UNIVERSITY OF NAIROBI

HEAVY METALS CONCENTRATIONS IN COAL, COAL ASH, SOILS AND GRASS SAMPLES FROM MAAMBA COAL MINE, ZAMBIA.

BY

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I56/7376/2017

A Thesis Submitted in Partial Fulfilment of the Requirements for the Award of the Degree of Master of Science in Environmental Chemistry of the University of Nairobi

January, 2020

DECLARATION

I declare that this thesis is my original work and has not been submitted elsewhere for any award. Where other people's work or my own work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.

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DEDICATION

This thesis is dedicated to all those who contributed to its development. Especially my wife and my daughter who have been there for me both financially and moral support for me to take this challenge. It is their desire for me to achieve greatness that helped to go through difficulties of this study.

ACKNOWLEDGEMENT

ABSTRACT

Maamba Collieries Limited (MCL), is a large coal mining concession in Zambia and manages the only coal-fired Thermal Plant in Zambia. Coal mining activities are generally associated with human and environmental health concerns. Therefore, the purpose of this study was to assess the concentration of heavy metals in coal, coal waste, soil and grass in Maamba coal mining area in Zambia. The concentration of Nickel (Ni), Lead (Pb), Copper (Cu), Cadmium (Cd), Iron (Fe) and Zinc (Zn) were determined in Coal, Coal ash (fly and bottom ash), Sandstone and Mudstone. Most of the samples were digested by wet method using a mixture of nitric, hydrofluoric and perchloric acid as recommended in the literature. The grass forages were digested using a combination of nitric, sulphuric and perchloric acid. The standards for the various metals studied were prepared and Atomic Absorption Spectrophotometer (AA − 6300) was used to analyse the resultant solutions. The levels of heavy metals in coal in their decreasing order were: Fe > Zn > Cu > Pb > Ni > Cd. The levels of heavy metals in coal ash in their decreasing order were: Fe > Pb > Zn > Cu > Ni > Cd. The concentrations of heavy metals in coal ash were higher than the parent coal. The order of selected heavy metals concentration in sandstone and mudstone in their decreasing order were: Fe > Pb > Zn >Cu > Ni > Cd. The mean levels of selected heavy metals in mudstone were higher compared to sandstone. The physiochemical properties such pH and conductivity of the surface soils collected were determined. The results revealed that the pH ranged from 3.2 – 7.4 and conductivity ranged from 0.2 – 589.0 ms/cm. The overall, mean concentrations ranges of heavy metals investigated in soils from Maamba Collieries Limited (MCL) such as Pb, Zn, Cu, Cd and Ni were below the World Health Organization and Food and Agricultural Organization (WHO/FAO) permissible limits. Contamination factor values (CF) were used to assess the level of pollution in soils. The heavy metal contamination from East and West transects were ranked as follows: Pb > Cu > Fe > Ni > Cd > Zn and Pb > Ni > Cu > Zn > Cd > Fe respectively. The CF values of heavy metals from North and South were ranked as follows: Ni > Cu > Cd > Fe > Pb > Zn and Fe > Ni > Cd > Cu > Zn > Pb respectively. Whereas the samples of grass forages analysed were found to be uncontaminated by Ni, however, there were slight contamination of the following metals Fe, Cu, Cd and Pb as their concentrations were above the concentration of the control sample and the permissible limits set by WHO/FAO for plant materials.

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LIST OF ABBREVIATIONS/ACRONYMS AND SYMBOLS

AAS   Atomic Absorption Spectrophotometer

ASTM   American Society for Testing Materials.

CF   Contamination Factor

CV   Coefficient of Variation

FAO   Food and Agriculture Organisation

GCV   Gross Calorific Value

M   meter

MCL   Maamba Collieries Limited

mg/kg   milligrams per kilogram

ppm   parts per million

STDEV   Standard Deviation

TCLP   Toxicity Characteristic Leaching Procedure

WHO   World health organization

XRF   X – Ray Fluorescence

CHAPTER ONE

INTRODUCTION

1.1   Background of the Study

Coal mining production has vastly increased in the world in both developed and developing countries, due to high demand of energy for the growing population and industries. According to Odunayo *et al.* (2016) nearly 8 giga-tonnes per year of coal is produced globally. China is amongst the largest user and miner of coal in the world (Abliz *et al.,* 2018). According to Bergh *et al.* (2011) South Africa is the fifth and fourth largest producer and exporter of coal in the world respectively. It has the biggest coal reserves in Africa estimated at 75 % of Africa's total current reserves. Zambia is one of the developing countries which is faced with energy crisis as it depends on imported crude oil for transport sector and hydro power for most of the industrial and domestic uses. These sources of energy are not sustainable for the growing economy. Therefore, there is need to explore other sources of energy such as coal rather than over dependence on crude oil and hydropower. Coal deposits in Zambia are approximated to be greater than 30 million tonnes while potential coal resources are approximated to be several thousand tonnes (Central Statistics Office, 2007). Maamba Collieries Limited (MCL), presently mines the largest portion of the coal and is the main coal company in Zambia. In Zambia coal is mainly utilized in the mining sector (54 %), commerce and industry (37 %), government and service sectors (9 %) (Central Statistics Office, 2007). Overall, the consumption of coal is very low (2 %) compared to two energy sources mentioned. MCL, is the largest coal mining concession in Zambia and manages the only coal-fired Thermal Plant in Zambia. MCL is the largest independent power producer in the country and caters to the growing demand for power. It contributes to the energy security and economic development of the nation.

Coal is solid fossil fuel derived from partial degradation of plants (Mukahopadhyay & Datta, 2007). Which contains high percentage (%) of carbon element and other elements: Hydrogen (H), Nitrogen (N), Oxygen (O) (Abdurrahman, 2010). For example, a chemical formula of Illinois bituminous coal is $C_{100}H_{85}S_{2.1}N_{1.5}O_{9.5}$. In its formation, plant matter is first converted into peat, lignite, bituminous and finally anthracite (Mukahopadhyay & Datta, 2007). Maamba Coal has high fusibility compared to Wankie Coal (about 1000 ℃) (Maamba Collieries Limited, 2014). When elements present in ash from coal melt, they clog the combustion units. Coal ash of higher fusibility is favoured because it requires high temperature for it to melt under normal conditions.

Environmental pollution is the contamination of our surrounding by substances which harm living things. These could cause diseases or intoxication and in extreme cases death. Environmental pollution is therefore of global interest. This fundamental problem is mainly due to the composition of the atmosphere changes due to natural and anthropogenic processes. Natural processes such as volcanic eruptions rapidly inject large amount of chemicals to the atmosphere. Anthropogenic sources of pollution are attributable to human activities such as mining, emissions from transport network, agricultural waste, and combustion of fossil fuel and dust from moving vehicles and discharge from industries. The comprehensive extraction of coal and mine fires in the area have resulted into many environmental threats such as geosphere and hydrosphere contamination (Pandey *et al.,* 2014). Mining of coal practices are always connected with the removal of large quantities of Sandstone and Mudstone (dump rocks). These dump rocks have potential for formation of acid mine drainage, which is an environmental concern (Pandey *et al.,* 2014). Combustion of coal results into production of airborne by products for example bottom ash and fly ash, which often contain heavy metals (Cu, Zn, Mn, Pb, As, Hg, Cr, Ni and Cd). Such heavy metals usually sediment or are deposited during precipitation or gravitation settling processes and cause soil pollution (Pandey *et al.,* 2014). During mining of coal, particulate matter which contains fine particles of heavy metals, Sulphur dioxide and other pollutants are emitted into the atmosphere. Abdurrahman (2010) reported that the availability of toxic trace metals in coal is a significant concern on the perspective of environmental safety and these toxic metals would be emitted into the atmosphere while other toxic metals are dispensed in bottom as well as fly ash.

Fabiane *et al.* (2010) revealed that utilization of coal as source of energy may result into grave environmental impacts due to discharge of contaminants resulting into pollution of soil, water and composition of air. Particles of toxic hazardous substances released in the atmosphere come back to the land by either gravity or wet deposition which affect the composition of soil, plants, buildings, surface water and even under ground water. In recent years, the world energy demands have increased tremendously and new technologies developed. However, to a large extent energy production is dependent on fossil fuels (Mandal and Sengupta, 2006). According to Mandal and Sengupta (2006), coal-fired power plants produce approximately 23% electrical power utilized globally. The generation of huge amount of ash caused by coal as a raw material in thermal power plants is a major contributor of environmental contamination. Fly ash has the ability to pollute the soil and groundwater of nearby places with the toxic heavy metals such as Cu, Fe, Zn, Pb, Cd and Cr.

Mishra *et al.* (2013) observed that the availability of heavy metals in particulate matter pose environmental problems including severe and persistent health problems. Long period of vulnerability to Cd, As, Ni, and Cr even at low levels can cause cancer (Akoto *et al.,* 2008)**.** Heavy metals levels in human organs at concentrations greater than the World Health Organization (WHO) permissible limits can cause teratogenic, carcinogenic, cardiovascular problems (Shang *et al.,* 2016). Cr, B, V and Sb have been recognised to limit the growth and survival of vegetation and population of microbes (Singh *et al.,* 2010). The major concern of effect of soil pollution by heavy metals on environmental health is because they undergo bioaccumulation and bio-concentration along food chain by vegetation, aquatic species like fish, and consumption of contaminated pastures by livestock and exposure to human populations via eating of contaminated vegetables and dairy products.

The natural and anthropogenic processes result into increased levels of heavy metals in the environment. Major human activities include industrial ventures, burning of oil and coal, building and demolition, movement of vehicles, crustal materials, and road dust re-suspension (Shah and Shaheen, 2012). Several mining activities, vehicular movement during transportation of coal and fire from the mine are the main origin of particulate matter which is associated with heavy metals pollution in the mining areas. Some studies reported higher level of toxic metals and particulate matter in coal mining regions (Dubey *et al.,* 2012: Roy *et al.,* 2012). Coal is also composed of different elements in trace quantities and high enrichment factors have been reported for some elements (Mishra *et al.,* 2013). Consequently, the wind-blown coal dust and combustion of coal are among notable origin of heavy metals contamination in the atmosphere near coal mining areas.

Heavy metals soil contamination is a growing concern globally due to increased human activities. This includes industrial, agricultural, mining, transportation and other related fields. They are dissipated by atmospheric forces with distance and carried up to many kilometres away from their origin and relocated to the geosphere and hydrosphere via precipitation or gravitational settling. Previous findings have disclosed that people subjected to excessive levels of heavy metals could result to their bioaccumulation in organs such as liver, kidney and bones (Ripin *et al*., 2014). Heavy metals naturally occur in rocks and in different amounts in soils based on their site and rock that has disintegrated to form soil's particles. Some of the heavy metals play an imperative function in human health (integral part of the protein, activator of enzyme reaction, stabilizer in biomolecules and co-factor in hormonal action) and are beneficial when

taken in the body as part of our diet or as supplements at recommended low concentrations. However, Pb, Cd, and Hg are toxic and harmful to people and have no recognised biological importance (Science Commission Unit, 2013). People living near coal mining areas are at higher risk of being exposed to toxic metals pollution through inhalation of suspended dust particles. This can also reveal the extent to which human populations are exposed to trace metals pollution arising from coal mining practices (Mishra *et al.,* 2013).

1.2   Statement of the problem

According to Niu *et al.* (2017) coal-mining activity generate large quantities of waste (tailings) and contribute to long-lasting environmental destruction such as disturbance of land surface, damage of biodiversity and ecosystems, soil erosion, mine subsidence, and environmental (air, noise, and water) pollution. Apart from that, production of dump rocks such as sandstone and mudstone lead to acid mine drainage and toxic metals pollution. During generation of electricity from the thermal power station, fly and bottom ash are produced and dumped in ash ponds which can contaminate the soil with toxic heavy metals. Dump rocks and coal ash may lead to pollution of the soil by trace metals through runoffs. High levels of toxic metals in soil, result into significant risk to human, plant and animal populations. Heavy metal ions could simply get into animals and human systems by breathing in, dermal absorption or eating (Sun *et al.,* 2010). Heavy metals exposure even in low concentration overtime accumulates and could be harmful to human health.

Heavy metals soil contamination pose risks and hazards to ecosystems and people via: direct eating or contact with polluted soils, the food chain (soil – plants – human or soil – plants – animals – humans) and consuption of contaminated underground water (Wuana and Okieimen, 2011). Heavy metals availability in the ecosystem is of considerable ecological importance because they are poisonous at certain levels, movement via food chains and persistence leads to their build-up in the environment (Opaluwa *et al.,* 2012). Vegetations may uptake heavy metals through three routes such as soil, water or air. Availability of coal mines in Maamba area and dumping of fly ash, bottom ash, mudstone and sandstone may contribute to the contamination of the soil, vegetation, underground and surface water with heavy metals. Heavy metal pollution near coal mine is a global issue because their adverse effect to human health.

1.3   Objectives

The study was guided by the following objectives.

1.3.1 Overall objective

The research's main objective was to determine the level of heavy metals concentrations such as Cd, Pb, Cu, Zn, Fe and Ni, in coal, coal waste products, soils and vegetation.

1.3.2 Specific objectives

(i) To determine the levels of selected heavy metals in coal, coal ash (fly ash and bottom ash), sandstone and mudstone.

(ii) To determine the levels of selected heavy metals in soil samples and compare them with permissible limits.

(iii) To determine the levels of selected heavy metals in grass from coal mining area.

(iv) To assess selected heavy metals pollution in soil and grass as the distance increases from the mining site.

1.4 Justification and significance of the study

Coal mining exploits continue to grow exponentially globally, the result of whose by products pose potential toxicities to humans and animals. For example animals that graze in the coal mining locality and may be subjected to high levels of toxic metals, from the grass, water and soil. Likewisely, human populations can get exposed to heavy metals through air, water, vegetables, milk and meat products obtained from polluted areas. Besides the above exposure route, heavy metals may also be introduced in the food chain through crops, and bio-accumulate in crops. Furthermore, pollutants could migrate from soil to water reservoirs and into ground water, leading to contamination of water used for consumption. Heavy metals can also be absorbed by vegetation (such as vegetables) and eventually eaten either by agricultural livestock, or by humans, resulting into elevated levels in human diet (SCU, 2013). Ingestion of soil (geophagia) is notably wide spread activity especially amongst Infants below three years, while playing outdoors. Children are believed specifically to be more vulnerable to pollutants, and are considered to be at highest risk from polluted soils (SCU, 2013). Working with soil emit particulate matter into the atmosphere and could also be inhaled during respiration process by construction workers and others nearby. Micro- particles may enter into the lungs, and there is a possibility that pollutants may be assimilated into the blood stream (SCU, 2013).

Literature review indicates that very few research works have been done on toxic metal contamination in soil and grass in the context of the coal mining sector in Zambia. Some studies in Zambia, reported heavy metals in soil and plants around Kabwe Town (former mining town for lead) (Tembo *et al.,* 2006). Therefore, the findings of this study would be beneficial by establishing the current status and creating awareness about the degree of heavy metals pollution

in the environment as a result of coal mining practices in the region. Besides, it will open doors for further research about heavy metals pollution, mitigation measures and make significant contribution to scientific knowledge.

CHAPTER TWO

LITERATURE REVIEW

2.1   Heavy metals pollution near coal mines

The utilisation of coal as source of energy has contributed to a chain of ecological and environmental concerns (Mandal and Sengupta, 2006). Chen *et al.* (2015) investigated the heavy metals content in soil samples, water and plants along Chongan River channel segment, downstream from the coal mining area. The study showed that most of wastewater standards have already exceeded the secondary Chinese discharge standards. It was also revealed that the effluent discharged did not meet the acceptable standards as it was contaminated by toxic metals as the result of coal mining in the area. The mining area had soil moderately contaminated by zinc and gravely contaminated by mercury. In addition, it was also revealed that all vegetation samples for instance rice seedlings, *Pteris vittata* L and vegetables, such as cucumber, tomato, capsicum, kidney bean, and eggplant, were contaminated by effluent from coal mine. These findings implied that the upper reaches of the Chongan River were gravely contaminated by heavy metals wastewater from coal mine, and hence, need imminent environmental management (Chen *et al.,* 2015).

Physicochemical characteristics and heavy metals content in soils nearby Jharia coal field in Jharkhand state of India were investigated to determine the concentration of pollution in the region (Mishra *et al.,* 2013). It was observed that the physicochemical characteristics of the soil were extensively changed by coal mining in the area. Areas around coal mining showed high concentrations of toxic metals. The mean concentrations of Zn, Cu, Pb, Cd, Cr, Fe, Ni and Mn were greater than the recommended critical soil levels of India. It was shown that heavy metals in soils near coal mining region such as Ni, Cu and Mn were approaching the toxic limits (Pandey *et al.,* 2014). The analyses of metals were done at different depths at the different sites using Atomic Absorption Spectrometry (AAS) to determine the concentrations of Cd, Zn, Pb, Mn and Ni, in coal ash. It was found that the concentrations of selected heavy metals in ash samples decreased in this order Pb, Zn and Ni (Miod, 2008).

The concentrations of Cu, Zn, Mn, Ni, Cr, Cd, Co and Pb were assessed in another study, for soils in close proximity to a lignite coal mine in Surat (Gujarat). It was shown that soils in close proximity of the coal mine were contaminated with Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn (Ladwani *et al.,* 2012). Spatial variations and changes in some heavy metals in soil were established near coal mining premises. Evidently, human activities, in particularly coal mining practices are

accountable for increased levels of heavy metals in soil. Pandey *et al.* (2014) also reported high enrichment of Zn, Cu, Cd and Pb in soils around coal mining regions. From the above studies, it can be deduced that coal mining is a serious source of heavy metals if control measures are not taken into consideration. Therefore, remediation measures should be implemented in order to protect people from ingestion of heavy metals directly (eating of soil), indirectly (from plants and animals) as well as other environmental exposure routes.

2.2 Heavy metals in soil and plants

A wide variety of activities and exposure routes could result into emissions of toxic metals to the environment. These could be discharged into the atmosphere throughout the course of burning, removal and processing and to surface water through runoff. Heavy metals can be liberated from storage and transported to the soil and ends up into underground waters and crops (Jarup, 2013). The availability of heavy metals in divergent varieties of soils with varying degree of solubility such as: in inorganic and organic constituents, in soil solution, structural constituents of the soil lattices and as precipitate with other soil constituent are important considerations. Notably, the first two types are able to be soaked up and used by vegetation (Zeng *et al.,* 2011).

Heavy metals accumulation by both leaves and roots of plants grown in polluted areas is well documented. Common indicators of heavy metals toxicity include characteristics such as decreased root length, biomass and shoot length (Street, 2012). Heavy metals transported by metal-tolerant plants has been of extensive interest due to repercussions for phytoremediation which has been reported (Street, 2012). Remediation of polluted soils by use of plants is viewed as having considerably promise contrast to traditional, civil engineering methods (Rahinimi *et al.,* 2012).

Grown plants are notably polluted by heavy metals, in particular cereal grains, lawn grasses and lettuces collected near the smelter (Pruvot, 2006). Additionally, due to the deposition of contaminated dust; the percentage of Pb available on lawn grasses may account for 50% of the total pollution of the vegetation. There was high metal concentration in grass of polluted lawns. In order to permit determination of the risk for people, the data of unwashed grasses was considered. Pruvot (2006) observed that people may be directly exposed to the polluted grass, particularly infants when they play in the lawns.

2.3   Heavy metals

These are a class of metals which have a density higher than 5 g/cm^3 (Lottermoser, 2007: Dzomba *et al.,* 2012). They could be categorised into two classes with respect to their toxicity; micronutrients like Mn, Cu, Fe, Zn, Cr, Mo and Ni which are vital in small quantities and poisonous ones like Cd, As, Hg and Pb which do not have biological significance. As a result of their non-biodegradability, they are exceedingly chronic in the environment, possess long biological half-lives, demonstrate stability to heat and ability to bio-accumulate and bio-concentrate to toxic concentrations in both animals and plants. They have been reported to have adverse health effects on humans and animals even at low concentrations, due to the absence of good processes for their removal from the body system (Adah *et al.,* 2013).

2.3.1   Cadmium (Cd)

Cadmium mainly occurs as sulphide minerals incorporated with zinc ores, lead ores and complex copper-lead-zinc ores (Marrow, 2001). Cadmium is non-essential for animal and plant life processes. However, some study revealed that cadmium is a trace metal which has some important role in life processes (Inam *et al.,* 2012). But its utilisation at present time are not understood. There are some beliefs that, it is involved in the plant metabolism but its position as a crucial trace metal is still not clear (Inam *et al.,* 2012). Exposure to Cd can result to harmful consequences, including; lung cancer, prostatic proliferative lesions, fracturing of bones, dysfunction of kidneys, and abnormally high blood pressure (Hu *et al.,* 2017).

