University of Nairobi

College of Architecture and Engineering

Institute of Nuclear Science and Technology

Impact of Iron Ore Mining on Heavy Metal Concentration in Soils of Kishushe area in Wundanyi, Taita Taveta County

by

Benard Kiprotich Cheneket

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Dedication

I dedicate this thesis to my wife, Peninah and sons, Ahaz and Andrew.

Acknowledgement

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List of Abbreviations

XRF -   X-Ray Fluorescence

IOSHIC -   International Occupational Safety and Health Information Centre

BIF -   Banded Iron Formation

IAEA -   International Atomic Energy Agency

XRD -   X-Ray Diffraction

EAC -   East Africa Community

ANOVA -   Analysis of Variance

PLI -   Pollution Load Index

EF -   Enrichment Factor

WHO-   World Health Organization

FAO-   Food and Agriculture Organization

LLD-   Limits of Detection

Abstract

The study of heavy metal deposition and accumulation in soils is of great interest due to the negative consequences it presents to environment and human health. Mining and milling activities such as ore grinding, ore concentration, and disposal of mine waste and waste water contribute to heavy metal pollution in the environment. These metals can be deposited in soils through discharge and dispersion to nearby agricultural soils. Once deposited in soil, they can be transmitted to ground water, surface water, food and atmosphere. Therefore, soil pollution directly threatens human health through its impacts on quality of food, drinking water and air. This study aimed at investigating and evaluating the impact of iron ore mining on heavy metal concentration in soils of Kishushe area in Wundanyi. The concentration levels as well as the distribution patterns were investigated. Fe was found to be the main constituent in soil samples at $8 - 12.5$ %. Other elements that were determined at substantial levels were Mn ($1,540 - 3,940$ µg g^{-1}), Ti ($2,472 - 17,300$ µg g^{-1}), Cu ($71 - 496$ µg g^{-1}), Zn ($76 - 130$ µg g^{-1}), Sr ($51 - 184$ µg g^{-1}), Zr ($259 - 590$ µg g^{-1}) and Pb ($26 - 68$ µg g^{-1}). The global average values for agricultural soils are Fe (5%), Ti ($10,000$ µg g^{-1}), Mn ($2,000$ µg g^{-1}), Sr ($1,000$ µg g^{-1}), Zr (550 µg g^{-1}), Zn (300 µg g^{-1}), Cu (120 µg g^{-1}) and Pb (70 µg g^{-1}). Pb, Zn, Sr and Zr levels were within the global values while Fe, Cu, Ti and Mn were slightly above. It was also observed that the levels were generally higher in study area than those recorded in the control area. The soil samples analysed by XRD technique showed the minerals quartz, albite, microcline and hornblende were present in substantial amounts. In conclusion, although the study showed that the contamination levels are low, it is important to put in place pollution mitigation measures and strictly adhere to them. It is also necessary to conduct follow-up studies to assess any changes.

CHAPTER 1

INTRODUCTION

1.1   Background

Heavy metal deposition and build up is of great research interest as a result of adverse effects presented to both environment and human health, at concentrations above set limits. Soil heavy metal contamination can emanate from both natural processes and anthropogenic activities.   Crustal composition greatly influences heavy metal concentration of a particular area, with natural processes such as weathering of rocks leading these metals to spread widely (Scroder et al., 2004; Abrahams, 2002). On the other hand, anthropogenic activities linked to vehicle emissions, industry, combustion of fossil fuels, agriculture, and exploration and metallurgy, in addition to their waste disposal are key sources of metal contamination (Likuku *et al.*, 2013).

Serious concerns have been raised over heavy metal pollution in soils. This is based mainly on three key reasons. First, as a consequence of anthropogenic activities, heavy metals can build up in the soils to levels that are toxic to plants. Second, their off-site mobility to both surface and ground water has the likelihood of contaminating drinking water resources. Third, heavy metals may build up in the food chain and have serious effects on human health through consumption of food grown on metal contaminated soils.

Once deposited in soil, heavy metals can be dispersed to far off areas. For instance, through wind and water erosion, these metals can easily be transported from the mines and waste disposal areas to far-off regions such as agricultural lands. In addition, they can move to lower soil profiles, with a potential to even pollute ground water. The downward mobility of heavy metals is determined by the soil characteristics like pH, organic matter and electrical conductivity   (Dudal *et al.*, 2005), which in turn affect chemical speciation and solubility.

Soil is not just a medium for plant growth and disposal of waste, but also a transmitter of numerous pollutants to ground and surface water, food, as well as the atmosphere.

Consequently, soil pollution directly threatens human health through its effects on food quality, drinking water and air (Likuku *et al.*, 2013). For instance, uncontrolled input of heavy metals into soil is undesirable considering that their removal is challenging, hence build-up in soils. The subsequent concerns of accumulation include plant toxicity, water resources contamination, and dietary exposures. However, unlike in the past, environmental pollution agencies, government, together with the environmental researchers and engineers have emphasized on the effects of soil contamination on its characteristics as well as biosphere (Salami *et al.*, 2007).

Mining sector is acknowledged to bring about significant environmental pollution, whilst mining waste loads are key sources of long term pollutants of water and the environment in general. The mining wastes have ecological concerns due to their characteristics such as huge volumes that occupy vast areas, approximately 70% of the entire excavated materials from exploration activities (Younger, 2004) and the subsequent landscape damages, the negative effects to underground and surface water, flora and fauna, as well human beings.

Exploration and milling operations like ore grinding and concentration, disposal of tailings, as well as mine and mill wastewater, can lead to heavy metal pollution in the environment, and soil in particular. The tailings and wastewater contain heavy metals, which are often deposited in soils through discharge and dispersion of these wastes to the local agricultural lands (Olatunji and Kayode, 2008). Even though some of these metals like copper, cobalt, iron, zinc and manganese, play an important role both in plant and human well being, their exposure in high concentration levels can be toxic (Kabata-Pendias, 2010). Degree of toxicity of these metals is due to the fact that they're non-biodegradable and also have a tendency to build up in the food chain (Sunday *et al.*, 2013).

Considerable progress has been made with regard to research in heavy metal pollution in soil, as a consequence of mining and metallurgical processes globally (Likuku *et al.*, 2013). The knowledge gained has played a key role in effective management of soil quality, as well as in designing pollution mitigation strategies (Su et al., 2014). It

has also been a positive step towards achieving better environmental quality and land use management.

Kenya is a country that is well endowed with iron ore mineral, which should to be fully exploited to support development and economic growth. Considerable iron ore deposits have been found in Marimanti in Tharaka Nithi County, Ikutha in Kitui County, Migori in South Nyanza, and Kishushe in Taita Taveta County, among other many areas (Maranga *et al.*, 2013). This particular study is designed around Kishushe iron ore mines in Taita Tavata County. From the geochemical studies of this iron ore mines carried out by Mines and Geology department, it was observed that the deposits are of acceptable commercial standards (> 65.9% Fe_2O_3; Maranga *et al.*, 2013). Subsquently, the mining contracts have been awarded, and exploration and processing of the mineral is set to commence soon.

A study by Olatunji and Kayode (2008), associated mining with various environmental challenges such as environmental degradation as well as heavy metal contamination around mining areas. The situation is expected to be no different in Kishushe iron mines once the exploration activities commence. Discharge of tailings and spoiled heaps of the iron ore into the physical environment is also anticipated. These metals can easily be dispersed to far off areas, polluting the agricultural lands and water resources. Through plants, heavy metals in the soils enter the food chain, and with continued consumption of the foods from such areas, these metals may accumulate in the body and interfere with proper functioning of various body systems, thus posing serious health problems like cancer, heart diseases, among others. It is in this understanding that this research was conducted. The research aims at establishing the benchmark heavy metal concentration levels in soils in the surroundings of Kishushe Mines in Wundanyi, in order to assess the environmental impacts of iron ore mining operations in the region.

1.2   Statement of the Problem

Soil is crucial for food production, filtration and storage of water, as well as nurturing numerous species by way of provision of a habitat. Hence, proper management of soil resources is imperative. It is essential to be cognizant of the physical, chemical as well as the biological changes taking place in the natural soil as a result of contamination.

Heavy metals are categorized as one of the most hazardous sets of ecological contaminants due to their toxicity and persistence in the environment (Olatunji and Osibanjo, 2010). Furthermore, the mobile heavy metals can readily reach the ground as well as surface water, thus contaminating them. Bearing this in mind, it is imperative to regularly assess and keep track of the fate and transfer of heavy metals in soils, with an aim of determining the degree of contamination and potential health risk.

The integrity of agricultural soils in iron ore producing countries in Africa is under great threat due to iron ore mining and processing operations (Olatunji and Osibanjo, 2010). Considerable amounts of iron ore consisting heavy metals in tailings, mine wastes and low-grade iron ore may enter into the soils through atmosphere and improper disposal of mine wastes. Since agriculture is the backbone of Kenya's economy, soil contamination should be assessed in order to ensure safe environment, and food crops that are free of toxic amounts of heavy metals. Iron ore mining operations are currently underway in Kishushe area, although there have been no research studies to assess the impact of ore mining to the quality of agricultural soils within the region.

1.3   Justification and Significance of the Study

Rapid global changes are introducing new challenges in protection and conservation of environment, thus leading to the need of scientific data to assess the impacts of contaminants in the ecosystems. Activities such as iron ore mining discharge a lot of tailings and mining wastes containing heavy metals to the environment and pose a great threat to the integrity of soils, food crops and water bodies (Jung, 2001, 2008;

Gutiérrez Ginés *et al.*, 2010). In addition, enrichment of soils with heavy metals directly affects the productivity of ecosystems and have potential negative impacts on human and animal health, thus posing a great risk on safety of the mine workers and the residents in the environs of the mining area (Lim *et al.*, 2008).

With increased mining activities, the levels of heavy metals in the agricultural soils may increase, with subsequent accumulation in food crops. Studies on effects of iron ore mining on soils in Kishushe, TaitaTaveta County, are lacking. Therefore, this research seeks to evaluate the baseline concentrations of various heavy metals in top soils around the mine. The study will provide the benchmark concentrations of the heavy metals as a basis for protection of environmental health, safety and sustainability. In addition, the study will help in identifying the contaminated areas, if any, for eventual environmental protection and remediation measures.

1.4   Objectives

1.4.1   General Objective

The overall objective of this research is to investigate and evaluate the impact of iron ore mining on heavy metal concentration in soils of Kishushe area, Taita Taveta County.

1.4.2   Specific Objectives

1. To determine spatial distribution and total heavy metal concentrations in soil samples from the vicinity of Kishushe Iron ore Mines by use of X-ray Fluorescence (XRF) Technique.
2. To determine mineralogy of soil samples from the environs of Kishushe Mines using XRD.
3. To assess the extent of heavy metal contamination due to iron ore mining operations in the region.

1.5   Scope

This research will mainly focus on the environmental impact of Fe ore mining with respect to heavy metal pollution in Kishushe, TaitaTaveta County. Total heavy metal concentration levels and variations will be assessed, both in the mining areas and the neighboring farmlands.   In addition, mineralogy of the soil samples will be determined.

CHAPTER 2

LITERATURE REVIEW

2.1   Global iron ore exploitation and consumption

Iron ore is the raw material of iron, a metal with the highest consumption in the world. The ores are formed by geological processes which concentrate a small fraction of the iron in earth's crust into deposits that contain as much as 70% of iron (Srivastava et al., 2001). The main ores of iron minerals are hematite, magnetite, siderite and goethite (Muwanguzi *et al.*, 2012; Maranga *et al.*, 2013). About 98% of iron ore consumed all over the world is used for production of iron and steel. The remaining 2% is used for production of cement, ballast, pigments and special chemicals. The iron mineral resources in the world are estimated to surpass 800 billion tonnes of crude ore, which has more than 230 billion tonnes of iron (MoEF, 2007). Iron ore is produced by more than 50 countries globally, but the bulk production comes from only a handful of them (MoEF, 2007). These include Brazil, China, Australia, India and Russia, accounting for 80% of iron production in the world in the year 2006 (MoEF, 2007).

Republic of China has the highest demand for iron in the world. Its astonishing demand growth lead the three leading production companies in the world (CVRD, Tinto and BHP Billiton), to invest large amounts of money in order to increase iron ore production to satisfy its demand (MoEF, 2007). In the period 2000 to 2006, China's consumption of the imported iron ore had grown tremendously from 70 million to 300 million tons (MoEF, 2007). Therefore, China's high demand for iron ore remained the main driver of increased global demand of iron. The world steel makers consumed about 1.5 billion tons of iron ore in 2006 of which approximately 759 million tons was shipped worldwide (MoEF, 2007).

