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Heavy metal pollution in soil and plants from a mining area in the North West Province, South Africa

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Dissertation submitted in fulfilment of the requirements for the degree *Master of Environmental Sciences and Management* at the North West University

Supervisor:Prof LG Palamuleni

Graduation: April 2019

Studentnumber:27457257

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NORTH-WEST UNIVERSITY
NOORDWES-UNIVERSITEIT
UNIBESITI YA BOKONE-BOPHIRIMA

DECLARATION

I, Iyioluwa Busuyi Raji, hereby declare that the work on which this thesis is based is original and neither the whole study nor any part of it has been, is being, or is to be submitted for another degree at this or any other university.

IB Raji

Date

ABSTRACT

South Africa is a mining country with a huge reserve of large deposits of gold, platinum, and coal, among others. However, contamination of soils and plants by heavy metals within the mining environment in South Africa has not been investigated as it should have been. Heavy metals have the tendency of entering the food chain and end up being consumed by humans either directly or indirectly. At high concentration in living body, heavy metals damage organs.

This study analyzed the concentration of heavy metals in soils and the plant found in the environment of a gold mine located in the North West Province, South Africa. The sampling depths for soil were 0-10 cm and 10-20 cm at various distances, namely 500 m and 1000 m around the mining site.

The soil and plant, *Eragrostic hynoides,* samples were analysed for Cd, Zn, Pb and As using inductively coupled plasma spectrometry (ICP-MS). Concentration factor was used for the determination of heavy metal uptake by the plant. The risk quotient was used in this study to determine the health risk associated with heavy metal contamination. A spatial variability of heavy metal contamination was created in the Geographical Information System environment by ordinary kriging.

The concentrations of heavy metals in the soil showed that the levels are within the South African threshold and below some other countries' thresholds. In the leaf and the root tissue of the sampled plant, the trend of heavy metal concentration was Zn > Pb > As > Cd. The results of the concentration factor (CF) revealed that *Eragrostic hypnoides* accumulated Zn and Cd from the soil. The CF was above 1. However, the CF of the arsenic and lead was below 1 in all the sampled locations except at the Northern part of the mine within the 1000 m radius of the mine. The map of spatial variability revealed that higher concentration of heavy metals were found close to the mining site.

In conclusion, the heavy metal concentration accumulated in the plant of the study area could be harmful to the health of the direct and indirect consumer. Future study should be done on agricultural products produced within this vicinity in order to assess the concentration of heavy metals in the crops most especially the extensive maize plantation within the locality.

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DEDICATION

I dedicate this research work most especially to my entire family members for giving me the inspiration and drive to pursue this career. Without their support, I will not be able to achieve my goals in life.

Finally, great thanks to almighty God for the wisdom and knowledge plus understanding to survive this long challenging journey, He is my backbone and ultimate provider.

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CHAPTER ONE

1. MINING AND SOIL CONTAMINATION

1.1 Introduction

Mining in general has adverse effect on the property of the environment (Donkor *et al.*, 2005). It destroys the natural ecosystems as a result of soil and vegetation excavation and burial beneath waste disposal sites. As a result, mining waste can be divided into two categories: 1) mine tailings, due to ore processing and 2) waste rocks generated when removing the ore body. Several exploration methods for ore body include crushing of rocks and ores, recovery of the desired amount and disposal of the wastes, often as slurry, to a tailing or retention pond. More than 99 % of the original material may finally become tailings when low-quality ores are utilized (Ledin *et al.*, 1996).

The high monetary value of gold made it a primary objective of heavy mining operations created in order to uncover the ore body in the most efficient way possible. Heavy machinery, strip mining and acid extraction techniques give miners access to the valuable metal, but they can have huge negative effect on the ecosystem. Gold exploration and extraction industries create different pollution types, and if not checked, they can have a large-scale damage within and beyond the mining environment.

Every mining operation influences the quality of atmospheric gas. Fragments are discharged in surface mining when overlaying rock or sediment is removed from the in-situ and stored or returned to the pit. When the sediment is uncovered, vegetation is also removed, exposing the soil to weather, making particulates to be carried by air through wind erosion and road traffic. Fragmented materials may be made of toxic materials such as arsenic (As), cadmium (Cd), zinc (Zn) and lead (Pb) which impact human health negatively, therefore leading to respiratory tract related illness such as emphysema (Farid *et al.*, 2015).

Mining can also cause physical interruption of the landscape, leading to displeasing sight such as waste-rock piles and open pits. Interruptions of this type result in the reduction of wildlife and plant species in an area. In most cases, it is impossible to restore pre-mining surface features after the termination of mining operation (Paluch, 2016). Another problem associated with mining is water pollution through acid mine drainage (Marara *et al.*, 2013), heavy metal contamination, and high sediment levels in streams. Sources can be dynamic or expelled surface and concealed mines, treating plants, waste-disposal areas, and haulage roads or tailings ponds. Sediments, typically from increased soil erosion, cause siltation or the smothering of streambeds (Farid *et al.*, 2015). This siltation affects the main usage of streams such as fishing, swimming, supplying local communities with portable water, irrigation etc.

Soil pollution originating from mining procedures is hazardous to biota and human health (Milton, 2007). Soil contamination was not ranked as harmful as air and water pollution many years ago, but this view has since changed in many developed countries (Su *et al.*, 2014). Mining operation, grinding, concentrating ores and removing of tailings provide obvious sources of contamination in the environment, along with mine and mill waste water (Barkouch *et al.*, 2015). The acid leaching out of mines tailings can contaminate groundwater, and the toxic substances and heavy metals present in the leftover materials can invade the topsoil and remain hazardous for decades (Karltorp, 2008). For example, mining actions in the Witwatersrand basin alone have resulted in several billion tons of mine waste comprising tens of million tons of sulphur and approximately 430 000 tons of uranium in the tailings storage facilities (Weiersbye *et al.*, 2006; Hobbs & Cobbings, 2007). Apart from generating ecological destruction, pollution emanating from leakage of chemicals, which is inevitable, also disturbs the wellbeing of humans within such environment (Evenson, 2003).

In addition, establishing a mining site is a significant habitat modification and smaller perturbations occur on a larger scale than the exploitation site (Jung, 1996). For example, mine-waste leftovers could contaminate the environment and the adverse effects can be observed long after the termination of the mining activity (Feris *et al.*, 2014). Direct poisoning caused by mine-extracted material and indirect poisoning through food and water, can also affect animals, vegetables and microorganisms (Jung, 1996). Besides, alteration of natural habitats together with man-made substances release, can have major impacts leading to biodiversity losses.

Established plants cannot move away from a disturbed area and will eventually be exposed to extinction if their habitat is contaminated by heavy metals or metalloids at concentration too high for their physiology (del Pillar Ortega-Larrocea, 2010). Some species have high opposition and will eventually endure these altitudes while other species that cannot tolerate these concentrations in the territory will migrate in the mine neighboring lands to occupy the ecological niche (del Pillar Ortega- Larrocea, 2010). Plant life can be affected through direct poisoning, for example, high concentrations of As in soils reduce bryophyte diversity (Banning et al., 2008). Soil acidification due to reduction in pH level by chemical contamination can also lead to lessening of numbers of some species. Change in soils' quality and marine content can be noticed in distressed locations, causing vegetation community changes in the environment (Mummey *et al.*, 2002). Several plant life forms have small heavy metal concentration acceptance in the topsoil and species' indifference varies. Grassland variety and coverage is less impacted by high contaminant concentration than forbs and shrubs (Mummey *et al.*, 2002).

Furthermore, animals that feed on heavy metal contaminated plants store these heavy metals in their systems. Heavy metals from such animals are transferred to the humans that feed on such animal products. Heavy metals of high contamination concentration have been found in dairy milk of animals (Ogabiela *et al.*, 2011; Zodape *et al.*, 2012; Abdulkhaliq *et al.*, 2012; Nyakairu *et al.*, 2012). Milk is an important diet for infants and adults, and the ingestion of heavy metals for example Pb, Cd, Cu and Zn can be determined by varied era of babies through different milk and baby diets (Gh, 2007). Besides infant food, developing fetuses are subjected to about 70 % of the mother's heavy metals released into her blood. Therefore, it is essential to be aware that heavy metals such as Pb and Hg can lead to autism, learning disabilities, low IQ and behavioral problems most importantly in children. Due to the importance of soil to the ecosystem, heavy metal concentrations have to be kept to the minimal, to prevent uptake by plants to animals and therefore, to humans or from the plant to humans directly, and also from soil to humans through ingestion of contaminated soil.

1.2 Problem statement

The budget of the North West Province is chiefly supported by exploration of mineral resources. Mining operations provides more than half of the provincial gross domestic product and generate employment for a section of its workers (Bokone Bophirima Provincial Government, 2015). The major minerals mined are gold, uranium, platinum and diamond. The eastern and southern locations of the province are noted for crop-growing producing maize, sunflower, tobacco, cotton and citrus fruits. Sheep and cattle farms and game reserves are established in the northern and western parts of the province. Despite the economic importance of these mines to the province and the country in general, there are negative environmental and social impacts.

Several studies from South Africa have focused on the environmental impact of mining. Examples of such studies include environmental impact of platinum mining in South Africa (Maboeta *et al*., 2005; Wahl *et al*., 2012; Jubileus *et al*., 2013), dams tailings in South Africa (Blight, 2012), acid mine drainage in South Africa (Naicker *et al*., 2003; Oberholster *et al*., 2010; McCarthy, 2011). Whereas extensive research on the environmental impact of platinum mining has been done by different writers, little published work has been done on the gold mine situated 60 km west of Mafikeng. South Africa is the world's largest gold mining country (O'Donnell, 2011) but the level of research that has been done on heavy metal pollution in the mining environment is very little or unpublished. Therefore, this study will investigate soil contamination and the health effect of heavy metals uptake within the surroundings of a gold mine in the western part of the North West Province.

1.3 Research aim and objectives

The primary aim of this research is to study heavy metal pollution in the environment of a gold mine in North West Province, South Africa.

The specific research objectives of this study are:

1) To define the concentrations of heavy metals in soils and plants.
2) To characterize the spatial variability of heavy metal contamination using Geographical Information Systems.
3) To determine the uptake of heavy metals by plants.
4) To evaluate the health risk posed by the heavy metal contamination.

1.4 Description of the study area

The gold mine studied is an open pit mine owned by the South African based Harmony Gold Mining Company. The mine is situated 60 km southwest of the town of Mafikeng, in the North West Province of South Africa. The North West province has a total area of 116 320 km^2 (9.5 % of the total area of South Africa) and is the third smallest province in South Africa. The North West Province is located geographically between 25° and 28°S and 22° and 28°E. Bordering the North West Province is the Northern Cape Province in the west, the Free State in the south, Guateng in the east and Limpopo in the north-east. It has a transnational boundary with the Republic of Botswana in the North (Figure 1). The topography of the North West Province is predominately flat and the highest elevations average about 1,393 m above mean sea level.

The North West Province is known as an arid province with high demands for water. Rainfall is highly different within the North West Province, both in volume and duration, often resulting in severe drought and extreme flooding. Within the province, it has been recorded that evaporation exceeds rainfall (Howard *et al.*, 2002).

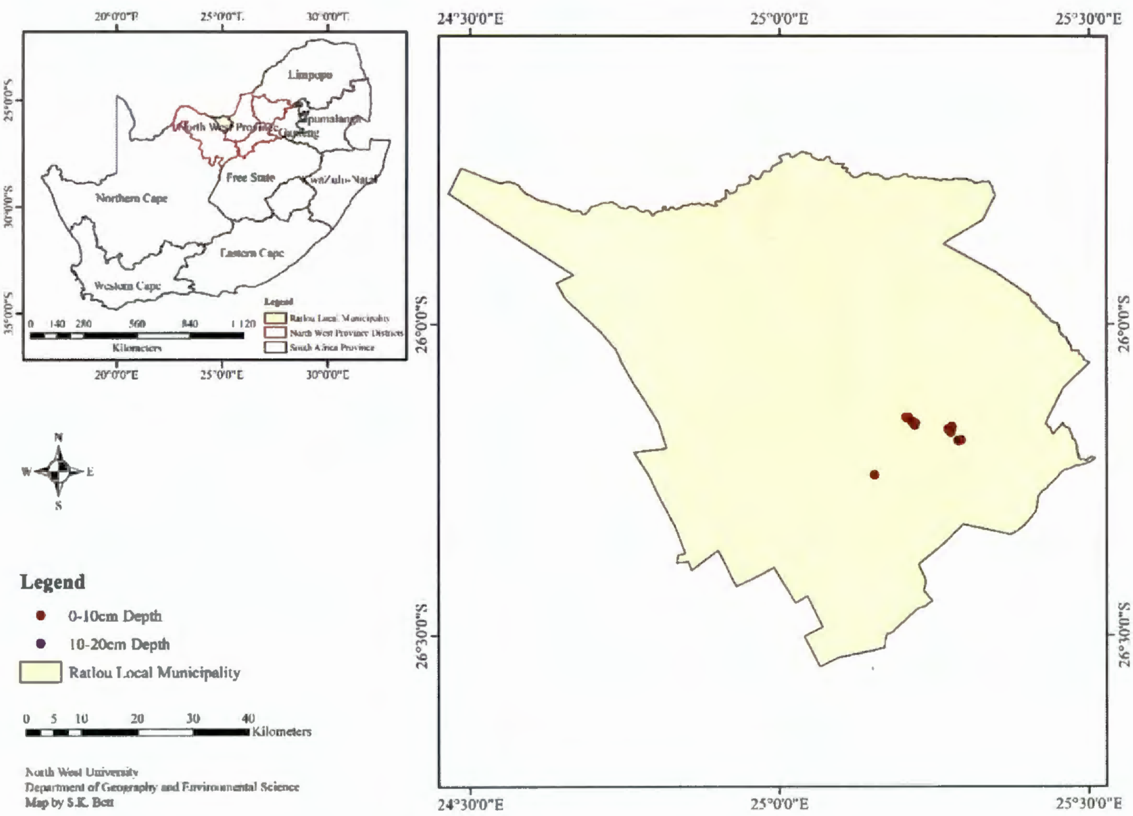


Figure 1: Map of the study area

Large part of the province is surrounded by the Savanna biome, while the remainder lies within the Grassland biome. There are four major ecological regions in the province: (i) the Highveld in the south-east, (ii) the Bushveld in the north-west, (iii) the Middleveld as a narrow zone between the Highveld and the Bushveld, and (iv) the Kalahari-desert in the west. The weather of North West Province is characterized by precise seasons with high temperature in summer and cold sunny winters. There is difference in the climate and rainfall from the rocky and raining eastern area to the drier, semi-desert plains of the Kalahari in the west. October to March is the rainy period.

Kalgold mine was commissioned in 1996. Before Harmony's merger with Kalgold, the West Rand Consolidated group owned South Africa's pre-eminent operation at Kalgold. The merger became effective in July, 1998. Gold is accessed in gold bearing ore in a banded formation in the Kraaipan greenstone belt. Tonnage mined at Kalgold is treated at the carbon-in-leach plant on site.

