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Heavy metal contamination and potential health risks from soils around a stone quarry in Tzaneen, South Africa

By

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Declaration

I, Mara Mthuthuzeli Kenneth, Student Number 11634857, declare that this dissertation, submitted to the University of Venda, is my own work and has not been previously submitted in whole or in part for any degree. All assistance and information from published and unpublished work have been fully acknowledged.

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Dedication

I dedicate this dissertation to my wife, Mabina Karabo Suzan, my daughters, Relebogile, Rorisang and my son, Prince Mara.

Abstract

Heavy metals exist naturally in the earth's crust as part of the composition. Their contents vary between regions resulting in spatial variations of background concentration. The concentration of heavy metals in the environment can increase to high levels through anthropogenic sources. Stone quarrying is one of the anthropogenic sources responsible for increase of heavy metals in the environment. Hence, the study aimed at assessing the contamination level and human health risks caused by heavy metals from soils around Tzaneen stone quarry. A total of 46 samples were collected and analysed for Cr, Pb, Cu, Co, Ni, Zn, Mn and Fe using AAS. The pollution level of the heavy metals in the study area was estimated using Pollution Index (PLI), Enrichment Factor (EF) and Geo-accumulation Index (Igeo). Non-carcinogenic and carcinogenic health risks were assessed for inhalation, ingestion and dermal absorption routes for infants, children and adults based on the hazard quotient (HQ), hazard index (HI), average daily intake and carcinogenic slope factor. Concentration of Mn and Fe were highest in the soil samples whereas Ni had the lowest concentration. Metal loading trends revealed a general decreased with distance from the quarry site. The PLI of heavy metals in the soil from the community ranged from 0.55 to 0.75 with an average value of 0.66 suggesting an unpolluted status. Metal enrichment at the quarry was in the order: Mn>Co>Pb>Cu>Ni>Cr>Zn while in the nearby community, it ranged from Co>Pb>Cr>Mn>Cu>Ni>Zn. The values for HQ and HI showed that infants, children, and adults in the study are exposed to potential non-carcinogenic health risks through dermal absorption compared to inhalation and ingestion. Children were the most at-risk population exposed to non-carcinogenic risk. Values for the incremental lifetime carcinogenic risk (ILCR), were lower than the US EPA tolerable range ($10^{-6} – 10^{-4}$), suggesting no immediate carcinogenic risks. However, prolonged exposure to quarry dust may still remain a potential health threat to the surrounding communities. It is recommended that quarry workers and residents in the study area should take protective measures against long-term exposure to heavy metals in the area.

Keywords: Stone quarry, heavy metal distribution, heavy metal toxicity, health risk assessment, carcinogenic assessment, non-carcinogenic assessment

Table of contents

CHAPTER THREE: METHODOLOGY...25

CHAPTER FOUR: RESULTS AND DISCUSSION……………......……………………….52

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS…………....………..…82

List of Figures

List of Tables

List of Acronyms

AAS	Atomic Absorption Spectrometry
CDI	Chronic Daily Intake
CF	Contamination Factor
CMZ	Central Marginal Zone
CSF	Cancer Slope Factor
DEA	Department of Environmental Affairs
EF	Enrichment Factor
GPS	Global Positioning System
HRSZ	Hout River Shear Zone
HQ	Hazard Quotient
Igeo	Geo-accumulation Index
ILCR	Incremental Lifetime Cancer Risk
LADD	Lifetime Average Daily Dose
LMB	Limpopo Mobile Belt
MGB	Murchison Greenstone Belt
NMZ	North Marginal Zone
PI	Pollution Index
RFD	Reference Dose
SMZ	South Marginal Zone
U.S. EPA	United State Environmental Protection Agency
VEB	Vertical Engineered Barriers

CHAPTER ONE: INTRODUCTION

1.1 Background of the Study

Stone quarry is a small-scale mine that supplies aggregate materials to the construction industry and contributes significantly to the development of most nations (Lameed and Ayodele, 2010). Stone quarrying results in several negative environmental impacts like the release of dust containing heavy metals, destruction of landscape, forests, and scenic beauty. Contamination of the environment with heavy metals is a major concern because of their toxicity, persistent nature, non-biogradability and a threat to human health. Heavy metals are defined as metallic elements with relatively high densities or atomic weights. Oves et al. (2012) defined heavy metals as metallic elements having an atomic weight higher than 40.04 (the atomic mass of Ca) and a relatively high density greater than 5 g/cm^3. Examples of heavy metals include Pb, Zn, Cd, Hg, As and Cr.

Heavy metals exist naturally in the earth's crust as part of the composition. They occur in the environment as products of biological and geochemical cycles in trace amounts (< 1000 mg.kg^{-1}) that are rarely toxic. Their contents vary between regions resulting in spatial variations of background concentration (Lar, 2013). The concentration of heavy metals in the environment can increase to high levels through anthropogenic sources (Wei et al., 2009). Stone quarrying is one of the anthropogenic sources responsible for increase of heavy metals in the environment; other sources include industrial discharge, wastewater irrigation, municipal waste, land application of fertilizers and pesticides (Bako et al., 2008). Quarrying is the process of extracting rocks from the earth through various processes including removal of the topsoil, drilling, blasting, crushing and screening of the rock materials to produce required aggregate sizes (Lameed and Ayodele, 2010).

Stone quarrying is an important industry because of its positive impact on socio-economic and infrastructure development of the nations (Ukpong, 2012). Quarrying activities are widely spread around the world, occurring mostly in developing countries such as Africa, Asia, Oceania, Central and South America (Ashante et al., 2014). Rapid growth of the stone quarrying activities due to the increasing population and high demand of quarry products has created job opportunities for both skilled and unskilled individuals, providing livelihood for many families (Lad and Samant, 2014). Despite the positive contribution, rock quarrying release huge amount of dust containing heavy metals into the atmosphere and the environment (Zhao et al., 2012).

Heavy metal distribution and accumulation in the environment is a serious problem around the world due to their toxicity and potential threat to human health (Hu et al., 2016). The distribution of these metals in the environment is governed by the properties of the metal and influences of meteorological conditions such as wind and rainfall (Khlifi and Hamza-Chaffai, 2010). Osu et al. (2018) indicated that dust containing Cu, Cr, Hg, and Zn metals was majorly dispersed from the source by wind which distributed dust containing metals in all direction at different magnitude, space and time. Once heavy metals accumulate in the environment, whether in small or large quantities, they cannot be removed due to their persistent nature, biodegradability and bio-accumulative potentiality (Islam et al., 2006). Heavy metals found at contaminated sites include Pb, As, Cd, Cr, Cu, Zn, Mn, Ni and Co (Avila et al., 2017). Ayodele et al. (2014) indicated that a granite stone quarry in Nigeria released dust containing heavy metals such as Fe, Pb, Cu, Cr, Ni, Mn, Cd and Co. Deposition and build-up of these metals in the environment above recommended background levels can affect the environment and human health directly and indirectly (Mahipal et al., 2016).

Heavy metals can damage the quality of the environment and affect human health indirectly through polluting soil, food crops, water, and the atmosphere (Oti-Wilberforce and Nwabue, 2013). They may also go into human body through ingestion, dermal contact and inhalation of soil particles thus directly damaging human health at different age groups including infants, children, and adults (Sun et al., 2010). Exposure risks to different populations is used to determine the overall incremental lifetime cancer risk. For instance, if a child is born and raised in the village until adulthood, what will be the potential health risk? Exposure to heavy metals is normally chronic due to food chain transfer or prolonged period of exposure in workplace and nearby communities (Guo et al., 2012). Acute (immediate) poisoning from heavy metals is rare through ingestion or dermal contact, but possible. This situation is critical for fish, other wildlife and humans at the top of the food chain. Since heavy metals are non-biodegradable, once ingested they accumulate in animal and human body tissues to toxic levels (Khan et al., 2008). Heavy metals such as Cu, Mn and Zn are necessary for good health in small amounts, but excessive levels may cause acute or chronic toxicity (Megateli et al., 2009).

Other heavy metals such as Pb, As, Cr and Cd are known carcinogenic metals with no beneficial effects in human health and are toxic even at very low concentration (Aloh et al., 2017). Exposure to As in soil can cause skin damage, increased risk of cancer, and problems with circulatory system

(Mazumber, 2008). Severe exposure to Cd can result in pulmonary effects such as alveolitis, bronchitis and emphysema (Adelokun et al., 2016). Cr (III) is an essential element; however, Cr (IV) compounds are known to be carcinogenic. Inhaling higher levels of Cr (IV) may cause asthma, shortness of breath and lung cancer (Podsiki, 2008). Hence, it is crucial to assess heavy metal contamination of the environment and identify potential health risks to human beings. The goal is to ensure protection of the environment and human health as optimum benefits are derived from such operations (Wahid et al., 2014).

1.2 Statement of the Problem

The study is aimed at assessing the concentration of heavy metals in near surface soil around a stone quarry. Rock blasting and crushing releases huge amounts of dust containing different heavy metals into the atmosphere and the environment (Zhao et al., 2012). The dust particles in the atmosphere can be distributed by wind around the mine. Deposition of heavy metals in soil above recommended regulatory limits pose a threat to human health (Avila et al., 2017). Long-term exposure to heavy metals can result in physical, muscular and neurological effects (Tasrina, 2015). Chronic exposure to carcinogenic metals such as Pb, Cd and Cr can lead to harmful effects, such as different types of cancer (bladder cancer, kidney cancer, skin cancer, lung cancer and liver cancer), bone fractures, kidney dysfunction and hypertension (high blood pressure) (Bollinger, 2010; Adelokun et al., 2016).

Given the proximity of Tzaneen quarry to residential areas and schools, the community may be exposed to potential heavy metal contamination, emanating from dust loading on nearby soils. Furthermore, the level of potential health risk to different populations (infants, children and adults) in the study area remains elusive.

1.3 Aim of the study

The aim of the study is to investigate heavy metal concentration and potential health effects from soils around Tzaneen Quarry, Limpopo Province, South Africa.

1.4 Specific objectives of the Study

The specific objectives of the study are:

- To determine distribution and concentration of heavy metals (Cr, Pb, Zn, Cu, Ni, Co, Fe and Mn) in near surface soils.
- To determine the degree of soil pollution by heavy metals using pollution indices.
- To assess potential human health risks from exposure to heavy metals for different age groups (infants, children and adults).

1.5 Research Questions

The research questions that will be addressed in this study include:

- What is the spatial distribution and concentration of heavy metals in near surface soils in the study area?
- Have the concentration of HMs in the soils attained the status of pollution?
- How does potential health risks from heavy meal contamination vary across the three age groupings (infants, children and adult).

1.6 Significance of the Study

Soil contamination by heavy metals resulting from anthropogenic activities is a serious environmental and health concern all over the world (Maas et al., 2010). Heavy metals in soil can be used to monitor the impacts of anthropogenic activities in the mining environment and provide evidence for decision makers (Hu et al., 2016). Stone quarrying is one of the anthropogenic activities responsible for addition of heavy metals in soil to toxic levels that are harmful to human health (Bako et al., 2008). Hence, a comprehensive understanding of the heavy metal pollution in the mining environment and their potential health risks will help to make informed decisions on the approaches to reduce contamination, minimize human exposure and identify human health risks (Suvarapu et al, 2014). This will allow for interventions that would balance between quarry productions and the protection of human health and environment (Wahid et al, 2014).

The current study seeks to generate data on the level of heavy metals in near surface soils around the Tzaneen quarry. This will contribute towards uncovering any inherent threat posed to the environment and human health (Hu et al, 2016). The information gathered from this study will add to the existing literature on heavy metal pollution of the environment in mining areas and serve as reference point for future studies. It is anticipated that findings from this study will assist the quarry operators, regulatory bodies and relevant government departments to create a safe working environment for mine workers and protect nearby communities from toxic heavy metals (Norbaya et al, 2014; Halwenge, 2015).

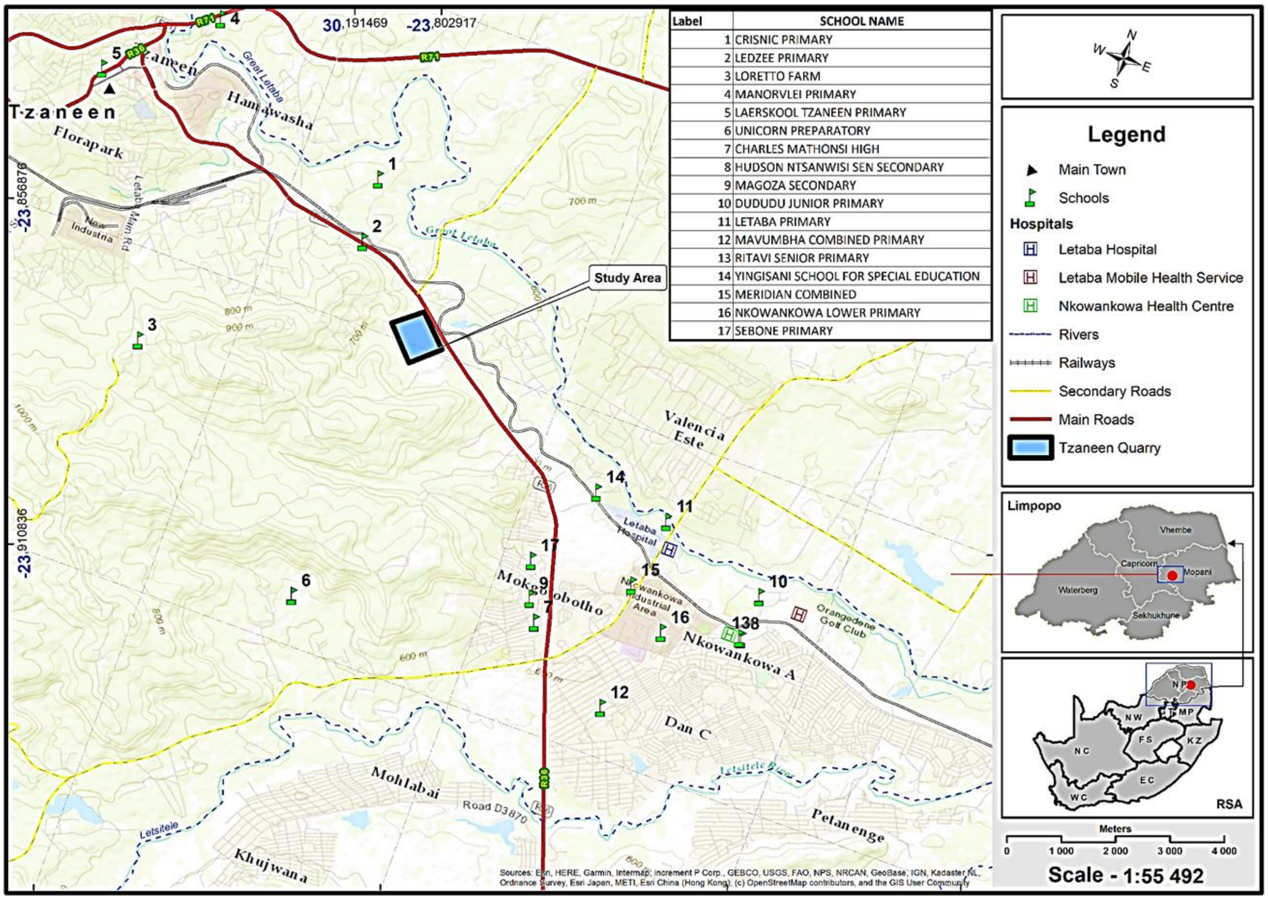
1.7 Delimitation of the study

Health risk assessment in the study focussed on the Mokgolobotho Community, which lies within 2 km to 2.5 km away from the quarry. The control site was at 10 km from the quarry towards Nkowankowa.

1.8 Study Area

1.8.1 Location

The study area is located about 8 km southeast of Tzaneen town along R36 road in the Great Letaba Local Municipality under Mopani district municipality, Limpopo province, South Africa. Wind direction is SE with relative to the nearby community from the mine. The geographic location coordinates of the study area are latitude: 23^{0}51’19” S and longitude: 30^{0}13’9” E at an altitude of 787 m above sea level (Figure 1.1).



Label	SCHOOL NAME
1	CRISNIC PRIMARY
2	LEDZEE PRIMARY
3	LORETTO FARM
4	MANORVLEI PRIMARY
5	LAERSKOOL TZANEEN PRIMARY
6	UNICORN PREPARATORY
7	CHARLES MATHONSI HIGH
8	HUDSON NTSANWISI SEN SECONDARY
9	MAGOZA SECONDARY
10	DUDUDU JUNIOR PRIMARY
11	LETABA PRIMARY
12	MAVUMBHA COMBINED PRIMARY
13	RITAVI SENIOR PRIMARY
14	YINGISANI SCHOOL FOR SPECIAL EDUCATION
15	MERIDIAN COMBINED
16	NKOWANKOWA LOWER PRIMARY
17	SEBONE PRIMARY

Sources: Esri, HERE, Garmin, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), (c) OpenStreetMap contributors, and the GIS User Community

Figure 1.1: Location map of the study area.

1.8.2 Climate

The climate of the study area is subtropical, with much less rainfall in winter than summer. Most of the rainfall is seasonal with more than 85% occurring during summer months. The peak rainfall months are January and February with an average annual rainfall is 965 mm (Kramers et al, 2014). The mountainous topography results in much higher rainfall with the mean average precipitation varying between 700mm - 1500mm in the mountainous region (Woodhall, 2005). The annual average temperature is 20.4 ^{0}C, varying during the year by 9.4 ^{0}C. The coldest month is July the average temperature of 9 ^{0}C and is the lowest average temperature of the whole year (Woodhall, 2005).

1.8.3 Topography

The study area is characterized by mountainous, inaccessible terrain in the west and south, and even topography (gentle slopes) to the north and east. The Tzaneen area is known for its hills and cliffs, such as Modjadjiskloof areas (Kressig et al, 2000). The study area falls within the low mountainous zone with surrounding undulated landscape. The topography around the quarry site is relatively flat.

1.8.4 Pedology and vegetation

The study area is composed of silty soils in the south-west and sandy soils in the rest of the study area from weathered granites (Figure 1.2). The soils vary from shallow to deep sandy and gravelly well-drained soils (Mokganya et al, 2012). The residual soils, where present, are usually between 1, 5 to 2 m thick, coarsely textured, non-cohesive and consist mostly of quartz and feldspar aggregates. This is a result of the deposition of arenaceous and argillaceous sediments within fluviatile and shallow water conditions that followed the period of volcanic activity (Brandl, 1981). The soil is red to yellowish in colour. Vegetation cover consists of Tzaneen bushveld. This is a deciduous, tall open bushveld with a well-developed, tall grass layer. The veld type occurs on low to high mountains with undulating plains mainly at the base and on the lower to middle slopes of the North-Eastern escarpment (Mucina and Rutherford, 2006). About 41% of the vegetation is transformed mainly by cultivation and plantations, very little is currently conserved. The most dominant veld type is the Lowveld sour bush, which is one of the inland tropical forest types (Brandl et al., 2006).

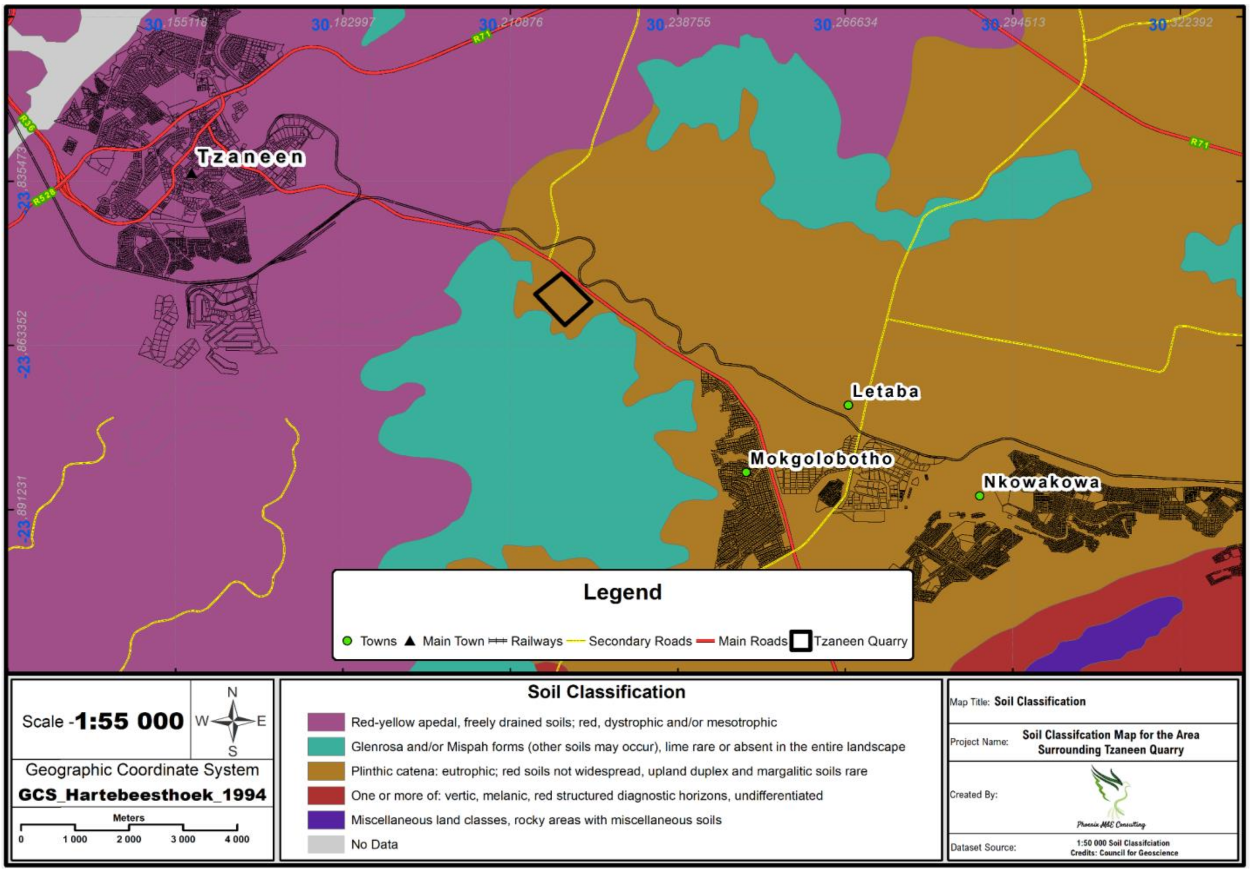


Figure 1.2: Showing soil classification map of the study area (Tshitangano, 2020).

1.8.5 Geology of the Study Area

The geology of the study area consists of Groot-Letaba Gneiss in the northern basement of the MGB (Figure 1.2). Groot Letaba Gneiss consists of a wide variety of closely fused gneisses such as fine to medium-grained tonalite, coarse-grained trondhjemite and minor banded and linear gneisses (Robb et al., 2006). The gneissic bodies are arranged from homogenous to strongly layered, leucocratic felsic to mafic minerals (Anhaeusser, 1992). The gneisses are generally migmatised with leucosome bands belonging to distinct generations of magma (Figure 1.3). Leucogranite gneiss in Tzaneen is of the various gneisses represented by Groot Letaba Gneiss (Figure 1.2).

