Faculty of Science, Engineering and Agriculture

Department of Earth Sciences

Environmental Impacts of Tin Mine Waste: A Case Study of the Zaaiplaats Tin Mine, Limpopo Province, South Africa

By

Student Name: Matodzi Bridget Nemadodzi
Student Number: 14002926

A Dissertation Submitted to the Department of Earth Sciences in the Faculty of Science, Engineering and Agriculture, in Fulfilment of the Requirements for the Degree of Master of Earth Sciences in Mining and Environmental Geology

Supervisor: Emeritus Prof. J.S. Ogola
Department of Earth Sciences
University of Venda

Co-Supervisor: Dr. H.R. Mundalamo
Department of Earth Sciences
University of Venda

September 2023

DECLARATION

I, Nemadodzi Matodzi Bridget, hereby declare that this dissertation submitted to the Department of Earth Sciences, at the University of Venda, for Master of Earth Sciences in Mining and Environmental Geology, is my original work and has not previously been submitted at this or any other institution of higher learning for a degree and that all reference materials contained therein have been fully acknowledged.

Student's signature Date 02 July 2024

Supervisor Date: 12 July 2024

Co-Supervisor Date: 15/07/2024

DEDICATION

I would like to dedicate this research work to my family.

ACKNOWLEDGEMENTS

Firstly, I would like to thank God for strength that got me to be able to fulfil this project.

Special thanks to my supervisor Emeritus Professor. J. S., Ogola for his advice, direction and guidance throughout the research together with my co-supervisor Dr. H.R., Mundalamo. I am also thankful to the owner of the Zaaiplaats tin mine for allowing me to conduct research at the mine. I am grateful to the Department of Earth Sciences for allowing me to use the equipment that was needed for this study and Mrs. N. Lilimu for her assistance during laboratory work.

I would like to thank my family members for their motivation, encouragement, and emotional support throughout the course of this study. I would also like to show appreciation to my fellow students; Mathebula L, Ngomane S.S. Mureri G.J, Tshitavha N, Nematenda P, Netshisaulu M, Munyai P.G, Maponya J and Mphanama T for their support and encouragement throughout the course of my research.

ABSTRACT

This research focused on the potential impacts of the Zaaiplaats tin mine waste on the environment and on human health. It investigated the heavy metals and their distribution pattern at the Zaaiplaats tin mine. Heavy metals were investigated in the tailings, water and plants found at the mine. A radiation survey was also conducted to check for the possibility of potential radionuclides induced by the mine.

Fieldwork involved collection of tailings within the old river channel, Heap A, B and C. A total of 65 samples were collected, 15 of them, across the river profile, while 6, 24 and 20 were collected from Heap A, B and C respectively. Samples were prepared and analysed at the Mining and Environmental Geology laboratory at the University of Venda using X-ray Fluorescence Spectrometry. The maximum values were 2842.4 ppm, 885.1 ppm, and 740.7 ppm for lead from Heap B followed by copper, and zinc from the river channel respectively. The distribution pattern of some metals like lead, zinc and copper were increasing with depth. The highest Pi (Environmental quality index of the pollutant) was registered by Pb followed by Cu and As and the values are 47.11, 29.95 and 26.89 respectively. Cu, Zn, As, Pb, Th and U had shown a higher degree of pollution which is presented by Pi values of 3 and above in all the different sampling locations of the tailings.

The total water samples collected were depending on the availability. Therefore, only 3 water samples were obtained by use of 250 ml bottles. Water samples were prepared and analysed using Atomic Absorption Spectrometry. There are no values for metals such as Cr, Ni and Co in water samples collected at Zaaiplaats tin mine. However, the maximum values of Pb and Cu metals were 0.67 ppm and 0.59 ppm respectively which is higher as compared to the South African water quality guidelines and it is thus polluted.

A plant commonly known as horsetail (*Equisetum ramosissimum*) was collected during dry and wet season for comparison purposes. A total of 9 plant samples were collected, prepared and analysed using Atomic Absorption Spectrometry. Bioaccumulation factor of these plant samples were higher during the dry season and lower during the wet season. The trend in the BAF for heavy metals during dry season are in the ranking order of Cr > Cu > Pb > Co. The trend in the BAF for heavy metals during wet season are in the ranking order of Co > Cu > Pb > Cr. Cr was transferred effectively in dry season while cobalt was transferred effectively in wet season. Cr and Cu metals were absorbed and accumulated during dry season as opposed to wet season wherein Co was absorbed and accumulated in wet season than in dry season. BAF and TF values were lower in both dry and wet season. The horsetail plant is a hyper-accumulator of these metals and can be used for their clean up as a remediation strategy paired with other remediation measures.

Radiation dose rate and dose surveying was also conducted by means of a portable radiation survey meter DP802i-RAYTECH Radiation Detector. Radiation dose is increasing from a higher elevation which is the first surveying point along the river channel to low elevation. Radiation dose rate is inconsistent and does not have a general trend. The radiation dose rate mean, minimum, maximum values in microsievent per year (mSv/y) were 4.03 mSv/y, 0.96 mSv/y, and 11.65 mSv/y respectively. The maximum value of radiation dose rate was slightly higher compared to UNSCEAR background radiation of 2.4 mSv/y to 10 mSv/y. However, Zaaiplaats tin mine tailings are of no immediate concern since there are some areas that have had a radiation dose rate of 10 times higher than that of UNSCEAR and no deleterious health effects were associated with this elevated radiation exposure.

Keywords: *Zaaiplaats tin mine, metals, tailings, water, plant, radiation survey.*

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMYS AND ABBREVIATIONS

As	Arsenic
AAS	Atomic Absorption Spectrometry
Cd	Cadmium
cm	centimetres
Co	Cobalt
Cr	Chromium
Cu	Copper
g	gram
km^2	kilometre squared
GPS	Global Positioning System
mSv/y	microsievent per year
mm	millimetres
Mo	Molybdenum
Pb	Lead
pH	potential of Hydrogen
rpm	revolution per minute
Th	Thorium
U	Uranium
Zn	Zinc

1 CHAPTER ONE: INTRODUCTION

1.1 Background

Mining is a major economic activity in both developed and developing countries. However, it is also greatly associated with the pollution of the environment with mine waste that contains toxic chemicals used in the dressing of the ore as well as heavy metals released from the ore (Tauli-Corpuz, 1997; UNEP, 2000). Tailings are mixes of crushed rock and treated fluids from mills, washeries or concentrators that remain after the extraction of valuable metals, minerals, mineral fuels, or coal from the mine resource (Kossoff *et al.,* 2014; Engel, 2012). Mining operations both small-scale and large-scale inherently are disturbing to the environment as they produce massive measures of waste that can have destructive impacts for years (Makweba and Ndonde, 1996).

According to Hudson *et al*. (1999), mining in the United States had progressed over the years from minor, simple operations to great, multifaceted production and processing systems and some notable mining activities that happened when environmental implications were poorly understood have left a tragic environmental legacy. Křibek *et al*. (2011) showed that mining in Africa had caused harmful effects of contamination on public health, agriculture, and the environment because of economic pressures and gradual evolution of environmental consciousness. Thus, mining is an economic activity with an adverse consequence on the environment.

Tin mine tailings are also associated with elevated amounts of heavy metals causing both soil and water contamination. Tin mining has both socio-economic and environmental impacts (Ibeanu, 2003; Nurtjahya *et al*., 2017; Ashraf *et al*., 2012).

The environmental impacts of mining have been studied in South Africa such as the Witwatersrand Basin, Olifants catchment, the Giyani Greenstone Belt as well as Messina mines (Nengovhela *et al.*, 2006; Nengovhela *et al.*, 2007; Munyangane, 2012; Netshitungulwana and Yibas, 2012; Ogola and Sebola, 2010; Ogola *et al.,* 2011; Matshusa *et al.*, 2012; Singo, 2013). Lishman, (2009), investigated the acid mine drainage possibilty in the Platreef of the Northern Limb of the Bushveld Complex. The mine waste impacts on the environment are site specific as this depends on the type of deposit and its associated minerals, scope of mining and weather conditions.

The current study focused on the potential environmental impacts of Zaaiplaats tin mine. The occurrence and quantity of toxic metals in tailings and radiation within the mine site were investigated.

1.2 Study Area

1.2.1 Location

Zaaiplaats tin mine is situated within the farm Zaaiplaats 223KR, approximately 35 km northwest of Mokopane town in the Limpopo Province, South Africa (Fig. 1.1). The mine lies at latitude of $24^0$2'55.2" S and longitude of $28^0$45'44.9" E.

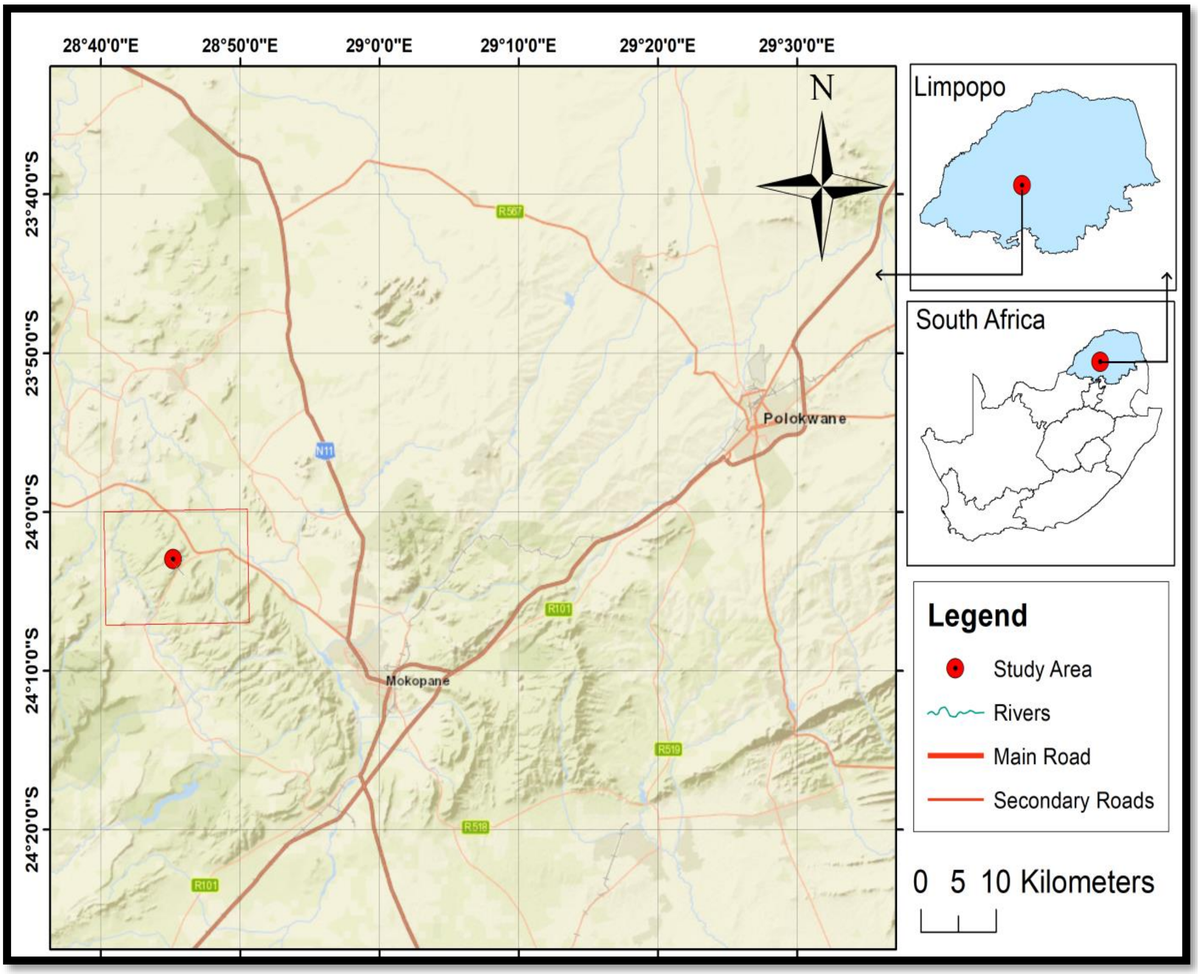


Figure 1.1: Location of Zaaiplaats tin mine (Esri, 2018)

1.2.2 Climate

Zaaiplaats mine is situated within the Mokopane area that has a semi-arid climate with little rainfall during the year (SAexplorer, 2018). The usual annual rainfall is 495 mm with an average temperature of 23^0C. January is the hottest month of the year with an average temperature of 32^0C while June is the coldest month, with temperatures of 13.0^0C (Climate-Data.org, 2018). Mokopane has dry periods in May, June, July, August and September. November is the wettest month and July is the driest month with precipitation of 95 mm and 8.5 mm respectively (World Weather and Climate Information, 2018).

1.2.3 Topography and Drainage

The Zaaiplaats tin mine is situated in the Makapaansberg Mountain which trends in the north-westerly direction from Mokopane town and is composed of the granite rocks of the Bushveld Complex as well as the felsites of the Rooiberg Group (Strauss, 1954). The gently dipping south-western slopes of the Makapaansberg Mountain are bordered by the valley of the Sterk River which is responsible for drainage of the area. The west side of the Sterk River consists of felsites of the Rooiberg Group which are overlain by the sediments of the Waterberg Group that gives rise to a steep descent to the west (Coetzee, 1984).

1.2.4 Soil and Vegetation

Zaaiplaats Tin Mine is situated within the Bushveld Complex which is a sub-tropical woodland eco-region characterised by well-grassed plains, dense clusters of trees and tall shrubs (Siyavula, 2018). Both tall and short trees occur within the mine. The grasses found are tall and turn brown or pale in winter but greener in wet season. The area is characterised by red to grey sandy soil.

1.3 Problem Statement

The Zaaiplaats Tin Mine ceased its operations in the 1990s. During mining, tailings were not being deposited in a well-engineered tailings dam but were being dumped along a non-perennial river nearby. Consequently, tailings had blocked the river channel. There are no known studies of the environmental impacts of the Zaaiplaats

Tin mine tailings, despite the fact that the tailings are currently being reworked and sold for construction purposes.

1.4 Justification

This study brings about understanding and knowledge of the potential environmental impacts of mine tailings at Zaaiplaats tin mine. Tin mine tailings are commonly associated with toxic metals, acidic waters, and radioactive elements (Ibeanu, 2003; Aliyu *et al*., 2015; Murciegoa *et al.,* 2011). The study involved analysis of the metals found within the Zaaiplaats mine tailings thus avail prerequisite information for future mining and environmental management. The information will also be useful for the Department of Mineral Resources, Environmental and Water Affairs that are responsible for environmental protection including protection of natural resources.

1.5 Research Questions

- Are there heavy metals in the Zaaiplaats tin mine tailings?
- Which metals occur in the tailings and how much of within Zaaiplaats mine waste?
- How is the occurrence and distribution of metals within the Zaaiplaats Tin Mine waste?
- Are there Zaaiplaats tin mine tailings radioactive and what are the radioactivity levels?
- To what extent is tin mine tailings impacting on the environment and on human health?

1.6 Objectives

The main objective of the study is to establish the potential impacts of the Zaaiplaats tin mine tailings on the environment and on human health.

Specific objectives are:

- Determine the type of metals found in tin tailings and their quantity and distribution.
- Determine the amount of metal values in water at the mine.

- Determine the concentration values of metals within plants found at Zaaiplaats Tin Mine and-
- Investigate the radiation of the Zaaiplaats tin mine tailings.

1.6 Dissertation Overview

A brief portrayal of the respective chapters is given here from the first to the last chapter. This dissertation starts with an introductory chapter (Chapter 1: Introduction) which gives a description of the study area and a justification of the study. It also provides the research questions, aim and objectives.

The second chapter is Chapter 2: Literature Review which positions the reader on the relevant literature. It covered the most importantly geology of the Zaaiplaats deposit and the history of how mining took place which consequently led to the potential environmental impact worthy of a study. Tin as an economic metal is also explored it terms of its properties, importance, production, geographical occurrence and its social and environmental impact.

Chapter 3: Materials and Methods details methodology used in this study. This chapter is broken down into three sections which is the Preliminary work, Fieldwork and the Laboratory work. Fieldwork section explains how sampling was conducted and how many tailings, water and plants samples were collected.

Chapter 4: Data Analysis and Interpretation is the bulk of the dissertation where the analysed data is being analysed, interpreted and displayed by tables, graphs and strip logs. The concentration values and distribution pattern of the metals had been presented and interpreted in this chapter. Chapter 5: Discussion, Conclusion and Recommendations is the last chapter of this dissertation. This chapter was purely for discussions, comparisons and conclusions of the research findings as well as recommendations for this study.

1.7 Chapter Summary

This is the introductory chapter which started by showing the background of this research dissertation which is that mining is a major economic activity and also has environmental impacts. The main objective of the study is to establish the potential impacts of the Zaaiplaats tin mine tailings on the environment and on human health. There is no research which have been done on the potential impacts of this study area and specifically to tin mine waste in contrary to gold and coal mine waste in South Africa.

Specific objectives are to determine the type of metals found in tin tailings, plants and water at the Zaaiplaats tin mine site. The last specific objective is to investigate the potential radiation of the Zaaiplaats tin mine tailings. The study area is in a semi-arid climate with the wettest and coldest month being November and June respectively. The mine is within the Bushveld Complex.

2 CHAPTER 2: LITERATURE REVIEW

2.1 Geology of the Bushveld Complex

The northern limb of the Bushveld Complex is where the Zaaiplaats tin mine is situated (Fig. 2.1). The Bushveld Complex is a great layered igneous intrusion and thus comprises of rocks which cooled slowly within the earth from molten magma (Schouwstra *et al*., 2000). It is in central north-eastern portion of the Kaapvaal Craton in Southern Africa and its of Paleoproterozoic age. The Bushveld Complex has an approximated total area of 65 000 km^2 and it contains most of the world's resources of vanadium, chromium, and platinum group elements (Lee, 1996; Hunter, 1976).

The Bushveld Complex consists of 4 groups of rocks which are the various satellite intrusions, Rashoop Granophyre Suite (RGS), Lebowa Granite Suite, and Rustenburg Layered Suite (RLS) (Fig. 2.1). According to Kinnard (2004), the Rashoop granophyric rocks occur broadly between the Rustenburg Layered Suite beneath and the Rooiberg Volcanics. The RGS consist of three units based on textural differences which are the Rooikop Granite Porphyry, the Stavoren Granophyre and the Zwartbank Pseudogranophyre (SACS, 1980).

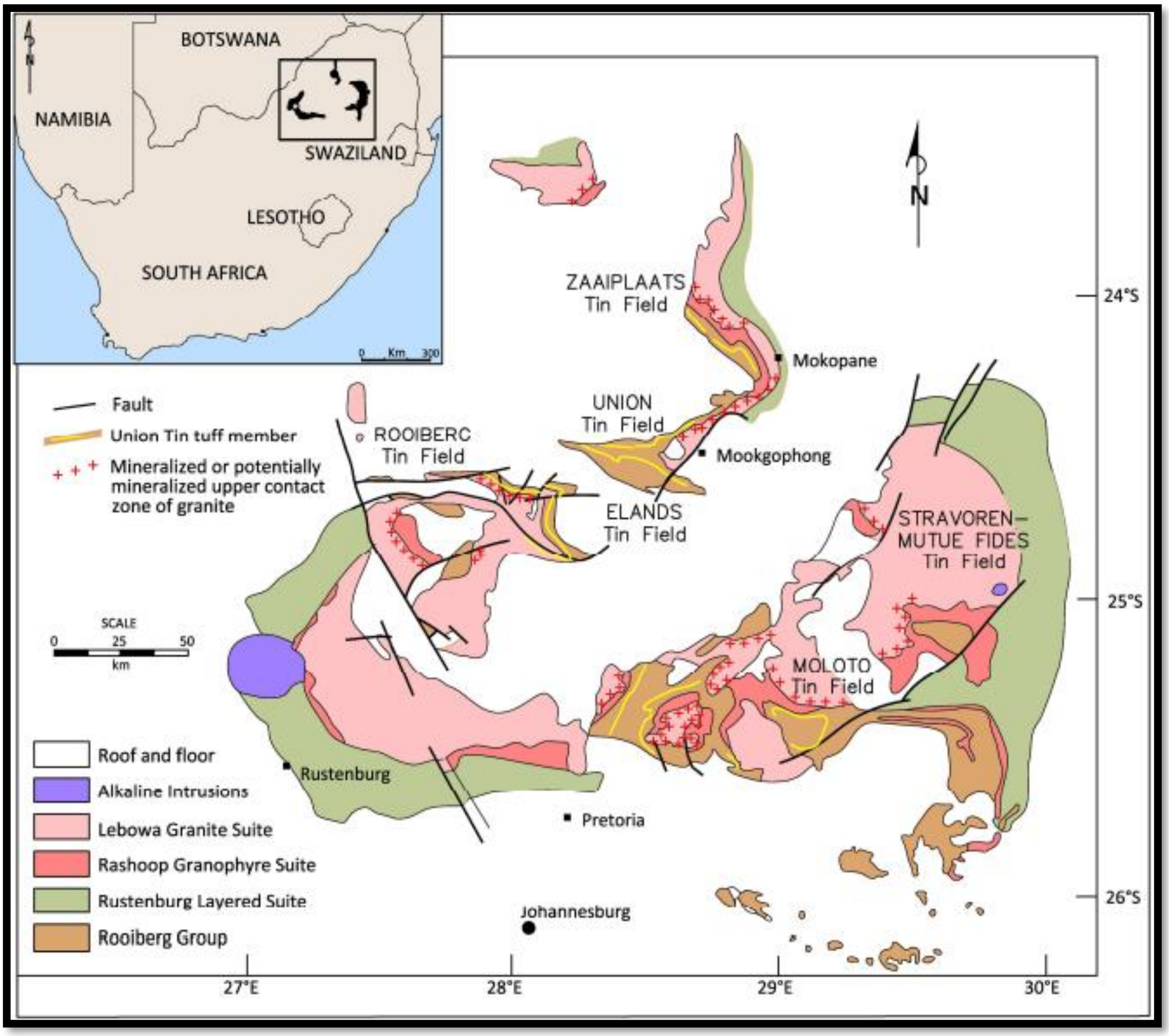


Figure 2.1: Geological map of the Bushveld Complex (Kinnaird *et al*., 2016)

The Rustenburg layered suite comprises a different type of rock, consisting of nearly 8 km of gabbro, norite, pyroxenite and other mafic to ultramafic (Harmer and Armstrong, 2000). The Rustenburg Layered Suite comprises of four main stratigraphic units which are the Lower Zone which is roughly 1500 m of harzburgitebronzitite and the Critical Zone which is also almost 1500 m of pyroxenite-anorthosite-norite. The Upper Zone has 2250 m of gabbronorite-magnetite gabbro-olivine diorite and the Main Zone is around 3 750 m of norite-anorthosite-gabbronorite, and their precise border line has been the matter of much discussion (Kruger, 1990).

The Bushveld granites or the Lebowa granites occur at around 3 km and 2 km thick sheet-like sill of batholithic parts and larger and the utmost familiar variety that occupies most of the middle core of the complex (Kleeman and Twist, 1989). Potassic, A-type granites, and magnetite-bearing are the principal granites of the Lebowa Granite Suite. (SACS, 1980).

The granites intrude and underlie the Rashoop Granophyre Suite. They also overlie the Rustenburg Layered Suite and the Rooiberg Group wherever these groups are present. The granites are cooled besides the granophyre and the contact is regularly noticeable by a zone of quartz-feldspar pegmatite correlated with late differentiate aplite. (Crocker *et al.*, 2001) This is close to referred to as the microgranite or Klipkloof granite. The manifestation of Klipkloof granite add up to towards the roof, and forms intrusive veins, sills, and in the Nebo granite (Crocker *et al.,* 2001)

2.2 Geology of Zaaiplaats Deposit

The Lease and the bobbejaankop granites are the members of the Lebowa Granite Suite of the Bushveld Complex. These granites accommodate the Zaaiplaats mineralisation (SACS 1980). They are a sheet like batholith which intruded near the contact amongst the Rustenberg Layered Suite and covering Rooiberg Group Felsites and Rashoop Granophyre Suite (SACS, 1980). The mineralized granites at Zaaiplaats intrudes granophyric granites, Rashoop Granophyre Suite which is the contact dipping at approximately 15^0 to the west.

In a vertical profile (Fig. 2.2), the granites are made up of the Lease granite which is a thin sheet of fine-grained and an upper, marginal pegmatite which are both underlined by Bobbejaankop Granite which is coarse-grained. (Cotzeee, 1984; Pollard *et al.,* 1989). The Lease and Bobbejaankop Granites are comprised broadly by quartz, alkali feldspar, chlorite, minor zircon, and magnetite. The Bobbejaankop and Lease granites are alkali feldspar granites which host tin-tungsten mineralisation.

Lease granites host the ore in sub-horizontal, low grade and tabular bodies. However, the Bobbenjaankop granites has a lower zone of disseminated cassiterite mineralisation nearly 50 m below the Lease Granite (Kinnard *et al.*, 2016) (Fig.2.2). In the dark, irregularly and randomly shaped tourmaline, tourmaline-rich pipes, frequently arises as radiating a circular crystal shifting microclinised feldspar with the interstitial relict quartz. In the micaceous rich core pipes, there is a plentiful of cassiterite and is accompanied by galena, wolframite, scheelite, molybdenite, arsenopyrite, pyrite, calcite, fluorite, and zinnwaldite (Kinnard *et al.,* 2016). Lease granites has the bleached haloes with quartz and albite nearer the pipes with the rims of pink microcline and there is an addition of chlorite in the Bobbejaankop granite. Countless minor pipes fluctuating in size from a few cm across to 1 m in size persist. The considerable pipes have been mined out and they were roughly elliptic, fit for 12 m across. Inconsequential sub-vertical veins with sulphides, calcite, fluorite, and quartz, crosscut the pipes and granites (Kinnard *et al*., 2016).

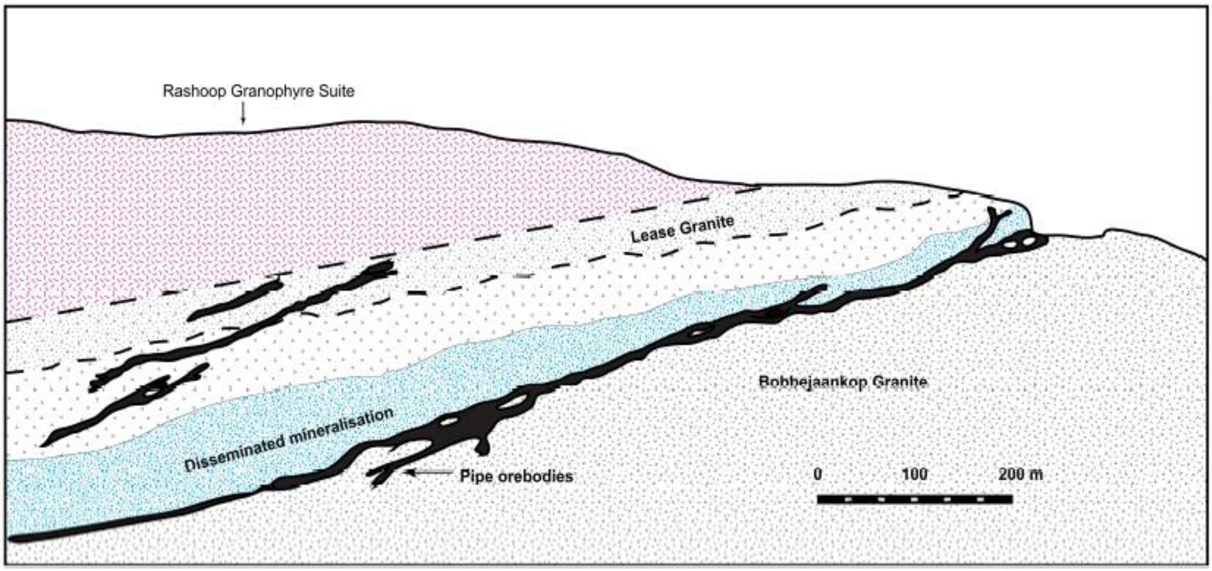


Figure 2.2: Schematic east-west section of the Zaaiplaats mine showing distribution of rock types and mineralisation styles (Pollard *et al*., 1991a, modified by Kinnard *et al*., 2016).

Miarolitic cavities are developed throughout the granites and vary from greater than ten volume percent in the uppermost part of the Lease Granite to fewer than one volume percent in the deepest part of the Bobbejaankop Granite (Pollard *et al*., 1991b). Miarolitic cavities contain a variety of infilling hydrothermal minerals incorporating fluorite, chlorite, albite, quartz, sericite, hematite, and calcite. Bobbejaankop and Lease facies has the interstitial fluorite appearing in pegmatitic miarolitic and pods spaces with enormous quartz crystals and seldom of euhedral calcite (Kinnaird *et al*., 2004).

2.3 History of Zaaiplaats Tin Mining

The Zaaiplaats 223KR, Groenfountein 227KR and Roodepoort 222KR were farms in which cassiterite was found in 1905 by prospectors (Lynn *et al.,* 2011). The development of the Zaaiplaats Tin Mining Company and Groenfontein Tin Mine were because of the discoveries of the cassiterite. Subsequently, tin deposits were encountered on neighbouring farms such as the Salomon's Temple 230KR. Cassiterite concentrate and tin metal were supplied by the Zaaiplaats Tin Mining Company constantly from its establishment to its shutting in 1989 (Lynn *et al.,* 2011).

It is between the year 1906 and 1989 that the Zaaiplaats Tin mine or the Zaaiplaats deposit produced over 100,000 tonnes of tin as of hard-rock mining. The simple processing methodology of stamp-milling of the ore was adopted and was later followed by gravity separation through shaking tables and spirals. The mine waste was later disposed of in a valley adjacent to the mine as a results of crude processing methodology employed. Substantial tin resource is considered to remain in the tailings dump (Miningatlas, 2018). Cassiterite occurred in irregular pipes with diameter fluctuating from ten centimetres to ten meters in lenses and the Zaaiplaats was producing 18 tonnes of tin per month. The mine is assumed to have shut down in the mid-1990s. The cassiterite was also found as disseminations in the granite rock (Mindat.org, 2019). The 90% of all the ore came from underground operations until 1927 and another ore was found surface workings of the pipes. Mining took place in fine and calm conditions of about 150 m below the surface (Mindat.org, 2019).

2.4 Tin

2.4.1 Properties and Occurrence of Tin

Tin has a symbol Sn and it's a chemical element (Bell, 2020). It is a silver to white and soft metal that is bright and simple to melt down and can be cut without much force. It is so soft and is seldom employed as a pure metal. It has an atomic number 50 in the periodic table (Calvert, 2002). Tin is a found within group 14 of the periodic table and it occurs as a post-transition metal (Fig 2.3). Tin is found completely and directly from the cassiterite that contains stannic oxide (SnO_2). Metallic tin does not effortlessly oxidize in air (Britannica, 2023)

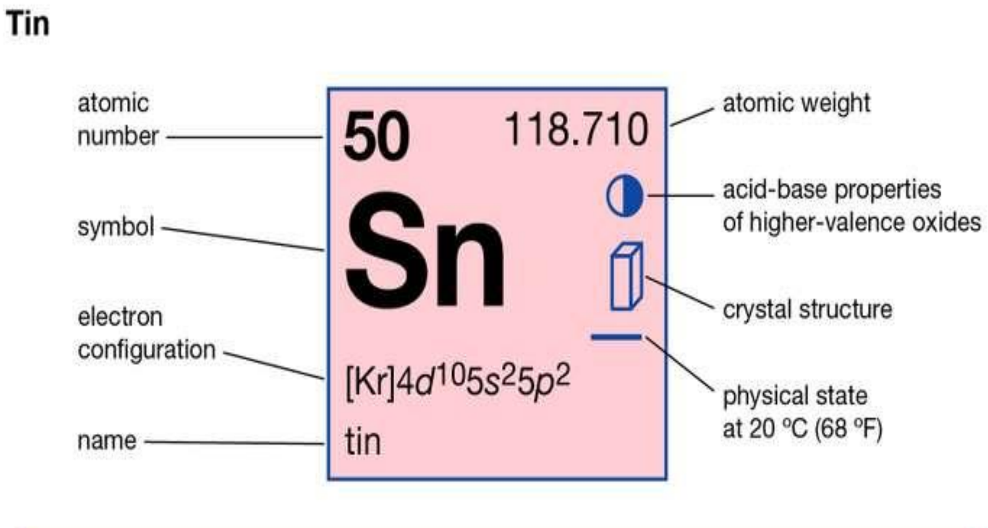


Figure 2.3: Properties of tin element (Britannica, 2023).

Physical Properties

Tin is a metal which is ductile, malleable, and greatly crystalline silver to white metal. Its melting point is further lowered to 177.3º and melts at very low temperatures of approximately 232ºC (Holleman *et al.,* 1985). It is divided into two allotropes which are named the α-tin and β-tin, which differ in terms of colour and uses. The white in colour β-tin is in metallic in form. β-tin is stable at, and above room temperature and it is malleable. α-tin has a diamond cubic crystal structure but does not have metallic properties entirely because of its atoms that forms a covalent structure and electrons cannot move freely (Holleman *et al.,* 1985). The β-tin and α-tin are generally known as White tin and gray tin respectively (Holleman *et al.,* 1985).

According to Woodford, (2019), tin is a typical metal that is easier to work with in numerous conditions. Tin is ductile and promptly makes a greyish protective oxide on its surface. However, it is not used as a construction material and its far weaker as equated to metals such as iron. Tin has a reasonably low melting but higher boiling point. It means that tin is a liquid over a widespread varying array of temperatures and may be exploited in several industrial processes.

Chemical Properties

Tin can be damaged by acids and alkalis, but it resists corrosion from water. It appears as a catalyst, and it assists in hastening chemical reaction when oxygen is in solution.

Tin is applied as a protective coat for other metals and can be greatly polished (Holleman *et al.,* 1985).

Occurrence

Tin is one of the elements which is never found as native element but is obtained from numerous ores. Tin is produced through the long s-process in low-medium mass stars and then by beta decay of the heavy isotopes of indium (Sutphin *et al.,* 1992). Cassiterite is the only economic ultimate source of tin and tin is extracted from. There are minor quantities of tin which are extracted from multifaceted sulphides ores. Approximately eighty percent of extracted tin is as of secondary deposits found downstream from the primary lodes and it because of elevated specific gravity of tin dioxide. Tin is mostly retrieved from granules washed downstream in ancient years and get deposited in sea or valley (Sutphin *et al.,* 1992). Dredging, open pits or hydraulicking are the most efficient and cheap ways of mining tin.

2.4.2 Importance of Tin

Tin is one of the important elements that can be used for so many applications. In present times, tin is utilized in alloys, meaning it is the alloys that have many different usages. Historic uses of tin were for weaponry, tin foil, collapsible tin tubes and tinplating. Tin is presently used is alloyed for bronze and pewter making, superconductive wire and solder, and electrically conductive coatings for frost-free windshields and panel lighting, window glass production and organ pipes. An alloy of copper and tin is bronze. Egypt to China presently are the locations in which bronze artifacts such as sickles, hatchets, and mirrors have been discovered. The known harmful well-being effects of lead, pewter, is presently made from alloying tin, cobalt, and antimony (Bell, 2020).

Solder

Electronic industry is the most recent application of tin as a solder. Tin is currently used in several purities and alloys. Solders of tin are suitable for boding materials because of having a low melting point (Bell, 2020). Tin’s use in solders is the foremost application. Legislation were established in 2006 for the prohibition of the use of lead in electronics, and then that is where tin became the main metal in solder. However, replacing lead has many glitches including formation of tin whiskers causing electrical problems and higher melting points (Black, 2005).

Tin Plating

Tin plating was done in the past and at our present day which is noteworthy usage of tin. The application of actual thin shielding coating of tin to steel, copper and other materials is called tin plating. Dipping of materials into molten tin is the process and is also known as electroplating. Tin and the material it wraps are protected by the dull, tin oxide that appears and forms on the surface of the tin plate (Woodford, 2019). As a result, to its low toxicity, tin-plated metal containers are broadly used for food preservation and packaging (given the name cans). The tin plate canister for preserving food form’s economic part for metallic tin. Safety pins, hair grips and paperclips are rustproofed using tin (Woodford, 2019).

Specialized Alloys

The other most prominent use of tin is the making of numerous alloys, including pewter, bronze, babbitt metal and solders of various kinds (2019). Tin forms a comprehensive type of beneficial alloys when combined with other elements although tin is generally alloyed with copper. Tin has been used sometimes in coinage. Tin minor percentages are used for the cladding of nuclear fuel when zirconium alloys have been added. Also, greatest metal pipes in a pipe organ are made of tin-lead alloy. The foremost benefits of using tin for pipes incorporate its resistance to appearance, corrosion, and workability. The most important alloys include die casting alloy, phosphor bronze fusible metal, babbitt metal, pewter, bronze metal, and white metal (Robert, 2006).

