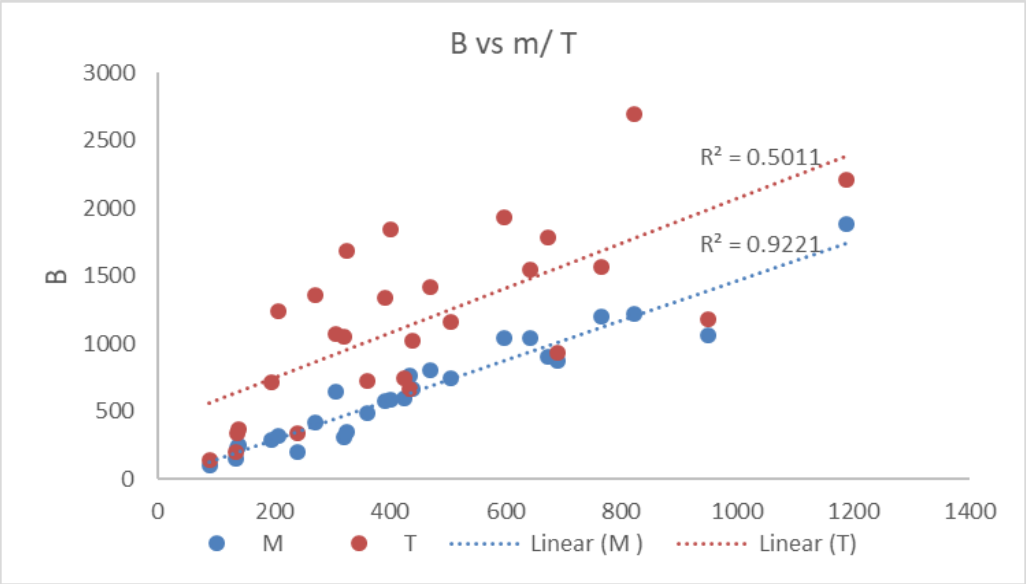

Figure 15: Correlation between different soil profiles B vs M/T of Mn

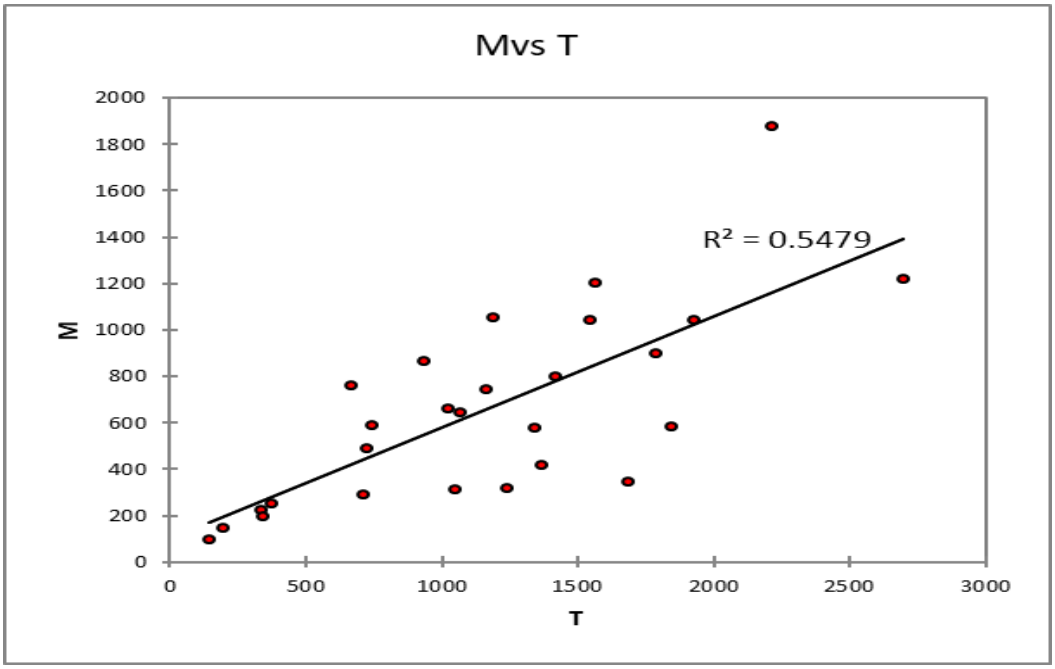

Figure 16: Correlation between different soil profiles M vs T of Mn

The moderate correlation among the soil profile demonstrated could be attributed to the fact that manganese metal is from anthropogenic source. Since the top soil was recorded

to have high concentration of manganese metal compared to the middle and bottom soil the contamination could be linked to deposition from diffuse pollution and anthropogenic contribution.

Zinc

The mean concentration levels of zinc in soil are shown in figure 17. These concentrations were recorded at levels below 0.01%. No significant difference in concentration levels between the three sampling profiles was reported. In addition, the three profiles were found to strongly correlate with one another as shown in figure 18. Zinc was also found to strongly correlate with iron, and weakly with other metals determined in this study. This could be due to the fact that the metals are from same origin. The Zn values are slightly lower than those reported by Mulwa (2011), at a range of 0.0035 – 0.0165 % and an overall mean of 0.0077 ± 0.0025% Additionally, the values were within the United States Environmental Protection Agency regulatory limits.