The study area falls under the Kalahari Desert in the west. Besides mining, cattle and sheep farming form the mainstay of the economic activity in this region as well as large scale irrigation from dolomitic rock formations, which takes place in and around the Pomfret- Tosca-Vergelee area (Tosca-area). Subsistence farming is another economic activity in this region. The largest portion of the study area is covered by recent sand deposits of the Kalahari group. The environment is dominated by sedimentary rocks of different types and sizes (North West Groundmaster Plan, 2010). The study area was chosen because it represents diverse land use, landscapes and, with the location of the mine in the area, it is crucial to study the heavy metals contamination in the soil and plants in order to publish the findings thereby contributing to knowledge on this important topic.

1.5 Organization of chapters in the dissertation

This dissertation is separated into six chapters.

Chapter 1 provides an overview of the study, the problem statement and the aims and objectives of the study and description of the study area.

Chapter 2 focuses on literature review, consisting of the findings of similar studies in the environments of mining areas and on the similar aspects of gold mining.

Chapter 3 discusses the research design and methodology. The chapter describes the research design and the methods of data collection, sampling procedures and the materials that were assessed in the study.

Chapter 4 presents the results obtained from the laboratory analysis of soil and plant samples. The results are presented in the form of tables, graphs, and statistical tests have been used to illustrate the relationships between the different variables. Also, it discusses the findings of the study and interpretation of results in relation to the research problem as well as existing literature.

Chapter 5 comprises of the conclusion and recommendations consisting of the summary of the whole research as well as suggestions on the remediation measures for soil contamination.

1.6 Summary

In chapter one of this study, the scope of this study was introduced, stating the problem statement and why it is necessary to evaluate heavy metal pollution in soils and plants from a mining area in the North West Province of South Africa and the aim and objectives of this research. The next chapter presents the literature relevant to this present study done by various researchers.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In order to totally appreciate the impact of this study, it is essential to understand the broader context in which it is situated. South Africa is a developing nation and mining is the chief contributor to the nation's economy. As a result, it is important to determine the impact of heavy metal pollution in soils and plants. Chapter two presents the literature review of this study, based on studies done on heavy metal pollution in soils and plants from mining environment by other researchers.

2.2 Soil pollution

Soil pollution is a direct result of man-made chemicals or modification in the original soil background. Industrial activities such as mining, agricultural chemicals or improper disposal of waste chiefly contribute to soil pollution. Concerns over soil pollution is based on health risks as a result of direct contact with the polluted soils, gases emanating from the contaminants and from secondary contamination of water supplies within and in the underlying soil (Thapa *et al*., 2012). Natural wastes such as lifeless vegetation, remains of wildlife and inedible fruits and vegetables, enhance the productivity of the soil. Nevertheless, leftovers generated from anthropogenic activities, are dominated by chemicals that are not normally found in nature and this could lead to soil pollution.

Industrial activities have enhanced the problem of soil pollution in the last century, mainly due to the expansion of mining and manufacturing industries. Many researchers have been able to address the negative impact of mining on the environment in numerous parts of the biosphere (Lee 2003; Navarro *et al*., 2004; Gomes & Favas, 2006; Sun *et al*., 2006; Moreno *et al*., 2007; Chopin & Alloway, 2007). The by-products of mining gold, platinum or coal are contaminated and are mostly discharged in ways that can be considered unsafe. For example, about 600 000 tons of uranium are confined in gold mine tailings located around the basin of Witwatersrand (Winde, 2008). Due to this, the industrial waste stays in the soil surface for many years and therefore rendering the soil useless (Ribadiya, 2015).

Several investigations have been piloted on heavy metal contamination in soils worldwide (e.g. Thorton 1980; Fuge *et al*., 1989; Merrington & Alloway 1994). The level of heavy metal pollution within the mining area differs accordingly to the geochemical individualities and the tailings mineralization. The open-pit mining activity has a great negative influence on soils and aquatic environment, generating several tons of sulphide-rich tailings (Bhattachararya *et al.*, 2006; Rodriguez *et al.*, 2009). Of concern is the effect that soil pollution has on the ecosystem (Science for Environment Policy, 2013).

While everybody is exposed to soil pollution, the degree of the impact of soil pollution in humans may vary based on age, general health status and other factors (Jagran, 2015). Chemicals in soils can also get intruded into ground water and pollute them. Njiru *et al.* (2011) stated that the ingestion of soil, either deliberately (geophagy) or accidentally (hand to mouth contact), may represent another exposure sequence. This increases the risk of tumors and several other imbedded long term health risks following chronic exposure (Njiru *et al.*, 2011). The correlation between drinking water containing high concentration of uranium, radium and the associated radionuclides, and the possibility of leukemia and tumors of the bone and other sites, have been theorized, even though the result is indecisive (Canu *et al.*, 2011). Furthermore, there is proof that uranium damages the endocrine glands, elevating the risk of reproductive cancers (Raymond-Whish *et al.*, 2007). Other forms of uranium are radium-226 and radon. When ingested, radium-226 end up in the bone while radon-222 finds its way into the lungs upon inhalation. The International Agency for Research on Cancer (IARC) Monographs pointed out that there is enough proof that radium-226 can lead to bone sarcomas (a harmful growth in the bone) and carcinomas (malignant tumor originating from epithelial tissue) of the paranasal sinuses and mastoid process, and that radon-222 results in lung cancer (Raymond-Whish *et al.*, 2007).

Heavy metals originating from mining activities generate a lot of interests due to several reasons. Primarily, heavy metals have the ability to stay in sediments and soils and they are not degradable. Secondly, they prevail in residues and soils from both natural and anthropogenic sources with sequence including inheritance from source rocks, use of water as well as native and long-range atmospheric and fluvial deposition of emissions from dust and mining (Getaneh & Alemayehu, 2006). Heavy metals can find their way into the nutrition chain through uptake by vegetation and wildlife (Aslibekian & Moles, 2003; Grzebisz *et al.*, 2002; Patel *et al.*, 2005). Conclusively, ecosystem contamination by heavy metals is of principal worry in the mining environment due to their poisonousness, perseverance and gathering in food chains (Donkor *et* *al*., 2005). It is therefore significant to categorize the origin of heavy metals, in addition to determining the concentrations and spatial variability in the soils.

2.3 Origin of heavy metals in the soil

Soil pollution resulting from heavy metals is a noteworthy ecological problem worldwide (Alloway, 1995). Of note of concern in several developing nations is the heavy metal pollution of top soils as a result of heavy industrialization and urbanization (Mireles *et al*., 2012; Wei & Yang, 2010; Yaylali-Abanuz, 2011). The deposition of heavy metals in top-soils is influenced by many environmental indices which include source material, soil properties and human activities which include mining, farming, industrial production and traffic. In comparison with other soil contaminants, heavy metals are more significant due to their accumulative hazardous consequence in topsoil and biomass and they are not depleted by ordinary degradation (Alloway, 1995).

Heavy metals can be classed into two: - essential and non-essential. The vital heavy metals exert biological and physical roles in plants and animals. Essential heavy metals are an important component of several enzymes and play central roles in innumerable oxidation-reduction reactions. Examples are copper and chromium but at high concentration, they become toxic. Other heavy metals like aluminum, cadmium, arsenic, lead, mercury etc. have no recognized biological functions and are considered as non-essential metals.

Natural background and human contributions are the major representatives upsetting the content of heavy metals in soils (Zhang, 2006). Natural background is the representative obtained from parental material while human additions stem from extensive human activities. Several investigations have revealed that natural background levels of many heavy metals (e.g. mercury (Hg), lead (Pb), and cadmium (Cd)) due to pedogenesis have been extended by anthropic additions to soils (Lu *et al*., 2012; Mico *et al*., 2006). Release from industries, automobile discharges, burning of fuels and mining have been established as the human origin of metals (Alloway, 1995; Imperato *et al*., 2003; Zhang, 2006). Furthermore, agricultural activities have the tendency of elevating the rate of accumulation of heavy metals in soils (Jaradat *et al*., 2010; Mico *et al*., 2006). Notwithstanding the source of heavy metal in soil, accumulations of heavy metals have the potential to lower soil quality, diminish crop yields and the quality of agricultural products, thereby negatively affecting the health of humans, animals and the ecosystem (Nagajyoti *et al*., 2010).

An increment in heavy metal level can absolutely influence people's health via diet intake, direct consumption and skin contact, predominantly for teenagers and elders. Chabukdhara & Nema (2012); Lai *et al.* (2010) reported that the concentration of Pb of >200 mg/kg in soils may up the likelihood of cerebral incapacity among young ones. Kabata-Pendias & Pendias, (2001) found that Cd, levels of ≥3 mg/kg, will have harmful impact in agricultural topsoils. At present, soil contamination is a significant problem in many countries, and this has increased the devotion of governments and people. Crop plantations within a close proximity of a mine might also be a problem. Several plants can germinate on fairly contaminated sites but yields will be lesser than it would have been in healthy growing environments (Jung, 1996). Furthermore, crops have the ability to amass metals in the aerial organs of the plant, potentially preceding human ingestion via fruits and vegetables (Wuana, 2011). Frequent ingestion may probably lead to health problems resulting from the long-term exposure. Tobacco planted on polluted soil might also have significant consequence on the cigarette-smoking human population, as tobacco amasses cadmium and zinc in its leaves (Jung, 1996).

2.4 Uptake of heavy metals and health effects

Although many heavy metals play an important part as nourishments for vegetation and animal health at low concentrations, some if encountered may become harmful leading to health challenges in human at greater proportion or concentrations and in certain forms (Lottermoser, 2001; Rowe *et al.*, 2004a; Rowe *et al.*, 2004b; Crounse *et al.*, 1983). Copper (Cu) and zinc (Zn) are examples of essential metals, playing a leading role for normal body metabolism at reduced concentrations but toxic at high concentration (Thorton, 1996). An increase in the quantities of Cu and Zn in human body potentially damage vital body organs. Arsenic (As), lead (Pb) and cadmium (Cd) are widely accepted as the cause of cancer, nervous and metabolic disturbances and other diseases (Getaneh & Alemayeyu, 2006; Patel *et al.*, 2005). Arsenic is a major predominant contaminant of drinking water worldwide, and leads to tumors of the skin, lungs, bladder and kidney. Lead, another metal of important note, results in brain, liver and kidney impairment in youngsters and neural impairment in adults while long term exposure to Cd, results in kidney failure, liver, bone and blood damage (Franco – Hernandez *et al.*, 2010). A large number of investigations relating to health issues as a result of high concentrations of heavy metals has been documented and published worldwide (Ogola *et al.*, 2002; Miller *et al.*, 2004; Heyden & New, 2004; El-Moselhy & Gabal, 2004)

Contamination negatively impact soil's ability to play its major roles in the ecological unit (State of Environment Report, 2010). Soil is a living resource, but when contaminated, the soil should be regarded as functionally lifeless. Pollution resulting from heavy metals as well as biological pollutants is unfortunately irrevocable (European Commission, 2012). The European Commission defined a contaminated site as follows: a site with a known presence, as a result of anthropic undertakings, of toxics to a level that could pose a noteworthy threat to man's wellbeing or the environment, with land use a factor to be put into consideration (Commission Proposal COM, 2006). Heavy metals result in oxidative stress in plants (Goncalves, 2007). Metal stresses disturb photosynthesis, chlorophyll fluorescence and stomata resistance (Monni *et al.*, 2001). As an example, Cu slows photosynthesis and the reproduction cycle; Pb diminishes chlorophyll generation and As negate the metabolic process. Consequently, plant growth is reduced or impossible (Franco-Hernandez, 2010).

Heavy metals are strongly harmful to living organisms and are transferred in the soil-plant-animal - human cycle (Isikli, *et al.*, 2003; Isikli, *et al.*, 2006). When plants are grown in heavy metal contaminated soil, the plants uptake metals through their roots (Intawongse & Dean, 2006; Phetsombat, *et al.*, 2006). Heavy metals can also accumulate on the plants externally (Akinola & Ekiyoyo, 2006). In both contexts, they will be transferred to animals or humans if the plants are ingested (Islam *et al.*, 2006). The Science for Environment Policy (2013) reported that the ingestion of mineral As for an extended duration results in chronic As poisoning (arsenicosis). Humans are exposed to As through drinking of water containing elevated concentrations of inorganic As, and food prepared with this water or food crops irrigated with this water high in As. The British Geological Survey in 2005 found that planting of some vegetables on garden topsoil close to a mine in the county of Devon showed a significant health danger. Of note, were beetroot, celery, tomato and lettuce as these do accumulate higher levels of As (Klinck *et al.*, 2005).

Cadmium (Cd) is found in soil as a result of zinc smelting. When Cd in soil accumulated in edible plants, it enters the human food chain when the edible plant is consumed (Science for Environment Policy, 2013). Crops uptake Cd from soils and the uptake proportion can be swayed through different conditions such as soil pH, salinity, amount of humus, crop types and diversities and the existence of other elements (e.g. zinc) (United Nations Environment Programme (UNEP), 2015). Some classes of populations are exclusively defenceless to increased contact and uptake of Cd (Science for Environment Policy, 2013). Vegans or personalities who consume enormous quantities of cereals and pulses advanced exposure than the general population, as cultivated produce (particularly watered rice) result for most of the Cd intake (Silva *et al.*, 2005). Tobacco vegetation uptake Cd from soil, similar to other crops, and are a significant foundation of Cd uptake for the chain-smoker. Non-smokers may be endangered as well via inactive exposure to secondary smoke (Science for Environment Policy, 2013). Animals can also accumulate Cd at a level tolerable for their health but can have effect on humans consuming animal products. The health implications of ingesting Cd are liver and kidney damage and low bone density (Science for Environmental Policy, 2013).

Cadmium can also damage the musculoskeletal system due to truncated bone mineralisation, an extraordinary frequency of bone fractures, high osteoporosis and extreme bone ache. These are attributes of the *itai-itai* disease, experienced firstly in Japan in the 1940s amongst individuals who had ingested rice cultivated in farms watered with cadmium-contaminated water. A small calcium intake in addition to high Cd exposure resulted in kidney disease followed by bone disease (Morgan, 2013).

Intawongse *et al.* (2006), investigated the uptake of heavy metals by vegetables planted on contaminated soils and their bioavailability in human gastrointestinal tract. They investigated the effect of Cd, Cu, Mn, Pb, Zn on several vegetables grown on compost contaminated at varying concentrations and control plants of each vegetable planted on unmodified soil. The results revealed that the uptake of Cd, Cu, Mn, Pb and Zn by vegetables corresponded to growing concentrations of soil contamination. Compost to plant transfer (TF) values reduced from Mn> Zn> Cd> Pb. Furthermore, the study revealed that individual plant types prominently vary in their metal uptake.