2.4.3 Metals associated with Tin

Tin elements that is associated with variety of metals. These metals differ in concentration based on locations e.g., tailings, soil, streams. Tin is associated with metals such as chrome (Cr), lead (Pb), vanadium (V), barium (Ba) and arsenic (As) and these metals are exposed during tin mining (Ashraf *et al*., 2011). Metals associated with tin are recognized for their negative impacts on the environment and on health and these negative impacts are harmful to the local residences (Ashraf *et al*., 2011; Asmarhansyah *et al*., 2017). Vanadium, barium, lead, chrome, lead, and arsenic are the most metals produced during tin mining and are concentrated in tin mine waste (Alshaebi *et al.*, 2009).

2.4.4 Production of Tin

According to Calvert, 2002, stannite is the main tin ore. Stannite is changed by supergene enrichment to cassiterite and is a mixed sulphide, Cu_2FeSnS_4. Cassiterite is the dark and heavy "tinstone" that is positioned in veins and at river gravels. Sulphides of lead, antimony, copper, zinc, bismuth, silver, and iron are considerably removed as much as possible when handling lean ores. These sulphides are heavy like cassiterite and cannot be rejected simply by gravity separation in water. Differential flotation had been an achievement. Elimination of sulphides, and leaching with hydrochloric acid to dissolve the zinc, iron, bismuth copper, and bismuth impurities is done after the ore had been roasted. It is then treated with chlorine to form chlorides of silver, lead, bismuth, and antimony which are leached out with dilute acids (Calvert, 2002).

Liquid tin is made when the concentrated ore is smelted in a blast furnace or a reverberatory furnace with coke or anthracite screenings. The slags generally have a reasonable measure of tin. Tin is lost in flue gases. The reverberatory furnace provides better recovery. The slag must be re-treated to salvage the 10% to 25% of tin that it includes (Calvert, 2002).

According to Woodford, 2019, tin ore is crushed to a powder and washed to free of the impurities before being heated with carbon (in the form of coal) and limestone in a giant furnace. Other metals, such as iron, copper and zinc, separate out. Molten tin sinks to the bottom of the furnace and is shaped into solid blocks known as ingots. Like most other metals, tin can also be separated or purified using electrolysis (an electrical-chemical process that works in the opposite way to a battery).

2.4.5 Economic aspects of Tin

Consumption of Tin

The consumption of tin varies in developed and developing countries. In 1960, developed countries consumed about 61% of world tin production while the rest is consumed in developing countries (International Tin Association, 2021). Industrialized countries' worldwide tin utilization in the post-war period has increased more gradually than that of other metals. United States of America is the most advanced purchaser of tin with the share of about 21% of overall world consumption and is followed by Japan, Germany, United Kingdom with 14%, 6%, 6% respectively (Chhabra *et al*., 1978).

Total consumption grew between 1960 and 1979 at an average yearly rate of only 0.5% per annum. The superior justification for this sluggish growth was the increasing replacement of tin-free steel and aluminium for tinplate in can production. Furthermore, technical innovation has cut down the amount of tin required in tinplate.

Trade

Also developing countries are the ones dominating tin trade just like they consume it. They report eight percent of tin metal world exports and approximately 92% of overall world exports of tin concentrates. In the chronicle of tin trade, the flow of trade has been in the form of export of tin-in-concentrates from producing developing countries to consuming developed countries (International Tin Association, 2021). In recent years, the direction of trade has remained the same, but tin metal has substituted for tin-in-concentrations. However, the significance of the trade-in tin concentrates has declined severely over the past 20 years as emerging producing countries have extended their smelting capacity (Chhabra *et al*., 1978)**.**

Market Prices of Tin

According to London Market Exchange, (2020), the current market price of Tin is in 16700 USD dollars per ton. According to Mongabay website, (2020), the market prices of tin were higher in the 1980s and had a sharp decrease in late 1990. However, there is an increase in the price of tin from 2014 to 2020. The figure displays the price of 99.85% of pure, clean refined tin from 2014 to 2018, containing a prediction until 2030. According to Garside, (2019), it is anticipated that in 2030, the price of tin will be close to 23,000 U.S. dollars per metric ton which is a considerable growth evaluated to the present price per metric ton (Garside, 2019).

2.4.6 Tin Mining Worldwide

There are about 35 countries that mine tin throughout the globe (Kinnaird *et al.,* 2016). According to the International Tin Association website (International Tin Association,

2021) tin mining started in 3000 BC (Bronze Age) in Europe and China. In current times large deposit of tin are being exploited throughout Asia, South America, and Africa. Europe or North America countries have no mining or production of tin. A substantial proportion of the worldwide tin supply mostly emanates from small-scale and artisanal mining operations which are undertaking in developing countries. The bulk of global tin production is from big formal extraction operations.

China

China is the largest producing country and is considerably the world's main market for tin, it is currently accounting for 40% of world refined tin production and consumption (International Tin Association, 2021). Various initiatives have been taken by the Chinese government to improve the environment performance of the industry (International Tin Association, 2021).

South America

South America is also one of tin producers in the world. Peru, Bolivia, and Brazil have reported for a foremost combined share of worldwide tin supply during current history, which in turn showing amid the world's major suppliers (International Tin Association, 2021). These three Latin American Tin producing countries currently tab for about 16% of world mine production (International Tin Association, 2021).

2.4.7 Tin in Africa

The foremost African countries traditionary recognized for their tin production are Democratic Republic of Congo (DRC), Nigeria, Namibia, South Africa, Rwanda, and Zimbabwe. The small niobium (Nb), tin (Sn), and tantalum (Ta) operations are also well-recognised from Uganda, Cameroon, Burundi, Egypt, Niger, Ethiopia, Somaliland, Madagascar, Sierra Leone, Sudan, and Mozambique (Kinnaird *et al.,* 2016). Presently, the main producers of tin in African continent are the artisanal miners and small-scale operation and they are producing 2.7% of the world's tin production with the DRC, Rwanda and Nigeria producing 3,000 tonnes, 1,900 tonnes and 570 tonnes respectively (USGS, 2013). Tin has been prospected for and mined in Nigeria since 1904 by western companies. Tin was the major revenue maker and basis of foreign exchange in the country before the discovery of oil (Kinnaird *et al.,* 2016).

The tin ore export from the DRC was approximated to be at 18,000 to 25,000 tonnes (Garrett and Mitchell, 2009). The DRC was the prominent African tin country producer with a yield of almost 3,000 tonnes of cassiterite in 2013 (Kinnaird *et al.,* 2016). Mineralisation occurs as a stockwork of north-south trending polymetallic cassiterite-bearing veins, 1 km to 3 km east of the contact between a medium-grained pink porphyritic granite to the west and micaceous schists, quartzites, phyllites and amphibolites, with minor calcareous rocks to the east (Witley and Leighton, 2015). Veins vary in thickness from 2 mm to 0.8 m being composed of massive, pinkish brown, fine-grained and often botryoidal cassiterite, and show compositional layering. Early cassiterite was followed by later chalcopyrite and bornite and then by galena and sphalerite mineralisation (Witley and Leighton, 2015). However, in the Atondo open pit mine, mineralised quartz veins are hosted by two-mica granites with cassiterite and muscovite at the contact between the quartz veins and the host rocks, and in fractures in the veins. A sub-vertical vein orientated 0-25°E consists primarily of quartz and muscovite, with minor fluorite (Dewaele *et al.,* 2015)

Rwanda had also produced tin and is regarded as the largest cassiterite producer on the continent in 2013 (USGS, 2015). The pegmatites of the Gatumba area, 50 km west of Kigali had been mined for columbite-tantalite and cassiterite, although they also contain beryl, apatite, spodumene, amblygonite, and rare phosphates (Dewaele *et al*., 2011). In the tin mining district of Rutongo in central Rwanda, 10 km north of Kigali, hundreds of cassiterite-bearing quartz veins occur on the eastern limb of a large anticlinorium that was intruded by G4 granite (Pohl and Gunther, 1990; Dewaele *et al.,* 2010). The medium-grained granite is sericitised and strongly kaolinised. The veins intrude thick sandstones and quartzites interbedded with minor pelites.

In Zimbabwe, the Kalinda and Kamativi mines were operational until 1994 and had produced about 1,200 tonne per year of cassiterite until the end of their production life (Kinnaird *et al.,* 2016). Cassiterite has been mined in Ta-rich pegmatites at the Bikita Mine in the Masvingo Greenstone Belt on the Zimbabwe Craton. These pegmatites host considerable lithium in amblygonite, lepidolite, petalite, spodumene, and eucryptite, as well as caesium in pollucite. They go along with by fergusonite, microlite, tantalite, wodginite, tapiolite, simpsonite, euxenite, and cassiterite (Martin, 1964; Von Knorring and Fadipe, 1981). The Sn-Ta ore occurs in marginal pockets of quartz-rich zones in substantial masses of lepidolite greisen. From 1916 to 1950, 160 tonnes of columbite-tantalite concentrate were produced and 188 tonnes of cassiterite concentrate were produced from 1916-1959 (Bartholomew, 1990).

2.4.8 Tin in South Africa

The operating tin-mining firms in South Africa were Zaaiplaats, Union Tin and Rooiberg which were all underground operations.

Rooiberg

Rooiberg Fragment is where tin has been mined for a minimum 500 years, and mining began in around 1906. The Rooiberg Minerals Development Company was registered in 1908 and operations on Olievenbosch farms and Hartbeestfontein where the current Rooiberg Mine is located. Miners of European descent reopened the historical tin mines of the Rooiberg area in1905. This tin has been mined in the Rooiberg area since 1905 until 1992 (Labuschagne, 2004). Rietfontein and Leeupoort and operating mine on Leeuwpoort mineral rights were bought in 1935. They were later followed by the purchase of Blaaubank Tin and Nickel Mines Limited, including Blaauwbank farm minerals rights in 1964 (Oxley-Oxland and White, 1974).

Vellefontein Tin Mining Company Limited was bought in 1970 with the mineral rights on Vellefontein and the operating Vellefontein Mine. The name of the company was changed to Rooiberg Tin Limited and a tin smelter was installed in 1979. The Rooiberg orebodies are incorporated in an ancient fragment of sedimentary rocks sited in the much younger rocks of the Bushveld Complex. The Rooiberg tin field is situated within the western lobe of the Bushveld Complex.Tin metal of 83,000 tonnes were produced from the Rooiberg from first production until 1992 (Labuschagne, 2004).

Union Tin

The Union Tin mine has the tin-bearing lodes which form an irregular stockwork and it occurs in shales in the vicinity of their contact with the overlying felsite’s. The arrangement is so irregular, and the lodes and veins are so difficult to find. There was a need for constant sampling and underground planning (Dagless, 1984).

Zaaiplaats

Zaaiplaats produced 18 tonnes of tin metal monthly from cassiterite. Cassiterite was occurring in irregular pipes with diameters varying from about 10 centimetres to 10 meters in lenses, and as fine disseminations in the granite rock. The ore was attained from surface workings of the pipes, but since then about 90 per cent of all the ore comes from underground operations until 1927. Mining took place in cool and calm conditions and was about 150 m below the surface. There were 37,079 tonnes of metallic tin produced from the Zaaiplaats tin field in 1909 (Falcon, 1985). Cassiterite has been mined from the six main regions of the Lebowa granites and the utmost productive ores being near to the contact with the metasedimentary rocks of the Transvaal Supergroup, (Groves and McCarthy, 1987).

2.5 Mine Wastes

Mine wastes are the soils, igneous, metamorphic, sedimentary rocks, and loose sediments which are heterogeneous geological materials (Srivastava, 2012). Mine wastes incorporate the overburden and waste rocks from surface and underground mine-workings. Mine wastes also have concentration of ore minerals fuels, minerals, industrial minerals, coal, metals that are sub-economic (Hitch *et al*., 2010). The standard of classification of materials as sub-economic or economic and the separation of waste rock from metalliferous ore is called the cut-off grade. (Lottermoser, 2013). The concentration of the ore element in any individual unit of mined rock and the rate of mining that unit is where the cut-off grade is established. Consequently, each mine has a diverse principle for separating mine waste from ore. Wall rock material which is also referred to waste rock is removed to retrieve and mine economic ore (Lottermoser, 2013).

Coal mining describes waste rocks as spoils. The physical and chemical characteristics of mine wastes differ according to moisture content, geochemistry, mineralogy, and particle size of the mined-out material (Hassinger, 1997). The foremost bases for mines waste material are soil, rock, and sediments from open pits, surface mining workings, and to a to a lesser extent considerable rock removed from shafts, haulage ways, and underground operations (Hassinger, 1997).

Types of Mine Waste

Tailings

Tailings are produced during mineral processing plants and are a combination of process effluents and ground rock. These tailings can be liquid, solid or slurry form of fine particles, and tailings are typically extremely toxic and possibly radioactive (Engel, 2012). The process of beneficiation of the ores and following discarding to surface containment facilities disclosures elements to speeded weathering and increased mobilization rates consequently. Tailings characteristics can differ significantly and are determined by the chemical and physical methods implemented to extract the economic product concurrently with ore mineralogy (Environment Australia, 1995).

Tailings are made up of liquids and solids. These solids are those released processed water into a tailing's storage facility (TSF) commonly known as tailings dam. The waste repository is the liquids in a form of surface and pore waters. Higher concentrations of processed chemicals are what these tailings liquids tend to have (Crock *et al.,* 1999). Tailings fluctuate greatly in their physical and chemical characteristics. The characteristics of tailings incorporates mineralogical and geochemical compositions; settling behaviour; viscosity characteristics; soil plasticity; pores water chemistry; tailings particles specific gravity; consolidation behaviour; permeability versus density relationships; leaching properties; and strength characteristics (Environment Australia, 1995).

Tailings dam

The gangue or by-products of mining operations following separation of the valuable mineral is stored in tailings storage facility which is an earth-fill embankment dam. Cross valley means that tailings dam has one or two dams constructed crossways a section of a valley, paddock impoundments that is 4-sided impoundments constructed on flat terrestrial, or side hill with one dam constructed perpendicular to the slope of a hill (Environment Australia, 1995).

Tailings dams require physical and chemical characterization for them not to break when using tailings, solids and waste materials as building materials for dam walls and banks (Fig. 2.4). The storage regions are also planned to remove any potential environmental impacts and to enhance the quantity of tailings stored. The processed waste is isolated by designed present tailings dams and other engineered structures

(Davies and Martin 2000). The foremost and insignificant environmental apprehensions with tailings dams are the probable release of tailings into the environment through pipeline failures, dam leakages and fallings-out, visual impact of the large, engineered erection and the structural stability of the dam (Davies and Martin 2000).

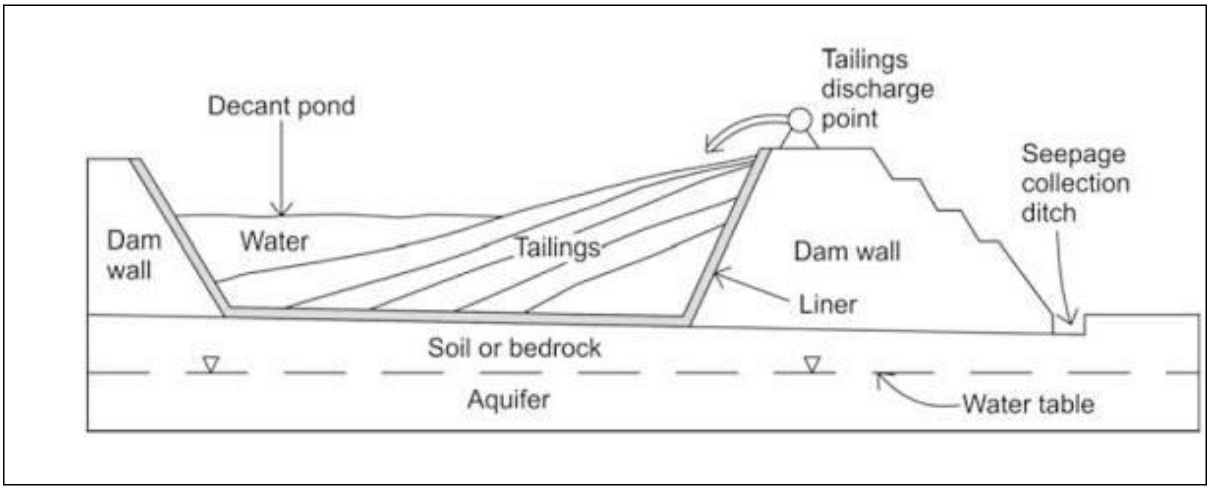


Figure 2.4: Simplified cross-section of a tailings dam (Davies and Martin 2000).

Waste rock dump

Mining workings yield enormous masses of waste rocks which frequently has minor or not at all valuable minerals. These waste rocks are comprised of blocky, crushed, or coarse material involving of varying dimension, from actual enormous rocks to fine particles (Tayebi-Khorami *et al*., 2019). The waste rock dump is comprised of low-grade material which has been unearthed and discarded to attain the high-grade ore (Lewis *et al*., 2020). Waste rocks with substantial minerals such arsenopyrite, pyrite, chalcopyrite, pyrrhotite, and which are sulphides from gold mining have the potential to produce AMD with potential for the release of heavy metals such as As, Cu, Zn, and Pb (Servida *et al*., 2013).

Mine water

Water is essential at mine site for vast activities such as mineral processing, dust suppression, hydrometallurgical extraction, and coal washing. Ground-water aquifers and surface water bodies are the sources of water. Tailings dams and ponds holds discharged water while some tailings are also a by-product of mine dewatering processes. The volume of mine water made, used, and discarded of at mine operations is far more significant than the volume of solid waste produced. Water gets to interact with minerals and dissolves them at mine sites and therefore water at mine sites contain dissolved and particulate matter. Flowing water can cause adverse turbidity and sedimentation when the laden waters reach receiving water bodies, lakes, and streams. This water can modify temperatures and their chemical constituents may have detrimental effects on flora and fauna (Kleinmann, 1989).

AMD is an example of poor mine water quality and is coupled with environmental impacts which arises when sulphide minerals get exposed to water and air. It is very difficult to halt or stop AMD when it begins because sulphide oxidation is an autocatalytic reaction (Demchak *et al*., 2004; Lambert *et al.,* 2004).

AMD can take place because of several processes such as when (Kleinmann, 1989);

- Ground water enters underground workings established above the water table and escapes via surface openings or is pumped to the surface;
- Meteoric precipitation and flood inflow enter mine or tailings disposal facilities;
- Run-off from rainfall interacts with mining, mineral processing, and metallurgical operations;
- Ground water enters pits and surface excavations;
- Meteoric precipitation comes in contact with pit faces;
- Meteoric precipitation infiltrates coal and ore stockpiles, heap leach piles, coal spoil heaps, and waste rock dumps (Fig. 2.5); and
- Surface water and pore fluids of tailings, heap leach piles, ore stockpiles, coal spoil heaps, and waste rock dumps may surface as seepage waters or migrate into ground water aquifers.

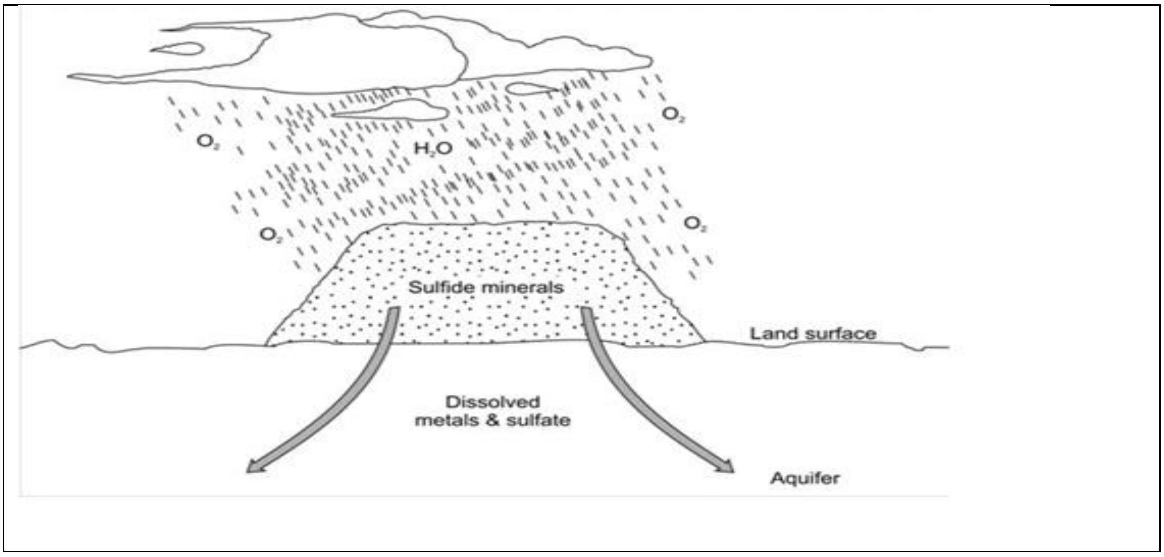


Figure 2.5: Conceptual process of sulphide oxidation and AMD development in waste rock dump (Kleinmann, 1989).

2.6 Environmental Impacts Associated with Mine Wastes

Mining activities are not environmentally friendly and negatively affects human heath directly and indirectly. On the other hand, mining activities are very undesirable as they provide job opportunities as well as economic benefits to citizens (Singh *et al.,* 2016) These impacts include effects on biodiversity, heavy metal contamination, water pollution, Acid Mine Drainage (AMD) including impacts on human health.

Effects on biodiversity

Animals, vegetation, and microorganisms are being negatively affected by direct poisoning and indirect poisoning. The indirect intoxication is mainly through water and food. Mine wastes impact aquatic biodiversity through direct poisoning when toxins are kinetic in the sediment and bioavailable in water (Steinhauser *et al., 2009;* Niyogi *et al.,* 2002). Pollutants in streams where there are excessive concentrations of suspended sediment causes turbidity can also affect aquatic organisms consequently destroying algae biomass (Niyogi *et al*., 2002; Ryan, 1991).

Heavy metal contamination

Heavy metals are the foremost source of environmental contamination because of their ability to accumulate and their toxic nature (Jaffar *et al.,* 2007). The dissolution and transport of metals by run-off and precipitation from mine waste or mine tailings results in heavy metal contamination. The transported metals from mine waste can move on the environment, thus, contaminating surface and groundwater, causing dermal diseases to animals and human, threatening biomass on the nearby environment, crippling plants and reducing productivities (Nuss and Eckelman, 2014; Diehl and Sanhudo, 2004).

Water pollution

Mine wastes have greater effects on the surrounding water resources that include surface and groundwater. Nuss and Eckelman, (2014), indicated that this may result in elevated by concentrations of chemicals, for instance, mercury, arsenic, and sulphuric acid in a greater part of ground and surface water. The dumped tailings contaminate the groundwater on the underlying strata. The movement of contaminated water from the waste dams into the underlying strata is subject to the relative permeability of the material (United Nations, 1996).

Acid mine drainage

The environmental impact of the mining business globally is acid mine drainage and is costly and considerable. It takes place whilst sulphide-rich wastes from the mines interact and get exposed to oxygen and water. AMD affect ground and surface water sources long after mining operations have ceased. Several studies on impacts of AMD have been conducted (Ogola *et al.,* 2002; McCathy, 2011). These include contaminated water with heavy metals, lowering water pH, contaminate soil, riverbed coating and blocking sunlight and through food chain will produce detrimental effects on human health.

The downstream use of water through drinking water, stock watering and irrigation are impacted by the generation acid mine waters with their higher salt and metal concentrations. The aquatic life is ruined by acidity levels, metalloid and metal concentrations which might have surpassed aquatic ecosystem toxicity restrictions. The irrigation of crops with impacted stream water and having metalloid and metal concentrations may be unacceptable and well exceeding threshold values can be phytotoxic to crops (Dolenec *et al*., 2007).

Effects on human health

Mine wastes also affect human health in many ways. The spread of contaminated water and air during both windy and rainy seasons initiate so many diseases such as silicosis, minamata and other neurological disease to humans. Dust emission is one of the hazards that is associated with mining activities which can last for several years during the active use of the tailing's dams or subsequently the mine closure (United Nations, 1996).

2.7 Environmental Impacts of Tin Mining

Land degradation

Mining of any mineral commodity has both positive and negative environmental, health and socio-economic consequences. The effects of tin mining had been studied in Nigeria because an abundance of tin mining operations. According to Ndace and Danladi (2012), the Bukuru area in Jos in the northern part of Nigeria was one of the predominant tin mining areas which had resulted in considerable erosion damages to land cover. The study had proven that tin has had a substantial impact on the natural ecology. Macro-organisms, micro-organisms and plants had been removed off their normal natural territory. There is a change in land use essential for agricultural and human settlement because of the removal of organic rich surface soils. The absence of natural flora had greatly improved the menace of gully erosion in mined out areas (Ndace and Danladi, 2012).

Radioactive contamination

Apart from land degradation, tin mining may result in production of radioactive ores and metals from the host rocks into the environment and this tends to pollute the environment because the associated accessory minerals are detrimental to fauna at low concentrations (Adiuku-Brown and Ogezi, 1991). According to Omotehinse and Ako, 2019 radioactive minerals such as monazite, pyrochlore and xenotime, which were obtained as by-products of tin mining in the Jos Plateau, Nigeria caused health problems. These minerals were left as waste in many mining sites in the Jos Plateau and led to the death of people which were connected to the high level of radiation from monazite-rich sand that was used for the construction of the houses the people lived in.

Metal loading

Tin mining is also associated with polluting the environment by heavy metals. According to Nurtjahya *et al*. (2017), Bangka Belitung Islands produced more than one third of worldwide tin supply which is an estimated number of 106,000 tonnes of tin in 2013 and the bulk of it is exported. In 2013, Tin mining is the main commercial driver in the area taking place offshore and inland with eighty dredges and around forty thousand floating tin mines off the coast of Bangka Island. Activities associated with tin mining has in water pH decreasing by 25% and the concentrations of Pb (0.223 ppm) and Total Dissolved Solids of 705 in solution offshore found to be above the ministerial regulations which are 0.008 ppm and 400 ppm respectively (Nurtjahya *et al*., 2017). There are almost 30 and 50000 independent smelters and artisanal small-scale mines in the Bangka Belitung Islands respectively (Nurtjahya et al., 2017).

The study done to produce data on the build-up of heavy metals for instance, arsenic, lead, tin, zinc, and copper in fish samples gathered from past tin mining catchment indicated an increased accumulation of these metals in fish. Sn > Pb >Zn > Cu > As is the order of heavy metals measured (Ashraf *et al*., 2012). These heavy metals on fish species were found to be because of a high influx of metals due to pollution from the dredged mined out ponds of the former tin mining catchment (Ashraf *et al*., 2012). Heavy and toxic metals incorporate the transition metals, metalloids, actinides and lanthanides and are elements that possess metallic properties (Gautam *et al.,* 2011).

2.8 Historical ways of storing mine tailings

Historically, tailings were consistently disposed of absolutely into the closest surface watercourse. This is still practised presently in some regions worldwide predominantly in regions of high rainfall, steep and unstable terrain (Engel, 2012). The Grasberg mine in Indonesia and the Ok Tedi mine in Papua New Guinea are the cases of prominent mining operations that discharge of their waste rock and tailings right into the native watercourse (Engel, 2012). The traditionally and historically used complementary to storage was to discharge of mine waste in a convenient and possible for instance river dumping which led to extensive environmental contamination in mining areas (Coil *et* *al.,* 2014). According to Vare *et al.,* (2018), deep-sea tailings disposal (DSTD) is still practiced in many regions of the world and mining industries disposed of processed tailings right into the marine environment as well as its shallow water counterpart, submarine tailings disposal (STD). Deep-sea tailings disposal can impact oceanic ecosystems additionally to more sources of stress for instance energy extraction, fishing, pollution, tourism, pollution, eutrophication, and climate change from deep-seabed mining presently and in the future.

Type and characteristics of tailings are some of the paramount factors that contribute to the environmental impacts. A study done by Franks *et al*., (2011), implied that tailings have the potential to degrade the environment by discharging toxic metals such as arsenic and mercury through acid drainage in addition to microbial action on sulphide ores by damaging aquatic flora and fauna that depend on clear water. The fine grain tailings cause dusty pollution in a dry background (Alshaebi *et al*., 2009).

2.9 Effects of Metals on Plants

Toxic metals contamination is a foremost environmental apprehension because plants absorb toxic metals, and it controls their development since toxic metals uptake take place alongside with fundamental elements from the soil. Plants absorb heavy metals through the root system from the soil or water. Metals are translocated from the plant roots to the aerial parts by means of the xylem (Mustafa and Komatsu, 2016). The foundation of phytoremediation is the aptitude of plants to accumulate heavy metals and is regarded as plants-based strategy executed in cleaning up contaminated soils (Mustafa and Komatsu, 2016).

Heavy metals for instance iron, zinc, and copper are vital for florae and faunas in considerable amounts. Metals for instance cobalt, manganese, molydenium, copper, nickel, zinc, and iron are vital micronutrients whose consumption in extra amounts to the plant results in poisonous effects (Asati *et al.,* 2016). The oversupply of these metals can be toxic to plants although plants need these metals for their growth. Plants have the capability to accumulate essential metals. It is when the concentrations within the plant surpass optimum levels that they unfavourably affect the plant both directly and indirectly and because metals cannot be broken down. Toxic effects associated with elevated metal concentration includes the inhibition of cytoplasmic enzymes and damaging of cell structures because of oxidative stress (Asati *et al*., 2016). The replacement of important nutrients at cation exchange sites of plants is the indirect toxic effect. The adverse effect of heavy metals on activities of soil microorganisms also indirectly affects the development of plants. A decrease in the quantity of valuable soil microorganisms because of excessive metal concentration leads to decline in organic matter decomposition and eventually to a lesser fertile of soil (Asati *et al.,* 2016).

Phytoremediation

Phytoremediation principally denotes to the usage of plants and related soil microbes to lessen the concentrations impacts of toxins in the environment (Ali *et al.,* 2013). It can be employed for elimination of organic pollutants, heavy metals, and radionuclides. It is an innovative, environmentally, efficient, eco-friendly, economical, in-situ applicable remediation strategy and its solar-driven (Ali *et al.,* 2013). Phytoextraction or phytoaccumulation, phytovolatilization, phytodegradation, phytostabilization, and phytofiltration are the techniques for phytoremediation (Ali *et al*., 2013). The absorption of pollutants from water or soils through plant roots and their accumulation and translocation in aboveground biomass is called phytoextraction (Mahar *et al.,* 2016).

2.9.1 *Equisetum ramosissimum* (Horsetail plant)

Equisetum ramosissimum plant was the dominant plant found within the Zaaiplaats tin mine. Below is a brief description of its physiology, origin, and distribution.

Physiology of the *Equisetum ramosissimum*

Equisetum ramosissimum comes from the *Equisetaceae* family and perennial fern. It breeds greatest in saturated soils. The black subterranean stem is typically upright and branches horizontally. The plants grow for up to 1 meter and the aerial stem raise above the ground. The thinner branches appear in whorls at each node beside the extent of the stem and it gives its communal name of “branched horsetail”. The scale-like leaves form a whorled sheath overhead each node laterally the aerial stem. The leaves are commonly of a shiny black colour and narrowly lanceolate with a single vein as explained by Szuman and Lall (Szuman and Lall, 2020). *Equisetum ramosissimum* Desf is an accepted name of a species in the genus *Equisetum* (family Equisetaceae) (The Plant List, 2013).

Origin and distribution of *Equisetum ramosissimum*

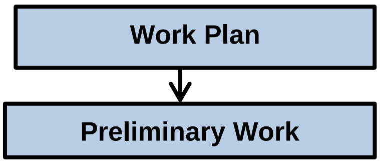
Equisetum ramosissimum is an ancient and common species which is occurring all over much of Africa, Europe, and Asia with the broadest spreading variety of some Equisetum species in the world (Schaffner 1930). It is also broadly distributed across South Africa in the Northern Cape, Mpumalanga, North-West, Fres State, Gauteng, Eastern Cape, Gauteng, KwaZulu-Natal, and Limpopo provinces and generally occurs in terrestrial areas, seasonally flooded areas and laterally perennial rivers and streams (Szuman and Lall, 2020).

Phytoremediation by *Equisetum ramosissimum*

As investigated by Ranđelovic *et al*. (2019), *Equisetum ramosissimum* display the capability to immobilize and phytostabilize existing tiny proportions of Mn, Fe, Sb, Pb and Zn in the environmentally threatened area (Ranđelović *et al.,* 2019). The presence of this horsetail plant as a primary settler on the flotation tailings proposes that biological remediation of the area is practical. *Equisetum ramosissimum* dominated abandoned tailings facility just about a year later the environmental disaster. It was also the early plant colonizer of the surrounding area in the western Serbia and the adjacent Kostajnicka River (Ranđelović *et al.,* 2019).

3 CHAPTER 3: MATERIALS AND METHODS

This chapter deals with the methods and procedures that were applied during the study (Fig. 3.1).



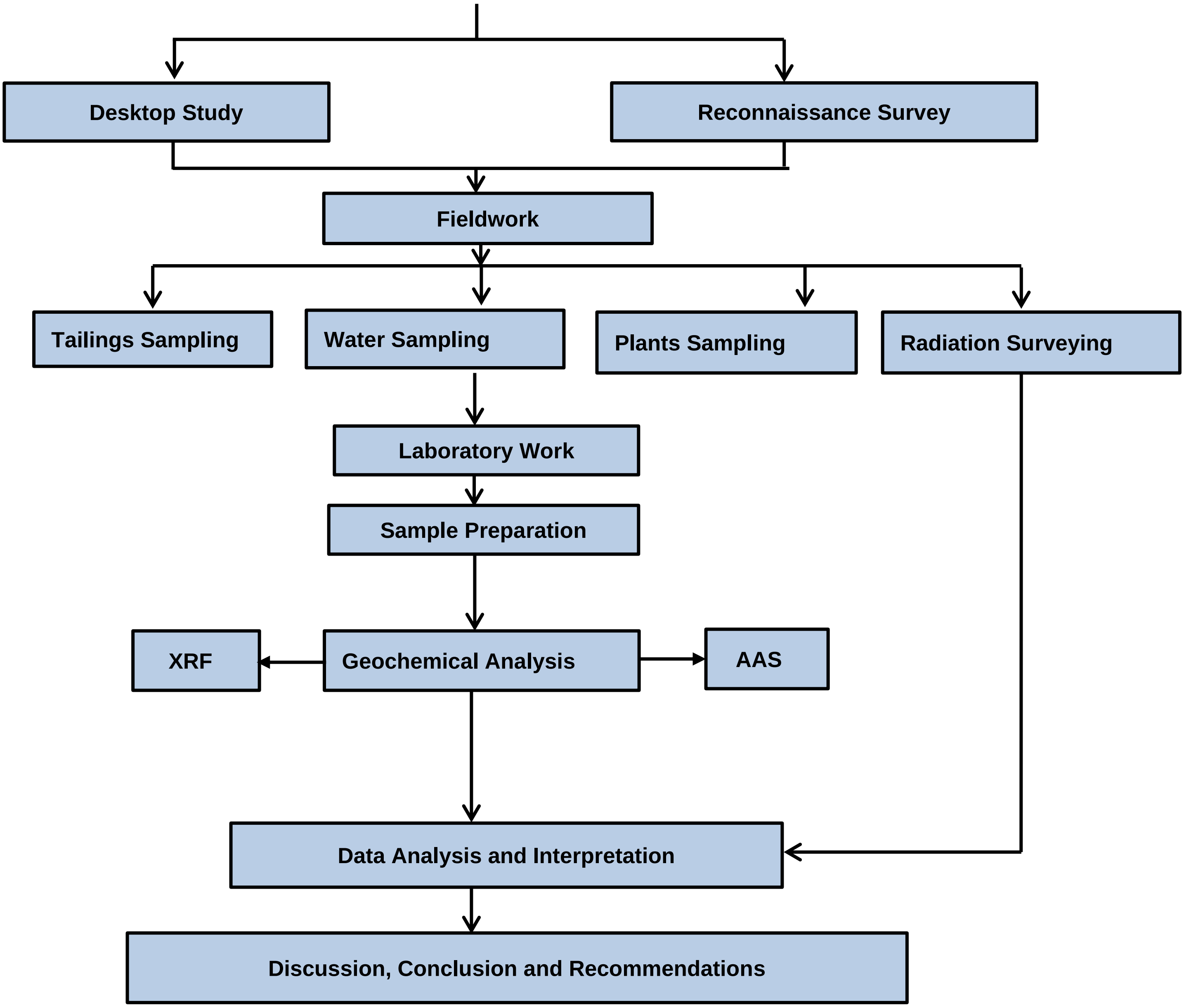


Figure 3.1: Flow-chart showing a summary of the methods and procedures that were applied in this study.

3.1 Preliminary Work

Preliminary work commonly refers to preparatory activities conducted before the actual fieldwork. These activities were undertaken to identify materials and methods which are necessary to carry out in the study. It involved both desktop study and reconnaissance survey.

3.1.1 Desktop Study

At this stage, preparatory work was done to gather information and materials that are relevant to the study. It involved acquiring of information around the study area from unpublished and published literature that assisted in steering the study. The literature used incorporates but is not limited to books, unpublished sources, theses, online resources, maps, photographs, and journals. Desktop study provided immediate information about the place, characteristics and the accessibility of the study area and the information obtained assisted with the preparation and planning of the work.

