Environmental impact of leach water from selected mine tailings materials in South Africa

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PREFACE

This dissertation consists of five chapters and forms part of the degree of Master of Science in Environmental Science. Chapter one consists of a background and motivation as well as aims, objectives and hypotheses. Chapter two consists of a literature review. Chapter three includes a detailed methodology. Chapter four consists of results and a discussion while Chapter five contains the final conclusions and recommendations for further research.

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Most importantly, I wish to thank the almighty God for being a pillar of my strength when all hope was lost.

Last but not least, I would like to convey my gratitude to my parents Mr G.E and Mrs A.M Mashimbyi for their love and encouragement during my long journey to this academic victory and my extended family for being with me spiritually.

DECLARATION

I declare that "Environmental impact of leach water from selected mine tailings materials in South Africa" was achieved in the School of Geo- and Spatial Sciences (Geology / Soil Science) at the NWU (Potchefstroom Campus) from March 2016 till November 2018.

This dissertation is my own work and may include the original leaching results of work done by Mr J.H de Wet on "Human health risk of South African mine tailings materials evaluated against international guidelines" within the same localities. All the sources used have been acknowledged and quoted according to the Harvard style of referencing both in text and complete references.

SUMMARY

Background and objective: Mine tailings materials pose severe impacts to the environment (soils, water and ecosystem). A variety of processes such as erosion or sedimentation and leaching disperse trace elements to the natural environment. The environmental impact of leach water from selected mine tailings materials in South Africa was studied.

Methods and materials: Sampling was done at sixteen different mine tailings materials, and detailed analysis was accomplished. Laboratory leaching for trace elements (TEs) was performed with the use of humidity cells as outlined in Chapter 3. The ICP-MS analysis method was further used to determine the concentrations of U, Cr, Co, Ni, Pb, Cu, As, Mn, Zn and Cd TEs. The level of TEs in soils was measured against the South African soil screening values (SSV) for all land-uses protective of the water resources to indirectly protect the ecosystem (NEMWA Act NO 59 of 2008). Uranium, As, Cu, Ni, Cr and Cd levels at sampling sites TJ3, TJ9, TJ15 and TJ20 were above the threshold limits.

Results: To classify soils and other fines i.e. tailings according to texture, particle size distribution analyses were performed. The size of tailings ranged from very coarse sand to clay. This contributed to understanding the mobility of TEs under study. Cation exchanged capacity (CEC) and anions analyses were also performed to support the results.

Conclusion: The pH of leached water ranged between 2.19 (TJ20) and 10.12 (TJ2), whereas EC ranged between 0.51 mS/cm (TJ23) and 60.7 (TJ1) respectively. Revegetation to hinder TEs from leaching was recommended. The addition of gypsum was also recommended to reduce the level of Na in mine tailings materials.

Keywords: Environmental impact, leaching, metal trace elements, soil, cations, anions

GLOSSARY

Acid Mine Drainage (AMD)- Is the outflow of acidic water from metal or coal mines after oxidation of sulphide minerals .

Cation Exchange Capacity (CEC)- is a measure of how many cations can be adsorbed on particle smaller than 2 mm by means of the negative charge on the surfaces and interlayers of these particles; it is mainly the clay fraction that is responsible for cation exchange and adsorbtion due to the negative charge of these colloidal fraction.

Concentration- is the abundance of a constituent divided by the total volume of a mixture.

Environment- Is the external conditions, resources, stimuli etc. with which an organism interacts.

Environmental impact- are harmful effects of human activity on the biophysical environment.

Electrical Conductivity- is the reciprocal of electrical resistivity and measures a material's ability to conduct an electric current; it is mainly soluble anions in a solution that is responsible for the electrical conductivity.

Humidity cell- It is a laboratory apparatus commonly used in the mining sector to estimate the long-term acid generation behaviour of sulphide-bearing tailings and waste rocks (ASTM D5744 2007, Technical Committee CEN/TR 16363 2012).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)- is a mass spectrometry analytical method which is capable of detecting metals and several non-metals at concentrations as low as one part in 10^{-15} (part per quadrillion, ppq) on non-interfered low-background isotopes.

Leaching- the movement of the chemical in the upper layers of soil into lower layers or into groundwater by being dissolved in water.

Macro-elements- are nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg); also refered to as macro plant nutriens

Micro-elements- are iron (Fe), manganese (Mn), zinc (Zn), boron (B), copper (Cu) and molybdenum (Mo) also refered to as micro plant nutrients.

Mine tailings materials- also called Tailings Storage Facilities (TSF), mine dumps, culm dumps, slimes, tails, refuse, leach residue or slickens, terra-cone, are the materials left over after the process of separating the valuable fraction from the uneconomic fraction (gangue) of an ore.

Particle Size Distribution- (PSD) of a powder, or granular material, or particles dispersed in fluid, is a list of values or a mathematical function that defines the relative amount, typically by mass, of particles present according to size.

pH- is a negative logarithmic concentration of the hydrogen concentration in a solution used to specify the acidity (pH<7), alkalinity (pH=7) or basicity (pH>7) or of an aqueous solution.

Soil screening value- concentrations of chemical substances found in soils below which there [were] not expected to be any adverse effects on wildlife such as birds, mammals, plants and soil invertebrates, or on the microbial functioning of soils.

Trace elements- are the metals subset of trace elements; that are, metals normally present in small but measurable amounts in soil, rock, animal and plant cells and tissues as well as mine waste. In some old literature the authors refer to Metal Trace Elements (TE) or even Heavy Metals.

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LIST OF ABBREVIATIONS

AMD	Acid Mine Drainage
CEC	Cation Exchange Capacity
EC	Electrical Conductivity (mS/m)
ICP-MS	Inductive Coupled Plasma Mass Spectrometry
pH	Pondus Hydrogenii
PSD	Particle Size Distribution
SSV	Soil screening values
TE	Trace elements
TJ	Sampling sites (also JT)
TL	Threshold Limit
TSF	Tailing Storage Facility

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CHAPTER ONE: INTRODUCTION AND CONCEPTUALISATION

1.1 BACKGROUND

Mining generates huge quantities of waste materials from ore extraction and milling operations, which then accumulate in tailings and open impoundments (Grangeia *et al.*, 2011). Regardless of the nature of mining or type of commodity being excavated, mining in South Africa plays a crucial role in socio-economic growth. However, mining is one of the main source of metals dispersion into the environment (Matshusa *et al.*, 2012). A footprint result after the extraction of valuable minerals from the earth's crust. This footprint may be in the form of a gaping hole, rock dumps and tailing dams. Despite the variety of waste materials from mining activities, only tailing dam's material of different commodities and locations were the area of interest in this study. This tailings material has a direct negative impact on the surrounding environment, water resources, plants and animals. In essence, this study focuses mainly on the environmental impacts of tailings materials. However, a study was conducted on "Human health risk of South African mine tailings materials evaluated against international guidelines" by De Wet (2017), at the same localities, but his focus was only directed to human health impacts of mining and not the environmental part of it.

Mining by its nature brings to communities enormous investment, thus contributing to the socio-economic development of the host communities (Mhlongo & Amponsah-Dacosta, 2014). Mining is the breaking up and extraction of economically valuable minerals from the earth's crust for human benefits. It engages a variety of processes such as conveyance of ore as well as downstream beneficiation processing of minerals and disposal of waste materials (Rembuluwani *et al.*, 2014).

The waste materials (solid or liquid) from mining activities contain a variety of toxic elements such as trace elements. Trace elements occur naturally in the soil environment from the initial processes of weathering of parent materials at levels that are regarded as trace (<100 mgkg^{-1}) and rarely toxic (Raymond *et al.*, 2011) but in new literature values >100 mgkg^{-1} are also allowable to use. According to (Lenntech,

2004) trace elements refers to any element that has a relatively high density and is toxic or poisonous even at low concentrations. However, trace elements are significant environmental pollutants.

Apart from mining, weathering of metal-bearing sulphide, silicate, oxide minerals and processing compounds cause extreme acidity in the tailings and the release of metallic elements such as aluminium that have potentially toxic effects on plants (Kossoff *et al.*, 2014). A large amount of waste materials generated from mining activities may result in severe effects such as AMD. According to (Stone *et al.*, 2002) AMD is considered one of mining's most serious threat to water resources and the surrounding environment. Acid mine drainage dissolves potential toxic elements such as copper, aluminium, cadmium, arsenic, lead and mercury from mine waste. Acid Mine Drainage is formed by the oxidation of sulphide minerals, mainly pyrite. In fact, the process is said to occur when sulphide ores are exposed to the atmosphere which can be enhanced through mining and milling processes where oxidation reactions are initiated (Akcil & Koldas, 2006; Allen, 2008; Johnson & Halberg, 2005).

The absorbed acidic material in TSF's poses a severe threat by means of the dissolution and subsequent release of some elements into the natural environment, and specifically on the growth of established vegetation cover for reclamation or rehabilitation processes. However, certain acid tolerating plant species and those that can survive on a very low pH is tested for phytotoxicity. Phyto-toxicity is defined as a delay of seed germination, inhibiting of plants growth or any adverse effects on plants caused by specific substances (elements, salts etc) or growing condition (Basiuk *et al.*, 2013; McCalla & Haskins, 1964; Olofsdotter *et al.*, 2002; Tam & Tiquia, 1994). Byrne *et al.* (2012), Grangeia *et al.* (2011), Watson *et al.* (2001), identified that the main geochemical signature of mine tailing contaminants is dependent on many factors such as lithology, porosity, mineralogy, total dissolved solids and pH of the pore water. Hence the effects of mining on the environment include the release of many chemical contaminants into water resources, which can cause damage to the environment (Förstner & Wittmann, 2012; Jolliet *et al.*, 2003; Kumar & Yadav, 2009; Tiwary, 2001). According to Alloway (2013), Ayman Ismail (2015) and Ene *et al.* (2010), the most significant source of TE's in the environment

are the anthropogenic activities such as mining, smelting procedures, steel and iron industry, chemical industry, traffic, agriculture as well as domestic activities. Discharge of waters with high concentrations of TE's from abandoned mines into surface streams or percolation of waste rock or ore leachate into groundwater systems can cause considerable issues like AMD (Fetter *et al.*, 2017; Hemanth Rajkumar, 2015; Lottermoser, 2003; Straskraba & Moran, 1990). However, this study focuses on mining as a source of trace elements into the environment.

1.2 PROBLEM STATEMENT

Mining plays a crucial role in the development of South Africa's economy; nevertheless, it amounts to the enormous quantity of waste materials via a variety of processes that poses detrimental impacts on the environment (soils, water and air), animals and human health. These waste materials are known to contribute to environmental impacts in the short to medium term, the long-term environmental effects of these facilities have not been established (Gupta, 1995; Frosch & Gallopoulos, 1989; Jubileus, 2008; Shrivastava, 1995). With that being mentioned the environmental impacts of mining has been investigated by many researchers and they acknowledged mining to be a prominent source of TE contamination on the environment, animals and human health (Förstner & Wittmann, 2012; Giusti, 2009; Kimani-Murage & Ngindu, 2007; Tiller, 1992; Zarcinas *et al.*, 2004). Acid mine drainage specifically is one of the environmental problems emanating from mining activities. This problem of AMD was reported to be an unavoidable issue causing severe negative effects to the soils, surface and groundwater sources, ecology and human health and is characterised by a low pH of approximately 2, sulphates and availability of TE's (Brown *et al.*, 2002; Dutta *et al.*, 2017; Kumari *et al.*, 2010; Meuser, 2010; Ngigi, 2009). However, this study focuses only on the environmental impacts of mine tailings, with emphasis given to TE concentrations by means of leaching method.

1.3 RESEARCH QUESTIONS

Frequently asked questions in connection with the environmental impact of mine tailings materials are the following:

1. What is the most suitable and appropriate method to obtain background information on the environmental impacts of mine tailings materials?
2. What is the concentration of trace elements on mine tailings materials?
3. What are the potential effects of trace elements on the environment?
4. What are the dispersion factors of such elements to the soil, surface water and plants?
5. What are the suitable strategies to control or manage the collective risk impacts of mine tailings materials?

These questions are not the objectives of this research study, but rather a helpful guide to identify the focus.

1.4 AIM, OBJECTIVES AND HYPOTHESES

1.4.1 General aim

The main aim of the study was to investigate the significant impact of leach water from sixteen different mine tailings material on the environment (soil, surface and groundwater and plants).

1.4.2 Specific objectives

Objective 1: To obtain background information on the environmental impacts of mine tailings materials

Objective 2: To determine the concentration of selected TE's on mine tailings material

Objective 3: To investigate the potential effects of selected TE's on the environment.

Objective 4: To assess the leaching technique of such TE's to the soil, surface water and its indirect effects on plants species. This aspect will focus on literature reviews and not on real time quantitave morphological charetristics of plants established in tailings because of the complicated and expensive analyses required

Objective 5: To evaluate the main environmental (water, soil and plants) risks of the above issues.

1.5 HYPOTHESES

Tailings material have a potential negative impact on the ecology, environment (i.e. land/soils, water sources and plants). Surficial processes such as erosion also play a contributing factor on the release of TE's to the environment in trace amount leading to potential pollution. This reprocessing is influenced by the instability of mine tailings dams of which is due to improper planning, design, or re-vegetation. Soil texture (sand, silt and clay) characterises the rate at which leaching will take place i.e. clay is much more reactive than sand due to the higher surface area of the clay but infiltration and leaching rates of sandy material are much faster in material. Leaching apart from surficial processes mobilises TEs to the natural environment.

The basic hyphothesis could be formulated that the influence of trace element concentrations in leach water will be related to physio-chemical-mineralogical characteristics of the tailings material and will have varies influences on environmental qualities in general.

1.6 THE SCOPE OF THE STUDY

For this study only, certain specific TE's were researched. This study also focused on the sources and transfer factors of potentially toxic elements into the soil environment, surface water sources and its effects on plants. Background information on the occurrence of AMD as a threat to the environmental system (soil, water and plants) was also covered. It extends to the fact of developing effective solutions to manage the risk from contamination of valuable and scarce resources such as water and agricultural land in South Africa, with special focus directed to

certain areas within the country. Although there are many methods of detecting the dispersion and or distribution of potentially toxic elements into the environment (soil, both ground and surface water source), the leaching method was used (Edet & Offiong, 2002; Ficklin *et al.*, 1992; Ju-Nam & Lead, 2008; Siegel, 2002; Siegel, 2003; Sullivan *et al.*, 2005).

1.7   AN OUTLAY OF THE RESEARCH PRODUCT

For the purpose of this research project to be completed in a more logical manner, a structure consisting of five chapters was constructed.

Chapter 1: Introduction and conceptualisation

This chapter provides direction to the study. It consists of a background to the study, problem statement, research questions, aims and objectives, hypothesis, the scope of the study and finally an outlay of the total project.