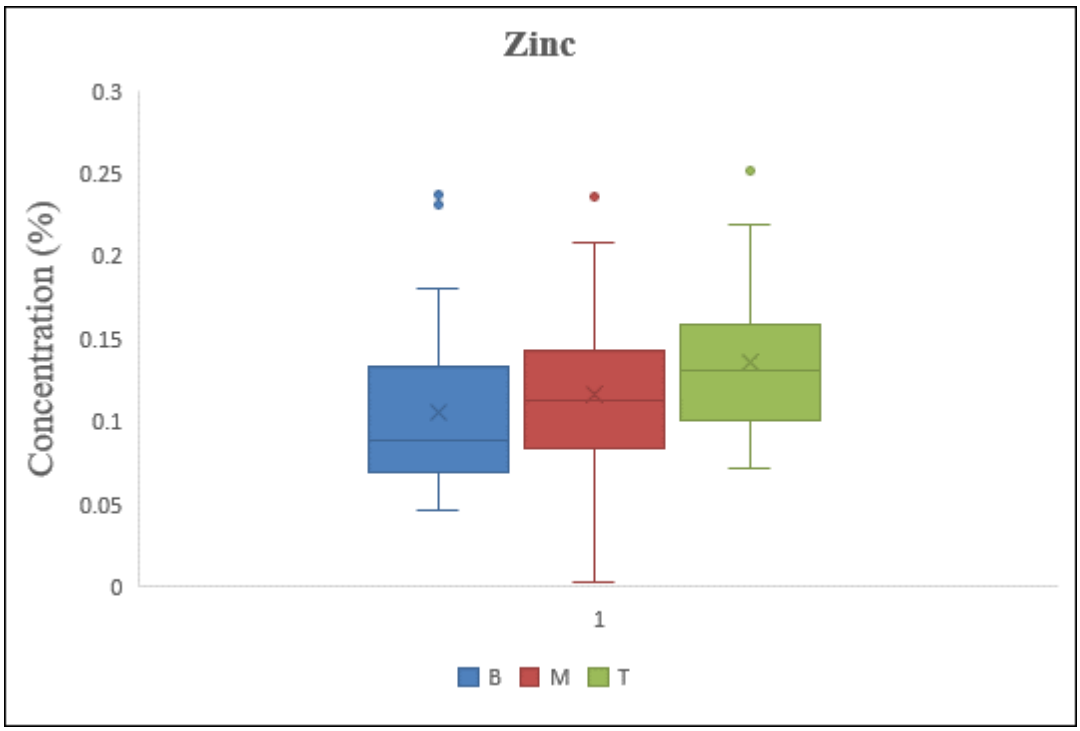

Figure 17: Zn content distribution in the three soil sampling profiles

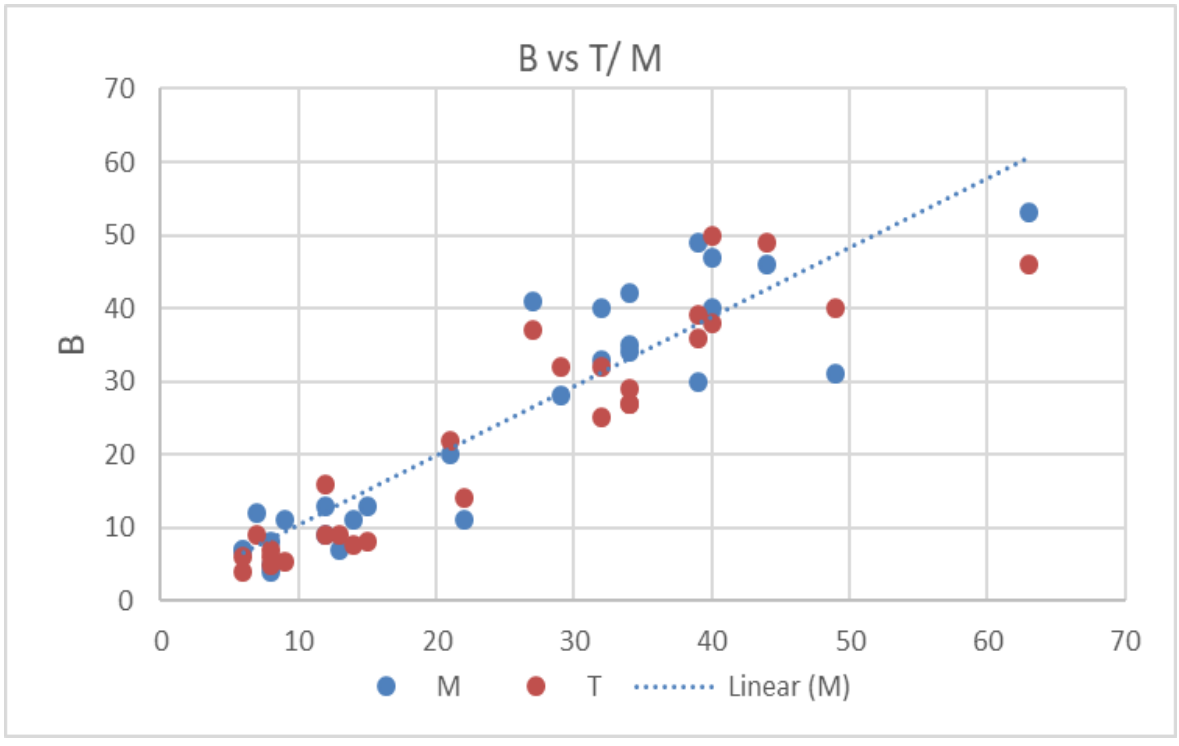

Figure 18: Correlation between different soil profiles B vs T/M of Zn

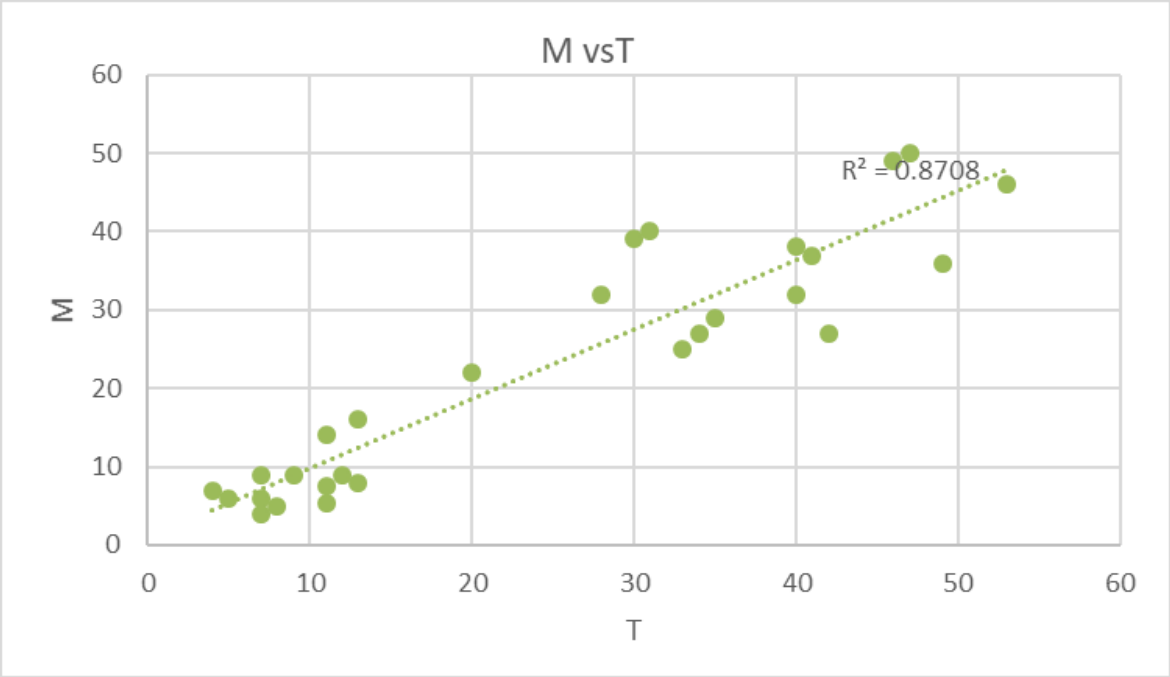

Figure 19: Correlation between different soil profiles(Zn)

There was a strong correlation was demonstrated among the soil profiles. This explains that Zn metal in the soil sample is from geogenic origin and not due to emissions, transformation or dilution in water, air or soil.

Lead

Lead is a toxic metal, with no known physiological role in human body. According to Kabata-Pandias and Pandias, (2011), the worldwide range of Pb in uncontaminated soils is below 0.01%. The mean Pb values recorded in the study fall within this range at between 0.002 – 0.0035 %. There was no significant difference between different sampling profiles. There was a strong correlation among the three soil profiles as shown in Figure 20 and Figure 21. Lead demonstrated a weak correlation with Iron and Zn. A moderate correlation was observed between lead and Manganese which could demonstrate possibility of similar parent source.