3.1.2 Reconnaissance Survey

Reconnaissance survey was conducted by travelling to the proposed area of study to be familiarized with the immediate surroundings. It aided the researcher in the identification of areas of relevance to meet the objectives of the project. It also assisted with the determination of the logistics, (arrangements for accommodation and meals) for the actual fieldwork. The researcher also dealt with issues such as contacting and acquiring permission from the owners of the Zaaiplaats tin mine.

3.2 Fieldwork

Fieldwork comprised of tailings sampling, water sampling, plant sampling and radiation surveying within the Zaaiplaats tin mine.

3.2.1 Tailings Sampling

Tailings involved classification of tailings within the mine. Tailings were sampled along and across the river profile and with the Heaps- A, B and C. Tools and materials used include hand auger, tape measure, polyethylene sample bags, tags, strings, permanent marker, pen, notebook, Geographic Positioning System (GPS).

3.2.1.1 Classification of Tailings

Tailings that are found within the Zaaiplaats Tin Mine were originally deposited in an irregular manner. The tailings are not dumped at the same place and are not in a well-engineered compartment. They have covered a large area in the mine. Tailings had been dumped at the edge of the river consequently covering the river. Some tailings were dumped at the same place making it a huge pile or heap, hence, the identified heaps that are within the mine and were recorded as Heap A, Heap B and Heap C. All the heaps were labelled and summarized based on their physical characteristics as shown in Table 3-1 below. There are also tailings covering approximately 2 km across a river and had been named the River Profile.

Generally, the physical characteristics of Heap A, B and C at Zaaiplaats mine vary but they also share some characteristics. They share physical attributes such as type of waste, colour and texture and differ in size, vegetation, and other properties (Table 3.1). The type of waste is tailings, they are all grey in colour and their texture is course. However, Heap A was found to be smaller in size; Heap B was found to be small to medium and Heap C was found to be large.

Heap B had short trees and grass while Heap A and Heap C had no vegetation. In terms of accessibility, all the tailings were accessible, however, Heap B was bushy, and Heap C was comparatively higher and too exposed to water and wind erosion. Heap A is located near the old processing plant while Heap C is at the edge of the river.

Table 3.1: Physical characteristics of the tailings within the study area

Characteristics	Heap A	Heap B	Heap C
Location	Located near the processing plant.	Located near the processing plant.	Located near the processing plant.
Colour	Grey	Grey	Grey

Texture	Course	Fine to course	Course
Vegetation	Clear-no vegetation	Short trees and grass	Clear-no vegetation
Size	Very small	Small-medium	Large
Accessibilty	Accessible	Accessible	Too high and accessible

3.2.1.2 Augering of Tailings

Tailings sampling across the river

Tailings were collected across the 5 river profiles and within the heaps (Fig. 3.2). The profiles were 500 m apart. The sampling interval was determined by firstly measuring the width of the river using a tape measure for determining the central point. The two samples were from the side part of the river while the other is in the central part of the river. Samples were collected at 1m depth, and a hand auger was used. Three samples were collected from the 5 profiles making a total of 15 samples from the river profiles.

Figure 3.2: Sampling points across and along the river profile and the Heaps at the Zaaiplaats Mine tailings.

Heap A sampling

A random method of sampling was employed to collect the tailings samples from Heap A due to the irregularity of the heap (Fig. 3.3). Samples were collected at 1 m depth with a hand auger. A sample bag and a string (cable tie) were utilized to store and string the samples to ensure accuracy and minimising cross contamination. Supplementary information concerning the location of the sampling point such as coordinates were recorded into the mini field notebook. A total of 6 samples were collected from Heap A. Heap A had undergone gully erosion (Fig 3.4).

Figure 3.3: Sampling points within Heap A at Zaaiplaats tin mine.

Figure 3.4: Heap A showing gully erosion.

Heap B sampling

A systematic method of sample collection was used to collect the tailings samples from Heap B (Fig. 3.5). In each point a hand auger was used to drill through the tailings from the surface to a depth of up 4 m. Samples were collected in a sampling interval of 1 m thus 4 samples were collected in each drill hole. The two profiles were approximately 45 m apart while sampling points were 50 m apart. A sample bag and a cable tie/string were used avoid cross contamination. A total 24 tailings sample were collected from the 2 profiles with 6 sampling points from Heap B. The extra information involving the location of the sampling point such as coordinates were recorded into the mini field notebook. Heap B is covered with grasses and short trees. It has fine to coarse texture tailings (Fig 3.6).

Figure 3.5: Sampling profiles and points in Heap B at Zaaiplaats tin mine.

Figure 3.6: Heap B at Zaaiplaats Tin Mine.

Heap C sampling

A systematic method of sample collection was used to collect the tailings samples from Heap C (Fig. 3.7). In each point a hand auger was used to drill through the tailings from the surface to a depth of up 4 m. Samples were collected in a sampling interval of 1 m thus 4 samples were collected in each drill hole. The two profiles were 50 m apart while sampling points were approximately 100 m apart. A total of 20 tailings samples were collected from the 2 profiles with 6 sampling points. Further information involving the location of the sampling point such as coordinates were recorded into the mini field notebook. Tailings from Heap C are currently being used utilised sold and used construction purposes (Fig 3.8).

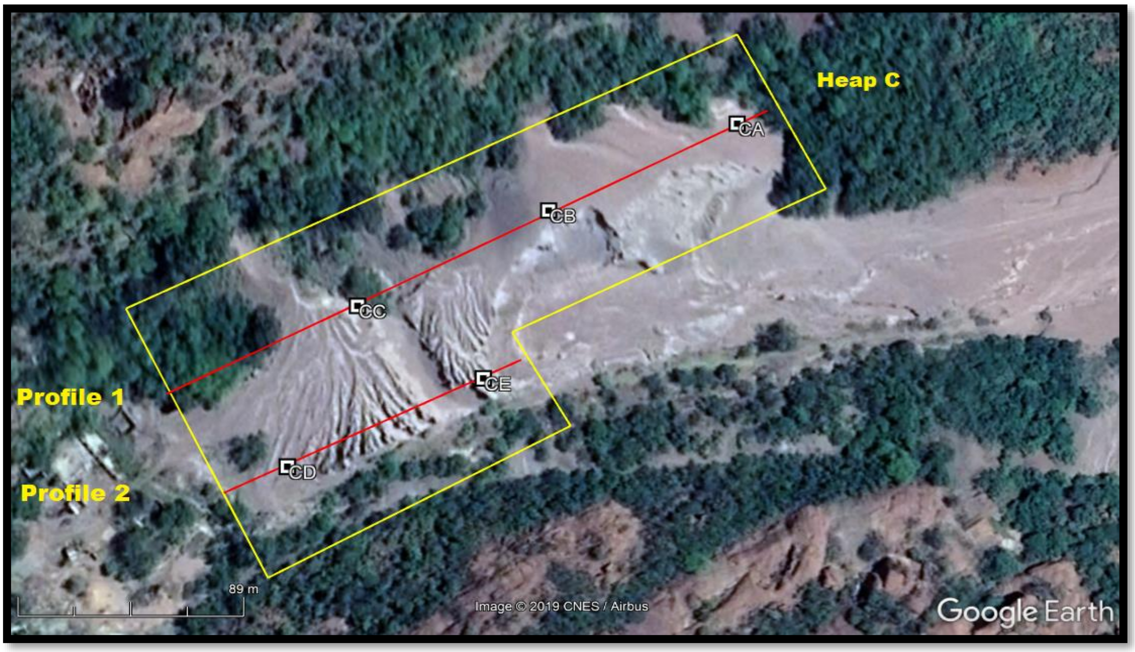


Figure 3.7: Sampling profiles and points in Heap C at Zaaiplaats Tin Mine.

Figure 3.8: Heap B at Zaaiplaats Tin Mine.

3.2.2 Water Sampling

Water Sampling is the procedure where water samples are collected to undertake chemical analysis for any available chemical characteristics of interest. The outcomes are used to determine the potential of that water in terms of water use or any implication; this is done by comparing it with the available water standards.

Water samples were collected within the mine standing waters, and it was not done systematically (Fig. 3.9). The total water samples collected were depending on the availability. Consequently, only 3 water samples were obtained using of 250 ml bottles. Immediate to sampling, the bottles were rinsed by the water to be collected so as to avoid cross contamination.

Figure 3.9: Water sampling at Zaaiplaats tin mine waste stagnant waters.

3.2.3 Plants Sampling

The same type of plant by the name of *Equisetum ramosissimum* plant was collected and it is also commonly known as horsetail (Fig 3.10). During dry season, a total of 5 plant samples were carefully handpicked in a random manner and stored in marked and labelled sample bags during dry season together with the tailings found below them. A shovel was utilized to collect the plant sample and tailings samples from the same point were collected. The 5 plant samples were collected within the tailings across the river profiles. To avoid contamination, the samples were tied securely with a string. The GPS was used to take the elevation as well as the coordinates of the sample points. During wet season, a total of 4 samples were collected within the tailings together with the tailings found below them.

Figure 3.10: Equisetum ramosissimum plants in both (a) and (b) pictures.

3.2.4 Radiation Survey

Radioactivity surveying was conducted by means of a portable radioactivity survey meter (DP802i-RAYTECH Radiation Detector) (Fig 3.11). It was conducted across and along the river profiles for an approximately 2 km distance. Survey locations were almost 500 m apart thus giving us 5 survey locations namely: A, B, C, D and E. The coordinates of the survey locations were recorded in the field book once the survey point had been identified. The survey points are like the tailings sampling points within the river profiles. Heap A, Heap B and Heap C were also surveyed for radioactivity as shown in Table 3.2 below. It was both the radiation dose rate and dose equivalent which were recorded and measured in microsievent per hour (µSv/h) and microsievent (µSv) respectively.

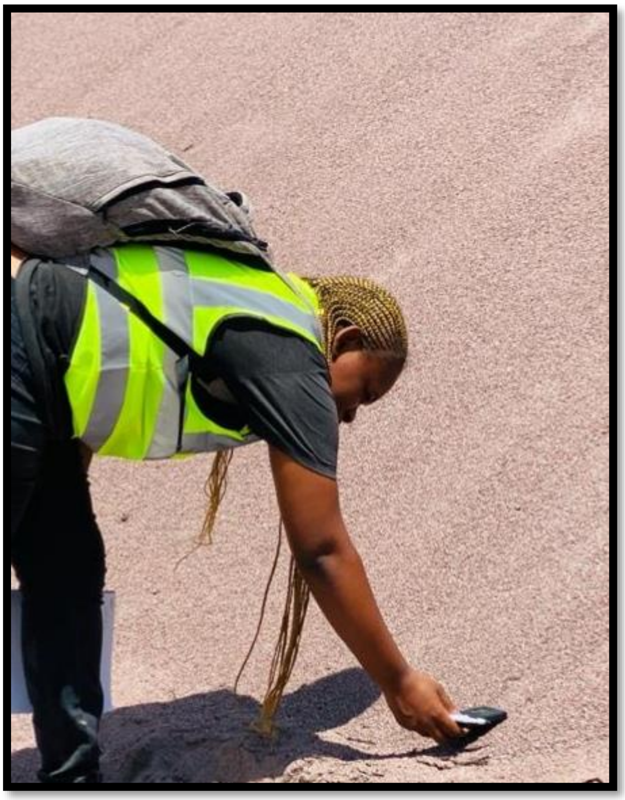


Figure 3.11: Radiation surveying using DP802i-RAYTECH Radiation Detector.

Table 3.2: Rate and Dose results found within the Zaaiplaats Tin Mine.

Surveying Point	**Rate (µSv/h)**	**Dose (µSv)**
Heap A	1.1	1.5
Heap B	1.65	2.10
Heap C	1.09	1.69
Location 1A	0.12	1.64
Location 1B	1.09	1.67
Location 1C	1.09	1.7
Location 2A	0.11	1.75
Location 2B	0.12	1.77
Location 2C	0.12	1.76
Location 3A	0.11	1.84
Location 3B	0.95	1.85
Location 3C	1.33	1.86
Location 4A	0.12	1.91
Location 4B	0.11	1.90
Location 4C	1.21	1.92
Location 5A	0.13	1.96
Location 5B	0.12	1.96
Location 5C	0.13	1.97
Control point	0.08	0.5

3.3 Laboratory Work

Laboratory work involved sample preparation and sample analysis. All the collected samples were prepared and analysed for metals. Sample preparations and analysis procedure were presented in this chapter and below.

3.3.1 Sample Preparation

3.3.1.1 Tailings Preparation for Metal Analysis using XRF

Tailings were subjected to geochemical analysis at the Department of Mining and Environmental Geology at the University of Venda. All the samples were homogenised and split using the riffle splitter at the University of Venda Mining and Environmental Geology (Fig. 3.12). During splitting, the initial sample weighing approximately 2 kg was split and reduced to approximately 300 g for drying and milling.

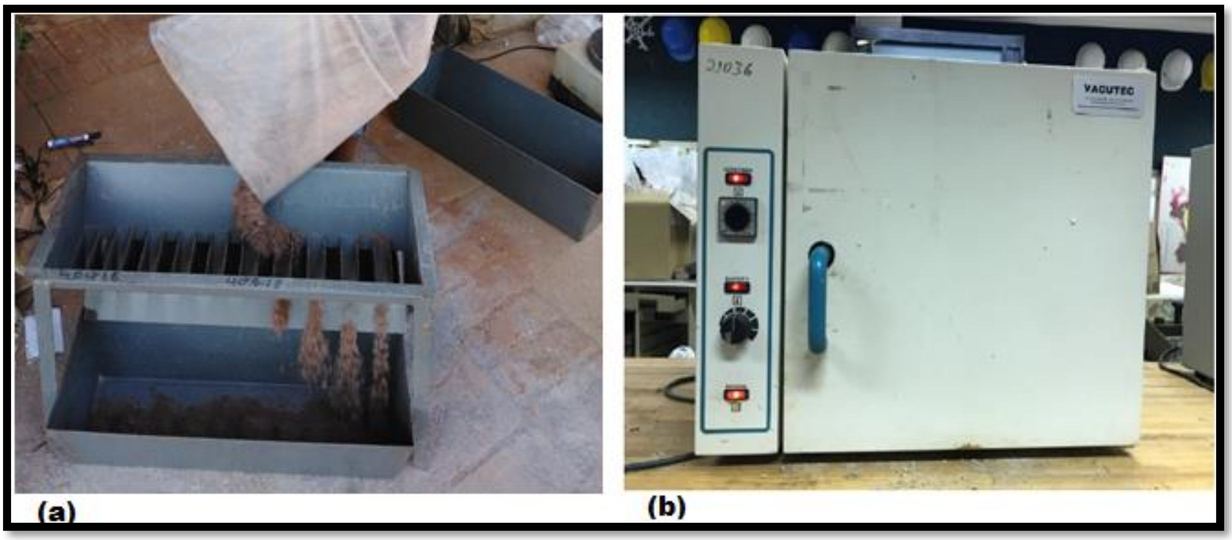


Figure 3.12: (a) Riffle splitter used for splitting the sample (b) Bench Vacutec laboratory drying oven used to dry the samples.

Drying of the samples was done using Vacutec drying oven at a temperature of 110 °C for at least 6 hours (Fig. 3.12). After drying, the samples were then removed from the oven and allowed to cool down at room temperature before milling. Milling was done using the Retsch RS 200 milling machine (Fig. 3.13). About 300 g of each sample will be placed in the milling pot for milling. The milling pots were cleaned with quartz prior to the milling process to avoid cross-contamination during the milling process.

Figure 3.13: Restsch model RS 200 milling machine used to mill the samples.

Following milling process, pressed pellets were produced using a hand operated pressing machine. Pressed powder pellets were for prepared with binding agent, Boric Acid (Fig. 3.14). Approximately 15-20 g of the milled powder were pressed in aluminium cups with a diameter of 40 mm on a 2.5 g bed of Boric Acid. A hand operated pressing machine was used, and 30 tons of pressure was applied for 20 seconds on each sample. Acetone was used to clean the aluminium cups upon removal of the pellets to avoid cross-contamination between the samples (Fig. 3.14).

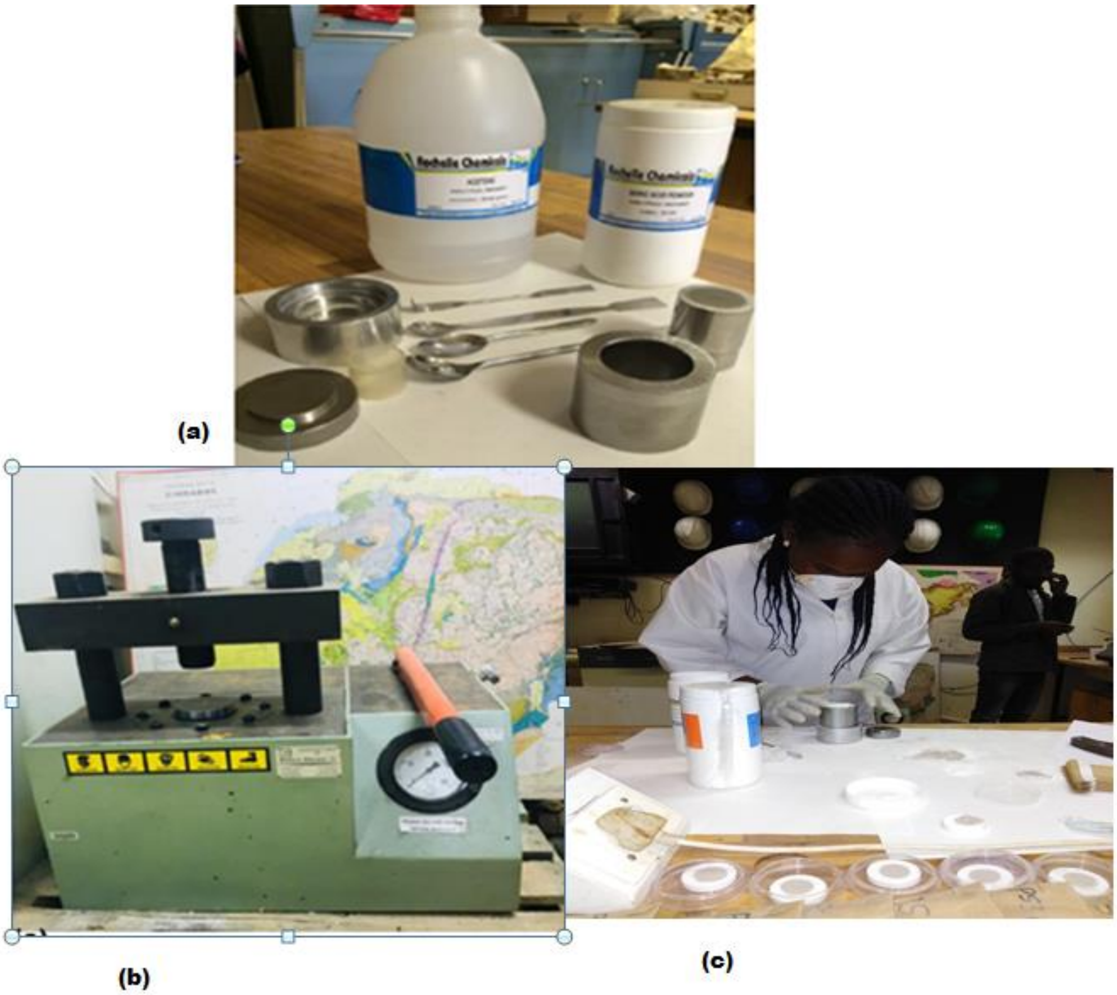


Figure 3.14: (a) Boric acid, acetone, and aluminium cups for making pellets. (c) Palletisation using a 40-ton pressure machine. (d) Prepared pellets ready for analysis.

3.3.1.2 Plant Sample Preparation for Metals Analysis using AAS

The plant samples were prepared at the University of Venda. The collected plants samples were transferred from the labelled paper sample bags and washed using deionized water. After washing, they were placed in an oven for drying for at least 24 hrs at 110 ˚C. The 14 of the dried samples (7 roots and 7 shoots samples) were accurately weighed into a porcelain crucible. Five grams of milled samples were placed into the decomposition beaker and approximately 2-5 ml of water to moisten the sample. In addition to water, aqua-regia (15 ml HNO_3 and 45 ml HCL) was also added. The samples were placed on the hot plate for decomposition for at least 90-120 minutes (Fig. 3.15). They were removed from the hotplate and allowed to cool to room temperature. They were then transferred to a 100 ml volumetric flask. They were allowed to settle after vigorously shaken. Standards were prepared for each metal to be analysed by diluting from standards of 1000 ppm to standards of 10, 20, 30, 50 and 100 ppm. These standards were used for calibrating the AAS equipment.

Figure 3.15: Digestion of plant samples using a hotplate.

3.3.2 Sample Analysis

3.3.2.1 Tailings Analysis

Sample analysis was carried out using X-ray Fluorescence Spectrometer (S2 Ranger) (Fig. 3.16). Calibration for the metal analysis was done prior to analysis. The analyses were carried out for Pb, Zn, Cu, As, Co, Cd, Cr and Mn. Sample results were stored on the computer. The results were later exported to Microsoft Excel for data analysis and interpretation.

Figure 3.16: A Ranger S2 XRF Machine used for analysis.

River Profiles

These are the results of a total of 15 samples collected across the River Profiles. Table 3.3 below shows the results of the metals analysed using X-ray fluorescence spectrometry and these includes Co, Cu, Zn, As, Mo, Cd, Pb, Th and U. Samples were collected at 1 m depth.

Table 3.3: Values of metals in samples collected across the River Profiles.

Sample ID	Cr (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Mo (ppm)	Cd (ppm)	Pb (ppm)	Th (ppm)	U (ppm)
P1S1	3,45	7,85	447,4	233,95	76,95	1,35	0,1	716,85	38,15	13
P1S2	4,65	7,65	449,95	238,65	95,6	0,45	0	890,65	40,35	14,5
P1S3	4,65	8,95	530,85	258	106,8	2,8	0,1	994,95	44,65	12,55
P2S1	8,55	8,45	413,05	240,25	90	1,5	0,1	807,1	37,5	13,35
P2S2	3,8	7,85	449,75	215	92,65	0,6	0,1	863,5	41,5	12,7
P2S3	5,2	7,35	464,55	219,7	108,75	0,6	0,1	1012,95	45	13,65
P3S1	51,4	9,5	459,35	236,15	103,05	3,2	0,1	960,15	49,55	14,9
P3S2	11,05	8,9	427,2	351,9	84,15	2,75	0,1	784,2	35,05	12,1
P3S3	18,45	9,9	564,8	308,6	109,2	0,5	0,1	1197,5	37,95	13,4
P4S1	11,3	6,95	370,2	220	91,05	0,5	0,1	847,95	46,95	10,2
P4S2	50,2	6,7	362,25	228,4	90,75	1,5	0,1	711,5	36,8	10,9
P4S3	4,85	8,4	404,9	269,6	98,2	1,55	0,1	915	56,85	12,85
P5S1	21,55	13,9	854,45	499,45	232,55	0,7	0,1	2166,6	92	17,45
P5S2	15,4	17,6	804,95	587,25	265,85	2,4	0,1	2476,9	116,55	24,25
P5S3	30,1	19,8	885,05	740,7	289,3	3,6	0,1	2318,2	141,8	29,6

Heap A

The following are the results of the 6 analysed samples collected from Heap A. Table 3.4 below shows the results of the metals analysed using X-ray fluorescence spectrometry. Samples were collected at 1 m depth.

Table 3.4: Values of metals in samples collected from Heap A.

Sample ID	**Cr (ppm)**	**Co (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**As (ppm)**	**Mo (ppm)**	**Cd (ppm)**	**Pb (ppm)**	**Th (ppm)**	**U (ppm)**
AA	13,4	8,95	420,1	264,1	109,7	1,85	0,1	1021,9	48,9	11,95
AB	4,95	7,45	419,25	231,1	91,35	1,45	0,1	850,8	43,25	14,25
AC	11,1	8,05	442,35	265,85	117,65	0,45	0,1	1096,25	49,5	13,5
AD	13,95	8,25	481,3	278,05	118,7	0,45	0,1	1106,25	50,6	14,1
AE	4,35	8,15	451,75	261,4	118,95	0,35	0,1	1108,25	48,75	13,5
AF	10,05	8,45	448,35	259,1	108,75	2,7	0,1	1013	49,8	14,5

Heap B

The following are the results of the 24 analysed samples that were collected from Heap B. The total of 24 samples come from the 6 drill holes. Sample marked 1, 2, 3 and 4 represent samples collected at 1 m, 2 m, 3 m, and 4 m depth respectively. The table below shows the results of the metals which were obtained using X-ray fluorescence spectrometry (Table 3.5).

Table 3.5: Values of metals in samples collected from Heap B.

Sample	Cr (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Mo (ppm)	Cd (ppm)	Pb (ppm)	Th (ppm)	U (ppm)
BA1	7,4	6,8	290,3	302,2	126,4	0,5	0,1	1177,7	40,8	15,7
BA2	6,1	6,4	281,3	282,6	138,5	0,5	0,1	1290,6	36,8	14,2
BA3	3,9	6,6	268,4	288	137	0,7	0,1	1276	38,7	14,5
BA4	13,4	6,5	259,3	306,9	133,5	0,5	0,1	1243,5	38,5	14,5
BB1	3,4	10,4	517,5	450	205	0,7	0,1	1909,6	76,4	22,6
BB2	4,3	11,4	580,6	529,4	260,8	0,8	0,1	2430,1	93	25,2
BB3	7,7	11,3	614,8	562,4	278,2	0,8	0,1	2591,9	89,8	24,8
BB4	4,6	11,3	596,5	519,8	253,9	0,8	0,1	2365,4	89,9	23,5
BC1	4,6	11,4	550,8	504,3	232	0,8	0,1	2161,1	88,4	23,9
BC2	9,4	11,4	576,1	513,3	242,8	0,7	0,1	2262	95,7	24,6
BC3	1,5	10,6	603,6	556,7	305,1	0,9	0,1	2842,4	89	23,4
BC4	5,5	11,3	581,3	529,7	253,5	0,8	0,1	2361,7	86,6	22,7
BD1	9,8	8,5	329,5	307,1	139,5	0,6	0,1	1300	43	13
BD2	6,3	8,3	356,3	331,9	145,3	0,6	0,1	1353,5	48	14,1
BD3	1,5	8,2	352,1	325,7	154,7	0,7	0,1	1441	52	14,2
BD4	10,2	9,1	381,6	369,2	170,1	0,6	0,1	1584,8	59,4	14,9
BE1	7,9	10,5	407,9	335,4	154,3	3,5	0,1	1437,4	57,7	15
BE2	2,8	9,2	396,6	382,8	213,2	3,4	0,1	1986,8	50,8	12,5
BE3	4,5	9,3	310,3	301,9	146	3	0,1	1360,4	47,9	14,4
BE4	10,2	10,7	387,3	375,8	182,1	3,2	0,1	1696,9	60,4	14,6
BF1	3	9,6	429,4`	385,8	213,4	0,9	0,1	1988,2	50,7	11,5
BF2	6,8	10,7	324,9	326,2	143,6	3,3	0,1	1337,7	52,7	11,6
BF3	1,3	11	435,2	363,7	174,2	2,7	0,1	1622,7	49	12,4
BF4	8	13,5	481,8	481,7	207,2	3,4	0,1	1930,4	74,6	18,7

Heap C

Table 3.6 shows the results of the 20 analysed samples collected from Heap C. The total of 20 samples come from the 5 drill holes.

Table 3.6: Values of metals in samples from the collected from Heap C.

Sample	**Co (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**As (ppm)**	**Mo (ppm)**	**Cd (ppm)**	**Pb (ppm)**	**Th (ppm)**	**U (ppm)**
CA1	8,6	384,2	260,3	59,5	0,2	0	554	32,2	11,4
CA2	8,4	520,1	226,9	72,5	0,5	0	675,1	35,5	12,8
CA3	8,6	595,3	228,6	66,3	0,6	0	617,9	36,9	12,6
CA4	8,6	518,8	214,8	63,6	0,4	0,1	592,6	35	12,7
CB1	7,7	382,3	313,5	53,9	0,3	0,1	502,5	32,6	14,5
CB2	8,2	412,8	282,1	51,5	0,4	0,1	480,2	30,4	12,6
CB3	8,6	506,5	219,5	54,2	0,5	0,1	504,6	37,5	13,1
CB4	8,3	471,7	261,1	59	0,4	0,1	549,3	34,5	14,6
CC1	8,2	421,9	254	77,8	0,6	0,1	724,7	37,6	13,1
CC2	8,1	423,4	252,1	99,6	0,2	0	927,5	38,4	13,7
CC3	7,9	443,7	255,7	103,5	0,4	0,1	964,7	38,5	14
CC4	8,1	398,9	249,1	77,6	2,5	0,1	723,3	36,7	13
CD1	7,6	535,2	283,4	99	0,4	0,1	922,8	43,8	15,2
CD2	7,7	506,5	255	86,9	0,4	0	810,1	36,5	15,3
CD3	7,9	521,4	250,7	82,7	0,5	0,1	770,5	39,4	16,6
CD4	7,8	506,7	249,9	77,1	0,4	0,1	718,2	37	16,7
CE1	8,2	456,3	272,7	73,4	2	0,1	683,4	35,8	11,4
CE2	9,2	523,7	264,4	83,3	0,4	0,1	776,5	38,1	12,6
CE3	10,4	507,2	241,4	83,7	2,4	0,1	779,4	38,4	11,4

CE4	10	538,2	243,5	80,7	2,5	0	752,2	37,8	11

3.3.2.2 Water analysis

Water samples were analysed using AAS. Samples were analysed to determine the metals which are more likely to be leached out during rainfall. The machine was first calibrated to ensure accuracy of the results using the standards prepared for each metal to be analysed through diluting from standards of 1000 ppm to standards of 10, 20, 30, 50 and 100 ppm. Table 3.7 below shows the results.

Table 3.7: Values of Metals in water.

	Cr (ppm)	**Co (ppm)**	**Cu (ppm)**	**Pb (ppm)**
S1	0	0	0.59	0.67
S2	0	0	0.03	0
S3	0	0	0.53	0.42

3.3.2.3 Plant analysis

The plant samples were analysed using AAS. Samples were analysed to determine the metals which are absorbed by the different parts of the plants. The machine was first calibrated to ensure accuracy of the results using the standards prepared for each metal to be analysed through diluting from standards of 1000 ppm to standards of 10, 20, 30, 50 and 100 ppm.

The concentration values of tailings samples collected below each plant is also presented. Table 3.8 to Table 3.10 shows the concentration values of metals within samples collected during dry season. The S and R in the table represent concentration values of metals in the Shoots and Roots of the samples respectively.

Table 3.8: Values of metals on the Equisetum ramosissimum plant from different locations within the study area from dry season.

Sample ID	**S1**	**S2**	**S3**	**S4**	**S5**
Cr (ppm)	15.79	15.72	15.71	15.58	15.66
Co (ppm)	1.01	0.52	0.18	0.15	0.14
Cu (ppm)	34.19	28.61	29.29	7.85	34.82
Pb (ppm)	3.81	3.64	3.65	4.73	4.99

Table 3.9: Values of metals on the Equisetum ramosissimum plant in the Shoot and Roots in different locations within the study area from dry season.

Metals	**S1**		**S2**		**S3**		**S4**		**S5**	
	S	**R**	**S**	**R**	**S**	**R**	**S**	**R**	**S**	**R**
Cr (ppm)	7.83	7.96	7.86	7.86	7.75	7.96	7.72	7.86	7.79	7.87
Co (ppm)	0.95	0.06	0.34	0.18	0.13	0.05	0.05	0.10	0	0.14
Cu (ppm)	5.79	28.4	6.71	21.9	6.59	22.7	3.33	32.9	4.52	30.3
Pb (ppm)	1.35	2.46	0.83	2.81	0.99	2.66	1.42	3.31	2.34	2.65

Lead and copper concentration values were lesser in the tailings samples as compared to the plant samples. The maximum values of lead and copper in the plant samples were 6.16 ppm and 34.82 ppm respectively.

Table 3.10: Values of metals on the tailings collected below Equisetum ramosissimum plant from different locations within the study area from dry season

Sample	**Cr (ppm)**	**Co (ppm)**	**Cu (ppm)**	**Pb (ppm)**
S1	2.52	0.06	13.37	5.07
S2	0.49	0	15.04	6.37
S3	1.11	0	22.89	9.92
S4	0.02	0	17.41	8.65
S5	0.02	0	13.09	9.31

Table 3.11 and Table 3.12 shows the concentration values of metals within samples collected during wet season. The S and R in the table represent concentration values of metals in the Shoots and Roots of the samples respectively.

Table 3.11: Values of metals on the Equisetum ramosissimum plant from different locations within the study area from wet season.

Metals	**S1**	**S2**	**S3**	**S4**
Cr (ppm)	0	0.7	0	0
Co (ppm)	1.04	0.72	0.65	0.75
Cu (ppm)	6.5	4.38	3.46	1.72
Pb (ppm)	3.22	1.54	0.84	0.76

Table 3.12: Values of metals on the Equisetum ramosissimum plant in the Shoot and Roots in different locations within the study area from wet season

Metals	**S1**		**S2**		**S3**		**S4**	
	S	**R**	**S**	**R**	**S**	**R**	**S**	**R**
Cr (ppm)	0	0	0	0.7	0	0	0	0
Co (ppm)	0.55	0.49	0.37	0.35	0.38	0.27	0.52	0.23
Cu (ppm)	2.79	3.71	1.97	2.36	1.49	1.97	0.17	1.55
Pb (ppm)	1.4	1.82	0.23	1.31	0.67	0.17	0.69	0.07

Table 3.13: Values of metals on the tailings collected below Equisetum ramosissimum plant from different locations within the study area from wet season.

Sample	**Cr (ppm)**	**Co (ppm)**	**Cu (ppm)**	**Pb (ppm)**
S1	0.13	0.31	3.71	3.08
S2	0	0.34	10.34	3.44
S3	0	0.42	14.92	4.59
S4	0	0.44	9.74	5.57

4 CHAPTER 4: DATA ANALYSIS AND INTERPRETATION

This section presents the analysis of results obtained from the study. It comprises of data from geochemical analysis and radioactive survey. The distribution pattern of the metals has been presented and discussed.

4.1 Metals Values in Tailings

The values of metals along and across the river and within the heaps was investigated and presented below.

4.1.1 Metals Values across and along the River Profile

The metals values (Table 3.3) at each sampling point were used to draw graphs and give comparison between these metals within the tailings. The Table 4.1 below shows the mean, maximum and minimum values of the metals from the River Profile. Lead has a maximum value compared to other metals and it's followed by copper, zinc, arsenic with a concentration of 2476.9 ppm, 885.05 ppm, 740.7 ppm, and 289.3 ppm respectively.

Table 4.1: The mean, maximum and minimum values of metals in samples collected from the River Profile

Sample ID	**Cr (ppm)**	**Co (ppm)**	**Cu (ppm)**	**Zn (ppm)**	**As (ppm)**	**Mo (ppm)**	**Cd (ppm)**	**Pb (ppm)**	**Th (ppm)**	**U (ppm)**
Mean	16,31	9,98	525,91	323,17	128,99	1,60	0,09	1177,60	57,38	15,03
Min	3,45	6,7	362,25	215	76,95	0,45	0	711,5	35,05	10,2
Max	51,4	19,8	885,05	740,7	289,3	3,6	0,1	2476,9	141,8	29,6

Figure 4.1 below shows the values of metals in bar graph. It clearly shows that the river profiles had higher lead values and is followed by copper, zinc, and arsenic. Chromium, cobalt, molybdenum, and cadmium have no peaks on the bar graphs due to their relatively low. River profile 1 was followed by River Profile 2 which is it approximately 500 m away from profile 1 and at a very low elevation compared to

River Profile 1 and. In this profile, the mean concentration values of metals in profile 1 are lower than that of profile 2.

River Profile 2 was followed by River Profile 3 which is approximately 500 m away from profile 2. Zinc concentration values are lower compared to the second profile. Profile 3 is also at a low elevation compared to profile 2. Concentrations values seem to increase with the distance and from higher elevation to lower elevation. The mean elevation of profile 1, profile 2 and profile 3 are 1156 m, 1131 m, and 1088 m respectively (Appendix 2). There are also higher values of lead, copper, zinc, and arsenic as compared to other metals and are shown by maximum peaks in the Fig. 4.1 below.

River Profile 3 was followed by River Profile 4 which is also approximately 500 m apart. There are also higher values of lead, copper, zinc, and arsenic as compared to other metals. Metals concentration values are higher than that of profile 3 above. There are higher peak in profile 4 than that of profile 3 and 2. However, lead seems to be at maximum followed by copper, zinc, and arsenic.