Chapter 2: Literature review

This chapter enables a researcher to develop a deep understanding of what is expected of him or her. This chapter provides all the factors that could have an influence on this study. It provides general knowledge on the properties that influence leaching of mine tailings materials. Environmental risks associated with leaching of mine tailings materials together with the consequences of each were discussed in this chapter. However, this study focuses on chemical properties of the soil, water quality and plants as influenced by the leaching of TE's from mine waste.

Chapter 3: Methods and materials

This chapter works as an engine of the research because it provides all the materials and methods used to obtain data. Varieties of mine tailings materials from different localities in South Africa, with different ore bodies, were used. Sampling, sample preparations (drying and sieving), particle size distribution, humidity leaching test, pH, EC, ICP-MS analysis for TE's and data processing were the methods and materials used to obtain final results.

Chapter 4: Presentation of results and Discussion

This chapter makes provision for a detail presentation and discussion of the results obtained during Chapter 3.

Chapter 5: Conclusion and recommendations

This chapter gives a brief summary of the results and also provides for what could be done in order to improve the present results during future studies.

CHAPTER TWO: LITERATURE REVIEW

2.1 ENVIRONMENTAL RISKS ASSOCIATED WITH MINE TAILING

South Africa has an amazing variety of mineralisation which has served as the catalyst in transforming the country from an agricultural to a mining and industrial-based economy. The nature of a mining operation being excavated determines the severity of contamination to the soil environment, water resources and plants. This is due to the toxicities status of by-products associated with the primary mineral resources and types of chemicals being employed during beneficiation processes. Ashton *et al.* (2001), Ekwue *et al.* (2012), Pappu *et al.* (2007), reported that mining gives rise to soil erosion and environmental contamination by generating waste during the extraction, beneficiation and processing of minerals. Amongst the waste materials produced from mining activities, only tailings materials of different elements and their effects on the environment were studied.

According to Jeeravipoolvarn *et al.* (2008), Ghose & Sen (2001) and Nkuli (2012), tailings are usually in the form of fine slurry, which is managed in ponds. Tailings result from mineral processing, which includes crushing, grinding, concentration, dewatering and finally tailings slurry disposal (Bussiere, 2007; Hamade, 2013; Wills & Finch, 2015). Coelho *et al.* (2013), Grangeia *et al.*, (2011) and Hiller *et al.* (2016) accentuated that tailings dams have long been associated with mining activities and has contributed major negative impacts to the environment.

Together with the mine waste rock, TSF and mine openings are recognised as the "legacy" impacts of mining. Tailings or mine waste disposal facility has proven the most contentious component of mining activities and has represented the source of significant environmental and economic impacts due in most of the cases, to poor management (Bakatula, Straker *et al.* 2015, Bakatula, Mosai *et al.* 2015). According to Hamade's (2013), Nkuli's (2012) and Xenidis's (2014) point of view, mine tailings dams are geotechnical structures that are designed to provide adequate and safe storage of tailings materials during and after the end of mine life. However, in the past, the primary aim was to provide a well-engineered structure into which the

tailings can be deposited without a great deal of attention being given to closure requirements or issues related to long-term management of the TSF (Ekwue *et al.*, 2012; Nkuli, 2012; Xenidis, 2004).

This research study focuses on the delivery of workable strategies for effective TSF management. In view, since the initial discovery of valuable minerals from the earth's crust, TSF's has been associated with numerous issues which negatively affect the soil environment, water resources and animals or human beings. These features alter the in situ geomorphological characteristics of the landscape prior to geological events of the past in relation to the origin of the earth (Blyth 2013; Griffiths *et al.*, 2012; Taylor & Eggleton, 2001). Management of tailings start with the first phase or step to mining which is prospecting. Prior to exploration the plan of what is to be done when and where at what time with what should be coupled or included on the mine plan. The aftercare part of it should be properly and effectively budgeted for with alternative solution also in place. These solutions will be implemented only if what is expected of the mine does not bear any fruits.

Regardless of the stability or technological design of TSF, tailings materials are being deposited or introduced to the environment i.e. land, air and water. The composition of tailings is dependent to the primary ore being mined (Fall *et al.*, 2010; Kossoff *et al.*, 2014; Van Jaarsveld *et al.*, 2000). For instance, Gold tailings materials contain far most diverse types of trace minerals and elements as compared to maybe, Diamond, Copper, Platinum, Andulisite and Coal tailings.

Ogola (2010), Pierzynski *et al.* (2005) and Smedley and Kinniburgh (2002) reported that gold mining activities generally take place in relatively large areas, and can have severe negative impacts on the natural environment including, soil, surface and groundwater quality and plants. This is because most of the mines, for example gold mines are associated with sulphide minerals which when oxidised, result in Acid Mine Drainage (AMD) and create low pH conditions. Low pH in these environments can increase solubility and mibility of the TE's. Despite a long history of gold mining activities, there is still a lack of thorough h investigation of mining wastes and their potential to produce AMD (Assawincharoenkij *et al.*, 2017 Müezzinoǧĭu, 2003;

Wolkersdorfer & Bowell, 2005). However, there is also a lack of proper sustainable rehabilitation which have a minimum maintenance and post-closure cost to it as well as financially viable post-closure land use activities been signed to it.

Tailings materials also contain some of the potentially toxic elements such as Hg, Pb, As, Cu and U (Alloway, 2013; Nagajyoti *et al.*, 2010; Wuana & Okieimen, 2011). These elements cause pollution in the soil environment and may negatively affect agricultural activities. The solubility and mobility of these elements from tailings take place in a variety of ways which include, leaching, erosion, flooding, wind transportation and/or weathering of parent materials. Leaching is the chemical removal of trace elements from ore deposit or waste materials deposited on the surface of the earth as tailings dams and appears in two forms of which are percolation leaching and flooded leaching (Hartman & Mutmansky 2002; O'Gorman *et al.*, 2004; Nilsson & Randhem 2008). The end results of the leaching end up in the toe of the TSF's, accumulate in the surface and ground water and also on the footprint of the TSF. TSF's are used to be re-mined to recover economic reserves and then the footprints are exposed which are suppose to be returned to arable land. It is these footprints that could have accumulations of potential toxic elements, especially for the rehabilitation vegetation and final end landuse i.e. crops, grazing etc.

2.2 ACID MINE DRAINAGE (AMD)

Byrne *et al.* (2012), Diz (1997:5) and Ewart (2011) reported that AMD from active and abandoned mines continues to be a vital source of water pollution in the United States and the globe. According to Diz (1997:5), Ewart (2011), McCarthy (2011), AMD is sometimes referred to as Acid Rock Drainage (ARD) of which is a well-understood process and arises primarily when the mineral pyrite ('fools' gold or iron disulphide) reacts with oxygen and water (referred to as oxygenated water).

Acid mine drainage is formed by a series of geochemical and microbial processes (Bond *et al.*, 2000; Taylor *et al.*, 1984; Tutu 2012). Acid mine drainage is the product of oxidation in abandoned mine lands and runs into surface water (Zhengfu *et al.*,

2010; Kirby 2014; Tutu, 2012). However, Zhengfu *et al.* (2010), Kimball *et al.* (2002) and Sobolewski (1999) proved through an experiment that AMD formed via a cascade of reactions. The sequence of chemical reactions in the oxidation of pyrite to form acid mine drainage took place in four steps (Reactions 1-4). From Wade *et al.* (2006), Johnson & Hallberg (2005) and Taylor *et al.* (1984), the reactions are summarised as follows:

$$FeS_2 + ^7/_2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

$$Fe^{2+} + ^1/_4 O_2 + H^+ \rightarrow Fe^{3+} + ^1/_2H_2O \qquad (2)$$

$$FeS_2 + Fe^{3+} + 12H_2O \rightarrow 12Fe^{2+} + 2SO_4^{2+} + 16H^+ \quad (3)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe\ (OH)_3 + 3H^+ \qquad (4)$$
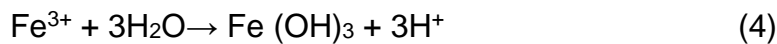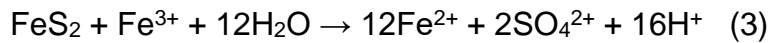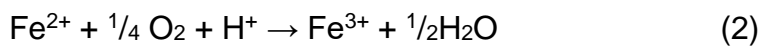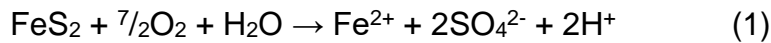
Chemical reactions in this context start with pyrite being exposed to oxygenated water and atmospheric oxygen. However, in the case of mine tailings, the cascade process begins with rain water percolating through the finely divided tailings to the oxidation of pyrite (Reaction-1) and ends with ferric iron precipitates (Fe $(OH)_3$ and hydrogen ion (H^+) (Reaction-4), of which a reaction apparently able to buffer the pH of acid mine drainage at 2.5-3.5 (Wade et al., 2006; cited from Zhengfu *et al.* 2010; Gazea *et al.*, 1996).

Furthermore, this sustained acidity leads to the dissolution of ores that occur alongside pyrite hence the presence of other ions or metal such as Silver, Gold, Cadmium, Cobalt, Nickel, Mercury, Molybdenum, Selenium, Copper and Zinc (Akcil & Koldas, 2006; Zhengfu *et al.*, 2010; McCarthy, 2011). Acidic metal-laden water resulted and percolated through the tailings heaps to recharge groundwater or leaches at the foot of the tailings dam into surface water or remain on the footprint of the TSF. (Akcil & Koldas, 2006; Acheampong, 2016; cited from Zhengfu *et al.*, 2010).

The procedure of this process is valid and motivates this study because it aims at investigating the environmental impacts of mine tailings putting more emphasis to leaching of the acidic and metal-rich solution being catalysed by rainfall infiltration into the tailings. The quantity of AMD produced depends primarily on the scale of the mining industry and the size of exposure of sulphides minerals to oxygen and water (Akcil & Koldas, 2006; Ferguson & Erickson, 1988; Gazea *et al.*, 1996). This also influences the concentration or acidity of the produced acid mine drainage. Acid mine drainage is one of the most significant and potentially persisting environmental issue of mining industries and if left abandoned, poses a long-term impact to surface and groundwater quality and or land (Ewart, 2011; Ogola *et al.*, 2010; El Tahlawi & Ahmed, 2006). Water found above the ground in dams, lakes, rivers, streams and the ocean is referred to as surface water. (Zhengfu *et al.*, 2010; Ogola et al., 2002; El Tahlawi & Ahmed, 2006).

Chavalala (2016), Ewart (2011) and Ogola *et al.* (2010) further reported that most of the existing surface water sources in South Africa are endangered by massive amounts of tailings dams' facilities available and in particular metal ores and coal within the country. Karanth (1987), Neitsch *et al.* (2011) and Udayabhanu and Prasad (2010) described groundwater to be such water that is enclosed within the aquifers below the earth's surface. Water quality is determined in terms of it's physical, chemical and biological characteristics and is evaluated according to DWA standards (Karanth, 1987; Udayabhanu *et al.* 2010; Winter 1998).

Groundwater is more prone to acid mine drainage contamination compared to surface water (Goel, 2006; Tiwary, 2001; Younger *et al.*, 2002). This is due to the geology of the country rock or the overburden. Once groundwater is contaminated it becomes difficult to purify from source resulting in a quality reduction for domestic, agricultural and or aquatic life. Wherein, on the other hand, quality reduction of surface water from AMD may be due to surficial processes such as surface run-off, erosion of leachate materials from the foot of the TSF's. The environmental issues of AMD result in degradation of such resources. Furthermore, the effect extends to agricultural lands, reducing the fertility of soil with an increase in acidity of such lands leading to low production.

Apart from surface and groundwater quality, AMD has tremendous negative impacts on ecology. Ecology refers to the interactions between biotic and abiotic environment (Borcard *et al.*, 1992; Soberon & Peterson, 2005; Vold & Buffett 2008). This impact is due to leaching of TE by AMD and then via erosion, dissolution weathering and runoffs or flooding then transported to a variety of natural environments (soil, water sources and agricultural land), including ecological systems of the environment (Hooda, 2010; Tayab, 1991; Tchounwou *et al.*, 2012).

2.3 ELEMENTS

Since 1886, mining has been identified to be the driving force in the South African economy, despite the wealth emanating from it, severe negative impacts of these industries cannot be ignored simply because of the introduction of waste materials concentrated with TE's, Macro and Microelements into the natural environment (Nkobane, 2014; Nujoma, 2009; Tayab, 1991). It takes a considerable period of time in years for environmental impacts of mining activities to graduate to a level that can be critical and by the era in which the effects start to show, the mine has already appreciated closure (Naidoo 2014; Nkobane 2014; Singo, 2013).

Macroelements (for plants) are nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg); also refered to as macro plant nutriens. Whereas Microelements are iron (Fe), manganese (Mn), zinc (Zn), boron (B), copper (Cu), molybdenum (Mo) and silicon (Si), also refered to micro plant nutrients. Thise mineral elements are present in much smaller amounts in plants and are important for the functioning of organic compounds (FSSA, 2OO7). However, Macro and Microelements leached in this study is only Ca, Mg, K, Zn, Mn and Cu.

Potassium (K) play a crucial role in plants. Plants require large amount of K compared to others elements. It plays a contributing function in the transportation of N in plants, translocation of starch and promote photosynthesis. Amongst other function K strengthen fibres and it has effects on the opening and closing of stomata. Nevertheless, K mobilises freely in plant (FSSA, 2007)

Magnesium also play a fundamental role in plant. It forms the nucleus of the complex chlorophyll molecule for photosynthesis to take place more effectively. Amongst other functions Mg contribute positively in the translocation of P and it moves freely in the plant (FSSA, 2007).

Calcium (Ca) as well form part of nutrients which contribute positively to the well being of a plant. Unlike K and Mg, Ca is immobile in plants and it promote protein formation. Calcium is also essential for the development and growth of plant cells. And therefore, it influences the quality of fruits and vegetables (FSSA, 2007). The importance of Microelements: Zn, Mn and Cu in plant has been discussed under TEs.

Trace elements are naturally occurring elements that form part of the soil environment or skin of the earth in trace amounts (Hooda, 2010; Singo, 2013; Tayab 1991) and in this study it derive from the ore, host rock or chemical additives in the reduction process.

Nyaba (2016), Pimentel & Coonrod (1987) and Singo (2013) described TE to be one of the categories of metallic elements and are toxic or poisonous at escalated concentration, however some of these metals such as Arsenic, Cadmium, Nickel and Chromium are unfriendly to agricultural produce even at low concentrations. The term TE was described by Moreno-Castilla *et al.* (1999) and Ricordel *et al.* (2001) to be any TE characterised by its association with pollution and toxicity. Furthermore, TE was the equivalent term for heavy metals, but it is not the case anymore; despite it applies to a group of elements like Cadmium, Copper, Chromium, Lead, Mercury and Arsenic.