2.3.2   Copper (Cu)

Copper metal exists naturally in animals and plants (Khajekar and Deshmukh, 2017). It also occurs in soil, rock, water and sediment. It is a required metal for all living organisms including humans, animals, and plants, in appropriate concentrations during consumption in food or as a supplement. For example, Cu is a major component of several metalloproteins (Khajekar and Deshmukh, 2017). Copper together with vitamin C, is vital in maintaining skin elasticity and blood vessels (Inam *et al.,* 2012). In addition, it assists in production of chemicals by the body that moderate pulse, blood pressure, and healing. The usual signs of Cu deficiency in the diet are; anaemia, arthritis, and many other health problems. However, high concentration of copper within the organic structure will cause abdomen and internal organ distress like nausea, vomiting, diarrhoea, and abdomen cramps (Khajekar and Deshmukh, 2017).

2.3.3 Lead (Pb)

Lead consists of four stable isotopes. It is not a commonly found metal, however, its ore deposits are easily found and vastly spread throughout the earth (Fang *et al.,* 2014). Its properties, for example low melting point, density and corrosion resistance make it a popular element in solder, weights, storage batteries and pipes (Fang *et al.,* 2014). Lead is a non-essential trace metal since it has no functions neither in plants nor humans. It has unfavourable health effects in people even in small quantities. Symptoms of Pb toxicity are anemia, colic, brain damage, nervous disorders and headache (Inam *et al.*, 2012 : Hu *et al.,* 2017).

2.3.4 Zinc (Zn)

It exists naturally in the earth's surface rocks and is not a native metal, and therefore, is not available as native element in nature (Mehdilo *et al.,* 2013). There are an estimated 55 mineralized forms of zinc and the most valuable zinc minerals in the world are smithsonite/ zinc spar ($ZnCO_3$), sphalerite/ zinc blende (ZnS), and hemimorphite ($Zn_4Si_2O_7$ (OH_2) H_2O) (Mehdilo *et al.,* 2013). Zn is a micronutrient metal, known to be a vital trace metal for people, animals and plants. It participates in over one hundred various chemical reactions in the body (Inam *et al.*, 2012). A number of these chemical reactions assist our body during formation and maintaining DNA - the compound which regulate how every single part of our bodies is formed and function. Deficiency in zinc can result in serious health defects in humans and animals (Inam *et al.,* 2012). Deficiency of zinc in the diet include the following symptoms; mental apathy, damage to reproductive organs and hair loss (Prasad, 2008). In addition, growth retardation and impaired mental capacity are also signs. High Zn concentrations could lead to impairing of cellular energy production through an inhibitory action on mitochondria and cause Parkinson's disease (PD) (Park *et al.,* 2014).

2.3.5 Chromium (Cr)

Chromium occurs in different chemical types showing variable valences from 0 to VI. Cr (VI) is a very poionous and exist as dichromate ($Cr_2O_7^{2-}$) or chromate (CrO_4^{2-}) and it has adverse effects on human health (Reczajska *et al.,* 2005). It was discovered that occupational vulnerability to Cr (VI) chemicals results to a number of health issues. Breathing in and retention of Cr (VI) bearing substances may lead to nasal septum perforation of the, bronchitis, asthma and larynx pneumonitis inflammation (Reczajska *et al.,* 2005). Cr (III) is less mobile and not very poisonous (Becquer *et al.,* 2003). It is a trace metal important for good functioning of living organisms. Contaminatin of ground water and soil is attributable to utilization of Cr in several

industrial practices has become the main genesis of concerns to animal and plant scientists for the previous ten years (Prasad , 2008).

2.3.6   Nickel (Ni)

Coal and oil contain significant quantities of Ni since organic matter (OM) demonstrate strong ability for uptake of the element (Lenntech, 1998 - 2018). Uptake of high levels of nickel has the following repercussions: nose cancer, lung cancer, prostate and larynx cancer, lung embolism, dizziness and sickness, asthma, respiratory failure, persistent bronchitis, birth disorders and allergic side effects such as heart disorders and skin rashes (Lenntech, 1998 - 2018).

2.4   Soil pH

The alkalinity and acidity of the soil are assessed by determining the pH of its solution. Among the properties of the soil, it plays the most significant function in evaluating solubility of minerals, metal speciation, movement, and finally bioavailability (Zeng *et al.,* 2011). The pH affects the level of heavy metals in soil, in acidic environment, heavy metals will easily dissolve in rain water and sink underground and affect the underground water and also increase bio absorption by plants. At high pH, the heavy metals will precipitate and will be found in surface soil in high concentration. Therefore, pH for each soil sample will be determined in this study.

2.5   Soil organic matter

Its constituents in soil is another significant soil property affecting heavy metals availability. Extensive investigations on the specific role of organic matter (OM) on presence of heavy metals shows that adsorption onto soil components decreased with decline in composition of OM content in soils (Zeng *et al.,* 2011). Dissolved organic matter is composed of fractions of humic and fulvic acids. In polluted soil, humic acid form insoluble complexes with heavy metals, reducing solubility. However, the fulvic acid fraction maintain heavy metals in the solution. Solution form of OM in soils may fuel the movement and absorption of heavy metals to vegetation (Zeng *et al.,* 2011).

2.6   Soil texture

Texture of soil performs a vital task in movement of heavy metals in soil. It gives the particle magnitude dispensation of the soil and thus the content of very small particle such as clay and oxides. These substances are vital uptake means for heavy metals in soils (Sherene, 2010). The proportion of three mineral particles; sand, clay and silt, contribute to soil texture properties.

CHAPTER THREE

MATERIALS AND METHODS

3.1   Description of the study area

Coal mining in Zambia is done by Maamba Collieries Limited (MCL), which is biggest firm in Zambia. The operations and head office for the firm are situated in southern province. Essentially, all activities take place in Sinazongwe district, Maamba town. Maamba town is approximately 350 km away from Lusaka. The mining firm has estimated reserves of 140 million tonnes made up of thermal and high-grade coal, distributed over 1070 hectares out of a total granted land of 7900 hectares (MCL, 2014). Mining is being carried out in two blocks, called Izuma A and Izuma B (MCL, 2014).
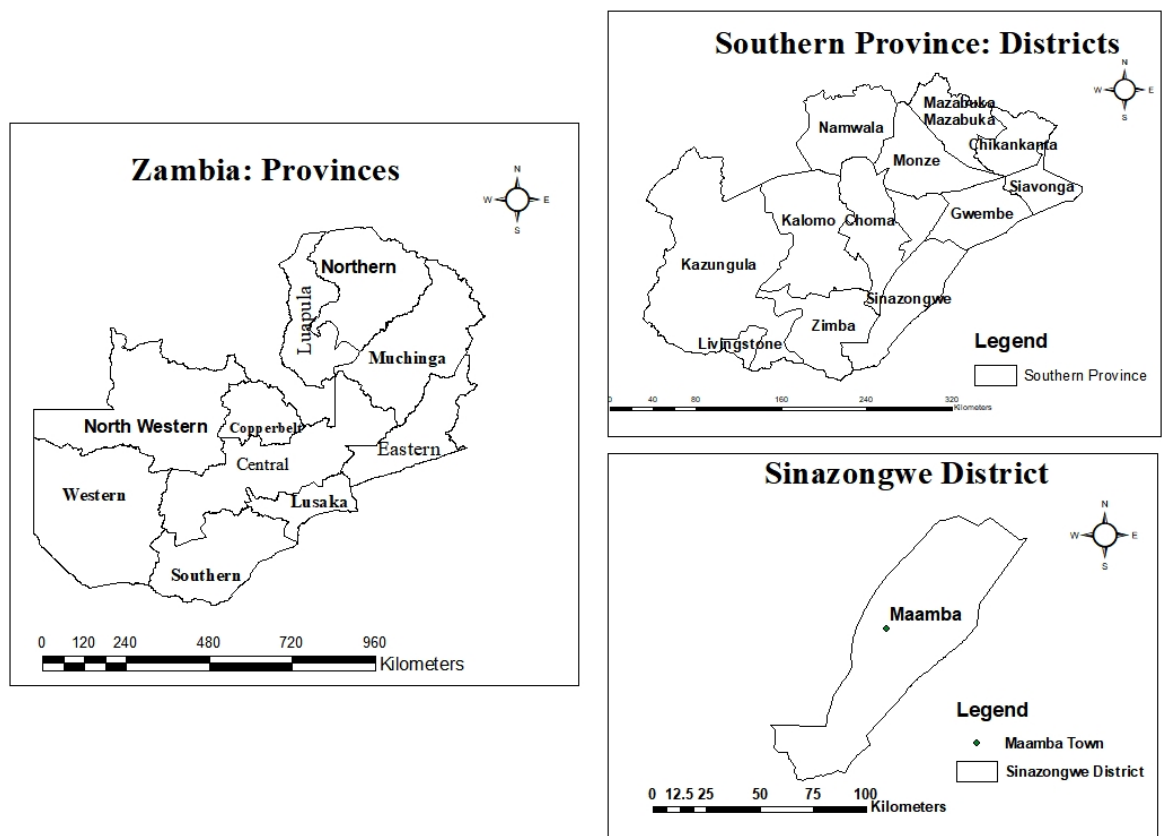
Figure 1   Maps showing the study area in Maamba, Zambia (Mbanga, 1992).

MAAMBA TOWN

1st September, 2018
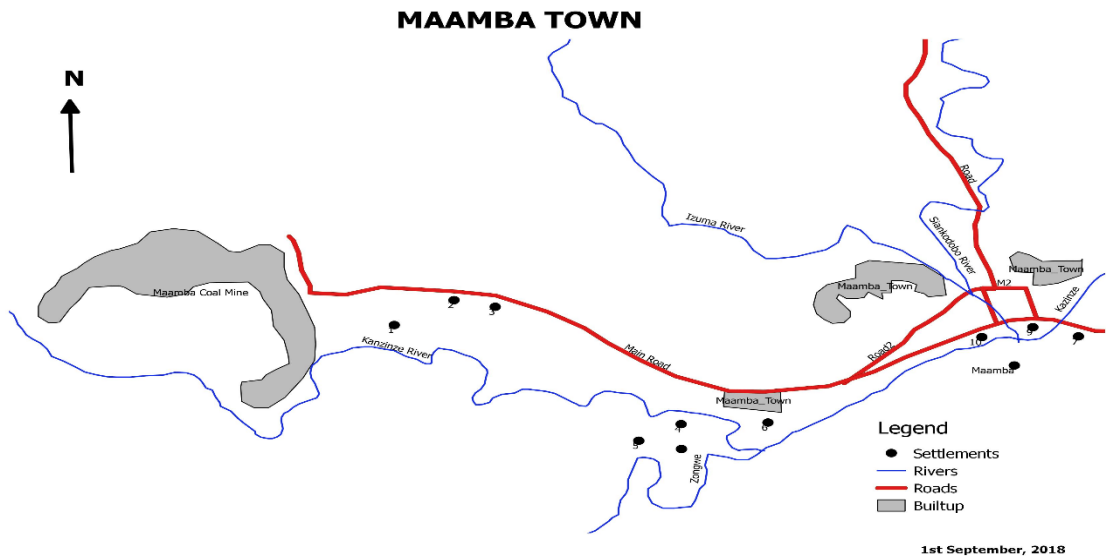
Figure 2   A map showing location of the mine in Maamba town, Zambia (Mbanga, 1992).

The area has three seasons like any other parts of Zambia. From May to mid-August cold season, late August to October hot season and November to April rain season.

3.2   Sampling

Samples of soil were collected systematically in four transects (North, East, West and South) of the mining area in distance intervals such as 10, 20, 30, 40, 50, 100,150 and 200 m. Road soils near the mine were also sampled and coded. The soils were scooped from 0 – 20 cm deep using clean stainless-steel core samplers. Each of the soil samples collected, were composed of 3 sub samples taken within 50×50 cm^2 area following the method detailed elsewhere (Mumie, 2013). The Garmin GPS 60 navigator was used to obtain coordinates and elevations of each sampling site and they were recorded. Soil samples were packed into plastic sample containers and closed tightly to avoid contamination. Other samples such as grades of Coal (peas, low grade and high grade), coal waste (bottom ash and fly ash) and waste rocks (mudstone and sandstone) were sampled from their piles and coded. The samples were taken, for analysis in the Department of Chemistry, University of Nairobi. A temperature of 105 ℃ was used to dry the samples and pulverised to go through a 2 mm mesh sieve and pieces. Powdered samples were packed into plastic sample containers and kept in an air-tight vessel for further work.

3.3   Grass sampling

Eight grass samples were taken by means of a scissors within the area of soil sampling and transported in plastic containers to the research laboratory at the Department of Chemistry, University of Nairobi for further preparations. The grass samples were air dried for four weeks

in the sun to a fixed weight. Finally, they were put in an oven and dried up to a constant temperature (105 ℃). Then pulverised to go through a 2 mm mesh sieve and pieces. The powdered sample were packed in sample containers and kept in an air-tight vessel for further work.
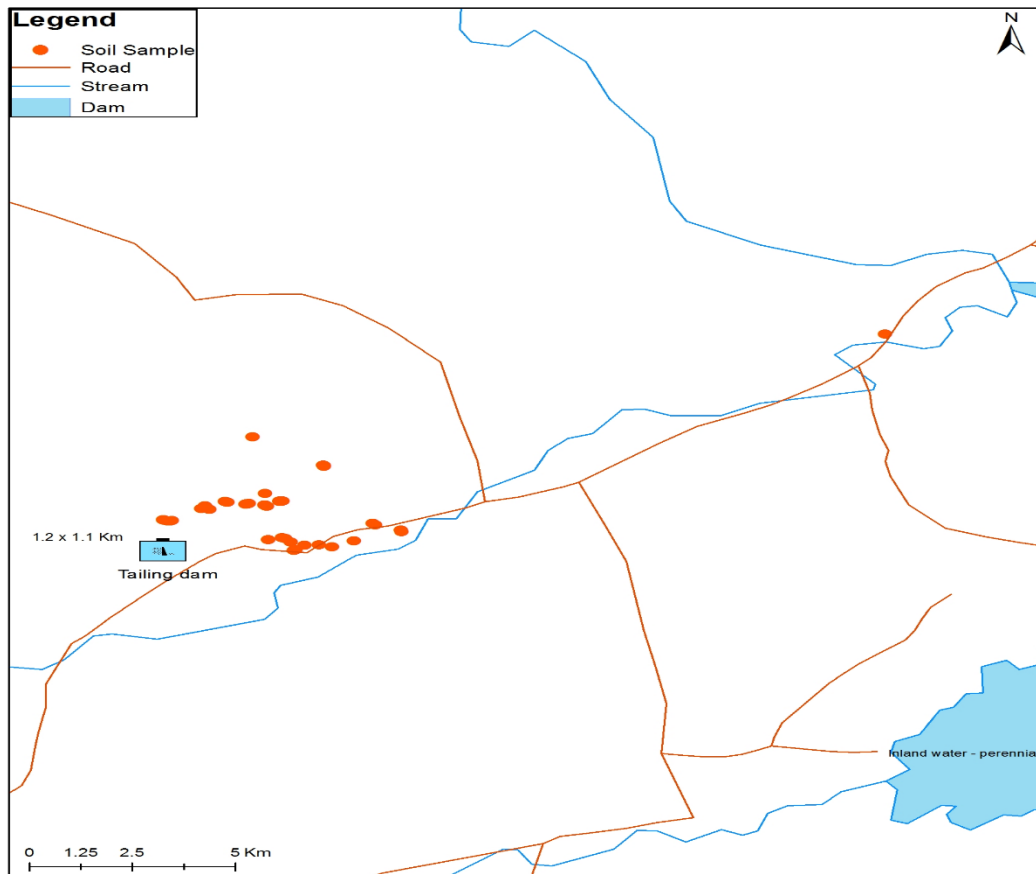
Figure 3   Map showing sampling points of soil samples collected from Maamba mine.

3.4   Instrumentation

The samples were analysed using Atomic Absorption and X − Ray Fluorescence Spectrophotometers.

3.4.1   Atomic Absorption Spectrophotometer

The instrument quantifies the quantity of light at the resonant wavelength which is taken in as it goes via a cloud of atoms of an element. When the number of atoms in the light route multiply, the quantity of light taken in increases in a foreseeable way. Quantitative determination of the quantity of analyte and metal available could be formulated by quantifying the quantity of light taken in. when the light with unique origin is utilised and care is taken during choosing of wavelength, this permit a particular quantitative determination of each metal in existence of others (Welz & Sperling, 1999). The instrument used for analysis is based on the Beer's Lambert

law, which states that the absorptive capacity of a solute is directly proportional to its level in a solution. By using linear regression, from a calibration plot of absorbance against concentration of standards, the concentration of heavy metals in samples were computed. The equation which shows linear relationship between absorbance and concentration is shown.

$$A = \varepsilon bC \qquad\qquad\qquad\qquad \text{eqn (1)}$$

Where A is absorbance, ε is absorptivity, b is the path length and C is the concentration Due of its specificity, sensitivity, precision and simplicity, the AAS is the most broadly recommended instrument used in analytical procedures for trace heavy metals analysis.

3.4.2 Optimum instrument parameters

The parameters of the instrument which yielded the most sensitive and reproducible results are given below in Table 1.

Table 1: Optimum operation conditions for Atomic Absorption Spectrophotometer (AA-6300).

	Zn	Cu	Fe	Ni	Cd	Pb
Lamp current intensity (mA)	8	6	12	12	8	10
Lamp mode	BGCD2	BGCD2	BGCD2	BGCD2	BGCD2	BGCD2
Wavelength (nm)	213.9	324.67	248.3	231.97	328.8	283.37
Spectral band pass (nm)	0.7	0.7	0.2	0.2	0.7	0.7

Note: BGCD2 = Background correction deuterium lamp.

3.4.3 X- Ray Fluorescence (XRF)

It is a method used to analyse elements and widely used in industry and science. It is built on the postulate that, when each atom is excited by absorption of energy from the external source, emit X-ray photons of a characteristic wavelength or energy. The elements available could be identified and quantitated by counting the number of photons of each energy released from a sample. The analysis is very fast and sample preparation is minimal. (James and Ferguson, 2012). The instrument was used for qualitative screening of selected samples in order to determine the major constituents.

3.4.4 Lab-ware apparatus

All lab-ware (digestion tubes, sample containers, pipettes, and volumetric flasks) were soaked 48 hours in washing detergent. After that, cleaned with running tap water and soaked in distilled water for 48 hours. The apparatus were removed from distilled water and transferred into aqua regia, in which they soaked for 24 hours. The washing procedures were completed by rinsing the lab ware when required for immediately use, with distilled water and dried at 80 ℃, where necessary.

3.5 Digestion of plant materials

A 1.000 – 1.155 g powdered samples was put into a boiling test tube and 68% nitric acid was added (10 mL). The content was heated between the temperatures of 90 ℃ – 100 ℃ for 30-45 minutes, in order to oxidise organic matter. Then content was left to cool, 5 mL of 70% perchloric acid was added and swirled for 1 minute and the content was heated till the appearance of white fumes. The content was left to cool, then 20 mL of distilled water was added and the content was heated for further discharge of any fumes. After allowing the content to cool to room temperature, the digested solutions were filtered into a 25 mL volumetric flasks using Whatman filter paper No 41 and washed thoroughly using warm distilled water and filled up to the mark as detailed elsewhere (Zeng-Yei, 2004**).** The samples were aspirated by using an AAS (AA-6300). The samples were prepared in three replicates and duplicate results were considered for each analysis for calculation of the mean. The concentrations of the analyte was determined from the calibration curve.

3.6 Digestion methods for coal, coal ash, mudstone and sandstone

3.6.1 Nitric-perchloric- hydrofluoric acid digestion

A 0.5000 – 0.5900 g samples were put into boiling tubes and 5 mL of 68% nitric acid was added and boiled at a temperature of 150 ℃ for 30 − 45 minutes. Then, the mixture was left to cool to room temperature. Hydrofluoric and perchloric acid (5.0 and 1.5 mL respectively) were measured and added to the mixture. The resulting content was heated using an aluminium block till dense white fumes of perchloric acid was seen (for 3 hrs). The residue was dissolved by adding concentrated nitric acid and distilled water (2.5 and 5.0 mL respectively). The Whatman filter paper No. 40 was used to filter the mixture into the 25 mL volumetric flask and toped up to the mark by using distilled water following the method detailed elsewhere (Sijakova-Ivanovai *et al*., 2011). The samples were prepared in three replicates and duplicate results were considered

for each analysis for calculation of the mean. The AAS (AA-6300) was used for analysis of heavy metals concentrations in samples.