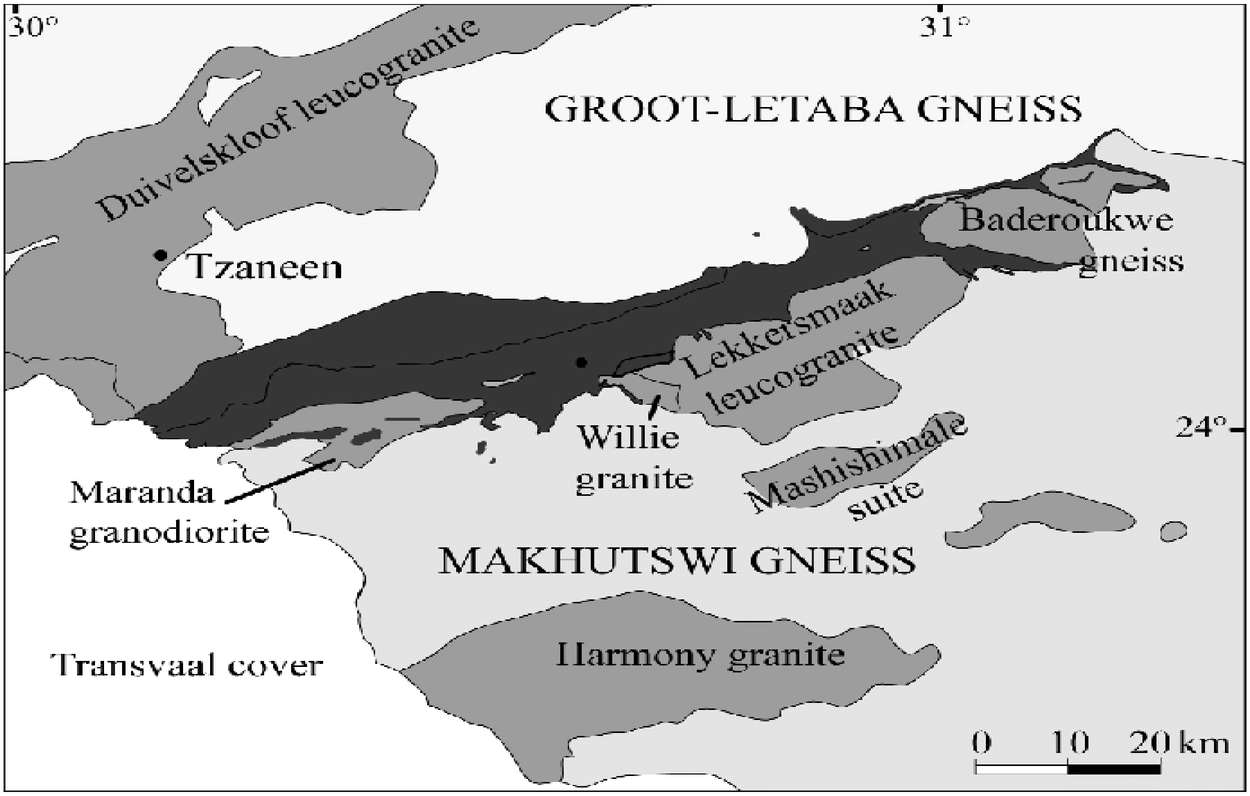


Figure 1.3: General map of the region with the surrounding granitoid of MGB (Robb et al., 2006).

The most widespread type is leucocratic biotite gneiss, probably tonalitic in composition and shows clear intrusive relationships (Brandl and Kroner, 1993). Small inclusions of mafic to ultramafic minerals are found in some areas, implying the intrusive nature of the gneiss protolith within the greenstone belt (Figure 1.3). The intrusive volcano-sedimentary outcrop comprised sub-aerially extruded basalts and minor pyroclastic materials with rare discontinuous intercalations of clastic sediments (Kroner et al, 2000). The deposition of sand and clay sediments within fluviatile and shallow-water conditions followed the period of volcanic activity (Brandl, 1981).

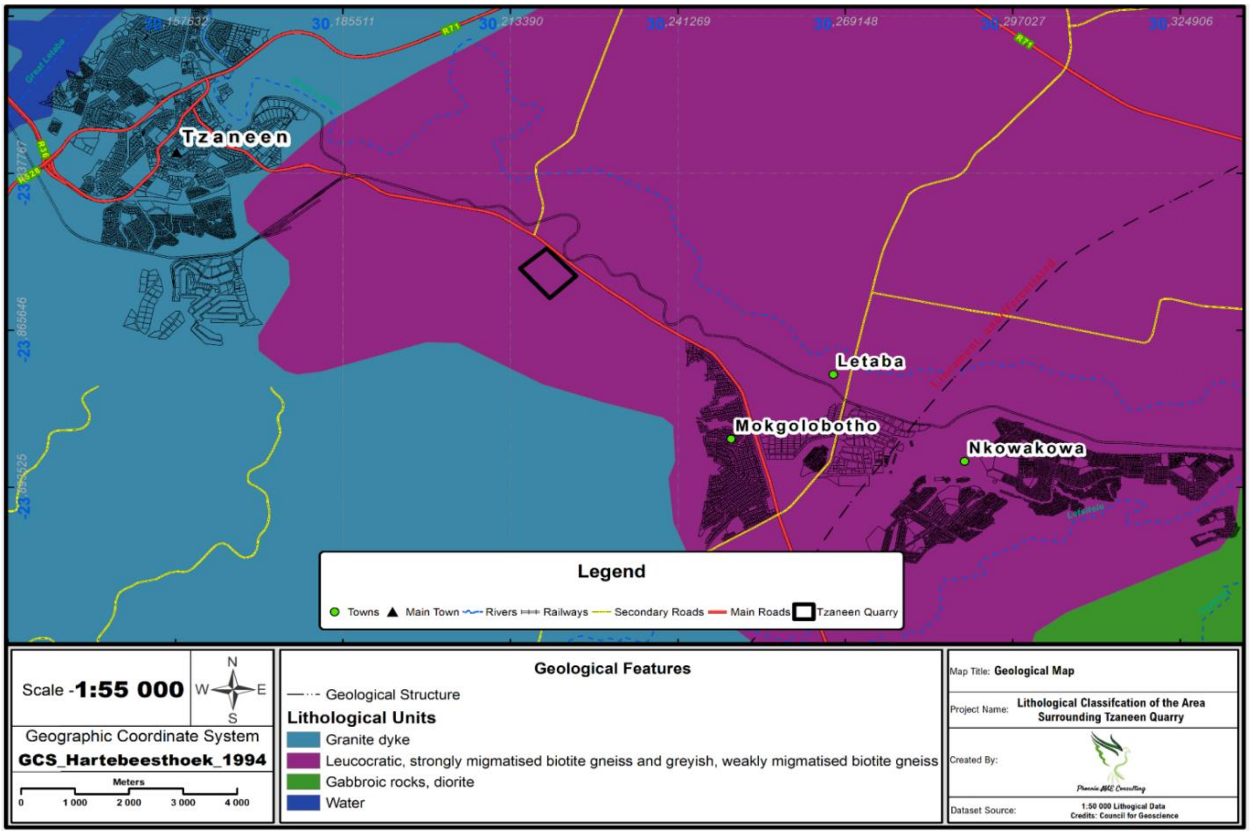


Figure 1.4: Showing geological map of the study area (Tshitangano, 2020).

CHAPTER TWO: LITERATURE REVIEW

2.1 Types of metals in the rocks found in the study area

Heavy metals occur naturally in the earth's crust and their contents in the environment vary between regions resulting in spatial variations of background concentration (Lar, 2013). Of the 92 naturally occurring elements in the earth's crust, approximately 35 metals and metalloids are heavy metals potentially toxic to humans (Figure 2.1). These metals include Be, B, Li, Al, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Mo, Pb, Ag, Cd, Sn, Sb, Te, Cs, Ba, W, Pt, Au, Hg, Pd and Bi (Tiimub et al, 2015). Previous studies have shown that heavy metals mostly found in granite stone quarries include Pb, As, Mn, Ni, Cu, Zn, Co, Cr, Cd and Hg (Ayodele et al, 2014; Tiimub et al, 2015; Osu et al, 2018). Hence, the study will analyse heavy metals such as Pb, As, Cd, Zn, Cu, Hg, Ni, Fe and Mn in soil samples of Tzaneen quarry, which also mines granite rock.

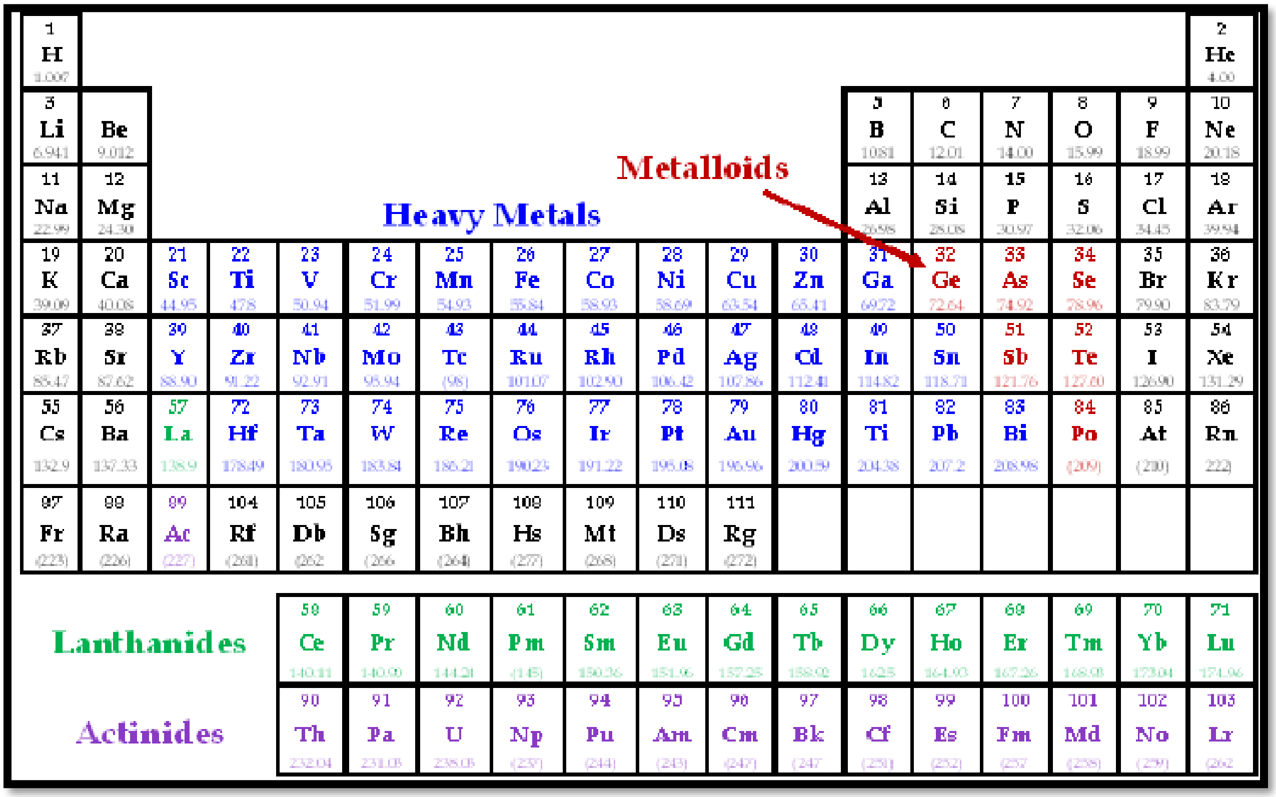


Figure 2.1: Showing the position of heavy metals in the periodic table.

2.2 Sources of Heavy Metals in Contaminated Soils

Soil heavy metal pollution has become a severe problem in many parts of the world (Hu et al, 2016). Although heavy metals may occur naturally in soil, additional contributions come from anthropogenic activities such as mining, municipal or industrial wastes, fertilizers/ pesticides, wastewater irrigation, and atmospheric deposition (Bako et al, 2008). Numerous studies have shown that pollution sources of heavy metals (Pb, Cr, As, Zn, Cd, Cu, Hg and Ni) in the environment mainly derive from these sources (Zhang et al, 2012). Mining and milling of metal ores coupled with industries contribute to wide distribution of metal contaminants in soil. Stack or duct emissions of air, gas or vapour streams and fugitive dust emission from mine tailing are some of the airborne sources of metals in soil (Smith et al, 1995). A limestone quarry in Florida was discovered to have been associated with exposure to hazardous levels of Hg metal (Etim and Adie, 2002).

Metals such as (As, Cd and Pb) can volatize under high temperature processing contributing significantly to the atmospheric concentration of metals. Avila et al. (2017) have reported highest concentration of As, Cu, Fe, Mn, Pb and Zn in mine tailings and places close to mining sites. Pb is a common heavy metal pollutant in mining/industrial areas with a high emission rate worldwide (Finzgar et al, 2006). Another major source of soil contamination is the aerial emission of Pb from combustion of petrol containing tetraethyl lead (Mahipal et al, 2016). This contributes substantially to the content of Pb in soils in urban areas and in those adjacent to major roads. Cd is emitted into the air by mines, metal smelters and industries using cadmium compounds for alloys, batteries, pigments and plastic. Cd may also be introduced in soils adjacent to roads, the source being tyres, and lubricant oils (Zhang et al, 2012). All solid particles in smoke from fires and other emissions from factory chimneys are eventually deposited on land or sea resulting in heavy metal contamination of the environment.

The application of municipal and industrial wastewater and related effluents to land is another source of heavy metals in soil (Reed et al, 1995). It is estimated that 20 million hectares of arable land worldwide are irrigated with wastewater. In several Asian and African cities, studies indicated that agriculture based on wastewater irrigation accounts for 50 percent of the vegetable supply to urban areas (Bjuhr, 2007). Although the metal concentrations in wastewater effluents are usually relatively low, long-term irrigation of land with such can eventually result in heavy metal accumulation in the soil. Wastewater irrigation causes heavy metals (Hg, Cd, Pb etc.) to continually accumulate and get fixed in the soil year by year (Su et al, 2014).

The use of fertilizers and pesticides to supplement crop yields has significantly increased the amount of heavy metals contained as impurities in soil (Jones and Jarvis, 1981). This led to substantial increase of heavy metals in soil, greatly exceeding background concentrations (Chiroma et al, 2014). Application of certain phosphatic fertilizers unintentionally added Cd and other potentially toxic elements to the soil, including Hg, and Pb. Such contamination has the potential to cause problems, particularly if sites are redeveloped for other agricultural or non-agricultural purposes (McLaughlin et al, 2000). Anthropogenic inputs of As in the soil include the use of arsenical insecticides, mining and fossil fuel combustion which are extremely important additional sources (Mazumber, 2008). Mercury may also enter the environment through the use of fungicides and seeds preservative in agriculture to protect crops (Reily, 1992).

2.3 Stone Quarrying

Stone quarrying is one of the anthropogenic sources responsible for an increase in certain heavy metals in soil. A quarry is an open pit mine from which rocks or minerals are extracted from the earth through various processes. This includes removal of the topsoil (overburden), drilling, blasting with explosives and use of machinery to crush and grade rock materials for transportation (Gamal El-Dine et al, 2009). Rocks deemed suitable for quarrying purposes include sand, slate, clay, sandstone, dolerites, limestone, granites, gneiss and basalt because they are found near the surface, easy to mine, beneficiate, and also allow the use of simple equipment and machinery (Dlambulo and Motsie, 2014). These rocks mined from stone quarries are used in the development of major infrastructures like laying roads, railway tracks, and dams (Birabwa, 2006).

2.3.1 Types of Stone Quarries

There are two types of quarries namely, crushed stone quarry and dimension stone quarry. Crushed stone quarries produce aggregates for construction industry and cement factories, while dimensioned stone quarries produce building blocks and ornamental stone for construction of buildings and cemetery tombstones (Halwenge, 2015). Crushed stone refers to rock that has been broken into small irregular fragments of specific particle size (Teoprdei, 2002). The bedrock is first drilled, filled partially with explosives, and stemmed with nonexplosive material (usually sand, crushed stone, or a manufactured plug). Controlled sequential blasting is employed to break the rock into pieces suitable for crushing. If the rubble is too large, secondary breaking may be required and usually is accomplished with hydraulic hammers, drop balls, or other mechanical devices (Smith and Collins, 2001). The blasted material is extracted using conventional earth-moving equipment, such as bulldozers, front loaders, backhoes, and hydraulic excavators.

Dimension stone refers to rock cut into building blocks and ornamental stone for building construction (Ashmole, 2004). Dimension stone is mined through splitting or cutting the stone into successively smaller pieces until the final desired block size is achieved, and saleable blocks are produced. There are two strategies employed in mining dimension stones. The first strategy involves loosening large volumes of rocks through primary cuts and then divided stepwise into smaller pieces until commercial blocks are obtained, discarding waste material as the process is performed. This is the main method employed in most granite and marble quarries (Hora, 2007). Under the second strategy, commercial blocks are directly cut from the rock body. This strategy is often employed in the production of sandstone, where blocks are often extracted from relatively thin layers or between bedding planes. In a case where natural slabs, curbs, paving stones, etc., are produced, a special case is considered where cautious blasting is employed, and suitable pieces are selected from the muck pile (Ashmole and Motloung, 2008). This latter case is often applied in the extraction of slates, and quartzite.

2.3.2 World View on Stone Quarrying

Stone quarrying is a global phenomenon and a cause of concern everywhere in the world (Sayara, Hamdan, and Basheer-Salimia, 2016). It plays an important role in the economies of many countries, creating employment to both skilled and unskilled employees, sustaining livelihoods and providing national income (Nartey, Nanor, and Klake, 2012). Stone quarrying activities are widely spread, occurring mostly in developing countries such as Africa, Asia, Oceania, Central and South America. The dependence on agricultural output in Africa could no longer provide financial security due to a continuous decline in farm yields as a result of climate change, causing loss of production yield (Ashante et al., 2014). This has compelled over 500 million people in developing countries such as Malaysia, India, Kenya, Nigeria, Ghana, and South Africa to engage in occupations such as small-scale surface mining and quarrying for survival (Wang et al., 2010). Nowadays, majority of poor people depend on quarry operations as the only alternative form of livelihood despite the dangers it poses to the environment and human health (Wells, 2000).

2.3.3 Stone Quarrying in South Africa

South Africa is one of the developing countries recognizing stone quarrying as a vehicle to foster socio-economic development of the nation (Ukpong, 2012). The history of quarrying is of gradual association, from early years of family-owned businesses geographically dispersed around the country, to the growth of the industry into larger companies (Solomons, 2012). The quarrying sector in South Africa has received inadequate attention until recently where significant percent of rock minerals remain largely unexploited because of their low economic value compared to gold and platinum group minerals (Dlambulo and Motsie, 2014). However, the sector presents an opportunity for South Africa to diversify the mineral portfolio, especially during times when the high-value mineral commodities such as gold and platinum group elements perform poorly (Malatsi et al., 2012).

Quarrying activities in South Africa are widespread in poverty-stricken regions such as Northern Cape, Northwest, Limpopo, and Eastern Cape provinces with known mineral availability (Ledwaba and Nhlengetwa, 2016). South Africa is estimated to have more than 881 stone quarrying operations with 10 000 to 30 000 number of people participating in the sector (Buxton, 2013). Some of the quarry operations include Silica Quartz (Pty) Ltd, PPC Ltd, WG Wearne, Larfage (Pty) Ltd, Afrisam (Pty) Ltd, Eagle Granite etc. Although only a few stone quarrying companies operating are recognized, the importance of the industry can’t be overstated as it provides for the economic growth of the nation and sustains the already socially depressed population. As key inputs in the construction industry, the demand for industrial minerals is expected to increase, creating opportunities for emerging and existing small-scale miners across South Africa (Ledwaba, 2017).

2.3.4 Tzaneen Stone Quarry

Tzaneen quarry is an advanced small scale mine opened in 1970 for the supply of rock materials to the construction industry. The quarry is mining granite rocks from a shallow open pit mine through the process of drilling, blasting and crushing which lead to addition of heavy metals in the environment. Ayodele et al. (2014) indicated that granite rocks mined at Nigeria contained heavy metals such as Fe, Pb, Cu, Cr, Ni, Mn, Cd and Co. Fe was the most abundant element in the topsoil (0-15 cm) and subsoil (15-30 cm), and Cd was below detectable level while other elements were present in the order: Mn>Cr>Pb>Ni>Cu>Co. The distribution of the heavy metals such as Fe, Pb, Cu, Cr and Ni were highest at 0 m and decreased with distance (Ayodele and Balogun, 2013).

Tiimub et al. (2015) indicated that granite quarry at Asonomaso in the Ashanti region of Ghana contained appreciable amounts of As, Hg, Mn, Cu, Zn, Pb and Fe. The AAS analysis of the soil samples collected from the quarry revealed relatively higher concentrations of As, Cu and Zn in the quarry soil than soil away from the site. The relative abundance of heavy metals across the study area was in the order of Fe > Mn > Zn > Pb > Cu > Cd (Onyedikach et al., 2018). There was statistically significant effect of quarrying activities on the concentration of the heavy metals (Fe, Mn, Zn, Pb, Cu, Cd) at $p < 0.05$ level. The concentrations of the selected metals in a stone quarry at Abia State, Nigeria showed a wide extent of variation with variable patterns in the order: Zn>Cu>Pb>Cr>Ni>Cd>As>Hg. There was a decrease in the concentration of Pb, Ni, Cd, Zn, Cr and As metals with increase in distance from quarry site (Osu et al, 2018). This suggested that the dispersion of Cu, Cr, Hg and Zn metals from the source could have been majorly by wind which distributed dust containing metals in all directions at different magnitude, space and time.

The average concentrations of Pb, Cd, Cr, Cu, Co, Mn, Ni, Zn and Fe in topsoil samples within a depth of 0 to 15 cm from 0 m to 500 m were presented by Etim and Adie (2012) from a limestone quarry in Nigeria. The concentration of various metals showed a wide range of variation with variable patterns in the order: Fe>Mn>Zn>Cu>Pb>Co>Cr>Ni>Cd. There is pattern in variation for each metal with increase in distance from the blasting and crushing area. This suggested that the dispersion of metals from the source could have been majorly by wind which disperses dust containing metals in all directions at different magnitude, space and time. Samples from 0 to 200 m showed higher concentrations for most metals than samples farther away (Etim and Adie, 2012). This could probably be due to their closeness to the exploration area and leaching of metals from the quarry tailings which were found within this distance. Analysis of the quarry material showed conspicuously higher level of Fe as compared to other metals investigated.

The trend showed by these metals could be as a result of their high content in topsoil samples possibly leached from quarry material or transferred by wind during blasting and crushing process. A similar spatial distribution of Ni in soils around an industrial facility in Mexico has been reported to be attributed to input from parent rocks in the surrounding environment (Morton-Bermea, 2010). Cd conspicuously indicated higher levels at 100 and 500 m from the mining area. It was thought that the source of Cd in these two sampling distances is a non-point source. *I-geo* rating indicated that all topsoil samples analysed ranged from practically uncontaminated (<0) to moderately contaminated (1 to 2). All metals showed varying enrichment from the quarry except Mn that showed *I-geo* of <0 for all samples implying that all samples were practically uncontaminated by Mn. This suggested that Mn input in the soil is associated with the parent material that formed the soil or other natural or small anthropogenic non-point sources.

2.3.5 Environmental Impacts of Stone Quarrying

Stone quarrying negatively affects the environment in a variety of ways from drilling, blasting, transport, and disposal of waste rocks (Lameed and Ayodele, 2010). Sati (2015) indicated that either small or large scale, stone quarrying is inherently disruptive to the environment, producing enormous quantities of waste that can have noxious impacts for long period. The major environmental effects are landscape destruction, scenic beauty damage, air pollution, water pollution, soil pollution, plant destruction and ecological disturbance (Lad and Samant, 2014).

The level of land degradation caused by stone quarrying puts forth questions as to whether or not the activity should be allowed to continue (Nartey et al., 2012). Rock blasting and crushing processes produce large quantity of dust, stockpiles and waste materials containing heavy metals in the mining environment (Zhao et al., 2012). Dust emission results in dispersal of these metals around the mine by wind and surface run-off (Avila et al., 2017). Highest concentration levels of heavy metals accumulate at mine sites resulting in soil contamination of such areas with toxic metals such as As, Pb, Cd and Mn, which are non-biodegradable and persistent in the environment (Aloh et al., 2017).

Soil pollution affects not only wildlife, vegetation, and water but also human health (Lad and Samant, 2014). The degree of pollution depends on the local microclimate conditions, the concentration of dust particles in the atmosphere, the size of the dust particles and their composition (Aigbedion and Iyayi, 2007). Although, the degradation of soil quality by pollution may be localized, the environmental impacts are usually larger (Wells, 2000). Heavy may be transported through soil to reach groundwater or taken up by plants, including agricultural crops (Avila et al., 2017). Accumulation of high concentration of these metals in plants growing in such contaminated soils can cause clinical problems when consumed by humans (Ayodele et al., 2014). Hence, it is necessary to assess the pollution status of the soil by heavy metals, take protective measures against excessive exposure and implement soil remediation measures to minimize high levels of these metals in soil.