Tailings are the results of ore processing after mining activities have occurred and they are the major source of TE dispersion to the natural environment (Doumett *et al.*, 2008; Feasby & Tremblay, 1995; Förstner, & Wittmann, 2012; Munyai, 2017). The dispersions of TE's to the environment manifest via a variety of processes such as erosion (water and wind), weathering and leaching. Distributed TE's are deposited either in soil (including agricultural land), surface water or leached to sub-

surface water and air. Due to their non-degradable nature, TE's are in all spheres of the environment (Förstner, & Wittmann, 2012; Munyai, 2017; Singo, 2013).

Some trace elements could cause severe negative impacts on the environment i.e. soil, plants and water. They reduce the fertility of agricultural soil or land leading to low or no production by means of replacing real nutrient elements, override the absorption of others, restrict the absorption of others and in combination with real plant nutrients they could become toxic substances (Mitchell, 2013 & Singo, 2013). Trace elements can also be mobilised at the acidic condition of pH less than 4. At this state, oxidation is at the focal point for AMD generation. Figure 1.1 below shows a variation in mobility of TE's from the different environmental condition. The black arrows indicate an increase in mobility according to the environmental condition. According to the diagram below Zn and U has high relative mobility in soil top profile (oxidising zone) and very low on-base profile (reducing zone).

Left diagram — Top Profile

Relative Mobilities	Oxidising (Environmental Conditions)
Very High	I
High	Mo U Se F Ra Zn
Medium	Cu Co Ni Hg As Cd
Low	Pb Be Bi Sb Ti
Very Low	Fe Mn Al Cr

Left diagram — Base Profile

Relative Mobilities	Reducing (Environmental Conditions)
Very Low	Al Cr Mo U Se Zn Co Cu Ni Hg As Cd Pb Be Bi Sb Ti
Low	
Medium	Fe Mn
High	F Ra
Very High	I

Right diagram — Humid

	Acid (Environmental Conditions)
	I
	Mo U Se F Ra Zn Cu Co Ni Hg
	As Cd
	Pb Be Bi Sb Ti Fe Mn
	Al Cr

Right diagram — Arid

	Alkaline (Environmental Conditions)
	Al Cr Zn Cu Co Ni Hg
	Pb Be Bi Sb Ti Fe Mn
	As Cd
	F Ra
	I Mo U Se

Figure 2. 1: The relative mobility of TE's in varying surface conditions (Plant *et al.*, 2000)

The transformation from former government to democracy contributed severely to TSF's present state due to rapid change of mine ownership via land claims, leaving

TSF's not rehabilitated. However, some of the tailings have been abandoned long before democracy. Regardless of the mining charter being recognised as the prime concern by government and industries, research proved on the magnitude of transformation in the mining industries is at best unreliable (Mitchell, 2013; Moraka & van Rensburg 2015; Yakovleva, 2017).

From the diverse existence of TE's on earth, only Cu, Zn, Cd, As, Pb, U, Co, Ni, Cr and Mn are of interest in this study. Their occurrence, uses and consequences to the soil, water and plants are discussed individually according to the element.

2.3.1   Copper (Cu)

Copper is the earliest industrial metal ever known to man. It occurs naturally within the crust in the form of sulphides minerals such as chalcopyrite, bornite and chalcocite as well as native copper. It is also found in the periodic table of elements having an atomic number of 29, the atomic mass of 63,546 g.mol,$^{-1}$ density of 8,9 g.cm,$^{-3}$ melting point of 1083° C and the boiling point of 2595° C (Clark et al., 1989; Nujoma, 2009; WHO, 2017).

According to Singo (2013) copper is that metal occurring naturally in every part of the environment; lithosphere, hydrosphere and biosphere. Copper is a prominent metal trace element used commonly in industries to manufacture electric conductors, air-conditioners, geysers and coins (Herselman, 2007; Nirel & Pasquin 2010; Nujoma, 2009).

Basic sources of copper metal are natural and anthropogenic sources. Natural sources include wind-blown dust, forest fires, decaying vegetation and sea spray, while anthropogenic sources of copper cover mining, metal production industries, phosphate fertiliser production industries and wood production industries. Copper metal does not mobilise easier and as a result, it is resistant to break down in the natural environment (Bonaventura & Johnson, 1997; Gavrilescu, 2004; Pilon-Smits & Freeman, 2006). Its resistant to breakdown makes it accrue in animals and plants tissues. The lowest acceptable concentration of copper in the soil for healthier plant growth is approximately 6 mg/kg. The toxicity of copper in soil environment occurs at

concentrations of approximately 150-400 mg/kg. (Baker & Proctor, 1990; Bradshaw, 1984; Raskin *et al.*, 1994).

Copper (Cu) as a microelements is located in the seed and growing parts of the plant and contribute positively in the respiration process, chlorophyll content and perform as a catalyst in many oxidation processes in plant. Dispite all its functions, Cu is immobile in plants (FSSA, 2007).

However, the target water quality range of copper is ≤ 0.2 mg/l. In certain site-specific basis for short-term irrigation, more than 5.0 mg/l of copper is acceptable (DWAF, 1996). The solubility of copper is controlled by a change in pH. Therefore, an increase in pH decreases solubility. As a result, in the acidic soil environment, the solubility of copper is high. From a geological point of view, copper metal is more abundant in mafic rocks comparing to sedimentary and metamorphic rocks (Barton & Johnson, 1996; Hemley & Hunt, 1992; Herselman, 2007). Apart from environmental impacts, copper also poses severe health impacts on human life.

2.3.2 Zinc (Zn)

Zinc is said to be the 24th diverse metal on earth crust (Dunham, 1974; Noble, 1974; Oro *et al.* 1990). Zinc is a trace element that occurs in air, water and soil. Mining, steel processing and combustion of coal and waste materials serve as anthropogenic sources of zinc. Zinc metal is characterised by an atomic number of 30, atomic mass: 65.37 g.mol,$^{-1}$ density: 7.11 g.cm,$^{-3}$ Melting point: 420° C and boiling point: 907° C. High concentration of zinc in the environment is influenced by mining activities. Like copper higher exposure to zinc negatively impact the survival of plants (Clark *et al.*, 1989; Gaur *et al.*, 2014; Renoux *et al.*, 2007).

Zinc plays a contributing role in plants. It activates enzymes, regulates the pH in the cell solution and positively contributes in the formation of chlorophyll and growth hormones. However, Zn deficiencies can be induced by an elevated soil-pH and has a severe negative effects on the structure, size, development of plant cells and it is relatively immobile in the plant (FSSA, 2007).

The movement of zinc metal is inversely proportional to change in pH. Geologically Zn is found more abundantly in magmatic rocks and some sedimentary rocks and materials such as shale and argillaceous sediments (Herselman, 2007; Kabata-Pendias & Pendias 2001; Kiekens, 1995). Zinc metal has both positive and negative impacts on human life. Zinc is an important nutritional trace element for plants and animals. Soil pH has a major effect on the concentration of Zn in the soil environment and its solubility increases with decreasing pH. The guideline value for Zn concentration in water ≤ 1.0 mg/l. However, > 5.0 mg/l of zinc concentrations in water is only acceptable for short-term irrigation and only for specific sites (Sharma *et al.*, 2007).

2.3.3   Cadmium (Cd)

Amongst all TE's, Cd is one of the greatest toxic element build-ups in the hydrosphere and lithospheric environments. Förstner and Wittmann (2012), Nagajyoti *et al.* (2010) and WHO (2017) reported that surface water contamination from Cd as a toxic TE's is due to industrialisation. Cadmium like Zn and Cu is known to enter the natural environment through processing from industries such as mining and phosphate mulch and it is insoluble in soil and that makes it to be more toxic (Gadepalle et al., 2007; Lombi et al., 2003; Osman, 2014). In a natural environment, Cd does not occur in segregation but as a patron element to Pb-Zn mineralisation (Snyder & Hendrix, 2008; WHO, 2017). According to ATSDR (2007), Singo (2013), Roberts (2014) cadmium is used as anticorrosive, electroplate on steel and, electric batteries, electronic components and nuclear reactors.

Cadmium is shining, silver-white, pliable and most resistent TE with an atomic number of 48, atomic mass$=112.4$ g.mol^{-1} and density of 8.7 g.cm^{-3} at 20° C. High concentration of Cd in soil threatens the entire soil ecosystem including the functioning of microorganisms together with earthworms which plays a primary role to proper soil structure (Aislabie *et al.*, 2013; Mao *et al.*, 2015; Snyder & Hendrix, 2008). However, Cd does not have any positive contribution to the wellbeing of animals, plants and human health (Corvalan *et al.*, 2005; Reganold & Wachter, 2016; Welch, 1993).

pH of soil plays a significant role in the concentration of Cd in the soil solution. The solubility of Cd in soil increases with a decrease in pH. The target water quality range of Cd is ≤ 0.01 mg/l. As a result, conservative measures are needed because of its potential to accumulate in plants and soils to concentrations that may be toxic to humans and animals. At concentrations > 0.05 mg/l of Cd, such water is only acceptable for short-term irrigation and only for specific sites. (dwarf). According to Nenwa (2012), the soil screening value of Cd for all land use is 7.5 mg/kg.

2.3.4   Arsenic (As)

Like other elements such as Zn, Cu and Cu to mention few, As is a TE occurring naturally in the earth's crust. The chemical classification of As fall under metalloids and this is due to As exhibiting the properties of both metals and non-metals; however, As is usually noted as a metal (ATSDR, 2007; Caudill, 2003). A report from Mandal & Suzuki (2002), NIEHS (2014), Wuana & Okieimen (2011) announced that arsenic is commonly found in water, air, soil and food.

It implies that As by its nature is found in almost every sphere of the environment. Arsenic is distributed to the environment from anthropogenic activities such as mining and commercial industries or during processing of most valuable metal such as gold from gangue or waste materials. Natural processes such as volcanic eruption contribute to the concentration of arsenic into the atmospheric environment (Fennelly, 1976; Pacyna, 1987; Smedley & Kinniburgh, 2002). Chemically arsenic has an atomic number of 33, atomic mass=74.91 g.mol^{-1} and is found in group four of the periodic table with valence electrons of five (ATSDR, 2007; Caudill, 2003; Pandey, 2004).

High concentrations of As in soil environment affect negatively the bioavailability of living organisms such as algae, fungi and bacteria from effectively playing their bioremediation role of minimising the toxicity of inorganic contaminants in soil environment (ATSDR, 2007; Caudill, 2003; Zou *et al.*, 2010). According to Brown & Ross (2002), Ng (2005), WHO (2010) subsurface water is more prone to Asa contamination and utilisation of such water, may cause detrimental health effects to

the soil (particular agricultural soils), humans and animals either by drinking or preparing food with such water. Soil pH has impacts on the concentration of As in the soil solution. Change in pH from acidic to alkalinity controls the solubility of arsenic in the soil solution. When pH decreases the solubility of As increases. According to NEMWA (2014), the soil screening value of arsenic is 5.8 mg/kg for all land uses. Concentrations of ≤ 0.1 mg/l of As in water satisfy the water quality standards for agricultural use. Depending on the type of plants, nutrients solution containing 0.5- 10 mg/l of As can induce toxicity. For short-term irrigation > 2.0 mg/l of As is allowed, but only for site-specific basis (DWAF, 1996).

2.3.5 Lead (Pb)

Lead is a TE occurring naturally in the earth's crust. It is occasionally found in isolation within the environment. It occurs in amalgamation with other elements as a compound (ATSDR, 2007; Caudill, 2003; WHO, 2010). Chemically Pb is characterised by its atomic number of 82, atomic mass=207 and is found in group 14 of the periodic table. Geologically, it is abundantly found in sedimentary rocks like black shale (McLennan & Taylor, 1991; Stallard & Edmond, 1983; Zou *et al.*, 2010). The concentration of Pb is low in the Earth's crust with respect to quantity and is usually found as a compound of lead sulphide. The wide distribution of lead throughout the environment are the result of many anthropogenic activities such as extraction of valuable metals from the earth's crust, metal processing, utilisation of Pb-rich fuel and manufacturing of Pb-rich batteries (Carter & Norton, 2007; do Costa, 1998; WHO, 2010).

Ecological functioning may be disturbed by the high concentration of Pb in soil and water. Plants uptake certain compounds of Pb from soil to its different parts or branches and as a result, its growth becomes affected. Most animals and or insects are affected by plants serving as a habitat or food. The banning of Pb for the production of fuel and paint to mention few have played a crucial role in the reduction of Pb concentration on the environment. At pH between 5.5 and 7.5 Pb availability for plants, uptake is usually found to be very low and this condition is controlled by phosphate or carbonate precipitates regardless of plants ability to absorb Pb. Soil pH

has a major effect on the concentration of Pb in soil solution and its solubility decreases with increasing pH. Toxic effects of lead have been observed in nutrient solution at concentrations of 1 mg/l. Lead concentrations tend to be higher in roots than in leaves, or in the fruit parts of plants. Guideline concentration of lead for agricultural water quality range is approximately ≤ 0.2 mg/l and higher than that is toxic. Lead concentration of > 2.0 mg/l is only accepted for short-term irrigation specifically on recommended sites. Furthermore, the NEMA (act no 107 of 1998) guideline value for concentrations of Pb in all land use is 20 mg/kg. However, the availability of Pb in soil and water is still a concern. (Sharma & Dubey, 2005; WHO, 2010).

2.3.6   Uranium (U)

Uranium is a radioactive and potential toxic element that occurs naturally within the earth's crust. It is found in soils, rocks, water and plants. Uranium occurs more abundantly than gold, silver or Hg, and it can be discovered in more than 50 minerals (Nilsson & Randhem, 2008; Pan *et al.*, 2018). Depending on the deepness of the deposit and ore grade U can be extracted by any mining method (Hore-Lacy, 2010; Nilsson & Randhem, 2008). With regards to it's chemical properties, U has an atomic number of: 92, atomic mass: 238.03 $g.mol^{-1}$ and the density:18.95 $g.cm^{-3}$ (Albright *et al.*, 1993; Grenthe *et al.*, 1992; Grenthe *et al.*, 2008).

Harrison (2001), Nielsen and Knudsen, (2013), Mello *et al.* (2013) reported that U is considered to be one of the first radioactive elements that was formed in times of the global-forming event and mainly occurs in the oxidised environment. The three types of mining methods usually used for extraction of U are; open cast mining for deposit located close to the earth's surface, underground mining for deposit located deep within the earth's crust and in situ leaching for deposit located in subsurface water sources. Underground mining for removing U was proved to be the dominant method in the world (Mtimunye, 2015; Seredin *et al.*, 2013; Tatiya, 2005).