3.6.2   Nitric-perchloric-hydrofluoric acid digestion soil

A 1.000 – 1.155 g powdered sample was put into a clean boiling tube. 5 mL of 68 % nitric acid was added to a sample and the mixture was boiled between the temperatures of 900˚C – 1000˚C for 30-45 minutes, in order to oxidise organic matter. The mixture was allowed to cool and 3 mL perchloric and 2 mL hydroflouric acid was added gradually. The mixture was boiled on an aluminium block for 3hrs. The resulting mixture was left to cool and Whatman filter paper No. 41 was used for filtration. The cooled solution was made up to 25 mL in volumetric flasks with distilled water and heavy metals were determination by Atomic Absorption Spectrophotometry following the procedure detailed elsewhere (Adaikpoh *et al.,* 2005). All the concentrations were in mg/kg and were calculated using the eqn 1 .

$$\text{Concentration in }\left(\frac{\text{mg}}{\text{kg}}\right) = \frac{\text{concentration of metal }\left(\frac{\text{mg}}{\text{L}}\right) \times \text{volume of digest(L)}}{\text{weight of the sample (kg)}}$$

<div align="right">eqn(2)</div>

3.7   Standard preparation of the blank solution

The blank solutions were prepared in the similar procedure as samples. The only exception is that the blank solution should not contain the sample. Same acids mixture used during sample digestion, same digestion time and temperature. All the procedures involved in each sample preparation for analysis were the same as those of blank solution preparation. The Whatman filter paper No. 40 was used to filter the mixture into volumetric flask and dilute up to the mark with distilled water and the solutions were ready for AAS analysis.

3.8   Preparation of standards for each metal

3.8.1   Calibration Standard for Zinc (Zn)

The 1000 ppm standard solution was prepared using zinc sulphate crystals ($ZnSO_4.7H_2O$, 99.5%) as recommended by the manufacturer. The salt was dissolved in 1:1 nitric acid and was diluted with distilled water in 1000 mL volumetric flask up to the mark to make 1000 ppm stock solution of zinc. From 1000 ppm, dilution was done to form 100 ppm using dilution formula $C_1V_1 = C_2V_2$. Where C and V are concentration and volume respectively. A series of dilution was done from 100 ppm to give working standards; 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 ppm zinc using the dilution formula. The absorbance for the standards were recorded in Appendix II and the calibration curve plotted (Appendix III).

3.8.2 Calibration Standard for Copper (Cu)

The 1000 ppm standard solution was prepared using copper (II) sulphate crystals ($CuSO_4.5H_2O$, 99.5%) as recommended by the manufacturer. The salt was dissolved in 1:1 nitric acid and was diluted with distilled water in 1000 mL volumetric flask up to the mark to make 1000 ppm stock solution of copper. From 1000 ppm, dilution was done to form 100 ppm using dilution formula $C_1V_1 = C_2V_2$. Where C and V are concentration and volume respectively. A series of dilution was done from 100 ppm to give working standards; 0.05, 0.1, 0.5, 1, 1.5 and 2 ppm copper using the dilution formula. The absorbance for the standards were recorded as shown in Appendix IV and the calibration curve plotted (Appendix V).

3.8.3 Calibration Standard for Iron (Fe)

The 1000 ppm standard solution was prepared using Ferric ammonium sulphate crystals ($NH_4Fe(SO_4)_2.12H_2O$, 98%) as recommended by the manufacturer. The salt was dissolved in 1:1 nitric acid and was diluted with distilled water in 1000 mL volumetric flask up to the mark to make 1000 ppm stock solution of iron. From 1000 ppm, dilution was done to form 100 ppm using dilution formula $C_1V_1 = C_2V_2$. Where C and V are concentration and volume respectively. A series of dilution was done from 100 ppm to give working standards; 0.5, 1, 1.5 and 2 ppm iron using the dilution formula. The absorbance for the standards were recorded as shown in Appendix VI and the calibration curve plotted (Appendix VII).

3.8.4 Calibration Standard for Nickel (Ni)

The 1000 ppm standard solution was prepared using Nickel chloride crystals ($NiCl_2.6H_2O$, 98%) as recommended by manufacturer. The salt was dissolved in 1:1 nitric acid and was diluted with distilled water in 1000 mL volumetric flask up to the mark to make 1000 ppm stock solution of nickel. From 1000 ppm, dilution was done to form 100 ppm using dilution formula $C_1V_1 = C_2V_2$. Where C and V are concentration and volume respectively. A series of dilution was done from 100 ppm to give working standards; 0.25, 0.5, 1, 1.5 and 2 ppm nickel using the dilution formula. The absorbance for the standards were recorded (Appendix VIII) and the calibration curve plotted (Appendix IX).

3.8.5 Calibration Standard for Cadmium (Cd)

The 1000 ppm standard solution was prepared using cadmium acetate crystals ($(CH_3COO)_2Cd.2H_2O$, 99%) as recommended by manufacturer. The salt was dissolved in 1:1 nitric acid and was diluted with distilled water in 1000 mL volumetric flask up to the mark to make 1000 ppm stock solution of cadmium. From 1000 ppm, dilution was done to form 100 ppm using dilution

formula $C_1V_1 = C_2V_2$. Where C and V are concentration and volume respectively. A series of dilution was done from 100 ppm to give working standards; 0.05, 0.1, 0.15, 0.2, 0.3 and 0.4 ppm cadmium using the dilution formula. The absorbance for the standards were recorded (Appendix X) and the calibration curve plotted (Appendix XI).

3.8.6 Calibration Standard for Lead (Pb)

The 1000 ppm standard solution was prepared using Lead (II) nitrate (Pb $(NO_3)_2$, 99.5%) as recommended by manufacturer. The salt was dissolved in 1:1 nitric acid and was diluted with distilled water in 1000 mL volumetric flask up to the mark to make 1000 ppm stock solution of lead. From 1000 ppm, dilution was done to form 100 ppm using dilution formula $C_1V_1 = C_2V_2$. Where C and V are concentration and volume respectively. A series of dilution was done from 100 ppm to give working standards; 0.1, 0.2, 0.3, 0.4, 0.5 and 1 ppm lead using the dilution formula. The absorbance for the standards were recorded (Appendix XII) the calibration curve plotted (Appendix XIII).

3.9 Determination of soil properties

3.9.1 Determination of the pH

A 2.00 g of soil was measured into a sample container and 5 mL of distilled water was added to get the 1:2.5 soil/water mixture. The sample containers with the soil/water mixture were placed on an automatic stirrer and stir for 30 minutes and finally the samples were removed from the automatic stirrer and were kept for 48 hrs. Finally, the electrodes were dipped into the mixture and pH was determined on the upper part of the suspension (Mumie, 2013). Electrical conductivity was determined from the same mixture prepared for determination of pH of the soil.

3.9.2 Contamination Factor (CF)

The contamination factor was computed by finding the quotient of the level of each metal in soil by the local background (Niu *et al.,* 2017). In case of this research, the local background was the concentration of the control sample.

$$CF = [C]_{heavy\ metal} / [C]_{background}$$ Eqn (3)

The extent of pollution was categorised based on their strength on a scale varying from 1 to 6, where 6 is very strong, 5 is strong to very strong, 4 is strongly polluted, 3 is moderate to strong, 2 is moderate, 1 is none to medium and 0 is none (Khan *et al.,* 2017).

3.9.3   Proximate and Ultimate analysis of coal

Proximate analysis determines the following: moisture content, volatile matter (VM), ash and the fixed carbon within the coal sample. These parameters were assessed using the following standard procedures: ASTM D3302M - 12 was used to determine moisture content, Ash was deduced by following ASTM D3174-12, Volatile matter was deduced by following ASTM D3175 - 11 and Fixed carbon was computed using the equation:

% fixed carbon = 100 – (% moisture + % volatile matter + % ash) (Zhu, 2014)   Eqn (4)

The major components of coal such as carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O) are determines by ultimate analysis (Zhu, 2014). Gross calorific (GCV) value was also assessed. Elemental composition of coal such as C, H, N and O were determined by following ASTM D5373 − 08 standard procedure. Sulphur composition and GCV were determined using standard procedures ASTM D 4239 − 12 and ASTM D 5865 − 12, respectively (Zhu, 2014).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1   X-Ray Fluorescence (XRF) Scan results

XRF was used for qualitative screening of selected samples in order to qualitatively establish the major and minor constituents. The samples which were screened are coal (Low Grade coal (LG1) and High-Grade coal (HG1), fly ash (F1), and grass from western direction of the mine, 1600 m from the pit (WG1600) and river sediments (KR1). The scan was done at University of Nairobi institute of nuclear science and the XRF spectra are presented in Figures 4 to 8.
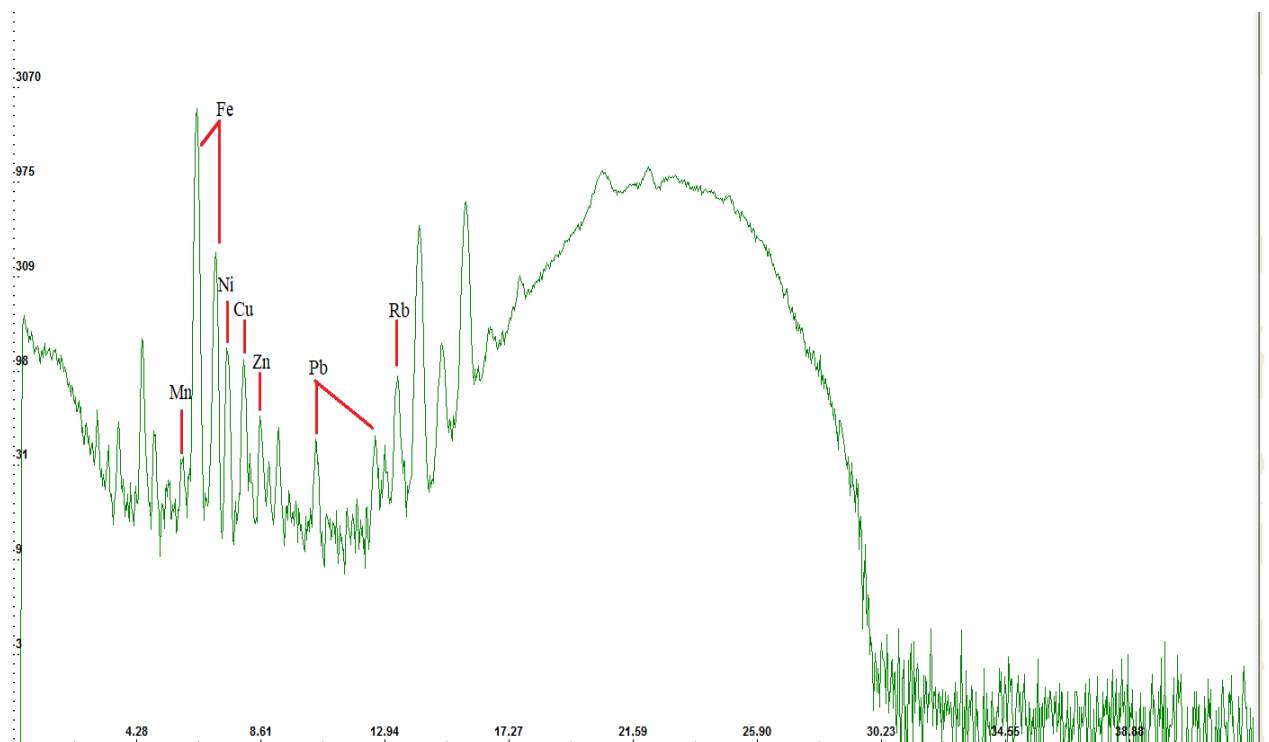
Figure 4: XRF spectra results for heavy metals in low grade coal (LG1) from Maamba, Zambia.
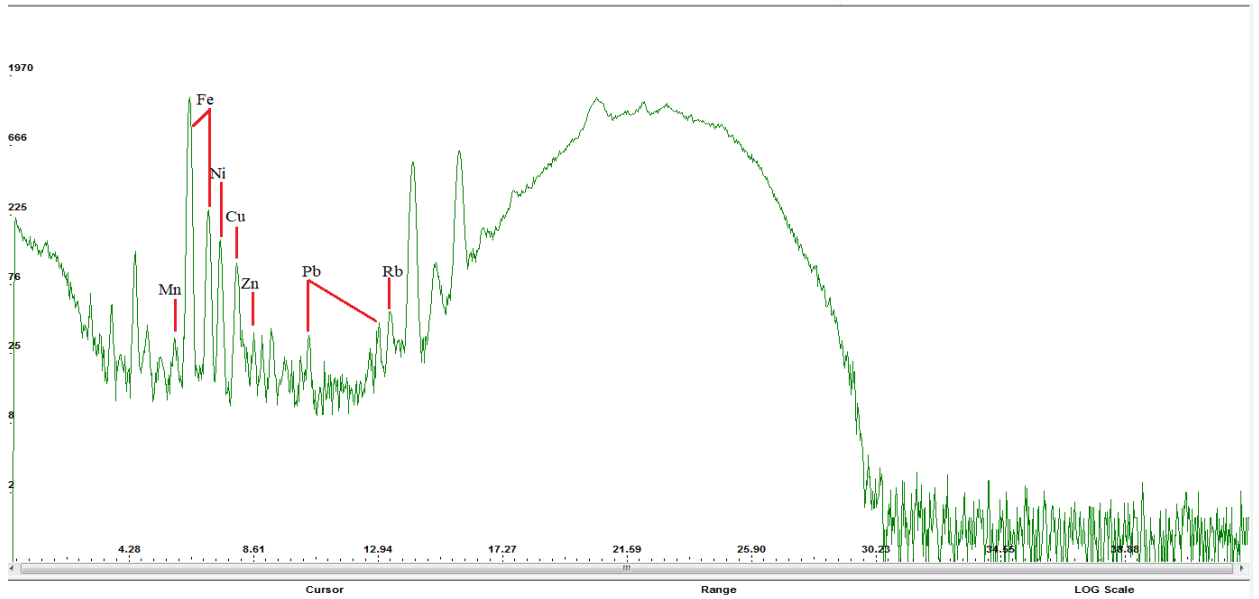
Figure 5: XRF spectra results for heavy metals in high grade coal (HG1) from Maamba, Zambia.
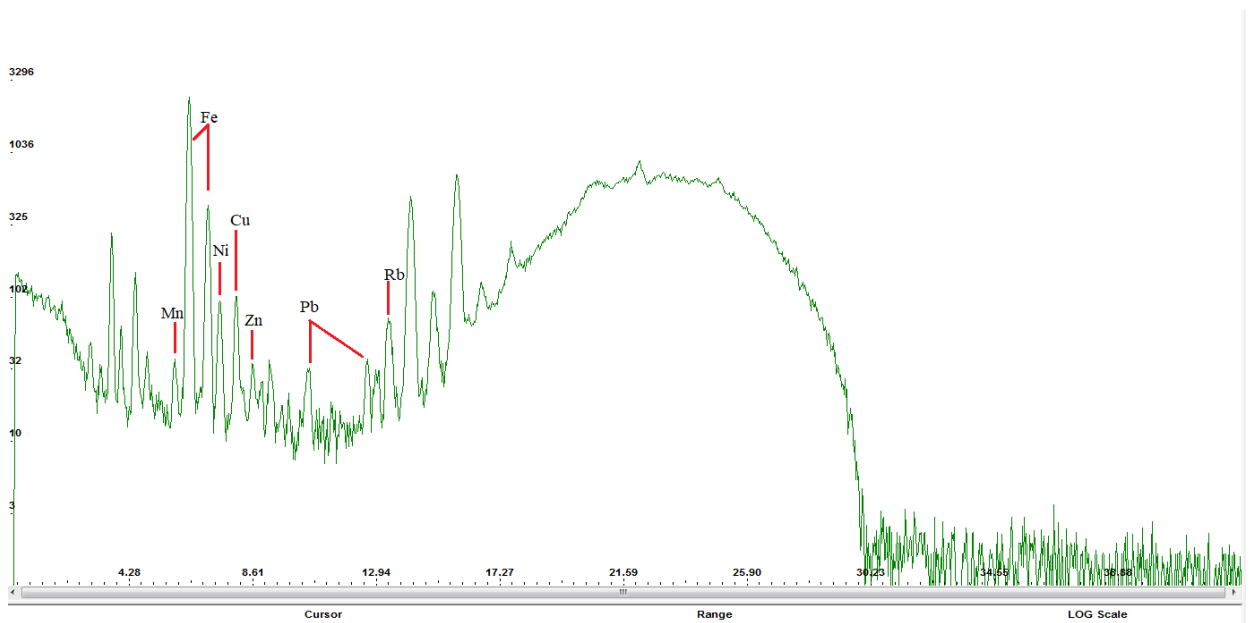
Figure 6: XRF spectra results for heavy metals in fly ash (F1) from Maamba, Zambia.
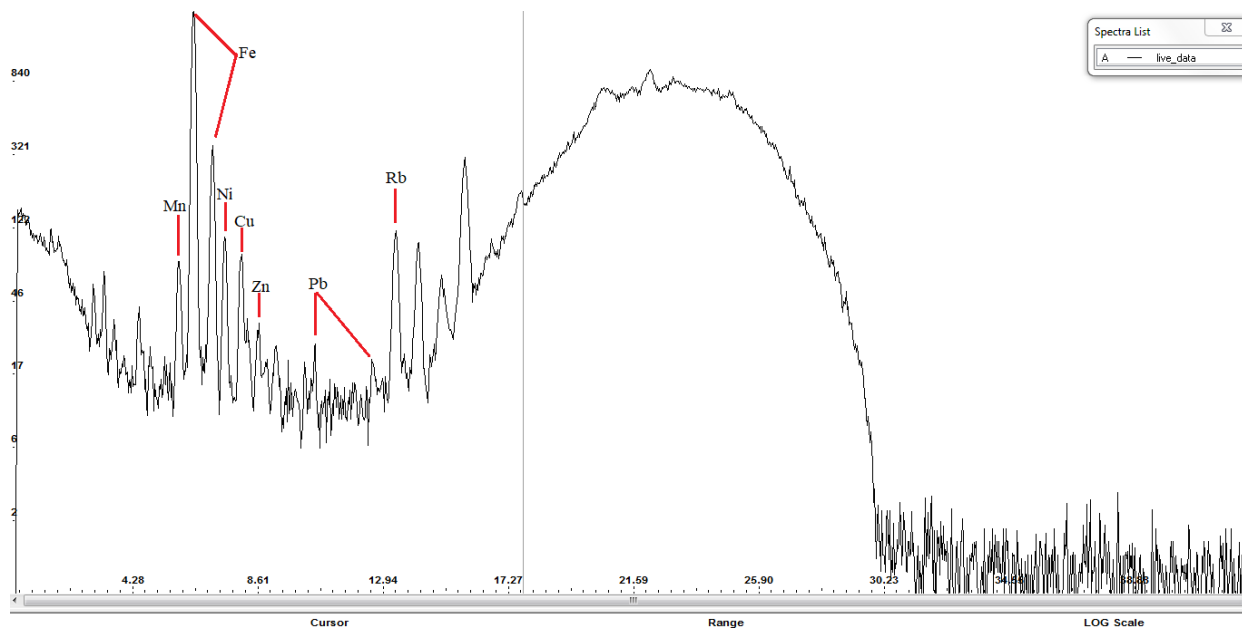
Figure 7: XRF spectra results for heavy metals river sediments (KR1) from Maamba, Zambia.
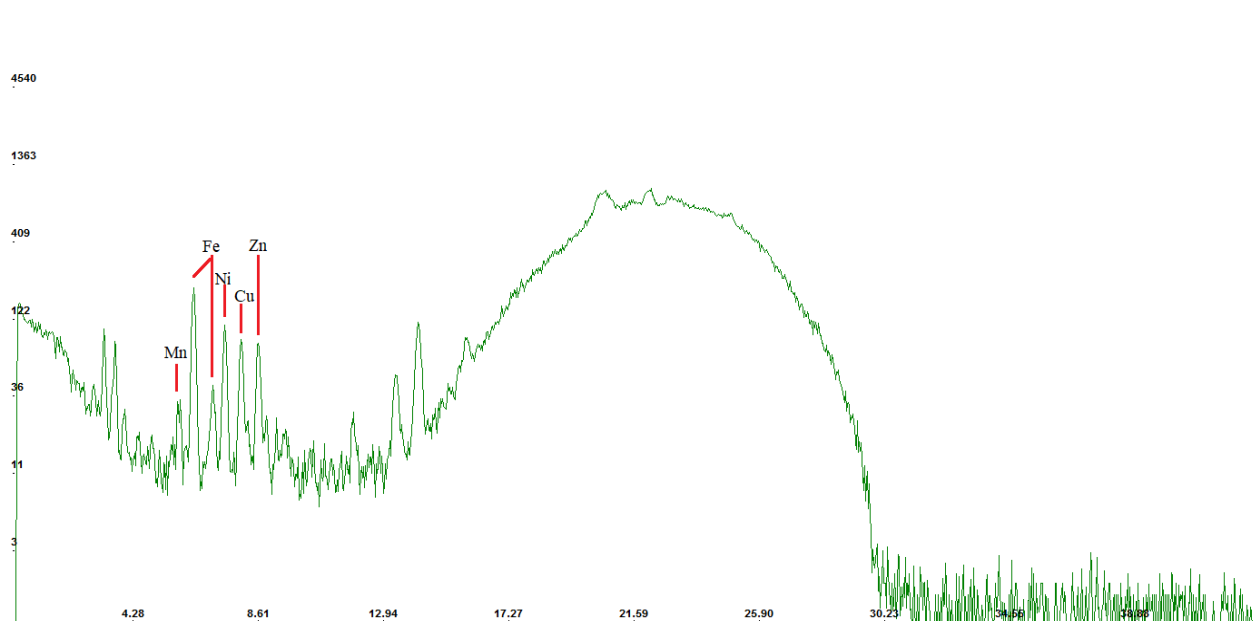
Figure 8: XRF spectra results for in heavy metal in grass (WG1600) from Maamba, Zambia.