Islam *et al.* (2006) reviewed the phytotoxic impacts and bioaccumulation of heavy metals in vegetables and other food crops and the soil heavy metal limits for possible nutritional toxicity. The study concluded that the dynamics influencing the limits of nutritional toxicity of heavy metals in the soil- crop coordination include: soil characteristics which includes soil pH, amount of organic matter, clay minerals and other soil chemical and biological properties; and crop types (cultivars) controlled by hereditary source for heavy metal mobility and gathering in plants. Islam *et al.* (2006) concluded that the relationship between soil - plant root microorganisms play a significant role in controlling heavy metal uptake from soil to the eatable portions of the plants.

Sen *et al.* (2007) undertook the foremost investigation on the impacts of Cd on the growth and hatching of eggs of *Loligo vulgaris*. The eggs were exposed to varying concentration of Cd ranging from 10 to 100 000 µg of Cd/I for a period of a month. Overall producing rates were then calculated to be 98.2 ± 1.6 % for the control group, 99.4 ± 0.6 for the 10 µg of the Cd/I group. Hatching successes were reported to be 69.5 ± 13.8 % for the control group, 84.5 ± 8.2 % for the 10 µg Cd/g group and 76.9 ± 5.9 % for the 100 µg Cd/I group. However, in the 10 000 Cd/I group, the eggs were deformed and 50-100 % of them died. In the 1000 µg Cd/I group, the eggs were deformed and 50-100 % of them eventually died. The result confirmed that Cd immensely influenced the growth, survival and hatching of *Loligo vulgaris*.

A national geochemical survey in the United Kingdom, UK, in the 1970s found elevated concentration of Cd, Pb, and Zn within the environment of a small mining town of Shipham in Somerset, UK. Houses had been built on land previously mined for zinc. Tested garden soils revealed Cd levels as high as 360 mg/kg (the median was 91 mg/kg), in comparison with the usual UK soil Cd levels of less than 1 mg/kg. This resulted in concern for local Shipham residents, and researchers undertook a series of investigation on residents and their interaction with Cd via soils (Morgan, 2013). Somewhere else in Japan, Cd concentration in soil of only 3 mg/kg had been found to affect the development of the musculoskeletal system in new-born babies, and osteoporosis in adult women.

Mercury (Hg) is found in soils around a gold mining environment. Mercury is a very long-lasting poisonous metal. In the metallic form, it can persist in soil for many decades, while minute quantity will be methylated by bacterial and end up in the food chain in the organic form or even as inorganic Hg^{2+} salts. Humans are exposed when Hg contaminated soil is consumed or ingested especially by children (World Health Organisation, WHO, 2013). This metal can also gather in the food chain and so can be concentrated in higher organisms, especially in fish which serves as food for humans (Breward, 1996). Ingestion of Hg can damage the central nervous system (CNS) and accelerate gastric system damage. It has effect on brain development causing in a lower intelligence quotient, IQ. Mercury ingestion also affects organization, vision, and the sense of touch in addition to impairing the liver, heart and kidney (World Health Organisation, WHO, 2016). Rice planted in a coal mining environment or smelting have been established to be affected recently.

Zhang *et al.* (2010) investigated dietary Hg contamination in rural, inland China - a region where a small number of people consume fish. Their study was concentrated on Guizhou province because the province has 12 large Hg-mining and smelting operations in addition to some other substantial coal-powered production. The researchers studied Hg levels in meals consumed by locals from different environments: a village situated inside a nature preserve, another location downwind of a major coal plant, people residing close to a defunct zinc smelter and a community whose air was polluted by mercury-mining operations. The Hg exposures for these societies differs extensively, however, rice accounted for 94-96 % of the probable daily intake of methyl-mercury in all the locals. Uniquely, rice paddies in the study area had same species of bacteria that is able to transform mineral Hg to a further poisonous methylated form. Therefore, the level of impurity of rice planted in another place, or exported, need further study.

Research done by Bellanger *et al.* (2013) projected that millions of youngsters in the EU are born with methyl-mercury exposures exceeding the harmless threshold of 0.58 µg/g, and an additional 200 000 group had levels beyond the WHO acceptable level of 2.5 µg/g. Conversely, not every child in Europe is equally at risk. A country by country analysis revealed that Portuguese and Spanish babies were mostly exposed to methyl-mercury, and those from Hungary had the minimum. Limiting Hg pollution and reducing prenatal exposure to methyl-mercury could save the EU billions of Euros per year, as suggested by the study. This is equal to averting exposure which causes loss of 600,000 IQ points yearly. The survey concluded that the intake of seafood is the chief origin of exposure of Hg contamination.

Epidemiological studies revealed that exposure to Pb during the initial stages of children's growth correlates with reduction in level of intelligence (Tong, 2010). Many investigations showed that for every 10 µg/dl (microgram per decilitre) of blood Pb there is a drop of 1-3 points of the IQ (Canfield *et al.*, 2003; Chen *et al.*, 2005; Morgan, 2013). Little drops of IQ level in many beings could result to weight problem to humanity, with low general knowledgeable ability and eventually monetary loss. Leaded fuel and mining undertakings are frequent causes for high Pb concentrations in soils. The implications of human exposure to Pb are not limited to the following: damage to the nervous system, reduced IQ and devotion, hand-eye coordination impairment, encephalopathy, bone weakening, high blood pressure, kidney disease (Brevik & Burgess, 2013).

A European site where most of the world's peak absorptions of arsenic (As) recorded in soil is found in the UK, and it is a direct consequence of quarrying. In Cornwall, UK, Phillip *et al.* (1984) revealed indication of a group of menacing melanomas (skin cancers) in communities with As concentrations as high as 30 mg/kg of soil. A direct link was also established between the concentration of As in garden soil and in house dirt. The investigation pointed out that the likelihood of increased high occurrence of malignant melanoma within the environment is connected to high level of As in soil, therefore confirming an earlier opinion of some epidemiologists studying melanoma patterns across the UK (Clough, 1980). The region has had more than two centuries of mining record, and this, joined with natural causes, has led to 722 km^2 of land with As concentration exceeding 110 μg/g of soil. This doubles the peak concentration expected in natural soil.

An investigation published in 1985 revealed that As concentrations of As in garden soils in Cornwall, UK, were extraordinary, and also differed extensively (144-892 μg/g). However, the concentration of As in salads and vegetables from those gardens barely exceed the normal acceptable concentration, and were not above the UK limit of 1 mg/kg fresh weight (Xu & Thornton, 1985). Hu *et al.* (2013) stated that it is of high importance to evaluate the extent of heavy metals in the topsoils, which assist as a significant link in understanding the total position of heavy metal pollution and the amalgamated environmental risk. The outcomes will be supportive in environmental management, most especially in regions experiencing rapid industrial revolution (Hu *et al.*, 2013).

2.5 Spatial variability of heavy metal contamination in soils

The familiarity of the regional variability, the background concentrations, and the human versus natural origin for possibly toxic substances in soils is of serious significance to evaluate anthropological impacts in order to have guiding values and quality standards (Facchinelli *et al.*, 2001). It is imperative to know the normal geographic level of heavy metals to find out their extensive range, to delineate their natural or anthropogenic origin and to determine the possible non-point sources of pollution.

There are a series of multivariate statistical approaches to assist in assessing soil contamination on a provincial scale. This approach includes the combination of Principal Component Analysis (PCA) and Cluster Analysis (CA) as a numerical tool. Geostatistics are used to create regional distribution maps which will be compared with geographical, geological and land use regional databases using Geographical Information System (GIS) software.

The PCA and its other derivative methods have also been extensively utilized in geochemical applications to specifically determine the sources of contamination as well as to delineate natural versus anthropic contribution. Application of these approaches to sediments (Binning

& Baird, 2001; Loska *et al*., 2003; Yang *et al*., 2013), and soils (Gao, 2006; Gergen, 2012; Wu, 2014) have been reported. The CA is most times integrated with PCA to authenticate results and group separate measures and variables. Cases of applications to sediments (Huang *et al*., 2012; Kalogeropoulos *et al*., 1994) are common.

The GIS software is gradually utilized in studying the extensiveness of environmental contamination due to its ability to establish nonpoint source (NPS) contaminants (Corwin and Wagenet, 1996). Further applications to metropolitan contamination control (Fistikoglu *et al*., 2002; Manta *et al*., 2002), GIS was precisely used in soil contamination investigations (Hamlett *et al*., 1992).

In soil contamination studies, the soil heavy metal content is usually a skewed normal distribution and is spatially autocorrected (Kishne *et al*., 2003; Hu *et al*., 2013). With consideration to the monetary value of selection and analysis of soil, dense and repeated sampling is most times not possible. Mapping the spatial distribution of soil contamination needs spatial interpolation methods. As a result, interpolation methods such as Inverse Distance Weighing (IDW), kriging and spline have been widely utilized in mapping and investigating soil contamination (Imperato *et al*., 2003; Mc Grath *et al*., 2004; Amini *et al*., 2005; Lee *et al*., 2006). Interpolation precision is connected to the exact classification of the contaminated area and its boundaries. This impacts directly the accuracy of contamination assessment. Numerous studies have used spatial interpolation approaches, but the outcomes have not been specific enough (Shi *et al*., 2009). Some researchers concluded that kriging method outperformed IDW (Panagopoulos *et al*., 2006; Yasrebi *et al*., 2009). However, some reported that the kriging method was not better than the other different methods (Gotway *et al*., 1996).

For evaluation of human and ecological risk, a growing body of evidence has vindicated the importance of determining the spatial variability of soil contaminants. Such spatial data assist scientists to accurately define areas with high risk and therefore aid decision-makers in locating areas where remediation efforts should be concentrated.

Dependent on the range and quantity of soil contamination, soil can be remedied by the following methods; 1) removing the soils for treatment and discarding, 2) preventing the spread of contaminates by introducing large plastic materials over the affected site, 3) remediating the soils with some harmless chemicals in order to inactivate the contaminants. Several studies have been done on soil contamination from a mining location remediation point of view (Charbonnier, 2001; Waggit, 2008; Pachon 2012).

Several investigations of heavy metal in soils have been done in advanced countries but insufficient studies were directed on the spatial variability of heavy metals in emerging countries (Imperato *et al*., 2003). Therefore, understanding the source and spatial variability of heavy metals in soil is relevant since it can serve as a background for assessing the quality of the environment and economic structure regulation.

2.6 Summary

This chapter has shown that a lot of work has been done extensively on heavy metal pollution in soils and plants from mining areas. The environmental degradation caused by mining plus health effects of consuming heavy metals either by consumption of soils or by consumptions of plants cultivated on heavy metal polluted soils or consumption of animals that once grazed on polluted plants in the environment of a mining site were discussed. Communities are exposed to health risks due to consumption of soils and plants found and planted in the environment of a mining area.

Having discussed the literature review. the next chapter will focus on the research methodology used in this study.

CHAPTER THREE

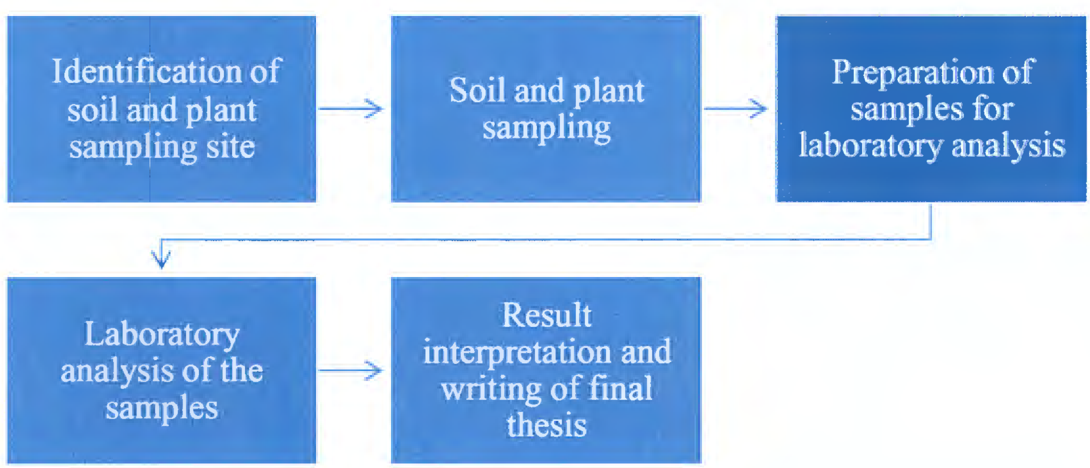
METHODOLOGY

3.0 Introduction

In the previous chapter, the literature review of studies done related to this study was elaborated. Having discussed soil pollution, sources of heavy metals in soil and the uptake of heavy metals by vegetation as well as the spatial variability of heavy metals in soils, this chapter will discuss the methods used in this study to achieve the set objectives of this research.

3.1 Research design

This study followed an experimental quantitative design which included heavy metal laboratory experiments and statistical analysis. The research design or process is shown in Figure 2:



3.2 Identification of soil and plant sampling sites

Spatial patterns of various climatic factors were taken into account to determine possible contamination areas as well as the extent of heavy metal contamination. The spatial factors which were taken into account during sampling include: rainfall, soils and geology of the area. The sampling sites were systematically distributed. Soil and plant samples were taken out at a distance of about 1 km around the mining area in each direction and the average distance between samples would be approximately 500 m.

The most fundamental factor to consider when selecting sample spots are (1) even spread of sample locations to provide a standard geostatistical fit, (2) diverse but representative land uses of the region, (3) collection from topographically flat areas to avoid morphological situations where intense runoff or collection of rain water could occur. (4) reduction of human input by avoiding of sites close to roads. houses.

Considering the large scale variability relating with both the parent rocks and the non-point source contamination. it was appraised that even a rather limited data set (32 samples for 4-6 metals) could be large enough to represent the study area and to allow for preliminary statistical and geostatistical evaluation.

3.3.1 Soil sampling

Branquiho *et al.* (2008) stated that the spatial dust impact seems to be local and ranges from 250 m to 1000 m. Soil samples were collected south, south-east, south- west, north, north-east, north-west, east and west around the mining site. Therefore, the samples were collected in each direction at 500 m and at 1000 m from the mining area and depending on the accessibility, less than 500 m from the mining area. At the two distances, two samples were collected at the depth of 0-10 m and the other at 10-20 cm. These depths were used in previous studies (Al-Khashman & Shawabkeh, 2006; Olowoyo *et al.*, 2013) and may indicate the difference in soil pollution at different depths. Studies have shown that heavy metals mainly stay at the topmost layer of the soil, 0-10 cm, therefore, if soil samples were collected from 0-20 cm as done by some researchers, the concentration of the heavy metals would be diluted by the lower concentration of the deeper soil layer. A control sample (background sample) was taken north, south, west and east approximately 50-100 km from the study area, where there are no human activities. at 0-10 cm and the other at 10-20 cm. Typically, this is done to avoid having a biased control sample. The study area and the control site have the same climatic conditions and soil type. At respective sample locations, 2-3 duplicate samples were collected. Approximately, ≥ 1 kg of soil were collected from each layer at each sampling point.