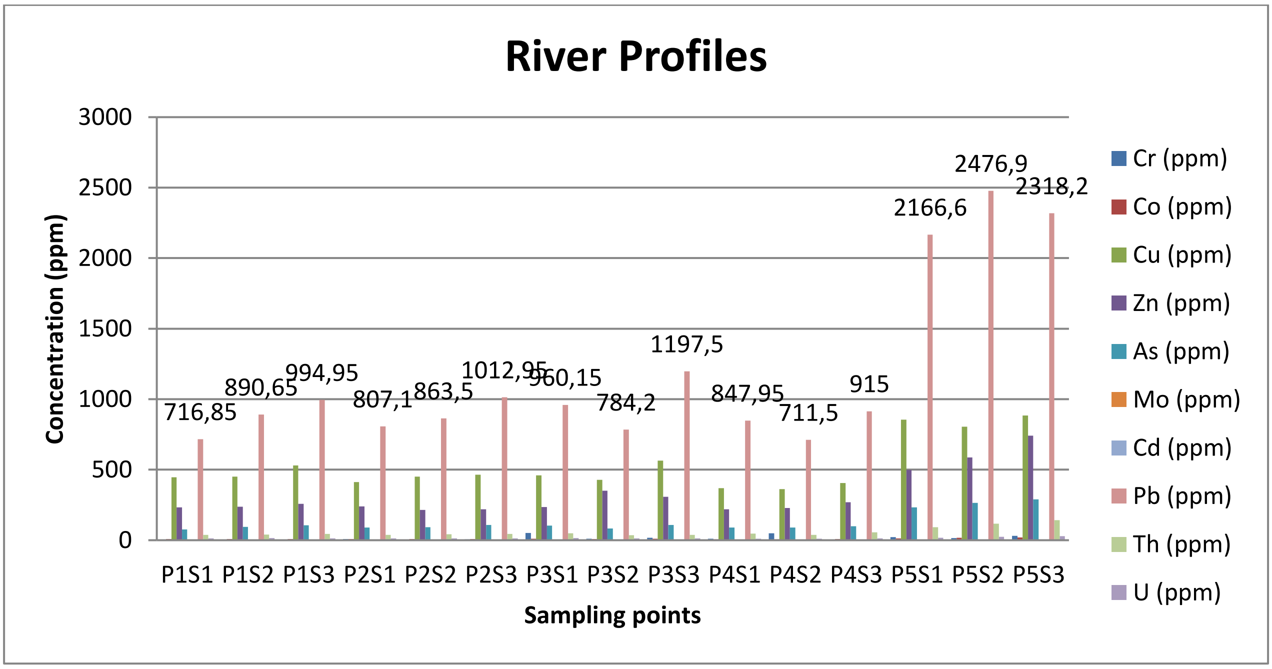


Figure 4.1: Values of metals in samples collected within the River Profiles

4.1.2 Metals Values within the Heaps (A, B and C)

The values of metals of the three heaps (A, B and C) was investigated and presented below.

Heap A

Table 4-2 below shows the mean, maximum and minimum values of the metals from the Heap A (Table 3.4). Lead has a maximum value compared to other metals and it's followed by copper, zinc, arsenic with a concentration 1108.25 ppm, 481.3 ppm, 278.05 ppm, and 118.95 ppm respectively.

Table 4.2: The mean, maximum and minimum values of metals in samples collected from the Heap A.

Sample ID	Cr (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Mo (ppm)	Cd (ppm)	Pb (ppm)
Mean	9,63	8,22	443,85	259,93	110,85	1,21	0,10	1032,74
Min	4,35	7,45	419,25	231,1	91,35	0,35	0,1	850,8
Max	13,95	8,95	481,3	278,05	118,95	2,7	0,1	1108,25

Lead has a maximum peak in all the analysed samples and is followed by copper, zinc and arsenic as shown in Fig. 4.2 below. Arsenic concentrations are ranging at the same level in all the points. Chromium, cobalt, molybdenum, and cadmium have no peaks on the bar graphs due to their relative low concentration.

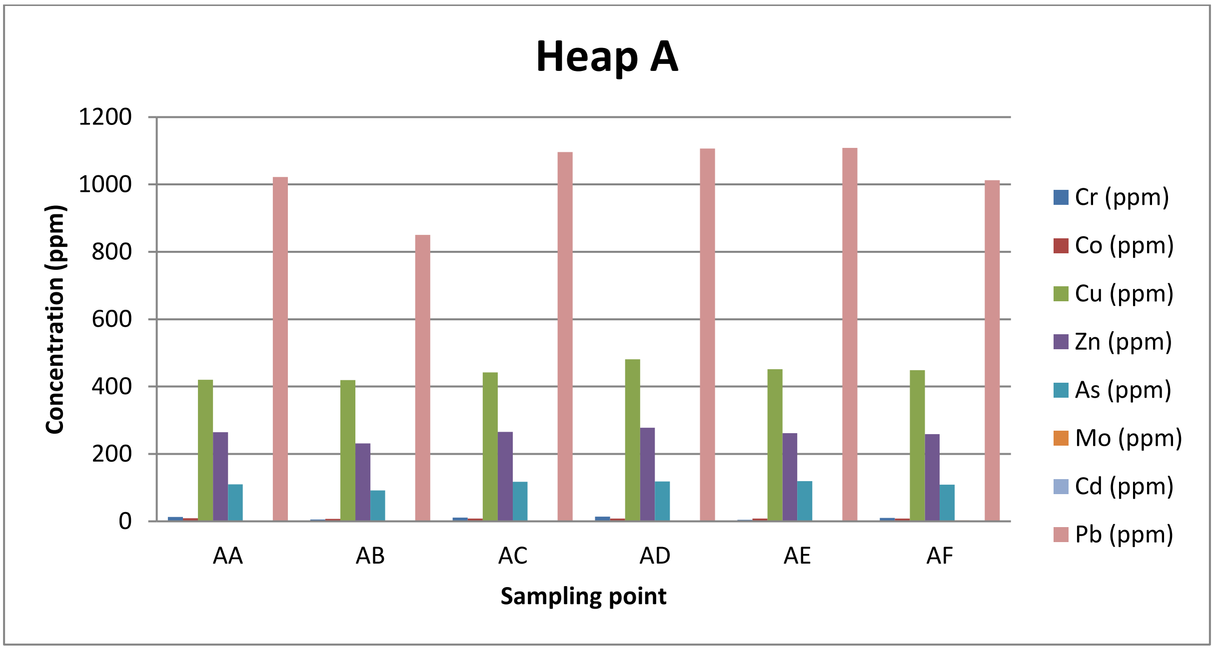


Figure 4.2: Values of metals in samples collected from Heap A

Heap B

The Table 4.3 below shows the mean, maximum and the minimum values of the metals from Heap B (Table 3.5). Lead has a maximum value of 2842.4 ppm which is higher compared to other metals and it's followed by copper, zinc, arsenic with a concentration of 614.8 ppm, 562.4 ppm and 305.1 ppm respectively.

Table 4.3: The mean, maximum and minimum values of metals in samples collected from Heap B.

	Cr	Co	Cu	Zn	As	Mo	Cd	Pb
Min	1.3	6.4	259.3	282.6	126.4	0.5	0.1	1177.7
Max	13.4	13.5	614.8	562.4	305.1	3.5	0.1	2842.4
Mean	6.0	9.8	429.7	401.7	192.1	1.4	0,1	1678.2

Lead has a maximum peak in all the analysed samples and is followed by copper, zinc and arsenic as shown in Fig. 4.3 to Fig. 4.8. Chromium and molybdenum and cobalt were very low. Cadmium was found to be constant throughout sampling point BA (Fig. 4.3)

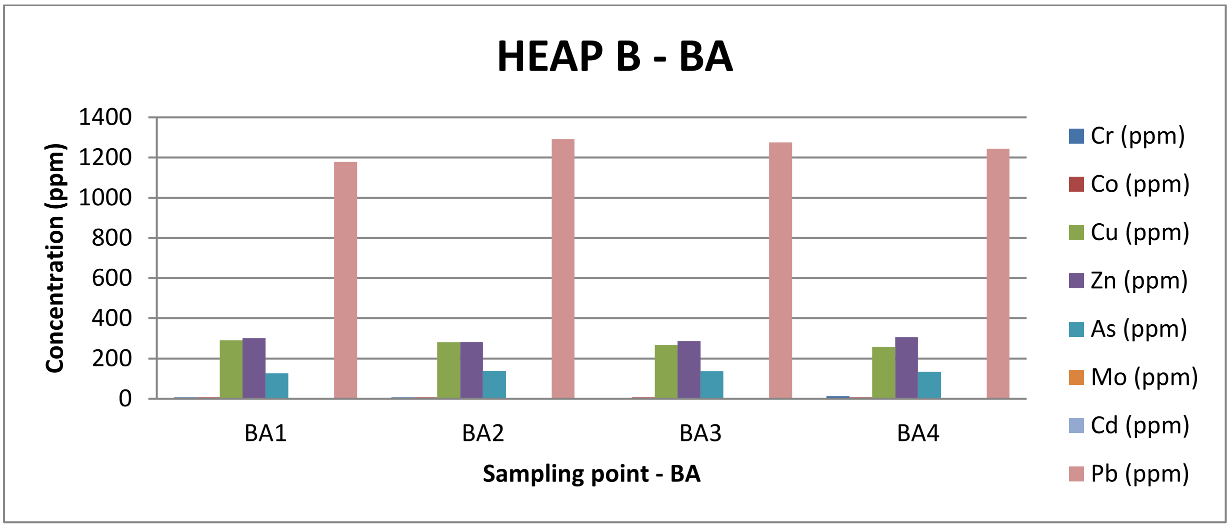


Figure 4.3: Values of metals in samples collected from point BA.

At sampling point BB, lead metal values are higher than that of cadmium. Copper and zinc showed a good relationship because their values levels seem to be a bit close to each other. The levels of arsenic seem to be less than those of zinc and copper but higher than those of chromium, cobalt, and molybdenum whereas cadmium was found to be constant throughout point BB (Fig. 4.4).

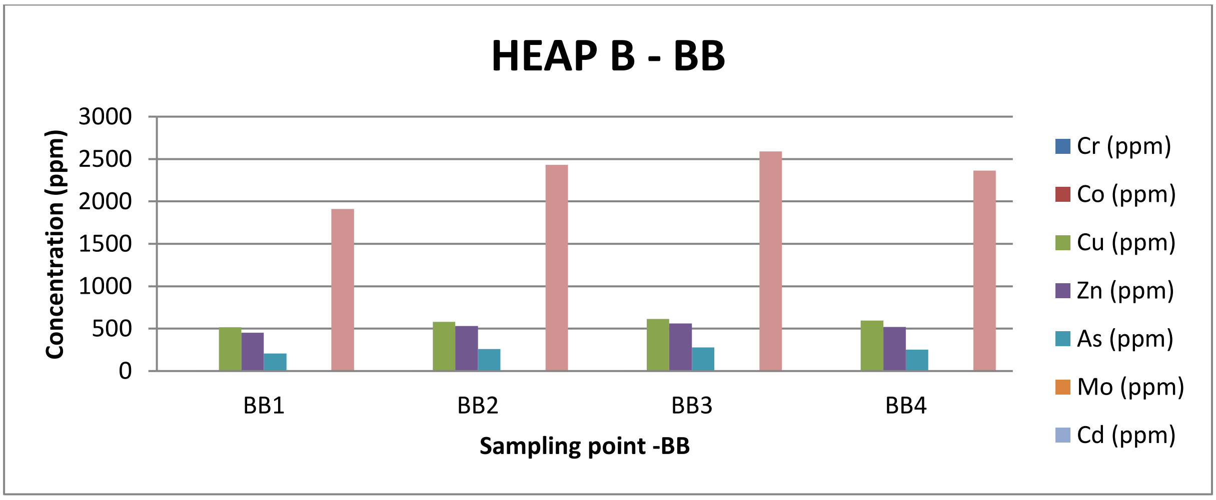


Figure 4.4: Values of metals in samples collected from point BB.

The bar graph (Fig. 4.5) below shows metals values at sampling point BC. Lead seems to be the leading element based on its metal value because the graph shows that it was the metal with levels throughout the sampling point. Copper, zinc, and arsenic are shown to have moderate levels. However, cadmium was found to be constant throughout the sampling point BC.

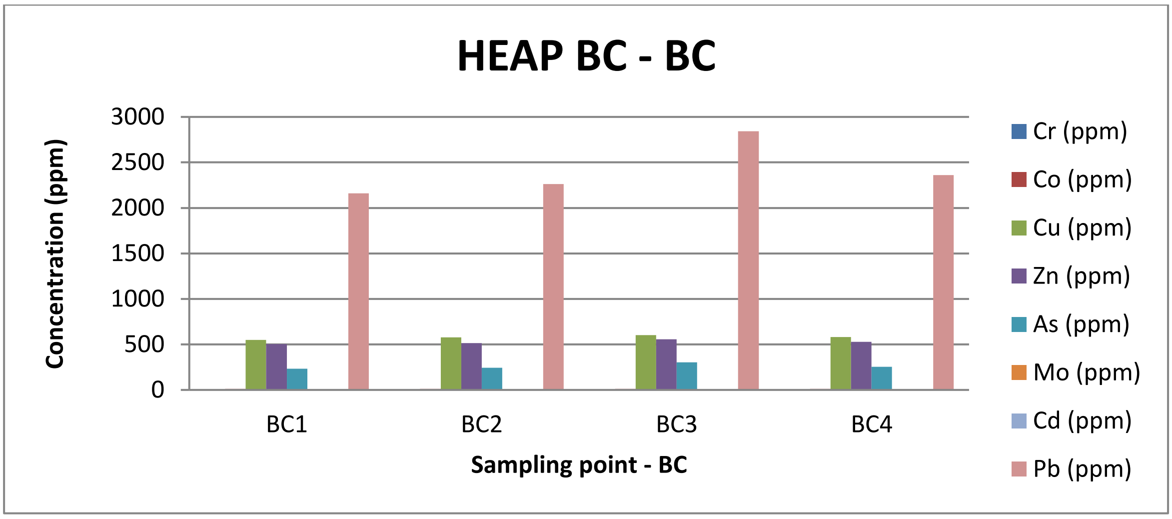


Figure 4.5:Values of metals in samples collected from point BC.

The metal values of lead seem to be lower at the top and higher at the bottom. Zinc and copper values are slightly at the same level. Chromium, cobalt, and molybdenum seem to be of low levels while cadmium was constant throughout (Fig 4.6).

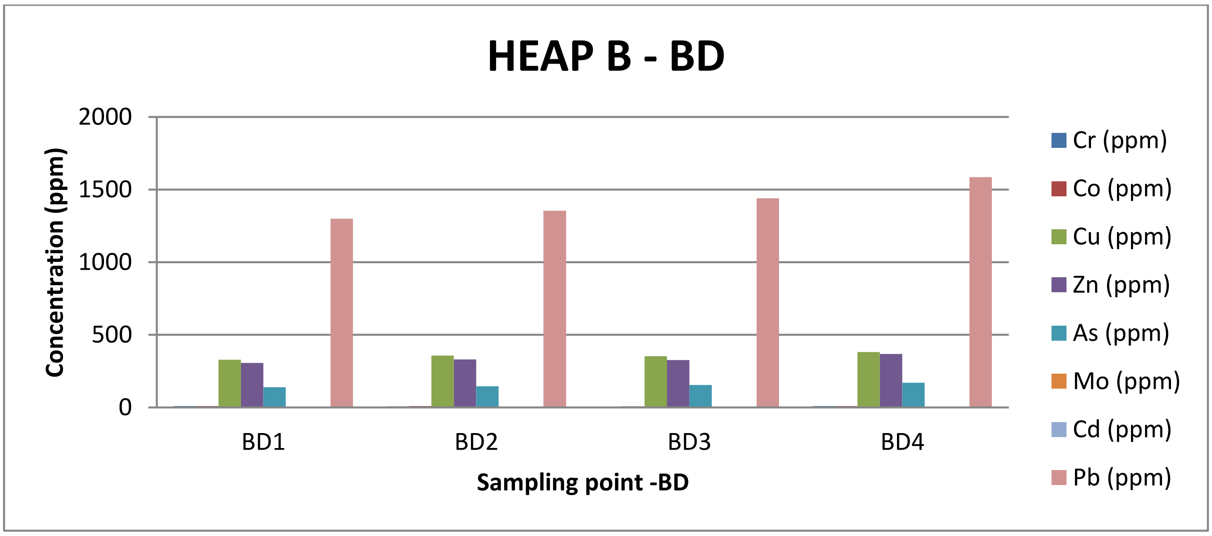


Figure 4.6: Values of metals in samples collected from point BD.

The metal values of lead at sampling point BE shown in figure 4.7 seem to have erratic behaviour but it is having higher levels compared to other metals. Lead is followed by copper, zinc, and arsenic with moderate metal values. Chromium, cobalt, and molybdenum have low levels and cadmium was constant.

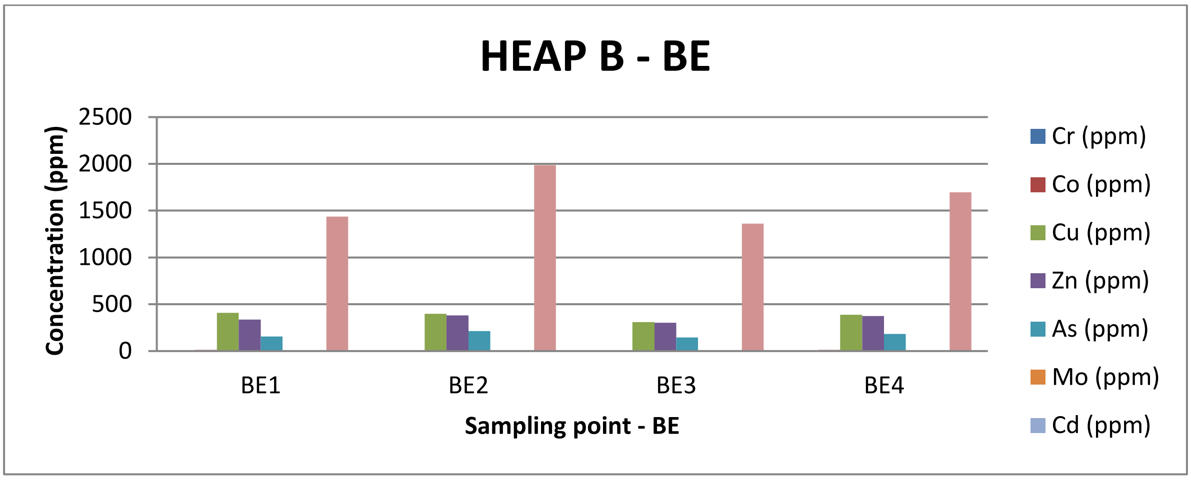


Figure 4.7: Values of metals in samples collected from point BE.

At sampling point BF lead was high on concentration level while cadmium was at its lowest concentration level. Copper and zinc showed a good relationship because their concentration levels seem to be a bit close to each other. The concentration levels of arsenic seem to be less than those of zinc and copper but higher than those of chromium, cobalt, and molybdenum whereas cadmium was found to be constant throughout (Fig. 4.8).

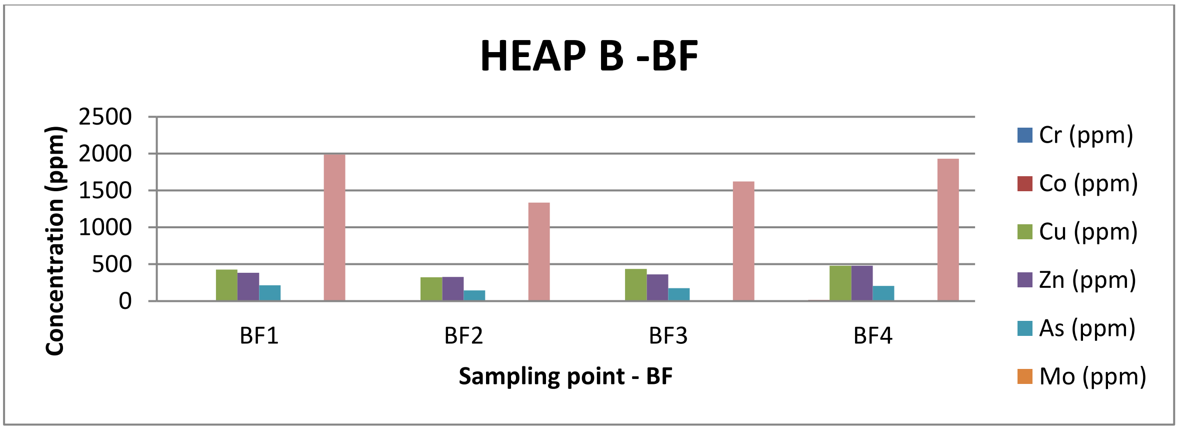


Figure 4.8: Values of metals in samples collected from point BF.

Heap C

The Table 4.4 below shows the mean, maximum and minimum values of the metals from Heap C (Table 3.6). Lead has a maximum value compared to other metals and it’s followed by copper, zinc, arsenic with a concentration of 964.7ppm, 595.3 ppm, 313.5 ppm and 103.5 ppm respectively.

Table 4.4: The mean, maximum and minimum values of metals in samples collected from Heap C.

Sample	Cr (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Mo (ppm)	Cd (ppm)	Pb (ppm)
Mean	9,71	8,40	476,26	253,75	76,45	0,79	0,07	712,31
Min	0,1	7,6	382,3	214,8	51,5	0,2	0	480,2
Max	37,6	10,4	595,3	313,5	103,5	2,5	0,1	964,7

Lead has a maximum peak in all the analysed samples and is followed by copper, zinc and arsenic as shown in Fig. 4.9 to Fig. 4.13. The concentration levels of arsenic seem to be less than those of zinc and copper but higher than those of chromium, cobalt, and molybdenum whereas cadmium was found to be constant throughout.

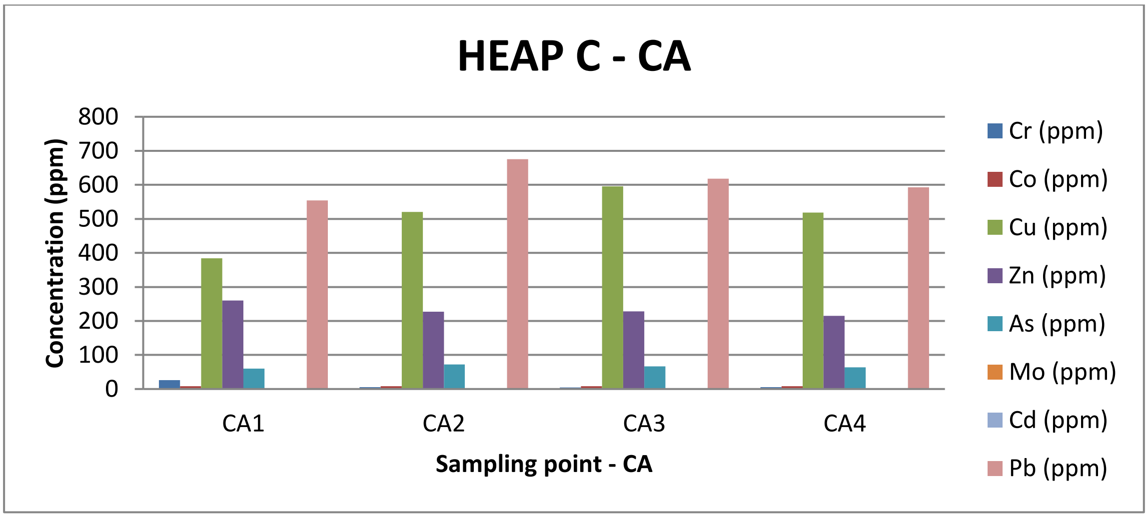


Figure 4.9: Values of metals in samples collected from point CA.

The bar graph (Fig. 4.10) below shows the concentration levels of metals at sampling point CB which is found within profile 1 of Heap C. Chromium, cobalt and arsenic have the lowest concentration values. In this point, lead, zinc, and copper concentration values are lower than those of sampling point CA.

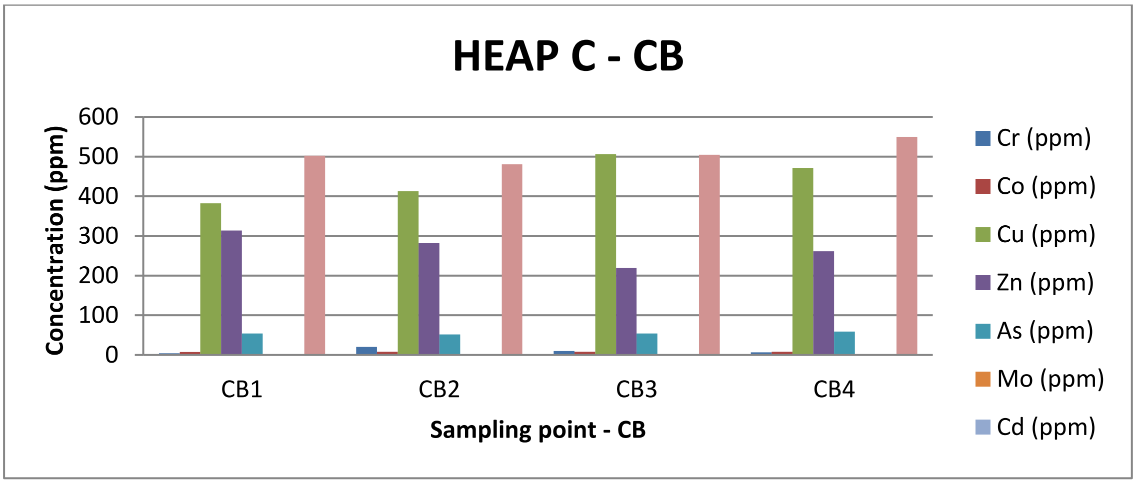


Figure 4.10: Values of metals in samples collected from point CB.

The bar graph (Fig. 4.11) below shows the concentration levels of metals at sampling point CC, and it found within profile 1 together with sampling point CA and CB. Copper concentration values are lower than that of drill CB while lead concentration are higher that of drill CB. There are low concentration values of copper in CC compared to that of CB. Zinc concentration values are very low compared to point CB.

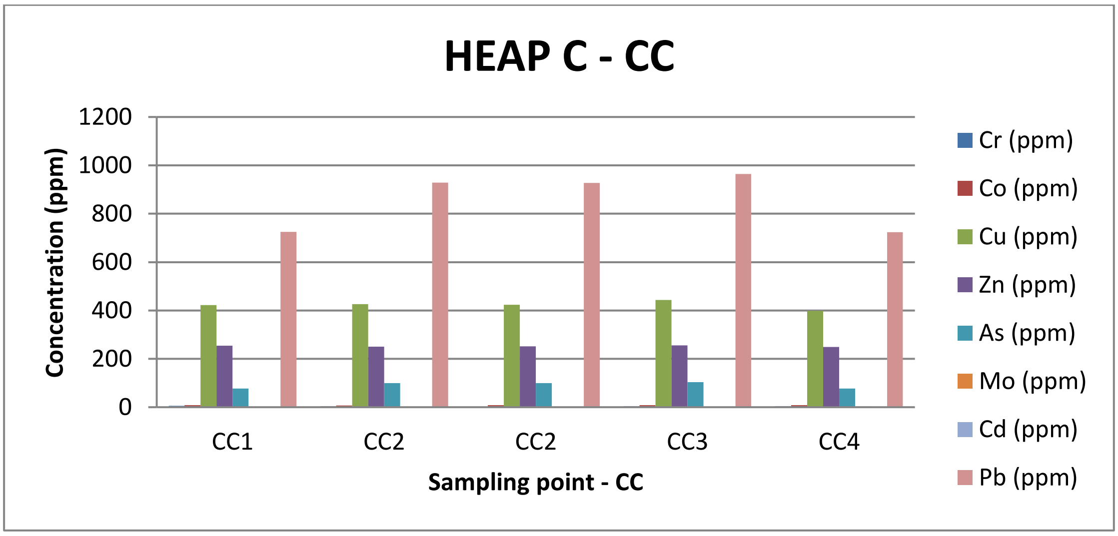


Figure 4.11: Values of metals in samples collected from point CC.

The bar graph (Fig. 4.12) below shows the concentration levels of metals at sampling point CD which is at profile 2. In this drill hole, the concentration of lead and zinc is decreasing with depth. There are very small peals of cobalt and chromium.

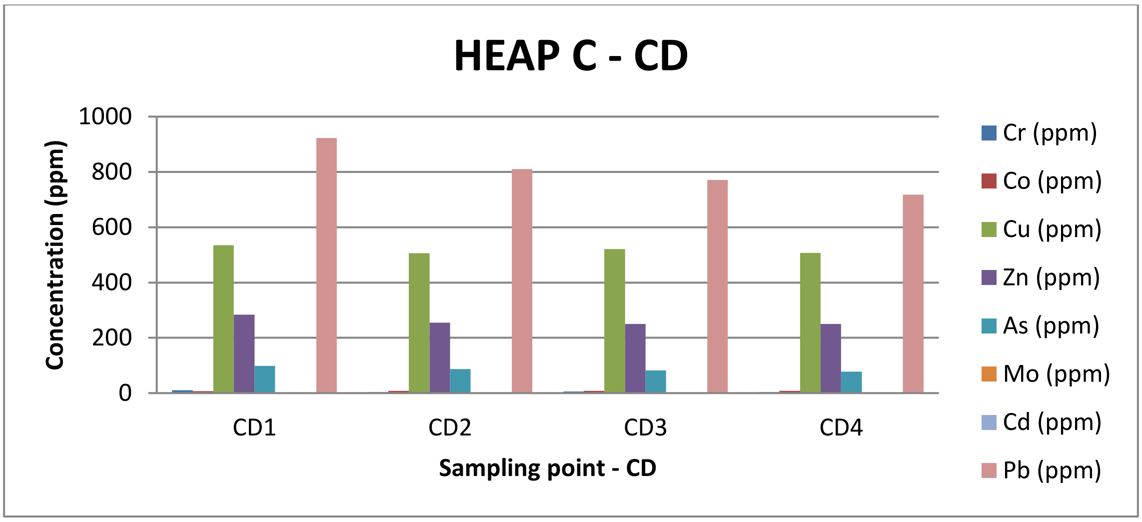


Figure 4.12: Values of metals in samples collected from point CD.

The bar graph (Fig. 4.13) below shows the concentration levels of metals at sampling point CE. There is a higher concentration of lead, copper, zinc and arsenic. Cadmium, molybdenum, and cobalt have very low concentration. The concentration values of CE and CD are more or likely the same.

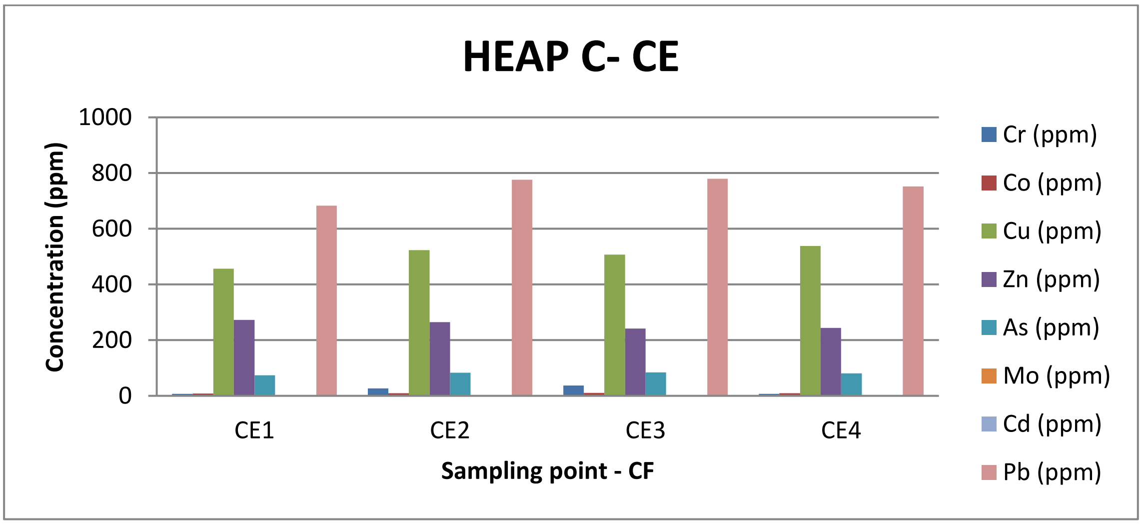


Figure 4.13: Values of metals in samples collected from point CF.

4.2 Distribution Pattern of Metals within the River Profile

The distribution pattern of metals across and along the river within the tailings was investigated along and across the river profiles. Data from the five profiles across the river were used to determine the distribution pattern.

4.2.1 Distribution Pattern of Metals across the River Profile

The distribution pattern of metals across the river profiles had been present below by means of Fig. 4.14 and Fig. 4.15. In Profile 1, P1S1 has low values of metals as compared to P1S3. The Pb, Cu, Zn and As metals values are higher at P1S3 which may be as a result of erosion and its low elevation level. In Profile 3, P3S1 and P3S3 are both at low elevation as compared to the central point and they have higher metals values than the central point. P3S3 has higher metals values although it is at a higher elevation than P3S1. The central point (P3S3) has low values of metals and it is at a higher elevation as compared to its counterparts (Fig. 4.14).

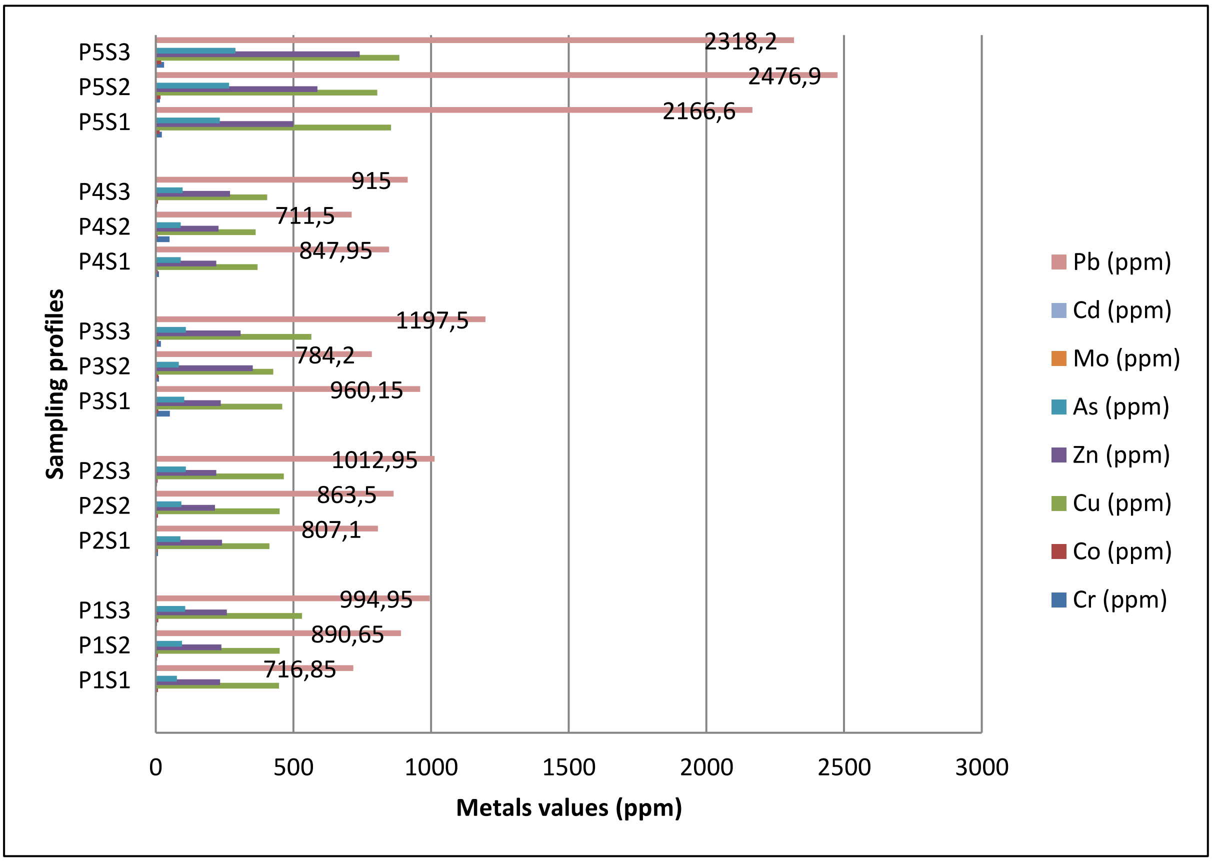


Figure 4.14: Distribution pattern of metals across the river profile.

The general trend of this assessment is that the higher metals values are associated with low elevation level of the sampling point across the river profiles.

4.2.2 Distribution Pattern of Metals along the River Profiles

Data collected from five profiles across the river were used to determine the distribution patter along the river. The mean value was computerised from the three sampling points in each profile so as to determine the distribution pattern along the river profile (Fig. 4.15). The profiles were spaced approximately 500 m apart. These metals, lead, copper, and arsenic are increasing with distance, for an example, P1 had a lead concentration of 867.48 ppm and P5 which is 2000 m away from P1 had a concentration of 2320.57 ppm. However, the concentration values of these metals had sharp decrease in P4 and increase in P5. These may be due to an increase in elevation in P4. The mean elevation values are 1156 m, 1131 m, 1089 m, 1105 m and 1078 for P1, P2, P3, P4 and P5 respectively (Appendix 2). It can also be concluded that water is responsible for the redistribution of these metal from a higher elevation to lower elevation.