2.4 Human Exposure Routes to Heavy Metals in Soil

The contamination chain of heavy metals always follows cyclic order: industry, atmosphere, soil, water, plants, animals and humans (Oti-Wilberforce, and Nwabue, 2013). Individuals working with soil in mining or agriculture are exposed to suspended particles from soil into the air. Very small particles may lodge in the lungs and the contaminants may have chance to be absorbed into the bloodstream (Ming-Ho, 2005). Compared to ingestion, this is far less significant source of exposure but may be relevant to those exposed repeatedly over a long period, for example, mine workers (Guo et al., 2006). Soil contaminants may also move into ground or surface water through leaching resulting in contamination of drinking water (Mahipal et al., 2016). Heavy metals in soil may be taken up by plants which are subsequently consumed by humans or by agricultural livestock, causing them to enter human food chain (Khan et al., 2008). The health effects could be chronic, as in the case of toxic metals significantly accumulating up the food chain through soil-plant-human or soil-plant-animal-human routes (Oti-Wilberforce and Nwabue, 2013).

Human beings may get heavy metals in soil through skin contact with contaminated soil and ingestion of soil particles, which can result in skin damage or stomach cancer (Mazumber, 2008). Children are very likely to contact and ingest soil while playing outdoors, which puts them at high risk of exposure to these metals (Sun et al., 2010). It has been estimated that adults may ingest up to 100 mg of dust/day from soil (Adaramodu et al., 2012). Accidental ingestion may also occur in adults, for example, eating vegetables with some soil still attached. However, in some instances people (more especially women and children) deliberately eat soil as a result of pica and geophagy. Pica is a disorder characterized by craving or having appetite for non-edible substances, such as ice, clay, chalk, dirt or sand while geophagy is a practice of eating earthly substances such as clay and chalk, often thought to augment a mineral-deficient diet (Mahipal et al., 2016).

Food is the major source of lead exposure. Other sources include lead dust, petrol and drinking water. Plant food may be contaminated with lead through its uptake from ambient air, soil and animals may then ingest the lead contaminated vegetation. In humans lead ingestion may arise from eating lead contaminated vegetation or animal food. Other source of exposure is through inhalation of lead dust from the soil. Cd metal is readily absorbed by plants in soil and can accumulate in animal milk and fatty tissues when ingested (Khan et al., 2008). Therefore, people are exposed to Cd when consuming such plant and animal-based foods. Inhalation of Cd metal from soil particles contribute significantly to the total body burden compared to ingestion. When inhaled, absorption of Cd from the lungs is much greater than from the gastrointestinal tract.

Mercury can bio-accumulate in animals and humans through food chain. High levels are often found in marine foods (Reily, 1992). Therefore, elevated mercury concentrations are mainly found in liver of lean species and fatty fish species. Methyl mercury has a tendency to accumulate with fish age and with increasing trophic level as a result of long-term exposure. This has led to accumulation of in old fatty predators like tuna, halibut, red fish, shark and sword fish in toxic levels (Murata et al., 2007).

2.5 Potential Health Risks of Heavy Metals

Heavy metals are of great concern to human health due to their toxicity, bio-accumulative potentiality, biodegradability and persistence nature in the environment (Aloh et al., 2017). Heavy metals such as Zn, Cu and Mn are necessary for a good health in small amount, but excessive levels affect human health. Some heavy metals such as Pb, Cd, As and Hg do not perform any known physiological function in human body and are toxic even at extremely low levels of exposure (Sumner, 2000). Heavy metals such as As, Cd and Ni are known carcinogens associated with cancers of the lung, liver, nose and kidney (Aloh et al., 2017). Chronic intake of these metals has undesirable impacts on humans and the associated harmful effects become perceptible only after several years of exposure (Khan et al., 2008). There are screening levels or regulatory limits for metal concentration in soil set up to protect wildlife, environment and human health.

Table 2.1 below shows the WHO and EPA regulatory limits of heavy metals in soil. Exceeding these concentrations is unacceptable for protection of natural resources and human health.

Table 2.1: Showing maximum allowable limit of heavy metals in soil (mg.kg^{-1})

Country	As	Pb	Hg	Cd	Cr	Cu	Zn	Ni
Germany	50	70	0.5	1.0	60	40	150	50
UK	32	450	10	10	130	-	-	130
Australia	20	300	1	3	50	100	200	60

China	30	80	0.7	0.5	200	100	250	50
WHO guidelines	20	100	-	3	100	100	300	50
EU guidelines	-	300	-	3	150	140	200	75
South Africa	5.8	20	0.93	7.5	6.5	16	240	91

Lead

Lead (Pb) is a non-essential element to the human body and excessive intake of the metal can damage the nervous, skeletal, circulatory enzymatic, endocrine and immune system of those exposed to it (Zhang et al., 2012). Once in the bloodstream, lead is primarily distributed among blood, soft tissues, and mineralizing tissues resulting in a dysfunction of the kidney, liver, brain, reproductive and central nervous system (Ming-Ho, 2005). Pb has developmental and neuro behavioral effects over a broad range of doses on fetuses, infants, children and elevated blood pressure in adults (Lin and Aarts, 2012).

Adults usually experience fatigue, loss of memory, nausea, anaemia, insomnia, anorexia; gastrointestinal problems and weakness of the joints when exposed to soil Pb (Levy et al., 1992). Children are particularly sensitive to this metal because of their more rapid growth rate and metabolism, with critical effects in the developing nervous system. This puts them at risk of impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, with those under the age of six being at a more substantial risk (Zhao et al., 2014). Hence, the WHO provisional guideline of 100 mg. kg-1 has been adopted as the maximum allowable limit of lead in soil, whilst DEA set the standard at 20 mg. kg-1 (Table 2.1).

Chromium

Chromium (VI) is the form of Cr commonly found at contaminated sites, which can also occur in the form of Cr (III), depending on pH and redox conditions. Chromium (VI) can be reduced to Cr (III) by soil organic matter under anaerobic conditions (Mazumber, 2008). Although, Chromium

(III) is an essential nutrient, long-term exposure to Cr (VI) compounds can cause damage to the liver, kidney, circulatory and nerve tissues, as well as skin irritation. Effects of chromium (VI) inhalation include asthma, nasal infection, shortness of breath, coughing, wheezing, and gastrointestinal effects such as abdominal pain and vomiting. Chromium is also associated with allergic dermatitis in humans (Podsiki, 2008).

Arsenic

Arsenic (As) is a metal that commonly occur as a component of sulphur containing ores such as metal arsenide and arsenate compounds. These compounds are toxic to the environment and carcinogenic human health (Mahipal et al., 2016). Exposure to arsenic compounds in soil can cause skin damage, increased risk of cancer, and problems with circulatory system (Mazumber, 2008). The toxic effects of arsenic depend specially on oxidation state and chemical species among others (Singh et al., 2007). Inorganic As is considered carcinogenic and related mainly to lung, kidney, bladder and skin disorders. The toxicity of As in its inorganic form has been known for decades under the following acute toxicity, synchronic and chronic toxicity, genetic toxicity, developmental and reproductive toxicity, immunotoxicity, biochemical and cellular toxicity (Mudhoo et al., 2011). Hence, the WHO provisional guideline of 20 mg.kg-1 has been adopted as the standard for As metal in soil (Table 2.1).

Cadmium

The target organs for Cd toxicity have been identified as liver, placenta, kidneys, lungs, brain and bones (Sobha et al., 2007). Depending on the severity of exposure, the symptoms of effects include nausea, vomiting, abdominal cramps, dyspnea, muscular weakness, pulmonary edema and death. Pulmonary effects (emphysema, bronchiolitis, alveolitis) and renal effects may occur following subchronic inhalation of Cd and its compounds (Adelokun et al., 2016). The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction (Campbell, 2006). The DEA contaminant level for Cd in Soil is 7.5 mg.kg-1 whereas the WHO the adopted the provisional guideline of 3 mg.kg-1 (Table 2.1).

Copper

Copper (Cu) is the third most used metal in the world essential for plant and animal growth (Wuana et al., 2008). In humans, it helps in the production of blood haemoglobin while in plants; it helps with seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses exceeding 16 mg. kg^{-1} can cause anaemia, liver and kidney damage, stomach and intestinal irritation (DEA, 2010). In the soil, Cu strongly complexes to the organic matter implying that only a small fraction of copper will be found in solution as ionic copper, Cu (II) (Martin and Ruby, 2004).

Mercury

Mercury is one of the most toxic heavy metals in the environment. The toxicity of Hg depends on its chemical form (ionic, metallic or organic) (Essumang et al. 2007). Exposure to high level metallic, inorganic, or organic Hg can permanently damage the brain, kidneys, and developing fetus. Organic Hg compounds easily past across biomembranes and are lipophilic.

Nickel

Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts of 50 mg. kg-1 are exceeded (Chiroma et al., 2014). This can cause various kinds of cancer within the human body, mainly of those that live near mines and refineries (Khodadoust et al., 2004). Ni is also responsible for health issues such as depression, heart attacks, hemorrhages and kidney problems. Workers who are in close contact with the nickel powder are more likely to suffer from respiratory cancer. The content of Ni in the environment is positively correlated with nasopharyngeal carcinoma (Chen et al., 2015).

Manganese

Mn is essential in trace amounts, but excessive level of exposure and absorption leads to toxicity and detrimental health effects (Ykateryna et al., 2011). Excess Mn interferes with the absorption of dietary Fe and long-term exposure may result in Fe-deficiency anaemia and the impairment of the activity of copper dependent metalloenzymes. Significant increase in Mn concentration has been observed in patients with severe hepatitis, dialysis and cardiac arrests (Rollin, 2011).

2.6 Remediation of Heavy Metal Contaminated Soils

The purpose of soil remediation approach is to reduce metal bioavailability with reduced risk for a long term in order to bring solution that is protective of human health and the environment

(Norbaya et al., 2014). Remediation is based on assessments of human health and ecological risks subject to an array of regulatory requirements where no legislated standards exist, or standards are advisory (Guo et al., 2012). Failure to mitigate high concentration of heavy metals in soil may result in mobilization of heavy metal contaminants into flora, fauna and subsequently into man with consequent deleterious health effects. However, the effects of heavy metals on the ecosystem can be mitigated by immobilization (Dermont et al., 2008). Research continues on the effective, less expensive and environmentally friendly methods of immobilizing heavy metals in contaminated soil thereby making them less bioavailable. One of the currently researched decontamination methods for heavy metal polluted matter is phytoremediation which is the use of plants to accumulate heavy metal contaminants and also to restrict their dissemination from the polluting source (Kumar et al., 1995).

Soil contamination can be determined by comparison of observed heavy metal concentrations with soil quality standards for a particular regulatory domain, or by performance of a site-specific risk assessment. Remediation goals for heavy metals may be set as total metal concentration or as leachable metal in soil or combined. Remediation technologies include, gentle in-situ remediation, in-situ harsh soil restrictive measures, and ex-situ harsh soil destructive measures (Wuana et al., 2008). The goal of the last two harsh alleviating measures is to avert hazards either to man, plant, or animal while the main goal of gentle in situ remediation is to restore the malfunctionality of soil (soil fertility), which allows a safe use of the soil (Wang et al., 2010).

USEPA (1989) has broadly classified remediation technologies for contaminated soils into source control and containment remedies. Source control involves in situ and ex situ treatment technologies for sources of contamination. In situ or in place means that the contaminated soil is treated in its original place; unmoved, unexcavated; remaining at the site or in the subsurface (Martin and Ruby, 2004). Whilst ex-situ means that, the contaminated soil is moved, excavated, or removed from the site or subsurface for removal of the contaminant. Containment remedies involve the construction of vertical engineered barriers (VEB), caps, and liners used to prevent the migration of contaminants (Guo et al., 2006). Five categories of remediation approaches include isolation, immobilization, toxicity reduction, physical separation, and extraction (Dermont et al., 2008).

Once soil suffers from heavy metal contamination, it is difficult to be remediated. In practice, it may be more convenient to employ a hybrid of two or more of these approaches for more cost effectiveness (Wang et al., 2010). The key factors that may influence the applicability and selection of any of the available remediation technologies are: (i) cost, (ii) long-term effectiveness/ permanence, (iii) commercial availability, (iv) general acceptance, (v) applicability to high metal concentrations, (vi) applicability to mixed wastes (heavy metals and organics), (vii) toxicity reduction, (viii) mobility reduction, and (ix) volume reduction (Finzgar et al., 2006)

CHAPTER THREE: METHODOLOGY

3.1 Introduction

This chapter describes all steps undertaken to investigate a research problem and the rationale for applying specific procedures used to generate the data through the laboratory analysis of samples. Figure 3.1 shows the steps and procedures adopted in this study in form of a flow chart.

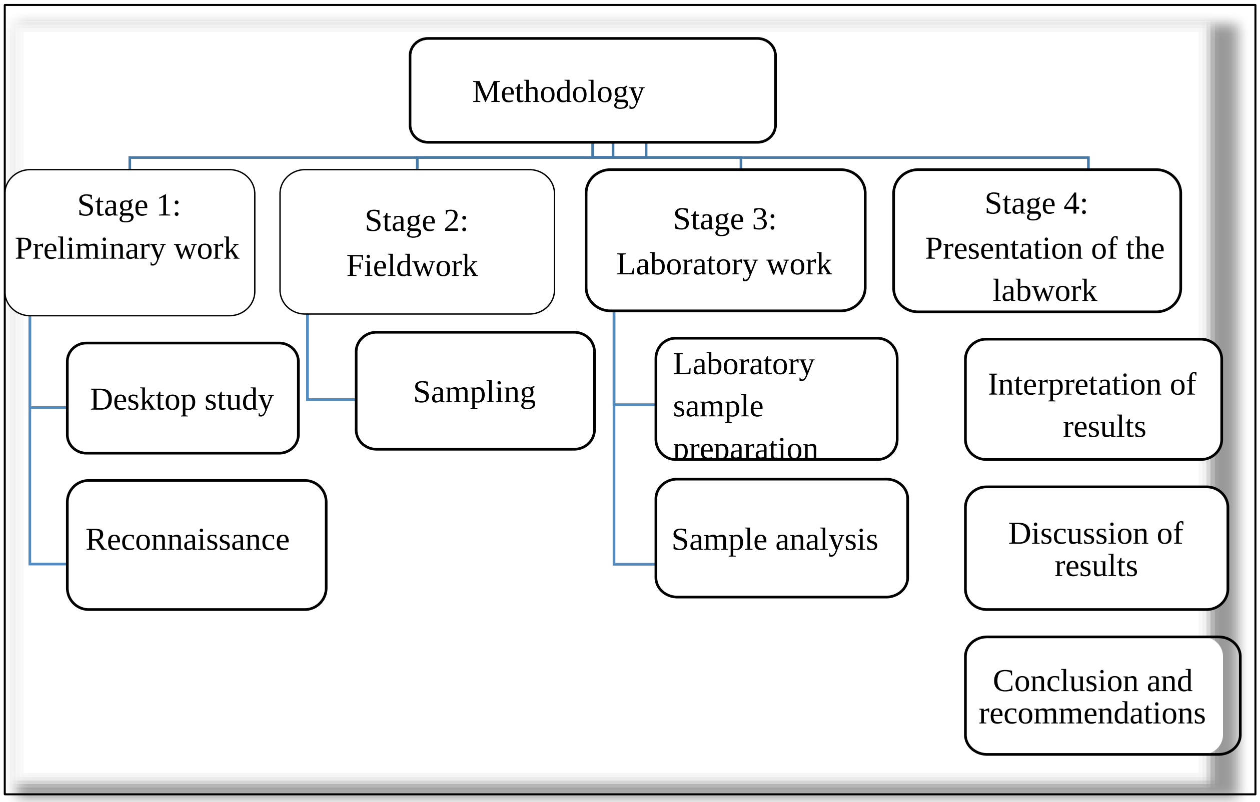


Figure 3.1: A Flow chart showing the methods and procedures used in the study.

3.2 Preliminary Studies

3.2.1 Desktop Study

During the desktop study, existing data from the public domain, scientific, government published data and commercial databases and available project sources was gathered and analysed with the aim of gaining broad information about the study area. Relevant materials providing information about geology and economic mineral occurrence within the granite rocks were gathered from books, journals, thesis, and dissertations. This review was conducted on materials such as; books, journals, reports, and maps. Internet websites were also visited to obtain other reference materials.

3.2.2 Reconnaissance survey

The study area was surveyed to acquire the preliminary data and generalize geology, pedology, vegetation, and topography. A snap survey of the soil, rock types and vegetation cover was done to deduce geological information of the study area. The presence of agricultural activities, rivers, and neighbouring communities was checked to see how far they are located from the mine site in order to assess the magnitude of heavy metals pollution in the study area. Rock and soil samples were collected from the mine to assess pollution status of heavy metals and their health risks.

3.3 Research Design

Research design is the plan for connecting the conceptual research problems to relevant empirical research. Quantitative research method was adopted in the study following a simple randomized sampling procedure (Maree, 2016). Samples were collected at specific points with distance away from the mine. Samples collected were analysed for their metal contents using AAS. Pollution indices were used to determine the degree of heavy metal pollution in soil and then use EPA health risk assessment to identify potential health risks. The quantitative data generated from these sources was analysed using computer Statistical Package for Social Sciences (SPSS 12.0.1 edition) software, specifically with the aid of frequency, mean, range, and variance and perform the least significant difference (LSD) of the total metal concentration in soil.

3.4 Data collection methods

Primary data was collected where actual soil sampling is carried from the mine with distance towards the nearby community to determine distribution and concentration of heavy metals in the study area. Below is the outline of the data collection method for soil sampling method and analysis of heavy metals.

3.4.1 Soil Sampling Method

Soil samples were collected at 0-15 cm depth using a soil auger in the study area and the pits were filled back (Ayodele et al., 2014). Soil samples were collected along a straight line moving away from the mine towards the nearby village of Mokgolobotho approximately 2 to 2.5 km from the quarry. Sampling distance constituted 0m, 25m, 50m 100m with subsequent intervals set at 100m apart towards the nearby village (Wu et al., 2010). Soil samples collected at the crushing area represent samples at zero meters (Figure 3.2). A total of 10 soil samples per site were collected (Figures 3.2 and 3.3).

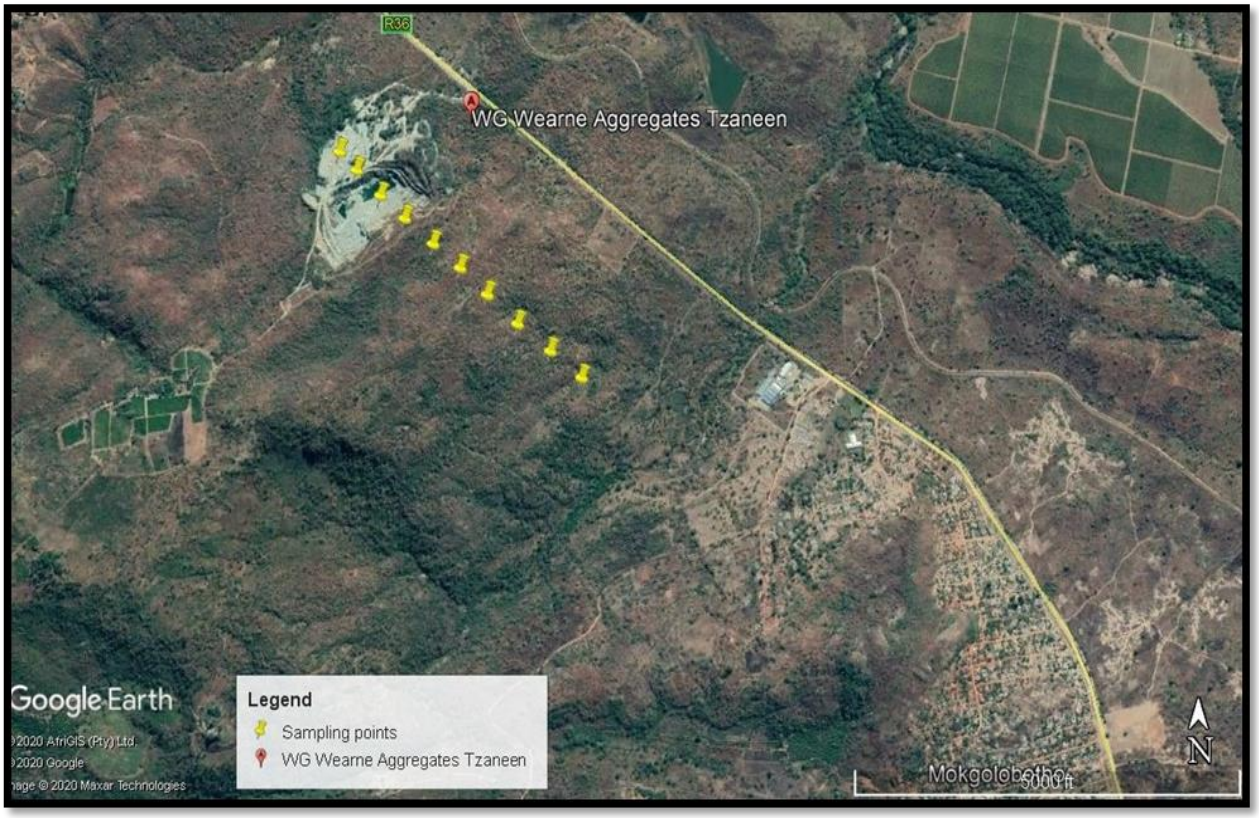


Figure 3.2: Soil sampling map of the study area.

Each sample was stored in a paper sample bag and labelled. The co-ordinates of the sampling locations were recorded with a hand-held GPS (Table 3.1). It was discovered that fine dust from the soil samples collected are itchy to the eyes and nose. As result the researcher took protective cover against prolonged exposure to the soil.

Figure 3.3: Photo showing soil sampling at the quarry.

Table 3.1: Sampling point coordinates of the quarry with distance away

Sampling point name	Latitude	Longitude	Elevation	Altitude
QS1	23^{0}51’34.65”	30^{0}13’20.91”	659 m	1675 m
QS2	23^{0}51’37.02”	30^{0}13’23.52”	661 m	1675 m
QS3	23^{0}51’40.36”	30^{0}13’26.97”	662 m	1675 m
QS4	23^{0}51’43.22”	30^{0}13’30.77”	693 m	1675 m
QS5	23^{0}51’46.66”	30^{0}13’34.86”	722 m	1675 m
QS6	23^{0}51’49.69”	30^{0}13’38.84”	755 m	1675 m
QS7	23^{0}51’52.86”	30^{0}13’42.73”	755 m	1675 m
QS8	23^{0}51’56.28”	30^{0}13’47.28”	718 m	2825 m
QS9	23^{0}52’00.23”	30^{0}13’51.82”	680 m	2825 m
QS10	23052’04.00”	30013’56.61”	657 m	3028 m

A total of 10 rock samples was collected from the quarry in order to analyse their metal contents (Figure 3.4). It was discovered that there are three rock types different in colours. There was a black rock (basalt), light grey-whitish rock (granite gneiss) and brown-yellowish rock (overburden rock).

Figure 3.4: Photo showing rock sampling at the quarry.

A total of 12 samples was collected from the community as shown in Figures 3.5 and 3.6 below. The samples were collected randomly along a straight line in order to discover the metal trends with distance from the quarry. Table 3.2 below shows the sampling coordinates in the nearby community.

Figure 3.5: Soil sampling map of Mokgolobotho area

Figure 3.6: Showing soil sampling from the nearby community of Mokgolobotho village

Table 3.2: Sampling points coordinates of the nearby community

Sampling point name	Latitude	Longitude	Elevation	Altitude
V1	23^{0}52’17.14”	30^{0}14’26.77”	629 m	2823 m
V2	23^{0}52’17.03”	30^{0}14’37.27”	639 m	2823 m
V3	23^{0}52’18.97”	30^{0}14’47.91”	627 m	2823 m
V4	23^{0}52’27.94”	30^{0}14’49.91”	630 m	2823 m
V5	23^{0}52’38.38”	30^{0}14’51.36”	629 m	2823 m
V6	23^{0}52’49.52”	30^{0}14’53.42”	612 m	2823 m
V7	23^{0}53’01.39”	30^{0}14’55.97”	608 m	2823 m
V8	23^{0}53’14.72”	30^{0}15’58.40”	628 m	2823 m
V9	23^{0}53’26.46”	30^{0}15’01.01”	643 m	2823 m
V10	23^{0}53’37.61”	30^{0}15’02.23”	617 m	2823 m
V11	23^{0}53’47.21”	30^{0}15’04.12”	606 m	2823 m

V12	23^{0}53’58.78”	30^{0}15’05.41”	610 m	2823 m
Creche no.1	23^{0}52’29.3”	30^{0}14’51.6”	609 m	873 m
Creche no.2	23^{0}53’12.08”	30^{0}15’2.09”	618 m	682 m
Creche no.3	23^{0}53’12.24”	30^{0}15’2.31”	618 m	682 m
10 km away	23^{0}52’57.44”	30^{0}18’19.48”	549 m	2823 m

An additional 8 composite samples were obtained from a school playground area which was approximately 2.9 km from the quarry (Figures 3.7 and 3.8). The playground was divided into two sets of quadrants to ensure total coverage of the recreational area. Four sub-samples within each quadrant were homogenized to form one composite sample. In addition, 3 representative soil samples were collected from the creche from the nearby community which was approximately 2.5 km away from the quarry. Five background topsoil samples were collected from a control location about 10 km away from the study area for comparison purposes and combined to a composite (Etim and Adie, 2012).