XRF analysis revealed the availability of heavy metals in all the samples screened. As shown, Ni, Zn, Cu, Fe and Pb peaks were observed. The other heavy metal (Cd) of interest was not detected, since samples were not digested, and the instrument is not very sensitive and requires longer scanning time. The AAS was used for quantitative analysis and other heavy metals were detected such as cadmium which cannot be detected by XRF due to the radiation source used. Other elements which are not the focus of present study were also observed as shown.

4.2   Determination of heavy metals by Atomic Absorption Spectrophotometry (AAS).

4.2.1   Sensitivity

The parameters finally chosen as optimum for the operation of the instrument as shown in Table 1, were verified by comparison of selected concentration of the standards (expected value) for each metal and the instrumental values as shown in Table 2. The instrumental values were in accordance with the standard concentrations (expected values) and the sensitivity of the instrument was monitored by running the standard at the interval of 50 samples. Where there was decrease or elevation in concentration, a re-slope standard was used for recalibration.

Table 2: Sensitivity check.

Element	Expected value (mg/l)	Instrumental value (mg/l)
Zn	0.4	0.40
Cu	2.0	1.99
Fe	1.0	1.00
Ni	2.0	2.00
Cd	0.2	0.20
Pb	1.0	0.99

4.2.2   Accuracy and precision.

In analytical chemistry, accuracy is the ability of an experiment to obtain the correct, desired experimental value/ standard value whereas precision refers to the closeness of two or more measurements to each other. In this study, the concentrations obtained from each set of data showed minimal variations as it could be noticed from the standard deviation computed for each metal in the statistical tables.

4.3   Coal from Maamba

4.3.1   Maamba Coal Quality Characteristics

Four grades of Coal collected from Maamba region in Zambia were analysed namely: Low grade (LG), high grade (HG), washed Coal peas (PE) and Coarse mixed rejects coal (RE) using the methods summarised in 3.9.3. The characteristics of these grades of Coal are listed in the Table 3.

Table 3: Characteristics of Coal from Maamba.

Grade	Ash %	Volatile matter %	Fixed Carbon %	Sulphur %	Gross Calorific Value (Kca/kg)
LG	$30.0 - 60.0$	$12.0 - 19.0$	$27.5 - 49.8$	$0.2 - 1.5$	$2530 - 5353$
HG	$17.0 - 30.0$	$15.0 - 20.0$	$54.3 - 61.5$	$0.2 - 5.0$	$5353 - 6577$
PE	$16.0 - 22.0$	$18.0 - 21.0$	$59.2 - 61.2$	$0.2 - 1.5$	$6106 - 6671$
RE	$35.0 - 65.0$	$13.0 - 17.0$	$30.0 - 50.0$	$2.0 - 50.0$	$2060 - 4883$

The proximate analysis of subbituminous coal from Maamba was done as described in 3.9.3. The elemental composition was found to be % C 66, % H 3.5, % N 1.3, % S 1.5 and %O 65. Abdurrahman, (2010), conducted a proximate analysis of Hazro coal: % S 7.54, % Ash 18, % Fixed carbon 32.36, % Volatile matter 47.80 and Gross calorific value 6964.85 Kca/kg. The Hazro coal had slightly high gross calorific value, sulphur and volatile matter than the results obtained in this study. The % ash and % fixed carbon were less than the results obtained in this study. The coal ash was also analysed for the availability some oxides and results are summarised in Table 4.

Table 4: Coal ash analysis (using $X - Ray$ Fluorescence)

% oxides									
SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5
48.9	11.8	31.2	2.5	1.9	0.8	0.1	0.4	1.8	0.6

4.3.2 Determination of heavy metals concentration in Coal.

The levels of the Ni, Zn, Cd, Fe, Cu and Pb were determined in coal. The statistical information of heavy metals in coal are shown in Tables 5 and 6. Method 3.6.1 was adopted for digestion of Coal and Coal ash as it is recommended in other studies due to HF's ability to digest silica. The assortment of acids ($HClO_4$, HF, and HNO_3) were used for acid digestion since the combination has been shown to be the most effective for sample preparation for all the heavy metals in ash and in coal (Lachas *et al.,* 1999). Heavy metals (Zn, Cu, Cd, Fe, Pb and Ni) were analysed and found to be available in coal samples. The mean values, standard deviations and coefficient of variations were computed, and results are presented in Table 5 and 6. The mean concentrations

ranges were as follows: Fe (6776.79 − 24919.12), Zn (23.69 − 73.13), Pb (13.89 − 46.87), Cu (20.16 − 45.28), Ni (0.74 − 16.64) and Cd (0.35 − 1.20) mg/kg. The levels of heavy metals in coal samples in decreasing order were: Fe, Zn, Cu, Pb, Ni and Cd.

Table 5: The mean concentrations (mg/kg), standard deviation and coefficient of variation of Zn, Cu and Fe in coal samples.

	Zn			Cu			Fe		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
LG1	70.59	0.22	0.32	44.64	0.38	0.85	12810.75	17.86	0.14
LG2	73.13	0.19	0.26	45.28	0.41	0.91	12845.93	0.04	0.00
LG3	71.30	0.52	0.73	43.86	0.11	0.26	12794.78	7.37	0.06
HG1	34.44	0.39	1.15	22.24	0.27	1.20	8363.94	1.06	0.01
HG2	33.46	0.13	0.40	23.08	0.14	0.61	8362.44	1.06	0.01
HG3	35.51	0.68	1.91	22.93	0.05	0.21	8062.27	0.85	0.01
PE1	23.69	0.33	1.38	20.51	0.36	1.75	7334.05	0.00	0.00
PE2	23.78	0.04	0.16	20.16	0.33	1.65	6776.79	0.14	0.00
PE3	24.01	0.03	0.14	21.80	0.07	0.32	7335.70	0.76	0.01
RE1	24.58	0.28	1.12	28.56	0.32	1.13	24919.12	42.30	0.17
RE2	24.71	0.20	0.82	27.73	0.28	1.01	19954.68	0.71	0.00
RE3	24.34	0.07	0.29	29.31	0.07	0.24	23842.52	60.30	0.25

Note: STDEV = Standard deviation. CV = Coefficient of variation of the actual measurements.

Overall, the results shown in Tables 5 and 6 compared with other studies whose results are reported. Fabiane *et al.* (2010) reported the levels of toxic metals Pb (3.3 − 7.9) and Cd (0.05 − 015) mg/kg in coal samples from Brazil. The findings revealed that the level of Pb was greater than that of Cd and similar as obtained in this current study. The levels of Pb and Cd obtained in this study are greater than those revealed by Fabiane *et al.* (2010). In another study which was done in Nigeria by Adaikpoh *et al.* (2005) the level of heavy metals like; Pb (0.013 − 0.017), Ni (0.064 − 0.067) and Cd (0.036 − 0.043) mg/kg were determined in coal samples which were less than the concentrations obtained in this study.

Table 6: The mean concentrations (mg/kg), standard deviation and coefficient of variation of Ni, Cd and Pb in coal samples.

	Ni			Cd			Pb		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
LG1	11.36	0.24	2.11	1.02	0.08	7.36	46.87	0.05	0.11
LG2	11.84	0.20	1.72	1.12	0.01	0.62	44.56	0.07	0.17
LG3	12.28	0.40	3.26	1.20	0.01	0.51	46.64	0.04	0.09
HG1	4.12	0.03	0.72	0.35	0.00	0.00	13.95	0.00	0.00
HG2	4.00	0.00	0.00	0.39	0.00	0.49	14.04	0.06	0.45
HG3	4.32	0.04	0.86	0.41	0.01	2.21	13.89	0.00	0.00
PE1	0.89	0.14	16.08	0.62	0.00	0.36	16.42	0.11	0.70
PE2	1.03	0.01	0.76	0.62	0.01	1.05	16.97	0.00	0.00
PE3	0.74	0.05	7.29	0.57	0.01	0.99	16.20	0.14	0.88
RE1	16.64	0.10	0.60	0.42	0.05	11.16	32.77	0.28	0.86
RE2	5.55	0.26	4.78	0.38	0.01	2.13	37.75	0.35	0.92
RE3	16.54	0.06	0.39	0.39	0.01	1.57	32.94	0.06	0.17

Further, Odunayo *et al.* (2016) did a comparative study on the level of heavy metals in coal from two countries, Nigeria and South Africa. Several metals were analysed among of them were Zn (11.9), Pb (5.48), Ni (11.2) and Cu (23.7) mg/kg and Zn (38.6), Pb (7.02), Ni (20.6) and Cu (23.7) mg/kg respectively. Overall, the mean levels of these metals in this study exceed the reported concentrations in both countries. However, the level of trace metals like Zn (82.4), Pb (51.9), Cd (0.407), Cu (41.1) and Ni (20.8) mg/kg in coal sample reported by Chun-Gang, (2009) were higher than the levels obtained in this study. In retrospect, it is evident that Coal contains trace elements and utilisation of it as a source of energy may result in leaching of heavy metals, leading to environmental contamination if appropriate mitigation measures are not put in place. The overall mean level of Zn, Cu, Fe, Ni, Cd and Pb obtained in coal in this study, were 41.62, 29.62, 12783.58, 7.44, 0.66 and 27.39 mg/kg respectively. There were high deviations in the means since Coal samples were of different grades. The low-grade coal (LG), which is unprocessed/unwashed, yielded high concentration of metals compared to other grades such as high grade (HG), peas (PE) and rejects (RE) which are processed/washed products. You *et al.* (2016) observed that the levels of heavy metals gradually increase with prolonged mining duration, which suggest that extraction of coal processes could result into possible environmental

pollution implications. Therefore, there is need for continued monitoring and surveillance of levels of heavy metals in Maamba study area to ensure compliance with discharge standards set by regulatory agencies.

4.4 Determination of heavy metals concentration in Coal Ash.

Coal Ash is made up of bottom and fly ash generated by burning of coal from a thermal power station. Fly ash is finely separated remains generated from the combustion of fine particles of coal, which is conveyed from firebox to the boiler by mixture of gases whereas bottom ash is a rough, angular substance of permeable surface texture mainly sand-sized. Chemical makeup of bottom ash is comparable to the fly ash but typically consists of higher quantity of carbon (Kumar *et al*., 2014). Coal ash samples collected from Maamba were analysed using method 3.6.1 and the results of selected heavy metals are shown in Table 7 and 8. The mean concentration range of metals obtained in Coal ash were; Zn (45.94 − 77.28), Cu (39.15 − 81.04), Fe (11295.29 − 31124.11), Ni (1.11 − 16.59), Cd (0.75 − 1.34) and Pb (51.52 − 88.10) mg/kg. The concentrations of heavy metals determined in their decreasing order can be ranked as follows; Fe > Pb > Zn > Cu > Ni > Cd. The findings revealed that there was higher level of heavy metals in coal ash than in parent coal. This is attributed to less organic matter (carbon) in coal ash and metal become concentrated due to dumping coal ash in ash ponds. Sijakova-Ivanovai *et al*. (2011), reported the mean concentration range of Cu (61 − 80), Pb (43 − 50), Ni (58 − 68), Cd (6 − 14) and Zn (93 − 114) mg/kg in fly ash from Macedonia. In comparison between levels of heavy metals in fly ash from Macedonia and from this study: the mean concentration range of Zn, Ni and Cd in this research were less than those reported, Cu was similar and Pb was higher than those reported in fly ash from Macedonia. Abdurrahman (2010) studied the heavy metals content in subbituminous coal bottom ash from Turkey. It was shown that the mean level of Fe (200.50 ± 2.030 mg/kg) was the highest followed by Zn (0.85 ± 0.013), Ni (0.22 ± 0.014), Pb (0.15 ± 0.006) and Cu (0.13 ± 0.005) mg/kg. The concentration of heavy metals reported by Abdurrahman (2010) and Olushola *et al*. (2012) were less than those of this study. Israa (2018) reported concentrations of heavy metals in fly ash from middle and south of Iraq. The mean concentration range of Ni (5.579 ± 0.473), Zn (31.92 ± 0.005), Fe (1100.5 ± 0.105) and Pb (2.241 ± 0.112) mg/kg were less than those obtained in this study. However, the mean concentration range of Cd (2.043 ± 0.025) and Cu (104.7 ± 0.039) mg/kg were more than those obtained in this research.

Table 7: The mean concentrations (mg/kg), standard deviation and coefficient of variation of Zn, Cu and Fe in coal ash samples.

	Zn			Cu			Fe		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
F1	72.16	0.24	0.33	70.81	0.16	0.23	21930.75	44.40	0.20
F2	77.28	0.24	0.31	68.73	0.09	0.13	11671.31	0.00	0.00
F3	71.97	0.51	0.70	78.98	0.57	0.72	15530.33	44.43	0.29
F4	75.37	0.26	0.34	79.93	0.40	0.50	11600.96	4.58	0.04
F5	73.36	0.29	0.39	81.04	0.07	0.09	11295.29	0.66	0.01
F6	76.28	0.02	0.03	70.86	0.14	0.19	15498.47	0.24	0.00
B1	57.07	0.55	0.97	42.78	0.35	0.82	30303.25	15.32	0.05
B2	59.57	0.14	0.23	40.58	0.12	0.30	31111.40	17.11	0.06
B3	46.60	0.17	0.37	39.15	0.37	0.96	27380.51	0.06	0.00
B4	57.83	0.13	0.23	43.06	0.01	0.02	31124.11	0.02	0.00
B5	45.94	0.08	0.16	40.00	0.01	0.03	27489.62	0.10	0.00

Table 8: The mean concentrations (mg/kg), standard deviation and coefficient of variation of Ni, Cd and Pb in coal ash samples.

	Ni			Cd			Pb		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
F1	6.34	0.39	6.18	0.88	0.08	8.57	76.50	0.26	0.33
F2	6.46	0.00	0.00	1.12	0.11	9.40	80.21	0.40	0.49
F3	6.78	0.06	0.95	0.76	0.00	0.62	87.61	0.14	0.16
F4	6.34	0.04	0.70	0.75	0.07	9.24	84.67	0.01	0.01
F5	6.74	0.07	0.99	1.22	0.04	3.03	88.10	0.01	0.01
F6	6.31	0.01	0.14	0.98	0.00	0.41	79.85	0.07	0.08
B1	1.63	0.30	18.48	1.34	0.31	23.40	55.69	0.14	0.25
B2	1.11	0.00	0.22	1.10	0.04	3.37	51.52	0.66	1.28
B3	16.23	0.01	0.07	1.11	0.17	15.49	59.14	0.63	1.07
B4	16.46	0.05	0.30	1.01	0.01	0.60	59.95	0.07	0.12
B5	16.59	0.06	0.34	0.98	0.01	0.61	55.94	0.06	0.11

Note: F1 to F6 (fly ash samples). B1 to B5 (bottom ash samples).

Table 9: Comparison of mean concentration values of heavy metals (mg/kg) in coal and coal ash.

Metals	Coal	Coal Ash
Fe	6776.79 − 24919.12	11295.29 − 31124.11
Zn	23.69 − 73.13	45.94 − 77.28
Pb	13.89 − 46.87	51.52 − 88.10
Cu	20.16 − 45.28	39.15 − 81.04
Ni	0.74 − 16.64	1.11 − 16.59
Cd	0.35 − 1.20	0.75 − 1.34

As shown in Table 9, coal ash had higher concentration of heavy metals than parent coal. This is due to dumping of coal ash in dumping ponds as a result the metals become concentrated. This may lead into leaching of metals in agricultural soil, surface and underground water. Coal ash also has less carbon content hence high heavy metal content compared to coal. The runoffs from coal ash can cause severe environmental pollution with heavy metals. The disposal and storage of coal fly ash could result into emission of leached metals into soils, surface and underground waters. Most metals accumulate in sediment and soils, and most of them are chronic and very toxic to people, plants and animals via water, air and soil uptake (Olushola *et al.,* 2012).

Literature is abundant with publications on the effects of coal-fired power plants and wastes produced by them, on the environment and human health (Fahad and Bertug, 2016). Sushil and Batra (2006) investigated levels of heavy metal in fly ash and disposal. The results revealed that the ashes contained Ni, Mn, Zn, Pb, Co, Cu and Cr. It was revealed that high levels of heavy metals were observed in coal ash, Zn and Cr level were the highest while Co level was the lowest. Israa (2018) reported significant contamination of metals like Zn, Cu, Cd and Fe in fly ash samples from Iraq. The results from literature agree with the one obtained in this research since high heavy metals content was observed at some sites as shown in tables 7 and 8.
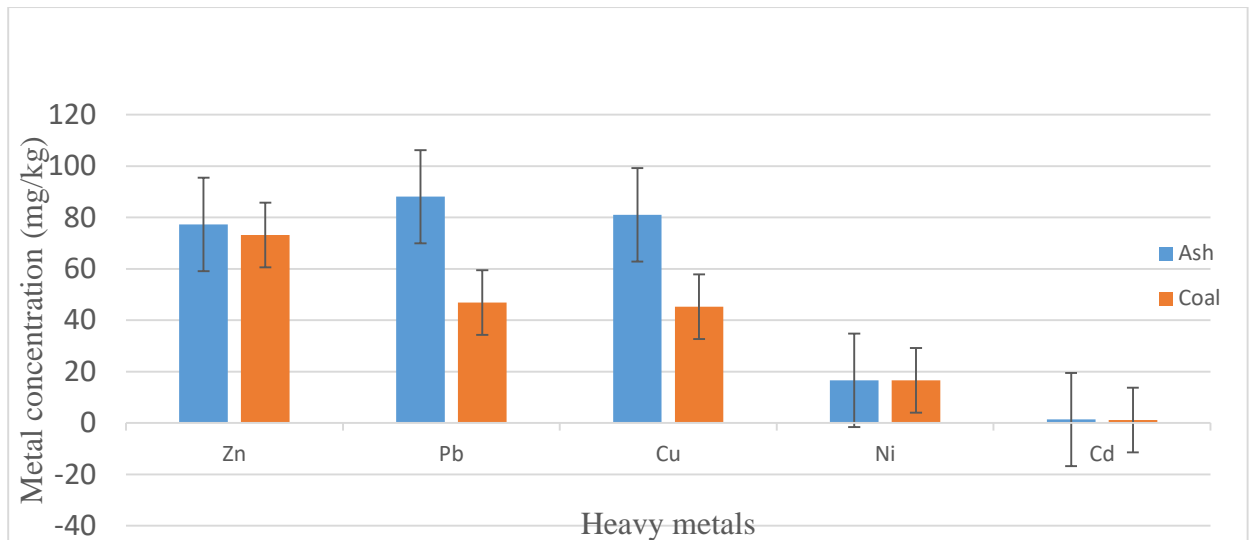
Figure 9: Graphical comparison of concentration of Zn, Pb, Cu, Ni and Cd in Coal and Coal Ash.

Figure 9 shows that Coal ash had high concentration of heavy metal than parent coal as reported in other studies. Odunayo *et al.* (2016) observed that fly ash samples showed highly elevated levels of Co, Nb, Ni, Pb, V, Zr and U in the electric precipitated fly ash than the parent coal. This was attributed to the evaporation of these metals in combustion chambers during disposal process in the gaseous product. The overall mean levels of Zn, Cu, Fe, Ni, Cd and Pb in coal ash were: 65.32, 60.43, 21357.82, 8.27, 1.00 and 71.46 mg/kg respectively. It was also revealed that fly ash had high levels of Zn, Cu, Fe and Pb than bottom ash but bottom ash had high concentration of Ni and Cd.