2.2   Iron Ore Mining in Kenya

In Kenya, the mining sector contributes to about 1% of the country's GDP, the bulk of which are non-metallic minerals (Delloite, 2016). Only a few mining activities of metallic minerals such as iron ore, lead, titanium and gold are underway (EAC, 2016). However, with intensive mineral exploration going on, and with several mining projects being initiated, mining exports are expected to increase contributing about 3% of GDP by 2030, thus becoming the fourth largest foreign exchange earner (EAC, 2016).

Iron ore deposits have been discovered in Taita-Taveta County in the coastal Kenya (Maranga et al., 2013). Some of the areas identified as having deposits that can be economically viable include, Kishushe, Shelemba, Kasighau, Mwandongo, Mwambirwa, Oza, Kamtonga and Daku locations (Maranga et al., 2013). These deposits exist in Banded Iron Formation (BIF), alluvial and reef deposits.According to Keller (1996), these deposits could be attributed to the fact that Taita-Taveta region lies within the Mozambique belt, which is a geological zone rich in gemstones and metallic minerals. Iron deposits have also been found in other areas in Kenya such as Meru, Ikutha, Embu, Lolgorien, Samburu, Marimanti, Samia and Funyula.

Kishushe iron ore mineral deposits are mainly hematite (Fe_2O_3) and magnetite (Fe_3O_4), and chemical analysis shows that the ores are of high quality; greater than 65 % Fe content (Maranga *et al.*, 2013). The records at Kenya's mines and geology department (MoMG, 2016), show that an exploration contract has been awarded to Wanjala Mining Company. The mining process is ongoing, with an annual iron ore production estimate of 100,000 tons. According to Maranga *et al.* (2013), two mining methods are being employed; mobile screening method for alluvial and BIF deposits, and open cast mining for reef deposits. The two methods entail clearing of vegetation as well as removal of topsoil and rocks of low grade of <58% Fe content (Maranga *et al.* 2013). Consequently, these can lead to widespread pollution and destruction of ecosystem.

Most of the mined iron is meant for export market. Prior to its exportation, the iron ore is semi-processed as part of value addition. At Kishushe, the ore semi-processing involves use of jaw crushers for size reduction (< 100mm), and vibrator screen for rock size classification. Rock sizes of between 10 - 60 mm are then fed on to magnetic separators, with sizes above 60 mm being conveyed into a cone crusher, while those less than 10 mm are separated using magnetic drums to obtain iron fines (Maranga *et al.*, 2013). Stock piling of beneficiated iron ore fines is done before transporting them for export and a separate area is used for stock piling of low grade ore which are further crushed into fine particles and beneficiated using magnetic separating drums. The non-magnetic fines are utilized in refilling the excavated areas (Maranga *et al.*, 2013).

2.3   Environmental Impact of Iron Ore Mining

Occurrence of huge iron ore deposits in Kishushe area is good and timely news for Kenya. It will help contribute towards the country's development agenda, as well as in diversifying the economy. However, there is a downside to these development; environmental degradation. Some of the most significant environmental concerns resulting from iron ore mining include; change in land-use patterns, land degradation, deterioration of flora and fauna, and impact on both surface and underground water as well as the drainage system (Erraiyan, 2014; Bhumika, 2014). Above all, elevation of metal content of soil and water resources is a key concern (Pereira *et al.*, 2008; Angelovičová and Fazekašová, 2014). The significance and magnitude of these effects on the environment depend on size and scale of exploration activities, in addition to topography, climatic conditions, nature of mineral deposits, method of mining, among others (MoEF, 2007).

In the case of iron ore in Kishushe, open cast mining method is mainly being used, as it is more economical, and the mineral deposits are close to the surface (Maranga *et al.*, 2013). Therefore, vast areas of land are being excavated, and forest cover destroyed. Consequently, apart from having adverse effects of benthic organisms, it may also have an impact on wildlife in the neighboring Tsavo National park, as well

as on availability of pasture to pastoral communities in the area. In addition, the soil structure will be affected resulting in enhanced soil erosion, low fertility, formation of sinkholes andsiltation of water systems e.g. rivers and dams (Tarras-Wahlberg *et al.*, 2001).

Contamination of agricultural soils and water resources with heavy metals is a major challenge associated with mining (Bhumika, 2014; Erraiyan, 2014; Humsa and Srivastava, 2015). For instance, during the pre-processing stage, the iron ore is ground into fine particles that are more mobile. The particles can easily be carried away by wind or water over long distances, with potential of contaminating not only the nearby lands, but also those that are miles away. In addition, the metals can find their way into river systems or even seep downwards polluting underground water.

Ediga *et al.* (2011) conducted a study on effects of pig iron slag on soil's biological, physico-chemical and enzymatic properties and found that soil pH increased marginally, while electrical conductivity, potassium, phosphorus and carbon contents were found to increase substantially in the polluted soil. These in turn had adverse effects on microbial population. Similarly, enzyme activities declined three-fold in the polluted area as compared to control area.

Another research conducted by Mghanga (2011) on mining and minerals in Taita Taveta raised the issues of environmental damage. The author noted that measures put in place by the government are rarely observed, since owners of the mines are more concerned with profit making than in environmental integrity. This could lead to environmental degradation and enhanced pollution levels not only in the mining area, but also surrounding agricultural lands. Similar observations were made by Kitula (2006), in a study on environmental and social economic impacts on mining in Geita District, Tanzania. Issues such as land degradation, deterioration in water quality, and harm to livestock and wildlife diversity were raised.

2.4   Trace elements and heavy metals in Iron Ore

In geochemistry, trace elements are the chemical elements whose concentration on the earth's crust is less than 0.1% by weight, while heavy metals refer to high atomic number elements including some of the trace elements. Although the former does not play an important role in the earth's crust make-up, they are of greater interest and significance in geology, metallurgy, ecology, agriculture, medicine, toxicology and many other fields.

Based on the level of impurities, iron ore can be categorized as high-grade ore (over 65 % Fe content), medium grade ore (62 – 64 % Fe content) or low-grade ore (< 58 % Fe content).   The other major constituents include silica, alumina, calcium, and magnesium. Heavy metals and trace elements such as Ti, P, Pb, Mg, Mn, Zn, and Cu are also present, though in small quantities (Srivastava *et al.*, 2001; Muwanguzi *et al.*, 2012).

Muwanguzi *et al.* (2012) conducted a study on characterization of various iron ores in Uganda. The deposits were found to be hematite (Fe_2O_3), of between 86.7 – 97.8 % Fe content (high grade). Manganese, zinc, lead and copper were determined at levels below 100 mg kg^{-1} while titanium was determined at between 200 – 1700 mg kg^{-1}. In a similar study by Olatunji and Kayode (2008) on heavy metal contamination of plants and soil in Itakpe iron ore mine in Nigeria, considerable amount of Pb, Mn, Ni, Cu, Ti, Zn and W were found in low-grade ore, tailings and wastes of mining operations. Consequently, if proper disposal mechanisms are not implemented, mine tailings and wastes can pose a great danger to the integrity of soils and rivers.

According to Kabata-Pendias and Pendias (2001), heavy metals like Pb, Cd, Ni, Cu, Mn, Zn, As, Cr, and tin are natural components of iron ore deposits, and therefore can be released into the environment in the process of extraction/ mining, smelting and refining of the ore. The study further reported an association between Ti^{2+}, Cr^{3+}, V^{3+}, Mn^{2+}, Pb^{2+}, Co^{2+}, U^{4+} and W^{5+} with iron (II) (Fe^{2+}) cations, and V^{4+}, Ti^{4+}, Cr^{3+}, Co^{2+}, Mn^{2+}, Pb^{2+}, U^{5+} and W^{5+} with iron (III) (Fe^{3+}) cations.

2.5   Heavy Metal Contaminants in Soils

Heavy metals may enter into the environment from mine wastes and tailings during mining and extraction operations or during the life cycle of the products (Figure 2.1). Contamination from landfills of mine tailings and waste from mining and extraction are important pathways besides the others. Through iron ore mining and extraction some heavy metals will be discharged as part of mine wastes and tailings (Boateng et al., 2012; EC, 2002). Studies have shown the following heavy metals are some of the composites of iron ore deposits: Ni, Cd, Mn, Pb, Cr, Cu, As, Zn and Ti (Olatunji and Osibanjo, 2012), which are released to the environment during mining, smelting and processing.

The heavy metal content in soils is the total sum of metals originating from human activities and natural sources. However, it is estimated that the human activities contribute a higher amount of heavy metals in the soils than natural sources (Nriagu and Pacyna, 1988). Generally, soils in the mined areas are biologically and chemically deficient (Vega et al., 2006), and are characterized by limited cohesion, instability, low nutrient, organic matter content and high concentrations of heavy metals (Boateng et al., 2012). Accumulation of heavy metal contaminants in soils, sediments and food crops can eventually lead to biodiversity loss and potential risks to animal and human health in the vicinity of mines area (Galan et al., 2003; Lee et al., 2001; Lim et al., 2008).
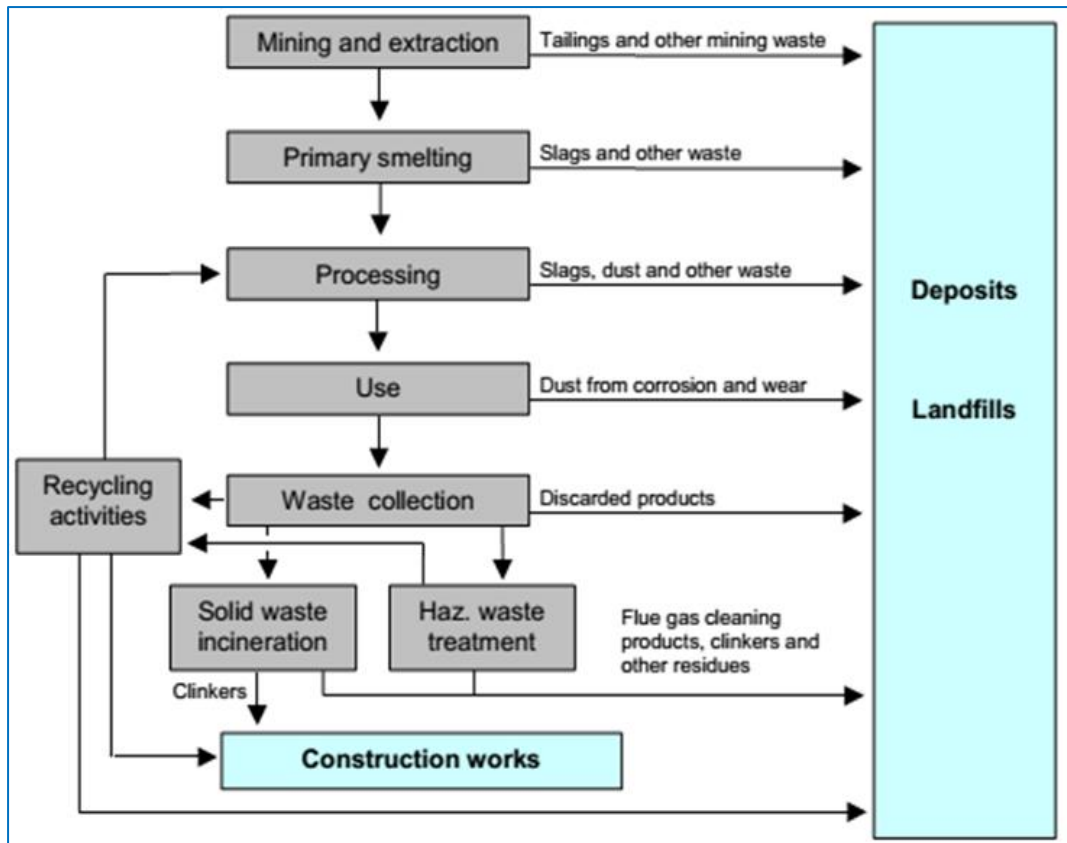
Figure 2.1:   Major pathways of heavy metals to soils, European Commission, EC
(2002).

Olatunji and Oladele (2012) conducted a baseline study on heavy metals in the topsoil
around iron ore mining field in Itkape North Central Nigeria. The mean
concentrations of the heavy metals were found to be: Zn, 43 - 75 $\mu g\ g^{-1}$; Cu, 33 - 51
$\mu g\ g^{-1}$; Pb, 18 - 33 $\mu g\ g^{-1}$; Mn, 6 - 20 $\mu g\ g^{-1}$; and Ni, 11 - 20 $\mu g\ g^{-1}$. Considering this
was a benchmark study, all the elements were determined within the natural
concentration range.   However, the author expressed fears that with the
commencement of exploration activities, the area could experience a surge in soils
heavy metal content.

On the other hand, Omono and Kakulu (2012) assessed the impact of iron ore mining
on various environmental samples from Itakpe Mine in Okene, Nigeria. Analyses of
the soil samples revealed that their heavy metal content was within the global average
values (Pendius A.K and Pendius H., 2001). However, these levels were higher than

those in soil samples collected from a nearby control area of similar geology. The author attributed this observation to aerial deposition, whereby dust laden metals resulting from iron processing find their way to soils, plants and water. Furthermore, the spatial variation of heavy metals in topsoil was indicative of their dispersion through erosion and wind.