Figure 3.7: Soil sampling map of the school playground area in the study area.

Figure 3.8: Photo showing soil sampling at the school playground area in Mokgolobotho village.

Table 3.3: Sampling points coordinates of the school playground.

Sampling point name	Latitude	Longitude	Elevation	Altitude
S1	23^{0}53’05.59”	30^{0}15’02.02”	609 m	880 m
S2	23^{0}53’05.02”	30^{0}14’59.83”	610 m	859 m
S3	23^{0}53’05.41”	30^{0}15’02.87”	608 m	894 m
S4	23^{0}53’05.78”	30^{0}15’01.66”	610 m	894 m
S5	23^{0}53’03.64”	30^{0}15’00.83”	608 m	859 m
S6	23^{0}53’04.56”	30^{0}14’58.45”	615 m	888 m
S7	23^{0}53’05.59”	30^{0}14’57.29”	615 m	859 m
S8	23^{0}53’06.27”	30^{0}14’59.41”	613 m	859 m

3.4.2 Physiochemical properties of the soil samples

Physicochemical characterization was carried out on air-dried soil samples in the MEG laboratory. 50 g of soil samples was poured inside a glass beaker and mixed with deionised water (1:2.5 soil: water ratio) for analysis of pH, electrical conductivity (EC) and total dissolved solids (TDS) (figure 3.9). The samples were suspended in the deionised water for at least 24 hours to allow sufficient saturation. The parameters were measured using laboratory pH meter, conductivity meter, and TDS meter, respectively. The measurement were repeated three times for each samples and averaged to obtain pH and hydrogen ion concentration. The glass beakers were thoroughly cleaned with soap to avoid cross contamination.

Figure 3.9: Physicochemical characterization of the soil samples

3.4.3 Sample preparation

The samples collected from the study area were transported to the University of Venda MEG laboratory for preparation and analysis. Firstly, the soil samples were oven dried at 110 ^{0}C for at least 12 hours to remove excess moisture, after which they were sieved through a set of sieves ranging from 4 mm to 32µm and the empty bottom pan. The mass of each sieve was weighed, recorded and stacked in ascending order. Each soil sample was carefully poured on top of the stacked sieves and the top was covered with its lid. The samples were agitated at 90 amplitude for about 10 min using AS 200 basic shaker machine (figure 3.9). The stack was allowed to rest to allow lightweight soil to settle. Then, the sieves were carefully removed from the stack and the corresponding masses were weighed and recorded. The researcher used personal protective equipments (gloves, lab coat, facemask and safety googles) throughout laboratory work Sampling implements and other work surfaces were cleaned thoroughly between samples during preparations and analysis to avoid cross contamination. The mass of the sieves/pan were subtracted from the previously recorded mass of soil and sieves/pan to compute the total mass of soil retained in all the sieve and pan. The data obtained was used to determine the percentage of different grain sizes contained within the soil sample and to get fine fractions for milling and chemical analyses (Ayodele et al., 2014).

Figure 3.10: The procedure of sieving soil samples.

Firstly, the rock samples were crushed with a sledge to reduce their sizes. The samples were then crushed furthermore into smaller pieces using a Jaw crusher (Figure 3.10). After crushing each sample, the jaw crusher was cleaned to avoid cross contamination. The crushed samples were grinded to powder form using RS 200 milling machine. The machine was set to operate at a rotational speed of 700 rpm and mill for a minimum of 4 min per sample. The milling pot was also thoroughly wiped with acetone between each sample to prevent cross contamination.

Figure 3.11: The process of crushing and milling rock samples.

3.4.4 Major elements analysis

The milled samples were also transported to ERM lab for analysis of major elements (such as SiO2, Al2O3, Fe2O3, MgO, CaO, and K2O) using a handheld XRF machine. Samples were filled into the liquid cup and sealed with a foil cover (Figure 3.11). The foil roll was placed gently on top of the sample cup. A plastic ring counterpart that is slightly wider than the sample cup was used to press down onto the ring gently but firmly to create a taunt smooth film on the top of the sample cup. After the sample cup is sealed with foil cover, it was placed into the XRF spectrometer for analysis. Once the analysis is complete, the sample can either be discarded or retrieved for further testing of use.

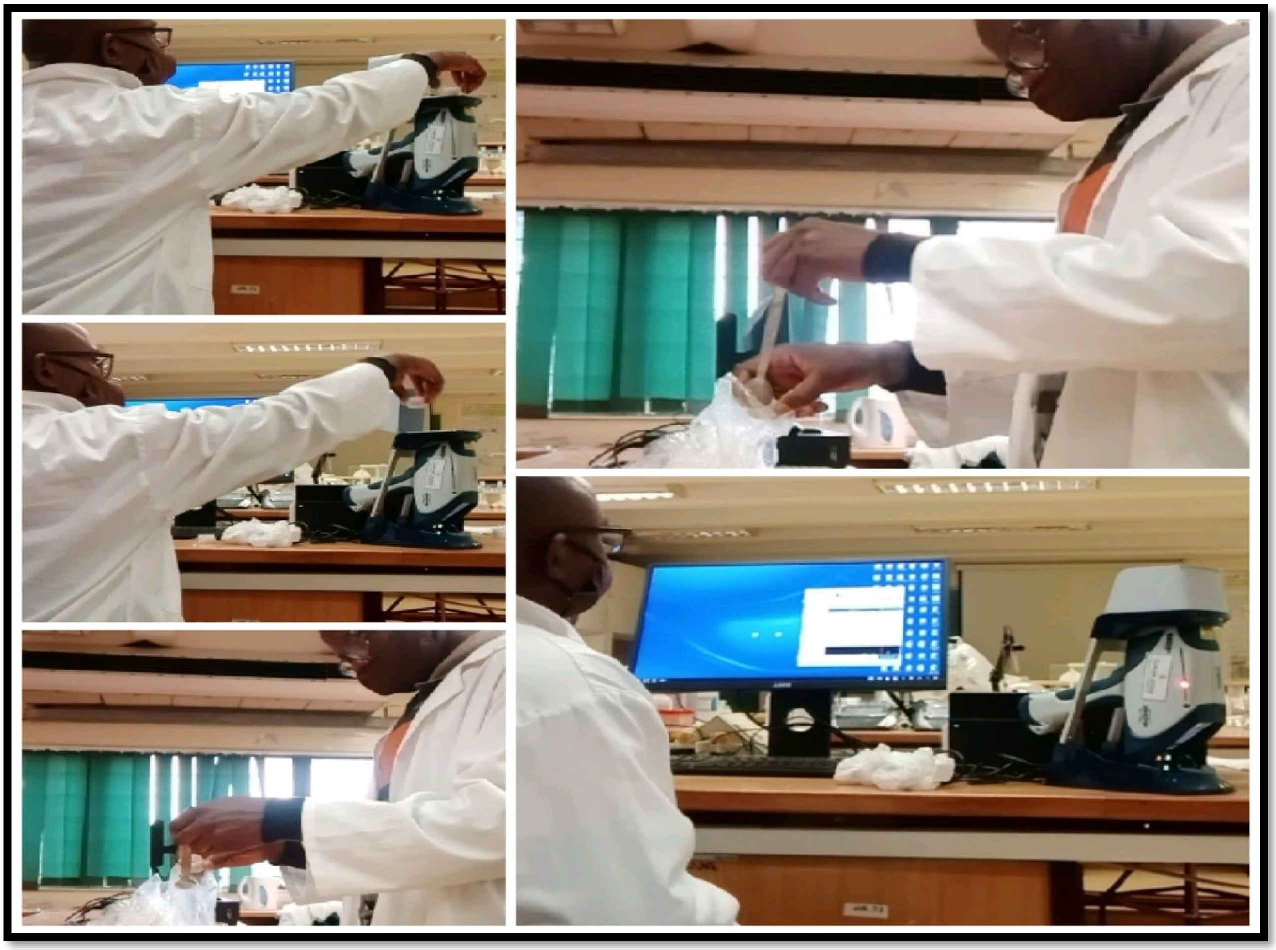


Figure 3.12: The analysis of major elements using handheld XFR machine.

3.4.5 Digestion of samples

The milled samples were transported to the HWR laboratory for digestion. Significant fraction of all metals was leached by weighing 0.5 g of each sample using a weighing boat, model AS 220.R2. The weighed samples were then transferred into the vessels and mixed with 9 mL of nitric acid and 3 mL of HCl. The mixture was done inside the gas fume machine; model 321 Midcap Captair, to prevent absorbing the smoke of the acid (figure 3.12). The samples were digested for 10 min at the temperature of 110^{0}C and allowed to cool for 20 min in the digestion machine, model 240/50, MARS ONE. After digestion, the samples were transferred into 50 mL centrifuge tube and mixed with deionised water for dilution. The samples were filtered into volumetric flasks using Whatman filter paper (Adie and Osibanjo, 2009). The samples were then labelled and put inside fridge at 4^{o}C until analysis.

Figure 3.13: Showing the procedure for digestion of samples.

The digested samples were transported to the chemistry lab for analysis. Heavy metals such as Cr, Pb, Cd, Zn, Cu, Ni, Co and Mn were analysed from the samples using AAS machine (Etim and Adie, 2012). The solution was fed into the AAS and computerized results read against the standard solution (Figure 3.13).

Figure 3.14: Analysis of the soil sample using AAS (Silvia et al., 2004).

3.5 Data Analysis

The data was analysed using AAS. The collected data was cleaned, edited for accuracy and analysed using descriptive statistics in order to give numerical summaries of central tendencies and measures of dispersion. Statistical tools were applied on the data to study the relationship between heavy metals distribution with distance from the quarry site and level of pollution compared with the background levels (Etim and Adie, 2012). Descriptive statistics such as mean, range, frequency, standard deviation and coefficient of variation of heavy metals were determined using statistical package for social sciences (SPSS) software, version 17.0 (IBM SPSS Inc., Chicago USA). Analysis of variance (ANOVA) was also performed to test the significance of differences in total metal concentrations in the soil samples of the study area (Maas et al., 2010). The data obtained was used to conduct pollution assessment and health risk assessment in the section 3.6 and 3.7 below.

3.6 Pollution Assessment Methods

The degree of pollution by heavy metals in the study area was assessed using geochemical indices such as contamination factor (CF), pollution load index (PLI), enrichment factor (EF) and geo-accumulation index (Igeo) (Zhao et al., 2012). The pollution status of heavy metals such as Cr, Pb, Cd, Zn, Cu, Ni, Co, and Mn was assessed using the background concentrations provided by Wedepohl (1995) in Table 3.4 below. The following geochemical indices as outlined in the proceeding sections were used to assess the heavy metal concentrations and pollution status of the soil samples.

Table 3.4: Showing background concentration for selected heavy metals in soils (Wedepohl, 1995).

Metals	Background concentration (mg/kg)
As	2
Pb	17
Cd	0.10
Cr	35
Zn	52
Cu	25
Ni	19
Co	12
Hg	0.056
Fe	43 200
Mn	716

3.6.1 Contamination factor (CF)

CF expresses the level of soil contamination by heavy metals in the study area using the equation below as indicated by Zhao et al (2012):

$$CF = Cn/Bn$$

Where, Cn (mg/kg) is the measured concentration of each heavy metal and Bn is background value for each metal. Contamination factor that is less than 1 (CF<1) refers to low contamination, 1≤CF<3 means moderate contamination, 3≤CF≤6 indicates considerable contamination and CF>6 indicates very high contamination. The contamination factors of all metals studied were used to determine the pollution load index.

3.6.2 Pollution load index (PLI)

PLI is expressed as arithmetic mean of the analysed metal pollutants. Site quality was evaluated for the extent of metal pollution by employing the method developed by Tomlinson et al. (1980). PLI was calculated using the following equation:

$$PLI = \sum CFn$$

Where n is the number of metals studied and CF is the contamination factor. PLI=0 means "background concentration", 0<PLI<1 means "unpolluted", 1< PLI<2 indicates "unpolluted to moderately polluted", 2<PLI<3 means "moderately polluted", 3<PLI<4 signifies "moderately to highly polluted", 4<PLI<5 depicts "highly polluted" whereas PLI > 5 corresponds to "very high polluted" (Zhao et al, 2012).

3.6.3 Enrichment factor (EF)

Enrichment factor (EF) is used to determine the pollution status of heavy metals in the soil due to the influence of the anthropogenic activity to the natural environment (Jayarathne et al., 2018). Only metals enriched in the soil samples with respect to average crustal composition were considered for health risk assessment (Caeiro et al., 2005). Element Fe was selected as the reference in this case because is an abundant metal in the earth crust, allowing EF to be calculated using the equation below.

EF= (Si/Sn) sample / (Bi/Bn) reference

Where, Si = concentration of heavy metal in the soil sample
Sn = Concentration of Fe in the soil sample
Bi = heavy metal concentration of the reference sample
Bn = Fe concentration of the reference sample

If the element EF is close to 2, it can be considered that the element showed no enrichment compared to the soil source and it is therefore mainly composed of soil particles. Values in the range of 2-5 show moderate enrichment, indicating that element is influenced by human activities in addition to soil sources (Jayarathne et al., 2018). If the element EF is >5, this is an indication of significant enrichment.

3.6.4 Geo-accumulation index (Igeo)

Geo-accumulation index (Igeo), first used by Muller in 1969, is a tool that provides the extent of soil pollution concerning the background concentrations of the polluting metals (Gupta et al., 2014). The index considers the influence of geological and anthropogenic factors on natural background values of heavy metals in soil (Wei et al., 2009). Therefore, a change in the index reflects the nature of the heavy metal distribution and the impact of external anthropogenic factors on the environment (Table 3.5).

The Igeo formula is expressed as shown below.

$I\text{-}geo = \log_2 (Si/1.5\ Bi)$

Where, Si = concentration of element in the sample

Bi = background reference concentration

1.5 = is the modified index, which is usually used to characterize geologic influences.

Table 3.5: Showing geo-accumulation index of heavy metals in soil (Gupta et al, 2014).

I-geo Contamination	Geo-accumulation class intensity	Index description
>5	6	Extremely contaminated
4-5	5	Strongly to extremely contaminated
3 – 4	4	Strongly contaminated
2 – 3	3	Moderately to strongly contaminated
1-2	2	Moderately contaminated
0-1	1	Uncontaminated to moderately contaminated
0	0	Uncontaminated

3.7 Human Health Risk Assessment

Human health risk assessment is a process used to estimate the potential health risks that might occur as a result of exposure to carcinogenic and non-carcinogenic metals. Health risk assessment is carried out using the guidelines and exposure factors released by the U.S EPA (Table 3.6). The risk assessment process is made up of four basic steps: hazard identification, exposure assessment, toxicity (dose-response) assessment, and risk characterization (Caeiro et al., 2005). Hazard identification basically aims to investigate metals that are present at any given location, their concentration, and spatial distribution (Zhao et al, 2012). Exposure assessment is carried out by measuring the possible average daily intake (ADI) of heavy metals by individuals via three exposure routes (Wang et al., 2010).

Toxicity assessment (dose-response) estimates the toxicity due to the level of exposure to heavy metals in soil. The carcinogenic and non-carcinogenic factors are two important toxicity indices for health risk assessment. Risk characterization predicts the potential carcinogenic and non-carcinogenic health risks as a result of exposure to toxic metals in the study area. The population was divided into three groups, which include infants, children and adults due to their behavioural and physiological differences (USEPA, 1989). All the information gathered was integrated to arrive at quantitative estimates of cancer risk and hazard indices for all individuals with different age groups (US EPA, 2004).

3.7.1 Exposure Assessment

Exposure to heavy metals in soil was estimated via three routes separately for infants, children, and adults. Average daily intake was used to determine the level of human exposure to heavy metals in soil. The general exposure equations used below are based on recommendations provided by USEPA (1989) in Table 3.6 and 3.7.

Inhalation of particles from soil

$ADI_{inhalation} = (C \text{ x } IR_{air} \text{ x } EF \text{ x } ED) / (BW \text{ x } AT \text{ x } PEF)$ .... (1)

Where, $ADI_{inhalation}$= average daily chemical intake through inhalation; C= concentration of heavy metal in the soil (mg/kg), IR_{air}= Inhalation rate through air (m3/day), EF= Exposure frequency (day/year); ED= exposure duration (years), BW= body weight (kg); AT= averaging time: for non-carcinogenic, AT= ED x 365 d x 24 hours; For carcinogens, AT = 70 x 365 x 24 hours, PEF = particulate emission factor (m3/kg)

Ingestion of soil particles

$ADI_{ingestion}$ = (C x IR x EF x ED x CF) / (BW x AT) .... (2)

Where, $ADI_{ingestion}$= average daily chemical intake through ingestion, IR= Ingestion rate (mg/day), CFfrgvtb5= conversion factor in kg/mg (10^{-6}) (Table 3.6).

Table 3.6: Shows receptor characteristics for infant, child and adults (US EPA, 1989).

	Infant	Child	Adult
Age	0-6 months	5-11 years	≥ 20 years
BW (kg)	8.2	32.9	70.7
AF (mg/cm^2)	0.1	0.2	0.07
FE	0.61	0.61	0.61
Conversion factor (CF) (kg/mg)	0.001	0.001	0.001
PET (m^3/kg)	1.3x 10^9	1.3x 10^9	1.3x 10^9
Ingestion rate (kg/d)	0.00002	0.00002	0.00002
Inhalation rate (m^3/d)	2.1	14.5	15.8
Time spent outdoors (h/d)	1.5	1.5	1.5
Skin surface area (cm^2)			
Hands	320	590	890
Arms	550	1480	2500
Legs	910	3070	5720
Total	3620	10140	17640
Soil loading exposed skin (g/cm^2/event)			
Hands	0.00010	0.00010	0.00010
Surfaces other than hands	0.00001	0.00001	0.00001

Table 3.7: Recommended Default Exposure Factors by (U.S. EPA, 2011a).

Symbol	Definition	Recommended value	Source
LT	Lifetime (years)	70	U.S EPA 1989 (pg. 6-22)
AT	Averaging time (days/year)	365	U.S. EPA 1989 (pg. 6-33) (equal to exposure duration for non-carcinogens and 70 years for carcinogens)
ET	Air exposure time		U.S EPA 1991a
	(hours/day) Worker (ETw)	8	The workday
	Resident (ETr)	24	The whole day
ED	Exposure duration (years)		
	worker (EDw)	25	U.S. EPA 1991a (pg. 55)
	Resident (EDr)	26	U.S. EPA 2011a (Table 16-108)
	adult (EDra)	20	U.S. EPA 1991a (pg. 15)
	Child (EDrc)	6	U.S. EPA 1991a (pg. 6 and 15)
EF	Exposure frequency		
	(days/year)	250	U.S. EPA 1991a (pg. 15)
	Worker (EFw)	350	
	Resident (EFr)		
BW	Body weight (kg)- Worker	80	U.S EPA 1991a (pg. 15)
	(BWw)		Weighted mean values for adults 21-78 years,
	Resident		Weighted average of mean body weights (birth to < 6 years)
	Adult (BWa)	80	
	Child (BWc)	15	
SA	Skin surface area (cm^2)		U.S. EPA (Table 7-2, 7-8, 7-12)
	Adult worker	3,527	-Weighted average mean values for head, hands and forearms (male and female 21+ years)
	Resident (SAr)		-Weighted average of mean values for head, hands, forearms
	Adult (SAa)	6,032	and lower legs (male and females 21+ years)
			-Weighted average of mean values for head, hands, forearms,
	Child (Sac)	2, 373	lower legs and feet (male and female, birth to < 6 years)
IRS	Resident soil ingestion rate (mg/day)		U.S EPA 2011a (Table 5-11)
	Adult (IRSa)	200	Upper bound values accounting for both soil and dust
	Child (IRSc)	100	ingestion
AF	Soil adherence factor adult (mg/cm^2)		U.S EPA 2011a (Table 7-2 and section 7.2.2) Arithmetic mean of weighted average of body parts-specific
	Worker (AFw)	0.12	(hands, forearms and face) mean adherence factors for industrial activities.
	Resident		
	Adult (AFa)	0.07	U.S EPA 2004
	Child (AFc)	0.2	

Dermal contact

ADI_{dermal} = (C x SA x FE x AF x ABS x EF x ED x CF) / (BW x AT) .... (3)

Where, ADI_{dermal} = average daily intake through dermal contact (mg/kg/day), SA= exposed skin area (cm^2), FE= fraction of the dermal exposure ratio to soil, AF= is the soil adherence factor (mg/cm^2), ABS= fraction of the applied dose absorbed across the skin (Table 3.8); EF, ED, BW, CF, and AT are as defined earlier in Equation (1).

Table 3.8: Relative dermal absorption factors (US EPA, 2011a).

Metal	Relative dermal absorption factor (unit less) (ABS)
As	0.03
Cd	0.14
Cu	0.1
Pb	0.006
Ni	0.35
Zn	0.02

3.7.2 Non-Carcinogenic Risk Assessment

Non-carcinogenic health risk is typically characterized by hazard quotient (HQ), a unit less number expressed as the probability of an individual suffering an adverse health effect as a result of exposure to toxic heavy metals (Caeiro et al., 2005). The HQ is defined as the average daily dose (ADI) divided by the reference dose (RFD) in mg/kg/day (US EPA, 2011a). The reference dose is an estimate of individual daily exposure to toxic metals that is not likely to present an appreciable risk of deleterious effects during a lifetime (US EPA, 2011a). Hazard quotient of a single element within a single route of exposure for all individual age groups was calculated using the equations below.

$HQ_{inhalation}$= $ADI_{inhalation}$ / RfD.. (5)

$HQ_{ingestion}$= $ADI_{ingestion}$ x RfD... (6)

$HQ_{dermal} = ADI_{dermal} / RfD$.. (7)

Where, ADI is the average daily intake (averaged over a 70-year lifetime). R*f*D is the reference dose (mg kg^{-1} day^{-1}) provided by USEPA (USEPA, 2010) in Table 3.9.

All HQs calculated were added to generate a hazard index (HI) in order to estimate the overall potential risk posed by more than one metal through each exposure routes. The hazard index was calculated using the equation below.

$HI = \sum HQ_i = HQ_{inhalation} + HQ_{ingestion} + HQ_{dermal}$.. (8)

If the HI value is less than one, the exposed population is unlikely to experience adverse health effects. If the HI value exceeds one, then there may be concern for potential non-carcinogenic health effects (US EPA, 2001).

Table 3.9: Oral reference dose of various heavy metals used for the determination of toxicity responses (*Adapted* from USEPA, 1991 and DEA, 2010).