3.3.2. Plant sampling

Plant samples were collected at exactly the spots of soil sampling. This was done because plants depend on the physical and chemical properties of the soil and are affected by these parameters. One plant species was collected for study, focusing on the roots, stems, leaves and seeds of the plant. Plant samples was washed with tap water, quickly rinsed with 0.1 mol L^{-1}. HCl and rinsed with deionized water. This was done to remove all the soil particles on the plant because soil particles can influence the result of the heavy metal concentration in the plant. Samples were then dried at 70°C for 3 days; this was done in agreement with the method of Ma *et al.* (2001). Every plant materials were grounded in a mill preceding laboratory examination and determination of metal concentration.

3.4 Determination of heavy metals

Analysis of the following heavy metals, cadmium (Cd), lead (Pb), zinc (Zn), and mercury (Hg), was done for both plant and soil samples because they pose a serious health challenge to humans, animals and plants, and they are associated with gold mining and processing. These metals are on the list of top most dangerous metals to human health. Preceding this, 0.5 g of every sample was digested with 0.6 ml H_2SO_4, 0.6 ml concentrated HNO_3 and 1.8 ml concentrated HCL for 2 hours at 95 °C. After cooling, the samples were diluted to 10 ml with deionized water; and the metal in the solution were then determined using an inductively coupled plasma/ mass spectrometer (ICP/MS).

3.4.1. Determination of heavy metals uptake by plants

Concentration factor (CF) was used to establish the association between the uptakes of metals from soil by plants. This is a token for soil-plant transfer that supports the understanding of plant uptake signature (Olowoyo *et al.*, 2013). It is the ratio of the metal concentration in the plant (M_{plant}) to the total metal concentration in the soil (M_{soil}). Ratios above 1 indicate that plants are enriched in elements (accumulator), ratios around and below 1, indicate that plants are not influenced by elements from uptake (excluder).

$$CF = \frac{M_{plant}}{M_{soil}}$$

Where CF is the concentration factor, M_{plant} is the metal concentration in the plant and M_{soil} is the metal concentration in the soil.

3.5 Spatial variability of heavy metal contamination using Geographical Information System

The concentrations of heavy metal in the soil were utilized as the input data for a grid based map to show the spatial variability of metals in the study area. The Global Positioning System.

GPS, was used to define the specific locations of all the sampling location. The GPS coordinates were then imported into ArcMap 10.3.1 software program, where a heavy metal pollution map was created. Each heavy metal variability map was created showing the concentration of the heavy metals at each location the sampling was done. Each heavy metal has two spatial maps indicating the two depths used in the study (0-10 cm and 10-20 cm) and their concentration at each depth.

3.6 Health risks associated with heavy metal contamination

The health risk assessment of this study was done using the risk quotient, which is the ratio of exposure and effect. It is useful in assessing whether the pollutant concentrations exceed threshold levels. In the circles of risk characterization and assessment, this is termed a tier 1 risk assessment approach. Determination of the risk quotients for all the pollutants under study was done using the following equation;

$$\text{Risk quotient} = \frac{\text{Concentration of pollutant}}{\text{regulatory limit for pollutants}}$$

Whereby if the risk quotient is less than 1, it means there is no alarming risk but if it is equal to or exceeds 1, it means there is a significant health risk.

3.7 Data analysis

Data produced from laboratory were subjected to both basic descriptive and detailed statistical analysis. A statistical analysis was performed using the results obtained from the laboratory analysis. The means and standard deviations were calculated and tabulated using SPSS software. The SPSS software was also used to perform *Chi*-square and one-way ANOVA. The *Chi*-square test was used to establish the deviation of heavy metal pollutants' concentration from the background sample concentration, while the One-way ANOVA was used to evaluate the significance of the difference in the concentration of the pollutants with respect to the different sampling points.

Kriging was used for the interpolation of concentration of heavy metals. The variogram was used mathematically to reveal the variance of property fluctuations over the surface based on the distance and direction separating two sampling locations. ArcMap was used to conduct the spatial analysis for the study.

Tier 1 risk assessment, RA, was used for screening process. The purpose of the Tier 1 RA was to ascertain two main points: 1) whether there was a complete path between the contaminant of concern and potential receptor and 2) if contaminant concentrations surpassed the standard values for the applicable receptors or media of concern.

3.8 Summary

This chapter focused on the research design and methodology which the study used and followed to collect data to address the research objectives given on the first chapter of this dissertation. It discussed research methods that were used for data collection. Soil and plants samples gotten from the mining environment were then analyzed to determine the level of concentration of the heavy metals and to conclude if the heavy metal concentration observed were as a result of the mine. The analysis of the soil and plant samples is presented in the next chapter.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 Introduction

This chapter presents results and discussion of heavy metal concentrations in the soils and plants from the study area, heavy metal uptake by plants, the health quotient as well as the spatial distribution of heavy metals from soils at two depths: 0-10 cm and 10-20 cm. The heavy metal concentrations of Zn, Cd, Pd and As at 500 m and 1000 m away from the mining area are discussed and compared to determine if the soils are contaminated and how distance affects the concentrations. All metal concentrations are reported in mg/kg.

4.1 Heavy metal concentrations in soil samples

The results of the described field sampling are summarized in Tables 1 - 4. The results depict the varying concentrations of selected heavy metals at each of the respective sampling points and depths; and the maximum threshold limit for agricultural soils in South Africa. These concentrations were obtained from the analyses of the soil samples as outlined in Section 3.3.1.

Zn concentration

The result for soil sample metal analysis shows that within the ≤500 m radius of the mining location, Zn concentrations ranged from 4.545-9.204 mg/kg at the depth of 0-10 cm to 5.704 – 32.79 mg/kg at the depth of 10-20 cm. At ≤1000 m, the Zn concentrations ranged from 6.894 – 12.8 mg/kg at the depth of 0-10 cm to 6.322 – 14.7 mg/kg at the depth of 10 – 20 cm. At ≤500 m from the mines, the mean value of Zn concentration at 0-10cm depth is 7.966 mg/kg and 11.90 mg/kg at the depth of 10-20 cm and 9.49 mg/kg and 8.915 mg/kg at 0-10 cm and 10-20 cm depths respectively, at ≤1000 m away from the mines (Table 1). The general concentrations of Zn at all the sampled locations were much lower than the maximum threshold of Zn concentration in South Africa's agricultural soils (Herselman, 2007) which stands at 200 mg/kg.

Table 1: Concentration of Zn in soil samples

Zn concentration (mg/kg)										
Location	Distance from mine	≤500m		≤1000m		Control sample 1		Control sample2		South African limit in Agricultural soil
	Depth (cm)	0-10	10-20	0-10	10-20	0-10	10-20	0-10	10-20	
North		8.86	5.73	12.80	14.70	7.25	17.14	10.08	9.17	200
Northeast		7.88	32.79	8.02	10.49					
Northwest		6.99	10.21	11.92	6.64					
East		8.78	6.52	8.20	6.67					
Southeast		8.69	12.89	6.89	8.68					
West		9.20	6.74	9.10	6.32					
Southwest		8.78	5.70	NA	NA					
South		4.55	8.14	NA	NA					
Mean		7.97	11.09	9.49	8.92					
SD		1.55	9.11	2.35	3.26					
Range		4.55-9.20	5.70-32.79	6.89-12.80	6.32-14.70					

NA means no access to collect samples due to fencing

In comparison with the control sample 1 of this study, located about 10 km away from the mining location where there are no obvious human activity, Zn average concentrations are higher but lower average concentrations are reported at a depth of 10-20 cm than the control sample 1 within 500 m of the mining area. At ≤1000 m away from the mining area, a Zn average concentration of 9.49 mg/kg is higher than control sample 1 but lower than the control sample 2 at a depth of 0-10 cm. At 10-20 cm depth, a Zn mean concentration of 8.915 mg/kg is lower than the control sample 1 and control sample 2, 17.14 mg/kg and 9.169 mg/kg, respectively.

Furthermore, the results on depth analysis basis show that the average concentration of Zn within the ≤500 m radius of the mines are lower at 0-10 cm than at 10-20 cm. This conforms to the report of Ekwue *et al.* (2011) which reported that the mean concentration of Zn at a primary gold mine in Ilesha, Nigeria, was higher at a depth of 15-20 cm than at 0-15 cm, a result attributed to the leaching effect at close proximity to the mining area. Within ≤1000 m radius of the mining site, the average concentrations of Zn are higher at 0-10 cm than at 10-20 cm. This is similar to the work by Raulinaitis *et al.* (2012) which reported higher concentration of Zn at the top soil, 36.77 mg/kg than at the subsurface soil, 18.31 mg/kg.

Overall, the concentrations of Zn are within the stipulated limits of Zn in the South African agricultural soil and also lower than the maximum limit of countries like Austria (111 mg/kg), China (74.2 mg/kg), Germany (225 mg/kg) and USA (60 mg/kg) (Wu *et al.*, 2014).

Cd concentrations

The Cd concentrations from the soil analysis indicate that within the 500 m radius of the mining area, Cd ranged from 0.008 to 0.023 mg/kg at the depth of 0-10 cm and 0.010 to 0.395 mg/kg at the depth of 10-20 cm. At approximately 1000m from the mining area, Cd ranged from 0.011 to 0.031 mg/kg at the depth of 0-10 cm and 0.014-0.039 mg/kg at the depth of 10-20 cm.

Within the 500 m radius of the mines, the average of the Cd concentrations at the topsoil (0-10 cm) are lower than at subsurface (10-20 cm) soil. This is also similar at 1000 m from the mines where the mean concentrations of Cd at the topsoil are 0.021 mg/kg and 0.022 mg/kg at the subsurface soil. The mean concentration of Cd at both locations (500 m and 1000 m from the mines) indicate that the soil is not contaminated because it is less than the South Africa maximum threshold of Cd in agricultural soil which is 3.00 mg/kg.

When Cd concentration is compared with the control sample 1 and control sample 2, the mean concentration of Cd at 0-10 cm depth, 0.015 mg/kg, is less than the control sample 2 but slightly more than the control sample 1. At 10-20 cm, the mean concentrations of Cd are higher than both the control sample 1 and 2 within the 500m radius of the mine. At 1000 m away from the mines, the Cd concentrations at 0-10 cm, 0.021 mg/kg, are less than the control sample 2, 0.025 mg/kg but more than the control sample 1, 0.014 mg/kg while at 10-20 cm, and the average of Cd is 0.022 mg/kg, lower than the control sample 1, 0.024 mg/kg and the control sample 2, 0.039 mg/kg. The result based on depth indicates that the Cd average concentrations at depth of 0-10 cm are more than those at 10-20 cm depth at both the distances from the mining area. This conforms to the reports of Ekwue *et al.* (2011) and Ranlinaitis *et al.* (2012) which also reported increase in the Cd concentration with increase in depth.

Table 2: Concentrations of Cd in soil samples

Cd concentration (mg/kg)										
Location	Distance from mine	≤500m		≤1000m		Control sample 1		Control sample2		South African limit in Agricultural soil
	Depth (cm)	0-10	10-20	0-10	10-20	0-10	10-20	0-10	10-20	
North		0.014	0.016	0.028	0.039					
Northeast		0.019	0.396	0.020	0.027					
Northwest		0.023	0.026	0.031	0.017					
East		0.013	0.011	0.019	0.014					
Southeast		0.020	0.034	0.011	0.017					
West		0.012	0.023	0.015	0.019	0.014	0.039	0.025	0.024	3.00
Southwest		0.008	0.010	NA	NA					
South		0.011	0.024	NA	NA					
Mean		0.015	0.068	0.021	0.022					
SD		0.005	0.133	0.008	0.01					
Range		0.008-0.023	0.010-0.395	0.011-0.031	0.014-0.039					

NA means no assess to take samples due to fencing

In comparison with reported Cd concentrations in other countries, the studied area reported lower Cd concentration than the mean concentrations reported in China (0.1 mg/kg), Japan (0.41 mg/kg), and UK (0.62 mg/kg) (Wu *et al.*, 2014).

Pb concentrations

The Pb concentrations from the soil analysis indicates that within the ≤500 m radius of the mining area, Pb ranged from 2.971 mg/kg to 3.855 mg/kg at the depth of 0-10 cm and 0.334 mg/kg to 5.077 mg/kg at the depth of 10-20 cm. At ≤1000 m from the mining area, the Pb concentration ranged from 3.191 mg/kg to 5.077 mg/kg at the depth of 0-10 cm and 3.155-4.987 mg/kg at the depth of 10-20 cm.

Within the 500 m radius of the mines, the average Pb concentrations at the topsoil (0-10 cm) are lower than at subsurface (10-20 cm) soil level. This is different at ≤1000 m from the mines where the mean concentration of Pb at the topsoil is 4.249 mg/kg and 3.958 mg/kg at the subsurface soil (Table 3). The mean concentration of Pb at both locations (≤500 m and ≤1000 m from the mines) indicate that the soil is not contaminated because it is less than the South Africa maximum threshold of Pb in agricultural soil, which is 100 mg/kg.

Table 3: Concentration of Pb in soil samples

Pb concentration (mg/kg)										
Location	Distance from mine	≤500m		≤1000m		Control sample 1		Control sample2		South African limit in Agricultural soil
	Depth (cm)	0-10	10-20	0-10	10-20	0-10	10-20	0-10	10-20	
North		3.501	3.871	4.448	4.987	0.058	0.742	0.138	1.080	100
Northeast		3.277	0.334	3.191	4.417					
Northwest		3.808	4.946	5.787	3.167					
East		3.145	2.612	4.213	3.445					
Southeast		3.796	5.077	4.493	3.155					
West		3.855	2.613	3.36	4.574					
Southwest		3.332	4.876	NA	NA					
South		2.971	4.68	NA	NA					
Mean		3.461	3.626	4.249	3.958					
SD		0.334	1.668	0.935	0.798					
Range		2.971 - 3.855	0.334 - 5.077	3.191 - 5.787	3.155-4.987					

NA means no assess to take samples

The mean concentrations of Pb at both distances and depth are more than the Pb concentration at the control sample 1 and control sample 2. This indicated that the concentration of Pb is high due to other factors like the mining activity or as a result of the farming activities at the proximity of the location of the mines (Statistics Canada, 2010).

The result based on depth indicates that Pb average concentrations at depth of 0-10 cm are less than at 10-20 cm depth within the ≤500 m radius of the mines but at ≤1000 m radius, the average concentration of Pb at 0-10 cm are more than at 10-20 cm. This suggests atmospheric deposition from vehicular activity (Zhang *et al.*, 2012) as majority of these locations are close to roads connecting different farms.

In comparison with reported Pb concentration in other countries, the studied area reported lower Pb concentration than the mean concentration reported in China (26 mg/kg), Japan (20.4 mg/kg), and UK (29.2 mg/kg) at every sampled location (Wu *et al.*, 2014).

As Concentrations

The As concentrations from the soil analysis indicate that within the ≤500 m radius of the mining area, As concentration ranged from 0.656 to 0.993 mg/kg at the depth of 0-10 cm and 0.153 to 3.663 mg/kg at the depth of 10-20 cm. At approximately 1000 m from the mining area, As concentration ranged from 0.642 to 1.303 mg/kg at the depth of 0-10 cm and 0.644-3.548 mg/kg at the depth of 10-20 cm (Table 4).