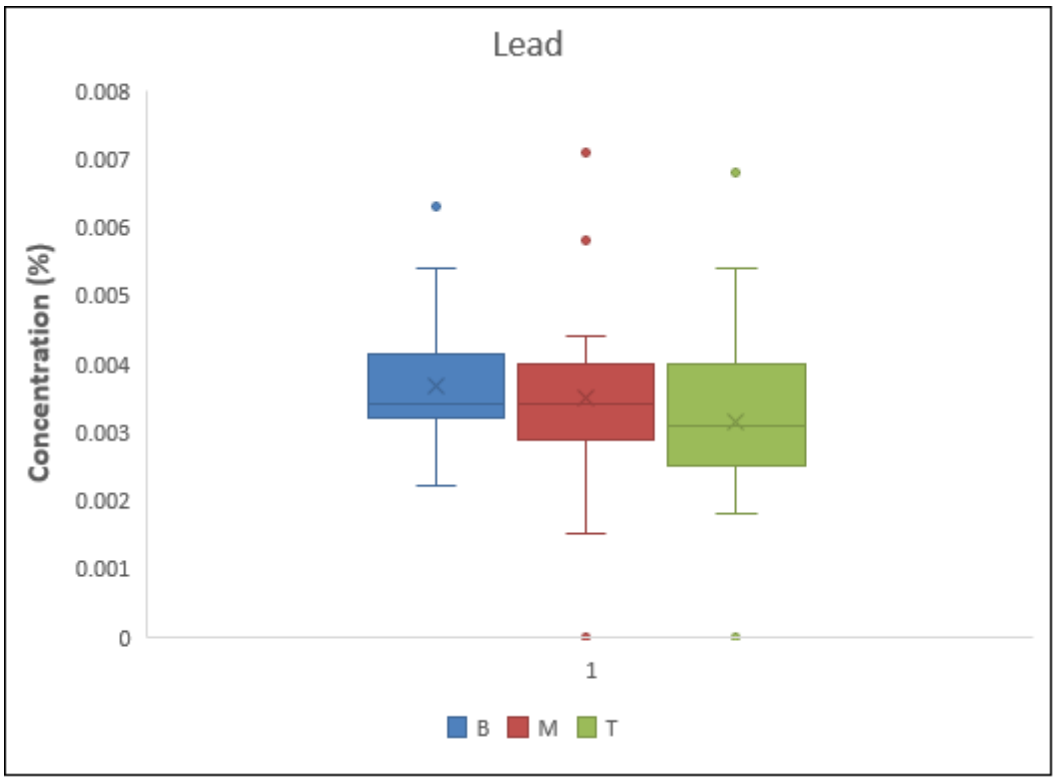

Figure 20: Pb content distribution in the three soil sampling profiles

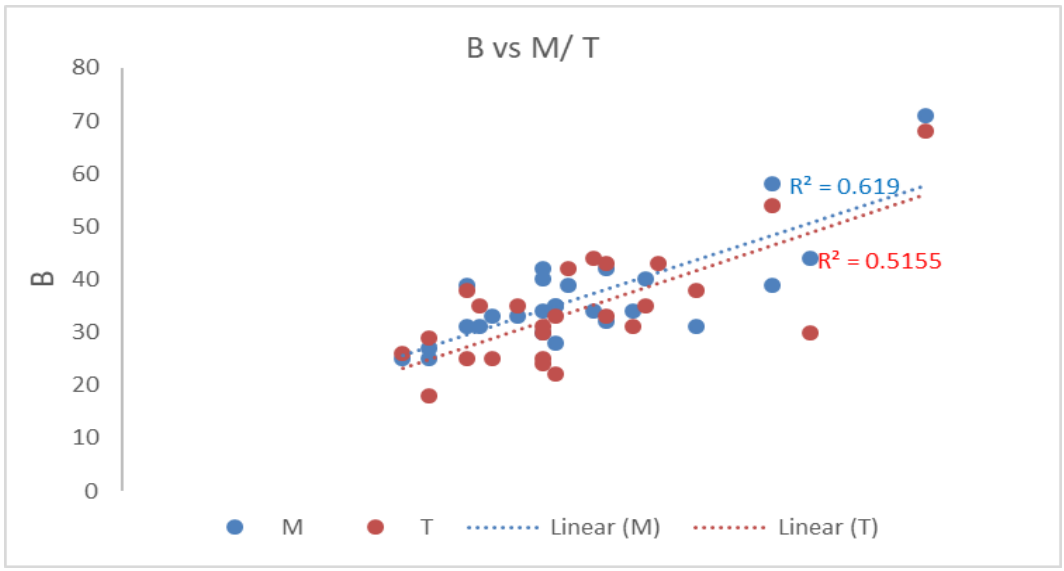

Figure 21: Correlation between different soil profiles B vs M/T of Pb

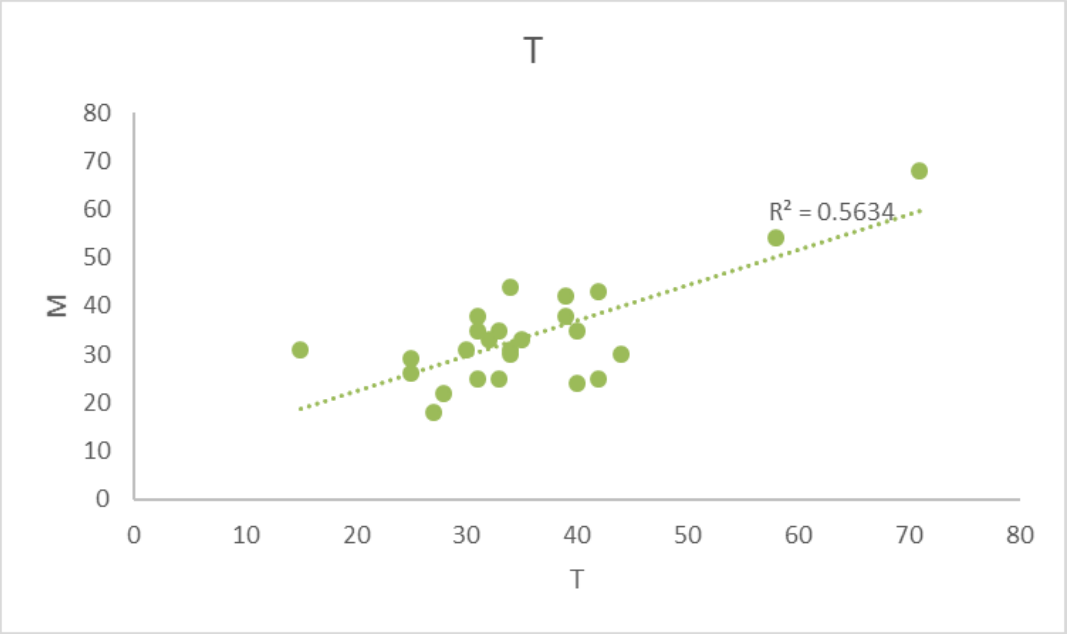

Figure 22: Correlation between different soil profiles T vs M of Pb

According to the correlation analysis conducted on the three soil profiles, a strong correlation was reported among all the three soil profiles. This strong correlation could be attributed to the fact that Pb metal origin is geogenic hence concentration levels do not vary significantly with the depth of the soil.

4.2.1 CORRELATION ANALYSIS OF THE CONCENTRATIONS OF HEAVY METALS

The correlations of the heavy metals determined in the collected samples were performed to test the coefficients. A value ranging from zero to one was used in determining the statistical implication of the correlation If the value was determined to be close to zero, it was concluded that there was no relation of the two elements and was labeled weak. The terms weak, moderate, and strong were used to represent coefficients of correlation of 0.2–0.4 for the ones considered weak, 0.4–0.6 for moderate, and the ones with correlation of >0.6, for strong. Correlation of a data set is important since it helps in determining possibility of any associations among the variables. The R values for Fe/Zn, Zr/ Ti were found to be highly correlated at 0.8208, 0.6827 respectively. Correlation between the other elements ranged between weak to

moderate correlation. The Pearson correlation matrix of the concentration of heavy metals are reported in the Table 6.

Table 6: Correlation Matrix of the concentrations of the heavy metals

Variables	Fe	Ti	Mn	Zr	Zn	Pb
Fe	1					
TI	0.2096	1				
Mn	0.5499	0.3369	1			
Zr	-0.0595	0.6827	0.4771	1		
Zn	0.8208	0.2510	0.4555	-0.1041	1	
Pb	0.1411	0.4795	0.5467	0.4928	0.0483	1

4.3 THE RADIOACTIVITY LEVELS

Radioactivity levels measurements were made by use of gamma-ray spectrometer. Radioactivity of the following radionuclides; thorium, uranium series, and 40K was determined in all the samples from Kinondo area. The most detected primordial radionuclides in the region were recorded to be 232Th, 238U and 40K.