Uranium is commonly used in the development of nuclear weapons, medical treatment, power supply etc. This process starts with mining as a source of U to

milling for separation of U from the unwanted materials, and enters the environment either contaminating water and soil. Plants respond to U concentration in the soil solution and similar to most TE's, U is absorbed by the soil. The solubility and speciation of U in the soil are controlled by pH, microorganisms and phosphate concentration. Uranium commonly accumulates within the roots of plants and it has been reported that vegetables can concentrate U to levels which are 100 times that of the irrigation water. The allowable level of U concentration in for agricultural water quality and suitability of soil is ≤ 0.01 mg/l. However, plants yield remains unaffected at U concentrations of less than 10 mg/kg in the soil. The maximum acceptable concentration of U in irrigation water is > 0.10 mg/l, and only under exceptional conditions (Harrison, 2001; Kabata-Pendial, 2010; Lábusová, 2013).

In geologic materials U is highly concentrated in igneous rocks, some of the sedimentary materials, and phosphate compounds. It is also abundance in seawater, subsurface water and surface water. In underground water, U concentration is influenced by rocks in contact with the flow of water and as such the level of U becomes elevated (Akcil & Koldas, 2006; Watanabe & Olsen, 1965; Zhou & Gu, 2005).

2.3.7 Cobalt (Co)

Cobalt is a naturally occurring TE within the earth's crust in carbonate rocks. It is chemically characterised in terms of atomic number: 27, atomic mass: 58.93 $g.mol^{-1}$ and a density: 8.9 $g.cm^{-3}$ at 20° C. Its application is dominant in nuclear reactors. However, most of the cobalt is concentrated in the core of the earth in amalgamation with other metals (Ambers & Hygelund, 2001; Liu & Motoda, 1998; Smith & Huyck, 1999). Cobalt usually occurs at an oxidation state of negative one to positive four and in nature, it is found as a Co compound. At acidic condition or low pH, Co becomes soluble and mobilised (Baralkiewicz & Siepak, 1999; Bosle *et al.*, 2016; Gill, 1956). In other words, Co mobility runs in a linear form with soil pH. Cation exchange capacity of soil with low organic matter like sandy soil influence leaching of Co to be moderate.

Can *et al.* (2012), Huijbregts *et al.* (2000), Wright & Welbourn (1994) reported that the environmental toxicity of Co differs according to the environment; terrestrial ecosystem, freshwater environment, continental aquatic environment and marine environment. Furthermore, excess concentrations of Co (up to 5000 mg.kg^{-1}) in the soil for uptake by plants severely affect photosynthesis processes leading to low production of chlorophyll. Soil pH has a significant impact on the concentration of Co in the soil solution and its solubility decreases with increasing pH. Cobalt by its nature is not classified as plant nutrients, but it appears to be of great importance for some plants. Cobalt concentration in the range of 0.1-5 mg/l has been found to be toxic to a number of food crops when added to nutrients solutions. Cobalt concentration of 0.1 mg/l was found to be toxic to tomatoes and this toxicity threshold also applies to other plants. 0.5 mg/l concentration of Co works for all soils. Therefore, ≤ 0.05 mg/l of Co determine the quality of irrigation water (Can *et al.*, 2012; Chatterjee *et al.*, 2010).

2.3.8   Nickel (Ni)

Nickel like other trace elements discussed above is a naturally occurring TE in the earth's crust and is rated twenty-fourth abundant element within the crust of the earth (Carpenter *et al.*, 1998; Tilman *et al.*, 2002; WHO, 2017). Nickel has an atomic number of: 28, atomic mass: 58, 71 g.mol^{-1} and density: 8.90 g.cm^{-3}. Unlike other TE's, nickel is unevenly distributed within the three layers of the earth namely; mantle, core and the crust (Hamilton, 1994; O'Neill & Palme, 1998). According to Hamilton (1994), Kabata-Pendias (2010), O'Neill and Palme (1998) Ni is a crucial TE in animal's health even though the biological importance of it has not yet been established. Geology plays a contributing factor on the background level of Ni in soils (Kabata-Pedias, 2010; Zhang *et al.*, 2002). It is dispersed to the environment via the burning of fuel oil, incineration of municipal waste, steel processing, Ni processing and suspended dust from wind erosion. It is used in different industries for the production of batteries, electroplating, coins, jewellery and in ceramics (Meena *et al.*, 2005; Purcell & Peters, 1998; Winder, 2004).

Nickel poses negative impacts on water, soils and plants. Generally, the concentration of Ni in unpolluted water is 0.0005 mg/l and in seawater is approximately 0.0006 mg/l. However abundant Ni concentrations may be found around mines where the ore yield Ni. The concentration of Ni in the soil is controlled by soil pH. Solubility and mobility of Ni in soil solution decreases with increasing pH. Nickel by its nature is not considered to be essential plant nutrient, but some evidence has emerged that in its small quantity it can improve growth of some plants. Guideline value for nickel concentration in agricultural water quality is ≤ 0.20 mg/l. The concentration of 0.5 mg/l in water culture is toxic to flax and > 2.0 mg/l is acceptable for short-term irrigation specifically for site-specific basis. Depending on plant species, nutrients solutions containing $0.5 - 1.0$ mg/l can induce nickel toxicity. The soil screening value of Ni for all land use is 91 mg/kg, but it can overlap up to 10000 mg/kg for commercial industries.

2.3.9   Chromium (Cr)

Chromium is a naturally occurring TE in the crustal rocks and it is more abundant in ultramafic rocks and sedimentary rocks such as shale. It has an atomic number of 24, atomic mass: 52 $g.mol^{-1}$ and density of 7.19 $g.cm^{-3}$. It exists in the environment in two forms; Cr(III) which is important for nutritional purposes and Cr(VI) which is highly toxic to humans and animals and may persist considerably in soils, sediments and natural waters (Al-hogbi, 2006; DeSarle, 2014; Fendorf, 1995). Chromium is also described as a transition TE that exists in varieties of isotopes in terms of oxidation state ranging from Cr(III) to Cr(VI) and it is used for industrial purposes such as leather tanning, Cr plating, timber preservation and corrosion protection (Darrie, 2001; DeSarle, 2014; Enghag, 2004).

In plants Cr(VI) imparts severe impacts on the event of photosynthesis and transpiration of stomatous functioning (Grybos *et al.*, 2007; Nkobane, 2014; Subrahmanyam, 2008). The pathways of Cr to the environment in particular surface water take place in either natural way of which the process is through weathering of rocks containing Cr or leaching from soils or TSF and man practices via direct discharge from industrial processes (Khandoker, 2017). The mobility of Cr(III) in soil

is controlled by soil pH (Grybos *et al.*, 2007; Kumpiene *et al.*, 2008; Nkobane, 2014). Chromium concentrations in the soil solutions are largely determined by sorption and desorption reactions with soil exchange complex. Chromium(III) oxidises readily to Cr(VI) under field conditions; organic matter and manganese oxides are significant electron acceptors in this reaction. The oxidation of Cr from one state to another depends on the prevailing redox condition of the soils. The solubility and mobility of Cr like other discussed TE's is controlled by a change in pH. Chromium solubility decreases with increasing pH. As compared to Cr(III), Cr(VI) is more mobile in soils and thus can be leached into groundwater. Like Cd, Cr is not an essential plant nutrient but at low concentration, it was found that it can be beneficial for the growth of certain plants. Both Cr(III) and Cr(VI) are found to be equally available to plants in nutrients solution. The toxic effects of Cr(VI) range from 5 to 500 mg/kg and 50 to 5000 mg/kg for Cr(III). Guidelines concentration of Cr in water is ≤ 0.10 mg/l and > 1.0 mg/l is only acceptable for short-term irrigation at certain sites. Depending on the type of plants, nutrients solutions containing 0.1 mg/l can induce Cr toxicity. Chromium (VI) soil screening value is 6.5 mg/kg and 46000 mg/kg of Cr(III) for all land use.

2.3.10 Manganese (Mn)

Manganese is a naturally occurring MTE in the earth's crust and it is rated number five in terms of its dominance and number twelve in terms of the gross elemental abundance. It has an atomic number of 25, atomic mass: 54.94 g.mol^{-1} and density of 7.43 g.cm^{-3} (Chakraborty, 2015; Martin & Whitfield, 1983; McLaughlin *et al.*, 1999). However, Greaney (2005), Maharaj (2003), Morgan & Maitland (1997), defined Mn as a naturally occurring element found in unspoiled water, flora and fauna. The concentration of Mn in the earth's crust ranges between 0.085% to 0.095% of the crust with special emphasis given to metamorphic and sedimentary rocks as primary host (Corfu & Stone, 1998; Spry *et al.*, 2007).

Anthropogenic sources of Mn are mining, mineral processing, burning of fossil fuels, contaminated water discharge, sewage sludge, iron and alloy processing industries (Fuge, 2013; WHO, 2004; Wuana & Okieimen, 2011). Manganese unlike few other

TE's like Cd has bio-importance properties. It is a vital micronutrient for human beings with the standard allowable consumption of 2-3 mg per day in the case of adults (Balkhair & Ashraf, 2016; Chen *et al*., 2016; Schowanek *et al*., 2004). Manganese play a contributing function in the photosynthesis and in oxidation-reduction reactions and promote the uptakeof nitrates, metabolism of iron in the plant and enzyme activities and it is immobile in the plant (FSSA, 2007). The effect of soil pH is to decrease the Mn concentration in the soil solution as soil pH increases. Manganese toxicity seldom occurs at soil pH above 5.5 – 6.0. Target water quality range ≤ 0.02 mg/l is good for crop yield and soil sustainability. Manganese concentration of > 10.0 mg/l is only acceptable for short-term irrigation on a certain specific basis. Soil screening value of Mn element for all land use is 740 mg/kg and it can overlap up to 12000 mg/kg for commercial use.

2.4 PHYSICAL and CHEMICAL PARAMETERS INFLUENCING THE MOBILITY OF TRACE ELEMENTS IN SOIL

2.4.1   Physical parameters

2.4.1.1   Particle size of tailings (texture)

Particle size distribution (PSD) and surface area of tailings materials perform an important part in the susceptibility kinetic and mobility of TE's. Small materials have a great surface area and therefore higher chemical activity i.e. adsorbtion, cation exchange, weathering, reaction with water, air etc wherein large materials have smaller surface area. The morphology and size of soil particles rely on the nature of mining method commissioned (Azcue, 2012; Blight, 2009; Dacosta & Reid, 2014). This property of tailings materials contributes a controlling role on the permeability of the materials (Benzaazoua *et al.*, 2004; Nehdi & Tariq, 2007; NRC, 2007). According to Buol *et al.* (2011), Eshel *et al.* (2004) and Isbell (2016), PSD provides a clear understanding of the textural classification of soil (sand, silt and clay).

2.4.1.2   Bulk density

Density is described as mass per unit volume of a material (Crawford, 2013; Gardner, 1986; Grossman & Reinsch, 2002). Bulk density is also described as the physical parameter employed for the characterisation of tailings materials or any other solid mediums together with the calculations of the volume of such materials denoted in $g.cm^3$. Bulk density as a physical property plays an important part in tailings analysis, however, it is rarely been done. It is an indicator of tailings compressibility and is controlled by certain factors such as soil structure, organic matter , porosity and the tailings mineral density (Jury & Stolzy, 2018; Ranjan & Rao, 2007; Van den Akker & Soane, 2005). The weight of dry tailings per unit volume is also referred to as bulk density. Therefore, this type of physical parameter plays a crucial role in the mobility and leaching of TE's. This is because bulk density reflects the tailings material ability to function for structural support, water and solute movement, PSD and tailings aeration (Hillel, 1998; Kay & Angers, 2001; Lal & Shukla, 2004).

2.4.1.3   Compaction

Compaction is explained as a mechanical technique that increases the bulk density of the tailings material (Hamza &Anderson, 2995; Multiquip, 2011; Smith *et al.*, 1997). Tailings material compaction takes place as tailings material bulk density increases due to energy into moist or wet tailings material. Compacted tailings cannot function properly because particles are interlocked with each other in a manner that no void spaces are left which result in poor establishment and production of crops. This results in decrease rainwater infiltration and aeration, which increases surface runoff and tailings material erosion (Greene *et al.*, 1994; Morin & Benyamini, 1977; Wallbrink & Murray, 1996). This factor positively contributes to trace elements leaching and mobility.

2.4.1.4   Hydraulic conductivity

Hydraulic conductivity is somehow mostly preferred than permeability. Hydraulic conductivity considers the characteristics of the fluid and sediments (Chapuis & Aubertin, 2003; Wang *et al.*, 2004; Vogel, 2000). Hydraulic conductivity varies in vertical and horizontal directions (transmissivity), huge strains take place in tailings dam materials, the occurrence of layering and commonly layers of clay (Bear, 2013; Blight *et al.*, 2010; Moldrup *et al.*, 2001). As a result, this property has a role on leaching and movement of TE's from mine tailings material.

2.4.1.5   Permeability

Permeability is one of the physical properties that positively influence the leaching of TE's from mine tailings material. It elucidates the capacity for a fluid to move via a porous medium. In situation where tailings dam is located next to the water system, permeability decreases more towards the centre of that particular pond or water body and that is due to particles size and volume of the pore spaces within the tailings materials and it varies according to particle size distribution of that particular tailing of which is due to a variation in segregation and sedimentation during tailings deposition (Blight, 2010; Verruijt, 2010; Vick, 1990).

2.4.1.6   Climate of the area

Climate is described as the average weather condition of an area and it is generally described in terms of variables such as wind, temperature and precipitation (Brower *et al.*, 1998; Goosse *et al.*, 2010; Stenseth *et al.*, 2003). The Republic of South Africa is characterised by the warm climate and almost the whole country experiences average annual temperatures of above 17° C and average annual rainfall of 450ml with four seasons: summer, winter, spring and autumn (Maurer *et al.*, 2002; Stewart & Oke, 2012). Therefore, for the process of leaching to take place rainfall is needed and as a result, high rainfall and temperatures   contributes positively to TE's solubility and mobility.

2.4.2   Chemical parameters

2.4.2.1   *pH*

pH is a measure of acidity or base of a mixture. According to McLean (1982) and Thomas (1996), pH is defined as the negative logarithm of the hydrogen ion concentration. Angelow *et al.* (2006), Singo (2013) and Turner *et al.* (1981) reported that pH ranges from 1-14 and subdivided into three segments; acidity (less than 7), neutral (equals to 7) and base (greater than 7). Tailings pH is an important tool to anticipate diverse chemical venture in tailings (Ansah, 2017; Nkobane, 2014). It plays a significant role in sorption, desorption, precipitation, dissolution and oxidation-reduction potential (Ansah, 2017; Draszawka-Bolzan, 2017; Singo, 2013). It impacts the process of continuous holding-up of TE's in the tailings. This process of TE's retention manifests either directly or indirectly in the soil. pH plays a crucial role in the movement of TE's from tailings to tailings environments. This is because pH has a significant impact on the solubility of TE's in tailings. In most cases, a low pH tends to lead to an increase in solubility and a consequent increase in the bioavailability and mobility of most TE's (Kabata-Pendias, 2004; Kabata-Pendias, 2010; Rattan *et al.*, 2005; Rieuwerts, 2007).