4.5   Soils near Coal mining area (Maamba).

Note:

S10 to S1800; soil samples collected at distances (10, 40, 60, 80, 120, 160, 180, 200, 1800 m) Southern transect, E10 to E1600; soil samples collected at distances (10, 40, 60, 80, 120, 160, 180, 200, 1600 m) Eastern transect, W10 to W200; soil samples collected at distances (10, 40, 60, 80, 120, 160, 180, 200 m) Western transect, N10 to N200; soil samples collected at distances (10, 40, 60, 80, 120, 160, 180, 200 m) Northern transect and R1200 to R3600; road soil samples collected at distances (1200, 1600, 1800, 2000, 2400, 2800 and 3600 m).

The physiochemical properties such as pH and conductivity of the surface soils collected were determined. The results revealed that the pH range from $3.2 - 7.4$ and conductivity ranged from $0.2 - 589.0$ ms/cm. The soil samples were found to be acidic in most samples, this could pose a

risk of infiltration of heavy metals into underground water during precipitation. The pH and conductivity values for soil samples from four transects are shown in Table 10.

Table 10: Physicochemical parameters of soils, selected grid reference and elevation of sampled sites.

Sample	East	South	Elevation (m)	pH	Conductivity (ms/cm)
S10	27.19442	-17.34688	610	4.7	0.265
S40	27.19432	-17.34696	610	3.8	139.6
S60	27.19424	-17.34697	611	3.2	113.4
S80	27.19414	-17.34699	611	3.5	58
S120	27.19405	-17.34699	611	3.4	117.7
S160	27.19398	-17.34702	609	4.9	0.64
S180	27.1939	-17.34704	608	5.1	0.26
S200	27.19384	- 17. 34709	607	3.8	0.23
S1800	27.1987	-17.3593	590	6	0.37
E10	27.19788	-17.34744	606	5.7	1.02
E40	27.19796	-17.34748	606	3.5	589
E60	27.19803	-17.34351	605	7.1	2.5
E80	27.19808	-17.34755	604	6	2.33
E120	27.19818	-17.3476	602	5.6	2.7
E160	27.19825	-17.34768	600	3.7	1.09
E180	27.19832	-17.34783	604	3.9	0.23
E200	27.19838	-17.34789	607	5.4	0.35
E 1600	27.20235	-17.35889	596	5.4	0.34
W10	27.18986	-17.34649	647	3.2	48.4
W40	27.18975	-17.34649	648	3.8	46.1
W60	27.18967	-17.34642	648	4.1	24.3
W80	27.18958	-17.34637	649	4.6	84.5
W120	27.18952	-17.34633	651	3.8	75.7
W160	27.18944	-17.34637	653	4.8	83.6
W180	27.18935	-17.34632	654	5	85.7
W200	27.18926	-17. 34621	654	6.8	0.27
N10	27.20117	-17.34619	600	4.9	0.37
N40	27.20125	-17.34619	603	6.6	136.5
N60	27.20133	- 17. 34617	604	5.3	0.38
N80	27.20143	-17.34615	604	4.9	140.2
N120	27.20151	- 17. 34612	604	5.9	0.85
N160	27.20162	-17.34611	605	6.9	0.61
N180	27.20111	-17.34608	605	6.4	0.86
N200	27.20181	-17.34604	604	3.5	103.1

4.5.1　The concentration of heavy metals in soils from the East transect

The mean concentration ranges of heavy metals in soils from eastern direction of the mine in their decreasing order are: Fe $(10856.95 - 27262.75)$, Pb $(25.15 - 45.53)$, Zn $(4.84 - 44.80)$, Cu $(10.51 - 33.22)$, Ni $(3.63 - 10.66)$ and Cd $(0.39 - 1.40)$ mg/kg. The samples had high levels of Fe followed by Pb, Zn, Cu, Ni and Cd. The strength of pollution of a trace metals is based on its levels in coal, its behaviour during the burning of coal and its movement in surface soils. Heavy metals that are available in higher levels in coal, have stronger tiny fragments association during burning of coal and are not very mobile in surface soils, reveal stronger pollution in soils near thermal plant (Mingzhe *et al.,* 2009).

Table 11: The mean concentration (mg/kg), standard deviation and coefficient of variation of Zn, Cu and Fe in soils from the East transect.

ID	Zn			Cu			Fe		
	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
E10	34.60	0.08	0.22	21.54	0.04	0.17	20282.01	1.77	0.01
E40	27.06	0.14	0.53	32.84	0.17	0.52	24767.89	0.40	0.00
E60	31.82	0.35	1.11	27.27	0.11	0.41	22583.23	0.13	0.00
E80	44.80	0.08	0.18	21.28	0.28	1.34	20186.63	3.63	0.02
E120	34.05	0.08	0.23	33.22	0.47	1.42	24278.06	1.44	0.01
E160	38.45	0.02	0.06	31.85	0.05	0.15	25719.58	1.16	0.00
E180	25.38	0.13	0.52	27.13	0.11	0.42	27262.75	13.93	0.05
E200	25.19	0.63	2.51	25.36	0.07	0.27	24554.52	1.63	0.01
E1600	4.84	0.54	11.13	10.51	0.09	0.90	10856.95	0.80	0.01

Table 12: The mean concentration (mg/kg), standard deviation and coefficient of variation of Ni, Cd and Pb in soils from the East transect.

	Ni			Cd			Pb		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
E10	7.26	0.08	1.10	0.54	0.02	4.15	38.33	0.16	0.41
E40	10.66	0.13	1.26	1.03	0.17	16.44	30.69	0.14	0.46
E60	10.23	0.20	1.92	0.53	0.01	2.66	35.38	0.21	0.59
E80	7.56	0.01	0.12	0.45	0.01	2.04	35.16	0.35	1.01
E120	9.48	0.20	2.13	0.62	0.00	0.62	32.43	0.07	0.22
E160	9.58	0.49	5.12	0.55	0.00	0.18	35.64	0.74	2.07
E180	7.41	0.00	0.04	0.46	0.00	0.00	37.10	0.09	0.24
E200	8.89	0.08	0.94	1.40	0.08	5.68	45.53	0.07	0.15
E1600	3.63	0.00	0.00	0.39	0.03	8.58	25.15	0.42	1.68
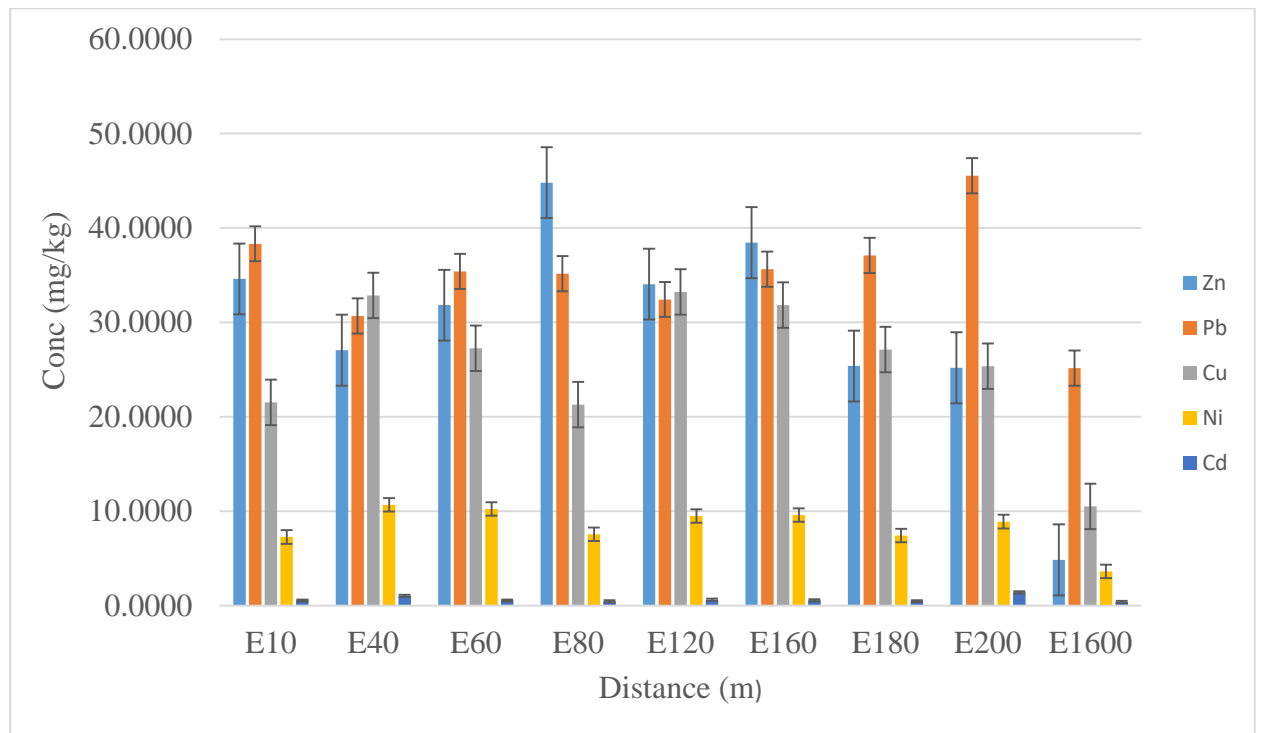
Figure 10: Concentration of Zn, Pb, Cu, Ni and Cd in soils as a function of distance from the mining site in the eastern direction.

The mean concentrations of heavy metals in the soil from eastern part of the mine fluctuated with distance away from subbituminous coal mine pit. This is due to some factors such as spillages of coal/ coal ash during transportation, windblown coal ash, atmospheric deposition,

terrains and most of the samples were obtain from old mines. Iron was not shown on this chart due to its extremely higher concentration than other metals. The highest level of each heavy metal was obtained at the following distances: Fe (180 m) Pb (200 m), Zn (80 m), Cu (120 m), Ni (40 m) and Cd (200 m). The lowest concentration of each metal was recorded at distance 1600 m, which suggests that the anthropogenic activity is responsible to elevation of heavy metal in soil.
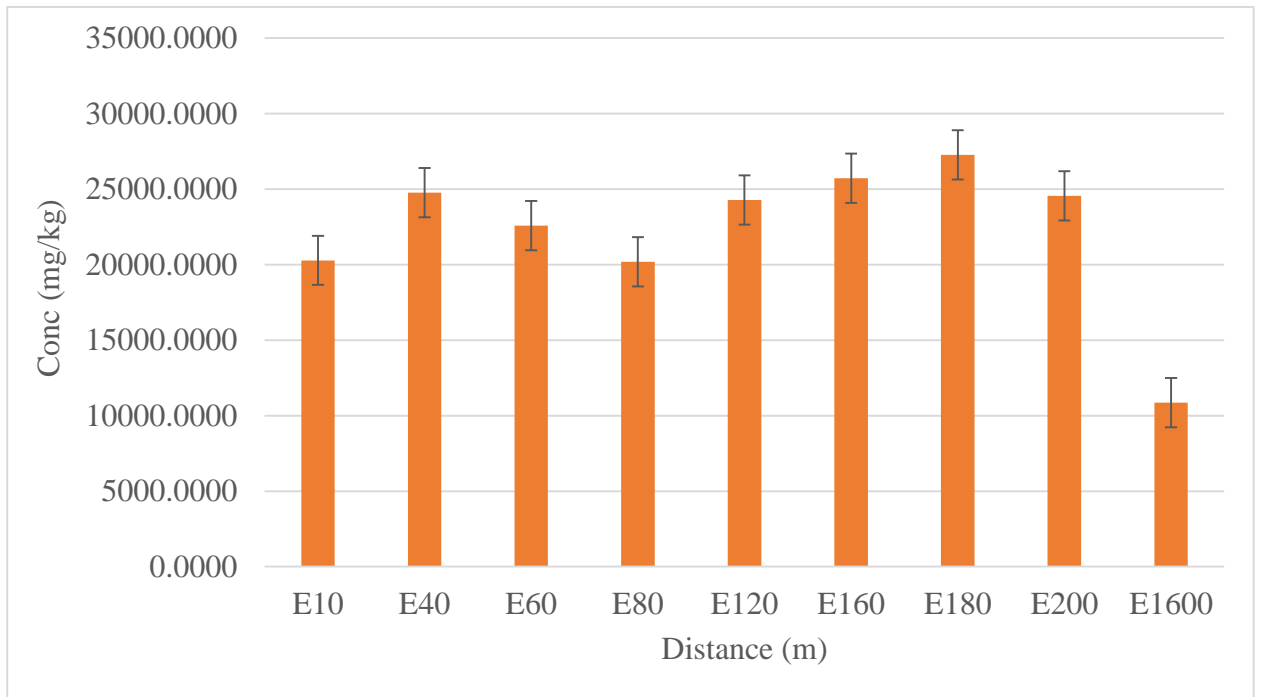
Figure 11: Iron levels as a function of distance from the mine in the eastern direction

The levels of heavy metals in this research were compared with world permissible concentration in soil and plants by WHO/FAO. Fosu-Mensah *et al.* (2017) reported world permissible concentration limit of heavy metals in soils and plants by WHO/FAO (2001). The reported world permissible concentration limit of heavy metals in soils are: Pb (50), Zn (300), Cu (100), Ni (50) and Cd (3) mg/kg. The levels of heavy metals in soil may vary below these values but not above stated concentration. Ladwani *et al.* (2012) reported the international standards of heavy metals in soil to be: Pb (10), Cu (30), Zn (50), Ni (40) and Cd (0.06) mg/kg. The control sample was also used to assess the effect of coal mining on soils near the mine in terms of heavy metals contamination. The control samples were collected approximately 50km away from Maamba coal mine.

Table 13: Comparison of mean concentration (mg/kg) of heavy metal from east transect with the control sample world permissible concentrations limit and international standards reported.

Metals	Sample	Control sample	WHO/FAO	International standards
Fe	10856.95 − 27262.75	14990.84	20000 − 550000	−
Zn	4.84 − 44.80	38.36	300	50
Pb	25.15 − 45.53	23.44	50	10
Cu	10.51 − 33.22	17.19	100	30
Ni	3.63 − 10.66	7.31	50	40
Cd	0.39 − 1.4023	0.6	3	0.06

The mean concentrations range of heavy metals in soils from the east of MCL such as Zn, Cu, Ni Pb and Cd were below the WHO/FAO (2001) permissible limits shown Table 13. For Fe, the mean concentrations were below and within the typical Fe concentration in soils range from 20,000 – 550,000 mg/kg. However, some of the mean concentrations were above the mean concentration of a control sample and the international standards reported. This shows that the soils were slightly polluted by heavy metals analysed, which is the same case in other studies. The mean heavy metals levels in soil samples decreased as follows: Fe > Pb> Zn > Cu> Ni > Cd. Shang *et al.* (2016) revealed that the mean levels of heavy metals were greater than background concentrations of Huaibei City topsoil. This was also observed in this study's results as most of the mean levels of all heavy metals were greater than the concentration of the control sample.

4.5.2   The concentration of heavy metals in soils from the West transect.

The mean concentration range of heavy metals in soil samples from the West transect descended as follows: Fe, Zn, Pb, Cu, Ni, and Cd. The mean range concentration of Fe, Zn, Pb, Cu, Ni and Cd are: 3575.98 − 12072.43, 5.01 − 44.51, 9.25 − 39.39, 5.01 − 32.82, 1.545 − 10.68 and 0.16 − 0.85 mg/kg respectively.

Table 14: The mean concentration (mg/kg), standard deviation and coefficient of variation of Zn, Cu and Fe in soils from west transect.

	Zn			Cu			Fe		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
W10	23.24	0.26	1.14	11.72	0.02	0.14	8871.36	1.17	0.01
W40	39.12	0.13	0.33	5.01	0.23	4.62	3575.98	0.57	0.02
W60	5.01	0.40	7.90	9.26	0.18	1.97	4994.04	2.37	0.05
W80	26.94	0.14	0.51	17.24	0.06	0.34	8497.20	2.99	0.04
W120	33.50	0.05	0.14	14.77	0.40	2.70	8922.72	0.02	0.00
W160	33.35	0.18	0.53	32.82	0.14	0.43	9617.64	5.29	0.06
W180	32.82	0.34	1.05	15.52	0.62	3.96	8178.56	2.19	0.03
W200	44.51	0.67	1.51	19.34	0.29	1.49	12072.43	2.31	0.02

Table 15: The mean concentration (mg/kg), standard deviation and coefficient of Ni, Cu and Pb in soils from west transect.

|	Ni			Cd			Pb		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
W10	1.55	0.39	25.00	0.22	0.05	23.75	9.25	0.40	4.31
W40	4.28	0.14	3.39	0.16	0.00	0.41	11.36	0.36	3.15
W60	5.12	0.05	0.92	0.23	0.02	9.02	16.66	0.00	0.00
W80	9.61	0.02	0.17	0.51	0.01	2.53	39.39	0.04	0.10
W120	10.68	0.25	2.35	0.22	0.01	2.68	27.00	0.48	1.79
W160	6.72	0.06	0.86	0.51	0.02	3.82	25.59	0.08	0.30
W180	7.40	0.21	2.88	0.72	0.02	2.44	24.55	0.29	1.18
W200	7.87	0.02	0.29	0.85	0.01	1.11	30.14	0.46	1.52
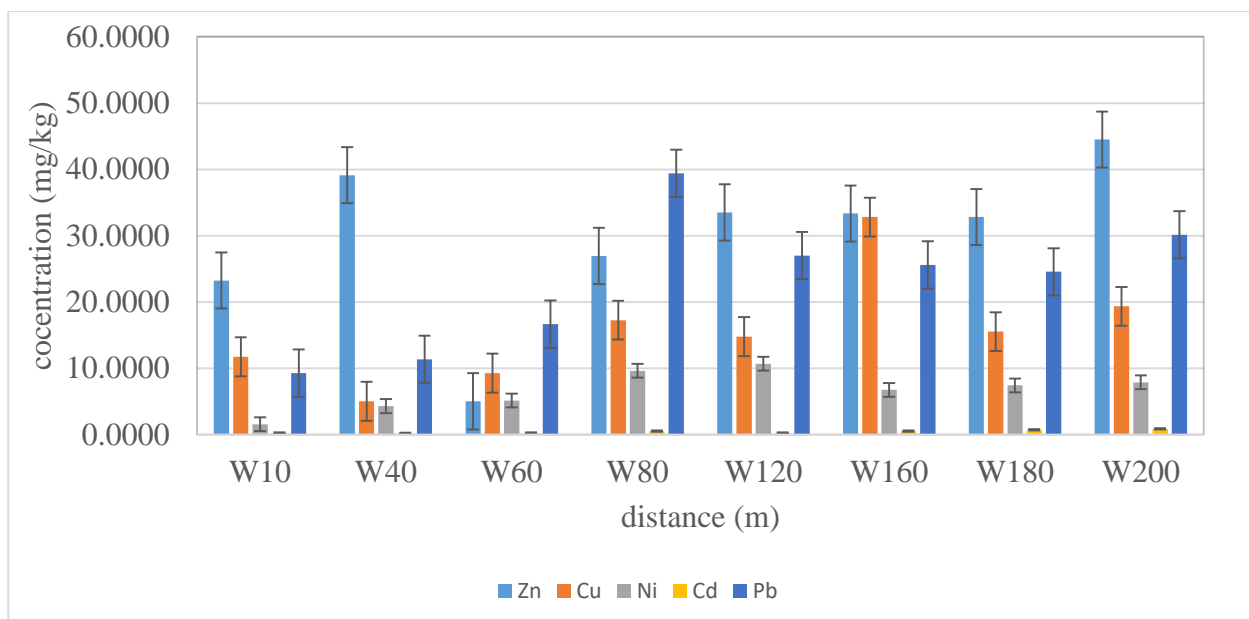
Figure 12: The levels of Zn, Cu, Ni, Cd and Pb in soils as a function of distance from the mining site in the western direction.

The concentrations of heavy metals in the West transect were lower than that of East transect. This was attributed to less transportation and lack of old mines on the western part of MCL due to the terrain. However, the level of heavy metals fluctuated with distance from the mining pit showing an increasing pattern as distance increase from the pit. The highest level of each heavy metal was recorded at the following distances: Fe (200 m) Pb (80 m), Zn (200 m), Cu (160 m), Ni (120 m) and Cd (200 m).