4.4 HPGE GAMMA SPECTROMETER ANALYSES RESULTS

High Purity Germanium (HPGe) gamma ray spectrometer was used for determining the activity concentrations of the soil samples. The spectral data was obtained and comparison method used for analysis using equation 3 below,

$$\frac{\mathbf{Ms}*\mathbf{As}}{\mathbf{Is}} = \frac{\mathbf{Mr}*\mathbf{Ar}}{\mathbf{Ir}} \quad \text{……. Equation 3}$$

Where;

Ms = the mass of sample

Mr = the mass of reference

As = the activity of sample

Ar = the activity of reference

Is = the intensity of sample

Ir = the intensity of reference,

The results of the radionuclide results and those for the standard reference; IAEA-RGK-1, IAEA-RGU-1 and IAEA-RGTh-1, were used. This method required similar preparation procedure and geometry for both samples and reference materials. This is to effectively minimize the matrix effects such as self-attenuation and coincidence summation. The certified reference material activity concentrations for High Purity Germanium detector are shown in the table 7 below,

Table 7: Certified reference material activity concentrations

Radionuclide	Certified Activity conc. ($Bqkg^{-1}$)	Certified range ($Bqkg^{-1}$)
^{232}Th	3250	3160 - 3340
^{238}U	4940	4910 - 4970
^{40}K	14000	13600 - 14400

The spectral lines recommended energy lines for gamma-ray emitters for environmental samples used for comparison is shown in the table 8 below,

Table 8: Energy lines for isotopes (IAEA, 2003)

Radionuclide	Isotope(s)	Spectral line (KeV)
K- 40	^{40}K	1460.81
Th- 232	^{212}Pb ^{228}Ac	238.63 911.21
U-238 (^{226}Ra)	^{214}Pb ^{214}Bi	351.92 609.31

Potassium radionuclide was analyzed using ^{40}K energy line 1460 where an intensity of 0.893 counts per second for RGK-1 was obtained. For ^{232}Th, average intensity of two daughters in the thorium series; ^{212}Pb at 238 KeV and ^{228}Ac at 911 KeV were used, and an intensity of 3.53 counts S^{-1} for the RGTH-1. Uranium was determined using the ^{214}Pb and ^{214}Bi daughters at 351 Kev and 611 Kev respectively. An intensity of 4.18 counts S^{-1} was recorded as shown in the table 9 below,

Table 9: Intensities of the radionuclides

Radionuclide	Isotopes	Intensity of sample (CS^{-1})
^{232}Th ($Bqkg^{-1}$)	Pb-212 Ac-228	3.536
^{238}U ($Bqkg^{-1}$)	Pb-214 Bi-214	4.185
^{40}K ($Bqkg^{-1}$)	K-40	0.893

Additionally, the minimum detectable activity (MDA) of the HPGe detector were calculated using equation 4 below,

$$\mathbf{MDA} = \frac{\mathbf{3} * \sqrt{\mathbf{Bg}}}{\mathbf{Pa}} * \mathbf{C}$$

Where;

Bg = the background count

Pa = the peak area

C is the activity concentration of radionuclide of interest.

The results were then presented in table 10 below,

Table 10: Minimum Detectable activities of Radionuclides

Radionuclide	Isotopes	MDA
^{232}Th (Bqkg^{-1})	Pb-212 Ac-228	3
^{238}U (Bqkg^{-1})	Pb-214 Bi-214	5
^{40}K (Bqkg^{-1})	K-40	45

The values were evaluated using a blank sample, which in this case, distilled water with similar packaging and geometry as the samples. The MDA depends on the counting effectiveness of the detector and also the probability of emission per disintegration of the selected gamma line (Knoll, 1999). In this study, the MDA for the detector ranged from 45 Bq kg^{-1} for ^{40}K to 3 Bq kg-1 for ^{232}Th.The higher MDA for ^{40}K, about ten times that of ^{232}Th and ^{238}U, could be attributed to the lower emission probability of ^{40}K which is about 10.7 % as compared 31 % and 45 % for thorium and uranium series respectively.

The measurements of concentration levels of activities of radionuclides U, Th and 40K of the soil samples studied are presented in the Table 11 below. The results were determined to range between 43-864 Bq. Kg-1 for 40K, 23-99 Bq. Kg-1 for Th and 15-68 Bq. Kg-1 for U. In some soil samples, high values were recorded which was attributed to the composition of the geochemical and source of the types of soils in a given area. This was attributed to the presence of phosphate, sandstone, granite and quartz which are radioactive rich.

Table 11: Radioactivity levels (Bq.Kg-1) of U, Th and 40K in the Soil Sample

SAMPLE SITE	K-40	Th	U
S1	746±0.153	55±0.0014	32±0.033
S2	452±0.905	36±0.958	23±0.648
S3	483±0.831	42±0.467	36±0.379

SAMPLE SITE	K-40	Th	U
S4	196±0.008	68±0.051	51±0.218
S5	102±0.216	23±0.561	17±0.892
S6	105±0.559	41±0.227	31±0.743
S7	85±0.249	31±0.743	20±0.262
S8	151±0.516	44±0.289	38±0.775
S9	100±0.613	39±0.812	22±0.268
S10	491±0.445	81±0.480	41±0.073
S11	102±0.142	41±0.073	27±0.795
S12	102±0.142	24±0.805	17±536
S13	545±0.371	81±0.714	41±0.337
S14	186±0.578	64±0.777	48±0.178
S15	855±0.210	99±0.612	53±0.345
S16	107±0.169	36±0.317	22±0.892
S17	79±0.678	26±0.366	21±0.859
S18	673±0.532	93±0.484	63±0.409
S19	633±0.190	66±0.361	40±0.385
S20	719±0.219	53±0.831	42±0.320
FS21	76±0.760	25±0.069	19±0.185
S22	43±0.803	34±0.24	15±0.524
S23	94±0.175	37±0.198	23±0.876
S24	110±0.879	26±0.767	19±0.647
S25	864±0.465	75±0.190	40±0.450
S26	84±0.459	28±0.234	21±0.532
S27	441±0.678	37±0.039	24±0.742
S28	204±0.539	71±0.673	68±0.402
Average	315.670	49.643	32.478
Standard deviation	274	22	14
Min	43±0.803	23±0.561	15±0.524
Max	864±0.465	99±0.612	68±0.402

According the study, the concentration of K-40 was determined to be greater than Thorium and Uranium in all the soil samples that were collected. Therefore, K-40 was concluded to be the most abundant radioactive element among the elements which were considered in the study. The distribution of concentration of nuclides is as shown in the figure 23 below.

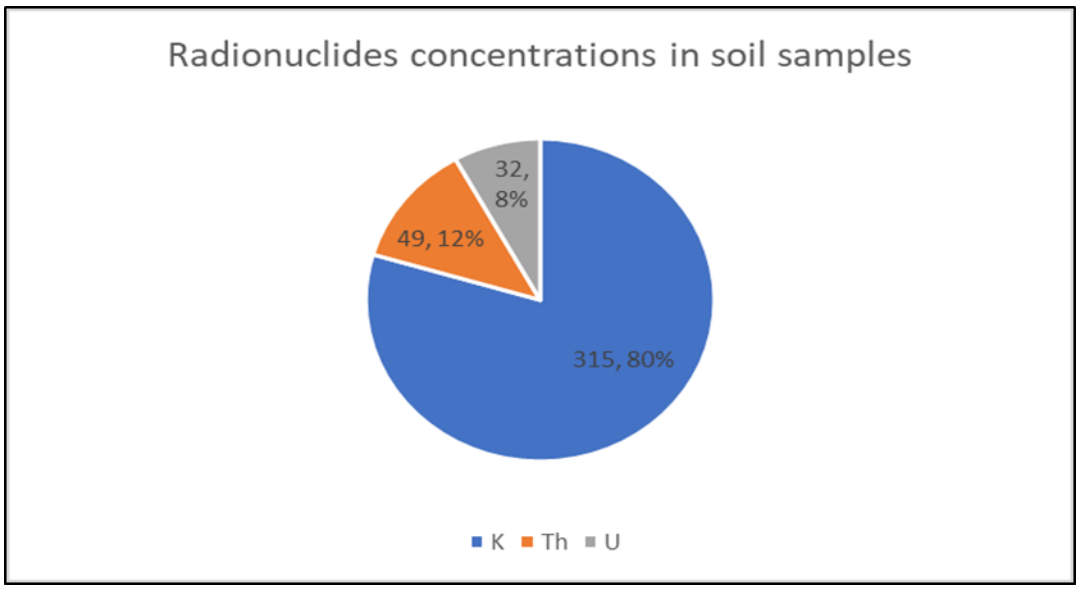

Figure 23: Pie chart orientation of the concentrations of K, Th and U

4.4.1 CORRELATION ANALYSIS OF RADIONUCLIDE ACTIVITY

The correlations between the radionuclides activities determined in the soil samples were performed to test the coefficients. The statistical significance of correlation among the samples was determined using values range between negative one and one. A positive correlation was used to signify that the existence of each radioactive affect the other and a negative correlation signify that existence of nuclide does not affect the existence of the other radioactive nuclide. The correlation test was presented in Figure 24 and Figure 25 below.