Heavy Metal	Oral R*f*D (mg/kg/day)	Dermal R*f*D	Inhalation R*f*D
As	3.0×10^{-4}	3.0 x 10-4	3.0 x 10-4
Cd	5.0×10^{-4}	5.0 x 10-4	5.7 x 10-5
Cu	4.0×10^{-2}	2.4 x 10-2	-
Pb	3.6×10^{-3}	-	-
Zn	3.0×10^{-1}	7.5 x 10-2	-
Mn	1.4×10^{-2}	-	-
Hg	3.0×10^{-4}	3.0 x 10-4	8.6 x 10-5
Cr (VI)	3.0×10^{-3}	-	3.0 x 10-5
Ni	2.0×10^{-2}	5.6 x 10-3	-

3.7.3 Carcinogenic Risk Assessment

Carcinogenic risk is estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogens. It is defined as the average daily intake (ADI) of a toxic over lifetime divided by the carcinogenic slope factor (CSF) (USEPA, 2010). The risk was calculated using the equation below.

$$CR = ADI \times CSF \qquad (9)$$

Where, CR is the probability of carcinogenic risk (dimensionless), ADI is the average daily dose and CSF is the carcinogenic slope factor (1/mg/kg/day). The carcinogenic slope factor (CSF) converts the estimated daily intake of a toxic metal averaged over a lifetime of exposure directly to the incremental risk of an individual developing cancer (USEPA, 1989). The incremental lifetime carcinogenic risk of toxic metals through all combined exposure routes was determined using equation (10) below:

$$ILCR = (ADI_{ingestion} \times SF_{oral}) + (ADI_{inhalation} \times SF_{inhalation}) + (ADI_{dermal} \times SF_{dermal}) \qquad 10$$

Where, ILCR is the incremental lifetime carcinogenic risk, equal to the sum of risk as a result of exposure to toxic metals through each route combined. The values of CSF for selected heavy metals in different exposure routes are provided by the USEPA (2010) in Table 3.10 below. The range of acceptable total risk for regulatory purposes is 10^{-6} to 10^{-4} (Park and Choi, 2013). In regulatory terms, ILCR less than or equal to 10^{-6} represent virtual safety and ILCR equal to or greater than 10^{-4} indicates a potential great threat (USEPA, 2002).

Table 3.10: Cancer Slope Factors (CSF) for the different heavy metals (USEPA, 2010).

Heavy metal	Oral CSF	Dermal CSF	Inhalation CSF
As	1.5×10^{0}	1.5×10^{0}	1.5×10^{1}
Pb	8.5×10^{-3}	8.5 x 10-6	4.2×10^{-2}
Cd	-	-	6.3×10^{0}
Cr (VI)	5.0×10^{-1}	-	4.10×10^{1}
Ni	0.84	-	-

3.8. Ethical Consideration

3.8.1 Informed consent

Informed consent is the process of telling potential research participants about the key elements of a research study and what their participation involved (Putman and Rock, 2016). The researcher informed the quarry operators about the purpose, procedures, risks, and benefits and obtained their consent before involving them in the research.

3.8.2 Confidentiality

Confidentiality is commonly reviewed as akin to the principle of privacy (Oliver, 2003). The name of the stone quarry was not used, meaning that the quarry operators remained anonymous. (Putman and Rock, 2016).

3.8.3 Permission to collect data

Permission to carry out the study was sought from the University of Venda Ethics Committee, while permission to collect soil samples for analysis was requested from the quarry operators in Tzaneen.

3.8.4 Risks/Benefits Information

No risks encountered. The quarry operators were assured of their protection during the data collection. They would also benefit from the implementation of the recommendations of the study.

3.9. Expected Outcomes

3.9.1 Potential Impacts

Two potential impacts are expected out of this study:

- It is anticipated that the study will create awareness about heavy metals, their distribution, toxicities, and potential health risks within the nearby community.
- The study will provide baseline data for identification and implementation of appropriate soil remediation studies and other sustainable pollution control measures.

3.9.2 Expected Outputs

The outputs will be the research dissertation and a publication of the findings in an accredited journal of international repute.

CHAPTER FOUR: RESULTS AND DISCUSSION

This chapter presents and discusses heavy metal concentrations and trends found within Tzaneen stone quarry. The data is presented in the form of tables and graphs in order to observe the trend in the data set.

4.1 Summary Statistics

Summary statistics of the analysed heavy metals from Tzaneen quarry rocks is presented in Table 4.1 below. The average concentration of heavy metals indicated abundance in the order of Mn>Fe>Cr>Co>Zn>Pb>Cu>Ni. The concentration of these metals was below the Wedepohl (1995) background concentration with a wide range of 1.11 to 624.06 mg/kg. It was observed that Mn and Fe had highest concentration than all other heavy metals in the quarry rocks with concentration values of 2585.02 and 1791.2 mg/kg respectively. Mn had the highest standard deviation of 231.36 than all other metals. This showed that Mn was dispersed with a wide range of 69.54 to 693.6 mg/kg. Ni had the lowest concentration of 6.14 mg/kg than all other metals.

Table 4.1: Descriptive statistics of the heavy metal concentration in quarry rocks found at Tzaneen

	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
Maximum	4.28	3.23	3.16	3.73	2.74	9.28	693.6	231.1
Minimum	3.17	1.89	1.72	2.73	0.02	0.11	69.54	149.5
Mean	3.58	2.34	2.21	3.04	0.61	2.70	258.50	179.12
SD	0.38	0.41	0.64	0.38	1.07	3.28	231.36	28.81
Background Concentration	35	17	25	12	19	52	716	43200

The concentration of heavy metals in soil samples from the stone quarry are presented below in Table 4.2. The metals showed a variable pattern in the order: Mn>Fe>Zn>Pb>Co>Cr>Cu>Ni. The average concentration of these metals was also below the Wedepohl (1995) background concentration. Similarly, Mn and Fe had the highest average concentration of 343.697 and 215.4 mg/kg. Mn had the highest standard deviation of 177.240 mg/kg. However, the concentration Mn and Fe decreased in soil compared to rock samples at the quarry (Figure 4.2). The range of heavy metals in the soil samples was 0.34 to 507.83 compared to rock samples. Cr, Cu and Co had highest concentration of 3.58, 2.21 and 3.04 mg/kg in rocks than the soil samples from the stone quarry (Figure 4.1). Conversely, the concentration of Pb, Ni and Zn were highest in soil samples than the quarry rocks with 3.20, 1.42 and 3.23 mg/kg, respectively.

Table 4.2: Summary statistics of heavy metal concentrations in soil samples from the stone quarry.

	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
Maximum	3.321	3.93	2.117	6.347	1.931	6.136	562.1	231.9
Minimum	1.721	2.499	1.777	2.146	0.131	0.031	54.27	165.5
Mean	2.544	3.200	1.869	2.887	1.416	3.233	343.697	215.4
SD	0.496	0.425	0.105	1.243	0.519	2.130	177.240	25.476

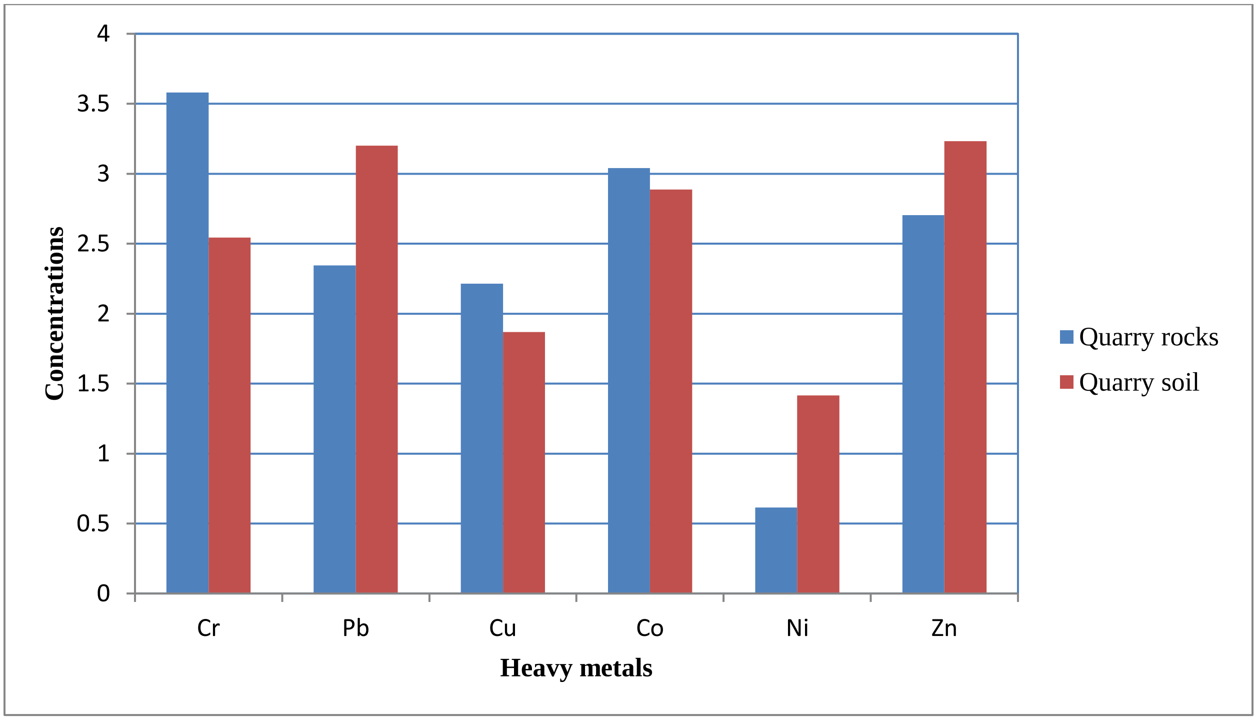


Figure 4.1: Comparison of heavy metals in quarry rocks and quarry soil from Tzaneen.

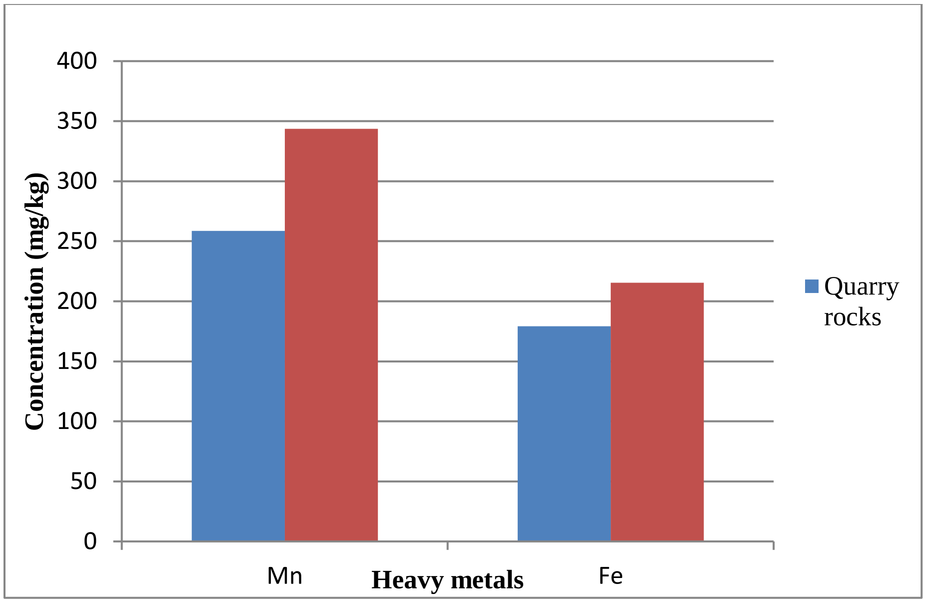


Figure 4.2: Comparison of heavy metals Mn and Fe in rocks and soils of the Tzaneen stone quarry.

4.2 Comparison of heavy metals from the stone quarry, community and control site

A comparison of heavy metal trends with distance from the stone quarry is showed below in Figure 4.3 and 4.4. The highest concentration of Cr was observed at the control site compared to the community and quarry in the following order: Control>Community>Quarry. Cu also had higher concentration at control site than the quarry and community in the following order: Control>Quarry>Community. Pb showed higher concentration of 3.20 mg/kg at the quarry site than the community and control location in the order: Quarry>Community>Control (Etim and Adie, 2012). Co showed higher concentration at the community than the other sites. The average concentration of Co at the quarry and control site was almost the same with values 2.887 and 2.875 mg/kg, respectively. Ni and Zn concentrations were highest at the quarry site with values 1.42 mg/kg and 3.23 mg/kg compared to the control location and the community in the following order Quarry>Control>Community (Figure 4.4). The concentration of Mn was higher at the quarry with values 343.70 and 215.4 mg/kg compared to the community and control site (Ayodele et al. 2014). Mn showed significant concentration in the following order: Quarry>Control site>Community whilst Fe concentration was in the order: Quarry>Community>Control site (Figure 4.4).

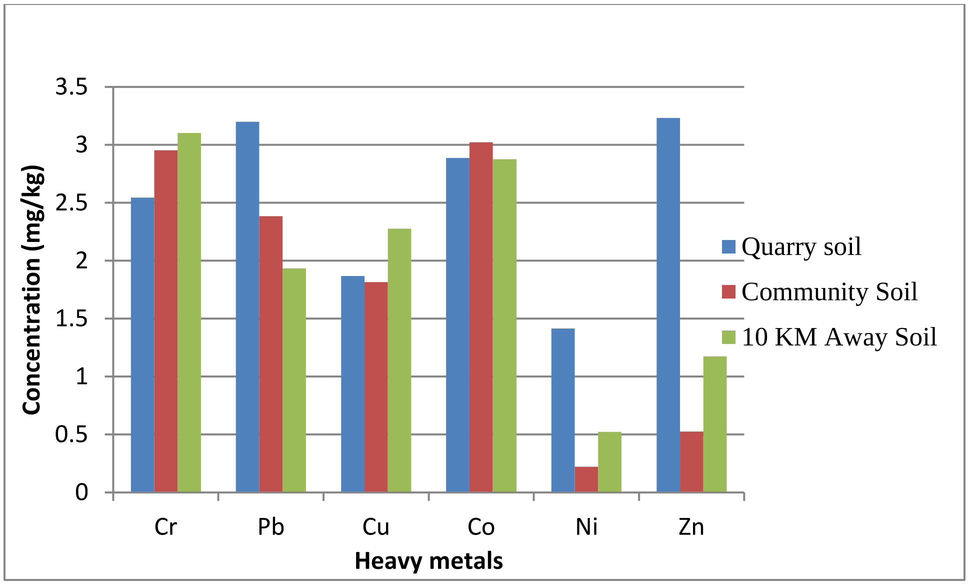


Figure 4.3: Comparison of heavy metals in soil samples from the quarry, community and control site.

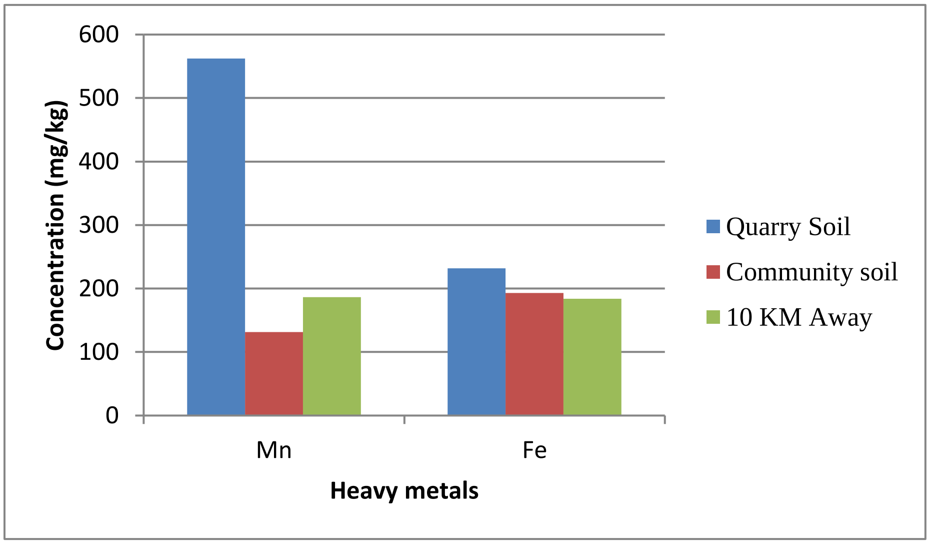


Figure 4.4: Comparison of heavy metals Mn/Fe in soil samples of the quarry, community and control site.

Table 4.3 below shows the comparison of heavy metals found in this study, Nigeria and Ghana. Nigeria and Ghana mined the same rock as this study. Ghana only analysed the following metals Pb, Cu, Zn, Mn and Fe (Aloh et al. 2017). The concentration of Cr, Co, and Ni was highest in Nigeria compared to this study. The concentration of Pb and Zn was in the order: Nigeria>This study> Ghana. Low concentration was recorded in Ghana compared to this study and Nigeria

(Table 4.3). Cu was low in this study compared to Nigeria and Ghana with 1.869 mg/kg, 2.63 mg/kg and 2.23 mg/kg, respectively. Mn and Fe were highest in this study compared to Nigeria and Ghana with 343.697 and 215.4 mg/kg. The lowest concentration was observed in Ghana with 1.3 mg/kg and 3.9 mg/kg.

Table 4.3: Comparison of heavy metals in this study, Nigeria and Ghana.

	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
This study	2.544	3.2	1.869	2.887	1.416	3.233	343.697	215.4
Nigeria	17.71	11.92	2.63	3.04	3.54	7.01	136.75	120.625
Ghana	-	0.235	2.23	-	-	0.4	1.3	3.9

4.3 Distribution of heavy metals with distance from the stone quarry

Distribution of heavy metals with distance from the quarry is presented in Table 4.4, Figure 4.5 and 4.6 below. The average concentration of Cr was higher at 200 m and lowest at 0 m. The metal showed an increasing trend from the quarry with distance towards the community. Pb was higher at 200 m and lowest at 10 km. It showed at decreasing trend from the 200m towards the community and the control site (Guo et al, 2012). Cu showed a decreasing trend from the 0 m up to 2.5 km but increased at 5 km and 10 km away. The lowest concentration was observed at 1.5 km and the highest concentration at 10 km away. Co was higher at the quarry decreasing with distance up to 500 m. The metal increased from 1 km decreasing towards 5 km and 10 km away. Ni showed a decreasing trend from the quarry moving with distance up to 100 m. the highest concentration was observed at 500 m and lowest at 1 km.

Ni was higher at the crusher with 1.653 compared to 10 km away, which was 0.522. Zn was higher at 50 m and lowest 5 km. It showed a decreasing trend moving away with distance from the quarry. Mn showed a decreasing trend from the crusher moving with distance towards the nearby community. The highest concentration was recorded at 500 m and the lowest concentration at 2.5 km. Mn was higher at the crusher than the control location (Ayodele et al. 2014). Fe showed a decreasing trend from the mine towards the community. The highest concentration was recorded at 50 m and the lowest at 1 km.

Mn had maximum concentration at 0 m, 50 m, 200 m, 500 m, 10 km compared to other metals. Fe also had maximum concentration at 100 m, 1 km to 5 km than all other metals. Ni had the minimum concentration at specific distance than all metals except at 500 m and 5 km, where Cu and Zn were the lowest with 1.845 and 0.106 mg/kg respectively. The average concentration of all heavy metals was highest at the following distances, 0 m, 50, 200m, 500 m.

Table 4.4: Distribution and concentration of heavy metals (mg/kg) with distance from the quarry.

Distance	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
0 m	2.277	2.973	2.117	6.347	1.653	2.596	407.5	224.7
50 m	2.489	3.476	1.825	2.56	1.602	6.136	408.7	231.3
100 m	2.475	3.154	1.777	2.325	0.131	0.757	54.27	165.5
200 m	3.321	3.742	1.811	2.855	1.557	5.704	380.3	229.2
500 m	3.274	2.844	1.845	2.367	1.931	2.917	475.8	228
1 km	2.478	2.268	1.798	3.091	0.001	0.515	24.07	132.8
1.5 km	2.635	2.937	1.75	3.077	0.084	0.203	9.409	150.8
2.5 km	2.9	2.143	1.77	3.057	0.023	0.343	3.634	168.1
5 km	3.193	2.45	2.165	3.301	0.565	0.106	20.34	186.3
10 km	3.103	1.933	2.277	2.875	0.522	1.175	186.5	183.7

The average concentration of Cr, Pb, Cu and Co almost showed similar distribution pattern compared to other metals (Figure 4.5). Co had an outlier of high concentration of 6.347 mg/kg at 0 m while Cu had an even distribution pattern throughout. Zn showed a variable distribution pattern compared to other metals with higher concentration at 25, 50 and 200 m away from the quarry (Megateli et al. 2009). A sharp drop was observed at 100 m with the concentration of 0.757 mg/kg. Ni showed the lowest concentration throughout with a sharp drop of 0.131 at 100 m compared to other metals. Fe showed a uniform distribution pattern throughout the distance, while Mn indicated a variable pattern (Figure 4.6). Mn showed a sharp drop in concentration at 100 m and 2.5 km away from the quarry. The highest concentration of Mn was observed at 0 m, 50 m and 500 m with 407.5, 408.7 and 475.8 mg/kg, respectively.

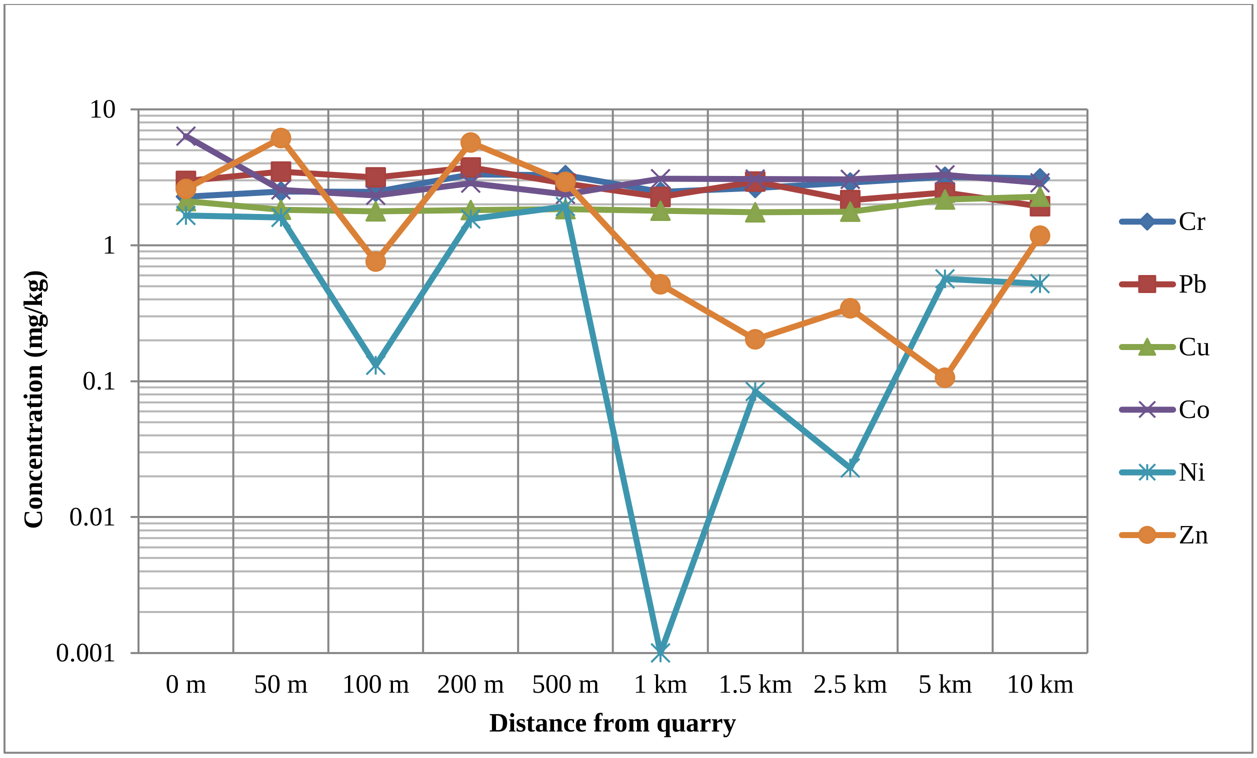


Figure 4.5: Distribution pattern of heavy metals with distance from the stone quarry.