2.6 Significance of Heavy Metals

Once heavy metals have been deposited in soil, they can have adverse effects on both plants and human beings. In plants, most of these metals are essential at low concentrations, however, above the tolerable limits they can lead to poisoning of the plant of even death. Their bio-availability to plants depends on soil's total metal content, soil pH and soil carbon/ organic matter content (Gupta *et al.*, 2008; Osman, 2012; Xu*et al.*, 2013). On the other hand, these metals can get into human body either directly through skin absorption and inhalation of dust, or indirectly through pollution of food, water and atmosphere (Su *et al.*, 2014). The effects of these metals on human health depend on type of metal and the level of exposure. In the next sub-sections, a brief discussion on various metals of interest in this particular study, their global abundance, as well as their effects on both plants and human beings is presented.

2.6.1 Lead

The principal sources of Pb contamination in soils, water and air are pyro metallurgical production of nonferrous metal, combustion of leaded fuel, cement production, combustion of coal, iron and steel manufacturing, and dumping of sludge (Weiner, 2000). Pb is also often found in mine waste, oil refineries, recycling facilities of lead-acid batteries and in lead-based paints. Globally, the soils lead content has been reported at a range of 10 to 67 $\mu g\ g^{-1}$, with anthropogenic sources constituting about 96% of global Pb emissions (Kabata-Pendias, 2010).

Pb is not an essential element, hence could be toxic to human beings and plants even at low concentration. In human beings, its poisoning could lead to loss of appetite, general weakness, anemia and colic. Other health effects include high blood pressure, peripheral nervous system damage and renal dysfunction (IOSHIC, 1999). In plants,

excessive lead accumulation could impair various physiological, morphological, and biochemical functions. It has been found that Pb strongly inhibits seed germination, seedling development, root elongation, transpiration, chlorophyll production as well as uptake of essential minerals (Pourrut *et al.*, 2011)

2.6.2 Zinc

Zn is contained in minerals in the form of sulphides, carbonates, oxides and silicates (Weiner, 2000). It occurs in both dissolved and suspended forms, and industries are a major source through waste streams such as steel industries with galvanizing operations, brass and Zn metal works, brass and Zn plating and manufacturing of ground wood pulp. The typical mean zinc concentration is between $60 - 120$ µg g^{-1} (Kabata-Pendias, 2010). Zn is an essential trace element for human health. However, excessive intake or exposure may cause abdominal pain, nausea, vomiting, dizziness, lethargy, skin irritation and anaemia. Extremely high levels of Zn may damage pancreas, interfere with metabolism of proteins and lead to arteriosclerosis. In plants, Zn is essential for lipid and carbohydrates metabolism at an optimum range of $10 - 20$ µg g^{-1} (Kabata-Pendias, 2010). However, only a few plants can survive in zinc-rich soils as it interrupts soil activity by reducing the activity of earthworms and other microorganisms, thus slowing down the breakdown of organic matter (Wuana and Okieimen, 2011).

2.6.3 Manganese

Mn is a widely distributed metallic element and rarely occurs as a pure metal (Weiner, 2000). It is found mostly in salts and minerals mainly with Fe compounds (Kabata-Pendias, 2010). The major sources of Mn are sediments, soils and rocks, although small amounts of Mn in water may be as a result of weathering of its deposits. Fe and steel industries and drainage of acid mines release large amounts of Mn to the environment (Weiner, 2000), and in the atmosphere it is dispersed by atmospheric deposition. It is a major component in soil, at a worldwide reported range of $100 - 9,200$ µg g^{-1} (Kabata-Pendias, 2010). It is important for normal physiologic functioning of humans, animals and plants. However, intake in excess of or exposure

to Mn (above 2,000 µg g^{-1}) may cause adverse respiratory, neurological and reproductive effects (EBO, 2009).

2.6.4 Copper

The global range concentrations of Cu in uncontaminated soil is between 10 - 24 µg g^{-1}, with levels as high as 144 µg g^{-1} being reported (Kabata-Pendias, 2010; Wuana and Okieimen, 2011). Cu generally accumulates in the upper soil profiles, and has been found to strongly correlate with Fe and Mn ions. In addition, it has been found to exhibit low mobility in soil (Kabata-Pendias, 2010). Cu is an essential micronutrient to both human being and plants. In human being, Cu is required in production of haemoglobin, while in plants it helps in desease resistance, seed production and water uptake. However, intake in excess of and accumulation of Cu has detrimental effects to human health. For instance, it may cause depletion of brain Zn supplies. Cu poisoning may cause vomiting, hematemesis, coma, gastrointestinal distress, hypertension and jaundice (Brewer, 2007). Long-term effects of Cu exposure may cause liver and kidney damage (Flemming and Trevors, 1989). In plants, Cu uptake in excess (above 100 µg g^{-1}) may lead to stunted growth and reduced yields (Wuana and Okieimen, 2011).

2.6.5 Iron

According to Kabata-Pendias (2010), Fe is one of the major elements in soil, with concentrations ranging between 0.4 to 5 %. It commonly occurs in soil as oxides and hydroxides, and is highly mobile depending on hydrolysis, soil pH, complexation and soil aeration.Fe plays a significant function in biology for it forms complexes with molecular oxygen in myoglobin and haemoglobin, which are used for transportation of oxygen in vertebrates. It is responsible for formation of white blood cells thus boosting the immune system of the body. The recommended daily intake of Fe is 10 - 15 mg for adults and 30 mg for pregnant women (Krayenbuehl et al., 2005). Symptoms of iron deficiency include impaired reactivity and coordination, inability to regulate body temperature, itching, fatigue and reduced immunity and physical fitness (Beard, 2001).

CHAPTER 3

METHODOLOGY

3.0   Overview

In this chapter, a brief description of the study area, that is, Taita Taveta county and Kishushe in particular is presented. The procedures employed during sampling, sample preparation, as well as sample analyses are also presented. Additionally, to have a better understanding of the analytical tools used, the operation principles of EDXRF spectroscopy and XRD technique will be discussed. Finally, the data analyses techiques used for this study are presented.

3.1   Description of the Study Area

This study was conducted within Kishushe iron ore mines in Taita Taveta County, which is in the Coastal region of Kenya. This area lies approximately 350 km southeast of Nairobi and 200 km northwest of Mombasa, at between 3.1° S and 3.3° S, and 38.1° E and 38.3° E (figure 3.1 and figure 3.2). The mine covers a total of 32 km^2, and is subdivided into eight blocks. This mine neighbours Tsavo National Park on the east and farmlands on the west. It is managed, explored and semi-processed by Shangani Group/ Wanjala Mines Limited.

The economy of the study area is diverse. It is characterized by farming activities, pastoralist and ranches, as well as mining activities. The area is known to lie within the Mozambique belt that extends along the eastern border of Ethiopia through Kenya to Tanzania. The belt is geologically rich in minerals and gemstones. For example, Fe ore, asbestos, limestone, chalk, gemstones, marble, magnetite, graphite, sand and construction stones are some of the minerals portfolio in TaitaTaveta. Apart from small scale farming and livestock keeping, large scale sisal farming, ranches and wildlife sanctuaries are also found in the area.

The area is well forested hosting a wide range of both exotic and indigenous tree species. It receives a mean annual rainfall of 650 mm and mean temperatures of $23°C$.

It has two rainfall seasons running from April to June and October to December particularly in the highlands. This makes the area prime for agricultural activities.

There is good drainage pattern in the area as it is well covered by lakes, rivers and springs. Lake Jipe, Lake Chala, Tsavo River, Voi River and Mzima springs are key water sources not only to the area residents but also to the wider coastal region. Other smaller rivers and springs are Njuguini, Maji Wadeni, Sanite, Lemonya and Humas Springs.
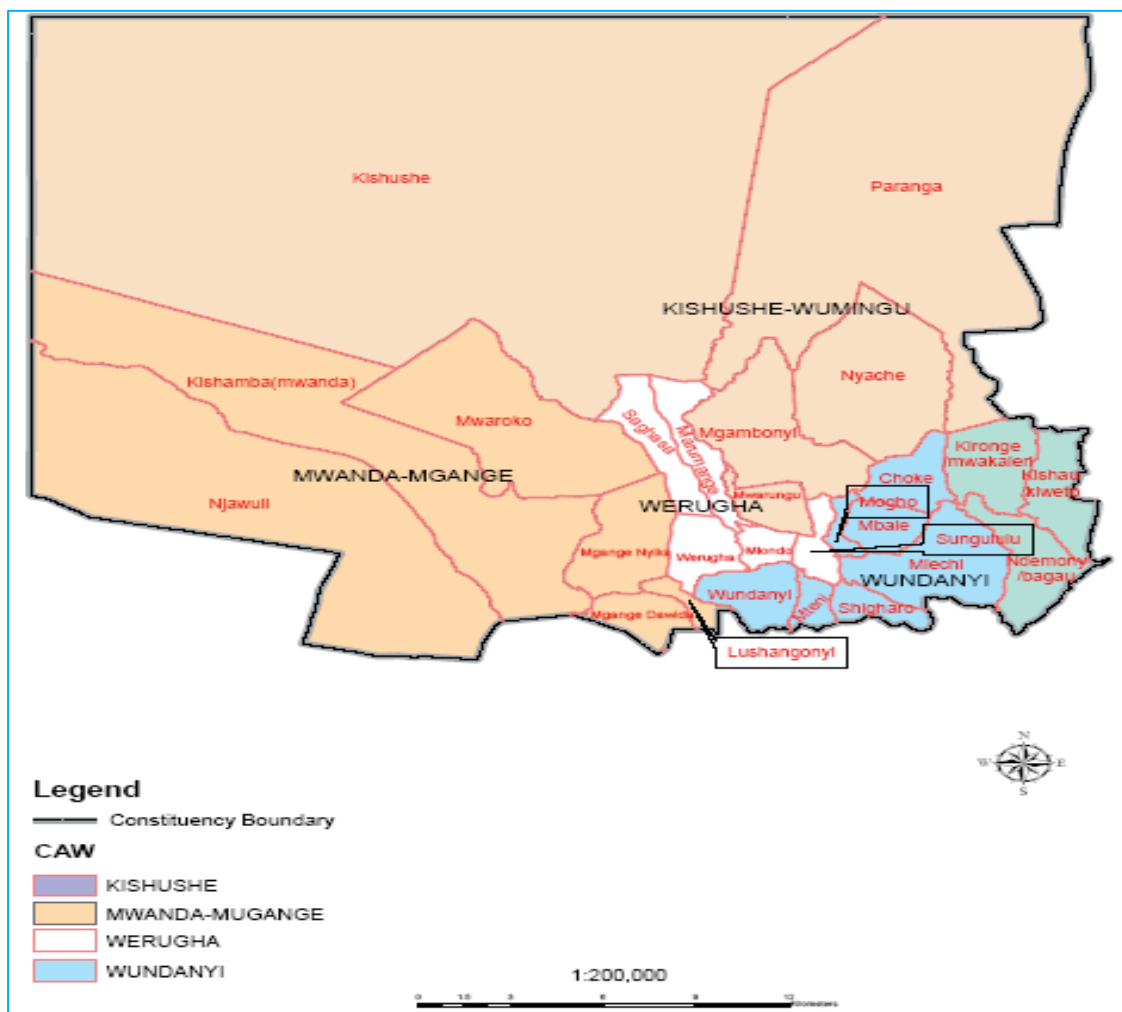
Figure 3.1:   Map of Taita Taveta County showing Kishushe area