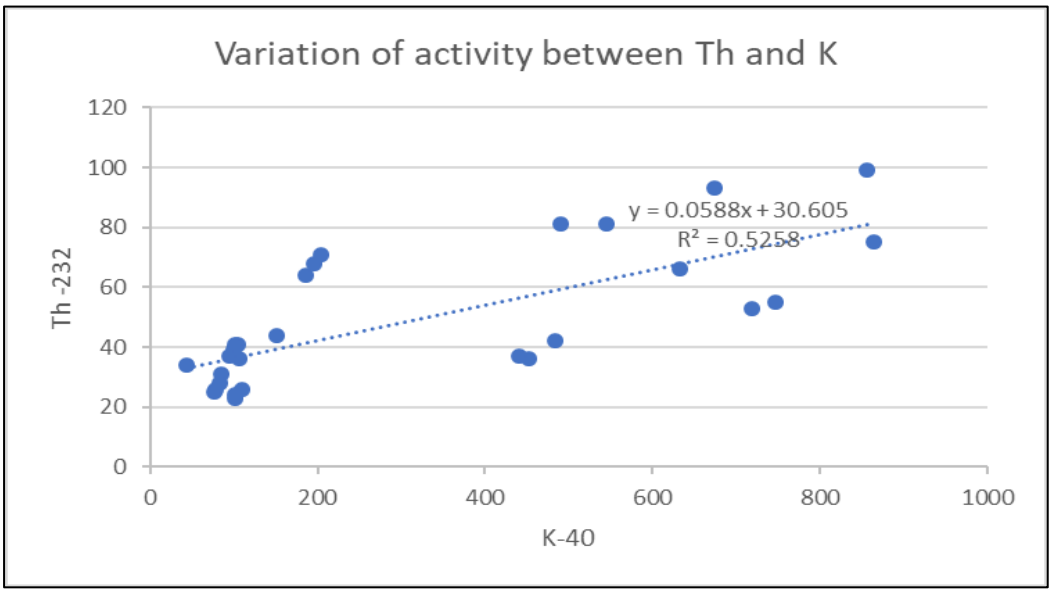

Figure 24: Variation of the Activity between Th -232 and K-40

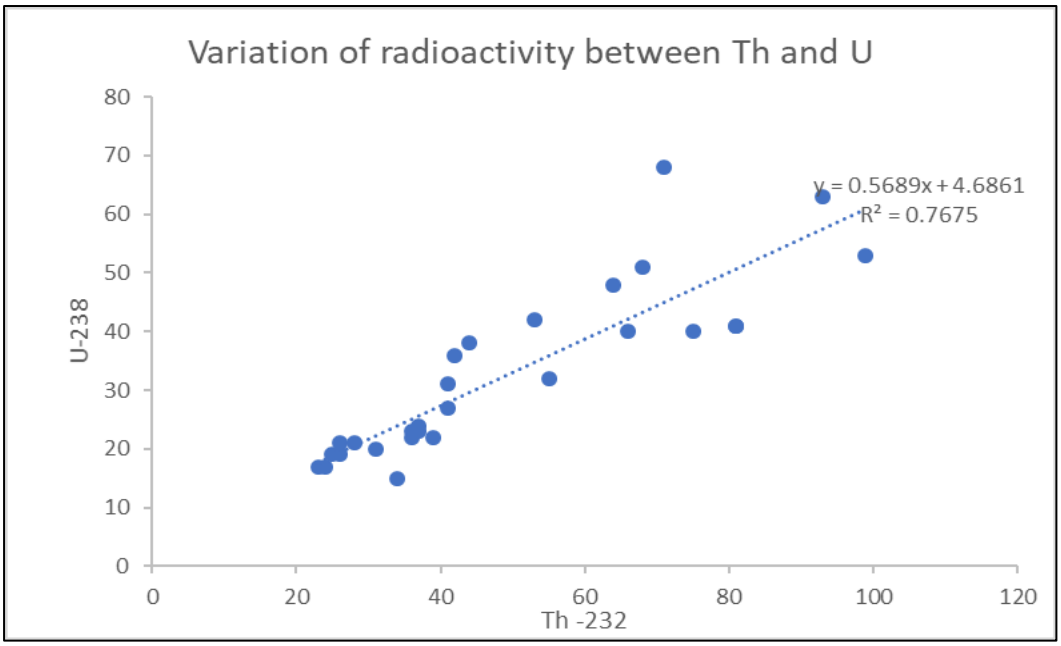

Figure 25: Variation of the Activity between Th-232 and U- 238

The figures 24 and 25 demonstrate a strong positive correlation that is between the activities from the K-40 and Th-232 since R=0725 and a strong positive correlation between the activities of U-238 and TH-232 since R=0.8760. These strong correlations

among radionuclides can attributed to the fact that they are from common origin and are therefore affected by the same geological factors

4.4.2 RADIATION HAZARD INDEX CALCULATIONS

The gamma-ray radiation hazards were determined using different indices. This is due to specific radionuclides of 226Ra, 232Th, and 40K. Since natural radioactivity in the soil is majorly from 238-U series, 232-Th series, and 40-K, determination of the radiation hazard indices is done by their radioactivity levels. The contribution due to the presence of 238-U is represented by the decay product 226-Ra due to the fact that 98.5% of its radiological effects is normally as a result of radium and the daughter products (Hamideen, M.S.; Sharif, J, 2012). The concentration activities of the radionuclides of interest for the 84 samples were determined using equation 3 as presented in appendix 4. Table 12 presents the mean activity concentrations values (± standard deviation) for 40-K, 232-Th and 238-U, at a 315 ± 74 Bq kg^{-1}, 49 ± 12 Bq kg^{-1} and 32 ± 10 Bq kg^{-1}, respectively. According to UNSCEAR (2000), the global mean of the reported activity concentrations is 420 Bq kg^{-1} for ^{40}K, 45 Bq kg^{-1} for ^{232}Th and 33 Bq kg^{-1} for ^{238}U this is comparable to the mean reported in this assessment. The activity concentration values recorded for the soil samples were further used to assess the radiological risks pose to the miners and residents. Various radiation hazard indices were used. A radiation hazards index is a single parameter representative of the measured activity levels of ^{40}K, ^{232}Th and ^{226}Ra (Uranium series) in the sample. The radiation hazard indices used in this study includes radium equivalent (Ra_{eq}) calculated using equation 5 below,

$$Ra_{eq} = A_{Ra} + 0.077A_{Ra} + 1.43A_{Th} \leq 370\ BqKg^{-1}$$

The representative gamma index I_γ was calculated using the equation 6 below,

$$I_Y = \frac{A_{Ra}}{150} + \frac{A_{Th}}{100} + \frac{A_K}{1500} \leq 1$$

And external and internal hazard index (H_{ex} and H_{in}) using equation 7 and 8 respectively,

$$H_{Ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1 \quad \text{..... Equation 7}$$

$$H_{In} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 8}$$

Radium equivalent is the weighted mean activity of three natural radionuclides, based on the assumption that 1 Bq kg^{-1} of ^{226}Ra gives a γ- ray dose rate equal to 0.7 Bq kg^{-1} of ^{232}Th, and 13 Bq kg^{-1} of ^{40}K, in the environment (Avwiri et al, 2007). According to this study the Raeq values varied from 57- 260 Bq/kg and average Raeq value was found to be 126 ± 61Bq/kg. The average Ra_{eq} values was estimated at a value less than the set limit of 370 Bq Kg^{-1} and at a mean of 126 ± 61 Bq kg^{-1}. For gamma representative index, a mean value of 0.91 ± 0.49 was recorded (UNSCEAR, 2000).