Within the ≤500 m radius of the mines, the average of As concentrations at the topsoil (0-10 cm) are lower than at subsurface (10-20 cm) soil. The same trend is noticed at ≤1000 m from the mines where the mean concentrations of As at the topsoil are 0.995 mg/kg and 1.338 mg/kg at the subsurface soil. This is similar to the research of Wahl (2014) which reported similar trend in heavy metal concentration in soils within the proximity of a gold mine in KwaZulu-Natal, South Africa. The mean concentrations of As at both locations (≤500 m and ≤1000 m from the mines) indicate that the soil in the sampled area is not contaminated because it is less than South Africa maximum threshold of As in all land- uses protective of the water resources (DEA, 2013) which is 5.8 mg/kg.

In comparison with the control sample 1 and 2, the mean concentrations of As at 0-10 cm within the ≤500 m radius of the sampled area is higher than of control sample 1 but lower than As concentration of control sample 2 at same depth. At 10-20 cm, the mean concentrations are lower than both the control sample 1 and control sample 2 at same depth. At ≤1000 m radius of the mines, As concentrations averaged 0.995 mg/kg at the topsoil, higher than the control sample 1 at the topsoil but lower than control sample 2 at the topsoil. Within 10-20 cm depth of the soil, the mean concentrations of As at the sampled location is lower than the control sample 1 and control sample 2 at both depth.

Table 4: Concentration of As in soil samples

As concentration (mg/kg)										
Location	Distance from mine	≤500m		≤1000m		Control sample 1		Control sample 2		South Africa Soil Screening Value
	Depth (cm)	0-10	10-20	0-10	10-20	0-10	10-20	0-10	10-20	
North		0.899	1.092	1.303	3.548					
Northeast		0.794	0.153	1.045	1.373					
Northwest		0.656	1.35	1.159	0.6437					
East		0.993	1.082	1.148	0.7295					
Southeast		0.800	3.663	0.6774	0.7149					
West		0.794	1.009	0.6415	1.016	0.742	2.029	1.084	1.448	5.8
Southwest		0.739	0.723	NA	NA					
South		0.788	1.081	NA	NA					
Mean		0.808	1.269	0.995	1.338					
SD		0.101	1.032	0.273	1.116					
Range		0.656-0.993	0.153-3.663	0.642-1.303	0.644-3.548					

NA means no assess to take samples

The result based on depth indicates that the As average concentrations at depth of 0-10 cm are more than at 10-20 cm depth at both distances from the mining area. The higher concentration noted at the top soil suggests atmospheric deposition (Ogundele *et al.*, 2015). This is similar to the report of Ekwue *et al.* (2011) which stated increase in As concentration with increase in depth at the environment of a secondary gold mine in Ilesha, Nigeria.

In comparison with reported As concentrations in other countries, the studied area reported lower As concentrations than the mean concentrations reported in Germany, 50 mg/kg (Lee *et al.*, 2011), Australia, 20 mg/kg, (EPA, Australia), China, 30 mg/kg, (EPA, China), (32 mg/kg) and Canada, 20 mg/kg, (Canada Ministry of Environment) at every sampled location.

In general, the overall soil concentrations of the studied heavy metals are within the threshold when compared to the control samples and also to other country's concentration. It suggests that the mining activity has not yet affected the concentration of the soil because the concentration of the control sample, $\geq$ 10 km from the mining site in an area presumed to be devoid of physical human activity, has similar soil concentration as that obtained around the mine.

4.2. Heavy metal concentrations in plant samples

Plants were collected and selected from the same genus and the metal immobilization capabilities are dependent on the availability of the metal concentrations present in the soil because it is responsible for the explanation of growth and differences between the metal concentrations (Saxena & Misra, 2010). Thus, the plant species studied, *Eragrostis hypnoides*, was analyzed to determine the metal contents and the results are presented in Tables 5 to 8. Plant samples of the same genus were collected from the exact locations where soil samples were collected to limit bias. Thus, this has limited the number of plant samples collected to four, two plant samples collected from the north and eastern direction within $\leq$500 m and the other two plant samples collected from the north and eastern direction within $\leq$1000 m of the mining location.

The trend of heavy metal concentrations in plants are Zn > Pb > As > Cd, and this is similar to the trend reported by Abdul-Wahab & Marikar, (2011); Ekwue *et al.* (2011); and Olowoyo *et al.* (2013). The concentration of metals in plants often serve to indicate the metal contamination status of the site, and also to reveal the abilities of various plant species to take up and accumulate the metals from the soil (Olowoyo *et al.*, 2013). A detailed discussion of the results obtained are given in the proceeding sections.

Zn concentration

The results for plant metal analysis revealed that the concentration of Zn ranged between 21.01 - 77.32 mg/kg in the root of the plant and 20.01 – 76.03 mg/kg in the leaf. The mean concentration in the leaf and the root tissue are 44.10 mg/kg and 44.98 mg/kg, respectively (Table 5). The mean concentration of Zn is higher in the root than in the leaf. In relation to the metal concentration in the soil, the concentrations of Zn in the plant are higher than the concentration of Zn in the soil where the plant sample was collected.

Table 5: Concentration of Zn in plant sample

Location	Distance (m)	Zn Concentration (mg/kg)	
		Root	Leaf
North	≤500	37.69	35.21
	≤1000	21.01	20.01
East	≤500	77.32	76.03
	≤1000	47.91	45.14
Mean		44.98	44.10
SD		23.65	23.66
Range		21.01 – 77.32	20.01 – 76.03
WHO limit		50	

WHO's recommended limit of Zn in plants is 50 mg/kg (Nazir *et al*., 2015). The concentrations of Zn at the eastern direction within ≤500 m only were above the WHO limit. At the remaining locations, the concentration of Zn were below the WHO recommended limit in both the root and leaf tissues. The concentrations of Zn were high within the ≤500 m of the eastern location because the sampling site is close to one of the mining plants and Zn has been reported to be associated with gold mining (Lecce *et al*., 2011). Zn is also easily dispersed by air (ATSDR, 2005) and so the reason for higher concentration of Zn at ≤1000 m of the eastern location.

Cd concentration

The permissible limit of Cd in plants as recommended by WHO is 0.02 mg/kg. At all the sampled locations, the concentration of Cd in the root and leaf is higher than the recommended permissible level (Table 6). It means that the plant is contaminated with Cd. The mean concentrations of Cd in the root are higher than the leaf's mean concentrations. This means that the plant does not have the potential to effectively translocate metals from the plants' root to the leaf. Bu-Olayan *et al*. (2009) reported that for a plant to be able to translocate heavy metals from the root to the leaves, it must have a translocation factor above 1 while plants with translocation factor below 1 have low tendency to transfer metal from root to the leaves thereby accumulating a large portion of the heavy metal concentration in the root.

When compared to the concentration of Cd in the soil where the plant samples were taken, the mean concentrations of Cd in the root and leaf of the plant were higher than concentration of Cd in the soil in the North within the ≤500 m radius of the mine but lower than the concentration of Cd within the ≤1000 m radius of the mine. The same trend was also recorded at the eastern direction of the mine within the ≤500 m and ≤1000 m radius of the mine. This may be due to the deposition of cadmium oxide which exist in the air as a result of mining activity due to the close proximity of the sample area to operational site of the mining location. ATSDR (2008) reported that cadmium is a widely dispersed element and dispersed into the environment through the air by melting and smelting activities as well as other man-made routes.

Table 6: Concentration of Cd in plant sample

Location		Cd Concentration (mg/kg)	
	Distance (m)	Root	Leaf
North	≤500	0.062	0.058
	≤1000	0.028	0.021
East	≤500	0.184	0.162
	≤1000	0.145	0.135
Mean		0.105	0.094
SD		0.072	0.066
Range		0.028-0.184	0.021-0.162
WHO limit		0.02	

Pb concentration

The WHO's recommended limit of Pb in plant is 2 mg/kg. The mean concentrations of Pb in the plant is higher than this permissible level due to the high concentration of Pb in soil at the North direction within the ≤1000 m radius of the mine. According to Punshon *et al.* (2017), the higher the total heavy metal concentration in soil, the higher the concentration of such heavy metal in plant. In the remaining locations, the concentrations of Pb are lower than WHO limit indicating that the plants are not contaminated. The range of concentrations of Pb in the root is 0.672 – 15.03 mg/kg and 0.512 – 14.81 mg/kg (Table 7). The mean concentrations of Pb is higher in the root than in the leaves of the plant in all the sampled locations.

Table 7: Concentration of Pb in plant sample

Location		Pb Concentration (mg/kg)	
	Distance (m)	Root	Leaf
North	≤500	0.672	0.512
	≤1000	15.03	14.81
East	≤500	0.906	0.775
	≤1000	0.734	0.621
Mean		4.336	4.180
SD		7.130	7.088
Range		0.672-15.03	0.512-14.81
WHO limit		2	

As concentration

The mean concentrations of As in the root is 0.893 mg/kg and 0.573 mg/kg in the leaf. Arsenic ranged from 0.208 mg/kg to 2.763 mg/kg in the root of the plant and 0.198 mg/kg to 1.531 mg/kg in the leaf (Table 8). The concentrations of As in plant is lower than the average concentrations of As in the soil where the plant sample was taken.

The WHO tolerance limit of As in food crops is 0.2 mg/kg (Punshon *et al.*, 2017). The concentration of As in the root of the plant is above this limit which indicate that the root of the plant is contaminated. The leaf part of the same plant, the concentration of As is also above the WHO tolerance limit (0.2 mg/kg) except for the plant sample collected from the North within the ≤500 m radius of the mine which is 0.198 mg/kg.

Table 8: Concentration of As in plant samples

Location		As Concentration (mg/kg)	
	Distance (m)	Root	Leaf
North	≤500	0.208	0.198
	≤1000	2.763	1.531
East	≤500	0.273	0.256
	≤1000	0.329	0.306
Mean		0.893	0.573
SD		1.247	0.640
Range		0.208-2.763	0.198-1.531
WHO limit		0.2	

In order to check for the dependence of the heavy metal concentration in the root and leaves of the plant, Chi-square test was used. The results are hereby displayed below for each of the heavy metal.

Table 9: Chi-square tests of As

	Value	df	Asymp. Sig. (2-sided)
Pearson Chi-Square	12.000[a]	9	.213
Likelihood Ratio	11.090	9	.270
Linear-by-Linear Association	2.997	1	.083
N of Valid Cases	4		

16 cells (100.0%) have expected count less than 5. The minimum expected count is 25.

Chi-square analysis for distribution of As in root and leaves

H0: concentration of As in the root and leaves are independent

H1: concentration of As in the root and leaves are not independent

Table 10: Chi square test of Zn

	Value	df	Asymp. Sig. (2-sided)
Pearson Chi-Square	12.000[a]	9	.213
Likelihood Ratio	11.090	9	.270
Linear-by-Linear Association	2.996	1	.083
N of Valid Cases	4		

a. 16 cells (100.0%) have expected count less than 5. The minimum expected count is 25.
Chi-square analysis for distribution of Zn in root and leaves
H0: concentration of Zn in the root and leaves are independent
H1: concentration of Zn in the root and leaves are not independent

Table 11: Chi-Square Tests of of Cd

	Value	df	Asymp. Sig. (2-sided)
Pearson Chi-Square	12.000[a]	9	.213
Likelihood Ratio	11.090	9	.270
Linear-by-Linear Association	2.987	1	.084
N of Valid Cases	4		

a. 16 cells (100.0%) have expected count less than 5. The minimum expected count is 25.
Chi-square analysis for distribution of Cd in root and leaves
H0: concentration of Cd in the root and leaves are independent
H1: concentration of Cd in the root and leaves are not independent

Table 12: Chi-square test of Pb

	Value	df	Asymp. Sig. (2-sided)
Pearson Chi-Square	12.000[a]	9	.213
Likelihood Ratio	11.090	9	.270
Linear-by-Linear Association	3.000	1	.083
N of Valid Cases	4		

a. 16 cells (100.0%) have expected count less than 5. The minimum expected count is .25.

Chi-square analysis for distribution of Pb in root and leaves

H0: concentration of Pb in the root and leaves are independent

H1: concentration of Pb in the root and leaves are not independent

From all the analysis in the above Table 9 – 12, the p-value 0.05 is less than the significance level 0.213. As a result, we can reject the null hypothesis and state that the concentration of these heavy metals (As, Zn, Cd and Pb) in the root and leaves are not independent.

In summary, from the overall result of the Chi-square test, we can see that the outcome of all the analysis are the same for all the metals. That implies that there are no other ways in which the heavy metals get into the plant except by absorption via the roots and are further translocated into the leaves, hence, the reason for the consistency observed across all the studied heavy metals.

4.3. Heavy metal uptake by plants

It is essential to acknowledge that plants have highly developed mechanisms to stimulate metal bioavailability in the rhizosphere and to improve uptake of heavy metals into the roots (Romheld & Marchner, 1986). Concentration factor is the ratio of the metal concentration in the plant (Mplant) to the total metal concentration in the soil (Msoil). Ratios greater than 1 indicate that plants are enriched in elements (accumulator), ratios around 1 indicate that plants are not influenced by elements from uptake (excluder) and ratios less than 1 show that plants exclude the elements from uptake (excluder) (Olowoyo *et al.*, 2012). The concentration factor is calculated using the equation:

$$CF = \frac{M_{plant}}{M_{soil}}$$

Where CF is the concentration factor, Mplant is the metal concentration in the plant and Msoil is the metal concentration in the soil.

Zn uptake by plant

In this study, the calculated concentration factor for Zn as observed revealed that the value of Zn in both the root and leaf is more than 1 at all the locations (Figure 2). This indicated that the plant is a good accumulator of Zn and can be used for phytoremediation of Zn contaminated soils. However, the consumption of crop with high Zn concentration is toxic to human (Su et al., 2014). This agrees with the findings by Pitchel *et al.* (1999) in which they suggested that metal uptake into roots occurs from the aqueous phase.