3.2   Sampling

Soil samples were collected from the mining area and a control area that was located approximately fifteen kilometers away.   The mining area was divided into eight blocks. For each block, two sampling points were identified as illustrated in figure 3.2, giving a total of sixteen sampling points within the mining area. For control samples, four sampling points were established in a farmland. Samples were picked from each sampling point (4 sampling points for control area and 16 sampling points for mining area) using a soil auger at depths of 0 – 20 cm, 20 - 40 cm and 40 – 50 cm giving a total of 60 samples. Approximately 300 g of each sample was stored in well labeled zip-lock polythene bags, sealed and transported to the laboratory for preparation and analyses.
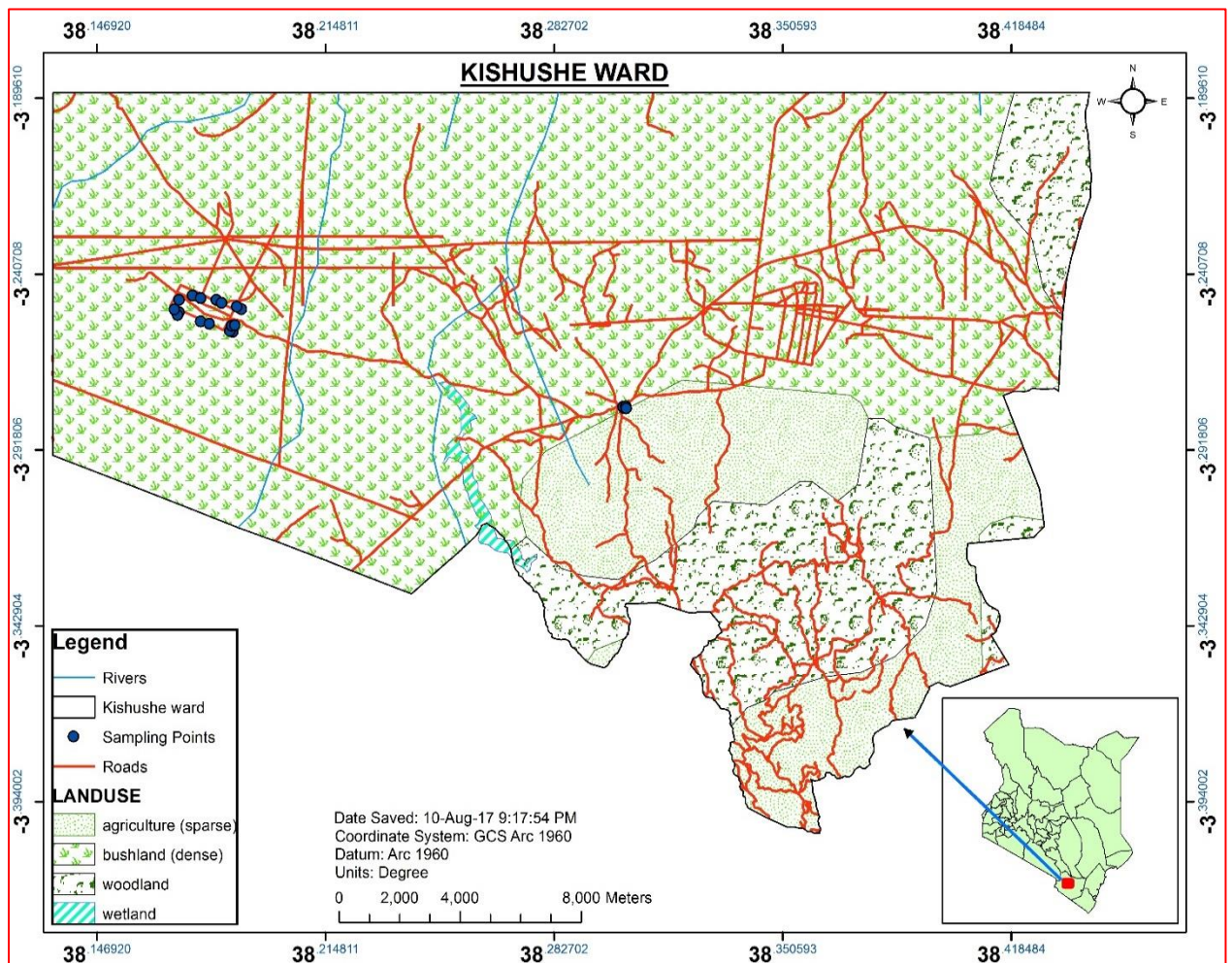
Figure 3.2: Map showing the sampling points in the study area
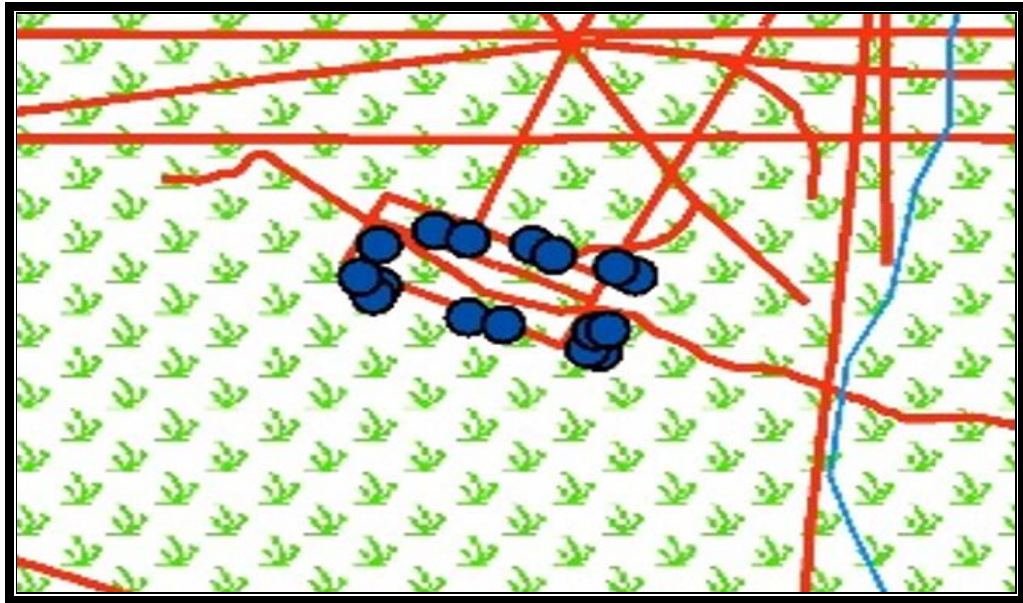
Figure 3.2 (a): Sampling points for Study area
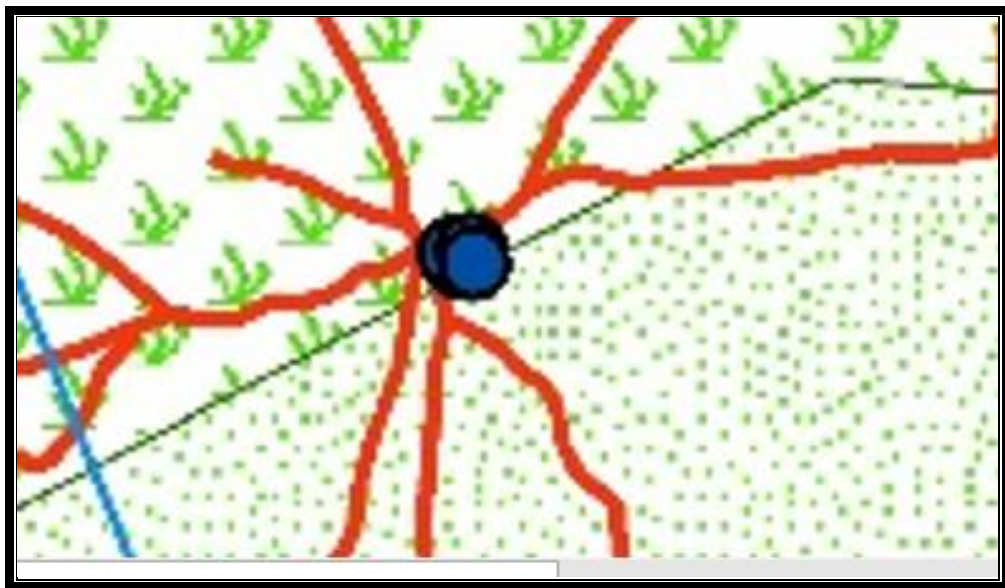
Figure 3.2 (b): Sampling points for Control area

3.2.1 Sample Preparation for EDXRF Analyses

In the laboratory, soil samples were air dried for one week. To further reduce the moisture content, the samples were then placed in an oven at 103 °C, till a constant weight was achieved. To remove rocks, roots or any other large particles, the samples were ground and sieved through a 2-mm sieve. The samples were further

pulverization using a pestle and mortar to reduce particle size to less than 75 μm. Pellets were then made from the powdered samples.

A hydraulic press was used for the pelletization process. Approximately 1.5 g of the sample was weighed and uniformly spread in a die (figure 3.3a). The die was then set in the hydraulic press, and pressure of between 5 – 8 tons was applied to form a pellet (figure 3.3b). The pellets were made in triplicates, weighed and stored in a well labelled petridish (figure 3.3c). To avoid cross contamination, both the die and pestle and mortar were thoroughly cleaned with a wet cloth and allowed to dry before a new sample was prepared. The preparation area was also properly maintained during the exercise.

| (a) | (b) | (c) |

Figure 3.3: (a) Soil sample loaded in the die; (b) The sample die placed in the hydraulic press; (c) The resultant sample pellet

3.2.2 Sample Preparation for XRD Analyses

One of the objective of this study was to determine mineralogy of soil samples. XRD technique was employed for this task. To achieve this, six soil samples were sent to the World Agro-forestry Centre (ICRAF), in Nairobi for analyses. The ICRAF standard procedure (2011) was used for sample preparation, as described below.

First, the samples were ground using pestle and mortar. Three grams of the sample were put into a milling cup, and an equivalent of nine grams of ethanol added to it. The mixture was then capped and milled for fifteen minutes. Afterwards, the milled sample was transferred into a 50-ml centrifuge tube set at 4,000 rpm, and allowed to run for 10 minutes to separate the supernatant liquid. Finally, hexane was added at a ratio of 1 ml to 2 g of the sample. The resultant paste was dried at between 85 $^{\circ}$C to 105 $^{\circ}$C for an hour. The dried sample was then sieved through 250 µm sieve, ready for XRD analyses.

3.3 Elemental Analyses

3.3.1 Energy Dispersive X-ray Florescence (EDXRF) Method of analysis

In this study, the elemental analysis of the soil samples was done using a benchtop EDXRF spectrometer, at the Institute of Nuclear Science &Technolgy, University of Nairobi (figure 3.4). The source of X-rays is a tube with a silver target/ anode. Based on the fundamental principles of XRF, electrons generated from the cathode are accelerated towards the silver target that is held at relatively higher potential difference. Once the fast-moving electrons impinges on the target, charactaristic X-rays as well as bremsstruhlung radiation are emitted. The X-rays escape through a beryllium window towards the sample.
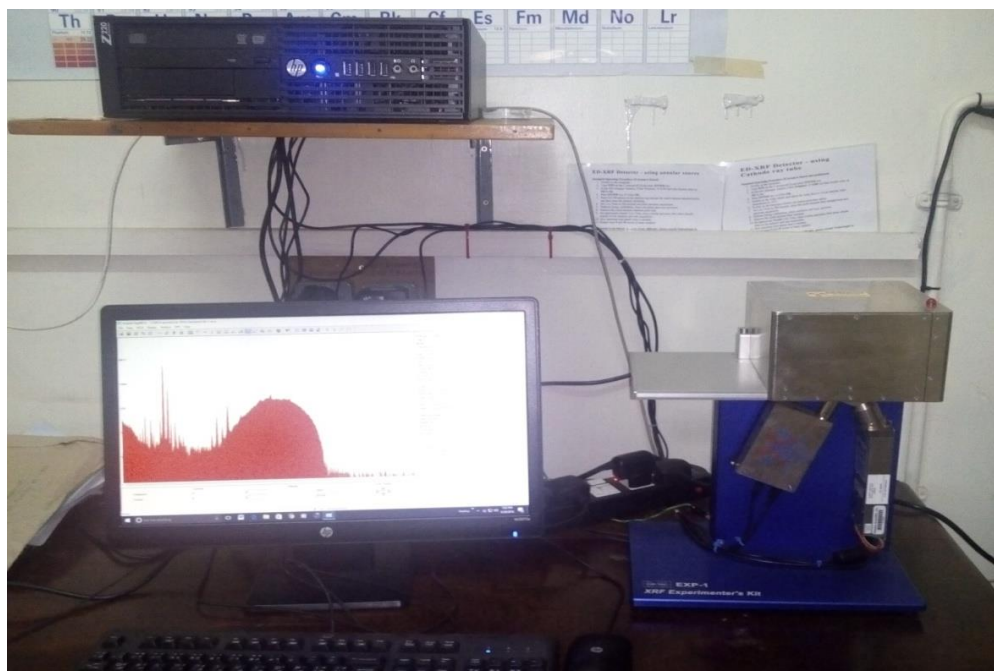
Figure 3.4: EDXRF setup at INST, University of Nairobi

As soon as the X-rays reach the sample, they ionize an inner electron shell through emission of a photo-electron, leaving the atom in an excited (unstable) state. This requires the energy of the photon to be higher than the energy that binds the electron to the nucleaus of the atom. To stabilize the atom, a higher energy electron transitions to fill the lower energy shell, emitting characteristic X-rays, whose energy is equivalent to the energy difference between the two orbitals. Therefore, simply by determining the energy/ wavelength of the emitted X-rays, one can idenitify both the element and the transition that occured. The count rate i.e. the number of emitted photons per unit time is indicative of the quantity of the analyte in the sample. Elemental peaks are generated by the detector, relative to the count rates for each energy line.