The availability of macro and microelements in water is controlled by the pH. Potassium availability is more abundant at pH 7.5 and 6.0 then decreases with pH, Ca is more abundant between pH 6.5 and 8.5, Mg between pH 6.5 and 8.5, Zn between pH 5.0 and 7.0, Cu between pH 5.0 and 7.0, Mn between pH 5.0 and 6.5 respectively (FSSA, 2007: 94)

2.4.2.2   *Electrical Conductivity (EC)*

According to Babu & Chempakam (2010), Mitchell *et al.* (2013) and Moleme (2017) EC can be defined as the capacity of substances to disseminate or conduct an electrical current and is habitually indicated in units of mS/m or dS/m. It has a great effect on soil microbial population, organic matter quantity and salinity. In terms of salts, EC only indicates the presence but not the type of such salts. For instance, EC methods can only detect the availability of salt but not the specific type of salt (e.g.

Na, Mg, K / sulphates, chlorides, or nitrates salts etc.) (Bernstein, 1975; Halliwell, 1978; Parida & Das, 2005). Tailings are commonly sandy to silty and they have an EC up to 10000 times that of natural soils and is an indication of the total soluble salts contents of the primary minerals. The variation in EC is influenced mainly by the mineralogy of the host rock and climatic factors such as rain and temperature (Cappuyns & Swennen, 2008; Fellet *et al.*, 2011; Förstner & Wittmann, 2012)

Hatje *et al.* (2003) and Marchuk (2013) further outlined that salinity is a primary driver for EC to take place in the tailings solution. It has some negative effects on agricultural practices only if it is in excess and it results in negative osmotic pressure (Marchuk, 2013; Rengasamy, 2010; Du Laing *et al.*, 2007a). It was elucidated that an increase in mobility of TE's in tailings is directly proportional to the increase in salinity (De Laing *et al.*, 2007a; Hatje *et al.*, 2003; Paalman *et al.*, 1994).

Conductivity is classified interms of low-1, medium-2, high-3 and very high-4 (FSSA, 2007: 71). Sodium adsorption ratio (SAR) and EC determine the salinity hazard of irrigation water (FSSA, 2007). Water with Low salinity harzard can be considered to be good water for irrigation. Water with medium salinity hazard ,may only be considered on certain conditions such as well drained soils with regular monitoring of salts and Na. However, water with high salinity hazards should not be used for irrigation (FSSA, 2007). Therefore, conductivity increases with increasing salinity in tailings and that can be controlled by means of effective monitoring of Na and salts in tailings (FSSA, 2007)

2.4.2.3   *Soil organic matter*

Organic matter forms through the process of decomposition of dead plants and or any perishable organic substances. Either via physical breakdown or biochemical processes (Bot & Benites, 2005; Brenner *et al.*, 1998; Salt *et al.*, 1995). The study conducted by Cong (2014) concluded that soil organic matter from the decomposition of plants increase biomass production, soil fertility and condemn emissions of greenhouse gases to the atmosphere. If the tailings are ameliorated with organic material i.e. compost and there are some TE's present in the tailings it

may affect typical soil fertility and reduces biomass creation (Anastassiadis, 2016; Nkobane, 2014; Singo, 2013). Application of organic matter is a common practice in tailings rehabilitation. It improves structure in tailings as well as CEC and water holding capacity and escalates soil carbon capacity and stimulates biological activities (Haller, 2017; Rahman *et al.,* 2016; Sharma *et al.*, 2018).

2.4.2.4 *Cations and anions exchange capacity*

The capacity of the soil or any fine particle like organic material to hold on to the cations is called cations adsorption capacity (sometimes also referred to cation exchange capacity) and the higher the organic carbon content, the higher the CEC. Whereas the lower the cations exchange capacity of soil or any fine particles the faster the pH will decrease with time and these is because low adsorption capacity for cations and H-ion will take the place of the cation on the exchange complex (Havlin *et al.*, 2016; Robertson & Groffman, 2007; Saichek & Reddy, 2003).

The leaching of cations and anions from mine tailings material and or in situ rocks are very much been influenced by redox and pH conditions. When the pH is lower than 4 at the acidic condition the rate of cation solubility and consequently the leaching ability increases. Examples of cations of importance in this study are Ca, Na, K and Mg and anions are sulphates, phosphates, nitrates, chloride for fertility purposes and the others for plant toxicity as well as negative influence to microbial activity etc. (Acosta et al., 2011; Gillman & Bell, 1978; Richter *et al.*, 2005).

2.4.2.5 *Redox potential*

Redox potential is described as a measure of the oxidation-reduction potential of electrode reactive components in the soil. Redox potential is an electrical measurement that shows the tendency of a soil solution to transfer electrons to or from a reference electrode. Redox potential measurements give an indication of either the soil or mine tailings is chemically oxidised or reduced (Albert *et al.*, 2013; Norby *et al.*, 2007; Vepraskas & Cox, 2002).

Oxidation and reduction conditions in mine tailings are subject to variations that affect the element it may contain, Fe and Mn in particular, although Cr, Cu and Pb are also influenced. The redox status of soil and tailings are described conceptually by using the aqueous electrons (Nkobane, 2014). When the redox potential value is high, the soil and water environments are well aerated. On the other hand, as the redox potential value is low, the soil environment is saturated, which means that there is no oxygen in the soil, causing other electrons acceptors to begin functioning (Chuan *et al.*, 1996; Miller *et al.*, 2004; Nkobane, 2014). Therefore both redox potential and pH greatly affects TE's solubility in the soil (Chuan *et al.*, 1996; Miller *et al.*, 2004; Nkobane, 2014).

2.4.2.6 *Water soluble elements*

Solubility is a chemical property referring to the ability of a given substance (solute) to dissolve in water. The resulting solution is termed saturated solution. Solubility range widely from infinitely soluble such as ethanol in water, to poorly soluble (chloride) in water (Beesley *et al.*, 2010; Schott, 1966; Vasconcelos *et al.*, 2007). Water is the vehicle for transport of solutes including TE's in soil. The mobility of dissolved trace elements in soils depends primarily on their concentration gradient spatially and the mass flow of water (Brown *et al.*, 2002; Naidu *et al.*, 1994). The water-soluble elements determine the concentration of substances in the soil solution. The toxicity of water-soluble elements may be due to their ability to generate free radicals via redox cycling with biological reductants (Brown *et al.*, 2004; Kabata-Pendias, 2001).

2.5 WATER QUALITY

Water can be defined as a natural resource that is fundamental to support any form of life (Tietenberg & Lewis, 2016). Whereas "water quality" is described as the suitability of water to support life (WHO, 1996). According to DWAF (1996), the term water quality defines the physical, chemical, biological and aesthetic properties of water which determines its fitness for a variety of uses and for protecting the health and integrity of aquatic ecosystems.

Leaching of TSF contributes severely to water quality reduction downstream or below the TSF. The extent of pollution is measured against the use of such water. The concentrations of chemical parameters such as TE's or any other pollutant is measured against the guideline standards for a different use (DWAF, 1996). The table below presents the SSV of TE's relevant to the objectives of this study.

Table 1.1 below shows different types of SSV (SSV1-SSV2) as published by the South African Department of Environmental Affairs on 19 March 2012. These national norms and standards were used as threshold limits or standard guidelines for remediation of contaminated land and soil quality.

"Soil screening value 1" refers to soil quality values that are protective of both human health and eco-toxicological risk for multi-exposure pathways, inclusive of contaminant migration to the water resources.

"Soil screening value 2" refers to soil quality values that are protective of risk to human health in the absence of a water resource.

Table 1. 1: SSV's for trace elements (TE's) (NEMWA, 2012)

Parameter (mg/kg)	SSV1	SSV2	SSV2	SSV2	Protection of Ecosystem Health
	All Land uses Protective of the Water Resources	Informal Residential	Standard Residential	Commercial or Industrial	
As	5.8	23	48	150	580
Cd	7.5	15	32	260	37
Cr (III)	46000	46000	96000	790000	
Cr (VI)	6.5	6.5	13	40	260
Co	300	300	630	5000	22000
Cu	16	1100	2300	19000	16
Pb	20	110	230	1900	100
Mn	740	740	1500	12000	36000
Ni	91	620	1200	10000	1400
Zn	240	9200	19000	150000	240
U	16				

CHAPTER THREE: MATERIALS AND METHODS

3.1 MATERIALS: GEOLOGY, MINERALOGY AND CLIMATE

A general description of the geology (lithology and mineralogy) and climate of each study area where the tailings samples were taken from are provided in this chapter. The motivation for geological and climatic information are there major influence on weathering potential as well as leaching and solubility of the primary minerals. It could also fit with Chapter two, but due to the very site and material specific characteristics and it's influence on the leaching quality, it was decided to to put it with Chapter three.

Figure 3.1 shows sampling localities and Table 3.1 is a stratigraphic summary of the main lithologies which are of concern in this research project.

Figure 3. 1: **South African Google Earth Photograph showing all sampling localities of this study**

Table 3. 1: Stratigraphic sequence of selected sites in South Africa that is applicable to this research study (Johnson *et al.*, 2006)

Age (from young to old)	Regional geology	Local geology	Locality	Sample no.
225-150 Ma	Karoo Supergroup	Ecca Group & Vryheid Formation	Witbank CoalField (TSF)	TJ3
1200 Ma	Pre-Karoo Kimberlite Intrusion	Kimberlite	Cullinan area, Gauteng	TJ2
1200-1000 Ma	Namaqua Natal Metamorphic Complex	Bushmanland Group	Aggeneys (TSF)	TJ6
		Nama Group-Spektakel Suit	Spektakelberg mine (TSF)	TJ1
		Okiep Group-Koperberg Suit	Okiep copper mine (TSF)	TJ9
1759 Ma	Post-Karoo Kimberlite	Kimberlite	Samada diamond mine	TJ12
2060-2050 Ma	Bushveld Complex	Merensky Reef	Paardekraal mine	TJ19
2060.6±0.5 Ma	Phalaborwa Complex	Carbonatite complex	Phoscorite & PMC mine	TJ23
2555-2222 Ma	Griqualand West Basin	Ghaap Group & Gamagara Formation,	Manganese mine (TSF)	TJ25
			Sishen Iron mine	TJ5
		Maremane Formation		
2650-2970 Ma	TransvaaL Supergroup	Chuniespoort & Black ReefFormation	New Machavie mine (TSF)	TJ20
3074-2714 Ma	Witwaterrand Supergroup	Central Rand Group	East rand gold mine (TSF)	TJ15
3090-2970 Ma	Murchison Greenstone Belt	Weigel Formation	Antimony (TSF)	TJ22
3500-3200 Ma	Barberton Complex (Barberton Greenstone Belt-Barberton Supergroup	Fig Tree Group-Mapepe Formation	Revolvervlei gold mine (TSF)	TJ24
		Swaziland Supergroup	Kalgold gold mine (TSF)	TJ 4

3.1.1 TJ1-Spektakelberg and TJ9-Okiep copper mines, Springbok (Northern Cape)

Spektakelberg copper mine is located west of Springbok, Northern Cape Province of South Africa, between latitude 29º 39' 48.32" south and longitude 17º 52' 47.47" East. See Figure 3.2 and Table 3.1 for more detail.
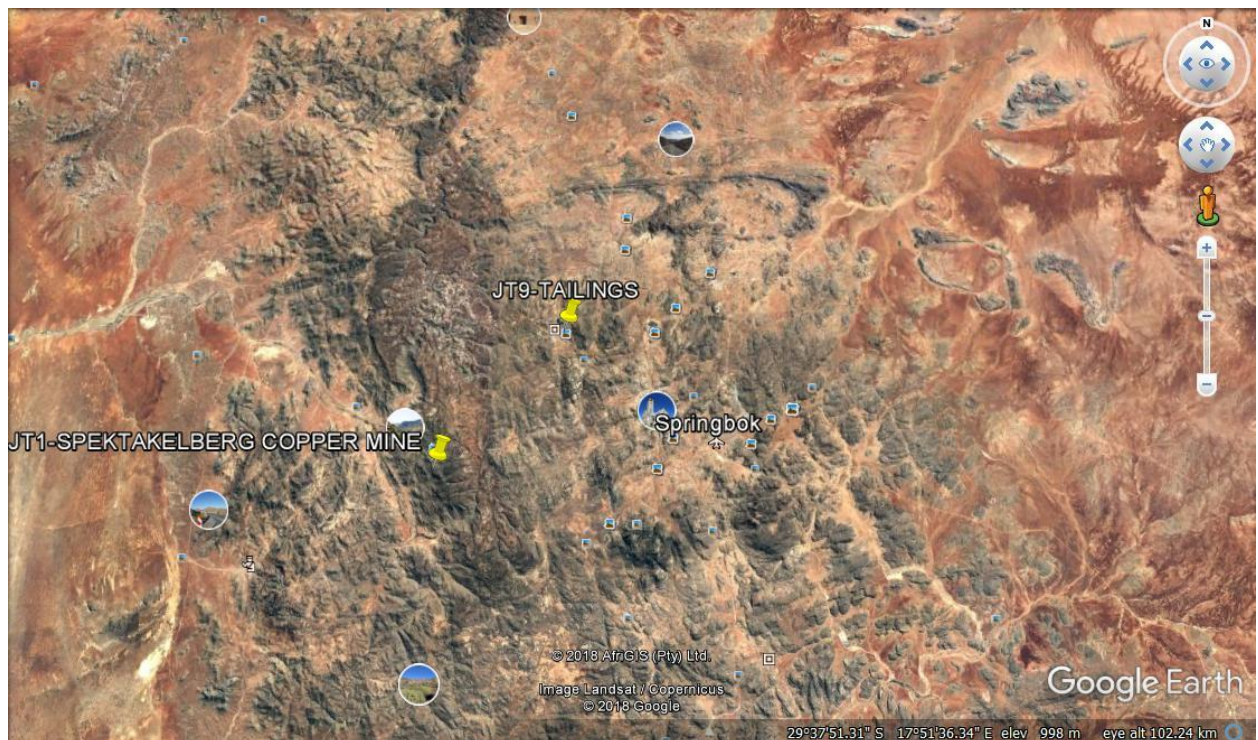
Figure 3. 2: **Google Earth Photograph showing the location of Spektakelberg (JT1) and Okiep copper mines (JT9) in Springbok, Northern Cape of South Africa**

Whereas the Okiep copper mine is located north-west of Springbok in the Northern Cape Province of South Africa, between latitude 29º 34' 59.49" south and longitude 17º 47' 06.92" East. It is the oldest formal mining area in South Africa. Historically copper in this area was mined and gained in Namaqualand by indigenous Namaqua people long before the explorer Piet Van Meerhof (Clifford & Barton, 2012; Tutu *et al.*, 2008).