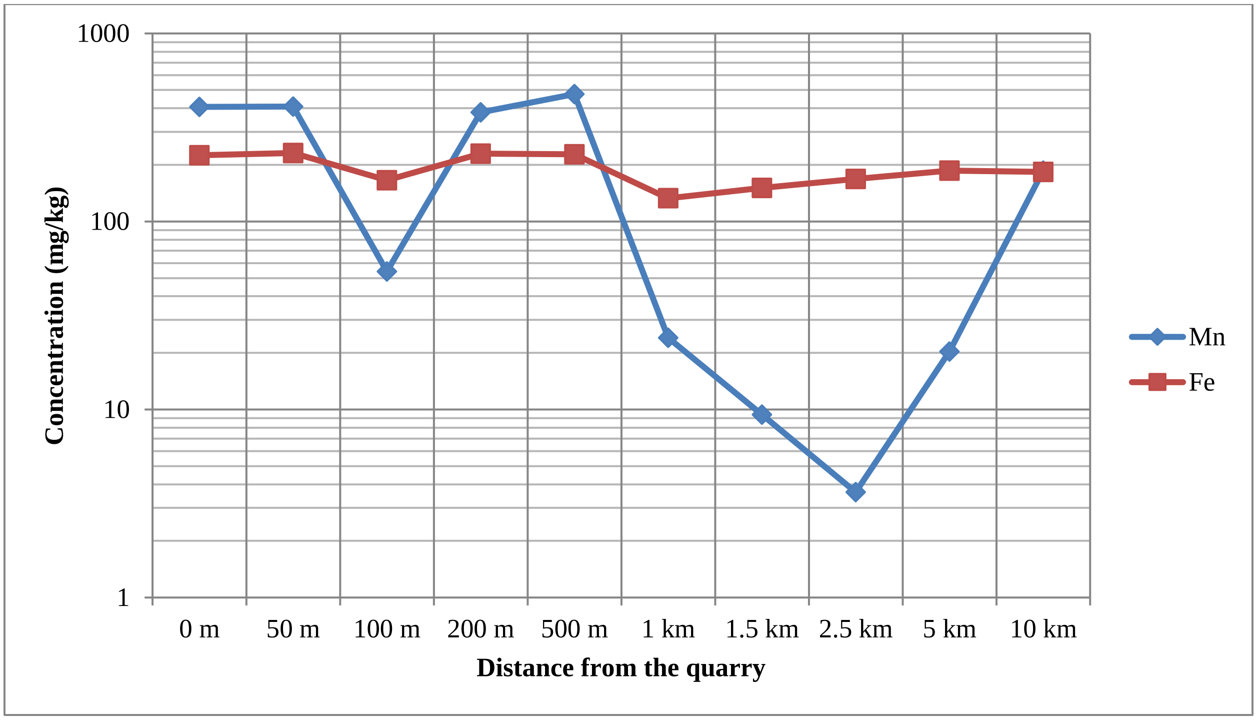


Figure 4.6: Distribution pattern of Mn and Fe with distance from the stone quarry.

4.4 Concentration of heavy metals in the school playground of Mokgolobotho village

The average concentration of heavy metals found in the school playground of Mokgolobotho village is presented in Table 4.5 below. The concentration of metals showed abundance in the following order: Mn>Fe>Zn>Cr>Co>Pb>Cu>Ni. The average concentration of Mn was higher with (377.32 mg/kg) followed by Fe with (186.375 mg/kg) compared to other metals. The lowest average concentration of 0.475 mg/kg and 1.888 mg/kg was recorded for Ni and Cu, respectively. The average concentration of heavy metals in the rock samples (SGR) collected from the school playground was highest for Cr, Pb, Ni, Zn, Mn and Fe compared to soil samples (Table 4.6). Only Cu and Co had higher concentration of 2.1895 and 3.008 mg/kg in the soil samples compared to rock samples. The average concentration of heavy metals found in the playground of Mokgolobotho community creche is also displayed in the Table 4.5 below. The metals showed abundance in the following order: Fe>Mn>Cr>Co>Pb>Cu>Zn>Ni. Fe had the highest concentration of 181.667 mg/kg compared to all other metals. Mn was second highest with 88.63 mg/kg concentration (Table 4.5). All other metals had low concentration that ranged from 0.268 to 3.038 mg/kg respectively.

Table 4.5: Concentration of heavy metals found in the school playground of Mokgolobotho village (mg/kg).

	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
Max	4.267	4.009	1.982	3.717	1.561	20.49	814.4	207.1
Min	3.308	2.16	1.796	2.91	0.121	0.354	85.96	153.9
Average	3.718	2.653	1.888	3.139	0.475	4.797	377.32	186.375
SD	0.351	0.614	0.071	0.342	0.456	6.910	270.981	19.414
SGR	3.2555	2.215	2.1895	3.008	0.2315	1.641	232.305	175.2
Creche	3.038	2.386	2.123	2.849	0.268	1.221	88.63	181.667

4.5 The concentration of major elements in the analysed soil samples

The concentration of elements in the rock samples collected showed abundance in the order: SiO_2>Al_2O_3>Fe_2O_3>CaO>MgO>K_2O. The average concentration of SiO_2 was higher with 62.12% and ranged from 70.45% to 44.26% compared to other elements. Al_2O_3 was the second highest element with the average concentration of 12.29% and range of 10.72% to 14.64%. Other elements such as Fe_2O_3, CaO, MgO and K_2O had low average concentration of 3.32, 2.715, 1.198 and

2.991%, respectively. The average concentration of elements in rock samples was higher than in soil samples (Table 4.6 and 4.7).

Table 4.6: Major elements concentration (%) in the rock samples collected from the stone quarry (%).

	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O
Max	14.64	70.45	10.81	8.81	4.3	4.07
Min	10.72	44.26	0.72	0.61	0.36	1.34
Average	12.286	62.116	3.32	2.715	1.198	2.991
SD	1.211	9.364	3.961	3.176	1.623	1.154

The concentration of Al_2O_3 and SiO_2 in the soil samples collected from the quarry was lower than the soil samples from the community (Table 4.7 and 4.8). The concentration of the elements increased with distance from the quarry towards the community. Conversely, the other elements Fe_2O_3, CaO, MgO and K_2O decreased with distance from the quarry towards the community (Table 4.8). CaO and MgO had lowest concentration of 0.838 and 0.458%, respectively. However, the concentration of all elements increased at 10 km away from the quarry (Table 4.8).

Table 4.7: Major elements concentration in the soil samples collected from the stone quarry (%).

	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O
Max	14.19	64.68	8.97	7.51	3.54	3.31
Min	8.57	37.16	0.57	0.43	0.32	1.16
Median	11.89	54.7	2.99	1.99	0.745	2.13
Average	11.659	54.44	3.21	2.65	1.141	2.304
Range	5.62	27.52	8.4	7.08	3.22	2.15
SD	1.902	8.608	2.532	2.094	0.986	0.805
%RSD	16.309	15.812	78.874	79.034	86.447	34.956
Total	116.59	544.4	32.1	26.5	11.41	23.04

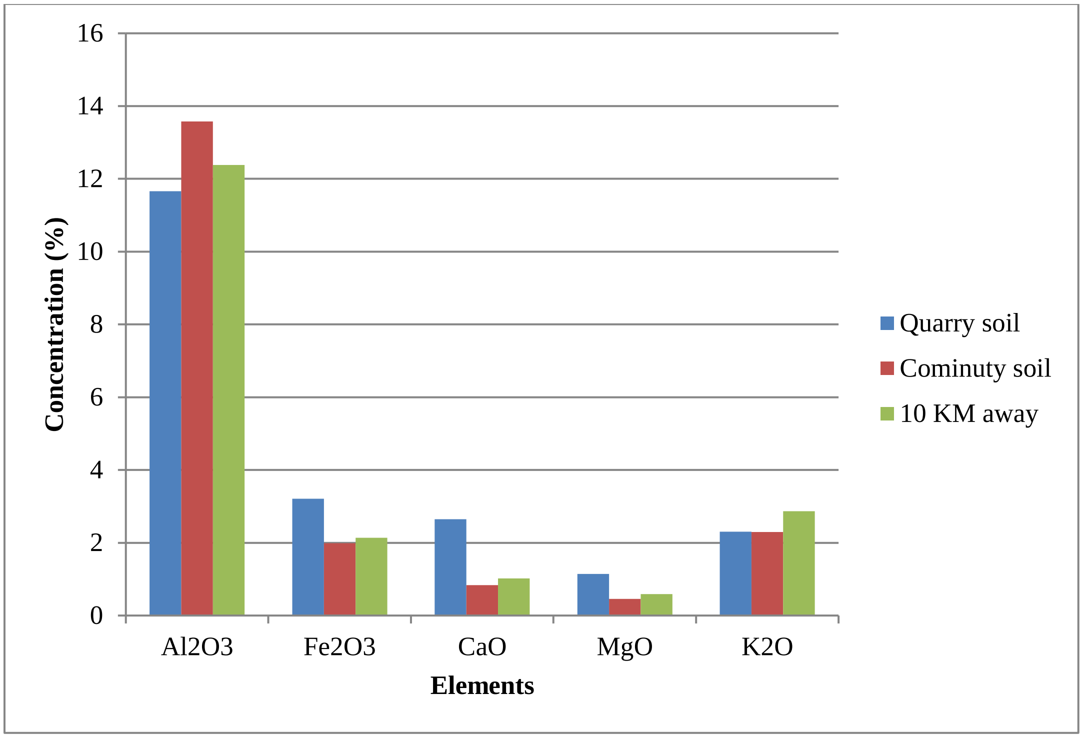


Figure 4.7: Major elements concentration in the soil samples collected from the quarry, nearby community and control site.

The concentration of SiO_2 increased with distance from the mine in the following order: Quarry>Community>Control. The highest concentration of SiO_2 was recorded at the control site.

4.6 Physicochemical properties of soil samples collected from the study area

The average soil pH at the quarry compared to the community and 10 km away with pH values of 6.73, 6.45 and 6.43. Similarly, EC and TDS showed the same trend with soil pH. Both increased with distance away from the quarry (Table 4.8). High EC and TDS at the quarry were likely to be influenced by disintegration (weathering) of minerals and rocks from the blasting and crushing area (Sati, 2015). As a result of mining activities and possibly evapotranspiration, soluble salts, inorganic and organic matter tend to accumulate and remain near the soil surface, resulting in higher EC and TDS.

Table 4.8: Summary of the physiochemical properties of the soil samples collected from the study area.

Location	pH	EC (dS/m)	TDS (mg/l)
Quarry soil	6.73	167.00	115.53
Community soil	6.45	150.2	105.65
10 Km soil	6.43	147.6	104.7

The average soil pH ranged from 7.32-6.17 within 500 m away from the stone quarry. The highest pH of 7.77 was recorded at 25 m away from the quarry decreasing with increase in distance (Figure 4.8 and 4.9). The average pH of background soil was 5.88 at 10 km away compared to the blasting and crushing site. Soil pH decreased with increase in distance from the quarry site. Soil pH values within 100 m from the exploration zone were comparable with the soil samples at 0 m, while pH values of soil samples further than this distance were more acidic. This indicated no influence from the quarry rocks, which are alkaline in nature. A slight decrease in pH occurred in near surface soil samples 200 m away and further from the exploration area, which is comparable with the background pH. Soil pH showed higher values of 6.76 and 7.5 at 1.5 km and 4 km away, compared to the control location. The lowest pH values of 5.97, 5.9 and 5.88 were observed at 1 km, 2.5 km and 5 km away comparably. This suggests lesser influence from the stone quarry. Generally, most metals do not exist in free form in the pH range of 6.0-9.0 (Ayodele et al., 2014). The pH for all topsoil samples analysed in this study fell within this pH range.

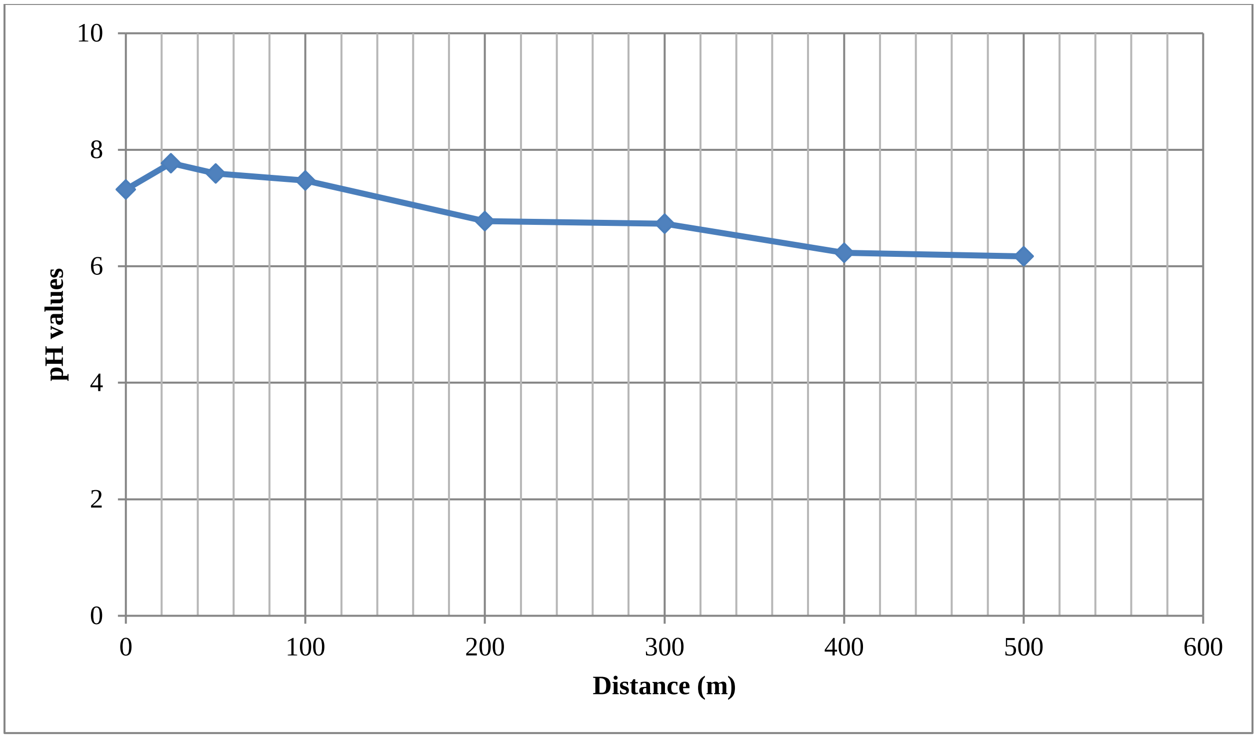


Figure 4.8: Soil pH with distance from the quarry.

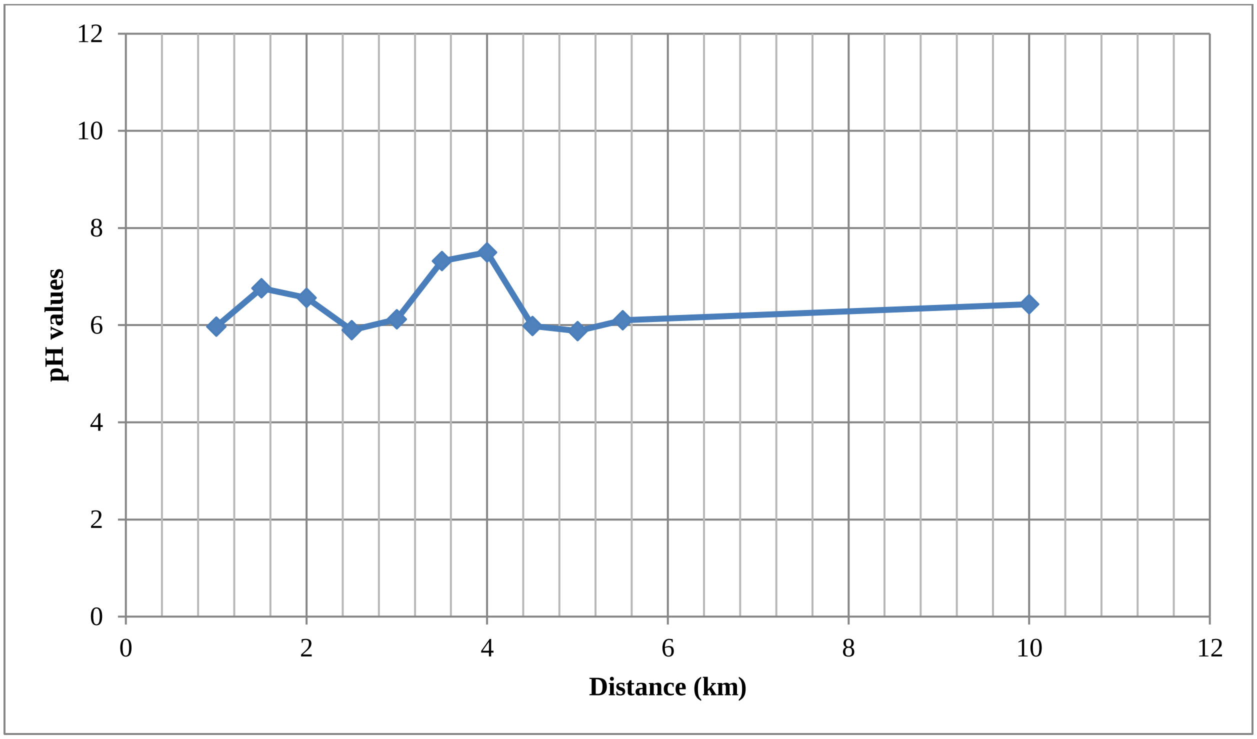


Figure 4.9: Soil pH with distance away from the quarry towards the community and control site

4.7 Particle Size Distribution

Figure 4.10 below shows the soil classification of the study area. The soil at the quarry was composed of sand 84.54 %, Silt 4.27%, Clay 1.38%. The percentage of sand was high at the quarry decreasing with distance from the mine. The percentage of sand in the study area showed a decreasing trend in the following order: quarry>community>control with 84.54%, 80.26% and 70.17%, respectively (Smith and Collins, 2001). Gravel percentage was high with 28.62% at the control site compared to the quarry and the community. The amount of silt and clay was high at the community than the quarry and control site. The soil in the study area was more sandy compared gravel, silt and clay.

The coefficient of uniformity (Cu) of soil samples from the quarry and control site shows that the soil is well graded compared to soil from the community, which is less graded (Table 4.9). This indicates that the soil mass consists of soil particles with different size ranges (Teoprdei, 2002). The soil in the study area showed Cu in the order: quarry>control>community respectively. The coefficient of curvature (Cc) for the soil at the quarry also implied that it is well graded compared to community soil, which are poorly. The Cc of control site was highest showing that the soil is highly graded compared to the quarry and community. The particle size distribution indicated that soil from the quarry and control site are well graded compared to soil in the community (Figure 4.11).

Table 4.9: Particle size distribution of the soil samples collected from the study area

Location	Particle size (%)				Effective size (mm)				
	Gravel	*Sand*	*Silt*	*Clay*	*D60*	*D30*	*D10*	*Cu*	*Cc*
Quarry	14.08	84.54	4.27	1.38	1.79	0.42	0.13	14.09	2.48
Community	6.37	80.26	26.75	13.38	0.37	0.08	0.04	9.28	0.06
Control	28.62	70.17	2.74	1.21	2.58	0.70	0.19	13.71	6.65

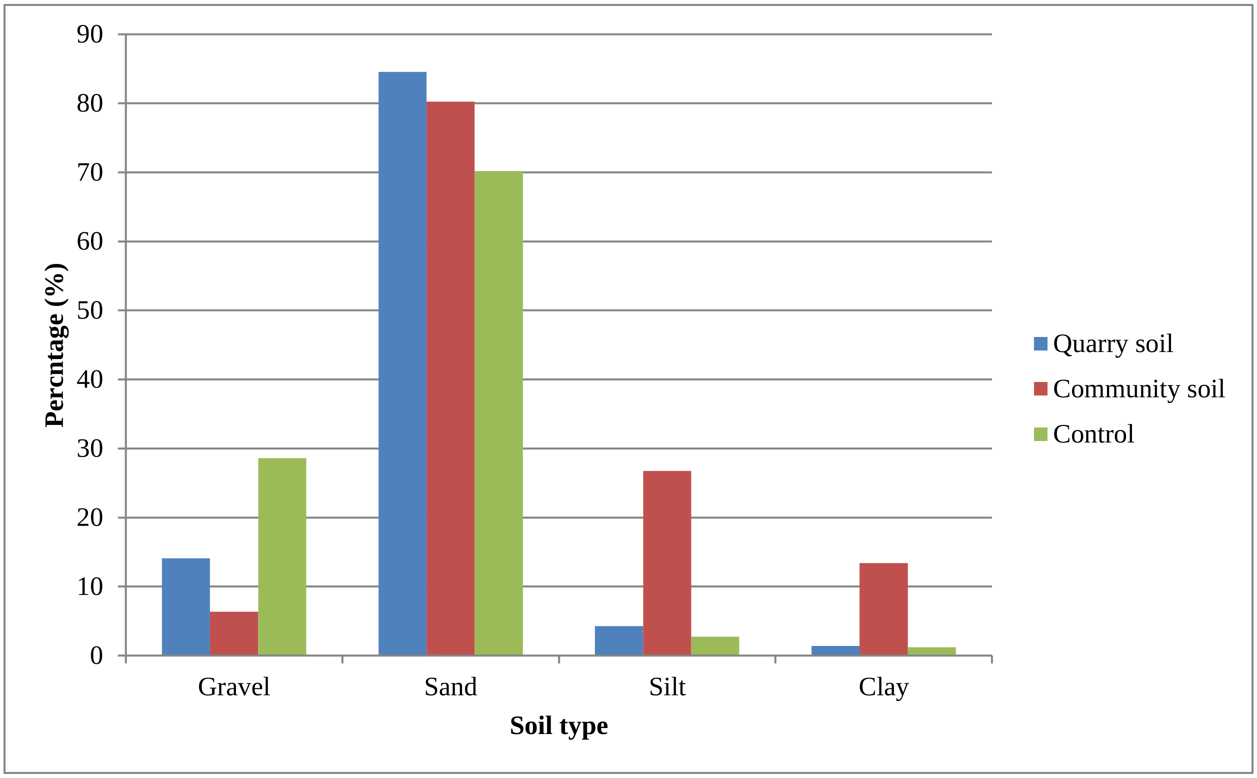


Figure 4.10: Showing soil classification of the study area.

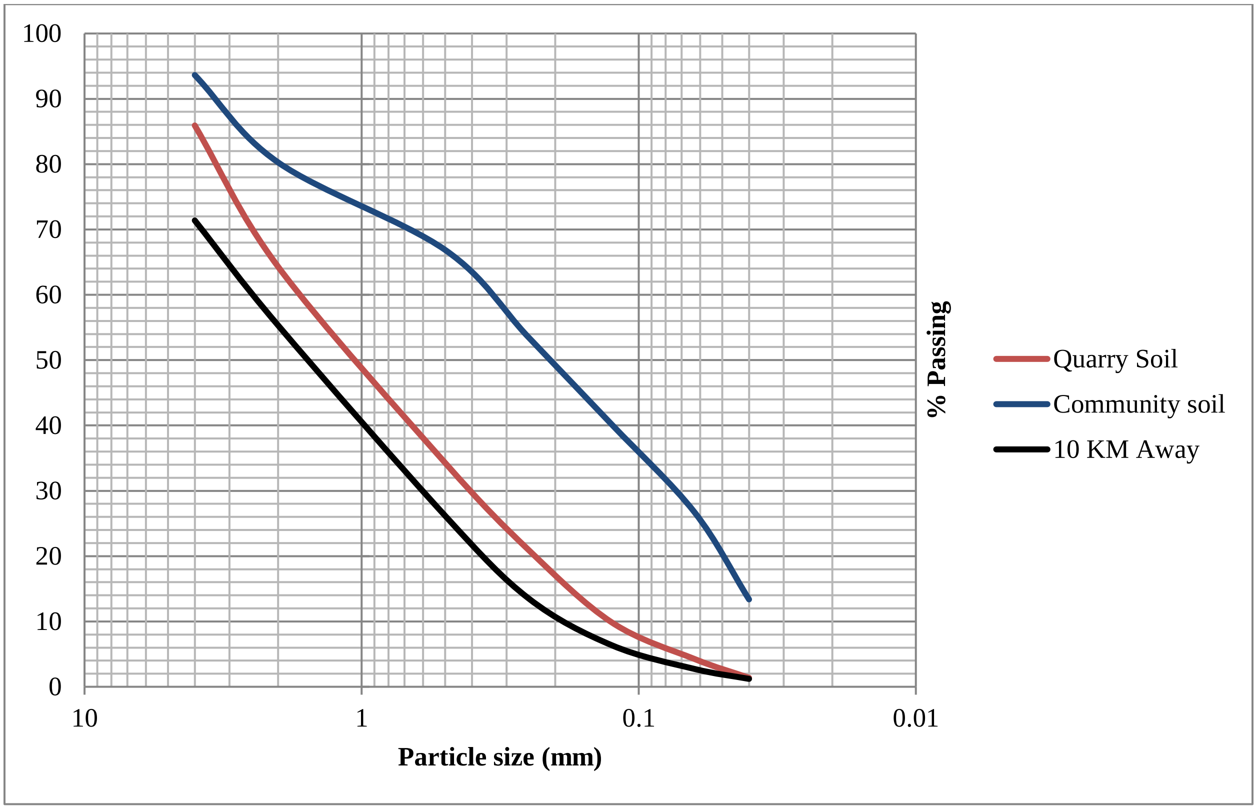


Figure 4.11: Showing the particle size distribution curve of the soil in the study area

4.8 Relationship between heavy metals in soils and soil properties

Correlation of heavy metals with soil pH was presented in the table below. Cr, Ni and Mn had negative correlation (r = -0.4, -0.32 and -0.14) with soil pH at the stone quarry compared to community soil which showed positive correlation of (r = 0.04, 0.24 and 0.19). This means that when Soil pH increase, the concentration of Cr, Ni and Mn decrease at the quarry compared to the community. Cu and Co showed negative correlation at the community compared to the quarry site, which had positive correlation of (r = 0.38 and 0.35). All other metals showed positive correlation with soil pH at the quarry and community, respectively.