The prepared soil pellets were irradiated using tube source for 200 seconds to give a spectrum. The tube current was optimised at 80 μA while the voltage was set at 30kV respectively. Analysis of X-ray Spectrum by Iterative Least-squares fitting (AXIL) software was used for spectrum de-convolution and quantification.

3.3.2   X-ray Diffraction Analyses

In this study, six samples will be analyzed using XRD for mineral characterization at ICRAF. The technique is dependent on constructive interference of monochromatic beam of X-rays with a crystalline sample. The X-rays which are produced by a cathode ray tube, are filtered to generate monochromatic radiation, and then collimated in order to minimize interference from scattered radiation. A constructive interference is produced once the incident radiation interacts with the sample on condition that it satisfies the Braggs Law ($n\lambda = 2d \sin \theta$), Moore (2008). This particular law relates the wavelength of electromagnetic radiation to the lattice spacing and the diffraction angle in a crystalline sample. The characteristic x-ray diffraction pattern that is produced in an XRD analysis gives a distinctive "fingerprint" of the minerals contained in the sample. When correctly interpreted in comparison to standard reference patterns and measurements, then the fingerprint allows identification of the crystalline form (Particle Analytical, 2016).

3.4   Data Analysis

3.4.1   Qualitatitave Analyses of EDXRF Spectra

In quantitative analyses of EDXRF spectra, the peak intensities (count rate) for the detected elements are converted into concentrations, by factoring other parameters such as Analyte concentration, sample type, sample matrix and operating conditions (Sitko and Zawisz, 2012). Two methods of analyses can be used; compensation method and matrix correction method. The compensation method is less popular as it allows for one or just a few elements to be determined (Sitko and Zawisz, 2012). Therefore, matrix correction method was applied.

Matrix effects constitute all the factors that prohibit the acquization of a simple relationship between the elemental concentration and peak intensities. This include the absorption, enhancements as well as sample non-uniformity and inhomogeniety (Mantler *et al.*, 2006). The two most common methods used for correction of matrix effects are the Emission-Transmission (ET) method and Fundamental Parameters (FP) method. The ET method is often used for intermidiate thick samples, and is founded

on the transmission measurement of the X-rays emitted by constituent elements of a target located in an adjacent position to the sample (Adams *et al*., 1991). On the other hand, FP method is based on a relationship between the analyte concentrations and measured x-ray intensities, applying the fundamental physical parameters of X-ray emission process as well as instrumental and sample parameters (Adams *et al*., 1991). Both methods are components of the AXIL software used for the analyses.

The fundamental parameter method was used for the analyses of spectra data. This involved two key steps; calibration using pure element samples, and analyses of the unknown sample using the generated calibration curve. The pure element standards used for calibration were Fe, Cu, Zn, Pb, Sn, Ti and W. They are represented by K-lines and L-lines. Figure 3.5 gives the steps followed during spectral analyses of the samples.
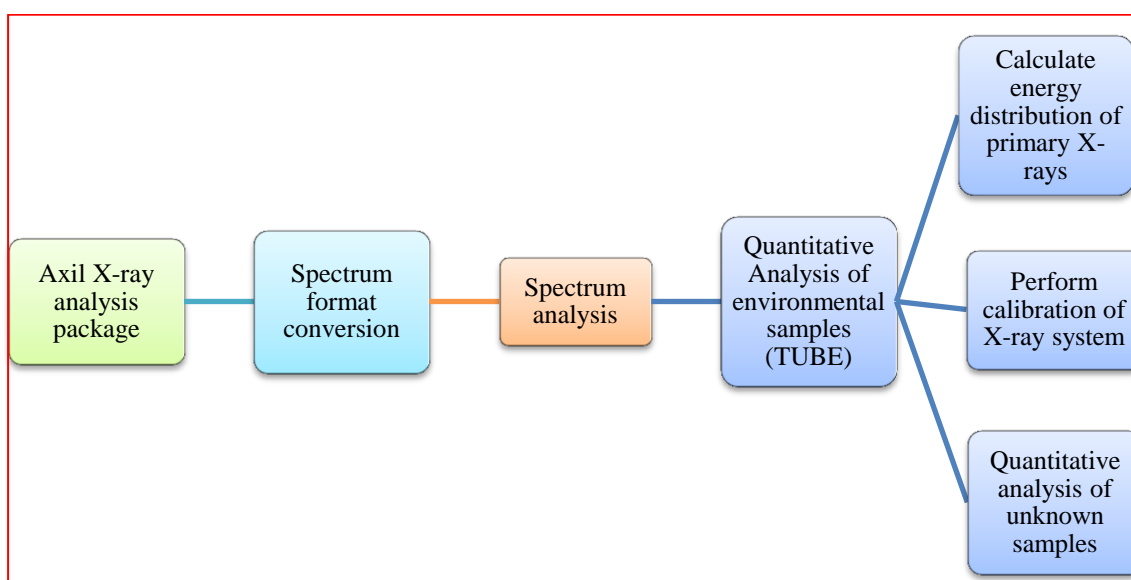
Figure 3.5: Block diagram illustrating the steps followed in spectral analysis (Adams *et al*., 1991)

3.4.2 Validation

To validate the methods used and the results, certified reference materials (CRMs) from IAEA (PTXRF-09) were used. The CRM was prepared and analyzed using a similar procudure to that used for samples. The obtained experimental values were

compared to the certified values. In addition, the values obtained from the analyses of CRM were used in calculation of detection limits using equation 3.1.

$$LLD = 3 * \frac{C}{P} \sqrt{R_b} \quad \dots\dots\dots\dots\dots\dots \text{ equation 3.1}$$

Where; R_b: background area of the element,

P: peak area of the element,

c: concentration of the element in µg g^{-1}

LLD: Limit of Detection

3.4.3: Pollution Indices

To assess the degree of heavy metal contamination in the study area, the Enrichment Factor (EF), Pollution Load Index (PLI), and geo-accumulation Index (Igeo) were employed.

Enrichment Factor (EF)

Enrichment Factor evaluates the abundance of heavy metals in the soils by use of the equation 3.1 introduced by Buat-Menard and Chesselet (1979).

$$EF = \frac{\left(\frac{Cn}{Cref}\right)Sample}{\frac{Bn}{Bref}} \quad \text{`}\dots\dots\dots\dots\dots \text{ equation 3.2}$$

Where; C_n is the analysed heavy metal concentration in the sample, C_{ref} is the analysed heavy metal concentration in the reference environment, B_n is the concentration of the reference heavy metal in the investigated environment and B_{ref} is the concentration of the reference heavy metal in the reference environment.

Enrichment Factor categorizes soil contamination into six classes as presented in table 3.1. Increase in EF means increased heavy metal contributions from anthropogenic activities (Sutherland et al., 2000). The commonly used reference metals are Fe, Mn and Al (Liu et al., 2009). The most abundant metal in the investigated and natural environment is usually used as a reference metal. For this study, Fe was selected.

Table 3.1: Degree of contanination based on EF (Acevedo-Figueroa et al., 2006)

S/N	EF Value	Level of Contanination
1	EF = < 3	minimal enrichment,
2	EF = 3-5	moderate enrichment
3	EF = 5-10	moderately severe enrichment
4	EF = 10-25	severe enrichment
5	EF = 25-50	very severe enrichment
6	EF > 50	extremely severe enrichment

Pollution Load Index (PLI)

The PLI was calculated using equation 3.3, proposed by Thomlinson et al. (1980).

$$PLI = (CF_1 * CF_2 * CF_3 * ……. * CF_N)^{1/N}$$ …………… Equation 3.3

Where; CF is the contamination factor calculated by Equation 3.4 and N is the number of metals analysed.

$$CF = \frac{Metal\ Concentration}{Metal\ Reference\ value}$$ ………………. Equation 3.4

The *PLI* is used as an estimate of the degree of metal contamination and an indictor of the measures that needs to be put in place. A PLI value > 1 indicates polluted soil while PLI value < 1 means no pollution. On the other hand, contamination factor is classified as shown in table 3.2.

Table 3.2:   Classification of contamination factor (Wu *et al.*, 2014)

S/N	CFValue	Degree of Contamination
1	CF< 1	Minimal contamination
2	1 < CF < 3	Moderate contamination
3	3 < CF < 6	High contamination
4	CF > 6	extreme contamination

Geo-Accumulation Index

The degree of heavy metal contamination in soil can be assessed using geo-accumulation index (I_{geo}), which was proposed by Muller (1969). The method generally compares the concentration levels before contamination to the present levels. It is computed using equation 3.5, and degree of contamination classified as shown in table 3.3.

$$I_{geo} = Log_2 \left(\frac{Cn}{1.5 \, Bn}\right) \quad \text{..........................} \text{ Equation 3.5}$$

Table 3.3   Classification of Geo-accumulation Index (Muller, 1969).

I_{geo} Value	Class	Degree of contamination
$I_{geo} < 0$	0	Non-contamination
$0 < I_{geo} < 1$	1	Light to moderate
$1 < I_{geo} < 2$	2	Moderate
$2 < I_{geo} < 3$	3	Moderate to strong
$3 < I_{geo} < 4$	4	Strong
$4 < I_{geo} < 5$	5	Strong to extremely serious
$5 < I_{geo} < 10$	6	Extremely serious

CHAPTER 4

RESULTS AND DISCUSSION

4.0   Overview

In this chapter, the results for elemental and minerological analyses of the soil samples collected from Kishushe Iron ore mining area are presented. The chapter begins with validation of the analytical procedure used for elemental analyses using certified reference material, PTXRF-IAEA09 from International Atomic Energy Agency, and calculation of detection limits.

4.1   Accuracy and Precision of Method

Certified Reference Material

To assess the accuracy of the analytical method used (EDXRF), certified reference material (PTXRF-IAEA09), which is a river clay sample was used. The experimental results obtained from the analyses of CRM were compared to the certified values as presented in table 4.1. It was observed that for the metals of interest to this study, the experimental values are within the range of the certified values. In addition, most elements had relative standard deviation below 10 %, indicating that the method could be applied for this study.

Detection limits

Detection limits for the EDXRF technique were also calculated using the obtained results of the certified reference material, by applying the equation 3.1.

In general, the detection limits improve (lower) with increase in atomic number. Therefore, elements with higher atomic numbers can be more acurately determined even at lower concentrations in comparison to their low atomic number counterparts.

Table 4.1: Results of analysis of CRM, PTXRF-IAEA09

Element	Experimental Values	Certified Values
Ti	4,108 ± 328 ppm	4,300 ± 230 ppm
Mn	965 ± 95 ppm	1,000 ± 60 ppm
Fe	3.24 ± 0.1 w%	2.97 ± 0.1 w%
Zn	97 ± 8 ppm	96 ± 8 ppm
Sr	108 ± 5 ppm	106 ± 8 ppm
Zr	273 ± 12 ppm	302 ± 20 ppm
Pb	41 ± 5 ppm	37 ± 3 ppm

Table 4.2:   Detection limit values (ppm) of various elements

Element	Atomic Number	Detection Limit
Ti	22	500
Mn	25	120
Fe	26	70
Cu	29	25
Zn	30	20
Sr	38	15
Zr	40	10
Nb	41	10
Pb	82	10

4.2 Heavy Metal Concentrations in the Soil Samples

In this study, Fe, Ti, Mn, Cu, Sr, Zr, Zn and Pb were determined above the detection
limits. Fe was found to be the most abundant element followed by Ti, Mn, Zr, Cu,

Zn, Sr, and Pb in that order. In this sub-section, we are going to discuss in detail the obtained results for each of these metals.

4.2.1 Iron

The Fe distribution pattern in the samples, as well as control samples and their variations with depth are presented in figure 4.1. In general, the mean concentration range in the soil samples was determined at between 8 -12.5 %, with an overall mean of 10.4% in the study area. A significant difference (P< 0.05) was observed between the Fe concentrations recorded and that of the control area located about 10 km away using ANOVA, where a range of 6.8 – 9.3 % with a mean of 8.1 % was recorded.

As observed in figure 4.1, there is no much variation in the concentration levels between the sampling depths apart from site S4, S8 and S11. This observation was further confirmed using ANOVA (SPSS V.18), which showed that there is no significant difference between the two sampling depths (P> 0.05). However, higher mean concentrations were generally recorded in the lower profile (subsoil). For instance, a mean of 10.9 % was recorded in the subsoil (> 40 cm), in comparision to 10.4 % at 0 – 20 cm depth and 10.5 % at 20 – 40 cm depth. Considering that this is an iron ore mining area where the mineral deposits are found from the subsoil level downwards, this observation could be anticipated (Maranga et al., 2013). A similar trend was reported by Maldonado et al. (2008), where Fe concentrations were noted to increase with depth. The author attributed this observation to downward mobility of the metal ions. Similarly, Kabata-Pendias (2010) noted that Fe is highly mobile depending on factors such as hydrolysis, soil pH, complexation and soil aeration.