This index is used as a tool for screening construction material where it correlates the excess external radiation to the annual dose rate. The limit for Iγ is set at one, that is corresponding to an annual effective dose of ≤ 1 mSv (Avwiri et al, 2007). Although the mean Iγ value is below one, there are some sampling site that surpassed the limit. For instance, S16 recorded a value of 1.91, almost double the limit. This means that if construction materials from such sites are used it can lead to higher exposure levels. H_{ex} and H_{in} were determined at a median of 0.33 ± 0.16 and 0.42 ± 0.2 respectively and recorded in the table 13 below. The values were determined to be within the set unity limit. This means that the external gamma radiation exposure as well as the internal exposure to respiratory organs in the dwellings can be considered insignificant.

Table 12: Average radioactivity levels (UNSCEAR, 2000)

	^{40}K (Bq kg^{-1})	**^{232}Th (Bq kg^{-1})**	**^{238}U (Bq kg^{-1})**
Average	315 ± 274	49 ± 22	32 ± 14
Min	43	23	15
Max	864	99	68
Global Mean*	420	45	33

Table 13: Calculated radiation indices* (UNSCEAR, 2000)

	I_γ	R_{aq} (Bq kg-1)	H_{ex}
Average	0.91 ± 0.49	126 ± 61	0.33 ± 0.16

Min	0.35	57	0.15
Max	1.91	260	0.7
Limit*	1	370	1

Similar radiological studies carried out in this region, coastal Kenya. Osoro et al. (2011) conducted a baseline study on radioactivity measurements around Maumba and Nguluku villages near the titanium mines. On comparing the measured mean values with other studies, the values reported are observed to be higher compared to the measured values of 27.5 ± 9.2 Bqkg $^{-1}$, 20.8 ± 7.7 Bqkg $^{-}1$ and 69.6 ± 16.4 Bqkg $^{-1}$ for ^{232}Th, ^{226}Ra, and ^{40}K. In Mrima Hill, comparatively higher mean activity concentrations of ^{238}U of ^{232}Th and ^{40}K were reported at; 207 ± 11 Bq kg^{-1}, 500 ± 20 Bq kg^{-1} and 805 ± 21 Bq kg^{-1}, respectively. Estimated annual average effective dose rate determined was at 1.1 ± 0.02 mSvy^{-1}, while the mean absorbed dose rate at 1 m distance above ground at 440 ± 16 nGyh-1. Similar findings were reported by Patel (1991), where external gamma radiation dose was reported fifty times the recommended limits. The area was hence declared a high background radiation area.

However, in this study, the average values of the obtained radiological effects: the external (Hex), the radium equivalent activity (Raeq) and the internal (Hin) hazard indices, the radioactivity level index (Iγ) were determined to be within the limits of the values internationally recommended. Therefore, there are no harmful radiation effects that are posed to inhabitants of the Kinondo area.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Heavy metals were identified in soil samples collected from Kinondo area. Their distributions in soil samples were also determined at substantial levels. The results showed concentrations of the following heavy metals; Fe, Zn, Pb , Mn , Zr and Ti. Based on the heavy metal concentrations, this study indicates that the major elemental constituents are Fe (0.5 – 8.5 %), followed by Ti (0.3 – 1.5 %). The values of levels of concentrations for other heavy metals like Zn and Pb were determined to be below 0.01%.

According to this study, there was non-uniform distribution of the concentrations of heavy metal in soil profiles. In some samples, concentrations of the heavy metal were found to be higher at a 0-20 cm depth compared to 20-30 cm depth, 30- 50 cm and vice versa. In other cases, there were similar concentrations of heavy metals in two soil profiles or even all the three soil profiles. This was attributed to the difference or similarity of the source of heavy metals contamination. In cases where the concentrations of the heavy metals were reported to be higher at the top soil profiles, it was deduced that heavy metals were of anthropogenic origin. However, in cases where the concentration of the heavy metals was determined to be higher at the middle and bottom soil profiles, the heavy metals were concluded to be of geogenic origin.

The results showed radionuclide content, distribution patterns and correlations in the soil profiles. The following radionuclides were determined; 238-U, 232-Th, 40-K. According to the study, 40-K was found to be the most abundant radionuclide followed by 232-Th and U-238. The level of natural radioactivity measured in soil samples showed normal radioactivity levels. The measured values of the radioactivity levels were determined to be all above the world average values but below the recommended ICRP limits.

The external radiation hazard index from the soil samples analyzed were determined to be below unity. The radium equivalent was reported to be below the 370 Bq kg^{-1} world average value. The values for Radium equivalent (Raeq), Radiation hazard index (Hex)

indicated that monitored areas have normal levels of natural radioactivity and therefore classified as a risk free area. Therefore, it was concluded that the area does not pose a radiation exposure hazard risks to the residents.

In general, according to the study on the levels of concentrations of the heavy metals in the samples, it was demonstrated that elemental content is within the reported global averages hence non-toxic levels. The findings indicate that there has been no significant contamination of surface soils in Kinondo area due to the mining processes taking place at Base Titanium mines in Kwale County.

5.2 RECOMMENDATIONS

1. The study recommends that the concepts of the pH of the soil samples be assessed in order to ascertain the heavy metal solubility and mobility variations in soils. This will enable the assessment of the organism's uptake of heavy metals, environmental accumulation and the toxicological bioavailability.
2. Since this study only covered the soil, it would therefore be important that further research be conducted on the water samples. This should therefore cover activity levels in plants used for food and water used for cleaning and drinking to gauge the ingested radiation by the people living in Kinondo area either by drinking or through food.
3. According to the study, the variation in depth of the soil profiles did not report significant difference in heavy metal and radioactivity levels. Therefore, it is highly recommended that a research is undertaken to soil samples from depths greater than 30cm to enable more comparison in the variation of the concentrations with depth.
4. Even though the activity values recorded for this study are within recommended ICRP limits, the Government of Kenya, through the Kenya Nuclear Regulatory Authority should ensure continued and frequent monitoring of Kwale county and neighboring areas to monitor any enhanced radioactivity level that can put the workers and the public at risk.

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APPENDICES

Appendix 1: Concentration levels for Fe and Ti (%)

	Fe			Ti		
	B	**M**	**T**	**B**	**M**	**T**
S1	0.0391	0.0303	0.0231	0.0108	0.0123	0.0105
S2	0.0439	0.0049	0.0295	0.0089	0.0108	0.0086
S3	0.0354	0.0278	0.0308	0.0101	0.0106	0.0145
S4	0.0231	0.0115	0.0061	0.0075	0.0065	0.0048
S5	0.0103	0.0075	0.006	0.0083	0.0121	0.0064
S6	0.0372	0.0387	0.0321	0.0129	0.0132	0.0133
S7	0.00286	0.0158	0.0116	0.0093	0.0121	0.0065
S8	0.00418	0.0032	0.0319	0.0049	0.0085	0.0115
S9	0.00313	0.0314	0.0243	0.0088	0.0103	0.0108
S10	0.0076	0.0063	0.0061	0.0112	0.0009	0.0078
S11	0.0159	0.0172	0.0077	0.0031	0.0133	0.0075
S12	0.0046	0.0048	0.0055	0.0072	0.0101	0.0084
S13	0.0057	0.0083	0.0076	0.0011	0.0014	0.0121
S14	0.00305	0.0324	0.0244	0.0087	0.0101	0.0092
S15	0.0051	0.0054	0.0089	0.0104	0.0059	0.0113
S16	0.0039	0.0334	0.0267	0.0078	0.0081	0.0117
S17	0.00358	0.0381	0.0338	0.0061	0.0072	0.0077
S18	0.00323	0.0281	0.0319	0.008	0.0081	0.0066
S19	0.00301	0.0313	0.0225	0.0087	0.0032	0.0116
S20	0.0065	0.0104	0.0086	0.0142	0.0139	0.0124
S21	0.00259	0.0274	0.0203	0.0112	0.0125	0.0095
S22	0.00432	0.0546	0.0362	0.0011	0.0014	0.0133
S23	0.00266	0.0219	0.0109	0.0129	0.0119	0.0123
S24	0.00248	0.0278	0.0254	0.0071	0.0096	0.0096
S25	0.0089	0.0104	0.0009	0.0112	0.0111	0.0087
S26	0.00846	0.00771	0.00505	0.0062	0.00111	0.0062
S27	0.00052	0.0046	0.0052	0.0122	0.0113	0.0088