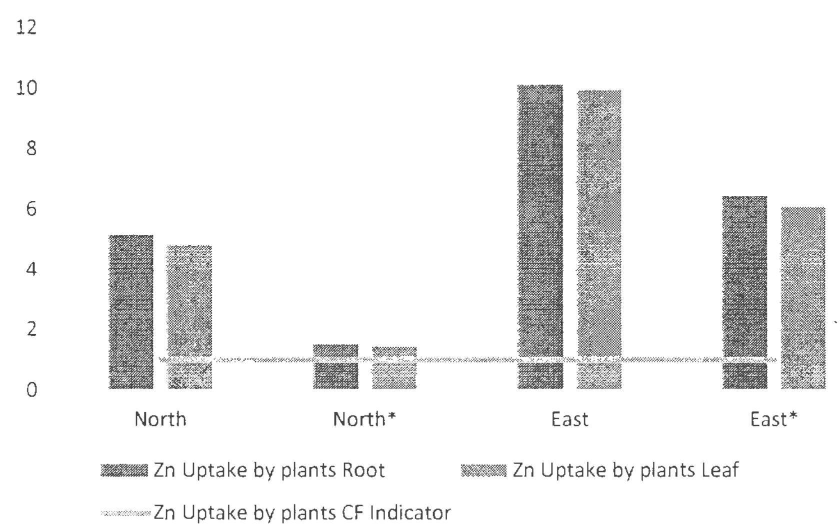


Figure 2: Zn concentration factor in plant's root and leaf

Cd uptake by plant

The result of concentration factor of Cd indicates that the roots and the leaf have a CF of > 1. The plants accumulated Cd from the soil in all the locations except at the northern direction within the ≤1000 m radius of the mine (Figure 3). The uptake of Cd is the highest in the eastern part of the mine within the ≤500 m radius of the mine. Overall, it can be suggested that the plant can be used for phyto-extraction of Cd from the soil for remediation purpose. Marques *et al.* (2009) suggested that plants with potential for phyto-extraction should among other factors be tolerant to high concentration of metal and also be able to accumulate high concentration of the metal in the harvestable parts of the plant e.g. plant portion above ground as well as roots.

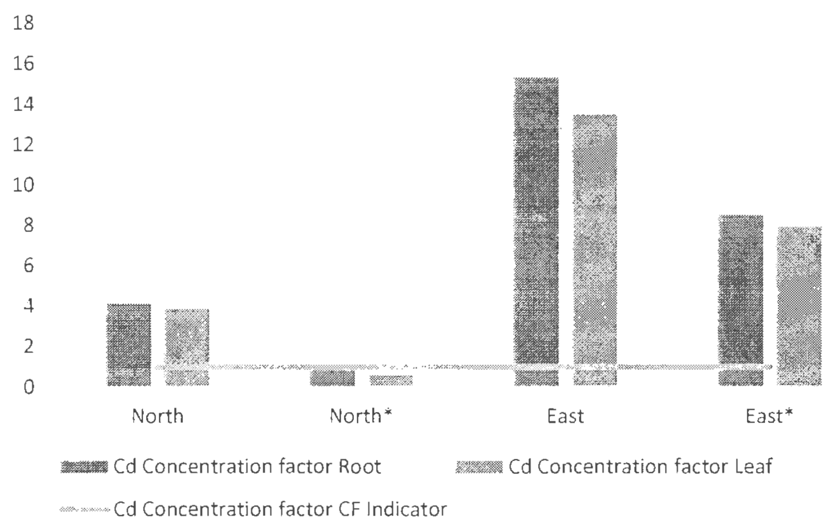


Figure 3: Cd concentration factor in plant's root and leaf

Pb uptake by plant

Plants generally have low tendency for Pb uptake (Intawongse & Dean, 2006). This can be explained by the fact that Pb binds to organic matter in soil, thereby, limiting uptake by plant (Wang *et al.*, 2004). Therefore, it is not surprising to note from the concentration factor calculation that in all the sampled area that the CF is less than 1 except in the northern direction within the ≤1000 m radius of the mine (Figure 4). This can be attributed to the high concentration of Pb in the plant and soil from this location (Table 4). It is also an indicator that this plant (*Eragrostis hypnoides)* cannot be used for phyto-extraction of Pb from the soil. This is confirmed by the research of Ana *et al.* (2009) which suggested that a plant can be used for phyto-extraction if the plant can accumulate heavy metal from the soil.

Where CF is the concentration factor. Mplant is the metal concentration in the plant and Msoil is the metal concentration in the soil.

Zn uptake by plant

In this study, the calculated concentration factor for Zn as observed revealed that the value of Zn in both the root and leaf is more than 1 at all the locations (Figure 2). This indicated that the plant is a good accumulator of Zn and can be used for phytoremediation of Zn contaminated soils. However, the consumption of crop with high Zn concentration is toxic to human (Su et al., 2014). This agrees with the findings by Pitchel *et al.* (1999) in which they suggested that metal uptake into roots occurs from the aqueous phase.

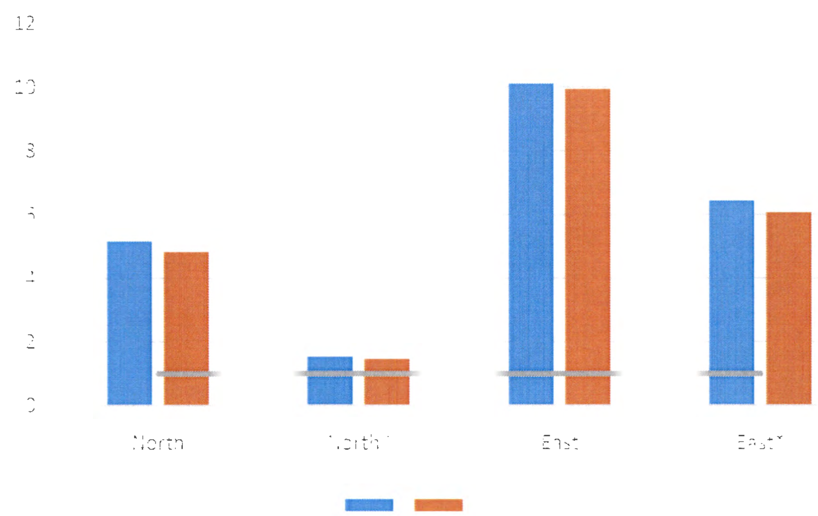


Figure 2: Zn concentration factor in plant`s root and leaf

Cd uptake by plant

The result of concentration factor of Cd indicates that the roots and the leaf have a CF of > 1. The plants accumulated Cd from the soil in all the locations except at the northern direction within the ≤1000 m radius of the mine (Figure 3). The uptake of Cd is the highest in the eastern part of the mine within the ≤500 m radius of the mine. Overall, it can be suggested that the plant can be used for phyto-extraction of Cd from the soil for remediation purpose. Marques *et al.* (2009) suggested that plants with potential for phyto-extraction should among other factors be tolerant to high concentration of metal and also be able to accumulate high concentration of the metal in the harvestable parts of the plant e.g. plant portion above ground as well as roots.

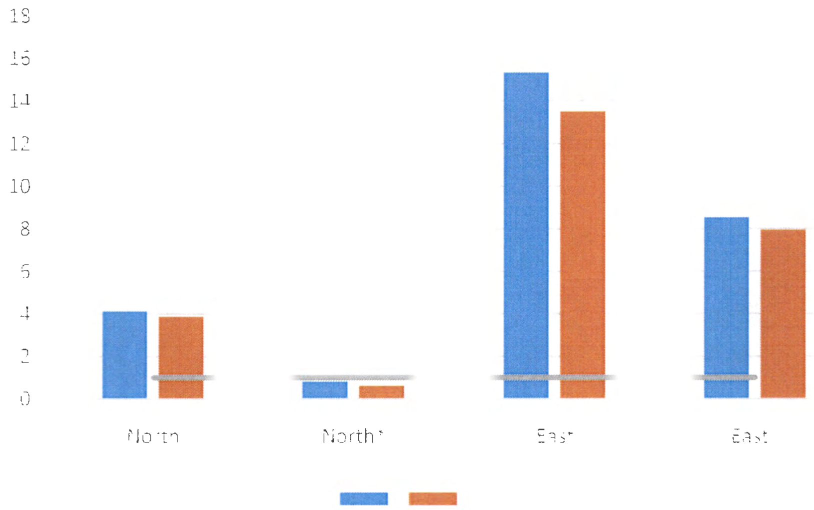


Figure 3: Cd concentration factor in plant's root and leaf

Pb uptake by plant

Plants generally have low tendency for Pb uptake (Intawongse & Dean, 2006). This can be explained by the fact that Pb binds to organic matter in soil, thereby, limiting uptake by plant (Wang *et al.*, 2004). Therefore, it is not surprising to note from the concentration factor calculation that in all the sampled area that the CF is less than 1 except in the northern direction within the ≤1000 m radius of the mine (Figure 4). This can be attributed to the high concentration of Pb in the plant and soil from this location (Table 4). It is also an indicator that this plant (*Eragrostis hypnoides*) cannot be used for phyto-extraction of Pb from the soil. This is confirmed by the research of Ana *et al.* (2009) which suggested that a plant can be used for phyto-extraction if the plant can accumulate heavy metal from the soil.

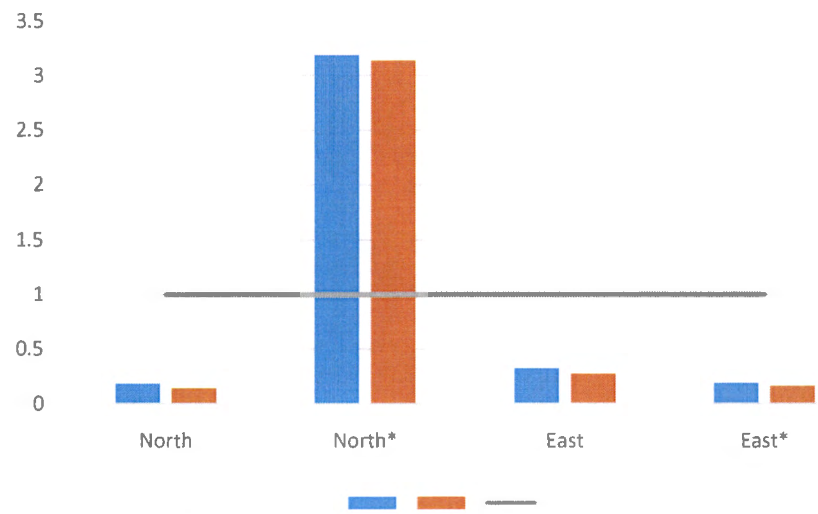


Figure 4: Pb concentration factor in plant's root and leaf

As uptake by plant

The concentration factor of As in this study is generally lower than 1 in all the sampled locations (Figure 5)

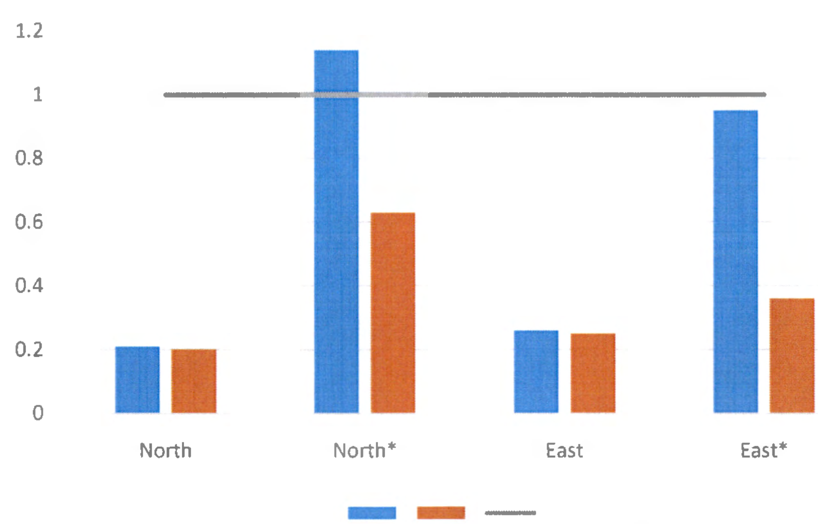


Figure 5: As concentration factor in plant's root and leaf

The only exception is found in the root of the plant at the northern direction of the mine within the ≤1000 m radius. From the concentration result of As, it can be concluded that the plant is an excluder and so cannot be used for phytoremediation of contaminated soil (Ana *et al.*, 2009).

4.4. Health risk associated with heavy metal contamination

Risk quotient is used to determine the health risk associated with heavy metal contamination. If the risk quotient is less than 1, it means there is no significant health risk but if it is equal to or exceeds 1, it means there is significant health risk. The results of the health risk associated with each heavy metal contamination are discussed in the proceeding sections.

Zn risk quotient

The highest risk quotient for Zn was recorded at the eastern part of the mine within the ≤500 m radius and the least recorded at northern part within the ≤1000 m radius of the mine. All points within the sampled area were below the maximum allowable risk quotient 1 except at the east location that is ≤500 m away from the mining site (Figure 6).

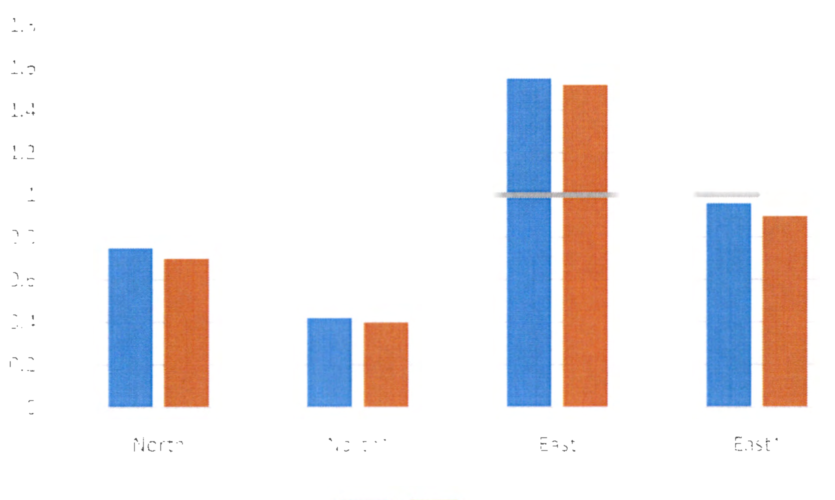


Figure 6: The Zn risk quotient

The risk quotient for element generally follows the same pattern as the concentration (Marara *et al.*, 2013). The chart indicated that the consumption of this plant does not pose any significant health risk for the primary consumer (animals, cow specifically) and secondary consumer (humans). Despite this, rearing of animals on the eastern side of the mine within ≤1000 m must be discouraged. This is because the risk quotient is close to 1 (Figure 6). Zn is an essential trace metal in the human body, but if the body takes excessive Zn from the outside environment, human health will be affected (Su *et al.*, 2014).

Cd risk quotient

The highest risk quotient for Cd was recorded at the eastern part of the mine and the least at the northern part of the mine within the ≤1000 m radius of the mine. All points within the sampled area are above the maximum allowable risk quotient 1 except the leaf of the plants located at the north of the mine within the ≤1000 m radius (Figure 7).

This confirms that consumption of these plants by animals most especially cattle poses a health risk as the Cd can be transferred to the animals and finally to human which always serve as the end consumer of such animals. Cadmium destroys the breakdown of calcium which results in calcium insufficiency and lead to cartilage disease and bone fractures, etc. (Su *et al*., 2014). The Agency for Toxic Substances Management Committee registered Cd as the sixth most toxic metal that affects man's wellbeing (Su *et al*., 2014).