Kabata-Pendias (2010), reported a typical Fe concentration range in soil at 0.4–5%. However, the values reported in this study are way higher. This can be attributed to the fact that this study was conducted in an iron ore mining area. Furthermore, this area lies within the mineral rich Mozambique belt (Maranga *et al.*, 2013).

Other studies conducted within this belt have also exhibited high Fe concentrations. For example, Patel and Mangala (1994), reported a concentration range of 5-30%, and a mean of 21% in Mrima Hill, Coastal Kenya. Despite these high reported Fe

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concentrations, none of the accessible literature that correlates high Fe levels to detremental effects either to human beings or plants. Instead, Fe has been shown to be an essential contributor to health.

Figure 4.1: Distribution of Fe (W%) in soil samples (A: 0 -20 cm; B: 20 − 40 cm and C: 40 − 50 cm), in both the study area (S) and control area(C).

4.2.2 Manganese

Figure 4.2 shows the distribution patterns of Mn in the sampling area and control area, as well as their variations with depth. Generally, the mean concentrations in the study area ranged between $1,540 – 3,940 \ \mu g \ g^{-1}$, where the highest value was recorded in site S4 while the lowest in site S11. For the control area, a range of $1,680 – 2,060 \ \mu g \ g^{-1}$ was recorded. These values are within the worldwide range of $100\text{-} 9,200 \ \mu g \ g^{-1}$ given by Kabata-Pendias, (2010). Additionally, the values are within the permissible limits set at $10,000 \ \mu g \ g^{-1}$ in agricultural soils, and above the threshold of $100 \ \mu g \ g^{-1}$ (Ondo et al., 2012). Considering the critical role that Mn plays in plant, we can conclude from these values that the soil is neither Mn deficient nor does it pose any

significant risk of toxicity in plants and human beings. The reported values are lower than those reported by Patel and Mangala (1994) in Mrima Hill.

In this study, relatively higher values were recorded in the upper profile with a mean concentration of 2,676 µg g^{-1}, as compared to a mean of 2,536 µg g^{-1} (20 – 40 cm) and 2,347 µg g^{-1} (40-50 cm) in the subsoil. On the contratry, a reverse trend was observed in the control area, with a mean of 1,894 µg g^{-1} in the topsoil (0 – 20 cm) and 2,062 µg g^{-1} in the subsoil (40-50 cm). However, the two profiles were statistically similar (P> 0.05), using ANOVA. It was also observed that the study area recorded higher values (2,026 – 3,939 µg g^{-1}) than the control area (1,681 – 2,062 µg g^{-1}).
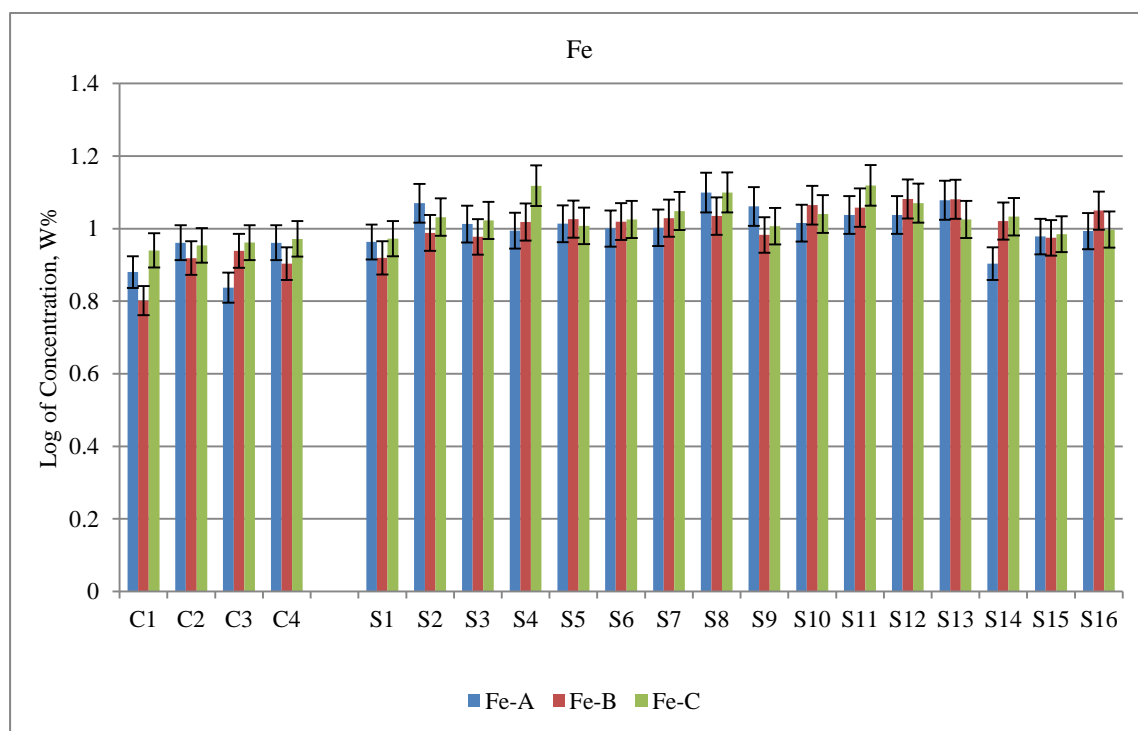

Figure 4.2: Distribution of Mn in soil samples (A: 0 - 20 cm; B: 20 – 40 cm and C: 40 – 50 cm), in both the study area (S) and control area (C).

4.2.3 Titanium

The titanium content in the soils samples, as well as their variation with depth is presented in figure 4.3. The study revealed a concentration range of between 2,472 – 17,300 µg g^{-1} in the study area, and 6,186 – 9,771 µg g^{-1} in the control area. This

reflects a significant difference (P< 0.05) between the study area (μ = 12,555 µg g^{-1}) and the control area (μ = 8,044 µg g^{-1}). With continued excavation/ mining activities, Ti can easily be dispersed to these control (agricultural) areas through erosion and wind dispersion, ultimately leading to elevated levels. Relatively higher concentrations have been reported in other mining areas in the region. While Patel and Mangala (1994) reported a mean of 46,500 µg g^{-1}, Maina (2008) reported a comparable mean of 12,850 µg g^{-1}.

Mixed trends were observed in Ti variations with depth, although statistically similar (P> 0.05). However, slightly higher means were reported in the topsoils in both the study area and control area. For instance, a mean of 13,126 µg g^{-1} for the upper profile (0 – 20 cm) and 11,900 µg g^{-1} for bottom profile (40 – 50 cm) was recorded in the study area. Similarly, in the control area, a mean of 8,110 µg g^{-1} was recorded in the topsoil (0-20 cm), in comparison to 7,969 µg g^{-1} in the bottom profile (40-50 cm).

Figure 4.3: Distribution of Ti in soil samples (A: 0 - 20 cm; B: 20 – 40 cm and C: 40 – 50 cm), in both the study area (S) and control area (C).

4.2.4 Copper

Cu is an essential metal in both plant and human health. Its concentration levels in the soil samples were investigated, and are presented in figure 4.4. The study area recorded higher Cu levels than the control area. A range of $71 - 496$ µg g^{-1} (µ = 177 µg g^{-1}) was recorded in the study area, and $47 - 157$ µg g^{-1} (µ = 123 µg g^{-1}) in the control area. The values are above the global range concentrations of Cu in uncontaminated soil is between $14 - 109$ µg g^{-1} (Kabata-Pendias, 2010).

Variation in Cu concentrations with depth was also assessed. Apart from site S4 and S11 where huge variations were observed propbably due to point contamination, all the others didn't exhibit substantial variation. However, slightly higher values were recorded in the top soil. Similar observation was made by Wuana and Okieimen (2011), where Cu was reported to generally accumulate in the upper soil profiles. Kabata-Pendias, (2010) associated this observation to low downward mobility of Cu.
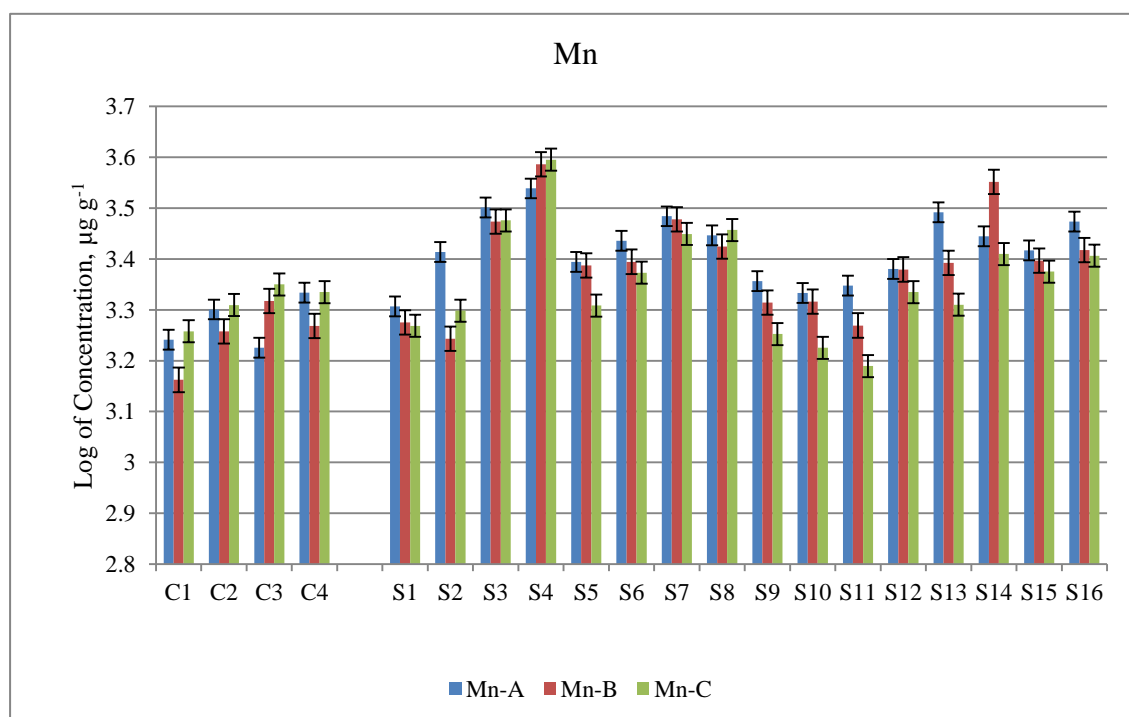

Figure 4.4: Distribution of Cu in soil samples (A: 0 - 20 cm; B: 20 – 40 cm and C: 40 – 50 cm) in both the study area (S) and control area (C).

4.2.5 Zinc

The worldwide reported concentration range in soils is 15 – 320 µg g^{-1} (Haluschak et al., 1998), while in uncontaminated soils, a global range of 15 – 135 µg g^{-1} has been recorded (Kabata-Pendias, 2010). In our study, apart from site S16, the soils Zn content falls within the range of uncontaminated soil (78 – 130 µg g^{-1}). There was no significant difference between the study area and the control area. Additionally, there was no significant difference between the two sampling depths, with very close values being recorded.

Figure 4.5:   Distribution of zinc in soil samples (A: 0 - 20 cm; B: 20 – 40 cm and C: 40 – 50 cm) in both the study area (S) and control area (C).