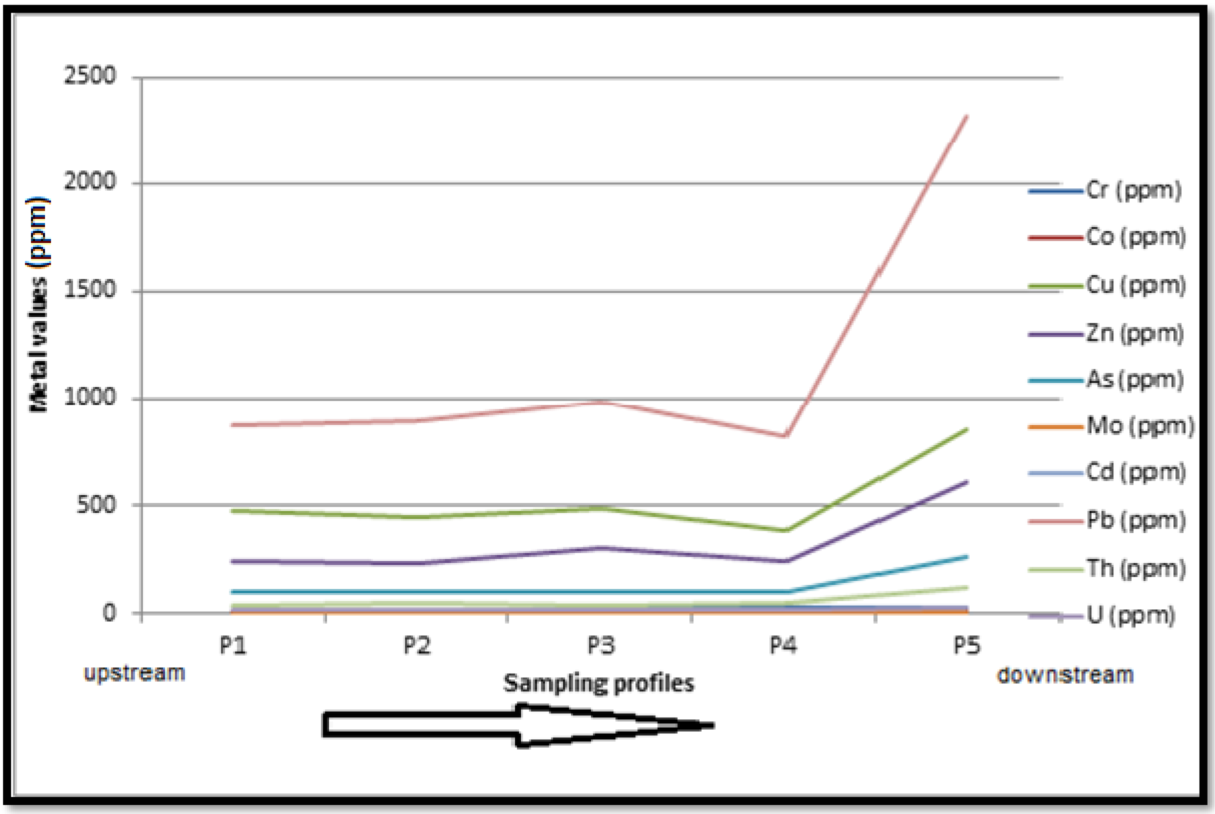


Figure 4.15: Distribution pattern of metals with along the river profile.

P5 is the last profile to be sampled and is approximately 2000 m away from River Profile 1. It is also the profile which is at the lowest elevation. It has very higher concentration of metals. This is due to water erosion thus metals had been washed from higher elevation to lower elevation.

4.3 Distribution Pattern of Metals within the Heaps

Data obtained from analysing metal values from Heap A, B, and C were used to determining metal values within these heaps and to ascertain any trends or behaviour of metals within such heaps.

Distribution pattern of Metals Heap A

Distribution pattern of metals cannot clearly be show because of its sampling procedure. A random method of sampling was employed for collection of the tailing's samples. Heap A tailings were very shallow, and samples were collected at only at 1 m depth only. However, its metals concentration values are clearly shown in Figure 4.2 and Table 3.4 above.

Distribution pattern of Metals Heap B

Drill hole BA

On the first sampling point along profile 1 named BA. The values of lead (Pd) were ranging between 1177.7 and 1243.5 ppm, increasing with depth. Cr values were decreasing from the top to level 3 m and then increased. Co values were decreasing to level 2 m and then increases thereafter and while Cu decreases with depth, and this depicts that water may be the transporting agent but metal values at each depth also depends on the mobility of the element itself. Mo had a slight increase in between level 2 m and 3 m and Cd had a constant distribution throughout the hole. Lead has a maximum value in all the analysed samples and is followed by copper, zinc and arsenic as shown in Fig. 4.16 to Fig. 4.21.

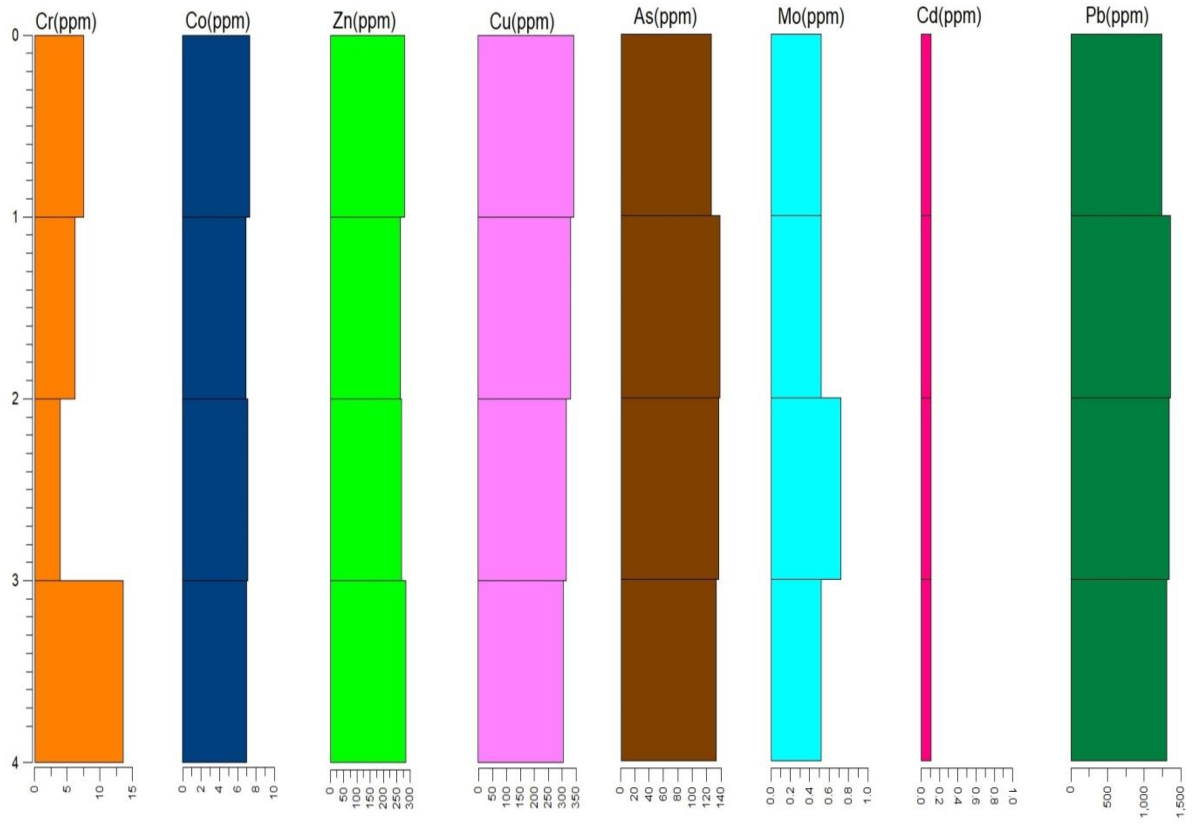


Figure 4.16: Distribution of metals with depth along BA drill hole within Heap B.

BB

The second sampling point was named BB and the Cd values were the same throughout the 4 m depth hole with a concentration of 0.1 ppm. Co and Mo values were increasing with depth from 1 m level to 4 m level. Cu, Zn, As, and Pb values increased with depth but decreased at 4 m level. Cu values ranges from 517.5 and 614.8 ppm. Mo values were increasing with depth. The maximum values were found at Pb which was ranging from 1909.6 to 2591.9 ppm. As values ranges from 205 to 278.2 ppm. In general, the metals in terms of concentration within this sampling profile were increasing to 3 m depth which is the level they settled to after being washed down (Fig. 4.17).

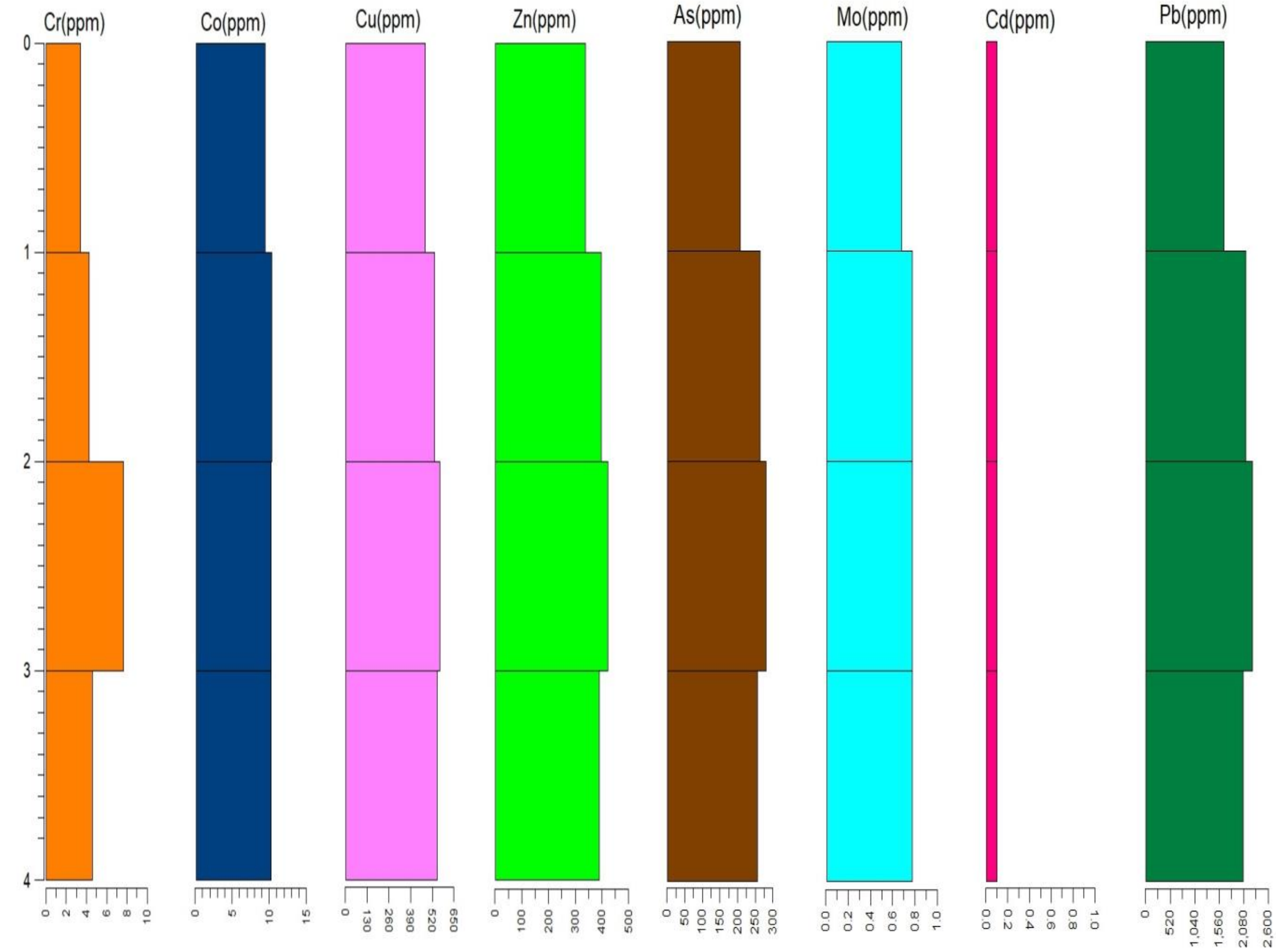


Figure 4.17: Distribution of metals with depth along BB drill hole within Heap B.

BC

The third sampling point was named BC along profile 1. Cr values were ranging 1.5 and 9 ppm. Co values ranges from 10.6 to 11.4 ppm. Co values decreased at 3 m depth and increased at 4 m depth. Cu, Zn, As, Mo and lead increased from 1 m depth to 3 m depth and then a sharp decrease at 4 m depth. Pb values are also higher with concentration ranging between 2161.9 and 2842.4 ppm. Cd values are also constant throughout with a concentration of 0.1 ppm (Fig. 4.18).

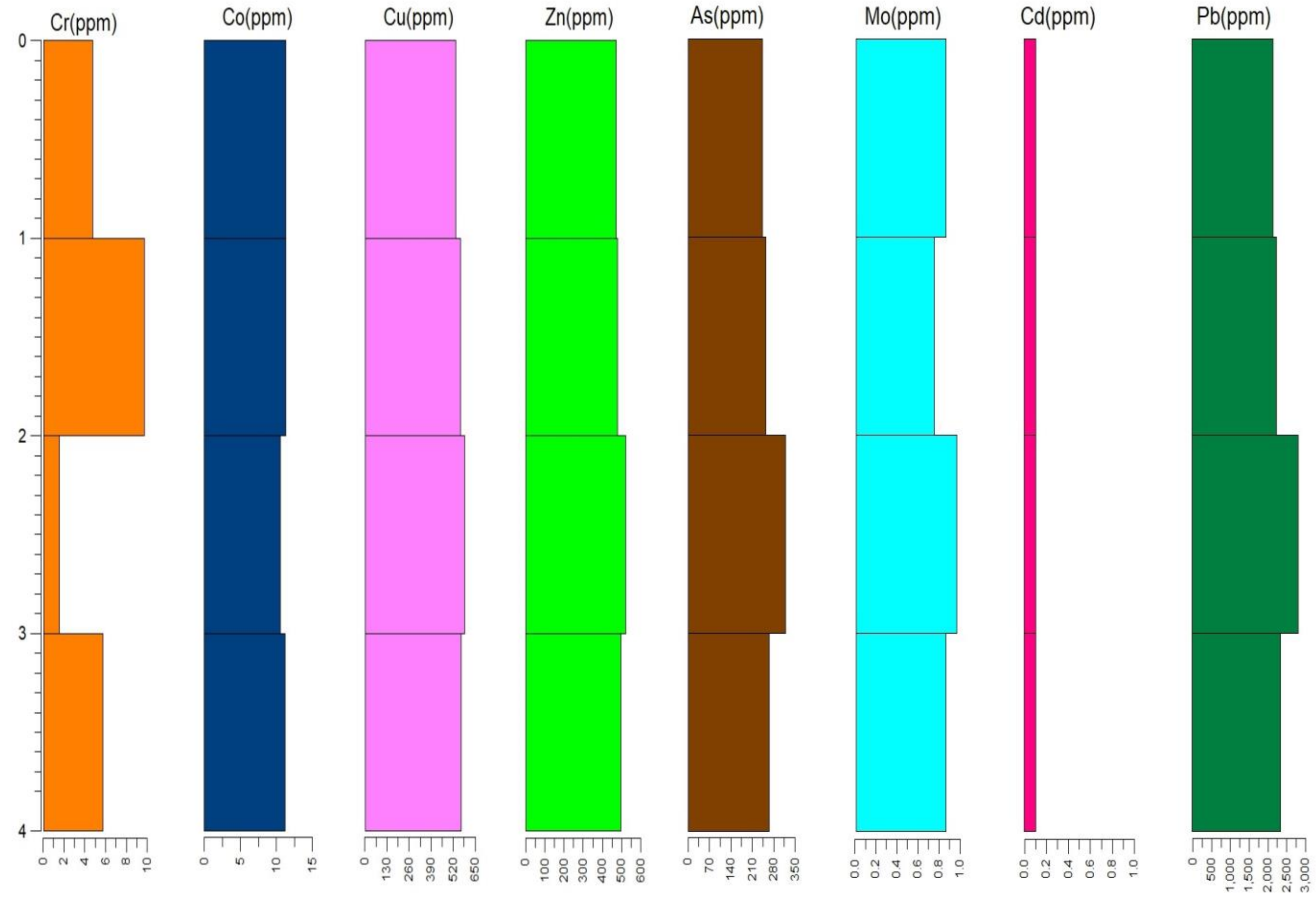


Figure 4.18: Distribution of metals with depth along BC drill hole within Heap B.

BD

The first sampling point along profile 2 was named BD where samples were collected for the same 4 m depth. The distribution pattern of metals along this profile was shown below (Fig. 4.19). The value of Pb ranges between 1300 and 1584, 8 ppm, thus increasing with depth. Zn, As and Cu values were also increasing with depth. Cr values were decreasing with up to level 3 m and then increased at 4 m. Mo was ranging between 0.6 and 0.7 ppm, meaning its concentration is very low while Cd is constant throughout the hole with a concentration of 0.1 ppm. In general, there was a slight increase in metals with depth.

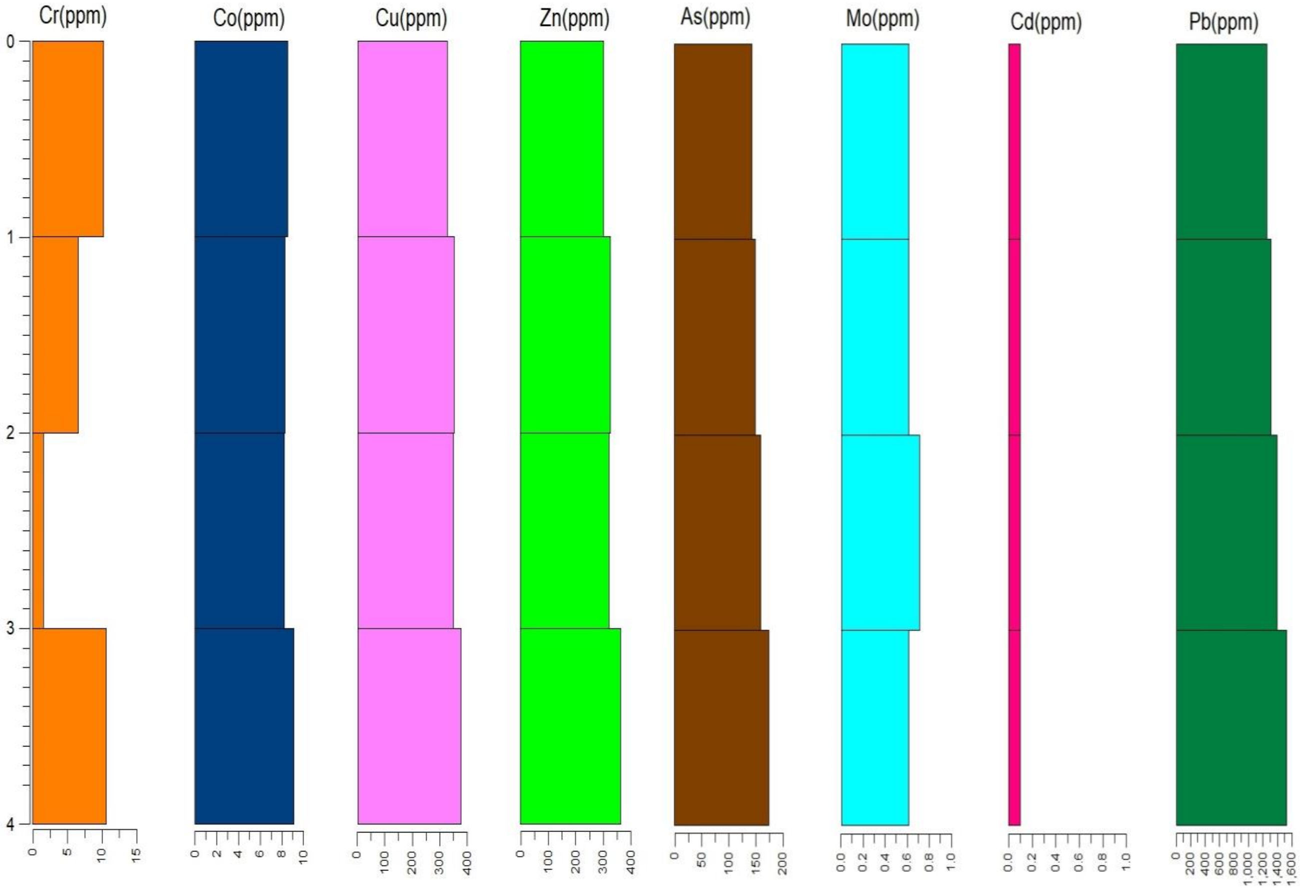


Figure 4.19: Distribution of metals with depth along BD drill hole within Heap B.

BE

The second point named BE along profile 2. Cr and Co values were higher at 1 m and the decreased at 2 m to 3 m and then increased at 4 m. Cu, Zn, As, and Pb increased to 2 m and then decreased at 3 m. Cd remained constant throughout with a concentration of 0.1 ppm (Fig. 4.20).

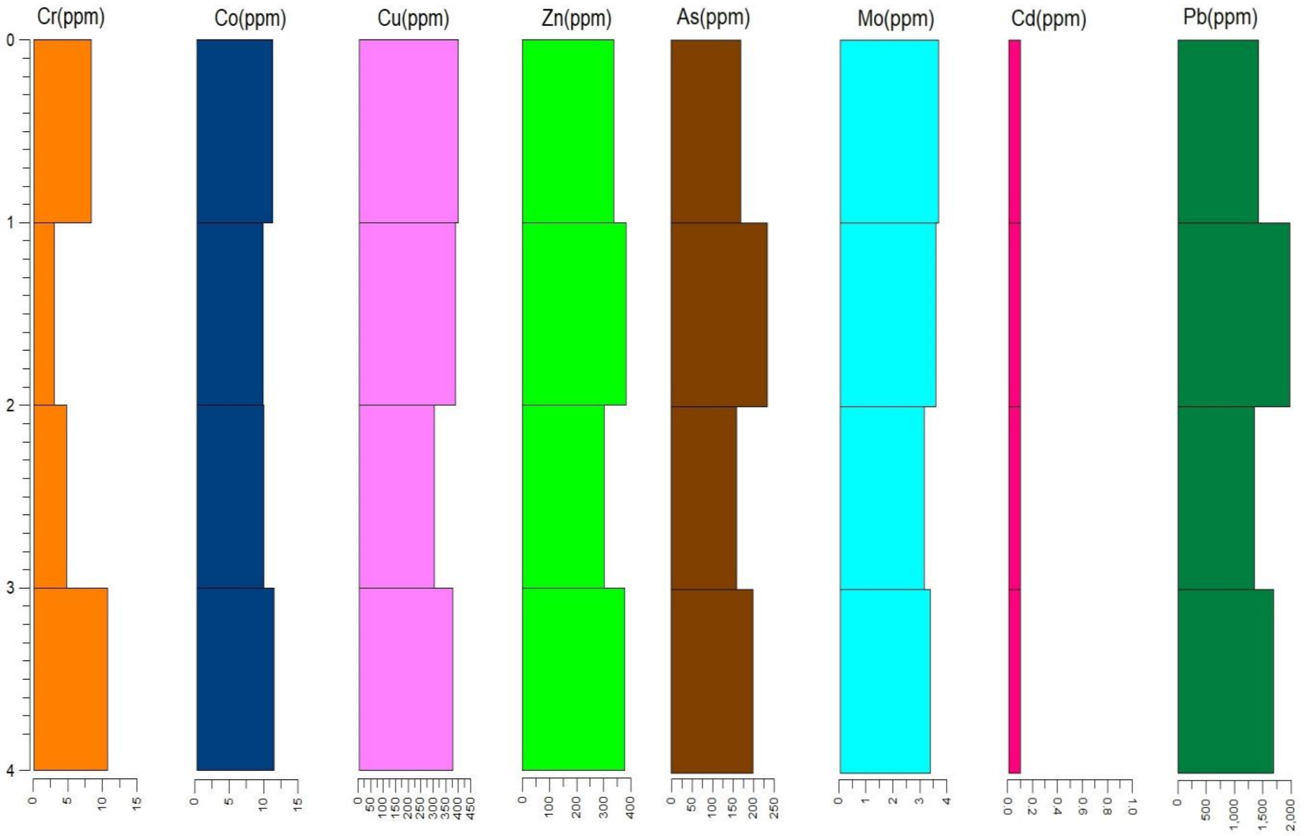


Figure 4.20: Distribution of metals with depth along BE drill hole within Heap B.

BF

The third sampling point was named BF along profile 2. The values of Cr were ranging between 1, 3 and 8 ppm. The concentrations of Co were increasing with depth which means that this metal can sink into the ground. Cu and Zn were distributed in such a way that it was increasing with depth. As values ranges from 143.6 to 207.2 ppm. Mo was found in low concentration and Cd was constant with a concentration of 0.1 ppm. However, Pb remains high in concentration compared to the other metals and ranges between 13337, 7 and 1988.2 ppm (Fig. 4.21).

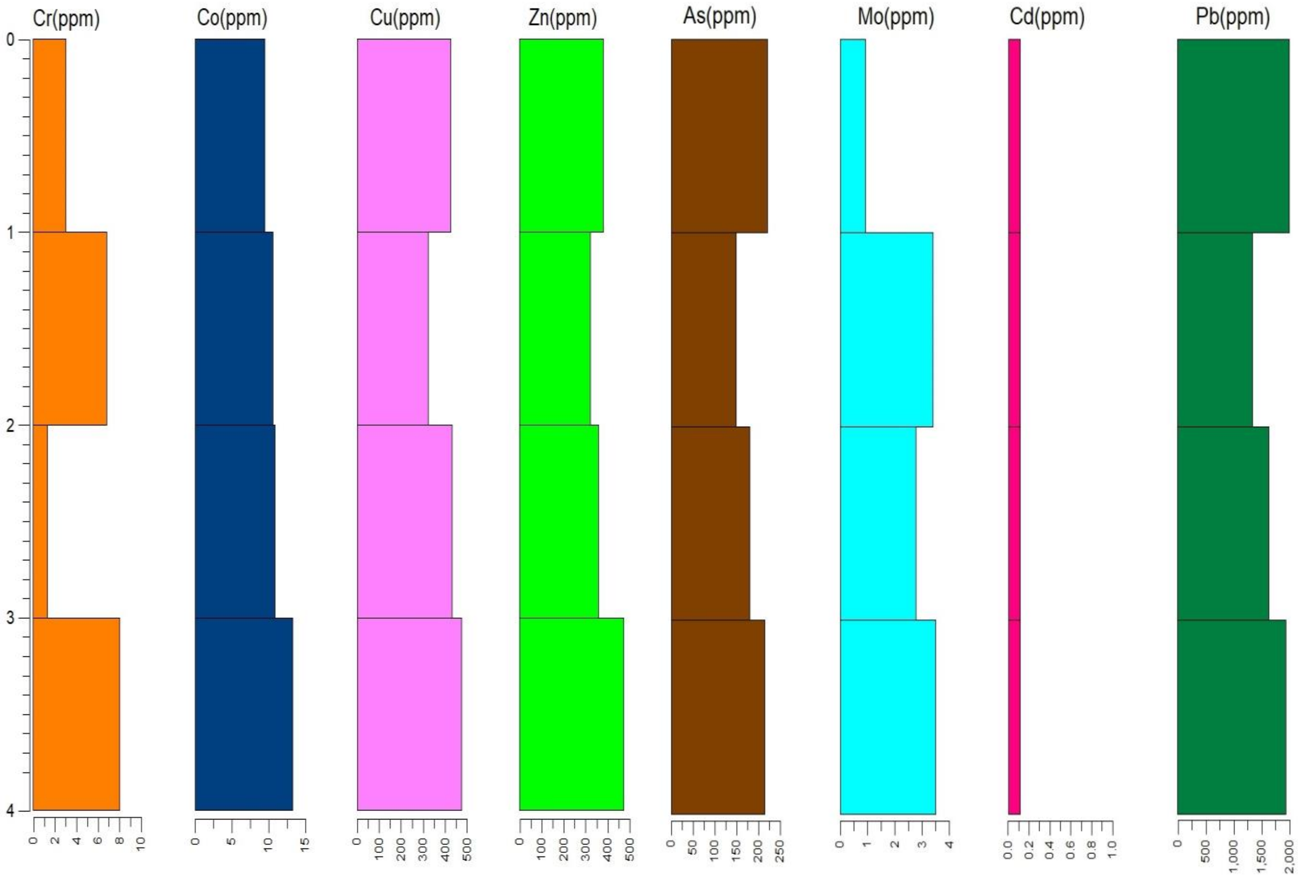


Figure 4.21: Distribution of metals with depth along BF drill hole within the Heap B

Distribution of metals within Heap C

CA

CA is the first sampling point along profile 1 in Heap C. The values of lead (Pb) were ranging between 554 and 675.1 ppm, increasing with depth. Lead has the ability to sink to the ground hence it is very low at the top of the hole and higher at the bottom. Cr values were higher at the top and low at the bottom. Co values were decreasing with depth. Cu, Mo and As concentration values had the same trend with Pb which is increasing with depth (Fig. 4.22). Lead has a maximum value in all the analysed samples and is followed by copper, zinc and arsenic. Overall, all the metals are increasing values with depth except for cadmium with a no concentration in drill hole

CA.

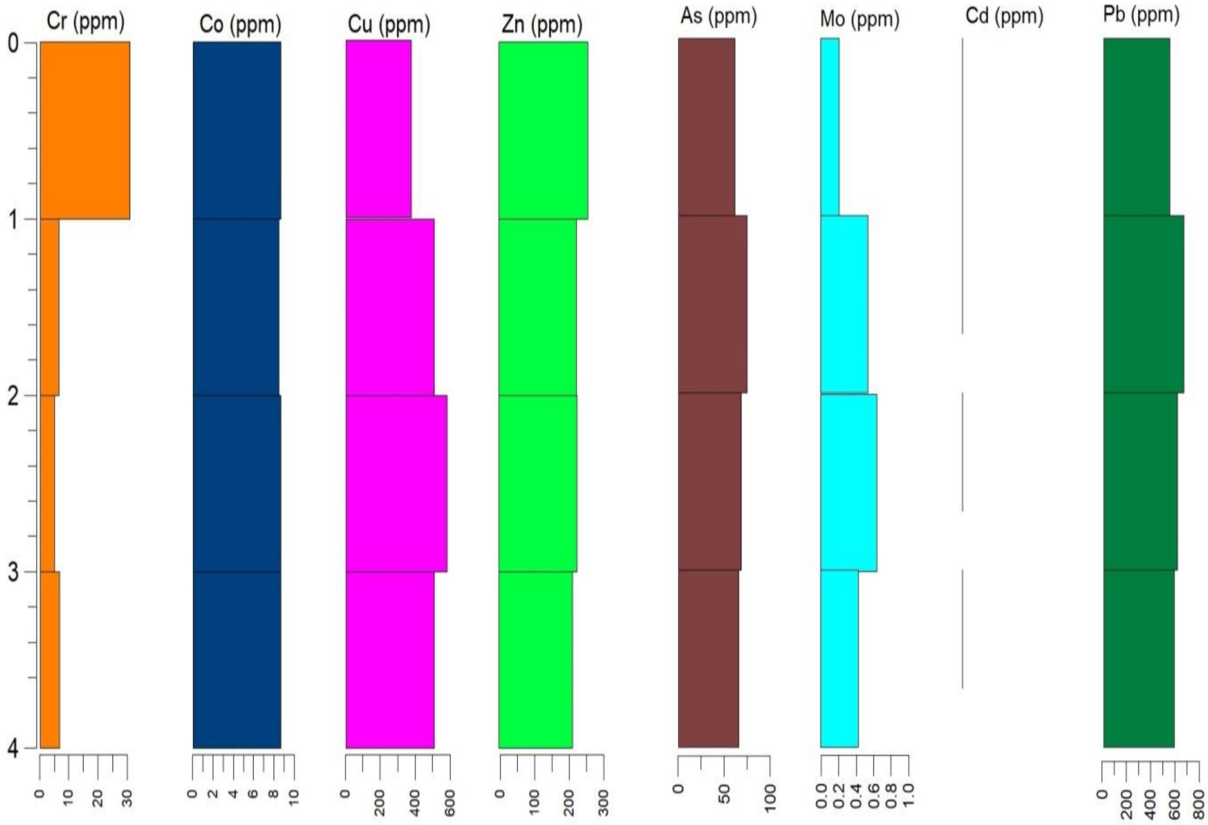


Figure 4.22: Distribution of metals with depth along CA drill hole within Heap C

CB

CB is the second sampling point along profile 1 in Heap C. There are maximum values of Pb, Zn, Cu and As with a concentration of 592.6, 506.5, 313.5 and 59 respectively. Co and Cup concentration values are increasing with depth while Cd and has a constant value of 0.1 ppm. Mo has also very low values of around 1.1 to 1.4 ppm. Pb, Cr, Zn and has erratic values in drill hole CB as compared to CA. Overall, all the metals are increasing values with depth except for cadmium with a constant concentration throughout the CA drill hole and a concentration of 0.1 ppm (Fig. 4.23).

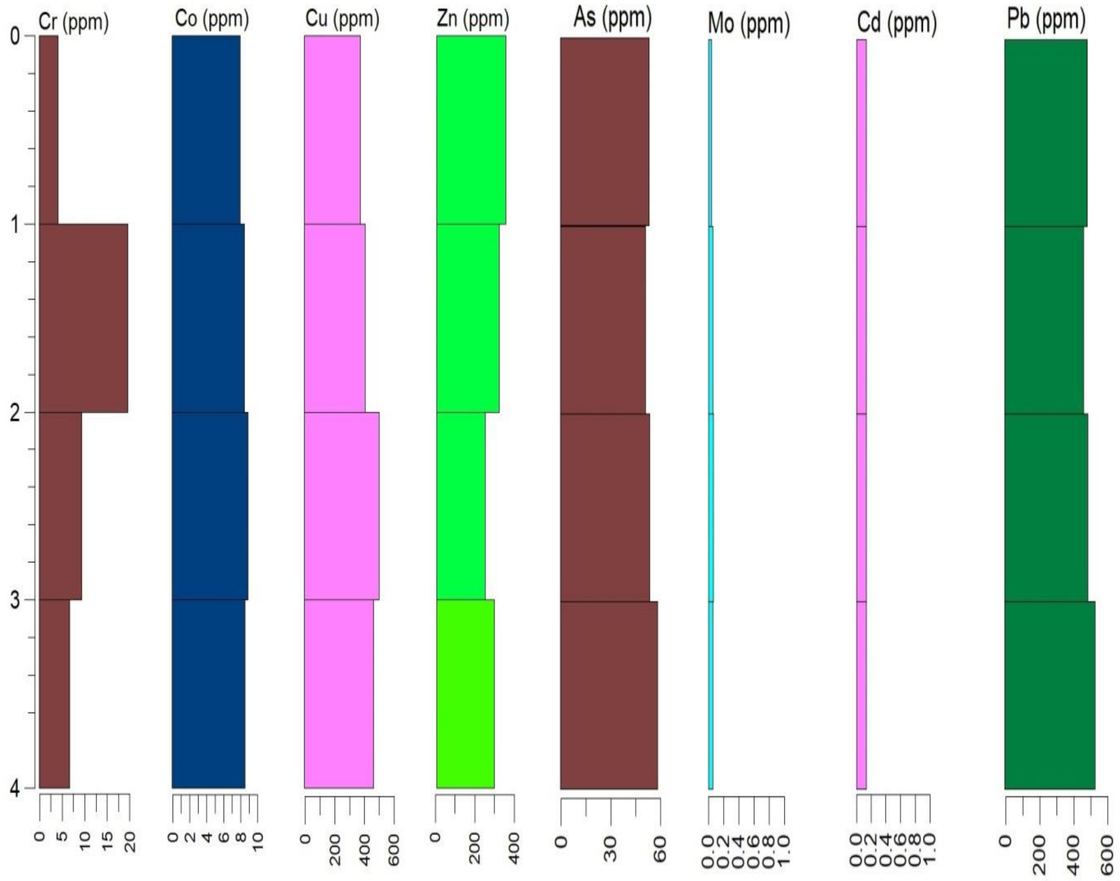


Figure 4.23: Distribution of metals with depth along CB drill hole within Heap C

CC

CC is the third sampling point along profile 1 in Heap C. Mo values increased at the bottom of the hole as compared to drill hole CB which had a constant concentration. The values of Pb are ranging between 724.7 and 962.7ppm, increasing with depth (Fig. 4.24). Cr values were higher at the top and low at the bottom. Co values were decreasing with depth. Cu, Mo and As concentration values had the same trend with Pb which is increasing with depth. Overall, all the metals are increasing values with depth except for cadmium with constant concentration in drill hole CC.