4.5.3   The concentration of heavy metals in soils from the North transect.

The mean concentrations of heavy metals in soil samples from the North transect decreased as follows: Fe, Cu, Zn, Pb, Ni, and Cd. The mean range concentration of Fe, Cu, Zn, Pb, Ni and Cd are: 15996.38 − 32859.51, 20.56 − 54.68, 31.55 − 44.58, 26.15 − 36.29, 13.96 − 27.59 and 0.83 − 1.08 mg/kg respectively. The statistical information of heavy metals in soil from the North transect are presented in Tables 16 and 17.

Table 16: The mean concentration (mg/kg), standard deviation and coefficient of variation of Zn, Cu and Fe in soils from North transect.

	Zn			Cu			Fe		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
N10	44.58	0.38	0.86	35.91	0.44	1.24	24179.92	0.89	0.00
N40	38.46	0.29	0.76	54.68	0.26	0.48	32859.51	5.24	0.02
N160	33.05	0.11	0.33	42.19	0.13	0.32	25436.56	13.53	0.05
N60	37.90	0.06	0.16	46.74	0.47	1.00	16817.73	3.09	0.02
N80	36.42	0.44	1.22	46.38	0.84	1.81	21112.89	0.00	0.00
N120	35.04	0.54	1.55	43.53	0.10	0.23	23430.33	5.80	0.02
N180	31.55	0.39	1.25	44.46	0.25	0.56	15996.38	1.77	0.01
N200	30.69	0.18	0.59	20.56	0.24	1.16	27899.18	0.00	0.00

Table 17: The mean concentration (mg/kg), standard deviation and coefficient of variation of Ni, Cd and Pb in soils from North transect.

|	Ni			Cd			Pb		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
N10	26.61	0.17	0.64	1.00	0.01	0.95	35.86	0.46	1.28
N40	27.59	0.44	1.58	0.92	0.01	1.10	33.38	0.53	1.58
N160	20.81	0.22	1.04	1.08	0.00	0.04	29.53	0.43	1.46
N60	24.73	0.40	1.63	1.04	0.01	1.18	31.99	0.54	1.69
N80	24.04	0.11	0.44	0.83	0.07	8.04	33.89	0.54	1.61
N120	21.47	0.26	1.22	1.07	0.11	10.67	26.15	0.08	0.30
N180	22.34	0.07	0.30	0.94	0.06	6.58	28.86	0.49	1.69
N200	13.96	0.27	1.94	1.07	0.03	2.68	36.29	0.49	1.36
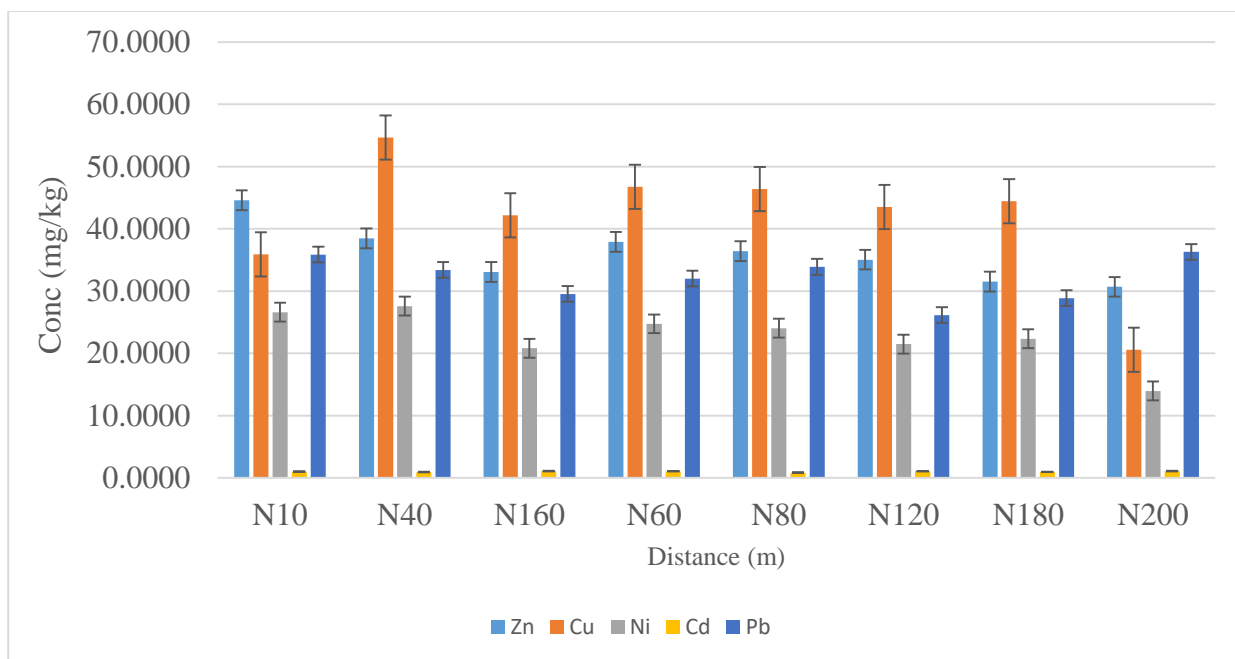
Figure 13: The levels of Zn, Cu, Ni, Cd and Pb in soils as a function of distance from the mining site in the northern direction.

The levels of heavy metals from the North transect were higher than that of East and West transects. This can be attributed to the make- up of the soil from the North transect as it is mainly made up of excavated soils (overburden). The levels of heavy metals fluctuated with distance from the mining pit showing a decrease in concentration, this is due to the reduction in amount of overburden as the distance increase away from the pit. The highest level of each heavy metal was recorded at the following distances: Fe (40 m), Cu (40 m), Zn (10 m), Pb (200 m), Ni (40 m) and Cd (160 m).

4.5.4 The concentration of heavy metals in soils from the South transect

The levels of heavy metals in soils from the South transect descended in this order: Fe, Zn, Pb, Cu, Ni and Cd. The mean concentration range for each metal is 9903.73 − 52349.91, 32.20 − 74.54, 15.41 − 35.86, 11.70 − 35.59, 6.87 − 18.11 and 0.47 − 1.35 mg/kg respectively. The statistical information of heavy metals in soil from South transect are shown in Tables 18 and 19.

Table 18: The mean concentration (mg/kg), standard deviation and coefficient of variation of Zn, Cu and Fe in soils from South transect.

	Zn			Cu			Fe		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
S10	62.02	0.18	0.29	33.89	0.05	0.14	29549.89	27.18	0.09
S40	32.44	0.54	1.68	19.82	0.33	1.69	19890.58	6.19	0.03
S60	32.20	0.55	1.71	35.59	0.10	0.28	52349.91	8.29	0.02
S80	35.76	0.31	0.86	26.11	0.12	0.45	49689.41	12.23	0.02
S120	57.94	0.62	1.08	26.56	0.28	1.07	23876.71	1.36	0.01
S160	73.25	0.16	0.22	32.83	0.13	0.39	27334.23	0.82	0.00
S180	74.54	0.18	0.24	27.36	0.50	1.81	14954.80	0.23	0.00
S200	53.74	0.11	0.21	30.39	0.10	0.34	20480.73	5.37	0.03
S1800	34.15	0.44	1.29	11.70	0.30	2.55	9903.73	5.72	0.06

Table 19: The mean concentration (mg/kg), standard deviation and coefficient of variation of Ni, Cd and Pb in soils from South transect.

|	Ni			Cd			Pb		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
S10	17.38	0.04	0.26	1.35	0.02	1.81	33.52	0.17	0.52
S40	13.00	0.54	4.20	0.71	0.03	4.45	15.41	0.24	1.57
S60	11.63	0.31	2.65	1.22	0.14	11.13	35.86	0.33	0.92
S80	8.49	0.41	4.80	0.84	0.10	12.44	33.85	0.61	1.80
S120	12.95	0.02	0.18	1.19	0.00	0.00	27.61	0.45	1.59
S160	15.23	0.09	0.59	1.14	0.00	0.00	27.66	0.14	0.50
S180	15.48	0.26	1.67	0.98	0.02	1.74	27.96	0.04	0.13
S200	18.11	0.47	2.62	1.22	0.02	1.69	27.95	0.35	1.24
S1800	6.87	0.09	1.33	0.47	0.01	2.05	29.20	0.00	0.00
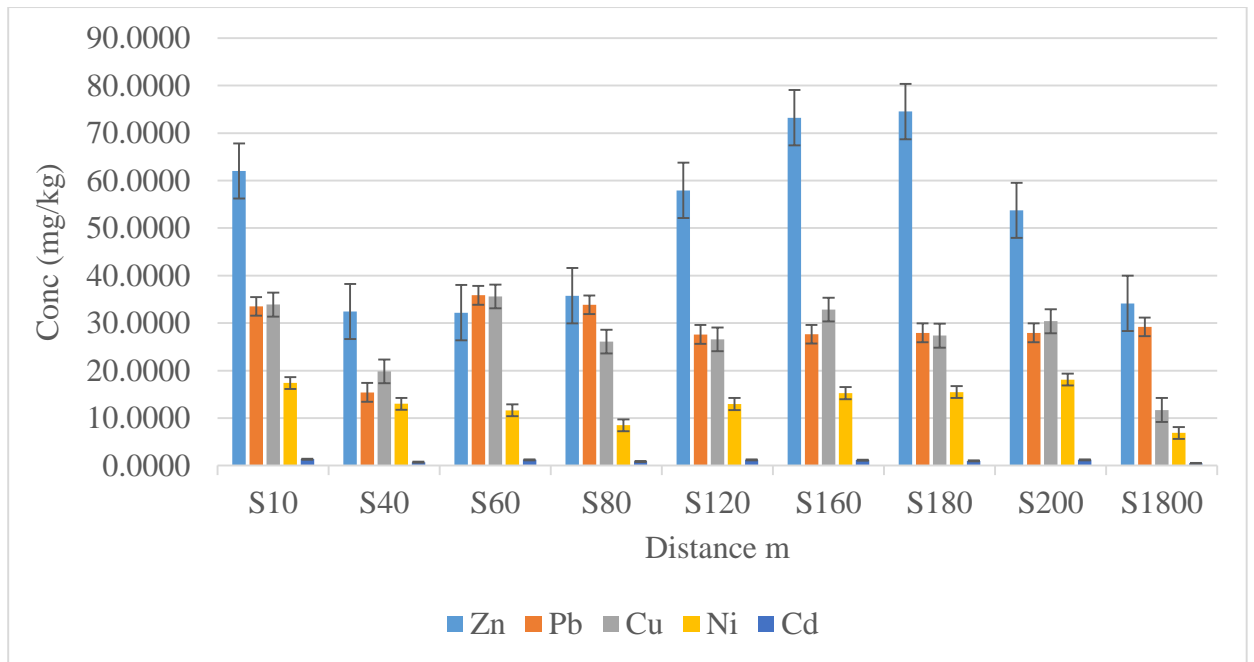
Figure 14: The levels of Zn, Cu, Ni, Cd and Pb in soils as a function of distance from the mine in the southern direction.

The maximum mean concentrations of Fe and Zn were higher than that from East, West and North. The concentrations fluctuated with distance from the mining pit and the highest level of each heavy metal was recorded at the following distances: Fe (60 m), Cu (60 m), Zn (180 m), Pb (60 m), Ni (200 m) and Cd (10 m). The concentration seemed to increase from the pit up to a distance of 200 m due to the presence of ash ponds on the southern part of MCL and at distance of 1800 m the levels reduced. The results obtained indicate that coal mining and dumping of its waste leads to soil contamination by heavy metals.

4.5.5   The concentration of heavy metals in road soils

Seven (7) soil samples were sampled starting from 1200 m from the mine up to Maamba Township. The mean concentration range of heavy metals obtained were Fe (8570.52 − 19297.54), Zn (10.70 − 52.27), Cu (5.94 − 38.80), Pb (22.54 − 35.85), Ni (4.09 − 11.78) and Cd (0.20 − 1.45) mg/kg. The mean levels of heavy metals in road soil descended as follows: Fe > Zn > Cu > Pb > Ni > Cd. The statistical information of heavy metals in road soil are shown in Tables 20 and 21.

Table 20: The mean concentration (mg/kg), standard deviation and coefficient of variation of Zn, Cu and Fe in road soils.

	Zn			Cu			Fe		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
R1200	28.23	0.36	1.28	19.36	0.06	0.31	8570.52	3.57	0.04
R1600	10.70	0.16	1.48	5.94	0.38	6.32	8941.33	2.29	0.02
R1800	27.92	0.07	0.26	30.46	0.21	0.68	17589.91	5.89	0.03
R2000	44.20	0.82	1.86	38.80	0.10	0.25	19297.54	9.75	0.05
R2400	29.95	0.36	1.21	19.97	0.47	2.34	13671.18	57.83	0.42
R2800	52.27	0.48	0.92	31.25	0.41	1.32	19091.76	1.31	0.01
R3600	39.41	0.23	0.58	15.22	0.16	1.08	13062.23	1.68	0.01

Table 21: The mean concentration (mg/kg), standard deviation and coefficient of variation of Ni, Cd and Pb in road soils.

	Ni			Cd			Pb		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
R1200	11.62	0.38	3.24	1.02	0.04	3.44	26.34	0.45	1.70
R1600	4.09	0.02	0.41	0.20	0.02	8.15	29.31	0.42	1.44
R1800	5.25	0.00	0.01	0.76	0.01	1.80	27.18	0.52	1.91
R2000	8.64	0.02	0.26	0.85	0.03	3.34	35.85	0.42	1.17
R2400	4.78	0.07	1.42	1.45	0.06	4.21	27.45	0.14	0.51
R2800	11.78	0.07	0.57	0.76	0.06	7.29	22.54	0.45	1.99
R3600	5.78	0.08	1.41	0.53	0.01	2.20	26.97	0.46	1.70
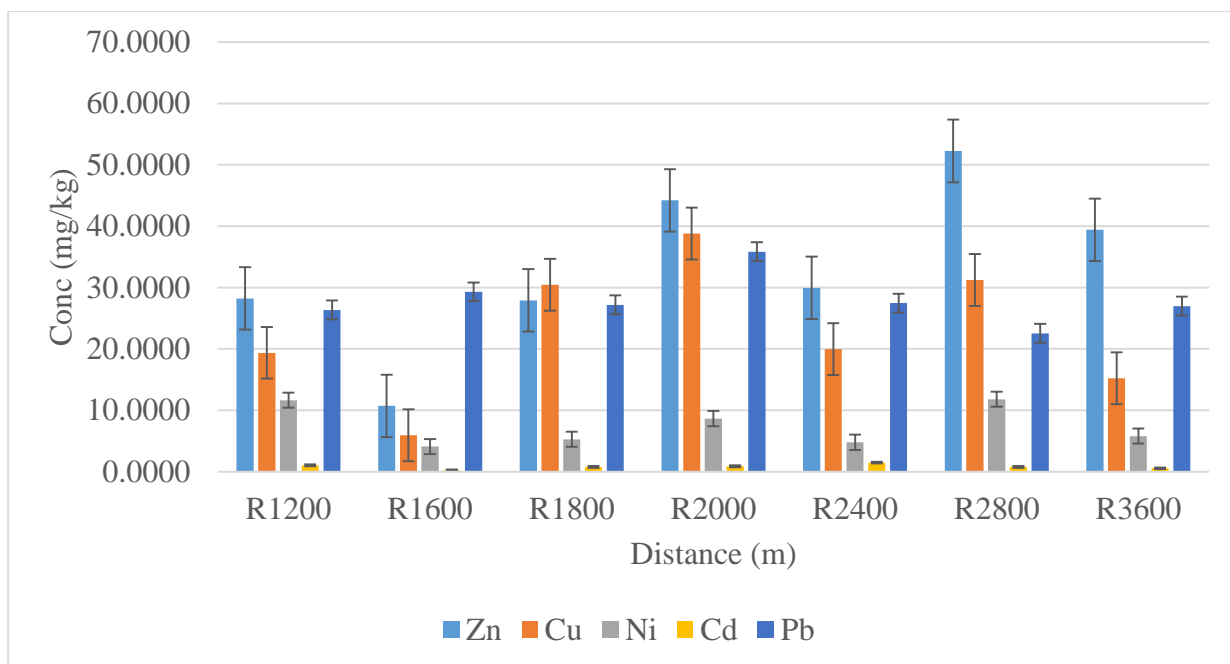
Figure 15: The levels of Zn, Cu, Ni, Cd and Pb in road soils as a function of distance from the mine.

The levels of heavy metals in road soils collected at various distances from the mine did not show any specific pattern. The surface soil from the road network had coal and coal ash spillages, this led to unevenly dispersal of heavy metals. The maximum mean levels of heavy metals were obtained from the following distances: Fe (2000 m), Zn (2800 m), Cu (2000 m), Ni (2800 m), Cd (2400 m) and Pb (2000 m). The sample collected at 2000 m contained mixed coal particles and that contributed to high levels of heavy metals. The mean concentrations of heavy metals obtained in this research were less than the results reported by Swaileh *et al.* (2004) (Zn $6.18 - 295$, Cu $4.37 - 321$, Pb $2.22 - 539$, Cd $0.09 - 0.59$ mg/kg). However, the concentrations obtained in this study were higher than values reported by Adedenji *et al.* (2013) (Cd $0.05 - 0.13$, and Fe $16.20 - 120.89$ mg/kg). The mean Concentration factor (CF) values obtained in this study for Zn, Cu, Fe, Ni, Cd and Pb were: 0.87, 1.34, 0.96, 1.02, 1.34 and 1.19 respectively. The soil generally varied from none to medium contamination classifications, though one sample had CF value of 2.26 (moderate contamination). The soil maybe said to be not very polluted currently, but precautions should be considered in order to reduce the addition of toxic metals in the environment by man activities. Pollution can elevate in future if measures are not put in place, because they have a tendency of bio accumulating in the environment.

4.5.6 Determination of heavy metals concentration in Sandstone and Mudstone samples

Sandstone and Mudstone are sedimentary layer of rocks found underground during mining of Coal. Sandstone is the first layer which is grey in colour and Mudstone is the second layer closer to Coal which is black in colour. These solid wastes are excavated in large quantities during mining especially open pit type of mining. At MCL these solid wastes have no economical use and they are dumped as part of overburden. Eight (8) samples of Sandstone and Mudstone were collected, and heavy metal content analysed. The mean concentration range for heavy metals in Sandstone are Zn (27.62 − 43.94), Fe (7826.10 − 17028.61), Cu (1.39 − 52.58), Ni (5.63 − 8.48), Cd (0.91 − 1.50) and Pb (50.34 − 62.83) mg/kg. The heavy metal content in sandstone in decreasing order is Fe, Pb, Zn, Cu, Ni and Cd. The mean concentration range of heavy metal in mudstone in decreasing order was found to be: Fe (9238.75 − 11785.53), Pb (58.80 − 71.71), Zn (42.90 − 88.09), Cu (1.39 − 52.58), Ni (6.78 − 8.64) and Cd (0.90 − 1.02) mg/kg. The mean concentration of heavy metals in mudstone were higher than in sandstone. The statistical information of heavy metals in Sandstone (S) and Mudstone (M) are shown in Tables 22 and 23.

Table 22: The mean concentration (mg/kg), standard deviation and coefficient of variation of Zn, Cu and Fe in Sandstone and Mudstone.

	Zn			Cu			Fe		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
M1	45.59	0.21	0.45	43.55	0.08	0.18	11713.17	19.61	0.17
M2	88.09	0.27	0.31	42.99	0.13	0.31	11741.99	61.56	0.52
M3	42.90	0.34	0.80	47.04	0.28	0.60	9238.75	57.38	0.62
M4	77.66	0.38	0.49	43.53	0.07	0.16	11785.53	0.00	0.00
S1	43.94	0.01	0.03	52.58	0.27	0.51	17028.61	55.32	0.32
S2	27.62	0.43	1.55	1.39	0.01	0.98	10039.32	0.74	0.01
S3	34.68	0.25	0.72	1.55	0.02	1.01	7826.10	0.64	0.01
S4	40.22	0.18	0.45	1.49	0.01	0.74	9879.81	0.08	0.00

Table 23: The mean concentration (mg/kg), standard deviation and coefficient of variation of Ni, Cd and Pb in Sandstone and Mudstone.