4.4.6 Lead

The mean Pb content for surface soils globally is 35 µg g^{-1}, and varies from 10 - 70 µg g^{-1} (Wuana & Okieimen, 2011). In this study, the Pb soil content falls within the range, where values between 28 – 64 µg g^{-1} were recorded in the study area (figure 4.6). Comparatively lower levels were observed in the control area (16 – 27 µg g^{-1}). At these concentrations, Pb does not pose any hazardous effects to plant and human

health. In addition, there was no significant difference between the two soil profiles, although the subsoils had slightly higher mean.
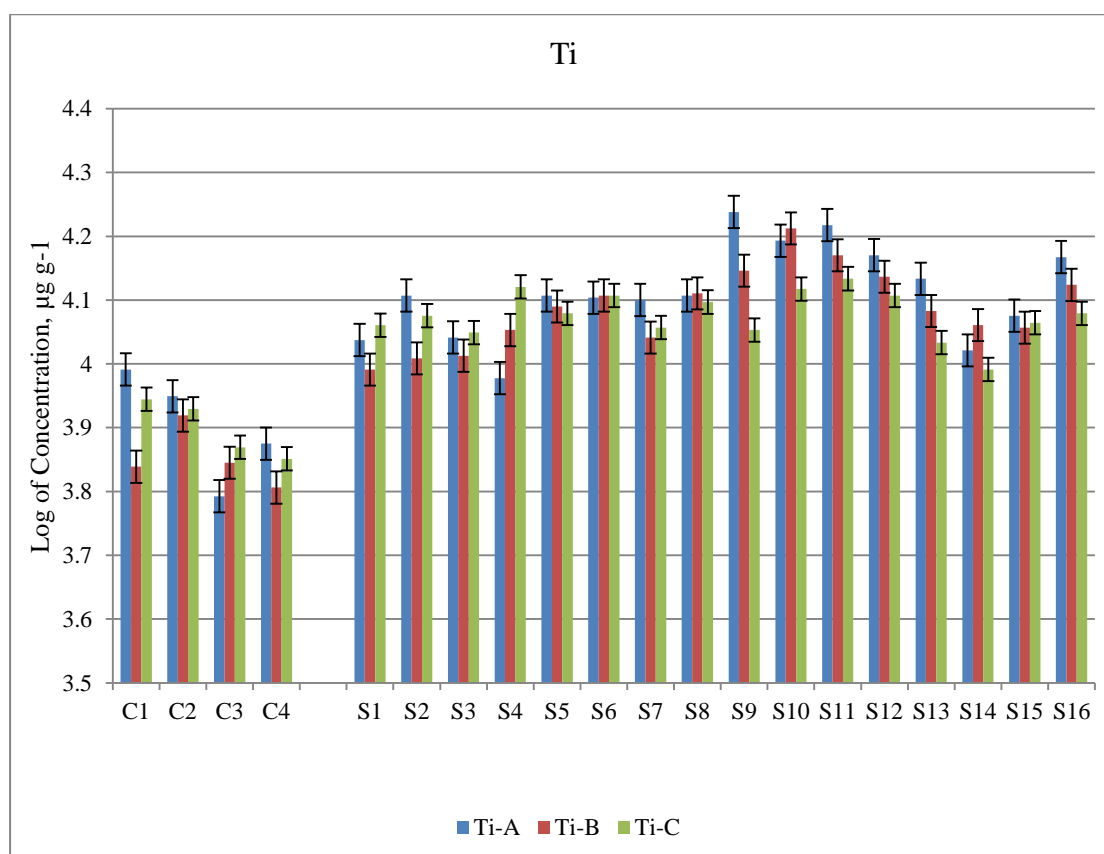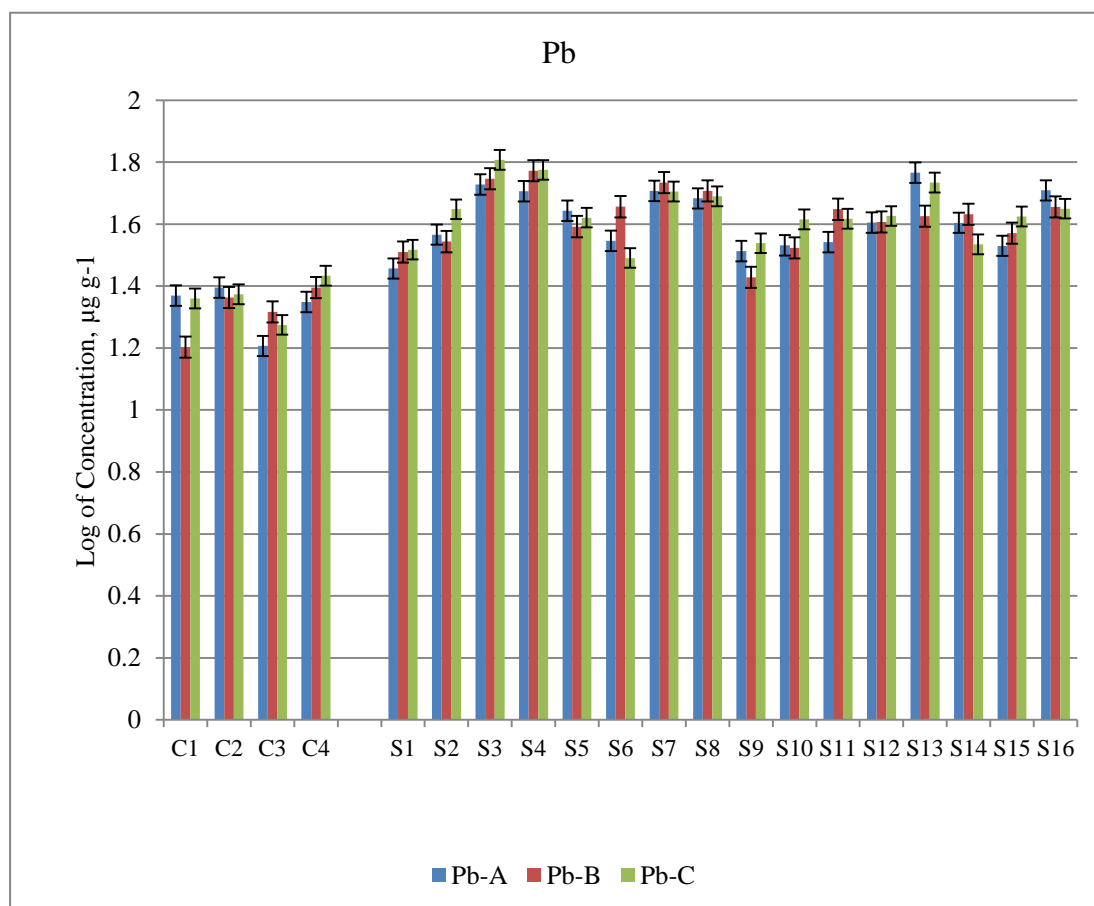

Figure 4.6:   Distribution of Pb in soil samples (A: 0 - 20 cm; B: 20 – 40 cm and C: 40 – 50 cm), in both the study area (S) and control area (C).

4.2.7   Strontium and Zirconium

Zr and Sr were also recorded above detection limits, and the obtained trends are presented in figures 4.7 and 4.8. Zr was determined at a range of $259 – 590$ µg g^{-1}, while Sr at between $51 – 183$ µg g^{-1}. Unlike the other heavy metals discussed in this subsection, Sr had higher concentrations in the control area. For Zr, significantly higher values were recorded in the topsoil.

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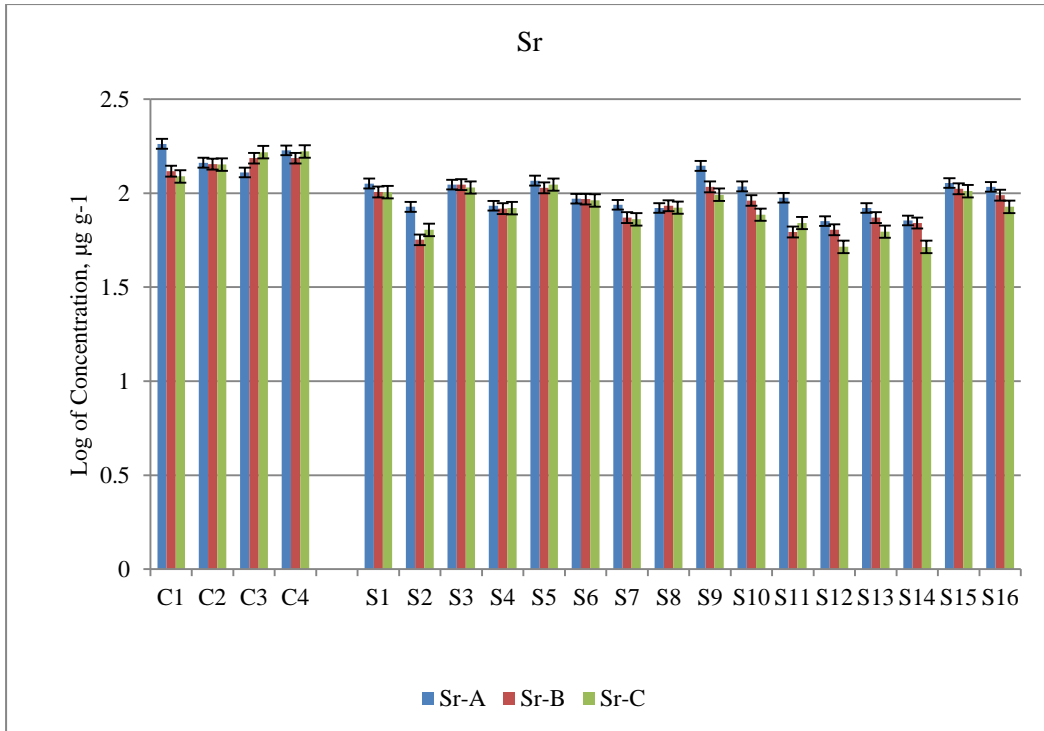
Figure 4.7: Distribution of Sr in soil samples (A: 0 - 20 cm; B: 20 – 40 cm and C: 40 – 50 cm) in both the study area (S) and control area (C).

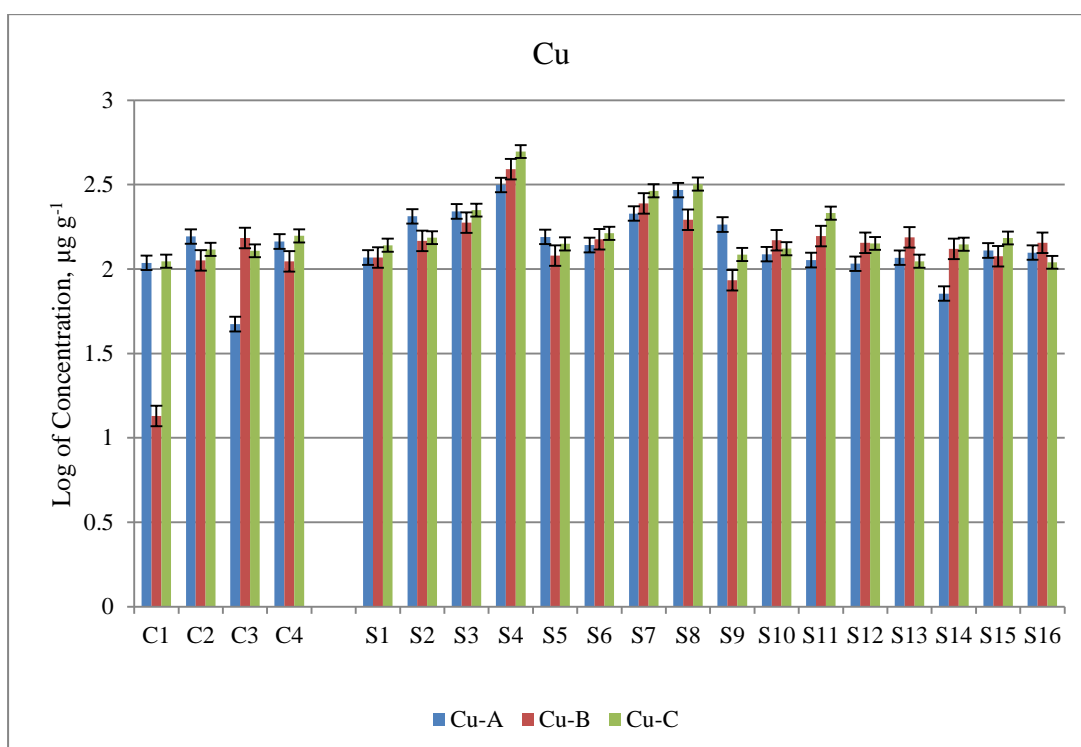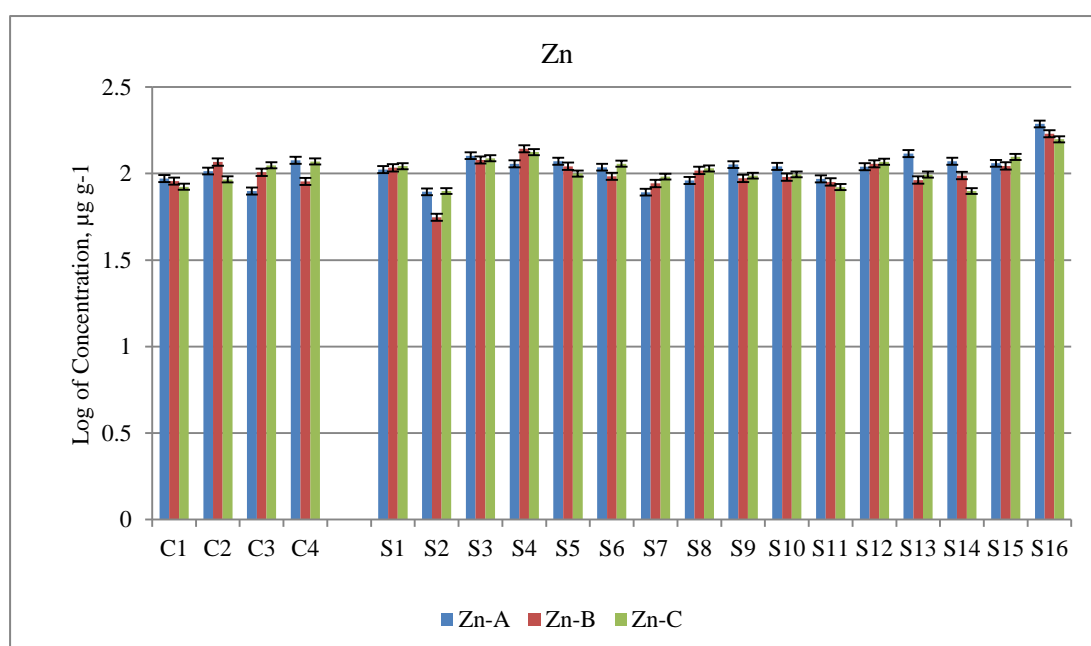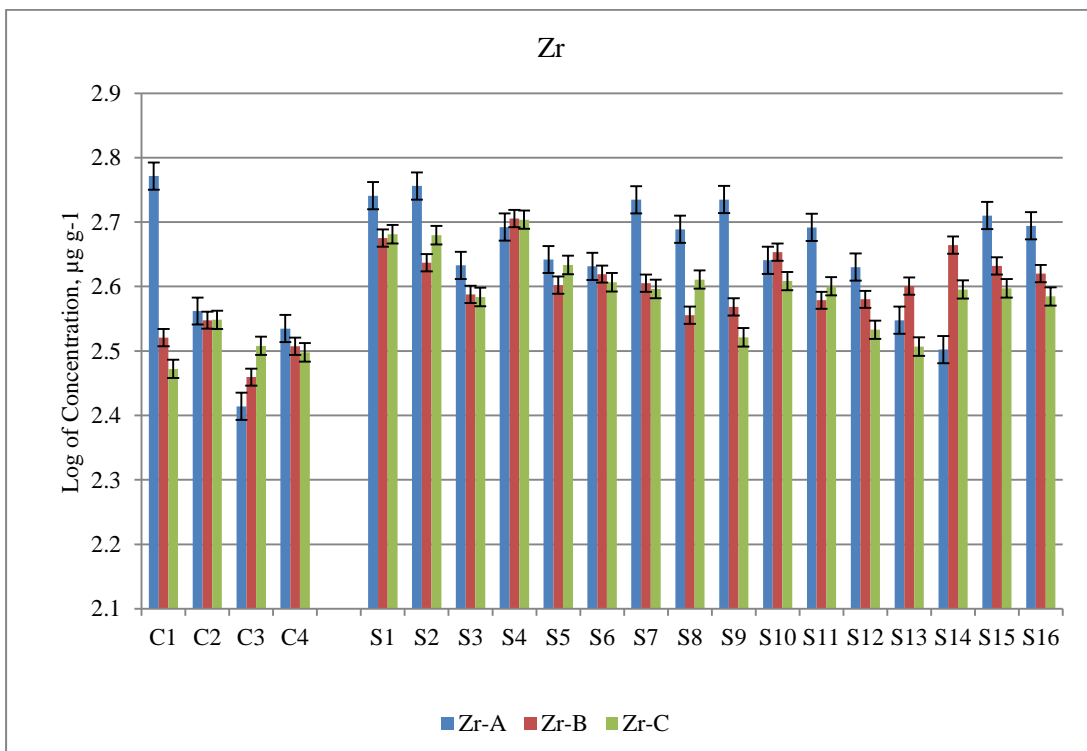**Figure 4.8**: Distribution of Zr in soil samples (A: 0 - 20 cm; B: 20 – 40 cm and C: 40 – 50 cm), in both the study area (S) and control area (C).