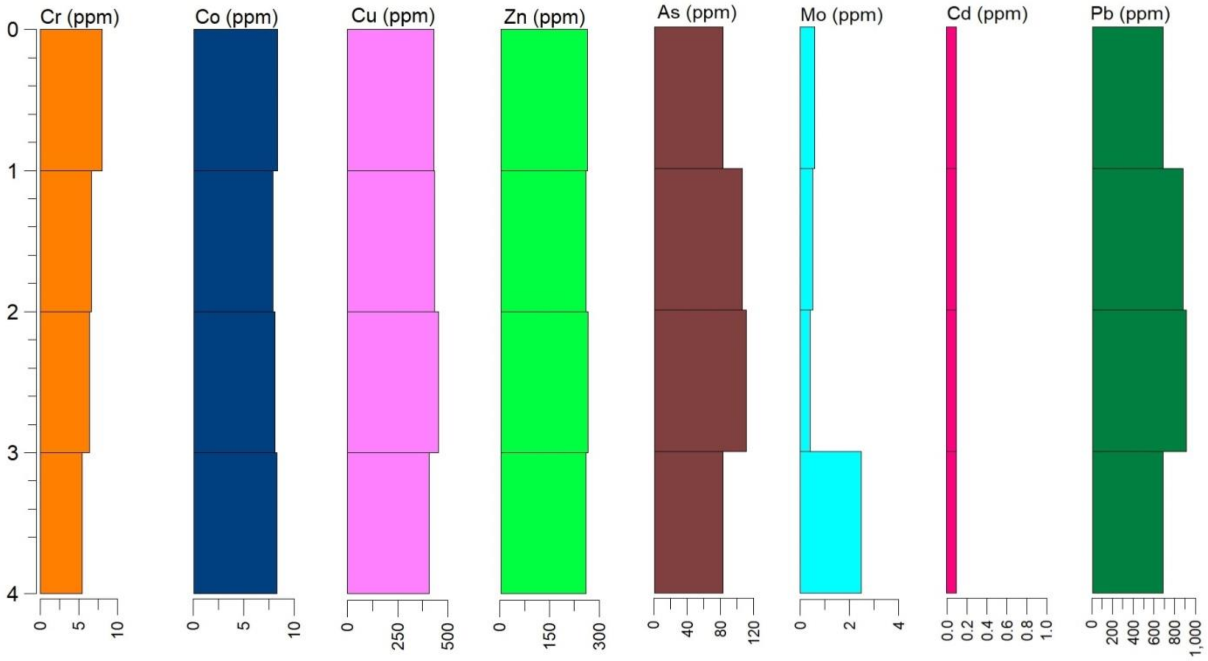


Figure 4.24: Distribution of metals with depth along CC drill hole within Heap C

CD

CD is the first sampling point along profile 2 in Heap C. Cr, As and Pb values decreasing from the 1 m to 4 m. Cadmium concentration value is either 0.1 ppm or 0 ppm (Fig. 4.25). Co and Cu values decreased at 2 m depth and then increased at 3 m depth. Zn values were higher at 1 m depth and then decreased to 4 m depth.

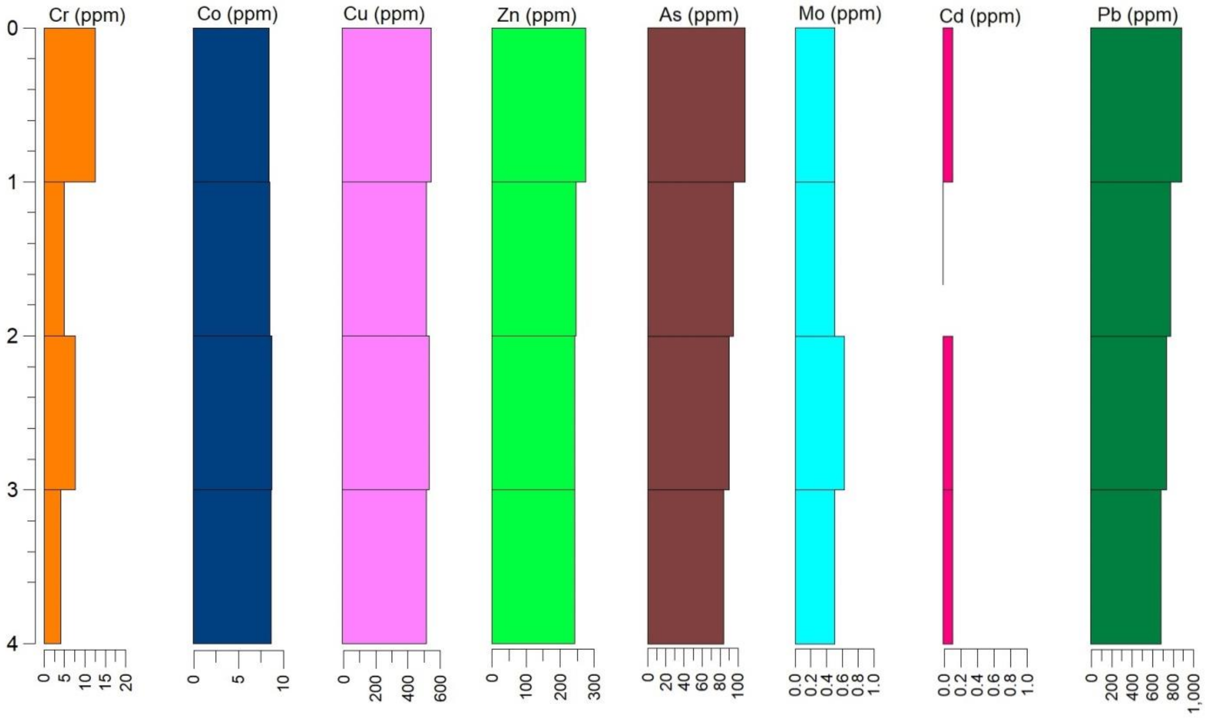


Figure 4.25: Distribution of metals with depth along CD drill hole within Heap C

CE

CE is the second sampling point along profile 2 in Heap C. Chromium and lead had the same trend and has the high concentration values at 2 m and 3 m depth. Cobalt, copper, zinc, arsenic have concentration values that are inconsistent with depth. Cadmium has a 0.1 ppm in and no concentration at bottom. These metals are increasing values with depth except for cadmium with a constant concentration throughout the CA drill hole (Fig. 4.26).

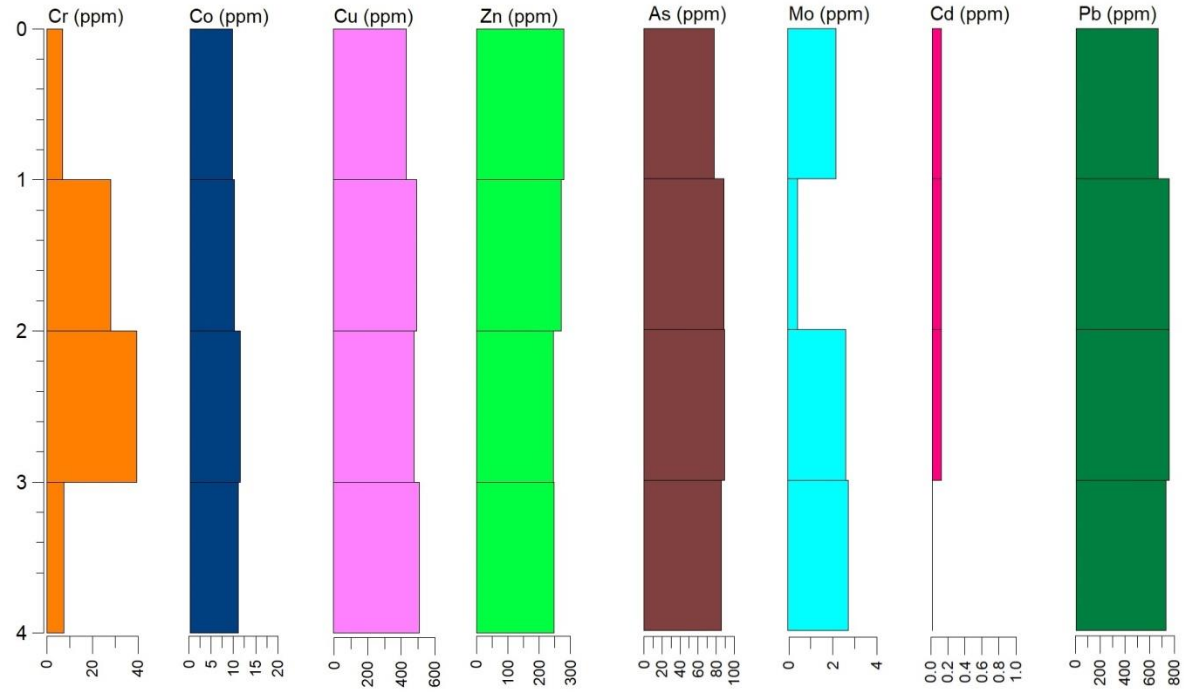


Figure 4.26: Distribution of metals with depth along CE drill hole within Heap C

In summary, some metals values are erratic with depth. However, the general trend is increasing with depth. Water is the transporting agent of these metals within the tailing’s heaps. The different metal values at different levels shows that there is a driving force responsible for their mobility which is in this case may be water from rain. However, Cd values were very low and remained constant throughout.

4.4 Pollution Condition of the Tailings

The Single Factor Index Method (SFIM) was the method used to establish the level of pollution of tailings within the study area. This method was developed by fang (Guazhang *et al*, 2005). This factor is calculated as shown in Equation 4.1.

$$Pi = \frac{Ci}{Si} \quad \ldots\ldots \quad (4.1)$$

Where,

Pi - Environmental quality index of the pollutant

Ci- Concentration on the spot survey of the pollutant

Si- Assessment standard of the pollutant

The assessment standard of the pollutant was taken from the work of Kabata-Pendias (2011) which is the world's average surface concentration of trace metals. The Pi values denote specific degree of contamination. In this $1 < Pi \leq 2$, denotes low degree of pollution, $2 < Pi \leq 3$ denotes moderate degree of pollution and $Pi > 3$ denotes high degree of pollution. The $Pi \leq 0.7$ indicates a minimum contamination potential. However, if $0.7 < Pi \leq 1$ displays that the heavy metal concentrations is less than the recommended quality standard, but the heavy metal pollution is approaching the warning conditions. Therefore, such soil can support plant growth and with no harm on human being (Guazhang *et al.*, 2005). The table below (Table 4.5) gives a summarised Environmental Quality Index (Pi) for the Zaaiplaats tailings and the lowest index calculated for each metal.

Table 4.5: Pollution condition of the tailings within the Zaaiplaats Tin Mine waste.

Pollution condition of the tailings within the River Profiles.										
Metals	Cr	Co	Cu	Zn	As	Mo	Cd	Pb	Th	U
Pollution Index of Metals (Pi)	0.08	1.01	19.26	3.47	16.37	0.25	0	28.46	4.6	2.76

Pollution condition of the tailings within the Heap A.										
Metals	Cr	Co	Cu	Zn	As	Mo	Cd	Pb	Th	U
Pollution Index of Metals (Pi)	0.33	1.2	29.95	3.73	19.44	0.25	0.09	34.03	5.27	3.23

Pollution condition of the tailings within the Heap B.										
Metals	Cr	Co	Cu	Zn	As	Mo	Cd	Pb	Th	U
Pollution Index of Metals (Pi)	0.04	0.93	18.53	4.56	26.89	0.28	0.09	47.11	4.49	3.11

Pollution condition of the tailings within the Heap C.									
Metals	Co	Cu	Zn	As	Mo	Cd	Pb	Th	U
Pollution Index of Metals (Pi)	1.10	27.31	3.54	10.96	0.11	0	19.21	3.93	3.08

The above analysis of the pollution index of the tailings revealed the following;

a) Tailings along the river profile were highly polluted with Pb, Cu, As, Th and Zn in that order.
b) Heap A was heavily polluted with Pb, Cu, As, Th, Zn and U in that order.
c) Heap B was heavily polluted with Pb, As, Cu, Th, Zn and U in that order.
d) Heap C was heavily polluted with Cu, Pb, and As in that order.

Cu, Zn, As, Pb, Th and U had shown a higher degree of pollution which is presented by Pi values of 3 and above in all the different sampling locations of the tailings. The highest Pi is found within the Pb metals and is followed by Cu and As and the values are 47.11, 29.95 and 26.89 respectively. Cr, Co, Mo and Cd show warning signals or no degree of pollution in the tailings. The minimum Pi values are found on the Cd and Mo which are 0 and 0.11 respectively. The general assessment is that the tailings are heavily polluted with Pb, Cu, As, Th, Zn and U.

4.5 Comparison of Metals in Water against South African Water Quality Guidelines

Table 4.6 contains metal values against South African Water Quality Guidelines, guidelines are standards that are used as the benchmark to denote if the water is polluted or not. The Target Water Quality Range (TWQR) is a management objective that is used to stipulate the anticipated ideal concentration range or water quality requirements for a specific constituent which in this case is a metal (Department of Water Affairs and Forestry, 1996). The Chronic Effect Value (CEV) is well-defined as that concentration or level of a constituent at which there is assumed to be a significant likelihood of measurable chronic effects (Department of Water Affairs and Forestry, 1996).

Table 4.6: Metal values against SA Water Quality Guidelines

Heavy metals	**Cr (ppm)**	**Cu (ppm)**	**Co (ppm)**	**Pb (ppm)**
SA Water Quality Guidelines: aquatic ecosystem (TWQR)	0,007	0,0008	none	0,0005
Chronic Effect Values (CEV)	0.014	0.0015	none	0.001
S1	0	0.59	0	0.67
S2	0	0.03	0	0
S3	0	0.53	0	0.42

There are no concentration values for metals such as Cr and Co in water samples collected at Zaaiplaats Tin Mine. Water having heavy metal concentration higher than the stipulated standards is said to be polluted or contaminated by that type of heavy metal. Heavy metals can bio-accumulate in aquatic plants and organisms. In the study area the water has higher metal values of Pb and Cu compare to the standards that are stipulated by the South African water quality guidelines and it is thus polluted. Lead values in sample 1 and 3 are above the TQWR and the CEV which means the surface water found within the mine is Pb polluted. Lead standards are 0.0005 and 0.001 ppm TQWR and CEV respectively

4.6 Metals Values in Plants

This section presents the concentration values of heavy metals within plants collected during the dry and wet season for comparison purposes.

Metals values in plants sampled during dry season

Table 4.7 below presents the mean, minimum and maximum values of metals on the Equisetum ramosissimum plant from different locations within the study area from dry season. Cu has a maximum value compared to other metals and it's followed by chromium and lead with a concentration of 34.82 ppm, 15.72 ppm and 6.16 ppm respectively. Cobalt has relatively low values than any other metals.

Table 4.7: The mean, minimum and maximum values of metals on the Equisetum ramosissimum plant from different locations within the study area from dry season

Sample ID	**Mean**	**Min**	**Max**
Cr (ppm)	15,69	15,58	15,79
Co (ppm)	0,4	0,14	1,01
Cu (ppm)	26,952	7,85	34,82
Pb (ppm)	4,164	3,64	4,99

Chromium values are almost at a slightly consistent manner as shown in Fig. 4.27 below. However, lead values are increasing with distance from S1 to S7 but other metals have no general trend with regards to sampling distance. Cobalt values are very low and have minimum peaks.

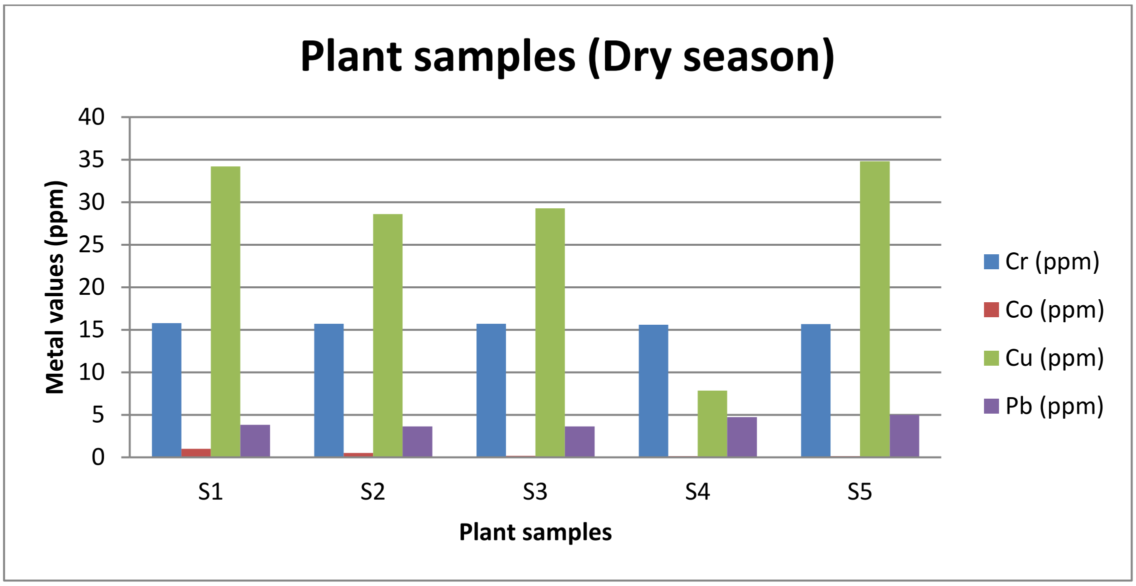


Figure 4.27: Values of metals on the Equisetum ramosissimum plant from different locations within the study area from dry season.

Cr has a maximum value compared to other metals and it is followed copper with a concentration of 7.86 ppm and 7.49 respectively. Copper values are consistent in the shoots of the plant as show in Table 4.8 below.

Table 4.8: The mean, minimum and maximum values of metals on the Shoots of the Equisetum ramosissimum plants from dry season.

Metals	**Mean**	**Min**	**Max**
Cr (ppm)	7,79	7,72	7,86
Co (ppm)	0,294	0	0,95
Cu (ppm)	5,388	3,33	6,71
Pb (ppm)	1,386	0,83	2,34

Cu and Cr metal values are higher with maximum values of 32.9 ppm and 7.96 ppm in the roots of the plant as compared to the shoots respectively (Table 4.9). In addition, lead values are also higher in the roots than on the shoots of the plant. However, cobalt values are lower at the roots of the plant than at the shoot.

Table 4.9: The mean, minimum and maximum values of metals on the Roots of the Equisetum ramosissimum plants from dry season

Metals	**Mean**	**Min**	**Max**
Cr (ppm)	7,90	7,86	7,96
Co (ppm)	0,11	0,05	0,18
Cu (ppm)	27,24	21,9	32,9
Pb (ppm)	2,78	2,46	3,31

It is evident that copper and lead values were higher in the roots of the plant during dry season as shown by maximum peaks as shown Figure 4.28. Chromium peak levels are consistent throughout.

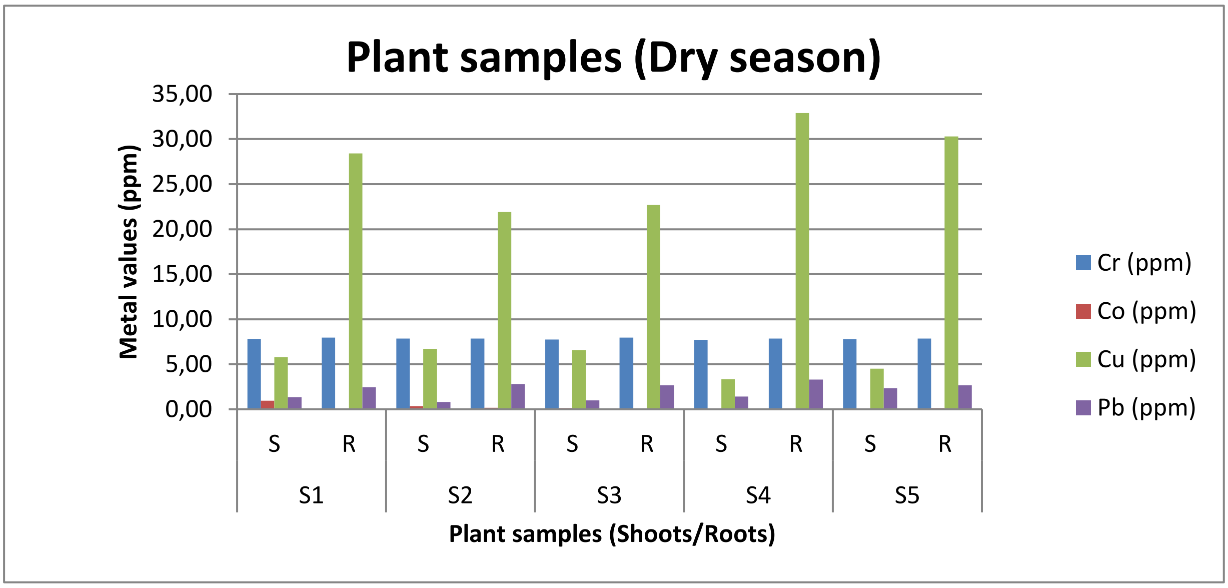


Figure 4.28: Values of metals on the Equisetum ramosissimum plant in the Shoot and Roots in different locations within the study area from dry season.

Table 4.10 below presents the mean, minimum and maximum values of metals on the tailings collected below the Equisetum ramosissimum plants from different locations within the study area from dry season. Cu has a maximum value compared to other metals and it is followed by lead and lead with a concentration of 22.89 ppm and 14.03

ppm respectively. Chromium and cobalt has relatively low values. In comparison with the whole plant metal values in Table 4.8 above, metal values found in the tailings are lower than that of a plant.

Table 4.10: The mean, minimum and maximum values of metals on the tailings collected below Equisetum ramosissimum plant during dry season.

Sample	**Cr (ppm)**	**Co (ppm)**	**Cu (ppm)**	**Pb (ppm)**
Mean	0,83	0,01	16,36	7,86
Min	0,02	0	13,09	5,07
Max	2,52	0,06	22,89	9,92

Cobalt has very low peak in Figure 4.29 below. Copper peak are at a maximum in all the sampled points and are followed by lead.

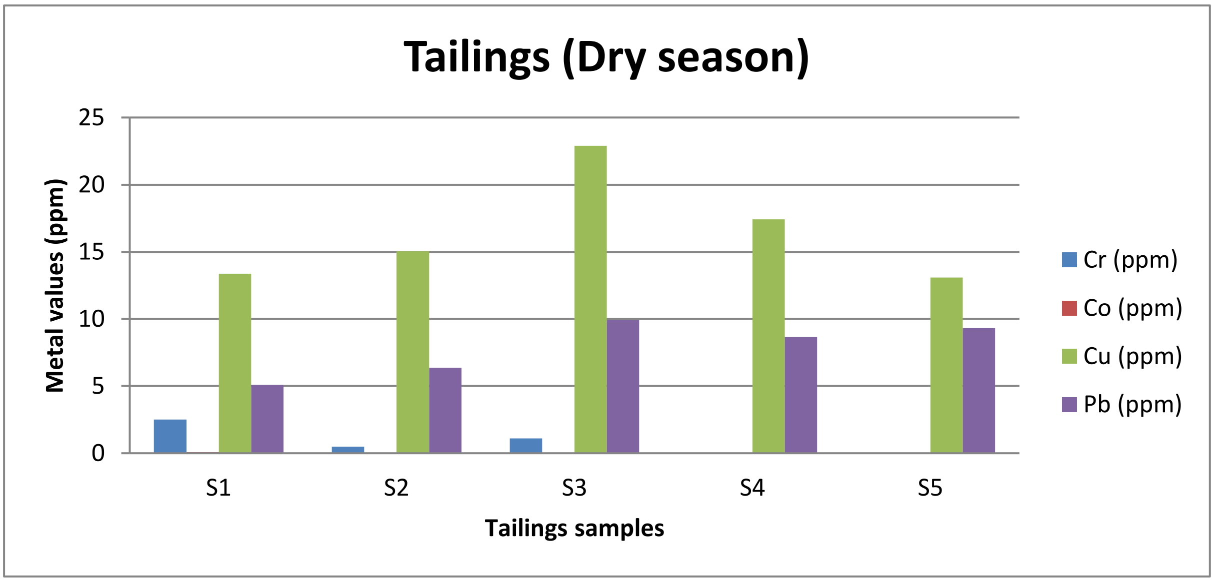


Figure 4.29: Values of metals on the tailings collected below Equisetum ramosissimum plant from different locations within the study area from dry season.

Metals values in plants sampled during wet season

Table 4-11 below presents the mean, minimum and maximum values of metals on the *Equisetum ramosissimum* plant from different locations within the study area from wet season. Cu has a maximum value and it is followed lead with a concentration value of 6.5 ppm and 3.22 ppm respectively. Chromium and cobalt have relatively low values. These metals from wet season are lesser as compared to metal values of dry season (Table 4-7).

Table 4.11: The mean, minimum and maximum values of metals on the Equisetum ramosissimum plant from wet season.

Metals	**Mean**	**Min**	**Max**
Cr (ppm)	0.175	0	0.7
Co (ppm)	0.79	0.65	1.04
Cu (ppm)	4.015	1.72	6.5
Pb (ppm)	1.59	0.76	3.22

Lead values have produced maximum peaks as shown in Fig.4.30. Chromium has only one peak in S2 which can be considered as an anomaly. Lead and copper values have a general trend which is the decreasing of its values with distance which is from S1 to S4.

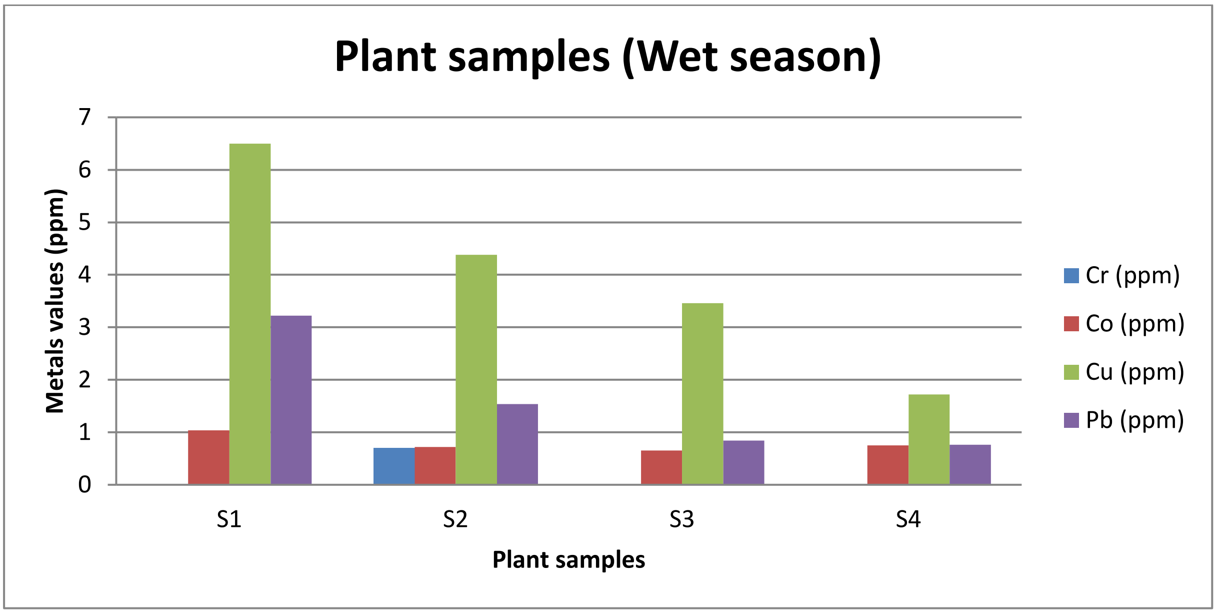


Figure 4.30: Values of metals on the *Equisetum ramosissimum* plant from different locations within the study area from wet season.

Cr has no value in the shoots of the plants collected during the wet season which is contrary to higher values found on plants collected during dry season (Table 4.8 and Table 4-12). Lead values are also lower in the wet season as compared to dry season.

Table 4.12: The mean, minimum and maximum values of metals on the Shoots of the Equisetum ramosissimum plants from wet season.

Metals	**Mean**	**Min**	**Max**
Cr (ppm)	0	0	0
Co (ppm)	0.45	0.37	0.55
Cu (ppm)	1.605	0.17	2.79
Pb (ppm)	0.75	0.23	1.4

Cu and Cr metal values are higher with maximum values of 3.71 ppm and 0.7 ppm in the roots of the plant as compared to the shoots respectively (Table 4-13). Lead values are higher in the roots than on the shoots of the plants. Cobalt values are lower at the roots of the plant than at the shoot.

Table 4.13: The mean, minimum and maximum values of metals on the Roots of the Equisetum ramosissimum plants from wet season.

Metals	Mean	Min	Max
Cr (ppm)	0.18	0	0.7
Co (ppm)	0.34	0.23	0.49
Cu (ppm)	2.4	1.55	3.71
Pb (ppm)	0.8	0.07	1.82

Copper and lead values are higher in the roots of the plant as shown by maximum peaks as shown Figure 4.31. The concentrations are values of the copper and lead are decreasing with distance from S1 to S4. Chromium peak levels are consistent throughout.

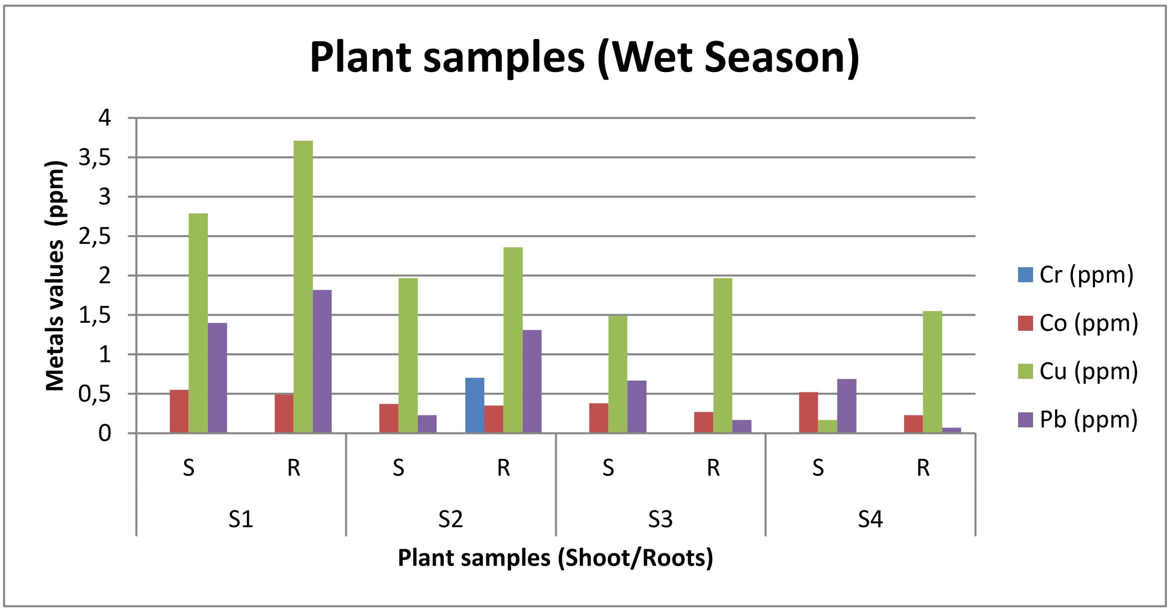


Figure 4.31: Values of metals on the *Equisetum ramosissimum* plant in the Shoot and Roots in different locations within the study area from wet season.

The values of metals on the tailings collected during the wet season are lower as compared to tailings collected during dry season. This is due to water erosion during wet season. Cu has a maximum value compared and it’s followed by lead with a concentration of 14.92 ppm and 5.57 ppm respectively. Chromium and cobalt has relatively low values. In comparison with the whole plant metal values collected in wet season in Table 4-11 above, metal values found in the tailings are higher than that of a plant.

Table 4.14: The mean, minimum and maximum values of metals on the tailings collected below *Equisetum ramosissimum* plant during wet season.

Sample	**Cr (ppm)**	**Co (ppm)**	**Cu (ppm)**	**Pb (ppm)**
Mean	0.03	0.38	9.68	4.17
Min	0	0.31	3.71	3.08
Max	0.13	0.44	14.92	5.57

Copper has very higher peaks in Fig. 4.32 below. Copper peak are at a maximum in all the sampled points and are followed by lead. Copper has very low peaks.

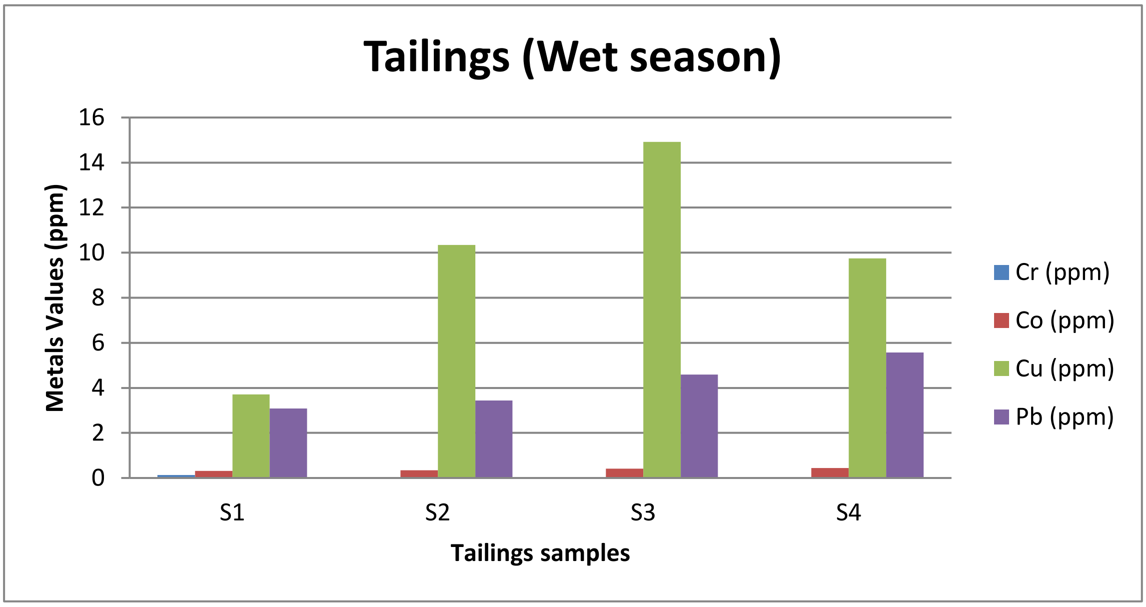


Figure 4.32: Values of metals on the tailings collected below Equisetum ramosissimum plant from different locations within the study area from wet season.

Chromium

Cr has a maximum value 15.79 ppm in the whole plant collected during dry season. Cr has a maximum values compared to other metals with metals values of 7.86 ppm in the shoots and 7.96 in the roots. Cr values in the tailings found below the plant were lower with a maximum value of 2.52 ppm. There is a higher concentration values of chromium in the roots corresponding to its upper shoots, for examples, S1 has a concentration value of chromium in the roots and shoot of 7.96 ppm and 7.86 ppm respectively. In addition, the concentration value of Chromium below S1 is 2.52 ppm. Chromium is been absorbed by the roots.

In wet season, Chromium had no values except an anomaly in the roots of S2 with a concentration value of 0.7. The tailings collected below the plants also had no concentration value of chromium with an anomaly of 0.13 ppm.

Copper

Cu has a maximum value of 34.82 ppm in plant collected during dry season. Cu has a maximum value of 6.71 ppm in the shoots and 32.9 in the roots. Cu had a maximum value of 22.89 ppm in the tailings found below the plant. There is a higher concentration values of copper in the roots corresponding to its upper shoots, for examples, S2 has a concentration value of copper in the roots and shoot of 21.9 ppm and 6.71 ppm respectively. The concentration value of Chromium in the tailings below S2 is 15.04 ppm; hence, there is higher metal absorption by the roots.

In wet season, copper concentration values decrease but still having the same trend of higher concentration values in roots than the shoot. The maximum values of the roots and shoot are 3.71 ppm and 2.29 ppm respectively. The concentration values copper of tailings below them is also much higher than that of the roots and shoots.

Lead

Pb has a maximum value of 4.99 ppm of in the whole plant collected during dry season. Lead had a maximum value of 2.34 ppm in the shoots and 3.31 ppm in the roots. PB had a maximum value of 9.92 ppm in the tailings found below the plant. There is also a higher concentration values of lead in the roots corresponding to its upper shoots, for examples, S7 has a concentration value of lead in the roots and shoot of 3.31 ppm and 2.34 ppm respectively. The concentration value lead in the tailings below S7 is 9.92 ppm. In this case, lead concentration values are much higher in the tailings found below the plant samples.

In wet season, lead concentration values decrease but still having the same trend of higher concentration values in roots than the shoot. The maximum values of lead in the roots and shoots are 1.82 ppm and 1.4 ppm respectively. The concentration values copper of tailings below them is also much higher than that of the roots and shoots.

Cobalt

Cobalt has relatively low values than any other metals. Cobalt values are lower at the roots of the plant than at the shoot in both dry season and wet season. Cobalt has a maximum value of 0.95 in the shoot and 0.18 in the roots. There is no cobalt concentration in the tailings below the plants during dry season.

For samples collected during the wet season, Cobalt values are still lower at the roots of the plant and are higher at shoot. There are concentration values of cobalt in the tailings during wet season.