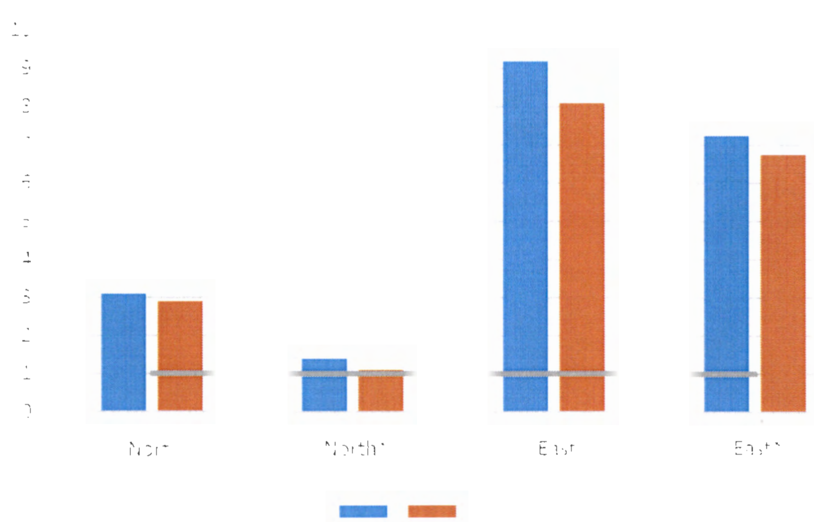


Figure 7: The Cd risk quotient

Pb risk quotient

The highest risk quotient for Pb was registered at the northern direction of the mine within the ≤1000 m radius and the lowest recorded to the eastern direction within same radius from the mine (Figure 8). The concept behind the high risk quotient recorded is a direct reflection of the high concentration of Pb recorded in the plant at this location (Table 7). All other locations sampled are below the maximum allowable risk quotient. This suggests that plants from the northern direction is contaminated with lead and so should be avoid.

This suggests that plants from the northern direction is contaminated with Pd and so could endanger the health of the end consumer. Lead enters the human body mainly through the digestive tract (through ingestion of Pb contaminated food, e.g. vegetables grown in contaminated soil or animals that fed on contaminated plants) and respiratory tract (via inhalation of Pb polluted fumes from the industries or mining area), and thereafter enters the blood flow in the form of solvable salts, protein complexes or ions, etc. Nearly 95 % of the insoluble phosphate lead accumulates in bones. Lead is strongly pro-organizational. It destroys various organs and system of human, for example kidney, liver, reproductive system, nervous system, urinary system, immune system and the basic physiological processes of cells and gene expression (Su *et al.*, 2014).

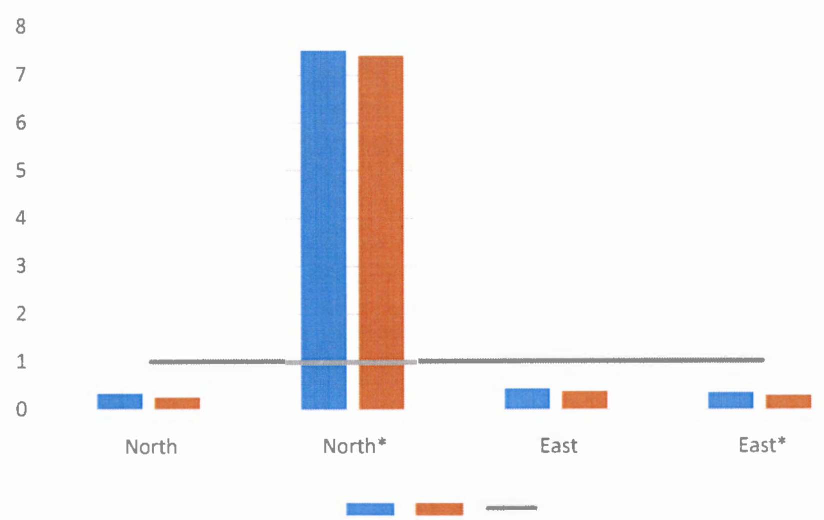


Figure 8: The Pb risk quotient

As risk quotient

All points within the sampled area were above the maximum allowable risk quotient 1. The highest risk quotient for As was recorded at the northern direction of the mine within the ≤1000 m radius of the mine. This was as high as 13.82 in the root of the plant. The lowest risk quotient for As was also recorded at the northern direction of the mine but at 500 m radius of the mine. The risk quotient stands at 1 and it is found in the leaf of the plant.

This suggests that consumption of the plant poses a significant health risk for the direct consumer (animals) and end consumer (humans). As poisoning can lead to plant death, it can also lead to human death due to various As-induced cancers: skin cancer, liver cancer, lung cancer, colorectal cancer, and uterine cancer among others (Su *et al.*, 2014).

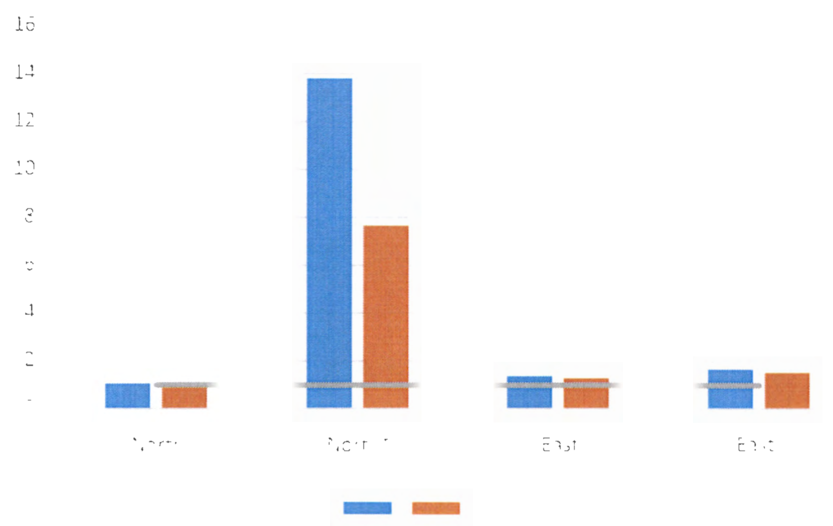


Figure 9: The As risk quotient

4.5 Spatial variability of heavy metal contamination

Figures 10 - 13 show the spatial variability of studied heavy metals (As, Pb, Cd, and Zn) for soil samples at a depth of 0-10 cm, created by ordinary kriging. As shown, the heavy metal values pointedly differed in different locations. The maps show that the higher heavy metal values were concentrated mainly in the central parts of the mining area, whereas, the lowest heavy metal concentration in soil were found in the southwestern part of the study area. These observations clearly demonstrates that the mining activities play a major role in the distribution of the heavy metals in this area. In all the studied heavy metals, the concentrations in the soil were reduced as the distance from the mining area increased. Preceding researchers have vindicated that heavy metals distribution in the soils is strongly influenced by different human activities such as mining, and also farming (Guo *et al.*, 2012; Qu *et al.*, 2013; Wu *et al.*, 2014).

At a depth of 10-20 cm, the spatial variability shows that the distribution of the heavy metals around the mines is low when compared to the distribution in the spatial map of 0-10 cm. Zinc shows high concentration at the eastern part of the mining location. In conclusion, concentrations of the studied heavy metals around the mines at a depth of 0-10cm is higher than at 10-20 cm. Figure 14 17 show the spatial variability of the studied heavy metals at a depth of 10-20 cm created by ordinary kriging.