4.3 Correlation Analyses

The results of total subsoil (40 – 50 cm) to topsoil (0 – 20 cm) correlation are presented in table 4.3. Other than Zr, the other elements exhibited a strong relationship. Pb had the strongest relationship (r = 0.906) followed by Cu at r = 0.809. On the other end, Fe showed a moderate relation (r = 0.575). It was observed that the elements that were in lower concentrations, displayed stronger relationships. The findings are contrary to what was observed by Galgallo (2015), where the major soil constituents showed stronger relationships than the minor constituents. The author argued that since these elements were in low concentrations; they tend to be strongly influenced by human activities. The alternate argument could hold for our study. Considering that the study area is in a gazetted forest, and large portion is yet to be excavated, we can presume a minimal pollution in most parts. As for Fe, the difference between the two profiles could be because of weathering process.

Table 4.3:   Results of Pearson's correlation for topsoil and subsoil concentrations

	Topsoil							
	Fe	Mn	Ti	Cu	Zn	Pb	Sr	Zr
Subsoil	**0.575**	**0.748**	**0.748**	**0.809**	**0.699**	**0.906**	**0.823**	0.389

NB: Strong correlation highlighted in bold

Strong positive relationship was observed for Fe and Ti, Fe and Cu, Fe and Sr, Cu and Mn, Mn and Pb, Pb and Ti, Ti and Sr, and Pb and Cu (table 4.4). The strong relations could due to lithologic association and presence of primary minerals biotite and pyroxene in the underlying geological strata (Smith and Huyck, 1999). The observed inverse relationship, such as Fe and Pb, Zr and Ti and Sr and Pb, could mean an enrichment of one element is accompanied by depletion of the other.

Table 4.4:   Results of Pearson's correlation between elements

	Fe	Mn	Ti	Cu	Zn	Pb	Zr	Sr
Fe	1							
Mn	0.401	1						
Ti	**0.747**	0.086	1					
Cu	**0.567**	**0.750**	0.134	1				
Zn	-0.031	0.397	0.122	0.002	1			
Pb	**-0.704**	**0.777**	**0.517**	**0.568**	0.340	1		
Zr	0.381	0.212	**-0.679**	-0.252	0.002	0.331	1	
Sr	**0.695**	-0.447	**0.509**	0.471	-0.060	**-0.671**	-0.334	1

4.4 Pollution Indices

Three different indicators were used to assess the extent of heavy metal enrichment/ pollution levels in the soil samples.   These were Pollution Load Index (PLI), Enrichment Factor (EF) and Geo-accumulation Index. The three pollution assessment methods are dependant on reference values; hence the key challege is to identify an appropriate reference value. Some of the commonly used reference values include the background, the regulatory, and the crust values (Wu *et al.*, 2014). In this study, the global average metal concentrations as reported by (Kabata-Pendias, 2010) were used as the background values in calculation of the pollution indices. However, the background value is a range rather than an obsolute value, and table 4.5 only presents the commonly used reference values. For the puposes of calculating the pollution indices, the depth of 0 – 20 cm (topsoil) and 40 – 50 cm (subsoil) were used.

Table 4.5: Summary of mean metal concentrations and reference values

Element	Study Area concentration		Control Area Concentration		Reference Values
	Top soil	Subsoil	Top soil	Sub soil	
Fe (%)	10	11	8	9	5
Mn (μg g^{-1})	2,676	2,347	1,894	2,063	850
Cu (μg g^{-1})	164	190	114	131	45
Zn (μg g^{-1})	112	107	98	101	95
Pb (μg g^{-1})	42	44	21	23	20
Sr (μg g^{-1})	97	82	156	149	375

4.4.1 Geo-accumulation Index

The level of contamination of the soil samples was assesed using Igeo, based on the seven descriptive classes as proposed by Muller (1969). The results show that there was no significant soil contamination in the study area (table 4.6), with slight contamination (class 1) being reported for Fe, Mn and Cu. On the other hand, the results showed there was no contamination with respect to Zn, Pb and Sr. Slightly higher I_{geo} values were recorded in the study area as compared to the control area. This was anticipated since it's a mining area and enhanced anthropogenic activities were being experienced.

Table 4.6: Calculated Geo-accumulation Index

Element	Study Area		Control Area	
	Top soil	Subsoil	Top soil	Sub soil
Fe	0.5	0.6	0.2	0.3
Mn	1.1	0.9	0.6	0.7
Cu	1.3	1.5	0.8	1.0
Zn	-0.3	-0.4	-0.5	-0.5
Pb	0.5	0.6	-0.5	-1.9
Sr	-2.5	-2.8	-1.8	-0.4

4.4.2 Enrichment Factor (EF)

The abundance of heavy metals in the soil samples was also assessed using EF, whereby Fe was used as the reference metal. From the results shown in table 4.7, all elements had an EF value less than three, indicating minimal contamination in the area.

Table 4.7: Enrichment Factor in the study and control area

Element	Study Area		Control Area	
	Top soil	Subsoil	Top soil	Sub soil
Fe	1.0	1.0	1.0	1.0
Mn	1.5	1.2	1.3	1.3
Cu	1.7	1.9	1.5	1.6
Zn	0.6	0.5	0.6	0.6
Pb	1.0	1.0	0.6	0.6
Sr	0.1	0.1	0.2	0.2

4.4.3 Contamination Factor (CF) and Pollution Load Index (PLI)

Contamination factor (CF) is the ratio between the obtained metal concentration and the reference value. On the other hand, PLI is an indicator of the overall soil's contamination status, where a PLI value > 1 indicates polluted soil while PLI value < 1 means no pollution. Table 4.8 presents the contamination factor and the resultant PLI value. Based on CF classification categories recognized by Wu *et al.*, 2014, the soil was considerably contaminated with Cu and Mn, moderately contaminated with Fe, Zn and Pb, but showed signs of low contamination with Sr. The PLI value in both control and study area was greater than one, indicating an overall contaminated status of the soil. However, the degree of contamination was higher in the study area compared to the control area.

Table 4.8:   Contamination Factor and PLI Values

Element	Study Area		Control Area	
	Top soil	Subsoil	Top soil	Sub soil
Fe	2.1	2.3	1.7	1.9
Mn	3.1	2.8	2.2	2.4
Cu	3.6	4.2	2.5	2.9
Zn	1.2	1.1	1.0	1.1
Pb	2.2	2.2	1.1	1.2
Sr	0.3	0.2	0.4	0.4
PLI	**1.6**	**1.6**	**1.3**	**1.4**

4.5   Mineralogical Analyses

Six samples were selected for mineralogical analyses using XRD method to assess the mineralogical composition. Four samples were selected from the study area (S1, S8, S11and S16), while two from the control area (C1 and C4). The obtained results (%) are presented in table 4.9.

The key compositions of the samples were quartz, albite ($NaAlSi_3O_8$), microcline ($KAlSi_3O_8$) and hornblende. Quartz is mainly composed of silica, while albite and microline is a sodium rich and potasium rich mineral respectively. On the other hand, there was hornblende which a complex inosilicate series mineral series (ferrohornblend-magnesiohornblende) with a general chemical formula of $(Ca,Na)_{2-3}(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$. Therefore, from these results, we can conclude that the key elements in the soil samples are Si, Na, K, Al and Fe. This concurs with the results of the elemental analyses where Fe was the major component. However, the other elements were not investigated during elemental analyses, partly due to limitations of the analytical technique, in addition to being outside the scope of this study.

Table 4.9:   Mineralogical composition of the various samples (%)

Site	Albite	Diopside	Hematite	Hornblende	Kaolinite	Microcline	Muscovite	Quartz
C 1	39	0	0	12	2	12	2	33
C 4	32	5	0	15	1	0	3	44
S 1	28	0	2	3	1	22	2	41
S 8	29	0	5	5	2	19	1	39
S 11	28	0	4	4	2	10	2	50
S 16	42	0	5	6	1	11	0	35

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1   Conclusion

All the three objectives set out for this study were achieved. Soil samples collected from Kishushe Iron ore mine were analyzed for elemental and mineralogical content, and degree of heavy metal contamination in soil assessed.

Analyses of certified reference material showed that EDXRF technique was suitable for the task. Detection limits for this technique were also obtained. Iron was found to be a key constituent in the soil. Other elements such as Mn, Ti, Cu, Pb, Zr, and Sr were also found in substantial amounts. Although most metals were determined at levels higher than those of uncontaminated soils, they were however within the global average values for agricultural soils. A strong positive correlation was found between elemental content in the topsoil and subsoil, where the two soil profiles showed no significant difference. In general, the study was able to show that the mining operations in the study area have not significantly affected the soil quality, with respect to elemental content.

Different pollution indices were used to assess the degree of contamination. This includes I_{geo}, EF, CF and PLI. These indices indicated that there was minimal contamination of the soil with heavy metals.

The soil samples analysed by XRD technique showed the minerals quartz, albite, microcline and hornblende were present in substantial amounts. The presence of hornblende mineral is a reflection of the high iron ore potential in the area.

5.2   Recommendations

1)   The study can be extended to cover a wider area; particularly those immediately neighbouring the mining area.

2)   It is also important to conduct studies on bio-indicators such as food crops and various plant species.

3)   Considering this study as a baseline study, other follow-up studies need to be undertaken to assess the impact of the mining operations in the area.

4)   More studies need to be conducted in the agrictural lands as well as the water bodies. In addition, impact of the mining process on air quality need to be assessed.

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