	Ni			Cd			Pb		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
M1	7.65	0.24	3.20	1.02	0.11	10.37	58.80	0.68	1.16
M2	6.78	0.00	0.00	0.95	0.02	2.24	59.59	0.00	0.00
M3	8.49	0.03	0.41	0.90	0.02	2.11	70.60	0.57	0.81
M4	8.64	0.06	0.71	0.99	0.00	0.36	71.71	0.03	0.04
S1	8.48	0.29	3.44	0.91	0.11	12.48	50.34	0.53	1.05
S2	6.06	0.09	1.53	0.91	0.01	1.56	59.46	0.35	0.59
S3	5.63	0.06	1.07	1.36	0.08	5.66	62.06	0.10	0.16
S4	5.74	0.07	1.16	1.50	0.00	0.01	62.83	0.10	0.14

The overall mean concentration of Zn, Cu, Fe, Ni, Cd and Pb in Sandstone and Mudstone are 36.62, 14.25, 11193.46, 5.77, 1.17, 58.67 and 63.56, 44.33, 11119.86, 7.89, 0.96, 65.17 mg/kg respectively. The mudstone rock contains high concentrations compared to sandstone. Generally, the concentration of heavy metals studied increased with depth from soil to sandstone, mudstone and Coal.

Table 24: The overall mean level of selected heavy metals in Sandstone and Mudstone and Low-grade Coal (mg/kg).

Metals	Sand	Mud	LG
Zn	36.62	63.56	71.64
Cu	14.25	44.33	44.48
Fe	11193.46	11119.86	12817.15
Ni	5.77	7.89	11.83
Cd	1.17	0.96	1.10
Pb	58.67	65.17	45.81

4.5.7 Determination of heavy metals concentration in Grass samples.

Seven (7) samples of grass forages were collected within coal mining area in 3 directions East, West and South. The northern side was characterised with huge mountains of overburden and

there was no grass nearby. The mean concentration range of selected heavy in grass samples were found to be: Fe (251.30 − 2252.76), Zn (25.79 − 60.63), Cu (2.87 − 8.23), Pb (0.57 − 4.75), Ni (0.00 − 2.52) and Cd (0.22 − 0.46) mg/kg.

Table 25: The mean concentration (mg/kg), standard deviation and coefficient of variation of Zn, Cu and Fe in grass samples.

	Zn			Cu			Fe		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
SG	33.54	0.36	1.09	5.74	0.29	5.08	2010.37	0.54	0.03
SG1800	45.80	0.32	0.69	7.76	0.18	2.33	2252.76	2.53	0.11
EG	65.87	0.38	0.58	7.32	0.05	0.68	1003.41	2.78	0.28
E1600	29.52	0.18	0.61	8.23	0.09	1.15	1326.33	0.31	0.02
E1800	25.79	0.27	1.06	6.08	0.12	1.98	1356.63	0.11	0.01
WG	60.63	0.16	0.26	3.98	0.05	1.19	251.34	0.00	0.00
WG1800	40.68	0.59	1.46	2.87	0.10	3.35	251.30	0.09	0.04

Table 26: The mean concentration (mg/kg), standard deviation and coefficient of variation of Ni, Cd and Pb in grass samples.

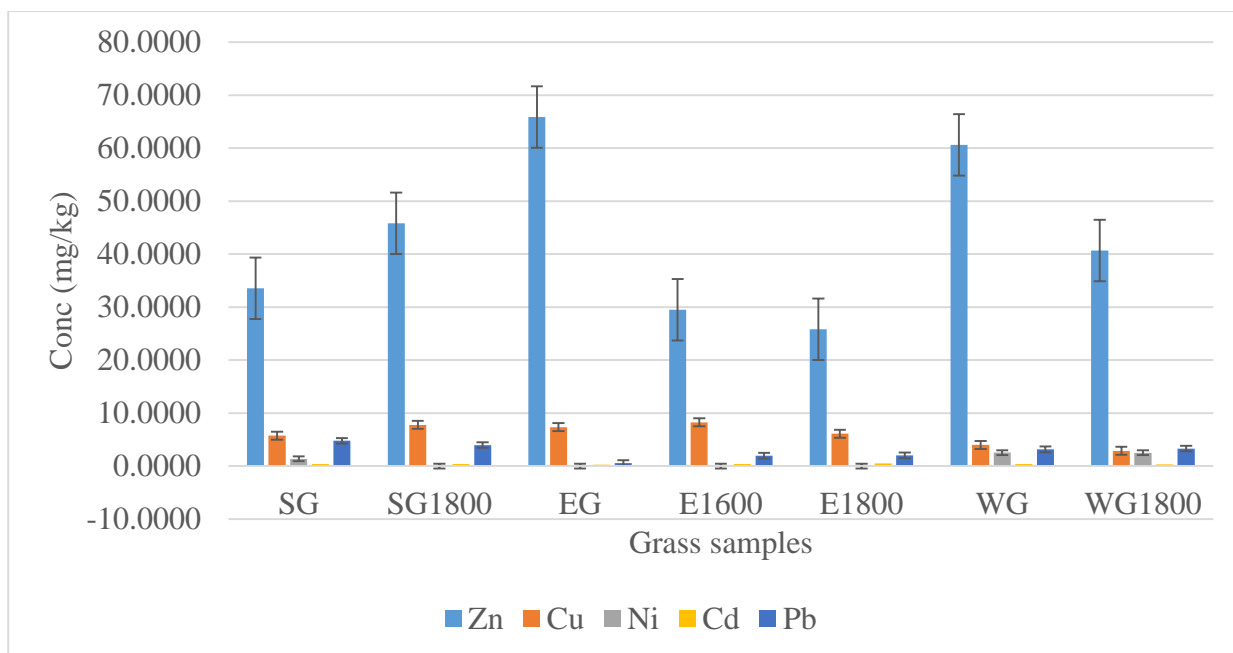|	Ni			Cd			Pb		
ID	MEAN	STDEV	%CV	MEAN	STDEV	%CV	MEAN	STDEV	%CV
SG	1.34	0.05	3.58	0.40	0.01	2.40	4.75	0.38	8.02
SG1800	0.00	0.00	0.00	0.35	0.01	2.68	3.95	0.56	14.03
EG	0.00	0.00	0.00	0.22	0.03	13.62	0.57	0.06	9.76
E1600	0.00	0.00	0.00	0.37	0.05	13.62	1.92	0.00	0.00
E1800	0.00	0.00	0.00	0.46	0.00	0.92	2.01	0.01	0.45
WG	2.52	0.42	16.84	0.36	0.05	14.45	3.16	0.02	0.77
WG1800	2.50	0.14	5.67	0.34	0.01	1.96	3.29	0.01	0.41

Figure 16: The levels of Zn, Cu, Ni, Cd and Pb in grass samples as a function of distance from the mining site.

The mean levels of heavy metals were higher in these samples: Fe (SG1800), Zn (EG200), Cu (EG1600), Pb (SG200) Ni (WG200) and Cd (EG1800). Ni was below detection limits in the following samples: EG200, SG1800, EG1600 and EGI800. Fosu-Mensah *et al.* (2017), reported permissible limits of heavy metals in plant materials by WHO/FAO (2001) and these are: Fe (400-500), Pb (0.43), Cd (0.20), Cu (3.0), Zn (27.3) and Ni (1.63) mg/kg. The maximum mean level of toxic heavy obtained are Fe (2252.76), Pb (4.75), Cd (0.46), Cu (8.23), Zn (65.87) and Ni (2.52). The maximum mean concentrations of the heavy metals were above the permissible limits set by WHO/FAO (2001) in plant materials. These concentrations of heavy metals constitute a considerable danger to animal that graze near the coal mining area. Fosu-Mensah *et al.* (2017) reported that animals that graze in e-waste dumpsite were more exposed to health dangers with respect to Pb toxicity via the eating of forage grasses growing in such areas.

4.6 Heavy metal pollution in soils near coal mine

The heavy metals levels obtained in soils near coal mine suggest an anthropogenic source, attributable to coal mining activities and the waste generated. Zn, Hg, Pb, Mo, Cd, As, Cu, Sb and V had broad concentration variations, attributable to human' activity sources (Liang *et al.,* 2017). The above statement indicated that surface soils near MCL have been polluted by heavy metals to various extent.

4.6.1 Concentration of Zn metal in soil near coal mine

The mean concentrations of Zn in four (4) transects vary as follows: East (4.84 − 44.80), West (5.01 − 44.51), North (31.55 − 44.58) and South (32.20 − 74.53) mg/kg. Similar concentration of Zn (47.84 mg/kg) was obtained by Abliz *et al.* (2018). The concentrations of Zn obtained in this research were lower compared to those reported by Niu *et al.* (2017) and Ladwani *et al.* (2012) (63.0 − 108.0 and 13.0 − 60.0 mg/kg respectively). However, Zn levels in the southern transect were greater than concentrations obtained by Ladwani *et al.* (2012) and by Khan *et al.,* (2017) (13.0 − 60.0 and 65.2 ± 4.9 mg/kg respectively). The maximum mean concentration of Zn in soils from East, West and North are almost the same. The similar distribution of Zn in the three transects indicates that metals predominantly emanated from soil parent matter. The South transect had the highest mean concentrations of Zn, this could be due to the presence of ash ponds, the garage and roads. Some of the mean concentrations obtained in this research are higher than the background concentration. The samples obtained from the eastern, western and north sides of the mine are less contaminated by Zn, because their contamination factor (CF) values fall below 1. However, some CF values were closer to and others are above 1, which shows that the soils were none to medium contaminated. The southern side was the most contaminated with Zn compared to the other three sides. The CF values were approaching two, which implies that the soils were moderately contaminated. The CF values of environmental concern from 4 transects ranged as: East (0.13 − 1.17), West (0.13 − 1.16), North (0.80 − 1.16) and South (0.84 − 1.94).

4.6.2 Concentration of Cu metal in soil near coal mine

The mean concentration of Cu in soils near coal mine ranged as: East (10.51 − 33.22), West (5.01 − 32.82), North (20.56 − 54.68) and South (11.70 − 35.59) mg/kg. The levels of Cu in selected soil samples were similar with the results reported by: (You *et al.,* 2016; Abliz *et al.,* 2018; and Ladwani *et al.,* 2012). The reported concentrations of Cu were 24.3 − 50.3, 19.28 and 9.1 – 57.0 mg/kg respectively. However, the mean concentration ranges of Cu obtained in this research were greater than those obtained by Niu *et al.* (2017) and Sawut *et al.* (2017) which are; 19.7 − 36.0 and 18.4 − 19.3 mg/kg respectively. Similar tendency was noticed in dispersal of Cu in surface soil near coal mine, though the highest mean level was acquired in the North transect. When the mean concentrations of this study were compared with the background concentrations, the concentrations were higher than the background level in selected soil samples. This suggested that human activities were responsible for elevated concentrations of Cu.

The contamination of copper in soils near coal mine was determined by calculating the CF values of each mean concentration in all four directions. The CF values of environmental concern from 4 transects ranged as: East (0.61 – 1.93), West (0.29 – 1.91), North (1.20 – 3.18) and South (0.68 – 2.07). The pollution degree could be categorised according to their strength on a scale varying from 1 to 6 (Muhammad *et al.,* 2011): none (0), none to medium (1) moderate (2), moderate to strong (3), strong pollution (4), strong to very strong (5), very strong (6). Most of the CF values in the East side were above 1 except one sample which had a value below 1. Therefore, the soil in the east transect was found to be none to medium polluted by Cu. The western side had CF values below 1 except three samples which had values above 1. Therefore, the western side of the mine is the least polluted by Cu. The northern side is the most polluted side of mine by Cu, the CF values are above 2 and the maximum was 3.18. Therefore, the soil is moderately and moderate to strong contamination by Cu. This is due to the fact that the soil on the northern part of the mine is made up of overburdens. The southern side is the second contaminated side with Cu, as the CF values are above 1 and the maximum was 2.07. Therefore, the soil is none to medium and moderately polluted by Cu.

4.6.3   Concentration of Fe metal in soil near coal mine

Iron has the highest mean level of all the metals analysed and its concentration ranged as follows: East (10856.95 − 27262.75), West (3575.98 − 12072.43), North (15996.38 − 32859.51) and South (9903.73 − 52349.91) mg/kg. The results obtained indicated that the mean concentration of Fe fluctuated in the four transects, the lowest was obtained in the West and the highest in the South transect. High levels of Fe in soils relatively to other metals have been outlined in several studies, affirming that natural soils contain higher concentration of Fe. The mean concentration range of Fe reported in this research is greater than those obtained by Osakwe and Okolie (2015) and Liang *et al.* (2017) which are; 142.93 ± 42.16 and 6.89 − 86.59 mg/kg. The CF values for Fe were: East (0.72 − 1.82), West (0.24 − 0.81), North (1.07 − 2.19) and South (0.66 − 3.49). Most CF values from the East were above 1 and very close to 2, hence the soil was moderately contaminated. The Western side showed the same trend with Fe as observed for Zn and Cu. It is the least contaminated side of the mine with Fe. The northern side was moderately contaminated by Fe, since the CF values were above 1 (2.19). Southern side is the most contaminated by Fe, the CF values are as much as 3.49. This implies that the soil can be classified as moderate to strongly contaminated.

4.6.4　Concentration of Ni metal in soil near coal mine

The levels of Ni in the soils from all the sites varied as follows: East (3.63 − 10.66), West (1.55 − 10.68), North (13.96 − 27.59) and South (6.87 − 18.11) mg/kg. The mean Ni content obtained in this study is comparable with the concentrations of Ni (7.1 − 16.0 mg/kg) obtained by Ladwani *et al.* (2012) and lower than those obtained by Niu *et al.* (2017) (26.2 − 43.7 mg/kg). The mean level of Ni was high in the North transect. The CF values of environmental concern from 4 transects ranged as: East (0.61 − 1.93), West (0.29 − 1.91), North (1.20 − 3.18) and South (0.68 − 2.07). The mean CF values for Ni in the Eastern direction of the mine is 1.13 which implies that the soil is none to medium contamination by Ni. However, one sample had CF value lower than 1. In the Western direction, like other heavy metals assessed the pollution was minimal with the mean CF value of 0.91. This means the soil is not polluted, but the value is closer to 1, this could be a threat in the near future. The maximum CF value obtained was 1.46, which means some samples were none to medium contamination. The Northern side of the mine was observed to be more polluted area with respect to heavy metals. The mean CF value was found to be 4.92, this means that the soil is strong contamination by Ni. The maximum CF value was found to be 6.10, this implies that some soil samples were very strong polluted by Ni. The southern side proves to be second in terms of heavy metal pollution due to the presence of road network, garage and ash ponds. There was a lot of variations in CF values and the mean value was found to be 1.81. The maximum value was 2.48, which means some soil samples were moderately polluted. The contamination load index derived from contamination factor showed that the sites around coal mining regions are most contaminated (Pandey *et al.,* 2014). Therefore, coal mining is responsible for increased levels of heavy metals in soils near mining area.

4.6.5　Concentration of Cd metal in soil near coal mine

Cadmium mean concentrations from all for transects ranged as follows: East (0.39 − 1.40), West (0.16 − 0.85), North (0.83 − 1.08) and S (0.47 − 1.35) mg/kg. These concentrations are greater than those obtained by Ladwani *et al.* (2012), You *et al.* (2016) and Shang *et al.* (2016) which are; 0.41 − 0.77, 0.07 − 0.28 and 0.16 − 0.51 mg/kg respectively and lower than those obtained by Liang *et al.* (2017) (0.05 − 8.71 mg/kg). The mean CF values for Cd in the Eastern direction of the mine is 1.10, which implies that the soil is none to medium contamination by Cd. The maximum CF value in the Eastern direction was found to be 2.34, this implies that some of the soil samples are moderately polluted by Cd. In the Western direction, like any other heavy metals assessed, the pollution was minimal with the mean CF value of 0.71. This means the soil is not polluted, but the value is closer to 1, this could be a threat in the near future. The maximum CF

value obtained was 1.42, which means some samples fall none to medium contamination category. The northern side was found to be more contaminated with Cd with a mean CF value of 1.66. This implies that generally the soils in the north direction can be classified as none to medium contaminated. The maximum CF value was 1.80 and the lowest was 1.38. The southern side was slightly more polluted than the northern. The mean CF value was found to be 1.69 and the maximum value was 2.24. Some soil sample were moderately polluted by cadmium and others were below 1.

4.6.6   Concentration of Pb metal in soil near coal mine

Lead concentrations in all the sites varied as follows: East $(25.15 - 45.53)$, West $(9.25 - 39.39)$, North $(26.15 - 36.29)$ and South $(15.41 - 33.85)$ mg/kg. The levels of Pb in this study are similar to those obtained by Abliz *et al.,* (2018), Fang *et al.,* (2014) in Xinzhuangzi and Panyi area, You *et al.,* (2016) and Shang *et al.,* (2016) which are; $7.22 - 33.00$, $16.6 - 39.5$, $11.3 - 36.2$ and $20 - 39.1$ mg/kg respectively. However, the Pb levels obtained in this research are notably higher than those obtained by Fang *et al.,* (2015) in Nihewan and Guqiao areas, Lwandani *et al.,* (2012) and Sawut *et al.,* (2017) which are; 26.1 ± 11.6, $3.4 - 9.0$ and $11.3 - 13.3$ mg/kg respectively. However, they were lower than those obtained by Liang *et al.,* 2017 and Niu *et al.,* 2017 which are; $8.69 - 744.70$ and $21.9 - 98.7$ mg/kg respectively. The mean CF values for Pb in the Eastern direction of the mine was found to be 1.50 which implies that the soil is none to medium contamination by Pb. The maximum CF value in the Eastern direction was found to be 1.94, this implies that some of the soil sample were almost moderately contaminated. In the Western direction, like any other heavy metals assessed, the pollution was minimal with the mean CF value of 0.98. This indicates that the soil is not polluted, but the value is closer to 1, this could be a threat in near future. The maximum CF value obtained was 1.68, which means some samples were none to medium contamination. The Northern side was found to be less contaminated with Pb than the Eastern side, with a mean CF value of 1.36. This implies that generally the soils in the north direction were none to medium contamination by Pb. The maximum CF value was found to be 1.55 and the lowest was 1.12. The southern side was slightly less polluted than the northern with Pb. The mean CF value was found to be 1.23 and the maximum value was 1.53.

Extraction of coal opencast mining and other anthropogenic activities substantially elevated the levels of heavy metals in soil. High levels of Pb were mostly dispersed near the coal mining region, chemical plant and down the road and even dispersions were noticed in the other parts of the research region. Abliz *et al.,* (2018) observed that consistent dispersion of Pb in the

research region revealed that large quantities of Pb occurs in soil parent material. As observed in this study, elevated level of heavy metals was observed near the open pit coal mining in Maamba. The increased levels of heavy metals in the mining areas revealed that the mining ventures such as mining, transportation, utilisation and waste disposal is one of the sources for toxic metals contamination in soil (You *et al.,* 2016).

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

5.1.1 Coal

This study has confirmed the availability of toxic heavy metals in coal, coal ash, solid waste (sandstone and mudstone), soils and grass forages near coal mining in Maamba, Zambia. The level of heavy metals in coal are ranked as follows: $Fe > Zn > Cu > Pb > Ni > Cd$. The Low Grade (LG) had higher concentrations than other grades of coal such as High Grade (HG), Peas (PE) and Rejects (RE). This observation may be attributed to the fact that HG, PE and RE are washed product of coal. Therefore, some of the heavy metals are washed away during processing with effluent. Although heavy metals concentrations are not very high but long period of mining coal may result into build-up of heavy metals in the environment. The mine may also lead to contamination of the surface water as the effluent is channelled into streams nearby. This can result to the addition of heavy metals into the food chain through eating fish from polluted reservoir. People may also ingest heavy metal from dairy product from livestock which drink water from polluted streams. In addition, runoffs from the piles of coal may potentially contaminate the surface soil and water reservoir during rainy season.

5.1.2 Coal Ash

Coal Ash is made up of Bottom and Fly Ash, which are the troublesome waste product generated from Coal Fired Plant. The by- products have economic use though they are not utilised in large quantities in Zambia. This has led to accumulation of these fine particle in ash ponds and very difficulties to manage as they can be blown by wind. Hence are irrigated by water using drip irrigation method and limestone added in order to neutralise the acid formed due to the presence of sulphur dioxide. Coal ash can cause leaching of heavy metal to underground water during rainy season and irrigation process. Heavy metals from fly ash can also be distributed in the environment by the following agents: wind, runoff and floods from ash ponds during heavy down pour. Heavy metals concentration in coal ash could be ranked as follows; $Fe > Pb > Zn > Cu > Ni > Cd$. Coal ash had high levels of heavy metals than parent coal. This could be attributed reduction of carbon content and the dumping of coal ash at one place results into concentrated level of heavy metals.