3.1.1.1 Climate of the area

The climate is typically that of desert and semi-desert areas. It is generally hot and dry region with fluctuating temperatures and generally low rainfall. The annual rainfall is sparse, only 50 to 400mm per annum. The average annual rainfall within the Northern Cape Province is approximately 202 mm. Namaqualand receives most of its rainfall during winter and the temperatures range 0^oC to 15^oC, whereas summer temperatures range between 25^oC to 35^oC. Physical weathering dominates the disintegration of primary minerals and the chemical phase is only applicable in the toxicity potential.

3.1.1.2 Geology and mineralogy

The geological setting of Okiep mine are within the Northern Cape province of South Africa in the Nama Group. The Nama Group together with Vanrhynesdorp Group is deposited in a peripheral Foreland Basin that developed inboard of the Damara, Gariep and Saldania Belts as a result of lithosphere flexure in response to thrust loading. Part of the Nama Group deposited in the Witwatersrand puts Basins exposed in the Nababeep Plateau between Vioolsdrif and Springbok and West of Upington. The Nama Group is subdivided into the Kuibis and lower Schwarzrand Subgroup. The Kuibis becomes more clastic and displays four Sandstone Shale cycles compared with two in Namibia. Features probably related to microbial mat binding of Sand in the Proterozoic occurs in the Kuibis and lower Schwarzrand sandstone (Germs & Gresse, 1991). The Nama Group shows an increasing intensity of deformation towards the West in the direction of Gariep Belt and its lithology is characterised by Quartz Microcline Granite, Biotite and Feldspar (van Deventer, 2016; Clifford, Tom & Barton, Erika, 2012).

Lower Fish River Subgroups forms part of the Nama succession (Gresse *et al.*, 2006). Schwarzrand Subgroup is extensively eroded by the Fish River unconformity. The Fish River Subgroup contains Cambrian trace Fossils in the Namibia side of the Nama Group. (Germs & Gresse, 1991; Gresse *et al.*, 2006). Although already discovered in 1685, mining of Copper deposit in Okiep District in the North-Western

Cape Province only started in 1852 and continued a relatively small scale until1931. Okiep Copper Company limited operated on ore produced and ore still in reserve from 1940 till the end of 1979. The Okiep district covers 3000 km^2 (Lombaard & Exploration Department Staff of the Okiep Copper Company Limited, 1986).

The geological setting of the Okiep Gold Mine is of special interest because of the confinement of the deeper part of the Copper-bearing Intrusive to a steep-dipping pipe of Megabreccia.

The revelation was provided by Gresse *et al* (2006), to further provides details on the size and shape of the copper-bearing intrusive ore body to be of knifed shaped and steeply extends upwards for about 1000 m through Nababeep granite gneiss, Modderforntein granite gneiss and of which was the emplaced horizontally, mainly focussing on the outcrops of the Schist and Quartzite. The genesis of the Copper ores of the Okiep District is inextricably related to the origin of the Koperberg Suite. Wyley, (1857) cited from Lombaard and Exploration Department Staff of the Okiep Copper Company Limited (1986), concluded that feldspar rock came up in a state of fusion from beneath and as a result Copper was brought along. See Figure 3.2 and Table 3.1 for more detail.

3.1.2 TJ2-Cullinan Diamond Mine

Cullinan diamond mine is located in Gauteng Province of South Africa. The study area is situated about 25km east of Pretoria city in Cullinan, between latitude 25° 39' 14.89" South and longitude 28° 31' 5.06" East. The diamond mine is also known as Premier mine. See Figure 3.3 and Table 3.1for more detail.

Figure 3. 3: **Google Earth Photograph showing the location of Cullinan diamond mine tailings (JT2) in Gauteng Province of South Africa**

3.1.2.1 Climate of the area

The study area is characterised by warm and temperate climate. It receives high rainfall in summer as compared to winter. The average annual rainfall is 668 mm with an average annual temperature of 17.8°C. Gauteng enjoys a mild climate, characterised by warm, moist summers and cool dry winters. Most rainfall occurs October to March, with a mean annual precipitation of 668 mm (Jones *et al.*, 2000). Chemical weathering domnates the weathering process in the kimberlite tailings in this case.

3.1.2.2 Geology and mineralogy

Cullinan diamond mine is located on a diamond bearing Kimberlite Pipe. The Carrot-shaped pipe with a volcanic neck is considered to be the largest Kimberlite pipe of the region.

The Cullinan pipe outcrops in the Pretoria Group, 25 km East Northeast of Pretoria. The pipe intruded rocks of the Transvaal Supergroup as well as igneous rocks of the

Bushveld Igneous complex. This pipe is one of the largest (32 ha at the surface) found in South Africa (Field *et al.*, 2008; Strydom, 2015; van Deventer, 2016). Pretoria Group in the Transvaal basins is dominated by numerous alternating quartsites, mudrocks and mudstone units with lesser diamictite/conglomerate members and volcanic units that represent an alternation of alluvial sedimentation with epeiric marine sedimentation (Catuneanu & Erickson, 1999; Moore *et al.*, 2001; Strydom, 2015).

The Pretoria Group is subdivided into fourteen formations namely: Houtenbek Formation, Steenkamsberg Formation, Nederhorst Formation, Lakenvleil Formation, Vermont Formation, Magaliesberg Formation, Silverton Formation, Daspoort Formation, Strubenkop Formation, Dwaalheuwel Formation, Hekpoort Formation, Boshoek Formation, Timeball Formation and Rooihoogte Formation (Bartman, 2013; Catuneanu, 2002; Erickson & Reezko, 1995).

Kimberlite is a volcanic to hypabyssal ultrabasic rock (<45% silica content) that originate from volatile-rich (high content of carbon dioxide and water) magma, which ascend to the earth surface at speed up to 30 km per hour from more than 150 km deep within the mantle where the pressure and temperature conditions are favorable for diamond formation. It ultimately requires an ultramafic composition, meaning more than 90% of the mineral content is magnesium and iron-rich. Amongst all the characteristics of an intrusive body to be classified as kimberlite, the classic carrot-shape of the diatreme not being one of them. Kimberlite also occurs as dikes or sills (Catumeanu, 2002; Eggler, 1989; Strydom, 2015). Morkel and Saydam (2008), Strydom (2015) and Van Deventer (2016) confirmed the dominant minerals of the Cullinan kimberlite to be Olivine, Phlogopite, Serpentine, Perovskite and Calcite. See Figure 3.3 and Table 3.1 for more detail.

3.1.3   TJ3-Witbank Coalfield, Mpumalanga

The area of study is located within the Province of Mpumalanga, South Africa between latitude 26° 02' 00.00" south and longitude 29° 10' 00.00" East of

Mpumalanga Province and It is also called a Coalville. See Figure 3.4 and Table 3.1 for more detail
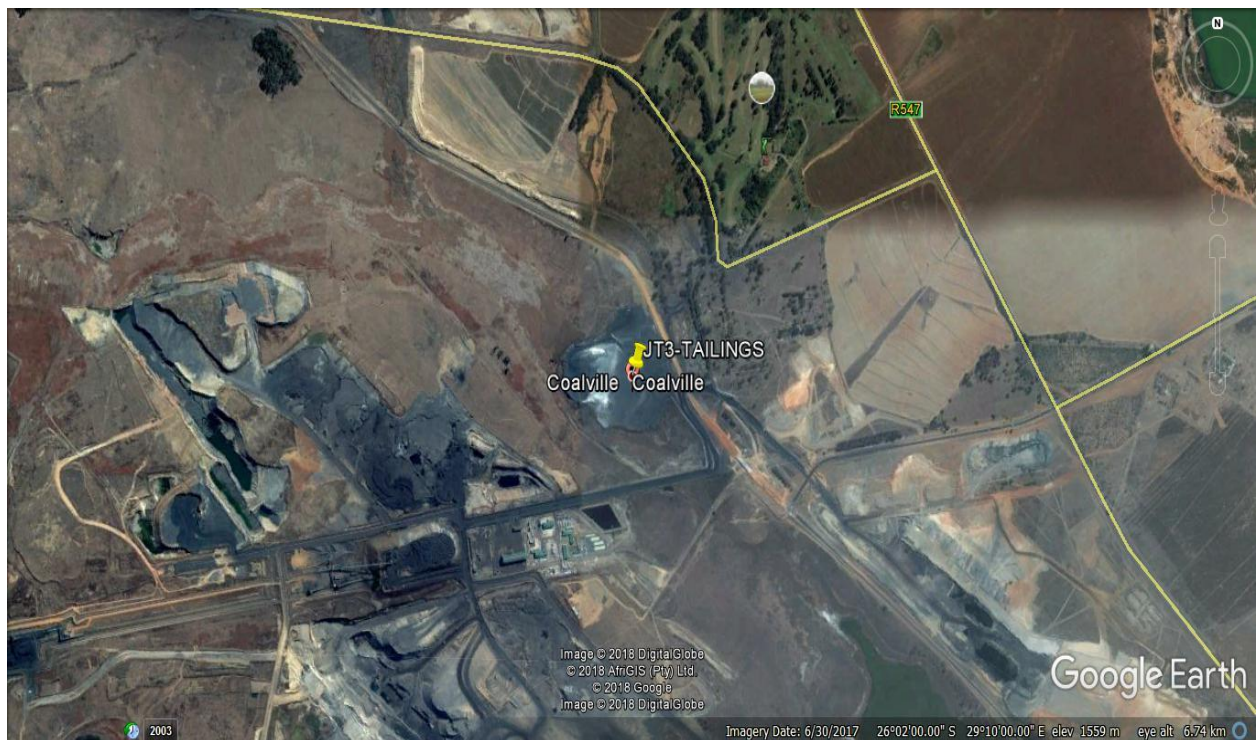
Figure 3. 4: **Google Earth Photograph showing the location of Witbank Coalfield (JT3) in Mpumalanga Province of South Africa**

3.1.3.1   Climate of the area

The study area is characterised by warm and temperate climatic conditions. It receives much more rainfall in summer as compared to the winter season. The average annual rainfall is approximately 756 mm, whereas the average annual temperatures range to an approximate number of 14.4°C. Chemical weathering of the primary minerals dominates the disintegration process.

3.1.3.2   Geology and mineralogy

The Witbank coalfields extend over a distance of some 180 km from the Brakpan and Springs areas in the west, to Belfast in the east and about 40 km in a north-south direction. Mining in the Witbank coalfield started in the Witbank area when four small collieries, Brugsprunt, Steenkoolspruit, Maggi's mine and Douglas colliery were

opened in 1889 (Singer, 2011). Witbank coal field is contained within the Karoo Supergroup which covers an extensive area of Southern Africa (Cairncross, 2001). The Karoo Supergroup is a thick sequence of sedimentary rocks deposited between approximately 300 and 180 ma (Cairncross, 2001). The Karoo Supergroup hosts all the coal of South Africa. The coal seams are virtually horizontal throughout the main basin. The wide range of depositional settings within which coal peats accumulated combined with a variation in climate and plants communities as well as Jurassic dolerite intrusions, impart to the coals significant differences in grade, types and rank (Cadle *et al.*, 1993; cited from Johnson *et al.*, 2006).

The peats of the Vryheid formation accumulated in swamps in a cool temperature regime (Cadle *et al.*, 1993; cited from Johnson *et al.*, 2006). Apart from the Dwyka and Beaufort Group, Ecca Group is of significant importance in this study because it directly hosts the Witbank coal deposits. Ecca Group comprises a total of 16 formations. These formations are grouped into three geographical areas; 1. Southern, 2. Western-North western and 3. North eastern geographical areas (Johnson *et al.*, 2006). The sediments of the coal-bearing Ecca Group of the Karoo Supergroup were deposited on an undulating pre-Karoo floor which had a significant influence on the nature, distribution and thickness of many of the sedimentary formations, including the coal seams (Smith & Whittaker, 1986).

Amongst all the formations only the Vryheid Formation of the north-eastern formation is of the area of interest in this study. Vryheid Formation thins towards the north, west and south. The formation rests directly on pre-Karoo rocks giving rise to marked variations in thickness. The different lithofacies of the Vryheid Formation are mainly arranged upward-coarsening cycles (up to 80 m thick in the south-east) which are essentially deltaic in origin (Johnson *et al.*, 2006).

The base of an idealised coarsening-upward deltaic cycle in the eastern part of the formation consists of dark-grey, muddy siltstone resulting from shelf suspension deposition in anoxic water of moderate depth. Bioturbated, immature sandstones dark siltstone and mudstones represent the prodelta sediment alterations. Vryheid Formation hosts the coal seams originated as peat swamps developed on broad

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abandoned alluvial plains and less commonly in interfluves (black swamps). Vryheid Formation can be subdivided into a lower fluvial-dominated deltaic interval, a middle fluvial interval and an upper fluvial-dominated deltaic interval. Sulphur and pyrite are sub-dominant minerals in the coal as well as some minor trace elements. The pyrite and sulphur cause in some cases extreme AMD with consequent low pH conditions and therefore high solubility of the TE's. (Tavener-Smith *et al.*, 1988; cited from Johnson *et al.*, 2006). As a result, most of the Witbank coal of economic importance is hoisted by the Vryheid Formation of the Ecca Group. See Figure 3.4 and Table 3.1 for more detail.

3.1.4   TJ4-Kalgold gold mine, Vryburg, North West Province

Setlagole mine, also known as Kalgold, is situated approximately 60 km south of Vryburg within the Kraaipan Greenstone Belt, between latitude 26° 09' 48.20" South and longitude 25° 15' 30.90" East. See Figure 3.5 and Table 3.1 for more detail

Figure 3. 5: **Google Earth Photograph showing the Kalgold mine tailings locality (TJ4)**

3.1.4.1   Climate of the area

Vryburg area in the North West Province of South Africa receives much of its rainfall during the month of January to April which amounts to 290 mm and October to December amounting to 144 mm. The lowest rainfall in this area is between May and September of which it amounts to approximately 43 mm. The lowest average temperatures at this area are approximate 9.3^o C during the month of July and maximum average temperatures are above 31^oC during the month January (https://en.climate-data.org/location/10658/).   Physical weathering dominates the disintegration process and the influence of chemical conditions are applicable in the final leachate products as well as in some potential toxicity and water quality conditions.