Table 4.10: Relationships between some soil pH and heavy metal contents in soils from the quarry and nearby community

	Soil pH	
Heavy metals	Quarry soil	Community soil
Cr	-0.4	0.04
Pb	0.57	0.23
Cu	0.38	-0.34
Co	0.35	-0.32
Ni	-0.32	0.24
Zn	0.5	0.46
Mn	-0.14	0.19
Fe	0.12	0.16

The correlation matrix of heavy metals analysed in the study is presented in Table 4.10 below. Correlation coefficients for all metals analysed at the quarry site are presented below. Strong correlation was observed between Cu/Co, Pb/Zn, Zn/Fe and Mn/Fe with 0.83, 0.86, 0.77 and 0.72 respectively. Weak correlation was observed between Cr/Mn, Pb/Fe, Cu/Ni, and Ni/Fe. Strong negative correlation was observed Cr/Cu with (r = -0.45). Cr also correlated negatively with Cu and Co at (r = -0.02) and (r = -0.17). Pb correlated negatively with Co, Ni, and Mn at (r = -0.07), (r = -0.14) and (r = -0.03).

Strong negative correlation was observed between Pb/Cu and Co/Mn (r = -0.60 and -0.55) (Table 4.11). Cr/Pb and Co/Fe had the same negative correlation (r = -0.42). Co/Zn also showed negative correlation (r = -0.38).

Table 4.11: Correlation matrix of all metals analysed at the stone quarry

	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
Cr	1							
Pb	-0.02043	1						
Cu	-0.45185	0.11037	1					
Co	-0.17224	-0.07351	0.832583	1				
Ni	0.080347	-0.13557	0.33505	0.149013	1			
Zn	0.075223	0.856784	0.193391	0.019912	0.29147	1		
Mn	0.406683	-0.02567	0.039383	0.240103	0.287625	0.271276	1	
Fe	0.234426	0.51271	0.345157	0.237494	0.462994	0.767497	0.71625	1

Cr had negative correlation with Zn, Mn and Fe, while Pb correlated negatively with Co, Ni and Mn. Negative correlation was also observed Cu/Zn (r = -0.02). Co also had negative correlation with Ni (r = -0.03). Ni had strong positive correlation with Zn, Mn and Fe of r = 0.63, 0.60 and 0.68, respectively. Zn also showed strong positive correlation with Mn and Fe (r = 0.73 and 0.52). Mn had strong correlated with Fe (r = 0.63). Heavy metals from soil samples collected from the nearby village were more negatively correlated compared to the quarry site, which showed more positive correlation (Table 4.12).

Table 4.12: Correlation matrix of heavy metals in the soil samples collected from the nearby community

	Cr	*Pb*	*Cu*	*Co*	*Ni*	*Zn*	*Mn*	*Fe*
Cr	1							
Pb	-0.4207	1						
Cu	0.2614	-0.5974	1					
Co	0.1646	-0.1668	0.10476	1				
Ni	0.2237	-0.0387	0.36876	-0.0354	1			
Zn	-0.1666	0.04535	-0.0155	-0.3753	0.62810	1		
Mn	-0.0231	-0.1054	0.31499	-0.5522	0.60121	0.72761	1	
Fe	-0.1079	0.10195	0.34873	-0.4151	0.675264	0.523436	0.63298	1

4.9 Pollution Assessment

4.9.1 Contamination Levels of Heavy Metals

All metals analysed showed low contamination (CF<1) at all distances from the mine (Table 4.13). The PLI value at the quarry site was 1.56, implying that the soil from the quarry was unpolluted to moderately polluted. Beyond 100 m from the quarry, PLI values of 0.62 were recorded, suggesting unpolluted state (Su et al. 2014).

Heavy metals such as Cr, Pb, Cu, Co and Mn showed generally low contamination (CF<1) within the community (Table 4.14). Other metals Ni and Zn showed background concentration at some distances in the community whilst, Fe showed background concentration at all sampling locations in the community. The PLI indicated low contamination of heavy metals in the soil from the community ranged from 0.55 to 0.75 with an average value of 0.66 (Table 4.14). The average PLI indicated that the soil at the community was unpolluted. The soil samples collected from the control site also revealed unpolluted status (PLI = 0.85) (Sun et al. 2010).

Table 4.13: Contamination factors of heavy metals from the stone quarry

Sample	Distance	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe	PLI
QS1	0	0.07	0.17	0.08	0.53	0.09	0.05	0.57	0.01	1.56
QS2	25	0.05	0.23	0.08	0.22	0.08	0.12	0.25	0.01	1.04
QS3	50	0.07	0.20	0.07	0.21	0.08	0.12	0.57	0.01	1.34
QS4	100	0.07	0.19	0.07	0.19	0.01	0.01	0.08	0.00	0.62
QS5	200	0.09	0.22	0.07	0.24	0.08	0.11	0.53	0.01	1.35
QS6	300	0.06	0.18	0.07	0.24	0.07	0.05	0.79	0.01	1.47
QS7	400	0.08	0.19	0.07	0.22	0.06	0.05	0.77	0.01	1.44
QS8	500	0.09	0.17	0.07	0.20	0.10	0.06	0.66	0.01	1.36
QS9	600	0.06	0.15	0.07	0.18	0.10	0.00	0.16	0.00	0.73
QS10	700	0.08	0.19	0.07	0.18	0.08	0.05	0.41	0.01	1.07
Average		0.072	0.189	0.072	0.241	0.075	0.062	0.479	0.008	1.198

Table 4.14: Contamination factors of heavy metals in the soil samples collected from the community and control site

Sample	Distance	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe	PLI
V1	800	0.08	0.15	0.07	0.20	0.01	0.02	0.18	0.00	0.72
V2	900	0.08	0.15	0.07	0.23	0.02	0.01	0.18	0.00	0.75
V3	1000	0.07	0.13	0.07	0.26	0.00	0.01	0.03	0.00	0.58
V4	1500	0.08	0.17	0.07	0.26	0.00	0.00	0.01	0.00	0.60
V5	2000	0.08	0.15	0.07	0.26	0.00	0.01	0.08	0.00	0.64
V6	2500	0.08	0.13	0.07	0.25	0.00	0.01	0.01	0.00	0.55
V7	3000	0.08	0.15	0.07	0.26	0.01	0.02	0.14	0.00	0.74
V8	3500	0.09	0.14	0.07	0.26	0.05	0.03	0.16	0.00	0.80
V9	4000	0.09	0.13	0.07	0.26	0.00	0.00	0.02	0.00	0.58
V10	4500	0.09	0.08	0.09	0.26	0.01	0.00	0.08	0.00	0.62
V11	5000	0.09	0.14	0.09	0.28	0.03	0.00	0.03	0.00	0.66
V12	5500	0.10	0.15	0.07	0.25	0.00	0.00	0.04	0.00	0.62
Average		0.08	0.14	0.07	0.25	0.01	0.01	0.08	0	0.66
Control	10000	0.09	0.11	0.09	0.24	0.03	0.02	0.26	0.00	0.85

4.9.2 Enrichment Factor

The average concentration of metals showed significant enrichment in the following order: Mn>Co>Pb>Cu>Ni>Cr>Zn. The average concentration of Mn showed higher enrichment compared to other metals indicating that the metal is influenced by human activities in addition to soil sources (Tasrina et al. 2015). Mn showed wide variation with range of 150.93 to 19.78 compared to other metals. The metal showed no pattern with distance away from the mine. Cr showed maximum significant enrichment at 100 m and lower enrichment at 25 m from the quarry. Cr showed enrichment with increase in distance from the quarry. Pb also showed higher enrichment at 100 m but lower at 500 m from the quarry. The enrichment of Pb decreased with distance from the quarry. Cu showed similar trend as Cr. The metal showed more enrichment at 600 m and low enrichment at 50 m from the quarry.

Conversely, Co showed good trend of enrichment with distance from the mine. High enrichment was observed at 0 m and low enrichment at 700 m away from the quarry. Ni showed higher enrichment at 600 m and low enrichment at 100m. The metal showed similar trend as Cr and Cu. Zn showed higher enrichment at 50 m and low enrichment at 600m. The metal showed similar pattern as Co and Pb. The average concentration Pb, Co and Mn showed highest enrichment at the quarry compared to other metals. Conversely, Cr, Cu, Zn and Ni showed lower enrichment at the quarry.

Table 4.15: Enrichment factors of heavy metals in the soil samples from the stone quarry.

Sample	Distance	Cr	Pb	Cu	Co	Ni	Zn	Mn
QS1	0	12.51	33.62	16.28	101.69	16.73	9.60	109.42
QS2	25	9.16	43.07	14.87	40.89	15.06	21.97	47.38
QS3	50	13.28	38.19	13.63	39.84	15.75	22.04	106.61
QS4	100	18.46	48.43	18.55	50.57	1.80	3.80	19.78
QS5	200	17.88	41.49	13.65	44.84	15.45	20.67	100.11
QS6	300	12.48	33.69	14.12	46.17	13.16	10.20	150.93
QS7	400	15.13	36.50	14.05	42.01	10.65	9.14	149.97
QS8	500	17.72	31.70	13.98	37.37	19.26	10.63	125.91
QS9	600	15.52	37.51	18.61	45.63	25.36	0.15	41.77
QS10	700	14.96	35.95	14.07	34.17	15.17	10.43	78.54
Average		14.71	38.015	15.181	48.318	14.839	11.863	93.042

The average values of metals in the nearby community showed significant enrichment in the following order: Co>Pb>Cr>Mn>Cu>Ni>Zn. The average concentration of Co showed high enrichment compared to other metals indicating that the metal is influenced by human activities in addition to soil sources. The metal showed wide variation in enrichment factor values ranging from 84.3 to 44.4 compared to other metals. The enrichment of Co decreased with distance away from the community. Low enrichment was recorded at 800 m and high enrichment at 5.5 km away. Cr showed similar trend with Co. Maximum enrichment of Cr was recorded at 5.5 km and low at 800 m in the community.

Pb, Ni, Zn and Mn showed no particular trend of enrichment with distance in the community. Cu showed similar trend as Cr and Co. The metal showed more enrichment at 4.5 km and low enrichment at 800 m in the community. The enrichment of Cu increased with distance away from the nearby community. The average concentration Cr, Pb and Co showed high enrichment compared in the nearby community compared to the control site (10 km away). Conversely, Cu, Zn, Ni and Mn showed low enrichment compared to the control site.

Table 4.16: Enrichment factors of heavy metals in the soil samples collected from the nearby community

Sample	Distance	Cr	Pb	Cu	Co	Ni	Zn	Mn
V1	800	18.01	34.22	16.07	44.40	3.13	5.37	39.37
V2	900	19.25	35.47	16.81	54.37	5.62	1.77	43.26
V3	1000	23.03	43.40	23.40	83.79	0.02	3.22	10.94
V4	1500	21.57	49.49	20.05	73.46	1.27	1.12	3.76
V5	2000	20.10	40.19	18.42	68.20	0.28	1.78	20.42
V6	2500	21.29	32.40	18.19	65.47	0.31	1.70	1.30
V7	3000	19.26	38.35	17.51	65.13	2.24	4.65	36.28
V8	3500	21.76	33.80	16.83	63.91	11.09	8.38	39.39
V9	4000	26.80	37.52	19.88	73.61	0.92	1.09	5.54
V10	4500	27.04	22.98	24.45	75.07	2.12	0.68	23.58
V11	5000	21.15	33.42	20.08	63.79	6.90	0.47	6.59
V12	5500	33.88	49.82	22.16	84.30	0.30	0.62	14.09
Control	10000	20.85	26.74	21.42	56.34	6.46	5.31	61.25
Average		22.76	37.59	19.49	67.96	2.85	2.57	20.38

4.9.3 Geo-accumulation index (Igeo)

Igeo values for all metals at the quarry was in the order: Fe>Mn>Zn>Cr>Pb>Cu>Co>Ni as shown in Table 4.17 below. The average Igeo values of Mn and Fe showed that the quarry site was extremely contaminated at 17.038 and 22.635 mg/kg respectively. Mn showed highest Igeo value at 300 m and lowest at 100 m. The average Igeo value of Cr was 5.866 mg/kg. Cr was highest at 200 m with (6.28) and lowest at 25 m with 5.33 mg/kg. Practically, the Igeo value of Cr in the quarry site and specific distances was >5 which means the metal was extremely contaminated in the area (Tiimub et al. 2015). Unlike Cr, Pb showed high Igeo value at 25 m and lowest at 600 m away from the mine. The Igeo values of Pb decreased with distance away from the mine. The average Igeo value of Pb was >5 which means that it was extremely contaminated in the mining area compared to other distances.

Similarly, Cu showed the same trend with Pb. The highest Igeo was at 0 m decreasing with distance away from the mine. The average Igeo of Cu was 4.961, which indicates that the soil was strongly to extremely contaminated with the metal. Co also showed a similar trend with Pb and Cu. The maximum Igeo was recorded at 0 m and lowest at 600m. This means that the Igeo Co decreased with distance from the mine. The average Igeo of Co showed that the metal was strongly to extremely contaminated in the mining area.

Ni showed no particular pattern. The minimum Igeo was observed at 100m and maximum at 500 m. The metal decreased from 4.39 at 0m to 0.73 at 100 m but increased from 4.3 at 200 m to 4.61 at 500m. The average Igeo of Ni showed that the metal is strongly contaminated at specific distances. Zn showed high Igeo at 25 and 50 m, while the lowest was observed at 600m away from the mine. The metal decreased with distance away from the mine. The average Igeo of the metal showed that it is extremely contaminated in the mine compared to distance away.

Table 4.17: Showing the Igeo of heavy metals in the soil samples collected from the mine

Sample	Distance	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
QS1	0	5.73	5.07	5.14	5.67	4.39	6.49	17.57	22.63
QS2	25	5.33	5.48	5.06	4.40	4.28	7.73	16.41	22.67
QS3	50	5.86	5.30	4.93	4.36	4.34	7.73	17.57	22.67
QS4	100	5.85	5.16	4.89	4.22	0.73	4.71	14.66	22.18

QS5	200	6.28	5.41	4.92	4.51	4.30	7.63	17.47	22.65
QS6	300	5.73	5.08	4.94	4.53	4.04	6.58	18.03	22.63
QS7	400	5.99	5.18	4.92	4.38	3.73	6.41	18.01	22.61
QS8	500	6.26	5.01	4.94	4.24	4.61	6.66	17.79	22.65
QS9	600	5.63	4.82	4.93	4.10	4.58	0.10	15.77	22.22
QS10	700	6.00	5.18	4.94	4.10	4.26	6.62	17.10	22.64
Average		5.866	5.169	4.961	4.451	3.926	6.066	17.038	22.555

The average Igeo values for all metals was in the following order: Fe>Mn>Cr>Cu>Pb>Co>Zn>Ni (Table 4.17). The average Igeo of Mn was high in the community, indicating that the area was extremely contaminated with the metal. Fe showed high Igeo of 22.4 throughout the community compared to other metals. The average Igeo of Cr was 6.098 ppm indicating that soil samples collected from the community was extremely contaminated with Cr. The Igeo of Cr increased with distance away from the nearby community. The highest Igeo was recorded at 5.5 km with (6.38ppm) and lowest at 2 km with 5.85 ppm. Unlike Cr, Pb showed high Igeo at 1.5 km and lowest at 4.5 km away. The average Igeo of Pb was within 4-5, which classifies the soil as ‘strongly to extremely contaminated’ in the community.

Cu showed the same trend with Cr. The Igeo of Cu increased with distance away from the nearby community. The average Igeo of Cu was 4.914, which characterize the soil as ‘strongly to extremely contaminated’ with the metal (Wei et al. 2009). Co also showed a similar trend with Cr and Cu. The maximum Igeo was recorded at 5 km and lowest at 800m. This means that the Igeo Co increased with distance away from the community. The average Igeo of Co showed that the metal was ‘strongly to extremely contaminated’ in the community.

Mn, Ni and Zn showed no particular trend with distance. The maximum Igeo was recorded at 3.5 km. At the following specific distances 1 km, 2 km, 2.5 km, 4 km and 5 km, Ni showed no contamination. The average Igeo of Ni showed that the community was uncontaminated with the metal. Zn showed high Igeo at 3.5 km, while the lowest was observed at 5.5 km away in the community. The metal showed a decrease with distance away from the community. The average Igeo of the metal showed that the community is strongly contaminated in the community than distance away.

Table 4.18: Showing the Igeo of heavy metals in the soil samples collected from the nearby community and control site.

Sample	Distance	Cr	Pb	Cu	Co	Zn	Mn	Fe
V1	800	6.04	4.88	4.90	4.25	5.43	15.87	22.40
V2	900	6.06	4.86	4.89	4.47	3.76	15.94	22.33
V3	1000	5.85	4.68	4.91	4.63	4.16	13.49	21.87
V4	1500	5.94	5.06	4.87	4.62	2.82	12.13	22.05
V5	2000	5.95	4.87	4.86	4.63	3.60	14.68	22.16
V6	2500	6.08	4.60	4.88	4.61	3.57	10.76	22.21
V7	3000	5.97	4.88	4.86	4.64	5.06	15.59	22.24
V8	3500	6.18	4.73	4.84	4.65	5.95	15.75	22.28
V9	4000	6.25	4.65	4.85	4.62	2.77	12.68	22.04
V10	4500	6.26	3.95	5.15	4.65	2.09	14.77	22.05
V11	5000	6.22	4.80	5.17	4.72	1.88	13.25	22.36
V12	5500	6.38	4.85	4.79	4.60	1.75	13.82	21.83
Control	10000	6.18	4.45	5.25	4.52	5.35	16.44	22.33
Average		6.098	4.734	4.914	4.591	3.57	14.061	22.152

4.10 Health Risk Assessment

The average daily intakes (ADIs) of selected heavy metals through each exposure route were estimated separately for infants, children, and adults (Table 4.19 – 4.22). Average daily intake was used to determine the level of human exposure to heavy metals in soil based on general exposure equations provided by USEPA (1989). The results were used to estimate non-carcinogenic and carcinogenic risk to the target population in the study area.

Table 4.19: Average daily intake of heavy metals by quarry workers from the mine

Heavy metals	Adult		
	ADIinh	ADIing	ADIdermal
Cr	7.49E-09	1.23205E-08	3.71E-03
Pb	9.42E-09	1.5502E-08	7.00E-04
Cu	5.50E-09	9.05137E-09	6.82E-03
Co	8.50E-09	1.3983E-08	-
Ni	4.17E-09	6.85658E-09	1.81E-02
Zn	9.52E-09	1.56614E-08	2.36E-03
Mn	1.01E-06	1.66484E-06	-
Fe	6.34E-07	1.04338E-06	-

Table 4.20: Average daily intake of heavy metals by residents living nearby the mine

Heavy metals	Infant			Child			Adult		
	ADIinh	ADIing	ADIdermal	ADIinh	ADIing	ADIdermal	ADIinh	ADIing	ADIdermal
Cr	3.35E-09	4.15E-08	1.20E-02	5.76E-09	4.81E-09	5.98E-03	8.94E-09	1.60E-08	8.26E-03
Pb	2.70E-09	3.34E-08	1.45E-03	4.65E-09	3.88E-09	5.51E-04	7.21E-09	1.293E-08	9.99E-04
Cu	2.06E-09	2.55E-08	1.84E-02	3.54E-09	2.95E-09	1.53E-02	5.49E-09	9.85E-09	1.27E-02
Co	3.42E-09	4.24E-08	-	5.89E-09	4.92E-09	-	9.14E-09	1.639E-08	-
Ni	2.51E-09	3.11E-09	7.88E-03	4.32E-10	3.61E-10	9.32E-03	6.71E-10	1.20E-09	5.42E-03
Zn	5.97E-09	7.39E-09	1.07E-03	1.03E-09	8.57E-10	5.33E-04	1.59E-09	2.855E-09	7.35E-04
Mn	6.53E-08	8.09E-07	-	1.12E-07	9.38E-08	-	1.74E-07	3.13E-07	-
Fe	1.85E-07	2.29E-06	-	3.18E-07	2.65E-07	-	4.93E-07	8.844E-07	-

Table 4.21: Average daily intake of heavy metals by children playing in the school playground of the nearby community

Heavy metals	Child		
	ADIinh	ADIing	ADIdermal
Cr	7.25E-09	6.05045E-09	7.53E-03
Pb	5.18E-09	4.31853E-09	8.06E-04
Cu	3.68E-09	3.07324E-09	9.56E-03
Co	6.12E-09	5.1081E-09	-
Ni	9.27E-10	7.73701E-10	4.86E-03
Zn	9.36E-09	7.80802E-09	8.42E-03
Mn	7.36E-07	6.14111E-07	-
Fe	3.64E-07	3.03336E-07	-

Table 4.22: Average daily intake of heavy metals by infants attending creche in the community near the stone quarry

Heavy metals	Infant		
	ADIinh	ADIing	ADIdermal
Cr	3.44E-09	4.26315E-08	1.23E-02
Pb	2.70E-09	3.34774E-08	1.45E-03
Cu	2.41E-09	2.97868E-08	2.16E-02
Co	3.23E-09	3.99793E-08	-
Ni	3.03E-10	3.7561E-09	-
Zn	1.38E-09	1.71293E-08	9.51E-03
Mn	1.01E-07	1.24372E-06	2.48E-03
Fe	2.06E-07	2.54928E-06	-

4.10.1 Non-carcinogenic risk assessment

The results of the HQ and HI calculations from the study area are listed in the Tables below. The HQ of the dermal absorption of soil particles for Cu, Ni and Zn was much higher than those of the inhalation and ingestion of soil particles for quarry workers (Table 4.23). The values of HQ and HI for exposure routes to heavy metals at the quarry site decreased in the order of dermal contact > ingestion> inhalation routes. The contribution of HQdermal to HI was the highest in exposure routes and accounted more with (3.54E+00) to the total risk. This result shows that the dermal absorption is a principal route of heavy metals damaging to human health. Conversely, the ingestion and the inhalation routes had relatively low values. The non-cancer risk of Ni was a major contribution to HI (with 3.23E+00), which was higher than the safe level compared to Cu and Zn. However, the HI for all metals in table 4.23 below was higher than the safe level (>1), which means there may be concern for potential non-carcinogenic health effects (US EPA, 2001). Therefore, the potential health risks for quarry workers cannot be overlooked.

Table 4.23: HQs and His of heavy metals in the soil samples collected from quarry.