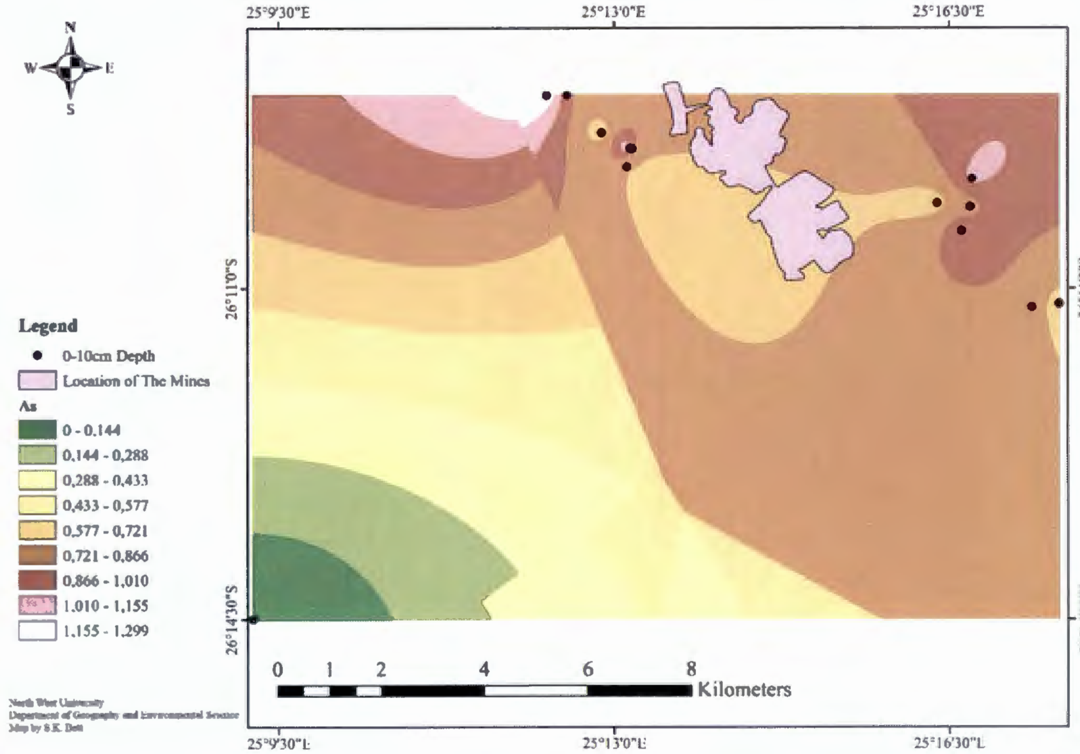


Figure 10: As spatial variability

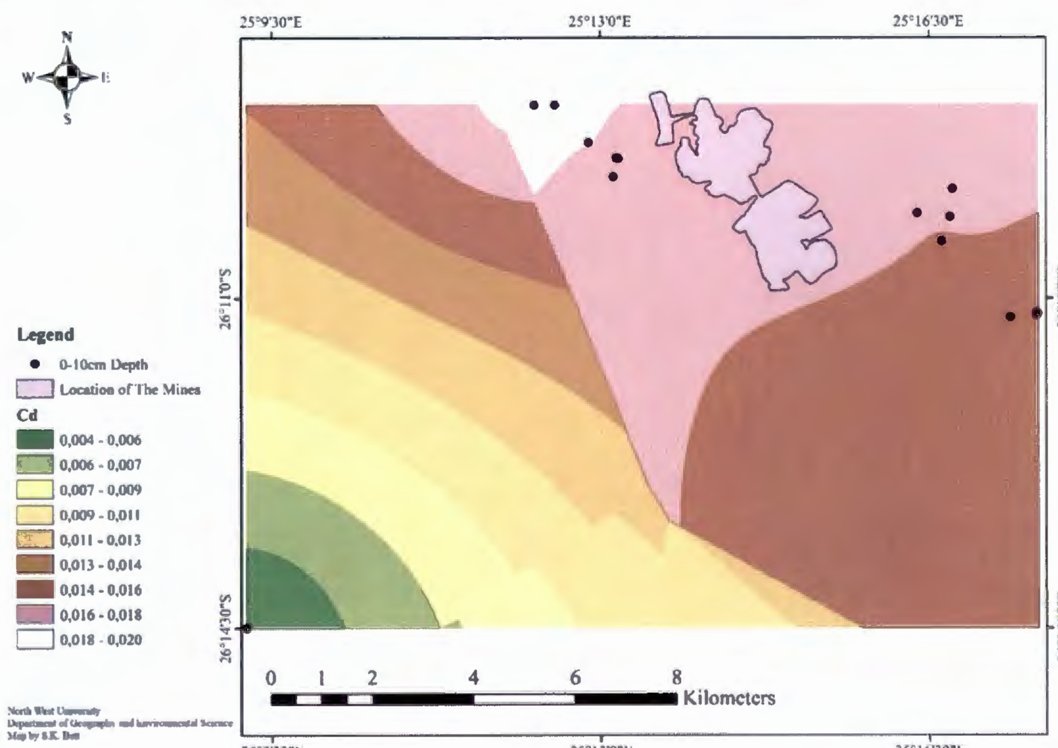


Figure 11: Cd spatial variability

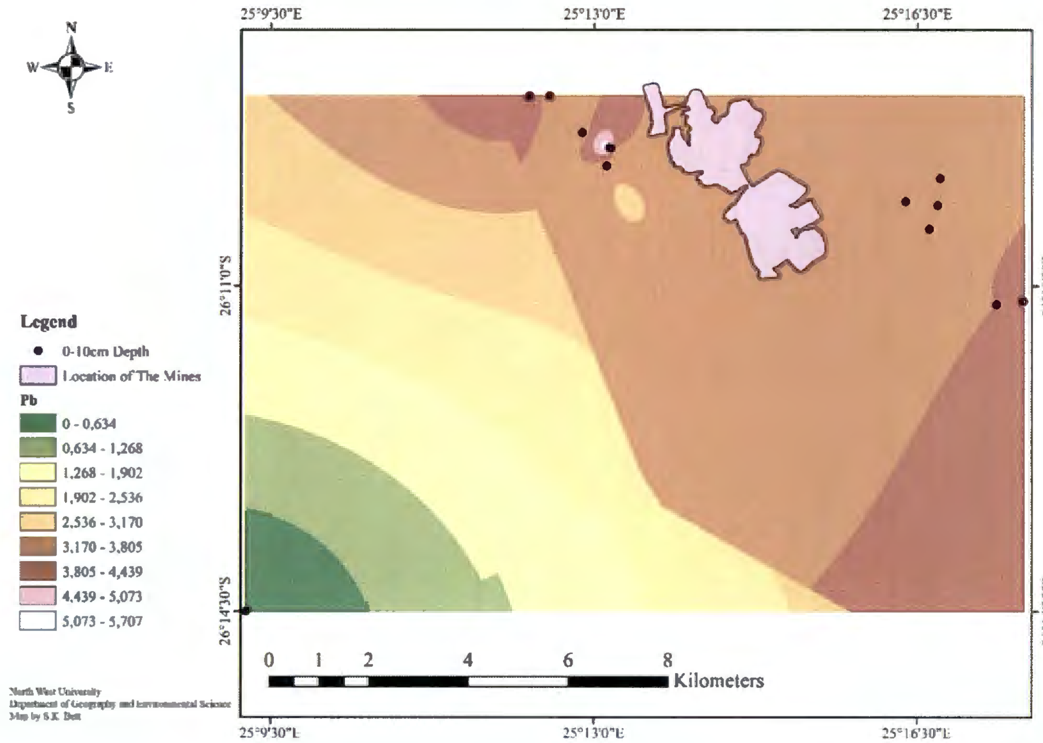


Figure 12: Pb spatial variability

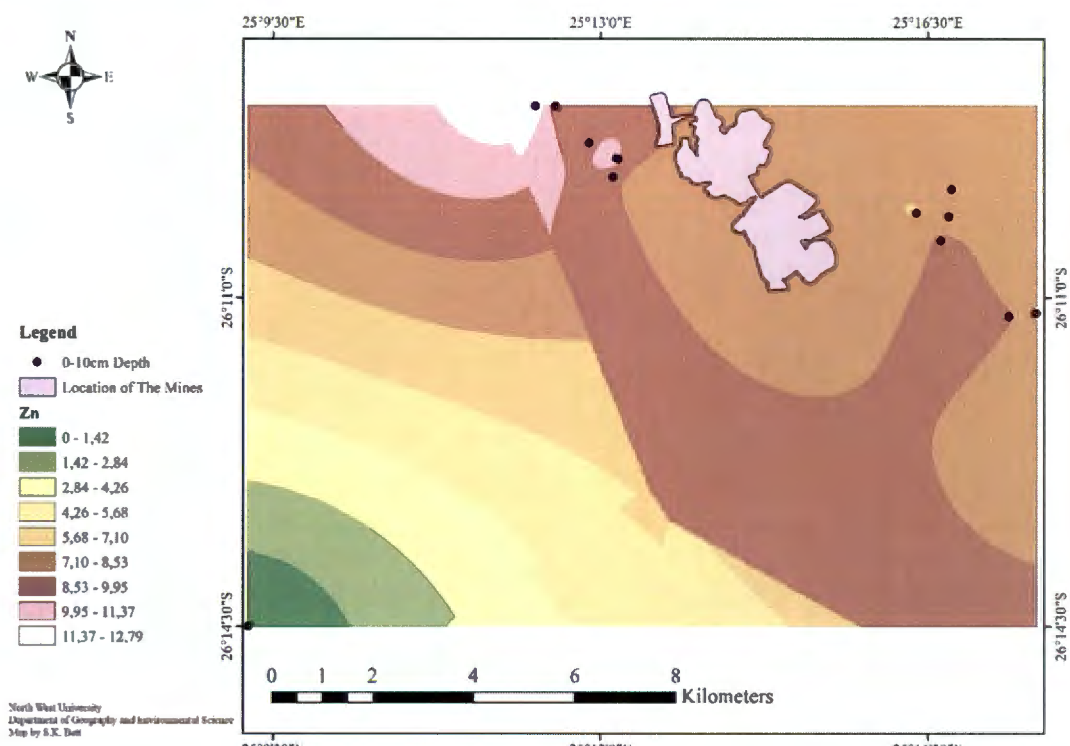


Figure 13: Zn spatial variability

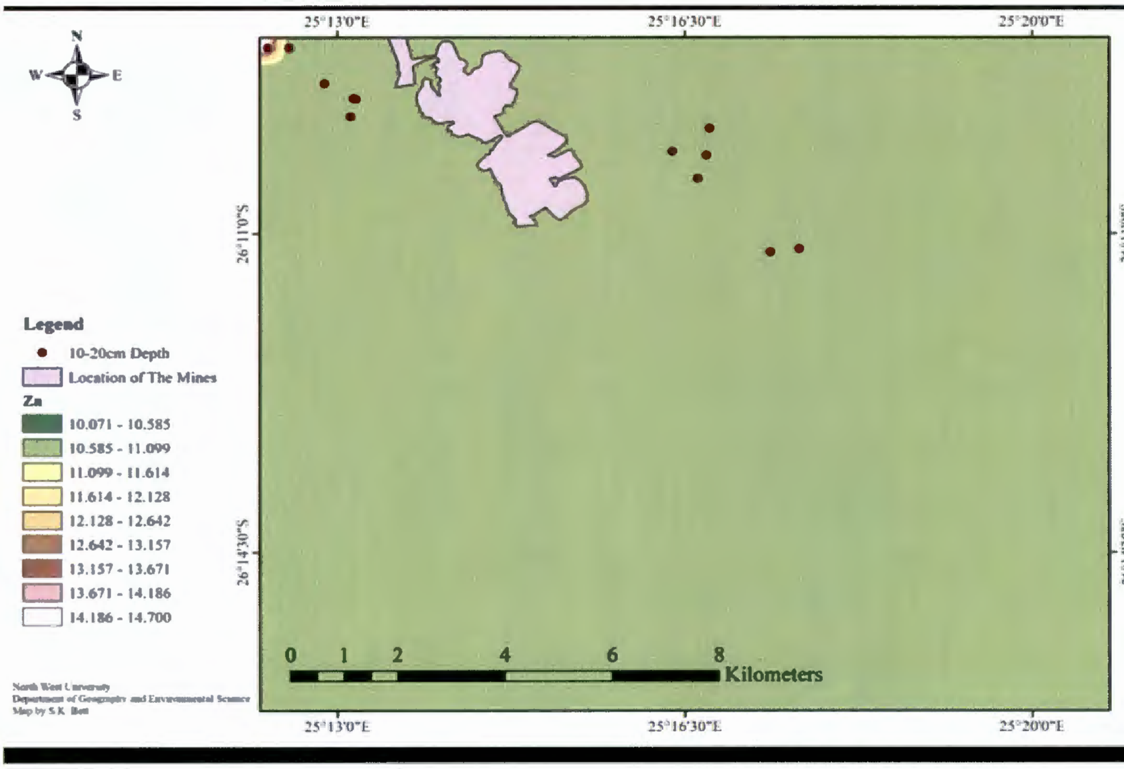


Figure 14: Zn spatial variability (10-20 cm)

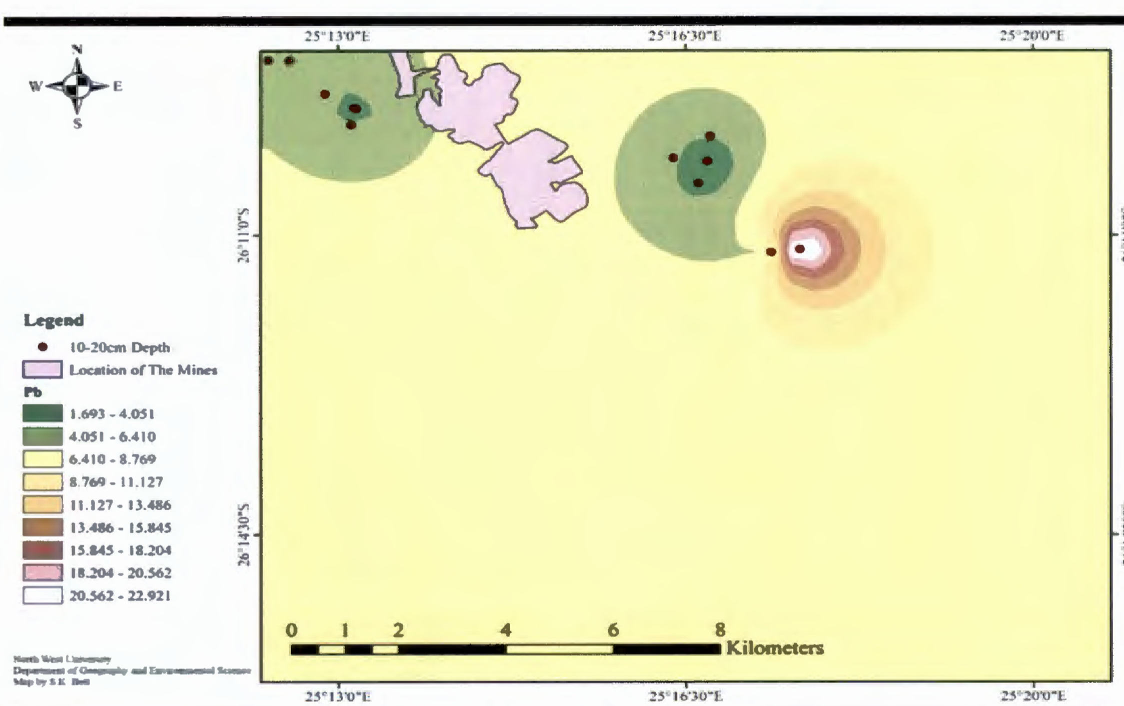


Figure 15: Pb spatial variability (10-20 cm)

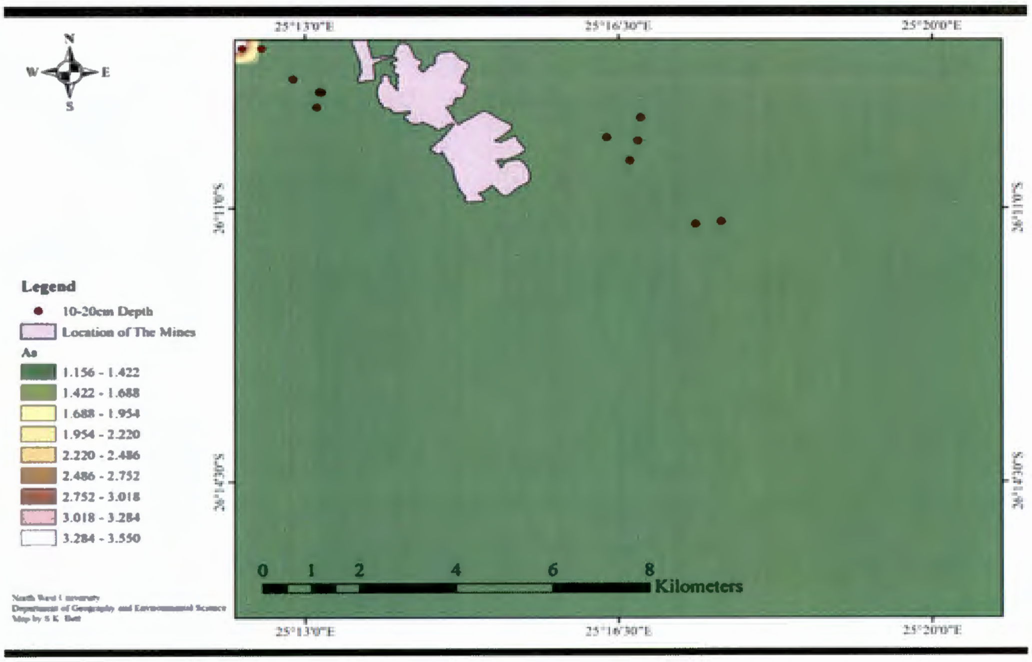


Figure 16: As spatial variability (10-20 cm)

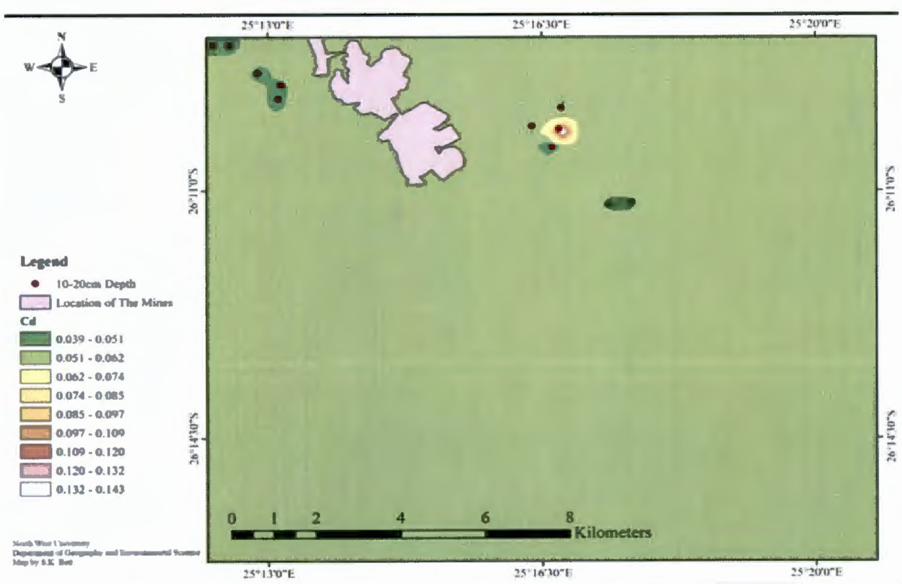


Figure 17: Cd spatial variability (10-20 cm)

SUMMARY

Based on the results presented in chapter 4, it can be deduced that As, Cd, Zn and Pb concentrations in soil are lower than the South African permissible limits in agricultural soil and the recorded limits of several countries. The concentrations of Cd and As in the plants' leaf and root are greater than the WHO tolerance limit while Pb (except in the North within ≤1000 m) and Zn (except in the northern locations of both distances) are lower than the WHO

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.0 Introduction

In the previous chapter, the results of the research were discussed with relevance to the objectives of this study. Chapter five will present the conclusions and recommendations.

5.1 Conclusions

The aim of this study was to examine the heavy metal pollution in the environment of a gold mine. The objectives were to determine the concentration of heavy metals in soils and plants, to determine the uptake of heavy metals by plants, to characterize the spatial variability of heavy metal contamination and to determine the health risk associated with heavy metal concentrations.

The methodology used and results obtained from the study have led to the following conclusions:

1) The trend of heavy metal concentrations in the soil and plant is Zn > Pb > As > Cd. This confirms that the metal content in plants is a direct reflection of such metal content in soils. This means that there is uptake of heavy metals by the plants within the mining area, which poses a health risk to the animals, most especially to the cattle grazing in this environment, and humans as the end consumer of beef meat.
2) The result of heavy metals concentrations in the soils are within the permissible limit of agricultural soils as approved by DEA, South Africa. Therefore, they are not of present danger to animals and humans. However, the concentration of heavy metals in *Eragrostis hypnoides* plants are higher than WHO permissible limit in most of the sampling locations. This proves that the consumption of such plants by animals and humans is of high risk. These environment has to be contained for quick remediation process, and all forms of animal grazing and farming activities must be immediately discouraged.
3) The sampled plant, *Eragrostis hypnoides*, accumulates Zn and Cd easily from the soil. In contrast, Pb and As are not enriched by the *Eragrostis hypnoides*, therefore, it is an excluder of Pb and As. This means that *Eragrostis hypnoides* can be used for the

phytoremediation of Zn and Cd contaminated soils but not for Pb and As contaminated soils.

4) The consumption of *Eragrostis hypnoides* have the tendency to induce Cd and As related diseases. This is because the health risk quotient of Cd and As are above the allowable limit, 1.

5.2 Recommendations

Emerging from the results of this study, the following recommendations can be made:

1) Regular study must be undertaken within the environment of all mining sites as well as farms and residence located within mining areas, to record any changes in the quality of the land, plants and animals within North West Province so that the appropriate measures can be appropriated.
2) The monitoring of heavy metal pollution should be enforced at all local municipalities in the North West Province, in order to ensure early detection of heavy metal pollution so that it does not impact on food security.
3) Allocations of residential land for humans living, as well as location of land for agricultural purposes, within a mining area must be discouraged.
4) Future similar research studies should be undertaken to;
   a) Determine the health risks of the maize plantation in this area since maize is one of the commonly grown and consumed crop.
   b) A detailed analysis to establish the factors that influence the spatial pattern and mobility of heavy metal pollution in soils and plants and make recommendation for possible future studies.

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