3.1.4.2   Geology and mineralogy

The Kraaipan Greenstone Belt (KGB) constitutes the larger portion of Amalia-Kraaipan Greenstone terrain which consists of north-trending linear belts of Archaean meta-volcanic and meta-sedimentary rocks, partitioned by granitoid units. Gold occurs in all of the main Greenstone lithologies and the deposits show a wide range of subtle variation in their structural style, mode of occurrences and ore mineralogy (Anhaeusser & Viljoen, 1986; Barton,1982; Kirk *et al.*, 2003). Most of the Archaean gold deposits may be regarded as epigenetic in origin, taking the form of ubiquitous, generally transgressive vein or shear zone gold-lode ore bodies of the type which characterises Archaean Greenstone Belts (Anhaeusser & Viljoen, 1986; Kirk *et al.*, 2003; Johnson *et al.*, 2006). A west-central portion of the Kaapvaal Craton hosts the Kraaipan Group. Approximately 20 km west of Kraaipan is a small Greenstone fragment centered on the settlement of Setlagole. Kraaipan succession consists mainly of mafic volcanic rocks with subordinate iron-formation and schist (Du Toit, 1908; cited from Robb *et al.*, 2006).

The Greenstones are intruded by various granitoid rocks including tonalitic and trondhjemite gneisses and post-tectonic granodiorite, adamellites and granite. Gold Ridge Formation that comprises mafic metavolcanic rocks, Ferndale Formation

comprising laminated ferruginous chert and jaspillitic chert and or Khunwana Formation having the same lithology with basal Gold Ridge Formation are the subdivisions of the Kraaipan sequence (Robb *et al.*, 2006; Poujol *et al.*, 2005; Robb & Meyer, 1995). According to Manahan (2017), Alloway (2013) and Prior *et al.* (2012), the geology and mineralogy of ore deposits play a crucial role in the chemistry of mine tailings materials. This is evidenced by the formation of AMD which is due to oxidation of sulphide minerals under the influence of oxygen and water. As a result of this chemical reaction, the risk of environmental (soil, water and plants) pollution is high. See Figure 3.5 and Table 3.1 for more detail.

3.1.5   TJ5-Sishen Iron mine, Kathu, Northern Cape

Sishen Iron ore deposit is located in the Transvaal Supergroup (Griqualand West) within the Northern Cape Province of South Africa, which is approximately 280 km North-west of Kimberly by road. It is between latitude 27° 44' 16.43" South and 22° 59' 47.20" East. See Figure 3.6 and Table 3.1 for more detail.

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Figure 3. 6: **Google Earth Photograph showing the location of Sishen Iron mine tailings (JT5)**

3.1.5.1 Climate of the area

The weather of the Northern Cape is typically that of desert and semi-desert areas. It is a generally hot and dry region with fluctuating temperatures and generally low rainfall. Evaporation levels exceed the annual rainfall which varies between 50 mm and 400 mm, of which the average rainfall of the Province is 202 mm. Namaqualand receives rainfall during the winter months (April to September). Temperatures range between 25°C to 35°C and winter is from 0°C to 15°C. However, the study area is characterised by semi-arid climatic conditions, with an annual average rainfall of approximately 202 mm and an average temperature of 18°C. Physical weathering dominates the disintegration process and the chemical influence is restricted to the leachate of potential toxic elements.

3.1.5.2 Geology of the area

Since 1958 the Sishen mine has been the country's main producer of iron ore, with an annual production of 20.8 Mt in 1994 (Vermaak, 1997; Hustrulid *et al.*, 2013). The iron ore of the Sishen mine generally consist of hard, high-grade material and conglomerate, as well as massive and laminated types, are found (Hustrulid *et al.*, 2013; Stoch *et al.*, 2018).

The geology of Sishen mine is in the Griqualand West Basin of the Transvaal Supergroup of which is subdivided into the Ghaap Group and Prieska Sub-basin (Hustrulid *et al.*, 2013). Furthermore, the Ghaap Group in Griqualand West Basin is subdivided in terms of the stratigraphic sequence into the following; Schmidtsdrif, Campbellrand, Asbestos hill and Koegas Subgroup (Van Schalkwyk & Beukes, 1986).

Sishen Iron Ore deposit falls within the Maremane dome defined by carbonate rocks of the Campbellrand Subgroup and iron-formation of the Asbesheuwels Subgroup of the Transvaal Supergroup dipping gently at less than 10° in an arc to the north, east

and south. The Gamagara Formation and underlying Manganore Iron-Formation in the northern part of the dome define the geological locality of the ore deposit at Sishen iron ore. In general, two ore types are present, namely laminated Hematite ore-forming, Illite, Chert, Quartz, Muscovite and Iron ore chlorite (Van Schalkwyk & Beukes, 1986).

In certain areas laminated hematite iron ore forms the top part of the Manganore iron formation which overlies the Wolhaarkop breccia. The Manganore iron formation is, in turn unconformably overlain by a basal conglomerate and shale unit of the Gamagara Formation (Van Schalkwyk & Beukes, 1986). The description is given above with regard to the geology and mineralogy of Sishen iron ore mine play a contributing factor on environmental impacts of mining. Leaching or weathering of in situ geological materials also pose an impact to the environment (soil, water and plants). However, this study only focuses on leaching from mine tailings. See Figure 3.6 and Table 3.1 for more detail.

3.1.6   TJ6-Aggeneys (Cu, Zn, Pb, & Ag) mine, Northern Cape

Aggeneys (copper, zinc, silver & lead) mining complex is located west of the town Aggeneys which is situated approximately 65 km west of Pofadder along the N14 highway to Springbok. It is located between latitude 29° 13' 15.89" south and longitude 18° 55' 35.23" East. See Figure 3.7 and Table 3.1 for more detail
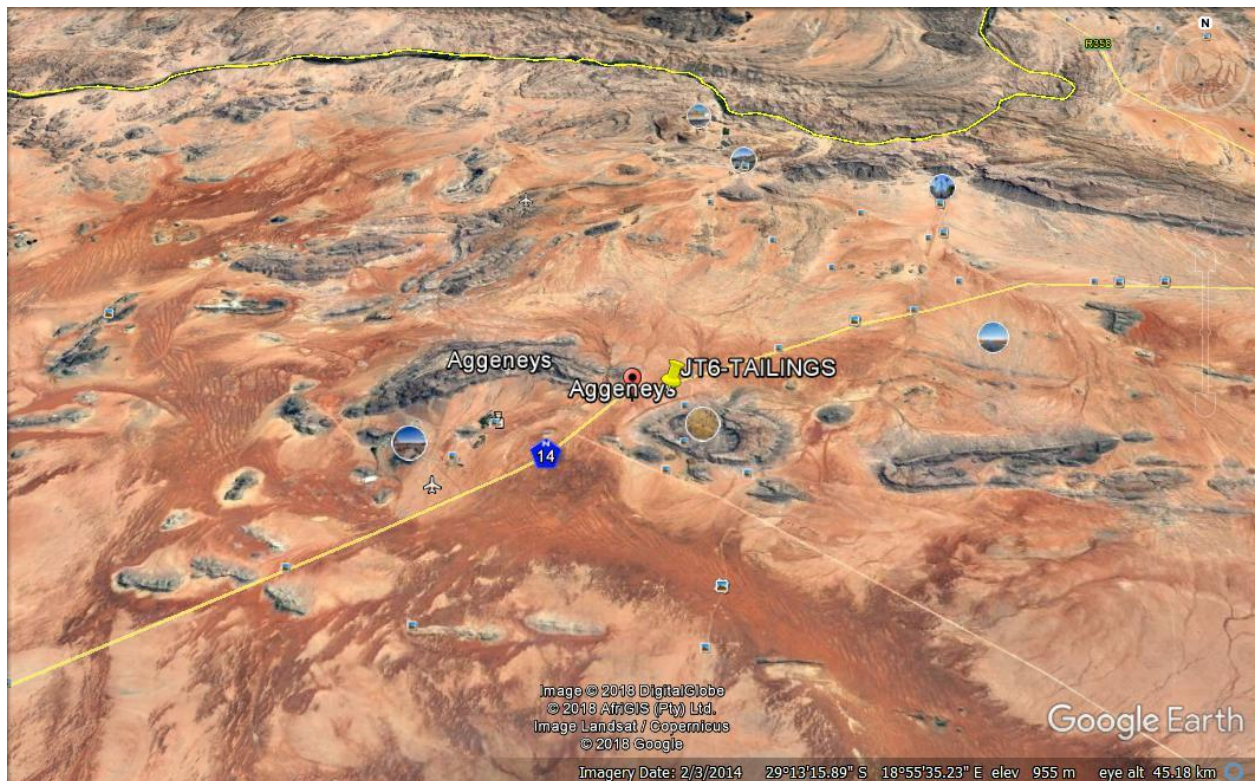
Figure 3. 7: **Gogle Earth Photograph showing the location of Aggeneys mine tailings (JT6)**

3.1.6.1   Climate of the area

The area is characterised by semi-desert, with generalised arid conditions, but advertises some of the most exquisite and infrequent Fauna and Flora around the globe. Aggeneys experience an annual rainfall of about 112 mm, with the highest precipitation taking place between the months of January and April.   Physical weathering dominates the disintegration process and the chemical influence is restricted to the leachate of potential toxic elements. Low pH and high salinity are a combination of first physical weathering followed by chemical disintegration.

In 2006, the highest recorded rainfall in this area was about 220 mm and the minimum was 11 mm in 1992. The minimum and maximum temperature in Aggeneys ranges from 15° C to 38° C in summer and 0° C to 18° C in winter (https://www.pathfinder.com/en/aggeneys).

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3.1.6.2   *Geology and mineralogy*

The Aggeneys deposits are located in the inner region of the Proterozoic Namaqua segment of the Namaqua-Natal Belt. This belt of highly deformed medium to high-grade metamorphic rocks to the south and west of the archean Kaapvaal craton of South Africa. The meta-volcano sedimentary supracrustal succession throughout the Bushmanland Sub-province is represented by the Okiep and Bushmanland Group which exist within the Okiep and Aggeneys District respectively (Bailie *et al.,* 2007). The older Namaqua segment rocks are unconformably overlain by the late syn or post-tectonic Kora's Group comprising the unfolded lavas, sediments and associated intrusive rocks. Most of the area is covered by wind-blown sand of the Kalahari Group and underlain by extensive calcrete deposits (Cornel *et al.,* 2006; Sithole, 2013). The Namaqua Province is divided into three Sub-provinces namely the Richtersveld Bushmanland, Gordonia and Kheis Sub-province; however, it is the Bushmanland Sub-province which is specific to the present study (Cornel *et al.*, 2006; Pettersson *et al.*, 2007; Sithole, 2013).

The lithology and mineralogy of the Bushmanland Group comprises ferruginous quartzite, shale, calc-silicate arrangements, amphibolite, sillimanite-quartzite, schist, garnet-quartzite, magnetite-quartzite, along with the associated Pb-Zn, Cu-Ag massive sulphide mineralisation at Aggeneys and Gamsberg (Bailie *et al.,* 2007; Ryan *et al.*, 2004; van Deventer, 2016). These massive sulphides are the primary source of the AMD. The age of the Bushmanland Group deposition had previously been bound between approximately 1.65 to 2.0 Ga (Reid *et al.*, 1987; Reid *et al.,* 1997; Robb *et al.,* 1999). The Bushmanland Group is divided into the Lortel and Konboom Subgroup and caped by the Koeris Formation (Mc clung *et al.*, 2006). See Figure 3.7 and Table 3.1 for more detail.

3.1.7   TJ12- Samada (Kaalvallei) diamonds mine, Welkom, Free State

Samada diamond mine is located in Free State Province of South Africa, between latitude 27° 58' 05.76" south and longitude 26° 41' 40.23" east of Welkom which is 7.5 km away. It is a small diamond mine in a Kimberlite pipe within the

Witwatersrand field. Kaalvallei (Samada) diamond mine was firstly found in the year 1890 and it was worked until the initial point of the Boer war in the year 1899. Therefore, the mine gained its operational power immediately after the resolutions of the Boer war and continued until the negotiations of the new dawn (Democracy) in 1990 (Field *et al.*, 2008). See Figure 3.8 and Table 3.1 for more detail.

Figure 3. 8: Google Earth Photograph showing the location of Samada diamond mine tailings (JT12) in Welkom, Free State Province of South Africa

3.1.7.1   *Climate of the area*

The climate of Welkom area within the Free State Province is influenced by ecoregion and experiences little rainfall throughout the year. The average annual temperature is 16°C, with average precipitation of 557 mm. August is classified as the driest months with 8 mm rainfall (https://en.climate-data.org/location/765253/). Physical and chemical weatehrings are about equal in this area, but the chemical disintegration dominates the final weathering process to release TE's.

3.1.7.2   Geology and mineralogy of the site

According to Mohs (1822), diamond is one of the precious metals classified to be the hardest gemstone on the Mohs scale. The Kimberlite pipe is the host rock of diamonds in South Africa. The age of Kimberlite pipes in South Africa ranges 1900 to 70 Ma and they are said to be younger than 200 Ma (Mesozoic). The Kaapvaal Craton was found to be the primary source of Kimberlite pipes; however, the off-craton kimberlite pipes also exist regardless of their deficiencies in diamond concentrations (Skinner & Truswell, 2006). Kimberlite is a hybrid, volatile-rich, potassic, ultramafic igneous rock derived from deep within the earth (i.e. less than 150 km in case of diamondiferous kimberlite (Skinner & Truswell, 2006).

Kimberlite has for example revealed complexes of antecedent dikes and sills cut by multiple pipe intrusions of various Kimberlite types (Clement, 1982; Field *et al.*, 2008; Skinner & Truswell, 2006). Kimberlite carrot shape in most cases is a result of magmatic crystallisation during intrusion (Skinner & Truswell, 2006). South African Kimberlites are originally subdivided into two groups termed "basaltic and micaceous" (Moore, 1986; cited from Skinner & Truswell, 2006). The "basaltic", also referred to as group one kimberlite, originates from an asthenospheric-type mantle and the "micaceous" on group two Kimberlite from enriched mantle materials (Agashev *et al.*, 2001; cited from Skinner & Truswell, 2006). The basaltic Kimberlites pipes are of global occurrence are the most hosts of diamond worldwide.

Lithologic classification of minerals associated with primary Kimberlite pipe are but not limited to euhedral olivine, phlogopite, monticellite, calcite, serpentine, diopside, melilite, apatite, perovskite, spinels and ilmenite (Skinner & Truswell, 2006). Kimberlite pipes in South Africa are subdivided into ten Provinces ranging from oldest to youngest; Pruissen province-dated 1950 Ma, Kuruman province-dated approximately 1650 Ma, Cullinan province approximately-dated 1200 Ma, Alldays Province dated at approximately 500 Ma, Group two micaceous province-dated approximately 200 Ma, Griqualand east province-dated approximately 194 to 150 Ma, Victoria west province-dated approximately 150 Ma, Kimberly province-approximately 99 Ma to 70 Ma, Lesotho province-dated approximately 90 Ma and

Gordonia province-dated approximately 80 to 54 Ma (Verwoerd *et al.*, 1995; Skinner, 1989; Kramers & Smith, 1983; all cited from Skinner & Truswell, 2006). However, this study only focuses on Kimberly province which occurs within the Karoo field of the Kaapvaal Craton in Welkom, Free State. See Figure 3.2 and Table 3.1 for more detail.