	Fe			Ti		
	B	**M**	**T**	**B**	**M**	**T**
S28	0.0004.03	0.0352	0.0322	0.0085	0.00786	0.0032
Average	0.00272	0.0256	2.03	0.0092	0.00103	0.0094
STDEV	0.00172	0.00167	0.00121	0.0025	0.0026	0.0027
Minimum	0.0046	0.0046	0.0052	0.0031	0.0032	0.0032
Maximum	0.0846	0.0771	0.0505	0.0142	0.0014	0.0145

Appendix 2: Concentration levels for Mn and Zr (%)

	Mn			Zr		
	B	**M**	**T**	**B**	**M**	**T**
S1	0.0672	0.0898	0.1789	0.0878	0.1438	0.1388
S2	0.0438	0.0663	0.1025	0.0902	0.1020	0.1241
S3	0.0471	0.0801	0.1416	0.0669	0.1129	0.1236
S4	0.0089	0.0096	0.0143	0.0764	0.0955	0.0926
S5	0.0138	0.0251	0.0371	0.0888	0.0026	0.0997
S6	0.0208	0.0321	0.1236	0.0995	0.1242	0.1294
S7	0.0643	0.1045	0.1543	0.0731	0.1155	0.1326
S8	0.0325	0.0347	0.1681	0.0658	0.1079	0.1045
S9	0.0401	0.0582	0.1841	0.0864	0.0793	0.1312
S10	0.0137	0.0227	0.0335	0.1373	0.1234	0.1318
S11	0.2704	0.3091	0.0814	0.2308	0.2081	0.2173
S12	0.0689	0.0869	0.0934	0.1144	0.1631	0.1148
S13	0.0506	0.0746	0.1164	0.2377	0.2362	0.2516
S14	0.0392	0.0581	0.1340	0.078	0.0954	0.1383
S15	0.0307	0.0643	0.1068	0.152	0.1418	0.1370
S16	0.0272	0.042	0.1363	0.0503	0.0834	0.1620
S17	0.0195	0.029	0.0710	0.0479	0.0451	0.0722
S18	0.0360	0.0491	0.0722	0.0757	0.1008	0.0982
S19	0.0823	0.122	0.2695	0.0661	0.0867	0.1331
S20	0.0134	0.0149	0.0196	0.1599	0.1536	0.1870
S21	0.0424	0.0592	0.0742	0.1803	0.1797	0.1680
S22	0.1188	0.188	0.2212	0.1122	0.1259	0.1499
S23	0.0949	0.1057	0.1185	0.1234	0.1397	0.2192
S24	0.0598	0.1044	0.1929	0.0806	0.1133	0.0887
S25	0.0435	0.0761	0.0667	0.1208	0.0795	0.1089
S26	0.0766	0.1203	0.1562	0.0468	0.0522	0.0880
S27	0.0240	0.0199	0.0339	0.1526	0.2027	0.1645
S28	0.0322	0.0312	0.1048	0.0689	0.0613	0.0808
Average	0.0529	0.0742	0.1145	0.106	0.1169	0.1352
STDEV	0.0492	0.0601	0.0615	0.0496	0.0504	0.0427
Minimum	0.0089	0.0096	0.0143	0.0468	0.0026	0.0722
Maximum	0.2704	0.3091	0.2695	0.2377	0.2362	0.2516

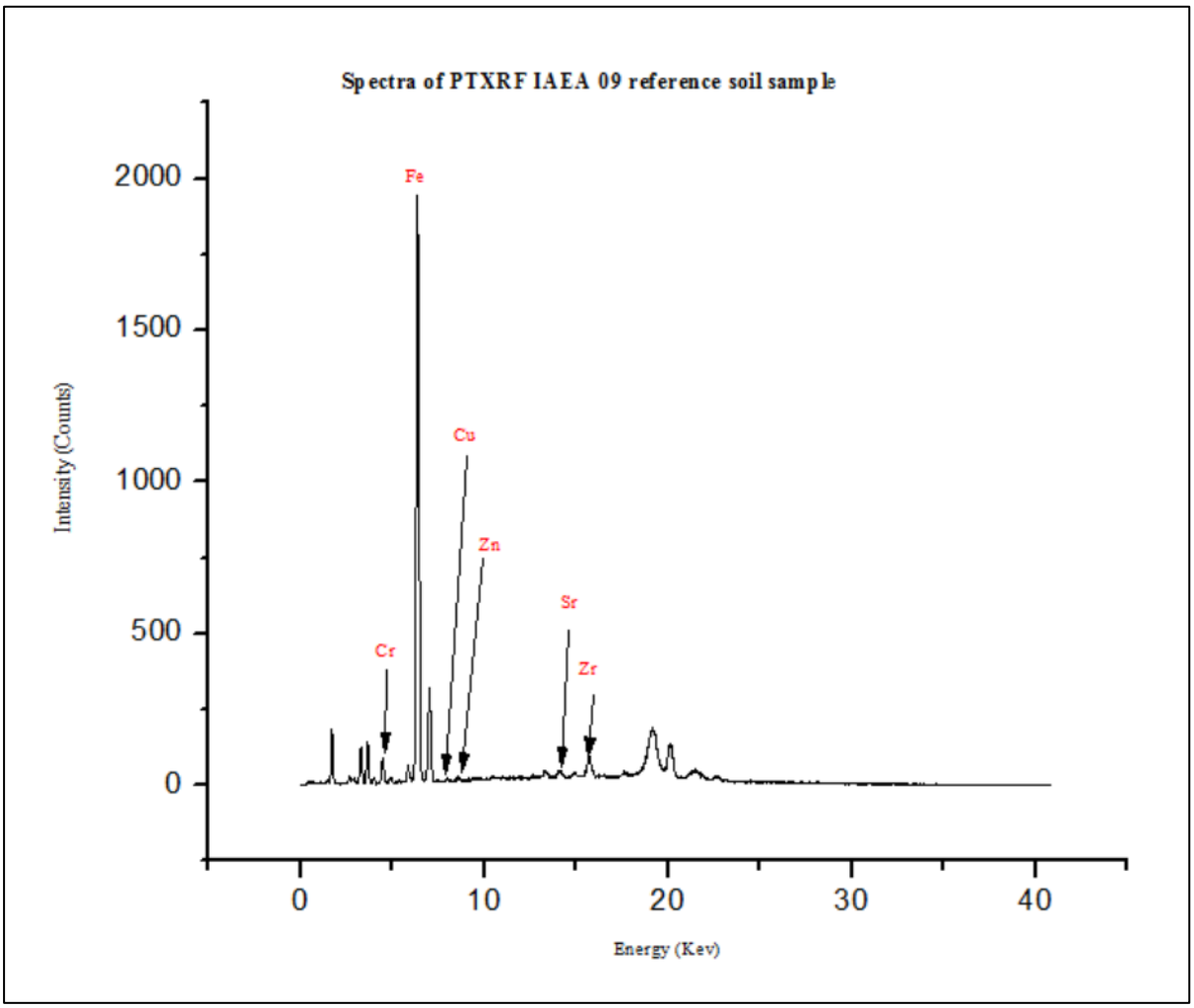
Appendix 3: Concentration levels for Zn and Pb (%)