4.7 Bioaccumulation factor and Translocation factor

The metals concentration values within the Equisetum ramosissimum plant from different location at Zaaiplaats tin mine tailings presented above were used for determination of the Bioaccumulation and Translocation factors. The mobility, bioaccumulation, and transfer of these metals; Cr, Co, Cu and Pb from the Zaaiplaats Tin Mine tailings to roots tissues and from roots tissues to shoots tissues of the plants are presented below.

Bioaccumulation factor

The bioaccumulation factor (BAF) is the ratio of heavy metal content in plants to the corresponding heavy metal content in soil, which reflects the degree of difficulty in accumulating heavy metals in soil (Zhang, 2021). It is also an index of ability of the plant to accumulate a metal, with respect to its concentration in the soil substrate (Branković *et al*., 2019). This factor is calculated as shown in Equation 4.2.

$$\text{BAF} = \frac{C_{plant}}{C_{soil}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.2)$$

Where C_{soil} is the concentration of heavy metal in soil and C_{plant} is the concentration of heavy metal in plant shoots and roots

Translocation factor

Translocation Factor (TF) defined as the movement of heavy metal from the soil to the roots and from roots to the other parts of the plant. It is the ability of a plant to move accumulated heavy metal from one part to another (Tudi *et al.*, 2020). This factor is calculated as shown in Equation 4.3.

$$TF = \frac{C\ shoot}{C\ root} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.3)$$

Where C_{shoot} and C_{root} are metal concentration in the shoot and roots, respectively. Wherein TF>1 indicates that the plants translocate metals effectively from roots to the shoots (Tudi *et al.*, 2020). Table 4-15 and Table 4-16 below shows the calculated Bioaccumulation Factor and Translocation Factor of plants samples and tailings samples collected from Zaaiplaats tin mine during dry season and wet season respectively.

Table 4.15: Bioaccumulation factor and Translocation factor within the Zaaiplaats Tin Mine during dry season

Metals	**S1**		**S2**		**S3**		**S4**		**S5**	
	BAF	TF	BAF	TF	BAF	TF	BAF	TF	BAF	TF
Cr	6.67	1	32.08	1	14.15	1	779	1	783	1
Co	16.83	15.83	-	1.89	-	2.6	-	0.5	-	0
Cu	2.56	0.20	1.90	0.31	1.28	0.29	0.45	0.10	2.66	0
Pb	0.75	0.55	0.57	0.3	0.37	0.4	0.55	0.4	0.53	1

Cr has BAF values of greater than 1 and higher and it was absorbed and accumulated. Cobalt metal has no BAF values except for an anomaly S1 sample hence it was not absorbed nor accumulated during dry season. Cu metal also has a BAF greater than 1 except for S4 sample; hence it was absorbed and accumulated. The BAF of Pb had been lower than 1 hence the metal was absorbed and not accumulated. Translocation factors of all these metals is also lower than 1 hence these metals where not transferred effectively from roots to shoots. There is a higher concentration amount of these metals in the roots than at the shoots during dry season. When BCF < 1 or BAF

= 1, it denotes that the plant only absorbs the heavy metal but does not accumulate, when BCF > 1, and this indicates that plant accumulates the heavy metals. The trend in the BAF for heavy metals during dry season is in the ranking order of Cr > Cu > Pb> Co. The trend in the TF for heavy metals during dry season is in the ranking order of Cr > Pb> Cu > Co. It is evident that the BAF and TF of Cr metal is higher than those of Cu, Pb and Co during dry season.

Table 4.16: Bioaccumulation factor and Translocation factor within the Zaaiplaats Tin Mine during wet season.

Metals	**S1**		**S2**		**S3**		**S4**	
	BAF	TF	BAF	TF	BAF	TF	BAF	TF
Cr	0	-	-	0	-	-	-	-
Co	3.35	1.12	2.12	1.06	1.55	1.41	1.70	2.26
Cu	1.75	0.75	0.42	0.83	0.23	0.75	0.18	0.11
Pb	1.04	0.77	0.45	0.18	0.18	3.94	0.14	9.86

Cr had a translocation factor of equal 1 in dry season and, but no movement of Cr metal occurred in wet season. There was also no movement of cobalt metal in the dry season but it is now being absorbed, accumulated and transferred effectively in wet season. Cu metal has low TF values in both dry and wet season. The values are much lower in dry season. The translocation factor of PB was very low or less than 1 with an exception of S5 during dry season and S3 and S4 during wet season which are the samples collected where Pb metal values where higher and also at a very lower elevation with a possibility of metal load by erosion. Generally, cobalt metal is being absorbed, accumulated, and transferred effectively in wet season while other metals are not in wet season.

In summary, Cr and Cu were absorbed and accumulated by the plants during the dry season while Co was not absorbed and not accumulated. In the wet season, Co was absorbed and accumulated by the plants while Cr, Cu and Pb were not. Hyper-accumulation refers to the natural ability of certain plants to clean up soil, air, and water contaminated with hazardous chemicals. Plant species show TF and BAF greater than one are suitable for phytoextraction of heavy metals (El-Amier *et al.,* 2017). *Equisetum ramosissimum* is a hyper-accumulator of Cr and Cu during dry season and Co during wet season and can be used for photostabilization and photoextraction of these metals. Mobility of these metals differs with seasons.

4.8 Radiation Surveying Analysis

The radiation dose rate and dose equivalent from each surveying point were used to draw graphs and give comparison of these values within the tailings. Radiation dose rate recorded and measured in microsievent per hour (µSv/h) and microsievent (µSv) respectively. The mean, minimum and maximum values of radiation dose rate during surveying were 0.46 µSv/h, 0.11 µSv/h and 1.33 µSv/h respectively (Table 4-17).

Table 4.17: The mean, minimum and maximum values of radiation dose rate and dose within the Zaaiplaats Tin Mine tailings.

Radiation Survey Measurements	**Radiation dose rate (µSv/h)**	**Radiation dose (µSv)**
Mean	0.46	1.83
Min	0.11	1.64
Max	1.33	1.97

Radiation dose is increasing from a higher elevation which is the first surveying point to low elevation which is the last surveying point as shown in the bar graph below (Fig. 4.33). Radiation dose is probably the result of thorium and uranium metals which were also increasing from upstream to downstream.

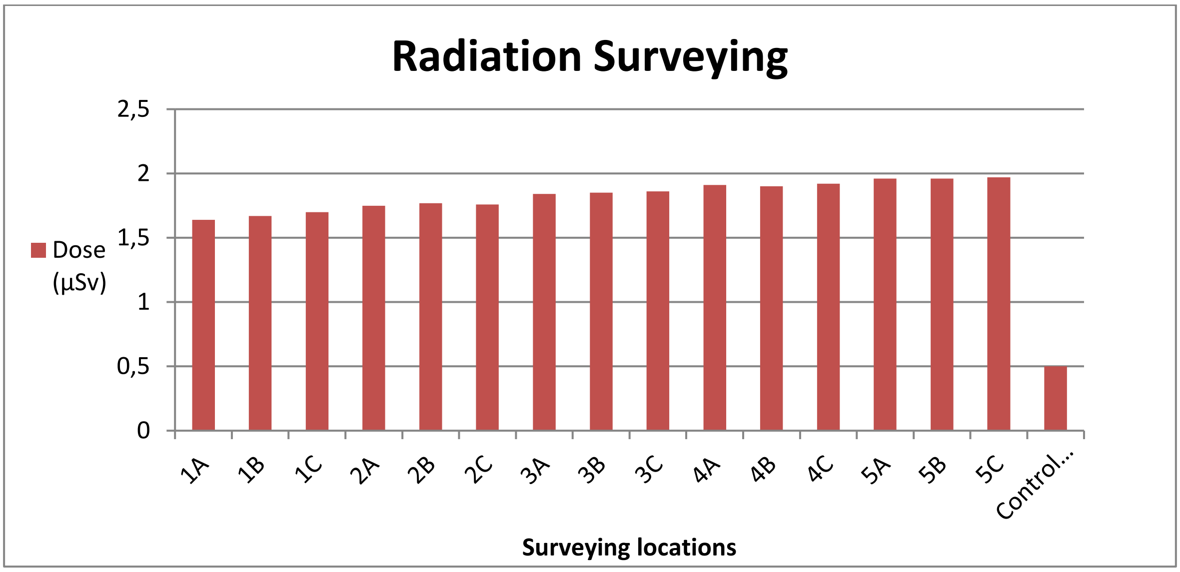


Figure 4.33: Radiation dose within the Zaaiplaats Tin Mine.

Radiation dose rate is erratic and does not have a general trend as shown in (Fig 4.34) below. The radiation dose rate had been converted to microsievent per year for comparison purposes (Appendix 16) and the mean, minimum, maximum values in microsievent per year (mSv/y) are 4.03 mSv/y, 0.96 mSv/y, and 11.65 mSv/y respectively.

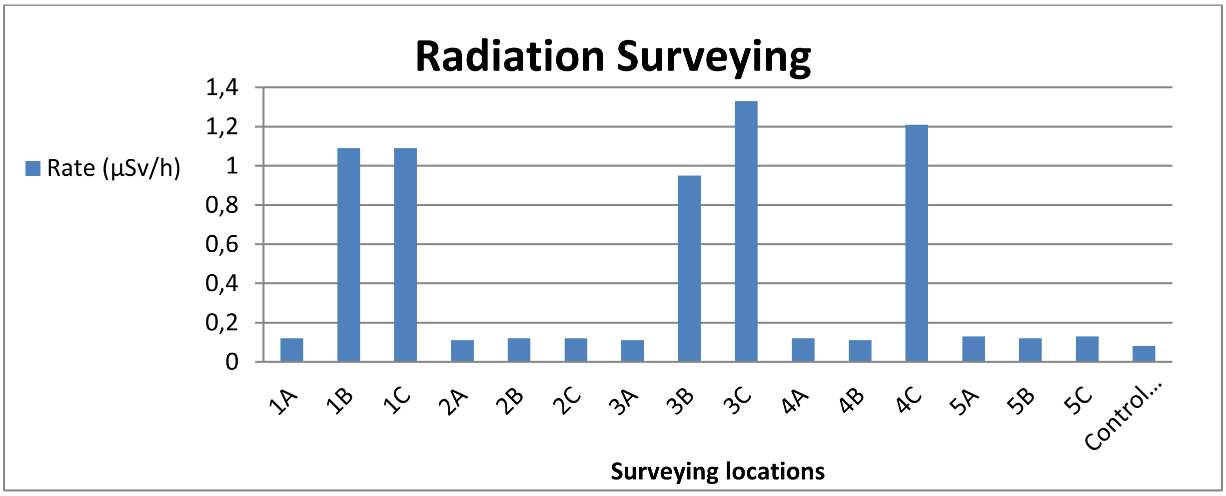


Figure 4.34: Radiation radiation dose rate within the Zaaiplaats Tin Mine.

In summary, radiation dose is increasing with distance from P1 to P5 which is from higher elevation to lower elevation. However, radiation dose rate is erratic.

5 CHAPTER 5: DISCUSSION, CONCLUSION AND RECOMMENDATIONS

The section discusses the conclusions of the study. The metals being investigated included Cr, Co, Cu, Zn, As, Mo, Cd, and Pb. Investigation of these metals was conducted along and across the river profile within the Zaaiplaats tin mine. Further analysis undertaken on tailings Heaps – A, B and C that are located at the bank of the river. Moreover, water and plants samples were also analysed from the mine.

5.1 Discussion

Lead had maximum values of up to 2842.4 ppm in tailings collected across and along the river profile and it was followed by copper and zinc with values of 885.05 ppm, and 740.7 ppm respectively. According to Hazrat *et al*. (2019), the standard mean values for Pb, Cu and Zn in surface soils worldwide averages to 32 ppm with a range of 10-67 ppm, 5 ppm to 70 ppm and 70 ppm with a range of 10-300 ppm respectively. However, the Zaaiplaats tin mine tailings have concentration values which are way above the unpolluted conditions soil conditions. The metal values from Zaaiplaats tin mine tailings are way too higher compared to metal values of some gold mine tailings that have been studied (Matshusa *et al*., 2012; Ogola *et al*., 2002). However, such high values of these metals implies that they may bear a great impact on the environment and human health. For example, higher metal levels of copper in tailings can accumulate in plants and negatively affect them. While zinc and lead can accumulate in the bodies of water and soil organisms which could lead to lead and zinc poisoning especially once they enter the food-chain.

The distribution pattern of these metals values is increasing with depth within Heap B and Heap C. Some metals had an erratic value but the general trend of metals is increasing with depth. In this study, there are higher values of lead, copper, zinc, and arsenic in tailings. On the other hand, Cd had a 0.1 ppm value which was constant throughout. These metals have the potential to be leached downwards into ground waters as well (Hazrat *et al.,* 2019).

Materials found within Heap B were fine to course while material collected from Heap A and C were course texture. River Profiles materials had a course texture at all profiles except for the last profile which is also at lower elevation. Higher concentration values are directly proportional to finer materials. The last profile had higher concentration values of metals and is being followed Heap B. The distribution pattern of these metals in Heap A is very irregular. This may be due to the gully erosion the tailings have undergone.

Tin mining is mainly associated with metals such as chrome, cobalt, zinc, arsenic, molybdenum, cadmium, barium, and vanadium (Ashraf *et al*., 2011). These metals at high concentration levels act as the major source of environmental contamination owed to their poisonousness and toxicity in the environment (Jaffar *et al*., 2017). Metals that are highly toxic even in minor quantity includes: zinc, selenium, arsenic nickel, cadmium, lead, cobalt, chromium, and mercury. Their presence in the environment results in several adverse impacts.

Metal toxicity on the environment is of absolute concern because the effect on the environment is difficult to eliminate. The current study established that the Zaaiplaats tailings contain metals with Pi greater than 3. For example, Pi for Pb was found to be 47.11 whereas Cu and As had Pi values of 29.95 and 26.89 respectively. These were above the standards. Consequently, there is a need for a clean-up.

Water collected along the river confirmed higher values of Pb and Cu assessed to the South African Water Quality Guidelines. These findings show that the Zaaiplaats tailings are highly polluted with toxic metals that are likely to impact negatively on the environment and human health. Analysis of water samples also confirmed higher values of Pb and Cu, apparently because of metal toxicity in tailings.

Cu, Cr and Pb have maximum values of 34.82 ppm, 15.72 ppm and 6.16 ppm respectively in plants collected during the dry season. There are also higher metal values of these metals in the roots compare to shoots. For example, Cu has a maximum value of 7.49 ppm and 32.9 ppm in the shoots and the roots respectively. Cobalt, however indicated lower values in the roots than in the shoots and it has lower values in the plants compared to other metals. Cobalt metal behaviour is contrary to that of Cu, Cr and Pb. There are no cobalt values in the tailings below the plants during dry season. However, there are concentration values of cobalt in the tailings during wet season which shows that cobalt is absorbed or there is movement of cobalt.

In a study conducted by Rashed, (2010), Cr, Co, and Cu metals were being absorbed and accumulated by the same type of a plant (*Aerva Javanica*) while lead was absorbed by the other type of a plant (*Acia Raddiena*). In this study *Equisetum ramosissimum* plant may be an absorber and an accumulator of Cr, Co, and Cu at different times but not of lead which showed lower values of BAF and TF in both dry and wet season. However, lead was also absorbed hence there was a higher concentration of it in plants roots. Cr was transferred effectively in dry season while cobalt was transferred effectively in wet season, and it is indicated by having higher concentration of these metals in the shoots corresponding to its roots. Accumulation of these metals imply that this plant had an excessive tolerance to these metals. Pb and Cr metals are not crucial for plants growth since they are not recognised to execute any physiological role in plants. Copper and cobalt are vital elements required for normal plant growth and metabolism, but when they are exceeding needed concentrations, they could constitute poisoning to specific plants (Abiya *et al*., 2018). The horse tail plant is a hyper-accumulator of these metals and can be used for their clean up as a remediation strategy paired with other remediation measures.

In the current study, radiation dose increased from higher elevation to low elevation. However, radiation dose rate was inconsistent and did not have a general trend. The radiation dose rate mean, minimum and maximum values in mSv/y were 4.03 mSv/y, 0.96 mSv/y, and 11.65 mSv/y respectively. The maximum value of radiation dose rate was greater than the United Nations Scientific Committee on the Effects of Atomic Radiation background radiation of 2.4 mSv/y to 10 mSv/y (UNSCEAR, 2000). However, there are areas of the world, such as parts of the Kerala state in India and the Pocos del Caldas plateau in Brazil, where levels of background radiation are up to 10 times higher than the average background level of 2.4 mSv/y but there are no detrimental health effects associated with this elevated radiation exposure that have been detected (UNSCEAR, 2000). The Zaaiplaats tin mine tailings pose no radiation threat to any of its surrounding fauna.

5.2 Conclusion

In this study the following conclusions were made:

- The higher values of chromium, cobalt, copper, zinc, arsenic, molybdenum, cadmium, and lead show that Zaaiplaats tin mine tailings have the potential to impact negatively on the environment and human health.

- The distribution pattern of metals along and across the river profile was increasing from higher elevation to lower elevation, while the distribution pattern of metals within the Heaps was found to be increasing with depth.
- Surface water had higher values of lead and copper compared to the standards that are stipulated by the South African Water Quality Guidelines and it is thus polluted
- The *Equisetum ramosissimum* plant from different locations at Zaaiplaats tin mine tailings had absorbed the metals within its roots during both dry and wet season. Equisetum ramosissimum is a hyper-accumulator of Cr and Cu during dry season and Co during wet season and can be used for both photostabilization and photoextraction of these metals.
- The radiation dose rates observed within the Zaaiplaats tin mine tailings are within the average background level of 2.4 mSv/y to 10 mSv/y and are of no threat.

5.3 Recommendations

The following recommendations were made:

- The study recommends environmental management plans for remediation and mitigation of the potential environmental impacts of Zaaiplaats tin mine tailings.
- The higher values of these toxic metals such chromium, cobalt, copper, zinc, arsenic, molybdenum, cadmium, and lead shows that Zaaiplaats tin mine tailings have the potential to pollute the environment, they require clean up.
- The study also recommends geotechnical studies for the alternative use of tailings from the Zaaiplaats tin mine.
- The study recommends the use of the *Equisetum ramosissimum* plant which is hyperaccumulater of Cr, Co, Cu and Pb as a strategy of rehabilitating the Zaaiplaats tailings.

REFERENCES

Abiya, S.E., Odiyi, B.O., Ologundudu, F.A., Akinnifesi, O.J. and Akadiri, S., **2018**, Assessment of Heavy Metal Pollution in a Gold Mining Site in Southwestern Nigeria. *J Genet Cell Biol,* Vol,1(2), pp 30-35.

Adiuku-Brown, M.E. and Ogezi, A.E., **1991**, Heavy Metal Pollution from Mining Practices: A Case Study of Zurak. *Journal of Mining and Geology*, Vol. 8 (1), pp. 71-77.

Ali, H., Khan, E, Sajad, M.A., **2013**, Phytoremediation of Heavy Metals - Concepts and applications. *Chemosphere,* Vol. 91 pp 869-881.

Aliyu, A.S., Mousseau, T.A., Ramli, A.T. and Bununu, Y.A., **2015**, Radioecological Impacts of Tin Mining. *Ambio*, Vol. 44, pp.778.

Alshaebi, F.Y., Yaacob, W.Z.W. and Samsuldin, A.R., **2009**, Sorption on Zero-valent Iron (ZVI) for Arsenic Removal. *European Journal of Scientific Research,* Vol 33(2), pp. 214-219.

Asati, A., Pichhode, M. and Nikhil, K., **2016**, Effect of Heavy Metals on Plants: An Overview. *International Journal of Application or Innovation in Engineering and Management,* Vol. 5(3), pp 56-66.

Ashraf, M.A., Maah, M.J. and Yusoff, I., **2011**, Heavy Metals Accumulation in Plants Growing in ex Tin Mining catchment. *International Journal of Environmental Science and Technology*, Vol. 8 (2), pp. 401-416.

Ashraf, M.A., Maah, M. J. and Yusoff, I., **2012**, Bioaccumulation of Heavy Metals in Fish Species Collected from Former Tin Mine Catchment. *International Journal of Environmental Research,* Vol. 6(1), pp. 209-218.

Asmarhansyah, R.B., Sanchez, P.B., Cruz, P.C.S. and Florence, L.M. ,**2017**, Land Suitability Evaluation of Abandoned Tin-mining Areas for Agricultural Development in Bangka Island, Indonesia. *Journal of Degraded and Mining Lands Management*, Vol. 4 (4) pp. 907-918.

Bartholomew, D.S., **1990**, Base Metal and Industrial Mineral Deposits of Zimbabwe Zimbabwe Geological Survey, Mineral Resources, Series 22, 157 p.

Bell, T., **2020**, The Properties, Production, and Applications of Tin. Availaible at: https://www.thebalance.com/metal-profile-tin-2340157 [Accessed 08 February 2020].

Black, H., **2005**, Getting the Lead out of Electronics. *Environmental Health Perspectives*, Vol. 113(10), pp. A682–A685.

Brime, C., **1985**, The Accuracy of X-ray Diffraction Method for Determining Mineral Mixtures. *Mineralogical Magazine.* Vol. 49, pp. 531-538.

Britannica, The Editors of Encyclopaedia. "tin". Encyclopedia Britannica, 1 June 2023, Available at: https://www.britannica.com/science/tin [Accessed 17 June 2023].

Brathwaite, R.L. and Rabone, S.D., **1985**, Heavy Metal Sulphide Deposits and Geochemical Surveys for Heavy Metals in New Zealand. *Journal of the Royal Society of New Zealand*, Vol. 15 (4), pp. 363-370.

Bunaciu, A.A., Udristiou, G. E. and Aboul-Enein, H.Y., **2015**, *X-Ray Diffraction: Instrumentation and Applications. Critical reviews in analytical chemistry / CRC. 45,* Available at: https://www.tandfonline.com/doi/full/1 [Accessed 23 May 2019].

Calvert, J. B., **2002**, *Tin*. Available at: mysite.du.edu/~jcalvert/phys/tin.htm#Intr [Accessed 08 February 2020].

Climate-Data.org., **2018**, *Climate Mokopane.* Available at: https://en.climate-data.org/location/953/ [Accessed 10 August 2018].

Chhabra, J., Grilli, E. and Pollak, P.,**1978**, The World Tin Economy: An Econometric Analysis, World Bank Staff Commodity Paper No.1.

Chibowski, S., **2000**, Studies of Radioactive Contaminations and Heavy Metal Contents in Vegetables and Fruit from Lublin, Poland. *Polish Journal of Environmental Studies,* Vol. 9 (4), pp. 249-253.

Coetzee, J., **1984**, A Geochemical and Petrographical Investigation of the Low-grade Tin Deposits in the Bobbejaankop Granite in the Zaaiplaats Tin mine, M.Sc. (Science), [Unpublished dissertation]: University of the Witwatersrand. Available at: http://wiredspace.wits.ac.za [Accessed 13 August 2018].

Coetzee, J., **1986**, The Lease granite – A Granophyric, Miarolitic Mineralized Granite at the Apical Region of a Tin-tungsten System, Transvaal. *Geological Society of South Africa*, Vol. 89, pp. 335-345.

Crocker, I. T., Eales, H. V. and Ehlers, D. L., **2001**, *The fluorite, Cassiterite and Sulphide Deposits Associated with the Acid Rocks of the Bushveld Complex*. Memoir of the Council for Geoscience, Pretoria, pp. 90-151.

Crock, J.G., Arbogast, B.F., Lamothe, P.J., **1999**, Laboratory methods for the analysis of environmental samples, In: Plumlee, G.S. and Logsdon, M.S. (eds) *The environmental geochemistry of mineral deposits. Part A: processes, techniques and health issues, Vol 6A*. Society of Economic Geologists, Littleton, pp. 265–287.

Dagless, J., **1984**, Manager, Union Tin Mine. Personal communication.

Davies, M.P. and Martin, T.E., **2000**, Upstream Constructed Tailings Dams – A Review of the Basics. In: Tailings and Mine Waste ’00. Balkema, Rotterdam, pp 3-15.

Diehl, E. and Sanhudo, C.E.D., **2004**, Ground-dwelling Ant Fauna of Sites with High levels of Copper. *Brazilian Journal of Biology*. Vol. 61(1) pp. 33-39.

Demchak, J., Skousen, J., McDonald, L.M., **2004**, Longevity of Acid Discharges from Underground Mines Located Above Regional Water table. *Journal of Environmental Quality*, Vol. 33, pp. 656 - 668.

Department of Water Affairs and Forestry, 1996.South African Water Quality Guidelines. Volume 7: Aquatic Ecosystems.

Dewaele, S., De Clerq, F., Muchez, P., Schneider, J., Burgess, R., Boyce, A. and Fernandez-Alonso, M., **2010**, Geology of the Cassiterite Mineralisation in the Rutongo area, Rwanda (Central Africa): Current State of Knowledge. *Geologica Belgica*, Vol.13 (1-2), pp. 91-112.

Dewaele, S., Henjes-Kunst, F.,Melcher, F., Sitnikova, M., Burgess, R., Gerdes, A., Fernandez-Alonso, M., De Clerq, F., Muchez, P. and Lehmann, B., **2011**, Late

Neoproterozoic Overprinting of the Cassiterite and Columbite-tantalite Bearing Gegmatites of the Gatumba area, Rwanda (Central Africa). *Journal of African Earth Sciences*, Vol. 61, pp.10-26.

Dewaele, S, Muchez, Ph., Burgess, R. and Boyce, A., **2015**, Geological Setting and Timing of the Cassiterite Vein Type Mineralization of the Kalima area, Maniema, Democratic Republic of Congo. *Journal of African Earth Sciences*, Vol.112, pp.199-212.

Dolenec, T., Serafimovski, T., Tasev, G., Dobnikar, M., Dolenec, M., and Rogan, N., **2007**, Major and Trace Elements in Paddy Soil Contaminated by Pb-Zn Mining: A Case Study of Kocani Field, Macedonia. *Environ Geochem Health*, Vol. 29, pp.21-32.

Du Toit, M.C. and Pringle, I.C., **1998**, Tin. In: Wilson, M.G.C. and Anhaeusser, C.R., Eds, *The mineral resources of South Africa: Handbook*, Council for Geosciences, pp. 613-620.

Dutrow, B.L and Clark, C.M., **2019**, *Geochemical Instrumentation and Analysis, X-ray Powder Diffraction (XRD).* Available at: https://serc.carleton.edu/research_educa [Accessed 23 May 2019].

El-Amier, Y.A., Alghanem, S.M., and Alzuaibr, F.M, **2017,** Bioaccumulation and Translocation of Heavy Metals from Coastal Soil by Wild Halophytes*. American Journal of Environmental Protection*, Vol. 5(2), pp. 52-60.

Engel, J., **2012**, *History of Tailings Storage Methods*. Available at http://www.tailings.info [Accessed 22 May 2019].

Eunice, E.U., Blessing, D.C. and Fabian, O., **2013**, XRD Characterization of Sand Deposit in River Niger (South Eastern Nigeria). *Journal of Applied Chemistry*, Vol. 3(3), pp. 287-293.

EL Hadi, H., **2015**, Spatial Distribution of Soil Heavy Metals in the Zaida Mine (Morocco) Based on Geostatistical Methods. *International Journal of Advanced Research*, Vol. 3, pp. 337-349.

Environment Australia., **1995**, Tailings Containment. Best Practice Environmental Management in Mining. Environment Australia, Canberra.

Environmental Systems Research Institute (ESRI). **2018**, ArcGIS Release 10.1. Redlands, CA.

Falcon, L.M., **1985**, Tin in South Africa. *Journal of South African Institute of Mining and Metallurgy*, Vol. 85, pp.333-345.

Garside, M., **2019**, Price for Refined Tin from 2014 to 2030, Available at: https://www.statista.com/statistics/469855/tin-price-forecast/ [Accessed 13 March 2020].

Garrett, N. and Mitchell, H., **2009**, *Trading Conflict for Development. Utilising the Trade in Minerals from Eastern Democratic Republic of the Congo for Development, Resource Consulting Services*. Available at: http://www.lse.ac.uk/internationa [Accessed 20 April 2019].

Gautam, N., Gupta R., Mishra, A and Singh, R., **2011**, Heavy Metals and Living Systems: An overview. *Indian J Pharma col*. Vol. 43(3), pp. 246-253.

Groves, D.I. and McCarthy, T.S., **1987**, Fractional Crystallization and the Origin of Tin deposits in Granitoids. *Journal of Mineralium Deposita*, Vol. 13, pp. 11-26.

Guazhang Z, Leping Y, Zhiper L. I and Chao C., **2005**, Assessment of Heavy Metals pollution of Agricultural Soil in Guazhang District. *Journal of Geographical Sciences* Vol. 16 pp 105-113.

Harmer, R. E. and Armstrong, R. A., **2000**, Duration of Bushveld Complex (seno lato) magmatism: Constraints from New SHRIMP Zircon Chronology. In: *Workshop on the Bushveld Complex*. Gethane Lodge, Burgersfort, South Africa.

Harvey, D., **2018,** Atomic Absorption Spectroscopy. Available at: https://chem.libretexts.org [Accessed 23 October 2018].

Hassinger, B.W., **1997**, Erosion. In: Marcus JJ (ed) *Mining Environmental Handbook: Effects of Mining on the Environment and American Environmental Controls on Mining*. Imperial College Press, London, pp 136–140.

Hazrat, A., Ezzat, K., and Ikram I., **2019**, Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. *Journal of Chemistry*, Volume 2019, Article ID 6730305, 14 pages https://doi.org/10.1155/2019/6730305.

Hitch, M., Ballantyne, S.M., and Hindle, S.R., **2010**, Revaluing Mine Waste Rock for Carbon Capture and Storage. *International Journal of Mining, Reclamation and Environment,* Vol. 24(1), pp 64-79.

Holleman, Arnold F., Wiberg, E., Wiberg, N.,**1985**, Tin. Lehrbuch der Anorganischen Chemie (in German) (91–100 ed.). Walter de Gruyter. pp. 793–800.

Hudson, T.L. Fox, F.D. and Plumlee, G.S.,**1999**, *Metal Mining and the Environment, AGI Environmental Awareness Series 3*, American Geological Institute, Alexandria, Virginia, pp. 7.

Ibeanu. I.G.E., **2003**, Tin Mining and Processing in Nigeria: Cause for Concern?. *Journal of Environmental Radioactivity*, Vol. 64, pp. 59–66.

IAEA (International Atomic Energy Agency), **2019**, *Radiation in Everyday Life*. Available at: https://www.iaea.org/Publications/Factsheets/English/radlife [Accessed 20 May 2019].

International Tin Association, **2021**, Mining Regions. Available at: https://www.internationaltin.org/market-analysis/# [Accessed 05 August 2021].

Jaffar, S.T.A., Chen, L., and Younas, H., **2007**, Heavy Metals Pollution Assessment in Correlation with Magnetic Susceptibility in Topsoil of Shanghai. *Environ Earth Sci*. Vol. 76, pp. 277.

Jamieson, H. E., **2011**, Geochemistry and Mineralogy of Solid Mine Waste: Essential Knowledge for Predicting Environmental Impact. *Elements*, Vol. 7 (6), pp. 381–386.

Isam S. M. M., **2019**, *Environmental Radiation: Natural Radioactivity Monitoring.* Available at: https://www.intechopen.com/online-first/environmental-radiation [Accessed 20 May 2019].

Järup, L., **2003**, Hazards of Heavy Metal Contamination. *British Medical Bulletin*, Vol. 68(1), pp. 167-182.

Jaishankar, M, Mathew, B.B, Shah, M.S. and Gowda, K.R.S., **2014**, Biosorption of Few Heavy Metal Ions Using Agricultural Wastes. *Journal of Environment Pollution and Human Health,* Vol. 2(1), pp. 1-6.

Kabata-Pendias, A., **2011**, Trace Elements of Soils and Plants Boca Raton: CRC press, Taylor and Francis Group, (4th ed) pp. 28–534.

Kamunda, C, Mathuthu, M. and Madhuku, M., **2016,** An Assessment of Radiological Hazards from Gold Mine Tailings in the Province of Gauteng in South Africa. *International Journal of Environmental Research and Public Health*, Vol.13, pp. 138.

Karishna, A.K and Govil P.K., **2005**, Heavy Metal Distribution and Contamination in soils of Thane-Belapur Industrial Development Area, Mumbai, Western India. *Jounal of Environmental Geology*, Vol. 47, pp. 1054-1061.

Kavehei, A., Hose, G. C., and Gore, D. B., **2020**, *History of Environmental Contamination at Sunny Corner Ag-Pb-Zn Mine, Eastern Australia: A Meta-analysis Approach. Environmental Pollution,* 2020.115742. *115742.* doi:10.1016/jenvpol.

Khan, S., Cao, Q., Zheng, Y. M., Huang, Y. Z. and Zhu. Y.G., **2008**, Health Risks of Heavy Metals in Contaminated Soils and Food Crops Irrigated with Wastewater in Beijing, China. *Journal of Environmental Pollution*, Vol. 152 (3), pp. 686–692.

Kinnaird, J. A., Hutchinson, D., Schurmann, L., Nex, P.A.M., and de Lange, R., **2005**, Petrology and Mineralisation of the Southern Platreef: Northern Limb of the Bushveld Complex. *Mineralium Deposita*, Vol. 40, pp. 576-597.

Kinnaird J.A., Kruger F.J. and Cawthorn R.G., **2004**, Rb-Sr and Nd-Sm Isotopes in Fluorite Related to the Granites of the Bushveld Complex. *South African Journal of Geology*, Vol.107, pp. 413-430.

Kinnaird, J, Nex, P and Milani, L., **2016**, Tin in Africa. *Episodes Journal of International Geoscience,* Vol. *39* (2), pp. 362-380.

Kleemann, G.J., Twist, D., **1989**, The Compositionally Zoned Sheet-like Granite Pluton of the Bushveld Complex: Evidence Bearing on the Nature of A-type Magmatism. *Journal of Petroleum Science and Engineering*, Vol. 30 (6), pp. 1383-1414.

Kleinmann, R.L.P.,**1989**, Acid mine drainage in the United States: Controlling the Impact on Streams and Rivers. In: 4th world congress on the conservation of built and natural environments. University of Toronto, pp 1–10.

Kossoff, D, Dubbin, W.E., Alfredsson, M., Edwards, S.J., Macklin, M.G., Hudson-Edwards, K.A., **2014**, Mine Tailings Dams: Characteristics, Failure, Environmental Impacts, and Remediation. *Journal of Applied Geochemistry*, Vol. 51, pp. 229–245.

Kruger, J.F., **1990**, The stratigraphy of the Bushveld Complex: A Reappraisal and the Relocation of the Main Zone boundaries. *South African Journal of Geology*, Vol.93, pp. 376-381.

Kříbek, B, Sinkamba, P, Maseka, K.K, Nyambe,K. I, Mapani, L.B, Kayula, W.G. and Čadská, R., **2011**, *Mining and the Environment in Africa*, Proceedings of the Inaugural Workshop IGCP/SIDA No. 594, KITWE/ZAMBIA, October 17th -18th, 2011.

Lambert, D.C., McDonough, K.M., Dzombak, D.A., **2004**, Long-term Changes in Quality of Discharge Water from Abandoned Coal Mines in Uniontown Syncline, Fayette County, PA, USA, *Water Research*. Vol. 38, pp. 277-288.

Labuschagne, L.S., **2004**, *Evolution of the Ore-Forming Fluids in the Rooiberg Tin Field, South Africa*, Council for Geoscience Memoir 96, pp.126.

Lewis, L., Hossain, M. and Rao, B.R., **2020**, Physicochemical Assessment of a Waste Rock Dump in the Hidden Valley Gold Mine: A Case Study for Bioremediation in Papua New Guinea. *Environmental Earth Sciences*, Vol. 79(5), pp.1-11.

Lishman, K.L., **2009**, *The Acid Mine Drainage Potential of the Platreef, Northern Limb of the Bushveld Complex, South Africa.* M.Sc. (Science) [Unpublished dissertation]: University of the Witwatersrand. Available at: http://wiredspace.wits.ac.za [Accessed 28 May 2018].

London Market Exchange, **2020**, LME TIN, Available at: https://www.lme.com [Accessed 3 March 2020].

Lottermoser, B., **2013**, Mine Wastes: Characterization, Treatment and Environmental Impacts, Springer Berlin Heidelberg, p.279.

Lynn, M., Hall, M. and Liebenberg, L., **2011**, *Mokopane Tin Project, South Africa*. Available at: http://www.bushveldminerals.com [Accessed 02 April 2019].

Mahar, A., Wang, P, Ali, A., Awasthi, M.K., Lahori, A.H., Wang, Q.,Li, R and Zhang, Z., **2016**, Challenges and Opportunities in the Phytoremediation of Heavy Metals Contaminated Soils: A Review. *Ecotoxicology and Environmental Safety,* Vol.126 pp 111-121.

Martin, H.J., **1964**, The Bikita tinfield. Southern Rhodesian Geological Survey Bulletin, 58: 114-131.

Matshusa, K, Ogola, J.S. and Maas, K., **2012**, *Dispersion of Metals at Louis Moore Gold Tailings Dam*, Limpopo province, South Africa; Proceedings of the International Mine Water Association Symposium; Bunbury, Australia, pp. 334A–334E.