5.1.3 Sandstone and Mudstone

The sandstone and mudstone are sedimentary rock excavated during mining of coal. These solid wastes have no economic benefits reported so far and are excavated in large quantities. Runoffs from these piles of rocks may contaminate the soil with heavy metals. Sandstone has low level of heavy metals analysed than Mudstone. The overall mean level of Zn, Cu, Fe, Ni, Cd and Pb in sandstone are: 36.62, 14.25, 11193.46, 5.77, 1.17 and 58.67 mg/kg respectively. Values obtained for Mudstone were as follows: 63.56, 44.33, 11119.86, 7.89, 0.96 and 65.17 mg/kg respectively. The rank of these heavy metals both in sandstone and mudstone were the same as follows: Fe > Pb > Zn > Cu > Ni > Cd. The solid waste contains high concentration of heavy metal which may spread in the environment by runoffs during rainy season.

5.1.4 Soil near coal mining area

The soils were generally slightly contaminated with heavy metals analysed, but there is need for monitoring as these metals are persistence in the environment. Most of soil samples analysed had the concentration of heavy metals greater than the control sample. This implies that there is elevation of heavy metal levels due to mining and the dumping of waste from utilisation of coal. The heavy metal contamination from East and West transect were ranked as follows: Pb > Cu > Fe > Ni > Cd > Zn and Pb > Ni > Cu > Zn > Cd > Fe respectively. The North transect was the most contaminated followed by the South transect. The contamination was ranked as follows: Ni > Cu > Cd > Fe > Pb > Zn and Fe > Ni > Cd > Cu > Zn > Pb respectively. The Northern was highly polluted by Ni with CF value 4.92. Heavy metals concentration fluctuated with distance from the mining pit due to spillages of coal, combustion by products (coal ash), solid waste (sandstone and mudstone) and old mines around. Most of the soils around the mine are no longer in their original form due to high overburden which is produced by open pit mine.

5.1.5 Heavy metal pollution in grass near Coal mine

The samples of grass forages analysed were found not to be contaminated by Ni. However, there were slightly contamination of the following metals Fe, Zn, Cu, Cd and Pb. The CF values for these metals are: 2.14, 1.43, 1.20, 1.08 and 0.66 respectively. From this study, it can be concluded that the pasture for livestock is slightly polluted by heavy metal which could result into health problem in future to the people in the study area. Livestock graze in old coal mines and water from steams where coal effluents are channelled, hence population may be exposed to heavy metals from consumption of dairy products.

5.2   Recommendations

This study has revealed that coal ash contains high concentration of heavy metals which potentially pose human health and environmental concern and a concern to human health. The recommendations for this study are listed below.

1. In order to reduce pollution of heavy metals, fly ash should be used in huge quantities in cement industries such as structural fill material in constructing highway embankments and road bases as ingredient in ultra - high strength concrete. It can also be used in manufacturing of concrete bricks, blocks and paving stones.

2. Studies on concentration of heavy metals in particulate matter at Maamba coal mine area should be conducted.

3. Mudstone and sandstone waste can also be used in manufacturing of concrete bricks, blocks and paving stones. Other innovations are needed for utilization of these waste as they occupy large portion of land and they cause environmental pollution.

4. Studies on heavy metals concentration in surface and under groundwater should be conducted.

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APPENDICES

Appendicx I: Pictures from Maamba Coal mine, Zambia.

(Low-Grade coal (LG), High Grade coal (HG), open-pit mine, Fly and Bottom ash)

a) Low-grade coal (LG)

b) High-grade coal (HG)

c) Open pit mine

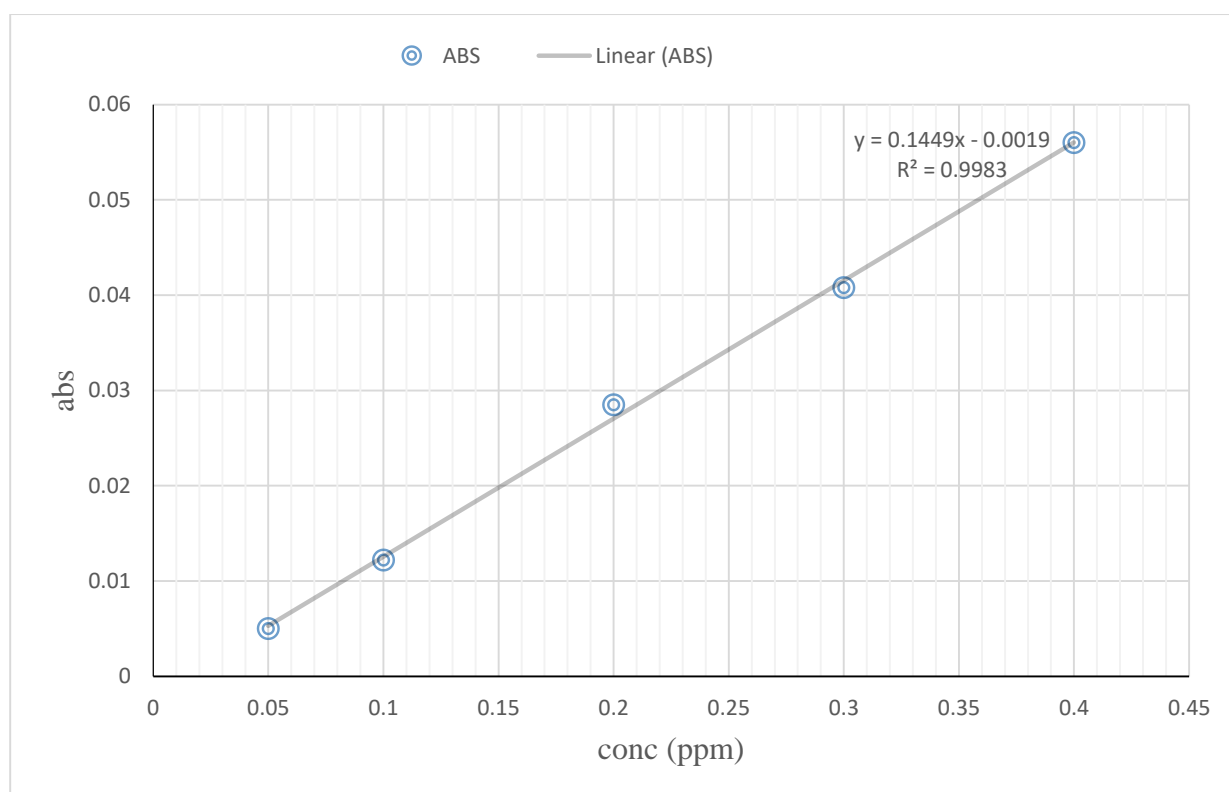

d) Fly ash and bottom ash

e) Sandstone and mudstone

f) Pit lake

Appendix II: Concentration and Absorbance for Zinc Standards.

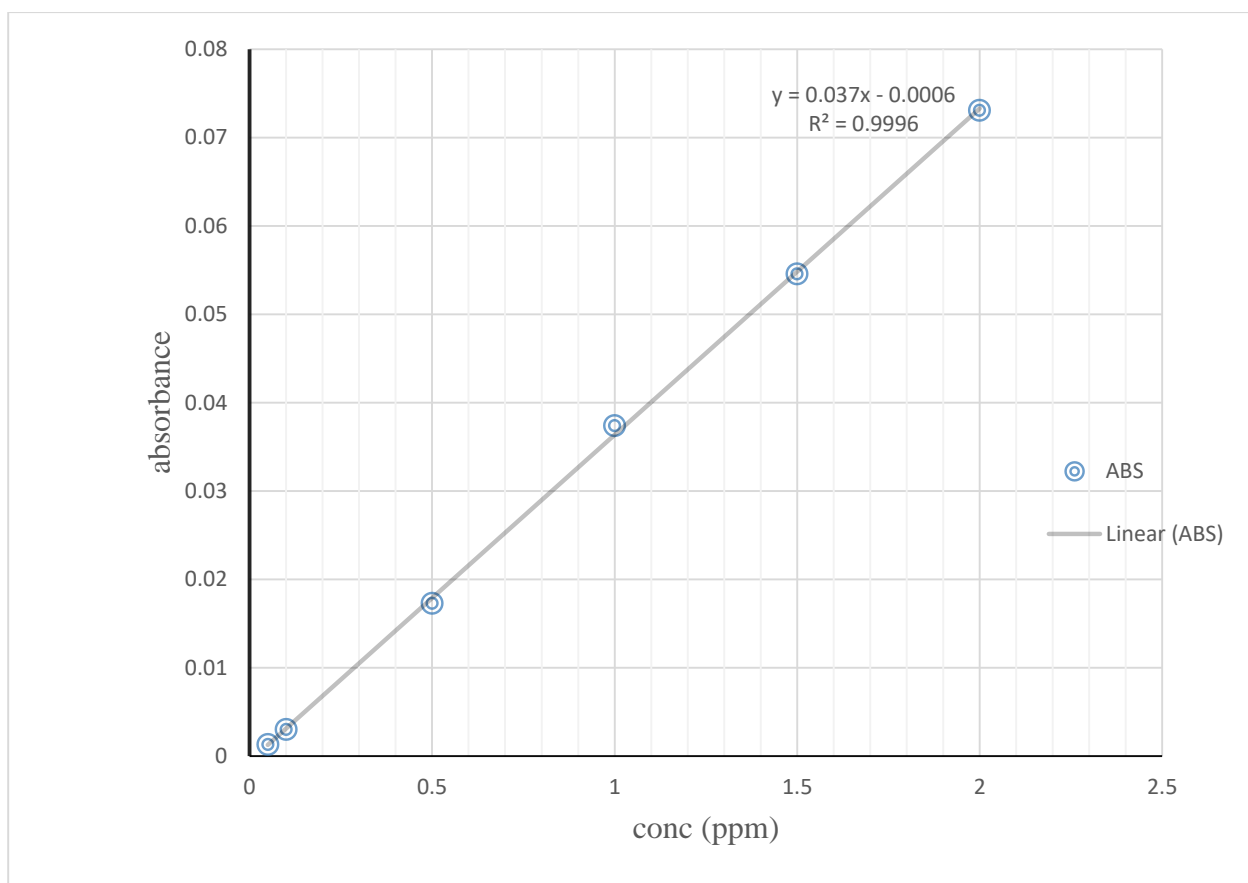| Standards	Concentration (ppm)	Absorbance
1	0.05	0.0050
2	0.10	0.0122
3	0.20	0.0285
4	0.30	0.0408
5	0.40	0.0560

Appendix III Calibration Curve for Zinc

Appendix IV Concentration and Absorbance for Copper Standards.

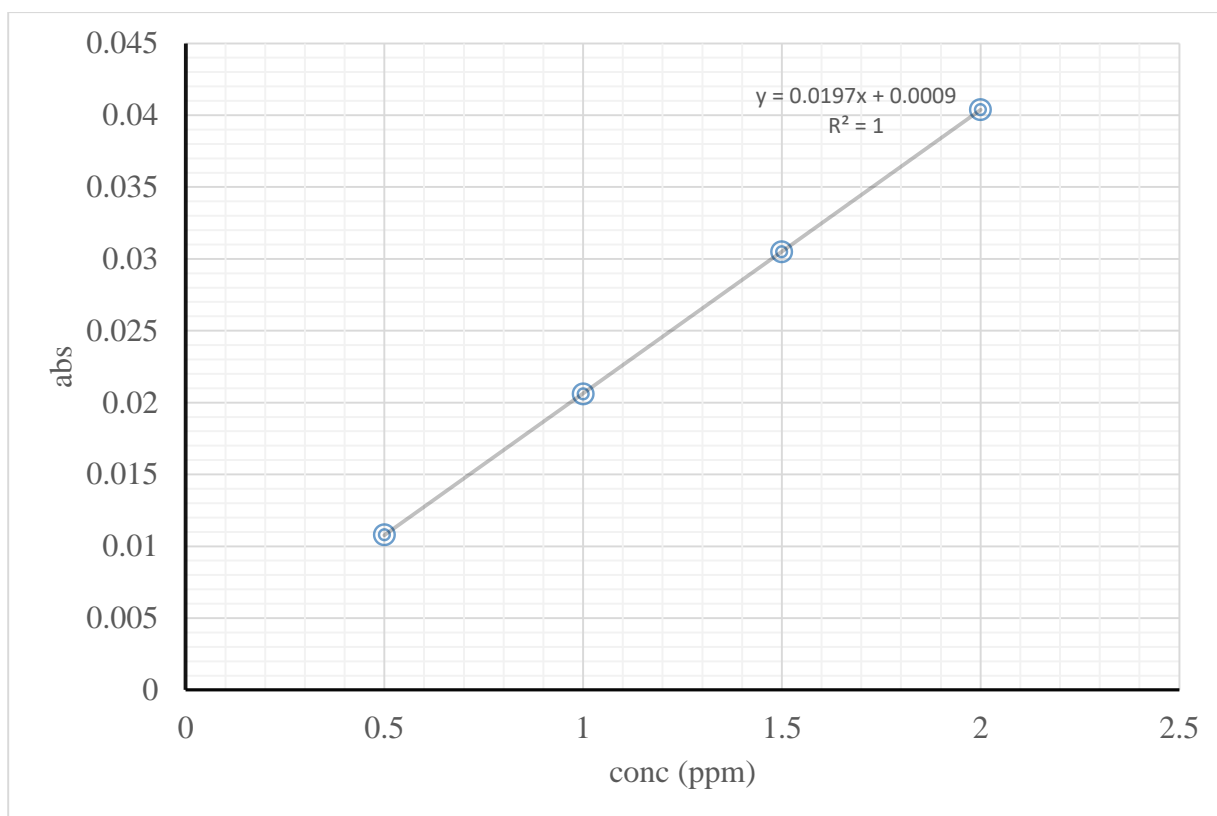| Standard	Concentration (ppm)	Absorbance
1	0.05	0.0013
2	0.10	0.0030
3	0.50	0.0173
4	1.00	0.0374
5	1.50	0.0546
6	2.00	0.0731

Appendix V   Calibration curve of Cu

Appendix VI: Concentration and Absorbance for Iron Standards.

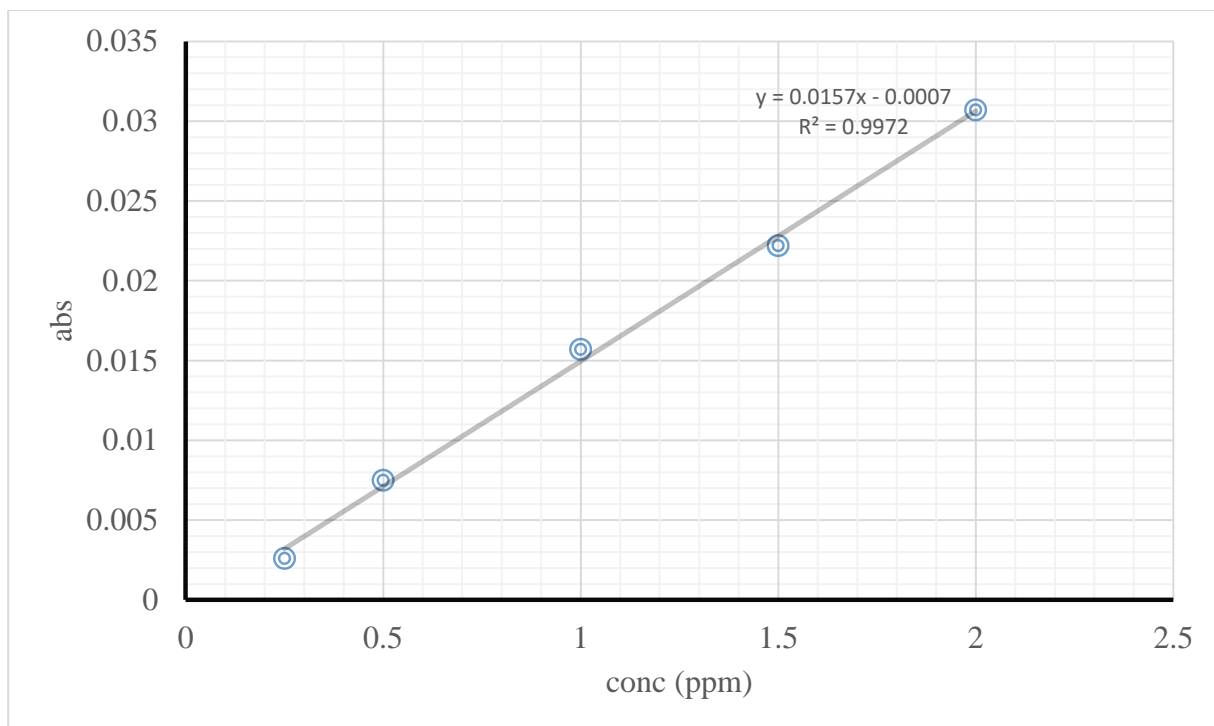| Standards	Concentration (ppm)	Absorbance
1	0.50	0.0108
2	1.00	0.0206
3	1.50	0.0305
4	2.00	0.0404

Appendix VII Callibration Curve for Iron.

Appendix VIII: Concentration and Absorbance for Nickel Standards.

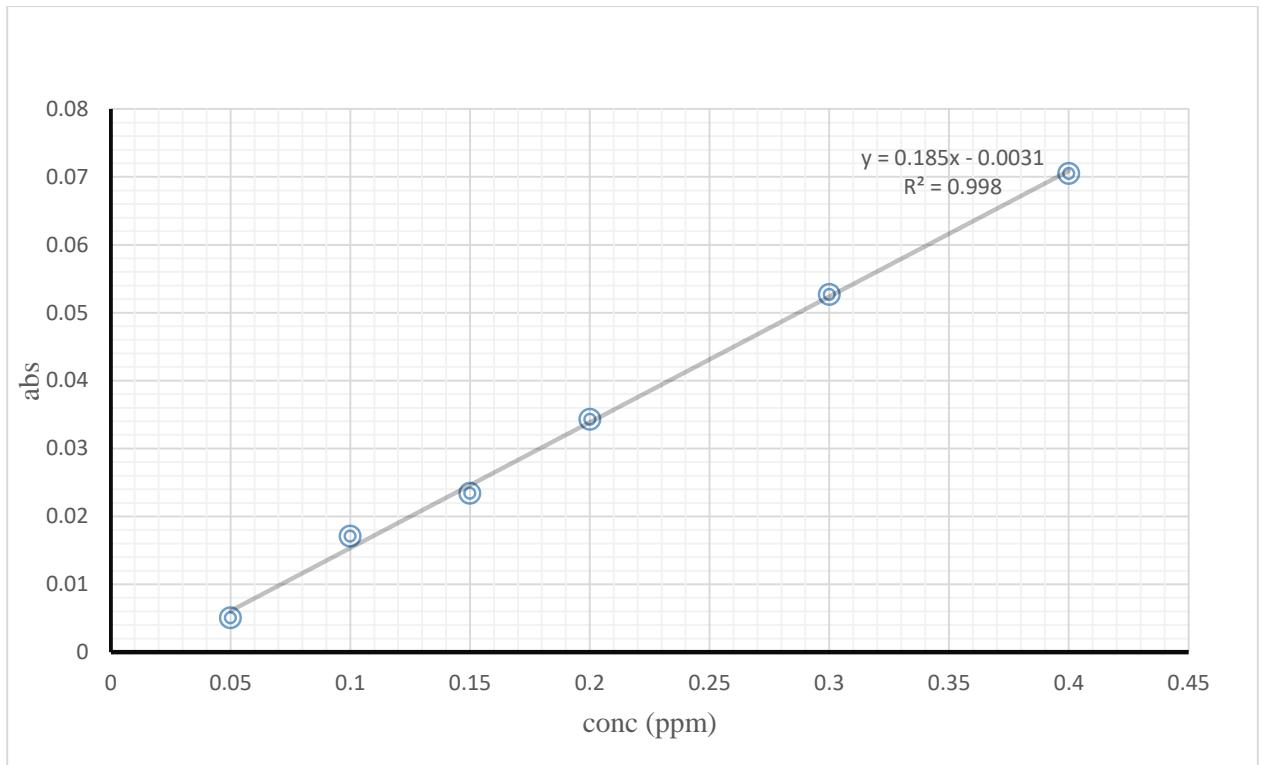| Standards	Concentration (ppm)	Absorbance
1	0.25	0.0026
2	0.50	0.0075
3	1.00	0.0157
4	1.50	0.0222
5	2.00	0.0307

Appendix IX Calibration Curve for Nickel

Appendix X   Concentration and Absorbance for Cadmium Standards.

Standards	Concentration (ppm)	Absorbance
1	0.05	0.0051
2	0.10	0.0171
3	0.15	0.0234
4	0.20	0.0343
5	0.30	0.0527
6	0.40	0.0705

Appendix X1 Calibration Curve for Cadmium

Appendix XII: Concentration and Absorbance for Lead Standards.

Standards	Concentration (ppm)	Absorbance
1	0.20	0.0016
2	0.30	0.002
3	0.40	0.0027
4	1.00	0.0048

Appendix XIII   Calibration Curve for Lead