	Zn			Pb		
	B	**M**	**T**	**B**	**M**	**T**
S1	0.0039	0.0030	0.0039	0.0029	0.0033	0.0025
S2	0.0034	0.0034	0.0027	0.0045	0.0031	0.0038
S3	0.0044	0.0046	0.0049	0.0028	0.0031	0.0035
S4	0.0014	0.0011	0.076	0.0024	0.0027	0.0018
S5	0.0009	0.0011	0.0526	0.0043	0.0015	0.0031
S6	0.0027	0.0041	0.0037	0.0033	0.0042	0.0025
S7	0.0012	0.0009	0.0009	0.0051	0.0058	0.0054
S8	0.0049	0.0031	0.004	0.0034	0.0035	0.0033
S9	0.0034	0.0042	0.0027	0.0037	0.0034	0.0044
S10	0.0006	0.0007	0.0006	0.004	0.0034	0.0031
S11	0.0013	0.0007	0.0009	0.0051	0.0039	0.0042
S12	0.0008	0.0004	0.0007	0.0041	0.004	0.0035
S13	0.0008	0.0005	0.0006	0.0038	0.0042	0.0043
S14	0.004	0.0047	0.005	0.0034	0.0035	0.0005
S15	0.0007	0.0012	0.0009	0.0042	0.0032	0.0043
S16	0.0063	0.0053	0.0046	0.0022	0.0025	0.0026
S17	0.0029	0.0028	0.0032	0.0033	0.003	0.0031
S18	0.0032	0.004	0.0032	0.0033	0.004	0.0024
S19	0.0034	0.0035	0.0029	0.0035	0.0039	0.0042
S20	0.0008	0.0008	0.0005	0.0024	0.0025	0.0029
S21	0.0021	0.002	0.0022	0.0027	0.0031	0.0025
S22	0.0039	0.0049	0.0036	0.0031	0.0033	0.0035
S23	0.0015	0.0013	0.0008	0.0054	0.0044	0.003
S24	0.0032	0.0033	0.0025	0.0027	0.0039	0.0038
S25	0.0012	0.0013	0.0016	0.0063	0.0071	0.0068
S26	0.004	0.0004	0.0038	0.0034	0.0028	0.0022
S27	0.0006	0.0007	0.0004	0.0033	0.0034	0.003
S28	0.0022	0.0011	0.0014	0.0038	0.0032	0.0033
Average	0.002489	0.0024535	0.002267	0.003657	0.0035814	0.0034153
STDEV	0.00152135	0.00158	0.001501	0.009529	0.001034	0.001039
Minimum	0.0006	0.0004	0.0004	0.0022	0.0015	0.0018
Maximum	0.0063	0.0053	0.005	0.0063	0.0071	68

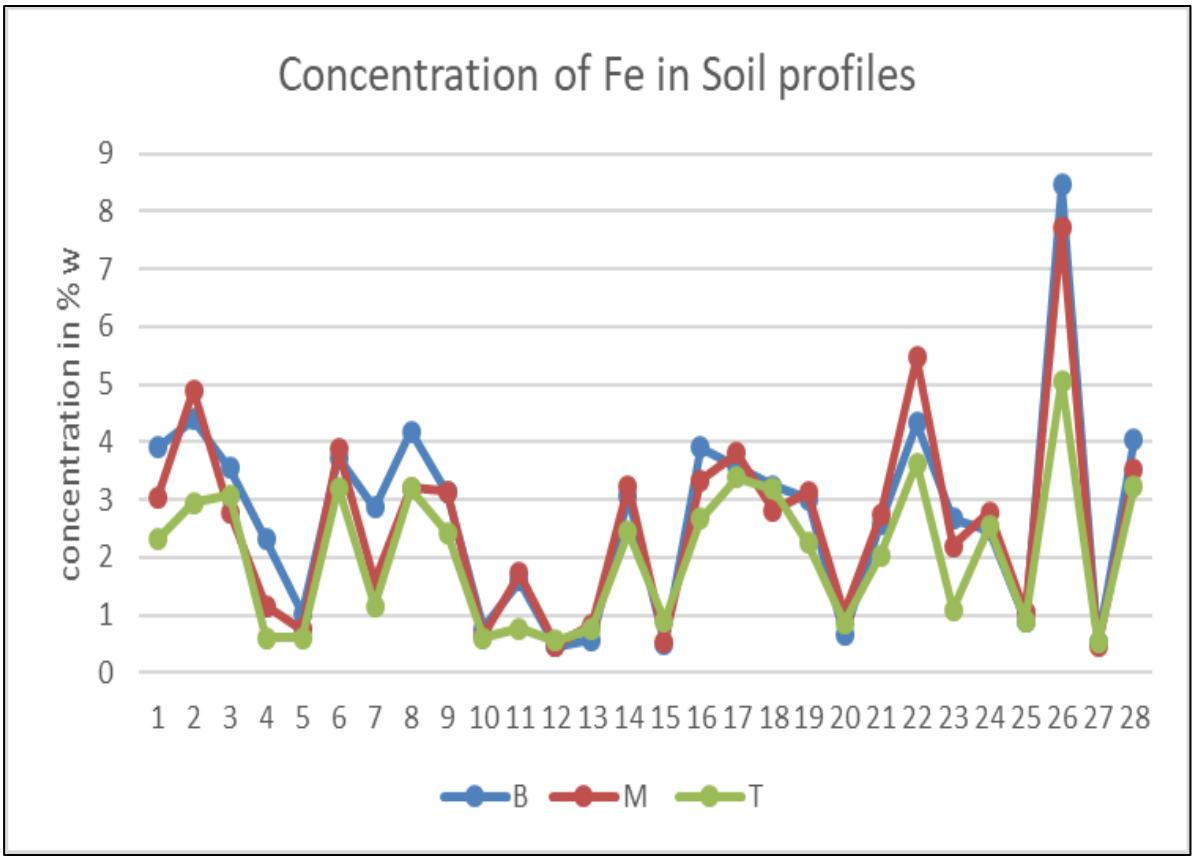
Appendix 4: Radionuclide concentration (Bq/kg) and respective radiation hazard indices (units)

	K	Th	U	Iyr	Raq (Bq kg-1)	Hex	Hin	Dr
S1	746	55	32	33	168	0.45	0.54	79
S2	452	36	23	23	109	0.29	0.35	51
S3	483	42	36	36	133	0.35	0.45	62
S4	196	68	51	51	163	0.44	0.57	72
S5	102	23	17	17	57	0.15	0.2	25
S6	105	41	31	31	97	0.26	0.34	43
S7	85	31	20	20	70	0.19	0.24	31
S8	151	44	38	38	112	0.3	0.4	50
S9	100	39	22	22	85	0.23	0.29	37
S11	491	81	41	42	194	0.52	0.63	88
S12	102	41	27	27	93	0.25	0.32	41
S13	102	24	17	17	59	0.15	0.2	26
S14	545	81	41	42	198	0.53	0.64	90
S15	186	64	48	48	153	0.41	0.54	68
S16	855	99	53	54	260	0.7	0.84	119
S17	107	36	22	22	81	0.22	0.28	36
S18	79	26	21	21	64	0.17	0.23	28
S19	673	93	63	64	247	0.66	0.83	113
S20	633	66	40	41	183	0.49	0.6	84
S21	719	53	42	43	173	0.46	0.58	81
S22	76	25	19	19	60	0.16	0.21	27
S23	43	34	15	15	66	0.18	0.22	29
S24	94	37	23	23	83	0.22	0.28	36
S25	110	26	19	19	64	0.17	0.22	29
S26	864	75	40	41	213	0.57	0.68	99
S27	84	28	21	21	67	0.18	0.23	30
S28	441	37	24	24	110	0.29	0.36	51
Avg.	315	49	32	32	126	0.33	0.42	57
Stdev.	274	22	14	14	61	0.16	0.2	28
Min	43	23	15	15	57	0.15	0.2	25
Max	864	99	68	68	260	0.7	0.84	119

Appendix 5: Typical Spectrum of PTXRF IAEA 09 Reference Soil Sample



Appendix 6: Concentration variation in Fe Soil Profiles



Appendix 7: Concentration variation in Ti Soil Profiles