Mahesh, B, Baburao, C., Bhargavi, S., Sreekanth, N. and Sreenu, D., **2012**, Inductively Coupled Plasma Mass Spectrometry (ICP-MS). *International Journal of Research In Pharmacy And Chemistry*. Vol. 2(3), pp. 2231-2781.

Makweba, M.M. and Ndonde, P.B., **1996**, *The mineral Sector and the National Environmental Policy.* In: Mwandosya, M.J, *et al,* editors, Proceedings of the Workshop on the National Environmental Policy for Tanzania (Dar es Salaam, Tanzania), 1994, pp.164-73.

Martin, H.J., **1964**, The Bikita Tinfield. *Journal of Southern Rhodesian Geological Survey Bulletin*, Vol. 58, pp.114-131.

Mattina MJI, Lannucci-Berger W, Musante C, White JC., **2003**, Concurrent plant uptake of heavy metals and persistent organic pollutants from soil. *Environmental Pollution*, Vol.124, pp.375-378.

McCathy, T.S., **2011**, The Impact of Acid Mine Drainage in South Africa. *South African Journal of Sciences,* Vol. 107 (5-6). pp.1-7.

Mcnaught, N. J, Pollard, P.J, Grove, D.J. and Taylor, R.G., **1993**, A Long-Lived Hydrothermal System in Bushveld Granites at the Zaaiplaats Tin Mine: Lead Isotope Evidence, *Journal of Economic Geology,* Vol. 88, pp. 27-43.

MEND.,**1994**, *Review of Waste Rock Sampling Techniques.* Mine Environment Neutral Drainage (MEND) Program Report 4.5.1. Prepared by SENES Consultants Limited, Golder Associe Ltee, and Laval University.

Meybeck, M. and Helmer, R., **1989**, The Quality of Rivers: from Pristine Stage to Global Pollution. Palaeogeogr., Palaeoclimatol, Palaeoecol. (Global Planet. Change Sect.), 75, pp. 283-309.

Mindat.org., **2019**, *Zaaiplaats Mine, Zaaiplaats Tin Field, Mokopane (Potgietersrus), Mogalakwena, Waterberg District, Limpopo, South Africa*. Available at: https://www.mindat.org/loc-26749.html [Accessed 02 April 2019).

Mininingatlas, **2018**, *Zaaiplaats Information.* Available at: https://mining-atlacs.com/operation/Zaaiplaats-Tin-Mine.php [Accessed 27 August 2018].

Mongabay, **2020**, *Price of Tin, (1980-2010) Price Chart*. Available at: https://data.mongabay.com/commodities/ [Accessed 13 March 2020]

Morais, S, Costa, F.G. and Pereira, M. L., **2012**, Heavy Metals and Human Health, in Environmental health – Emerging Issues and Practice, Oosthuizen, pp. 227-246.

Morrow, H., **2010**, *Cadmium and Cadmium Alloys*, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons, pp. 1-36.

Muindisi, A., **2012**, *Modelling and Evaluation of the Tin Resource on two farms on the Potgietersrus Limb of the Bushveld Complex,* M.Sc. (Geology) [Unpublished dissertation]: University of the Witwatersrand. Available at: https://core.ac.uk/download/pdf/39671169.pdf [Accessed 03 March 2019].

Munyangane L.P., **2012**, *Potentially Harmfully Heavy metals (PHTEs) in the Greater Giyani, Limpopo Province, South Africa: Possible Health Implications*. M.Sc.

(Geology) [Unpublished dissertation]: University of Johannesburg. Available at: https://ujdigispace.uj.ac.za/ [Accessed 28 May 2018].

Murciegoa, A., Álvarez-Ayuso, E., Pelliteroa, E., Rodríguezc, M. A., García-Sánchez, A., Tamayo, A., Rubio, J., Rubio, F and Rubin, J., **2011**, Study of Arsenopyrite Weathering Products in Mine Wastes from Abandoned Tungsten and Tin Exploitations. *Journal of Hazardous Materials,* Vol.186, pp. 590-601.

Mustafa, G. and Komatsu, S., **2016**, Toxicity of Heavy Metals and Metal-Containing Nanoparticles on Plants, *Biochimica et Biophysica Acta 1864,* pp 932–944.

Nassiri, O., Rhoujjati, A. and EL Hachimi, M.L., **2021**, Contamination, Sources and Environmental Risk Assessment of Heavy Metals in Water, Sediment and Soil around an Abandoned Pb mine Site in North East Morocco. *Journal of Environmental Earth Sciences,* Vol. 80, pp 96. https://doi.org/10.1007/s12665-021-09387-y.

Ndace, J.S. and Danladi, M.H., **2012**, Impacts of Derived Tin Mining Activities on Landuse/Landcover in Bukuru, Plateau State, Nigeria. *Journal of Sustainable Development,* Vol. 5, pp 90-100.

Nengovhela, A.C, Yibas, B. and Ogola, J.S., **2007**, Characterisation of Gold Tailings Dams of the Witwatersrand Basin with Reference to their Acid Mine Drainage Potential, Johannesburg, South Africa. Water SA. 32. 10.4314/wsa.v32i4.5290.

Netshitungulwana, R. and Yibas, B., **2012**, *Investigations of the Stream Sediments Geochemistry for the Metal Pollution Sources of the Olifants River Catchment,* Technical Report, Council for Geoscience, unpublished report.

Niyogi, D.K., William M., Lewis Jr., McKnight, D.M., **2002**, Effects of Stress from Mine Drainage on Diversity, Biomass, and Function of Primary Producers in Mountain Stream. *Ecosystems*, Vol. 5, pp. 554-567.

Nuss, P and Eckelman, M.J., **2014**, Life Cycle Assessments of Metals: A Scientific Syntheis. *PLoS ONE*. Vol. 9, No. 7, pp. 10-29.

Nurtjahya, E., Franklin, J., Agustina., U., and Agustina, F., **2017**, The Impact of Tin Mining in Bangka Belitung and its Reclamation Studies, MATEC Web Conference. 101 04010 (2017) DOI: 10.1051/matecconf/201710104010.

Ogola, J.S, Mitullah, W.V. and Omulo, M.A., **2002**, Impact of Gold Mining on the Environment and Human Health: A Case Study in the Migori Gold Belt, Kenya. *Journal of Environmental Geochemistry and Health*, Vol. 24, pp.141-158.

Ogola, J.S. and Sebola, A.M., **2010**, *Investigation of Heavy Metals Dispersion Around the Messina Copper Mine Tailings Dam*, South Africa, pp. 888-893.

Omotehinse, A. O., and Ako, B. D., **2019**, The environmental implications of the exploration and exploitation of solid minerals in Nigeria with a special focus on Tin in Jos and Coal in Enugu. *Journal of Sustainable Mining*, Vol.18(1), pp.18-24. doi:10.1016/j.jsm.2018.12.001.

10.1016/j.jsm.2018.12.001

Oxley-oxland, G., and White, H., **1974**, Ancient metallurgical practice in the Rooiberg area. *J. S. Afr. Inst. Min. Metall.,* Vol. 74. pp. 269-270.

Pierzynski, G. M., Sims, J. T and Vance, G. F., **2000**, Soils and Environmental Quality, CRC Press, London, UK, 2nd edition, 536 pp.

Pohl, W. and Gunther, M.A., **1990**, The Origin of Kibaran (Late Midproterozoic) Tin, Tungsten and Gold Quartz Vein Deposits in Central Africa: A Fluid Inclusion Study. *Journal of Mineralium Deposita*, Vol. 26, pp. 51-59.

Pollard P.J., Andrews A.S. and Taylor R.G., **1991a**, Fluid inclusion and stable isotope evidence for interaction between granites and magmatic hydrothermal fluids during formation of disseminated and pipe-style mineralisation at the Zaaiplaats tin mine. *Economic Geology*, Vol. 86, pp. 121-141.

Pollard, P.J. and Taylor, R.G., **1986**, Progressive Evolution of Alteration and Tin Mineralization: Controls by Interstitial Permeability and Fracture- Related Tapping of Magmatic Fluid Reservoirs in Tin Granites, *Journal of Economic Geology*, Vol. 81, pp 1795-80.

Pollard, P. J., Taylor, R. G., and Tate, N.M., **1989**, Textural Evidence or Quartz and Feldspard Solution as a Mechanism of Formation or Magg Spipe, Zaaiplaats Tin Mine, South Africa, *Journal of Mineralium Deposita,* Vol. 24, pp. 210-218.

Pollard P.J., Taylor R.G., Taylor R.P. and Groves D.I., **1991b**, Petrographic and geochemical evolution of pervasively altered Bushveld Granites at the Zaaiplaats Tin Mine. *Economic Geology*, Vol. 86, pp.1401-1433.

Mosby's Medical Dictionary, **2009**, Radioactive Elements. Available at https://medical-dictionary.thefreedictionary.com [Accessed 05 May 2019].

Ranđelović, D., Mihailović, N., and Jovanović, S., **2019**, Potential of Equisetum ramosissimum Desf. for remediation of antimony flotation tailings: a case study. *International Journal of Phytoremediation, 1-7.* doi:10.1080/15226514.2018.1556590

Rashed, N.M., **2010**, Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt. *Journal of Hazardous Materials*, Vol.178, pp 739–746.

Research and Development., **2018**, Atomic Absorption Spectrometer, Available at: https://www.iitk.ac.in/dordold/index.php?option=com [Accessed on 30 August 2018].

Rezapour, S., Atashpaz, B., Moghaddam, S. S., Kalavrouziotis, I. K., & Damalas, C. A., **2019**, Cadmium Accumulation, Translocation Factor, and Health Risk Potential in a Wastewater-irrigated Soil-wheat (Triticum aestivum L.) system*. Chemosphere.* doi:10.1016/j.chemosphere.2019.05.095.

Robert, P., **2006**, Pipe Metal. New York: Garland, p. 411.

Ryan, P.A., **1991**, Environmental Effects of Sediment on New Zealand Stream: A Review, New Zealand. *Journal of Marine and Freshwater Research*, Vol. 25, pp.26-41.

SAexplorer, **2018**, Potgieterus Climate, Available at: http://www.saexplorer.co.za [Accessed 10 August 2018].

SACS, **1980**, Bushveld Complex, In: Kent, .L. E. (Editor), *The Stratigraphy of South Africa, Part I, Lithostratigraphy of the Republic of South Africa, South West*

Africa/Namibia and the Republics of Bophuthatswana, Transkei and Venda. Geological Survey of South Africa, pp. 223-231.

Schaffner, J.H., **1930**, Geographic Distribution of the Species of Equisetum in Relation to their Phylogeny. *American Fern Journal,* Vol. 20(3), pp. 89-106.

Schouwstra, R. P., Kinloch, E. D. and Lee, C.A., **2000**, A Short Geological Review of the Bushveld Complex. *Journal of Platinum Metals Review*, Vol. 44(1), pp. 33-39.

Shrivastava, V.S., **2009**, X-ray Diffraction and Mineralogical Study of Soil: A Review. *Journal of Applied Chemistry and Resources*, Vol. 9, pp. 41-51.

Simate, G.S. and Ndlovu, S., **2014**, Acid Mine Drainage: Challenges and Opportunities. *Journal of Environmental Chemical Engineering.* Vol. 2, pp. 1785-1803.

Singh, P.K. and Singh, R.S., **2016**, Environmental and Social Impacts of Mining and their Mitigation, In *National Seminar ESIMM-2016*, pp. 17- 29.

Srivastava, J., **2012**, *Environmental Contamination*, IntechOpen, p. 234.

Srivastava, S. and Goyal, P., **2010**, *Novel Biomaterials: Decontamination of Toxic Metals from Wastewater*. Springer-Verlag. ISBN 978-3-642-11329-1.

Skoog, D.A., Holler, F.J. and Crouch, S.R., **2007**, *Principles of Instrumental Analysis*, Thomson Higher Education, 1039 p.

Singo, N. K., **2013**, An Assessment of Heavy Metal Pollution Near an old Copper Mine Dump in Musina, South Africa, M.Sc.(Science), [Unpublished dissertation] University of South Africa. Available at: http://wiredspace.wits.ac.za [Accessed 13 August 2018].

Siyavula, **2018**, Available at: https://www.siyavula.com/read/science/grade-10-lifesciences/biosphere-to-ecosystems/08-biosphere-to [Accessed 30 August 2018].

Steinhauser, G., Adlassnig, W., Lendl, T., Peroutka, M., Weidinger, M., Lichtscheidl, I.K., Bichler, M., **2009**, Metalloid Contaminated Microhabital and their Biodiversity at a Former Antimony Mining Site in Schlainng, Austria. *Open Environmental Sciences*, Vol. 3, pp. 26-41.

Strauss, C. A., **1954**, The Geology and Mineral Deposits of the Potgietersrust Tin-fields. *Journal of Geological Survey of Southern Africa*. Vol. 46, pp. 26-30.

Sutphin, David M.; Sabin, Andrew E.; Reed, Bruce L., **1992**, Tin – International Strategic Minerals Inventory Summary Report, pp.9.

Szuman, K., and Lall, N., **2020**, Equisetum ramosissimum. Underexplored Medicinal Plants from Sub-Saharan Africa, pp 93-98*.* doi:10.1016/b978-0-12-816814-1.00013-2.

Tauli-Corpuz, V., **1997**, *The Globalisation of Mining and its Impact and Challenges for Women*, Available at: https://www.twn.my/title/mining-cn.ht [Accessed 25 May 2018].

Tayebi-Khorami, M., Edraki, M., Corder, G. and Go lev, A., **2019**. Re-Thinking Mining Waste through an Integrative Approach Led by Circular Economy Aspirations, *Minerals*, Vol. 9(5), p. 286.

Taylor S. R. and McLennan S. M., **1985**, The Continental Crust: Its Composition and Evolution. Blackwell, Oxford.

Taylor S. R., and McLennan S. M., **1995**, The Geochemical Evolution of the Continental Crust. *Rev. Geophys*. Vol.33, pp. 241-265.

Taylor, R.G. and Pollard, P.J., **1988**, Pervasive Hydrothermal Alteration in Tin-bearing Granites and Implications for the Evolution of Ore Bearing Magmatic Fluids, In: Taylor, R.P. and Strong, D.E. (eds.), *Recent Advances in the Geology of Granite-related Mineral Deposits.* C.I.M. Spec. Vol. 39, pp. 86-95.

The Plant List. **2013,** Version 1.1. Available at: http://www.theplantlist.org/ http://www.theplantlist.org/ [Accessed 01 June 2021].

Tudi, M., Ruan, H. D., Yu, Y., Wang, L., Wei, B., Tong, S.,Yang, L., **2020**, Bioaccumulation and Translocation of Trace Elements in Soil-irrigation Water-wheat in Arid Agricultural Areas of Xin Jiang, China*. Ecotoxicology.*doi:10.1007/s10646-020-02267-4

United Nations, **1996**, Environmental and Safety Incidents Concerning Tailings dams at Mines, United Nations Environment Programme, Paris.

UNEP, **2000**, *Industry and environment, Mining and Sustainable Development,* Available at: http://www.uneptie.org/vol20no4 [Accessed 25 May 2018].

UNSCEAR (United Nations Scientific Committee on the Effects of Atomic Radiation), **2000**, Sources and Effects of Ionizing Radiation. Report to the General Assembly of the United Nations with Scientific Annexes. United Nations sales publication E.00.IX.3, New York.

USGS, **2013**, Minerals Yearbook, USGS, US Department of the Interior.

USGS, **2015**, Mineral Commodity Summaries, USGS, US Department of the Interior.

Vare, L.L., Baker, M.C., Howe, J.A., Levin, L.A., Neira, C., Ramirez-Llodra, E.Z., Reichelt-Brushett, A., Rowden, A.A., Shimmield, T.M., Simpson, S.L. and Soto. E.H., **2018**, Scientific Considerations for the Assessment and Management of Mine Tailings Disposal in the Deep Sea. *Journal in Frontiers in Marine Sciences,* Vol.5 (7), pp. 1-13.

Von Knorring, O. and Fadipe, A., **1981**, Niobium and tantalum minerals, Communications of the Geological Survey, Southwest Africa and Namibia, 1, pp. 85-88.

Witley, J.C. and Leighton, R.G., **2015**, NI 43-101 Technical Report Mineral Resource Estimate, Bisie Tin Project, North Kivu Province, Democratic Republic of Congo. MSA Group, pp. 178.

WHO (World Health Organization), **2019**, Ionization radiation. Available at https://www.who.int/ionizing_radiation/env/en/ [Accessed 20 May 2019].

Woodford, C., **2019**, Tin. Available at: https://www.explainthatstuff.com/tin.html [Accessed 08 February 2020].

World Weather and Climate information, **2018**, Climate Mokopane. Available at: https://weather-and-climate.com/average-monthly-Rainfall-Temperature-Sunshine,mokopane-limpopo-za,South-Africa [Accessed 13 August 2018].

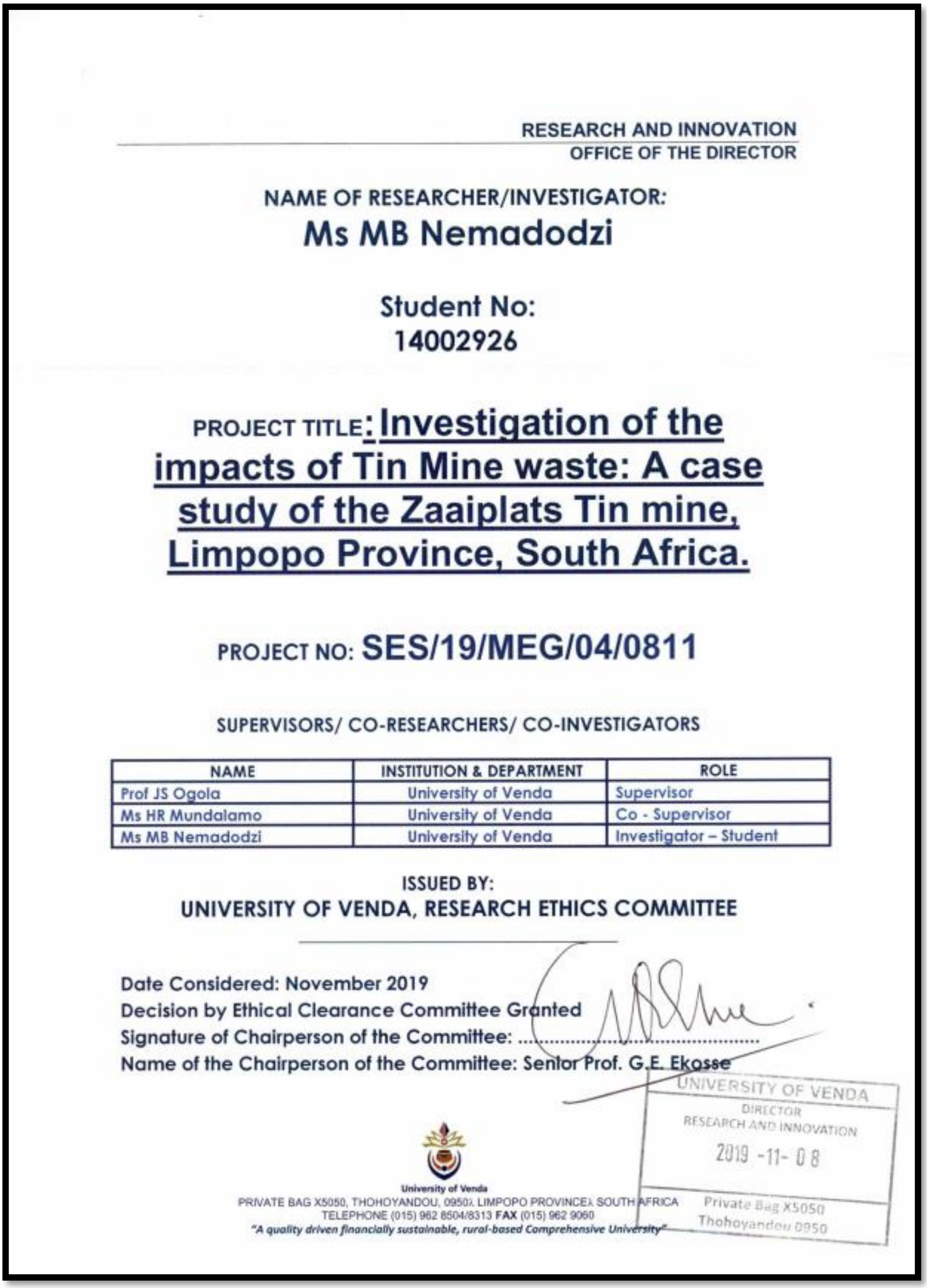
Zhang, C., Wang, X., Jian, S., Zhou, M, Li, F., Bi, X., Xie, S., Liu, J., **2021**, Heavy metal pollution caused by cyanide gold leaching: a case study of gold tailings in central

China. *Journal of Environmental Science and Pollution Research*. https://doi.org/10.1007/s11356-021-12728-w.

.

APPENDICES

Appendix 1: Ethical Clearance Certificate



RESEARCH AND INNOVATION
OFFICE OF THE DIRECTOR

NAME OF RESEARCHER/INVESTIGATOR:
Ms MB Nemadodzi

Student No:
14002926

PROJECT TITLE: **Investigation of the impacts of Tin Mine waste: A case study of the Zaaiplats Tin mine, Limpopo Province, South Africa.**

PROJECT NO: **SES/19/MEG/04/0811**

SUPERVISORS/ CO-RESEARCHERS/ CO-INVESTIGATORS

NAME	INSTITUTION & DEPARTMENT	ROLE
Prof JS Ogola	University of Venda	Supervisor
Ms HR Mundalamo	University of Venda	Co - Supervisor
Ms MB Nemadodzi	University of Venda	Investigator – Student

ISSUED BY:
UNIVERSITY OF VENDA, RESEARCH ETHICS COMMITTEE

Date Considered: November 2019
Decision by Ethical Clearance Committee Granted
Signature of Chairperson of the Committee: ....
Name of the Chairperson of the Committee: Senior Prof. G.E. Ekosse

UNIVERSITY OF VENDA
DIRECTOR
RESEARCH AND INNOVATION
2019 -11- 08
Private Bag X5050
Thohoyandou 0950

University of Venda
PRIVATE BAG X5050, THOHOYANDOU, 0950λ LIMPOPO PROVINCEλ SOUTH AFRICA
TELEPHONE (015) 962 8504/8313 **FAX** (015) 962 9060
"A quality driven financially sustainable, rural-based Comprehensive University"

Appendix 2: Coordinates of samples collected from the river profiles

Sample ID	**Longitude**	**Latitude**	**Elevation (m)**
P1S1	24^{0} 02' 57,6" S	28^{0}45'15.8" E	1157
P1S2	24^{0}2'58,5" S	28^{0}45'16" E	1156
P1S3	24° 2'52.24"S	28°45'51.10"E	1156
P2S1	24º 2’ 58.7” S	28º 45’ 32.9” E	1128
P2S2	24º 02’ 57.2” S	28º 45’ 32,6” E	1130
P2S3	24º 02’ 55,7” S	28º 45’ 32,3” E	1136
P3S1	24º 02’ 47.2” S	28º 46’ 08.1” E	1088
P3S2	24º 02’ 52.1” S	28º 46’ 09.7” E	1089
P3S3	24º 02’ 54.3” S	28º 46’ 10,1” E	1089
P4S1	24º 02’ 51,60” S	28º 46’ 6.81” E	1105
P4S2	24º 02’ 52,83” S	28º 46’ 6.46” E	1106
P4S3	24º 02’ 50,08” S	28º 46’ 6.38” E	1105
P5S1	24º 02’ 42,87” S	28º 46’ 22,23” E	1079
P5S2	24º 02’ 46,64” S	28º 46’ 22,99” E	1077
P5S3	24º 02’ 49,63” S	28º 46’ 23.67” E	1078

Appendix 3: Mean elevation values for river profiles

Sample ID	Mean elevation
P1	1156
P2	1131
P3	1089
P4	1105
P5	1078

Appendix 4: Coordinates of samples collected from Heap A

Sample ID	Longitude	Latitude	Elevation (m)
AA	24° 03’ 00,3” S	24° 45’ 58,3” E	1115
AB	24° 03’ 00.1” S	28° 45’ 58.0” E	1115
AC	24° 03’ 59,9” S	28° 45’ 57.7” E	1114
AD	24° 03’ 00.1” S	28° 45’ 57,4” E	1115
AE	24° 03’ 59,7” S	28° 45’ 58.0” E	1115
AF	24° 03’ 00,6” S	28° 46’ 57.4” E	1114

Appendix 5: Coordinates of samples collected from Heap B

Sample ID	Longitude	Latitude	Elevation (m)
BA	24º 03’ 00,9” S	28º 45’ 52.24” E	1142
BB	24º 02’ 59.18” S	28º 45’ 50.60” E	1148
BC	24º 02’ 58.37” S	28º 45’ 48.90” E	1138
BD	24º 02’ 59.47” S	28º 45’ 48.16” E	1143
BE	24º 03’ 0.31” S	28º 45’ 49.77” E	1145
BF	24º 03’ 1.18” S	28º 46’ 51.44” E	1140

Appendix 6: Coordinates of samples collected from Heap C

Sample ID	Longitude	Latitude	Elevation (m)
CA	24º 02’ 56.18” S	28º 45’ 14.58” E	1195
CB	24º 02’ 57.42” S	28º 45’ 11.82” E	1189
CC	24° 2'59.79"S	28°45'9.38"E	1145
CD	24º 03’ 0.94” S	28º 45’ 8.12” E	1173
CE	24º 02’ 59.75” S	28º 45’ 10.88” E	1177

Appendix 7: Pollution condition of the tailings within the River Profiles.

	Pollution Index of Metals (Pi)									
Sample ID	Cr	Co	Cu	Zn	As	Mo	Cd	Pb	Th	U
P1S1	0.08	1.14	32	3.77	16.37	0.75	0.09	28.67	4.65	3.51
P1S2	0.11	1.01	32.14	3.85	20.34	0.25	0	35.63	4.92	3.92
P1S3	0.11	1.30	37.92	4.17	22.7	1.55	0.09	39.80	5.45	3.39
P2S1	0.2	1.22	29.50	3.88	19.14	0.83	0.09	32.28	4.6	3.61
P2S2	0.09	1.08	32.12	3.47	19.71	0.33	0.09	34.54	5.06	3.43
P2S3	0.12	1.07	33.18	3.54	23.14	0.33	0.09	40.52	5.49	3.67
P3S1	1.22	1.38	32.81	3.81	21.93	1.78	0.09	38.41	6.04	4.03
P3S2	0.26	1.30	30.51	5.68	17.90	1.53	0.09	31.37	4.27	3.27
P3S3	0.44	1.43	40.34	4.98	23.23	0.28	0.09	47.9	4.63	3.62
P4S1	0.27	1.01	26.44	3.55	19.37	0.28	0.09	33.92	5.73	2.76
P4S2	1.20	0.97	25.9	3.68	19.30	0.83	0.09	28.46	4.49	2.95
P4S3	0.12	1.22	19.26	4.35	20.89	0.66	0.09	36.6	6.93	3.47
P5S1	0.51	2.01	35.68	8.06	49.48	0.39	0.09	86.66	11.22	4.72
P5S2	0.37	2.55	41.95	9.47	56.56	1.33	0.09	99.08	14.21	6.55
P5S3	0.72	2.87	52.91	11.95	61.55	2	0.09	92.73	17.29	8

Appendix 8: Pollution condition of the tailings within Heap A.

	Pollution Index of Metals (Pi)									
Sample ID	Cr	Co	Cu	Zn	As	Mo	Cd	Pb	Th	U
AA	0.32	1.3	30.01	4.26	23.34	1.03	0.09	40.88	5.96	3.23
AB	0.12	1.08	29.95	3.73	19.44	0.81	0.09	34.03	5.27	3.85
AC	0.26	1.17	31.6	4.29	25.03	0.25	0.09	43.85	6.04	3.65
AD	0.33	1.2	34.38	4.48	25.26	0.25	0.09	44.25	6.17	3.81
AE	0.10	1.18	32.27	4.22	25.31	1.19	0.09	44.33	5.95	3.65
AF	0.24	1.22	32.02	4.18	23.14	1.5	0.09	40.52	6.07	3.92

Appendix 9: Pollution condition of the tailings within Heap B.

	Pollution Index of Metals (Pi)									
Sample ID	**Cr**	**Co**	**Cu**	**Zn**	**As**	**Mo**	**Cd**	**Pb**	**Th**	**U**
BA1	0.18	0.99	20.74	4.87	26.89	0.28	0.09	47.11	4.98	4.24
BA2	0.15	0.93	20.09	4.56	29.47	0.28	0.09	51.62	4.49	3.8
BA3	0.09	0.96	19.17	4.65	29.15	0.39	0.09	51.04	4.72	3.92
BA4	0.32	0.94	18.52	4.95	28.40	0.28	0.09	76.38	4.70	3.92
BB1	0.08	1.51	36.96	7.26	43.62	0.39	0.09	97.20	9.32	6.11
BB2	0.1	1.65	41.47	8.54	55.49	0.44	0.09	103.68	11.34	6.81
BB3	0.18	1.64	43.91	9.07	59.19	0.44	0.09	94.62	10.95	6.70
BB4	0.11	1.64	42.61	8.38	54.02	0.44	0.09	86.44	10.96	6.35
BC1	0.11	1.64	39.34	8.13	49.36	044	0.09	90.48	10.78	6.46
BC2	0.22	1.64	41.15	8.28	51.66	0.44	0.09	113.70	11.67	6.65
BC3	0.04	1.54	43.11	8.98	64.91	0.5	0.09	94.47	10.85	6.32
BC4	0.13	1.64	41.52	8.54	53.94	0.44	0.09	52	10.56	6.14
BD1	0.23	1.23	23.54	4.95	29.68	0.33	0.09	54.14	5.24	3.51
BD2	0.15	1.20	25.45	5.35	30.91	0.33	0.09	57.64	5.85	3.81
BD3	0.04	1.17	25.15	5.25	32.91	0.39	0.09	63.39	6.34	3.84
BD4	0.24	1.32	27.26	5.95	36.19	0.33	0.09	57.50	7.24	4.03
BE1	0.19	1.52	29.14	5.41	32.83	1.94	0.09	79.47	7.04	4.05
BE2	0.67	1.33	28.33	6.17	45.36	1.89	0.09	54.42	6.20	3.38
BE3	0.11	1.34	22.16	4.87	31.06	1.67	0.09	67.88	5.84	3.89
BE4	0.24	1.55	27.66	6.06	38.74	1.78	0.09	79.53	7.37	3.95
BF1	0.07	1.39	30.67	6.22	45.40	0.5	0.09	53.51	6.18	3.11
BF2	1.16	1.55	23.21	5.26	30.55	1.83	0.09	79.53	6.43	3.12
BF3	0.03	1.59	31.09	5.87	37.06	1.5	0.09	64.91	5.98	3.35
BF4	0.19	1.96	34.41	7.77	44.09	1.89	0.09	77.22	9.10	5.05

Appendix 10: Pollution condition of the tailings within Heap C.

	Pollution Index of Metals (Pi)								
Sample ID	Co	Cu	Zn	As	Mo	Cd	Pb	Th	U
CA1	1.25	27.44	4.20	12.66	0.11	0	22.16	3.93	3.08
CA2	1.22	37.15	3.66	15.43	0.28	0	27	4.33	3.46
CA3	1.25	42.52	3.69	14.11	0.33	0	24.72	4.5	3.41
CA4	1.25	37.06	3.46	11.47	0.22	0.09	23.70	3.98	3.43
CB1	1.12	27.31	5.06	10.96	0.17	0.09	20.1	3.71	3.92
CB2	1.19	29.49	4.55	11.53	0.22	0.09	19.21	4.57	3.41
CB3	1.25	36.18	3.54	12.55	0.28	0.09	20.18	4.21	3.54
CB4	1.20	33.69	4.21	16.55	0.22	0.09	21.97	4.59	3.95
CC1	1.19	30.14	4.10	21.21	0.33	0.09	28.20	4.59	3.54
CC2	1.12	30.48	4.03	21.19	0.11	0	37.1	4.68	3.70
CC3	1.14	30.24	4.07	22.02	0.22	0.09	38.59	4.70	3.78
CC4	1.17	31.69	4.12	16.51	1.39	0.09	28.93	4.48	3.51
CD1	1.10	38.23	4.02	21.06	0.22	0.09	36.91	5.34	4.11
CD2	1.12	36.18	4.57	18.50	0.22	0	32.40	4.45	4.14
CD3	1.14	37.24	4.04	17.60	0.28	0.09	30.82	4.8	4.49
CD4	1.13	36.19	4.03	16.40	0.22	0.09	28.73	4.51	4.51
CE1	1.28	32.59	4.40	15.62	1.11	0.09	27.34	4.37	3.08
CE2	1.33	37.41	4.26	17.72	0.22	0.09	31.06	4.65	4.41
CE3	1.51	36.23	3.89	17.81	1.33	0.09	31.18	4.68	3.08
CE4	1.50	38.44	3.93	17.17	1.39	0	30.10	4.61	2.97

Appendix 11: Coordinates of Water Samples collected during within the Zaaiplaats Tin Mine tailings.

Sample ID	Longitude	Latitude	Elevation (m)
WS1	24º 02’ 57.4” S	25º 45’ 22.5” E	1139
WS2	24º 02’ 56.9” S	28º 45’ 34.4” E	1116
WS3	24º 02’ 55.8” S	28º 45’ 53.7” E	1103

Appendix 12: Properties of Water samples.

Sample ID	Electrical conductivity (µ/S)	pH	Salinity	Total Dissolved Solids	Turbidity (NTU)
WS1	140.5	5.43	70.2	93.4	5.7
WS2	125	6.1	65.4	87.5	5.4
WS3	138.4	5.1	66.3	89.1	5.8

Appendix 13: Coordinates of Plants Samples collected during dry season.

Sample ID	Longitude	Latitude	Elevation (m)
S1	24º 02’ 58.8” S	25º 45’ 18,5” E	1146
S2	24º 02’ 56.1” S	28º 45’ 21.4” E	1114
S3	24º 02’ 54.6” S	28º 45’ 35.5” E	1118
S4	24º 02’ 54.5” S	28º 45’ 49.5” E	1104
S5	24º 02’ 47.15” S	28º 46’ 11.08” E	1125

Appendix 14: Coordinates of Plants Samples collected during wet season.

Sample ID	Longitude	Latitude	Elevation (m)
S1	24º 02’ 57.1” S	25º 45’ 23” E	1141
S2	24º 02’ 55.8” S	28º 45’ 25.4” E	1139
S3	24º 02’ 54” S	28º 45’ 44.6” E	1104
S4	24º 02’ 47.4” S	28º 46’ 11” E	1084

Appendix 15: Coordinates of Radioactive Survey locations within the Zaaiplaats Tin Mine tailings.

Sample ID	**Longitude**	**Latitude**	**Elevation (m)**
Heap A	24º 02’ 59.1” S	25º 45’ 16.3” E	1149
Heap B	24º 02’ 56.9” S	28º 45’ 34.4” E	1116
Heap C	24º 02’ 57.9” S	28º 45’ 14.8” E	1195
Location 1A	24º 02’ 59.1” S	25º 45’ 16.3” E	1149
Location 1B	24º 02’ 58.4” S	25º 45’ 15.9” E	1156
Location 1C	24º 02’ 57.7” S	25º 45’ 16” E	1164
Location 2A	24º 02’ 55.8” S	28º 45’ 32.3” E	1121
Location 2B	24º 02’ 57.2” S	28º 45’ 32.6” E	1123
Location 2C	24º 02’ 58.6” S	28º 45’ 33.3” E	1121
Location 3A	24º 02’ 49.0” S	28º 45’ 01.3” E	1096
Location 3B	24º 02’ 57.2” S	28º 45’ 03.3” E	1096
Location 3C	24º 02’ 54.6” S	28º 46’ 06.9” E	1096
Location 4A	24º 02’ 49.6” S	28º 46’ 08.8” E	1090
Location 4B	24º 02’ 51.1” S	28º 46’ 10.0” E	1090
Location 4C	24º 02’ 51.7” S	28º 46’ 11.4” E	1089
Location 5A	24º 02’ 45.6” S	28º 46’ 21.9” E	1076
Location 5B	24º 02’ 43.8” S	28º 46’ 21.6” E	1075
Location 5C	24º 02’ 42.4” S	28º 46’ 19.0” E	1077

Appendix 16: Rate and Dose results found within the Zaaiplaats Tin Mine.

Surveying Point	Rate (μSv/h)	Annual ambient dose equivalent (mSv/y)
Heap A	1.1	9.64
Heap B	1.65	14.46
Heap C	1.09	9.55
Location 1A	0.12	1.05
Location 1B	1.09	9.55
Location 1C	1.09	9.55
Location 2A	0.11	0.96
Location 2B	0.12	1.05
Location 2C	0.12	1.05
Location 3A	0.11	0.96
Location 3B	0.95	8.33
Location 3C	1.33	11.66
Location 4A	0.12	1.05
Location 4B	0.11	0.96
Location 4C	1.21	10.61
Location 5A	0.13	1.14
Location 5B	0.12	1.05
Location 5C	0.13	1.14
Control point	0.08	0.70