Heavy metals	Worker		
	HQ inhalation	HQ ingestion	HQdermal
Cr	2.50E-04	4.11E-06	-
Pb	-	4.31E-06	-
Cu	-	2.26E-07	2.84E-01
Ni	-	3.43E-07	3.23E+00
Zn	-	5.22E-08	3.14E-02
Mn	-	1.19E-04	
Total	2.50E-04	1.28E-04	3.54E+00
HI	3.54E+00		

Table 4.23 below shows the results for HQs and HIs of heavy metals in the soil samples collected from the nearby community. The HQ of dermal absorption for infants, children and adults were higher than the inhalation (HQinh) and ingestion (HQing) exposure routes. The contribution of HQdermal (HQderm) to HI for infants and children was the highest in exposure routes compared with adults. However, in overall HQdermal for all infants, children and adults contributed higher to HI compared to other routes. Conversely, the ingestion and the inhalation routes had relatively low values. This result shows that the dermal absorption is a principal route of heavy metals in soil to the exposed population. The non-cancer risk of Ni for infants and children was a major contribution to HI was higher than the safe level compared to adults (Table 4.23). However, the HI for infants, children and adults exceeded one, showing that there may be a concern for potential non-carcinogenic health effects to the residents of the nearby community. The exposure risk to the target population was in the order of child>infant>adults. Children were more exposed to heavy metals in soil followed by infants and adults with HI of 2.31E+00, 2.19E+00 and 1.50E+00 respectively.

Table 4.24: HQs and HIs of heavy metals in the soil samples collected from the nearby community.

Heavy metals	Infant			Child			Adult		
	HQinh	HQing	HQderm	HQinh	HQing	HQderm	HQinh	HQing	HQderm
Cr	1.12E-04	1.38E-05		1.92E-04	1.60E-06		2.98E-04	5.34E-06	
Pb		9.29E-06			1.08E-06			3.59E-06	
Cu		6.37E-07	7.68E-01		7.39E-08	6.37E-01		2.46E-07	5.28E-01
Co		-							
Ni		1.56E-07	1.41E+00		2.16E-08	1.67E+00		6.01E-08	9.68E-01
Zn		2.46E-08	1.43E-02		2.86E-09	7.10E-03		9.52E-09	2.45E-03
Mn		5.78E-05			6.70E-06			1.25E-05	
Fe									
Total	1.12E-04	8.17E-05	2.19E+00	1.92E-04	9.48E-06	2.31E+00	2.98E-04	2.17E-05	1.50E+00
HI	2.19E+00			2.31E+00			1.50E+00		

Soil samples collected from the school playground also showed similar pattern with the ones collected at the village and quarry sites. The contribution of HQdermal to HI for infants was the highest with 1.38E+00 compared to other exposure routes. Inhalation and ingestion routes showed relatively low levels. The exposure risk was in the order: dermal>inhalation>ingestion routes. This result shows that the dermal absorption is the principal route of exposure to heavy metals in the school playground for children attending there. The HI was higher than the safe level (>1), which means that there may be concern for potential non-carcinogenic risks to children in the school.

Table 4.25: HQs and HIs of heavy metals in the soil samples collected from the school playground.

Heavy metals	Child		
	HQinh	HQing	HQdermal
Cr	2.42E-04	2.02E-06	-
Pb	-	1.20E-06	-
Cu	-	7.68E-08	3.98E-01
Ni	-	3.87E-08	8.67E-01
Zn	-	2.60E-08	1.12E-01
Mn	-	4.39E-05	-
Total	2.42E-04	4.72E-05	1.38E+00
HI	1.38E+00		

Soil samples were also collected to estimate the potential risk posed by metals through each exposure routes to infants attending crèche in the community. Similarly, HQdermal was high with 1.03E+00 and contributed more to HI compared to other exposure routes (Table 4.26). The overall potential risk of heavy metals to infants in the community was higher than the safe level. This means that there may be potential non-carcinogenic risk damaging to their health.

Table 4.26: HQs and HIs of heavy metals in the soil samples collected from the creche in the nearby community

Heavy metals	Infant		
	HQinh	HQing	HQdermal
Cr	1.15E-04	1.42E-05	-
Pb	-	9.30E-06	-
Cu	-	7.45E-07	8.98E-01
Ni	-	1.88E-07	-
Zn	-	5.71E-08	1.27E-01
Mn	-	8.88E-05	-
Total	1.15E-04	1.13E-04	1.03E+00
HI	1.03E+00		

4.10.2 Carcinogenic Risk Assessment

The carcinogenic risks according to inhalation, ingestion and dermal exposure routes to Cr, Pb, and Ni in soil samples collected from the study area are presented below (Table 4.27-4.30). Results showed that the exposure risks for Cr, Pb and Ni decreased in the sequence of inhalation>ingestion>dermal exposure routes for soil samples collected from the mine, nearby community and community creche, whereas for school playground, it was in the order of inhalation>dermal>ingestion routes.

Table 4.27: Carcinogenic risks for metal elements in soil collected from the mine.

Heavy metals	Workers		
	Inhalation CSF	Ingestion CSF	Dermal CSF
Pb	3.96E-10	1.32E-10	5.95E-09
Cr	3.07E-07	6.16E-09	-
Ni	-	5.75953E-09	-
Total	3.07E-07	1.21E-08	5.95E-09
ILCR	3.25E-07		
ILCR (70 years)	2.28E-05		

Inhalation was found to be the exposure route to heavy metals in the soil samples from all sites compared to Ingestion and dermal contact. The levels of carcinogenic risks for those metals were lower than the tolerable range (10^{-6}–10^{-4}), above which the environmental and regulatory agencies perceive as an unacceptable risk (Wuana et al. 2008). There were no immediate carcinogenic ricks to the exposed population in the study area. However, adults at the age of 70 years and older showed to be at a risk of cancer in the study area.

Table 4.28: Carcinogenic risks for metal elements in soil collected from the nearby community

Heavy metals	Infant			Child			Adult		
	Inhalation CSF	Ingestion CSF	Dermal CSF	Inhalation CSF	Ingestion CSF	Dermal CSF	Inhalation CSF	Ingestion CSF	Dermal CSF
Pb	1.13E-10	2.84E-10	1.23E-08	1.95E-10	3.30E-11	4.69E-09	3.03E-10	1.10E-10	8.49E-09
Cr	1.37E-07	2.07E-08		2.36E-07	2.40E-09		3.66E-07	8.01E-09	
Ni		2.61E-09			3.03E-10			1.01E-09	
Total	1.37E-07	2.36E-08	1.23E-08	2.36E-07	2.74E-09	4.69E-09	3.67E-07	9.13E-09	8.49E-09
ILCR	1.73E-07			2.44E-07			3.84E-07		
ILCR	1.21E-05			1.71E-05			2.69E-05		

Table 4.29: Carcinogenic risks for metal elements in soil collected from the school playground in the nearby community.

Heavy metals	Child		
	Inhalation CSF	Ingestion CSF	Dermal CSF
Pb	2.18E-10	3.67E-11	6.85E-09
Cr	2.97E-07	5.14E-11	-
Ni	-	6.49909E-10	-
Total	2.97E-07	7.38E-10	6.85E-09
ILCR	3.05E-07		
ILCR (70 years)	2.14E-05		

Table 4.30: Carcinogenic risks for metal elements in soil collected from the creche in the nearby community.

Heavy metals	Infant		
	Inhalation CSF	Ingestion CSF	Dermal CSF
Pb	1.13E-10	2.85E-10	1.24E-08
Cr	1.41E-07	2.13E-08	-
Ni	-	3.15512E-09	-
Total	1.41E-07	2.48E-08	1.24E-08
ILCR	1.78E-07		
ILCR (70 years)	1.25E-05		

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

A total of 46 representative samples were collected from the study area and the concentration of Cr, Pb, Cu, Co, Ni, Zn, Mn and Fe, as well as the contamination and health risk assessment, were investigated in this study. The objective 1 of the study was to determine the distribution and concentration of heavy metals (Cr, Pb, Zn, Cu, Ni, Co, Fe and Mn) in near surface soils. The average concentration of heavy metals in quarry rocks indicated abundance and distribution in the order of Mn>Fe>Cr>Co>Zn>Pb>Cu>Ni while in the near surface soil samples from the quarry, it was in the order: Mn>Fe>Zn>Pb>Co>Cr>Cu>Ni. The concentration of Cr, Cu and Co was highest in rocks than soil samples at the stone quarry, while, Pb, Ni, Mn, Fe and Zn were highest in soil than rock samples from the stone quarry. The concentration of Cu, Zn, Pb, Mn, Ni and Fe decreased with distance from the mine. Fe, Mn and Pb were highest at the quarry and lowest at the control location in the order: Quarry>Community>Control. Ni and Zn were higher at the quarry and lower at the community compared to the control site as in the following order: Quarry>Control>Community. This may be due to the blasting and crushing of quarry rocks, distributed these metals in the surrounding soil at the mine. Cr and Co were found to be increasing with distance away from the quarry. Co was found to be higher at the community than the quarry and control site.

High concentration of Cr and Cu was observed at the control site compared to the community and quarry. The concentration of Fe, Cr, Pb, Cu and Co showed the same distribution pattern with distance from the mine while Mn, Ni and Zn showed variable pattern. This suggests that the dispersion Mn, Ni and Zn from the source could have been, majorly by wind, which distributes dust containing metals from the mine in all direction at different magnitude, space and time. The concentration of metals in the school playground was variable in the order: Mn>Fe>Zn>Cr>Co>Pb>Cu>Ni compared the community, which was in the order: Fe>Mn>Co>Cr>Pb>Cu>Zn>Ni. Samples collected from the pre-school playground showed concentration in the order: Fe>Mn>Cr>Co>Pb>Cu>Zn>Ni. Cu, Pb, Co, Cr, and Fe were high in the community and pre-school playground compared to Mokgolobotho primary playground. Only Zn was found to be higher in the school playground to the community and the pre-school playground. The concentration of Mn, Fe, Zn, Co, Cu and Ni showed the same trend at the quarry and the school playground, except for Cr and Pb, which showed variable patter. Cr was higher at the school playground while Pb was higher at quarry. Samples from the control location showed abundance in the order: Mn>Fe>Cr>Co>Cu>Pb>Zn>Ni. Mn was higher at the quarry, school playground and control followed by Fe, which was higher at the quarry and pre-school playground. The concentration of Ni was low at all sampling sites. Cu was the second lowest at the quarry and school playground compared to other sampling sites while Zn was second lowest at the community, pre-school and control.

It was learned during sampling that Mokgolobotho village was used for agricultural activity before people can reside there. Hence, probably the use of fertilisers and pesticides could have also caused accumulation of heavy metals in the nearby community. It was also observed that the soil in the community had different colours, which may indicate variation in geochemical composition of the study area. The average pH of the soil samples collected from the study was higher at quarry compared to the community and control site as in the following order: Quarry>Community>Control. Cr, Ni and Mn had negative correlation with soil pH at the stone quarry compared to community soil, which showed positive correlation. Soil samples showed to be higher in sand particles compared to silt and clay. This characterises the soil in the study area as a sandy soil. Distribution of particle sizes indicated that soil from the quarry and control is well graded compared to the soil in the community. Correlation that is more positive was seen between metals at the quarry compared to the community, which showed negative correlation.

The objective 2 of the study was to determine the degree of soil pollution by heavy metals using pollution indices. The average concentration of the metals was below the Wedepohl (1995) background concentration. Similarly, the concentration of all metals analysed was found to be lower than the recommended maximum allowable limits from South Africa and WHO guidelines. All metals in the study area showed lower contamination. The PLI showed that the soil in the study area was unpolluted to moderately polluted by all metals analysed. Conversely, the Igeo mean value of all metals ranged from strongly to extremely contamination at the quarry and nearby community. Only Ni showed no contamination in the community. EF also showed significant enrichment of metals at the quarry in the order: Mn>Co>Pb>Cu>Ni>Cr>Zn while at the community it was in the following order: Co>Pb>Cr>Mn>Cu>Ni>Zn.

The objective 3 of the study was to assess potential human health risks from exposure to heavy metals for different age groups (infants, children and adults). Although, the average concentration of heavy metals in the study was below the maximum allowable limit set by South Africa and WHO guidelines, the ADI of metals by infants, children and adults through each exposure routes can result in adverse health effects. The values for HQ and HI showed that infants, children, and adults in the study are exposed to potential non-carcinogenic health risks through dermal absorption compared to inhalation and ingestion. Dermal absorption was found to be a principal route of heavy metals in soil particles to the exposed population. The exposure risk to the targeted population was in the order: Children>Infants>Adults. Children were more exposed to heavy metals in soil compared to infants and adults. Quarry workers were also found to be exposed to potential non-carcinogenic health risk through dermal absorption followed by ingestion and inhalation routes, respectively. Samples collected from the school playground showed that children in the school are exposed to potential non-carcinogenic health risks in the order: Dermal absorption>inhalation>ingestion routes. Infants (0-5 years) attending pre-school at the community were also found to be exposed to potential non-carcinogenic health risks through dermal absorption route.

The population in the study area was not exposed to carcinogenic health risk posed by metals analysed, since the ILCR was lower than the tolerable range (10^{-6} – 10^{-4}), above which the environmental and regulatory agencies perceive the risk to be unacceptable. However, adults born and grew in the study area were found to be at a risk of cancer at the age of 70 years and older. In conclusion, this quantitative evidence creates awareness about the health risks of heavy metals in soil, even at low concentration and demonstrates the critical need to protect residents, especially children from heavy metal pollution in the environment. The study is useful for both residents, in taking protective measures, and government, in alleviating heavy metals contamination, of the community members residing in close proximity to mining operations. Quarry operators will also use the results from this study to improve the working conditions for workers and protect them from potential non-carcinogenic health risks.

5.2 Recommendations

Based on the conclusion of this study, it can be recommended that:

- Quarry workers and residents in the study area should take protective measures against long term exposure to heavy metals in the area.
- Quarry managers and safety officers to ensure frequent wetting of roads to minimise dust production.

- Government authorities to provide the necessary oversight to ensure compliance.
- More intensive non-carcinogenic health risk assessment be done in the study area to assess the extent of health effects on quarry workers, nearby residents especially children who were found to be more exposed to heavy metals in soil.
- A comprehensive analysis of silica content can be done across the study area to evaluate health risks on quarry workers and nearby residents.
- Assessment of heavy metals in the groundwater used for drinking purposes be done to evaluate health risks to the target population in the study area

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Appendices

Appendix A: Average concentrations (mg/kg) of heavy metals in quarry rocks

	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
QR$_1$	3.413	2.101	1.716	3.080	0.149	0.243	97.57	149.5
QR$_2$	3.241	3.233	1.738	3.002	0.188	0.108	127.6	150.8
QR$_3$	3.374	2.753	1.762	2.950	0.148	1.483	315.7	173.9
QR$_4$	3.168	2.512	1.802	3.017	0.076	1.622	231.5	168.8
QR$_5$	3.569	2.438	3.128	3.734	2.539	8.316	654.6	229.2
QR$_6$	3.562	2.086	3.162	3.686	2.744	9.276	693.6	231.1
QR$_7$	4.054	1.887	3.127	2.731	0.113	2.162	183.1	181.3
QR$_8$	4.277	2.109	1.884	2.726	0.059	0.826	89.41	177.0
QR$_9$	3.893	2.002	2.013	2.732	0.018	1.684	122.4	168.5
QR$_{10}$	3.260	2.318	1.810	2.748	0.110	1.313	69.54	161.1

Appendix B: Average concentrations (mg/kg) of heavy metals loadings in near surface soils of the stone quarry

	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
QS$_1$	2.277	2.973	2.117	6.347	1.653	2.596	407.5	224.7
QS$_2$	1.721	3.930	1.995	2.634	1.536	6.134	182.1	231.9
QS$_3$	2.489	3.476	1.825	2.560	1.602	6.136	408.7	231.3
QS$_4$	2.475	3.154	1.777	2.325	0.131	0.757	54.27	165.5
QS$_5$	3.321	3.742	1.811	2.855	1.557	5.704	380.3	229.2
QS$_6$	2.272	2.979	1.836	2.882	1.301	2.760	562.1	224.7
QS$_7$	2.733	3.203	1.813	2.602	1.045	2.454	554.3	223.0
QS$_8$	3.274	2.844	1.845	2.367	1.931	2.917	475.8	228.0
QS$_9$	2.129	2.499	1.823	2.146	1.888	0.031	117.2	169.3
QS$_{10}$	2.744	3.203	1.844	2.149	1.511	2.843	294.7	226.4

Appendix C: Average concentrations (mg/kg) of heavy metals loading in surface soils of the nearby community

	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
V_1	2.814	2.596	1.793	2.378	0.265	1.247	125.8	192.8
V_2	2.861	2.560	1.784	2.770	0.453	0.390	131.5	183.4
V_3	2.478	2.268	1.798	3.091	0.001	0.515	24.07	132.8
V_4	2.635	2.937	1.750	3.077	0.084	0.203	9.409	150.8
V_5	2.655	2.578	1.738	3.088	0.020	0.349	55.16	163
V_6	2.900	2.143	1.770	3.057	0.023	0.343	3.634	168.1
V_7	2.689	2.600	1.746	3.117	0.170	0.964	103.6	172.3
V_8	3.114	2.349	1.720	3.135	0.861	1.781	115.3	176.6
V_9	3.259	2.216	1.727	3.069	0.061	0.197	13.77	150.1
V_{10}	3.293	1.359	2.127	3.134	0.140	0.123	58.73	150.3
V_{11}	3.193	2.450	2.165	3.301.	0.565	0.106	20.34	186.3
V_{12}	3.560	2.543	1.663	3.037	0.017	0.097	30.29	129.7
10KM	3.103	1.933	2.277	2.875	0.522	1.175	186.5	183.7

Appendix D: Average concentrations (mg/kg) of heavy metals loading in the soil samples of the school playground

	Cr	Pb	Cu	Co	Ni	Zn	Mn	Fe
SG_1	3.856	4.009	1.982	3.656	0.538	0.589	814.4	202.4
SG_2	3.941	2.819	1.881	3.717	0.281	0.693	762.4	194.4
SG_3	4.008	2.239	1.859	3.065	0.257	6.470	372.8	207.1
SG_4	4.267	2.219	1.982	2.921	0.121	7.246	361.3	206.9
SG_5	3.470	2.679	1.812	2.910	0.434	1.148	249.7	181.3
SG_6	3.308	2.160	1.796	2.987	0.273	0.354	189.7	173.2
SG_7	3.562	2.827	1.934	2.942	0.338	1.389	182.3	171.8
SG_8	3.328	2.275	1.860	2.910	1.561	20.49	85.96	153.9
SGR_{11}	3.455	2.215	2.185	2.906	0.051	1.253	60.11	153.9
SGR_{12}	3.056	2.215	2.194	3.110	0.412	2.029	404.5	196.5
C1	2.813	2.388	2.058	2.887	0.522	2.104	73.65	181.1
C2	2.987	2.257	2.076	2.832	0.152	0.751	94.32	181.6
C3	3.314	2.512	2.234	2.828	0.129	0.807	97.92	182.3

Appendix E: Average concentration (%) of elements found in the stone quarry rocks

	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O
QR_1	14.64	63.20	2.53	0.61	0.41	1.34
QR_2	12.06	65.80	2.05	1.22	0.39	3.74
QR_3	12.16	66.94	2.01	1.13	0.58	3.94
QR_4	11.92	70.45	0.72	1.25	0.36	3.24
QR_5	13.81	66.46	1.28	2.43	0.42	3.57
QR_6	11.12	45.69	10.81	8.81	4.30	1.37
QR_7	10.72	44.26	10.70	8.54	4.25	1.35
QR_8	12.67	68.02	1.26	1.15	0.38	3.83
QR_9	12.53	68.39	0.96	0.93	0.37	4.07
QR_{10}	11.23	61.95	0.88	1.08	0.52	3.46

Appendix F: Average concentration (%) of elements found in the near surface soils of the stone quarry

	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O
QS_1	13.07	64.68	1.02	1.07	0.37	3.31
QS_2	10.33	59.99	1.21	1.40	0.78	2.97
QS_3	11.96	64.27	1.39	1.54	0.62	3.10
QS_4	11.82	53.72	5.22	4.41	1.75	1.87
QS_5	9.71	48.04	432	3.84	1.82	1.61
QS_6	8.57	37.16	897	7.51	3.54	1.16
QS_7	13.80	54.42	3.10	2.26	0.69	2.08
QS_8	13.04	54.98	2.88	2.32	0.71	2.18
QS_9	14.19	46.76	3.42	1.72	0.81	1.46
QS_{10}	10.10	60.38	0.57	0.43	0.32	3.30

Appendix G: Average concentration (%) of elements found in the topsoil of the nearby community

	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O
V_1	15.79	50.86	3.61	1.56	0.46	1.55
V_2	16.23	50.81	3.07	0.81	0.68	2.17
V_3	12.62	67.51	0.93	0.97	0.37	2.50
V_4	12.58	68.44	1.46	0.86	0.38	2.13
V_5	13.16	62.45	1.73	0.99	0.44	2.74
V_6	12.46	70.69	0.57	0.49	0.37	3.56
V_7	16.44	54.48	1.94	1.31	0.50	2.00
V_8	10.48	63.72	2.42	1.24	0.74	2.29
V_9	10.88	72.50	1.47	0.76	0.39	3.12
V_{10}	14.41	58.41	1.36	0.66	0.39	3.12
V_{11}	21.55	46.38	4.06	0.17	0.40	1.12
V_{12}	6.34	80.50	1.18	0.23	O.37	1.28
10KM	12.38	64.61	2.14	1.02	0.59	2.87

Appendix H: Physiochemical properties of the soil samples collected from the mine.

	pH	EC (dS/m)	TDS (mg/l)
QS_1	7.32	117.8	80.8
QS_2	7.77	103.6	71.3
QS_3	7.59	176.8	120.3
QS_4	7.47	185.97	128
QS_5	6.774	308.3	224
QS_6	6.73	387.3	271
QS_7	6.23	162.03	104.3
QS_8	6.17	119.9	81.2
QS_9	5.74	41.97	23.6
QS_{10}	5.52	66.3	50.8

Appendix I: Physiochemical properties of the soil samples collected from the nearby community

	pH	EC (dS/m)	TDS
V_1	7.13	351	249
V_2	6.20	117.5	81.8
V_3	5.97	84.2	63.7
V_4	6.76	94.3	70.1
V_5	6.56	191.1	114.67
V_6	5.90	21.8	16.5
V_7	6.12	290.3	219
V_8	7.32	335.7	236
V_9	7.5	93.5	64
V_{10}	5.98	88.1	58.4
V_{11}	5.88	47	30.6
V_{12}	6.10	87.9	63.97
10KM	6.43	147.6	104.7

Appendix J: Physiochemical properties of the soil samples collected from the nearby community

	pH	EC (dS/m)	TDS
SG_1	6.57	42.7	30
SG_2	7.19	68.6	51.2
SG_3	7.92	150.9	104
SG_4	6.01	33.9	20.3
SG_5	6.21	100.03	80.6
SG_6	5.00	44.3	31.5
SG_7	5.48	47.7	34.7
SG_8	5.45	33.1	21.1
C1	7.02	103	66.07
C2	6.49	116.6	81.6
C3	6.31	42.6	83.1

Appendix K: Particle size distribution of soil from the stone quarry

Sieve size (mm)	Soil mass retained (g)	Cumulative mass (g)	% Mass retained	% Passing
4	109.835	109.835	14.079	85.921
2	168.831	278.666	35.721	64.279
0.5	233.925	512.591	65.707	34.293
0.25	104.001	616.592	79.038	20.962
0.125	86.726	703.318	90.155	9.845
0.063	43.515	746.833	95.733	4.267
0.04	22.545	769.378	98.623	1.377
Pan	10.743	780.121	100	0

Appendix L: Particle size distribution of soil from the community

Sieve size (mm)	Soil mass retained (g)	Cumulative mass (g)	% Mass retained	% Passing
4	26.086	26.086	6.365	93.635
2	54.821	80.907	19.741	80.258
0.5	179.951	135.728	33.118	66.882
0.25	125.463	190.549	46.494	53.506
0.125	112.101	245.37	59.871	40.129
0.063	40.947	300.191	73.247	26.753
0.04	14.063	355.012	86.624	13.376
Pan	6.507	409.833	100	0

Appendix I: Particle size distribution of soil from 10 km away from the mine

Sieve size (mm)	Soil mass retained (g)	Cumulative mass (g)	% Mass retained	% Passing
4	228.83	228.83	28.619	71.381
2	128.52	357.35	44.692	55.308
0.5	232.82	590.17	73.810	26.190
0.25	101.13	691.3	86.458	13.542
0.125	57.5	748.8	93.649	6.351
0.063	28.89	777.69	97.262	2.738
0.04	12.21	789.9	98.789	1.211
Pan	9.68	799.58	100	0