3.1.8 TJ15-East Rand gold mine, Springs, Gauteng Province

The study area is located in Springs, Gauteng Province of South Africa between latitude 26º 14' 21.44" S and longitude 28º 28' 34.89" E. See Figure 3.9 and Table 3.1 for more detail.
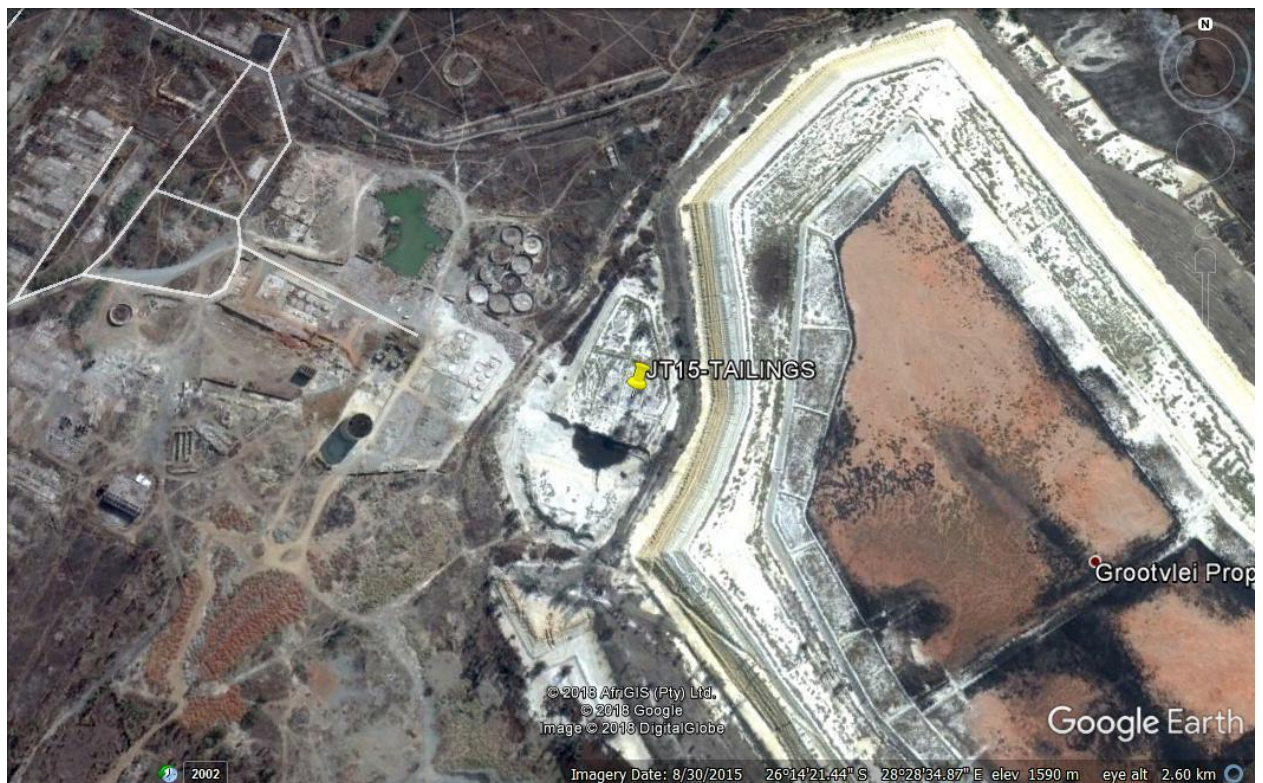
Figure 3. 9: Map showing the location of East Rand gold mine tailings (JT15) materials in Springs, Gauteng Province of South Africa

3.1.8.1 Climate of the area

The study area is characterised by mild and or warm climatic conditions. It has an annual average temperature of approximately 15.5ºC and annual average

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precipitation of about 699 mm. January month experiences the maximum average temperature of approximately 20°C and June the lowest temperature at 8.9°C. The weathering of the quarts-rich tailings material is dominated by chemical weathering.

3.1.8.2   Geology and mineralogy

The East Rand gold mine falls within the great goldfields of the Witwatersrand basin. In this area gold was initially discovered in quartz-pebble conglomerate during the year 1886 in the Witwatersrand Supergroup (Pretorius, 1986). The age of the Witwatersrand Supergroup is between 2300Ma and 2800Ma. It covers a great part or portion of Kaapvaal craton (Pretorius, 1986). Witwatersrand Supergroup is generally composed of the Central Rand Group and the West Rand Group. The Central Rand Group is subdivided into Turffontein Subgroup and the Johannesburg Subgroup, whereas the West Rand Group is subdivided into the following Subgroups; Jeppestown, Government and Hospital Hill Subgroup (Pearton & Viljoen, 2017; Pretorius, 1986). However, the West Rand Group together with Turffontein Subgroup of the Central Rand Group is of no interests in this study, but only the Johannesburg Subgroup is of interests.

Central Rand Group of the Witwatersrand Supergroup is believed to execute great disparities as compared to the West Rand Group, reason being the quartzite, shale ratio of the Central Rand Group is 12: 6 and the sequence consist of quartzite and conglomerate, whereas the West Rand Group of the Witwatersrand Supergroup is dominated by quartzite that is devoid of feldspar (Pearton & Viljoen, 2017; Pretorius, 1986). Furthermore, Central Rand Group (Turffontein and Johannesburg Subgroups) was proven by Pretorius (1986) to be the most producer of gold found in the Witwatersrand Supergroup. However, this study only focuses on the Johannesburg Subgroup. The Johannesburg Subgroup of the Central Rand Group consists predominantly of quartzite, deposited in a fluvial braid-plain environment (McCarthy *et al.*, 2006).

Up to date the geographical unit of the Witwatersrand Supergroup point towards the Central Rand Group (Pretorius, 1986; cited from McCarthy *et al.*, 2006).

Johannesburg Subgroup is represented by Blyvooruitzicht Formation of a conglomerate at its base, main Formation and latter commencing with the main Reefs/carbon leader. This was evidenced by erosive channels through the main Reef that is filled with argillaceous sediments derived from exposed Jeppestown Subgroup rocks on more proximal portions of the Palaeslope (Martin, 1994; McCarthy *et al.*, 2006; Pretorius, 1986). The Johannesburg Subgroup of the Central Rand Group is dominated primarily by quartz, pyrite and pyrophyllite (McCarthy *et al.*, 2006; Van Deventer, 2016). The sulphide minerals is the major source of AMD and together with the sulphides there are some trace elemnts too. The geology and mineralogy of this area play a crucial role in the chemistry of mine tailings facility. See Figure 3.9 and Table 3.1 for more detail.

3.1.9   TJ19-Paardekraal platinum tailings (T4), Rustenburg, North West Province

This study area is located between latitude 26º 06' 52.38" south and longitude 27º 46' 01.00" East. It falls within the Bojanala platinum district municipality of the northwest province with Rustenburg as the closest main town. It is located northeast of the Rustenburg central business district between Molapo drive and Egoli Street, in proximity to Sunrise Park. See Figure 3.10 and Table: 3.1 for more detail.

Figure 3. 10: **Google Earth Photograph showing the location Paardekraal platinum mine tailings (JT19) materials Rustenburg, North West province of South Africa**

3.1.9.1   Climate of the area

Rustenburg normally receives about 513 mm of rain per year, with most rainfall occurring mainly in summer. It receives the lowest rainfall (0 mm) in June and the highest (101 mm) in summer. The average temperatures range from 19.3°C in June and 29.4°C in January during the day and about 1.7°C when the mercury drops during the night in July (Weather Bureau, 1997; https://www.saexplorer.co.za/south-africa/climate/rustenburg-climate.asp).   The primary weathering process is equally influenced by chemical and physical weathering.

3.1.9.2   Geology and mineralogy of the area

The geology of the northwest province is primarily of the Bushveld Complex. Bushveld Complex is the world's largest layered intrusion and because of its unique character, most of the other layered intrusions are compared with it. The Bushveld Complex consists of eastern, western and northern limbs and it is seven to nine km

thick. As being the largest layered intrusion, the Bushveld Complex also hosts the largest concentrations of Platinum Group Elements (PGE's) in the world. Apart from the upper group chromite No.2 (UG-2) and Merensky Reef, the zone also hosts the plat reef mineralisation of the northern limb of the Bushveld Complex. However, the present study focuses on the Merensky Reef of the Bushveld Complex (Ballhaus & Sylvester, 2000; Johnson *et al.*, 2006; Schouwstra & Kinloch, 2000; Viljoen, 1999).

The Rustenburg layered suit of the Bushveld Complex is divided vertically into five zones, being the marginal zone, the lower zone, critical zone, main zone and upper zone. Regardless of the existence of other subdivisions of the Rustenburg layered suit, the platinum group metals-bearing Merensky Reef is hosted by the upper group (Cawthorn, 2010; Cawthorn, 2015; Johnson *et al.*, 2006; McDowell, 2011). The rock-forming minerals of the Merensky reef comprise approximately equal amounts of dark iron-magnesium silicate minerals and lighter calcium-aluminium-sodium silicate minerals (called feldspathic pyroxenite), under and overlain by thin (5 to 15mm) often discontinuous layers of chromatite concentrations. The Merensky Reef has traced for 300km around the entire outcrop of the eastern and western limbs of the Bushveld Complex, to depths of 5km. Approximately 40% Pyrrhotite, 30% pentlandite, 15% chalcopyrite and trace amounts of millerite, troilite, pyrite and cubanite also occur as base metals sulphides (Johnson *et al.*, 2006; Schouwstra and Kinloch, 2000; van Deventer, 2016; Viljoen, 1999). See Figure 3.10 and Table 3.1 for more detail.

3.1.10 TJ20-New Machavie gold tailings, Potchefstroom, North West Province

It is located between latitude 26° $45^{'}$ 6" S and Longitude 27° 11' 8" E. it is about 22 km west of Potchefstroom, a town which is about 120 km west-southwest of Johannesburg (Koch, 2014:24). See Figure 3.11 and Table 3.1 for more detail.

Figure 3. 11: **Google Earth Photograph showing the location of New Machavie mine tailings (JT20) materials**

3.1.10.1 Climate of the area

Potchefstroom normally receives about 615 mm of precipitation falls annually, with most rainfall occurring mainly during mid-summer. The temperatures range from 17.9ºC in winter and 29º C in summer during the day and up to Oº C in winter during the night (Koch, 2014). About 556 mm is experienced during the month of October to May and minimum rainfall is approximately 59 mm of which is experienced during the month of June to September (https://en.climate-data.org/location/27286/). Chemical weathering dominates the disintegration of the tailings material with major physical contributions.

3.1.10.2 Geology and mineralogy

Mineralisation in New Machavie is located in the Black Reef Formation, Malmani Sub-group of the Transvaal Supergroup. The Transvaal Supergroup covers the

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Pretoria Group, Chuniespoort Group, Segwagwa Group, Taupone Group, Ghaap Group and the Postmasburg Group, with the overall lithology of clastic sediments and volcanic rocks and or chemical sediments. and or Chuniespoort together with the Pretoria Groups are of Transvaal basin in South Africa (Button, 1986; Eriksson *et al.*, 2006). However, this study is only channelled towards the Chuniespoort and the Black Reef Formation. As referenced by Beukes (1987); Button (1986); Eriksson *et al* (2006), Transvaal Supergroup encompasses one of the world's earliest carbonate platform successions and it overlies the Archaean basement, Witwatersrand and Ventersdorp Supergroup.

Historically the development of Transvaal Supergroup rocks in the Transvaal basin was found to be influenced by intrusion occurred approximately 2060 Ma of the Bushveld Complex forming the floor rocks in most areas and this intrusion as well affected the Pretoria Group and Magaliesberg Formation (Eriksson *et al.*, 2006; Walraven, 1995). As explained in paragraph one above that only the Black Reef Formation (BRF) and Chuniespoort Group are of interest in this study. The BRF consist predominantly of relatively mature quartz arenites, with lesser conglomerates and subordinates mud rocks forms a thin veneer of arenaceous rock unconformably overlying older successions (Button, 1986; Eriksson *et al.*, 2006; Henry *et al.*, 1990). The BRF forms very widespread thin sheet quartzite with a varying thickness between 30m to 60m in the western part of the basin (Button, 1986; Eriksson *et al.*, 2006).

Historically the BRF has been traditionally regarded as time equivalent to Vryburg Formation in the Griqualand west (Nwaila, 2017). Despite, Walraven (1995) cited from Eriksson *et al.* (2006), differs with the above hypothesis, suggesting BRF's age to be of Oaktree Formation that is located in the Barberton Mountain Land (BML).

On the other hand, the Chuniespoort Group of Transvaal Basin comprises the Malmani Subgroup and Penge Formation. The Malamani Subgroup is dated between approximately 2600 and 2500 Ma, in spite, the age of its basement remains uncertain. The age difference between the Chuniespoort Group and the BRF lies between 2640 and 2650 Ma. However, both the BRF and Chuniespoort Group are

dominated by quartz, feldspar, pyrite, sphalerite, pyrrhotite, ilmenite, chalcopyrite and chromite (Antrobus *et al.*, 1986; cited from Koch, 2014; Button, 1986; Van Deventer, 2016). See Figure 3.11 and Table 3.1 for more detail.

3.1.11 TJ22-Antimony (Sb) Tailings, Gravelotte, Limpopo Province

Antimony mine tailings materials are located in Limpopo Province of South Africa, between latitude 23º 56' 30.38" S and longitude 30º 36' 28.77" E. See Figure 3.12 and Table 3.1 for more detail.

Figure 3. 12: **Google Earth Photograph showing the location of Antimony Gravelotte mine tailings (JT22) materials in Limpopo Province of South Africa**

3.1.11.1 Climate of the area

This area is characterised by semi-arid climatic condition with maximum rainfall experienced during summer and low in winter seasons. The average precipitation is approximately 598 mm with the average temperature of about 17.3ºC

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(). The high rainfall and tempratures control the chemical weathering process which is dominant.

3.1.11.2   Geology of the area

Murchison Greenstone Belt (MGB) is located in the North-eastern Kaapvaal craton, South Africa. It is situated 3km north of the village called Gravelotte which is between latitude 23° 56' 23" & longitude 30° 36' 29" and is the most abundant antimony deposit of the MGB. It is between the Drakensberg plato hills in the west and the Kruger National Park in the east. With respect to history antimony within the Murchison, range is inevitably connected to that of gold. The metal was found and mined simultaneously with gold; however, gold was given much attention due to its vital demand during this particular era. It was discovered in 1869 (Anhaeusser & Maske, 1986; Jonson *et al*., 2006; Verwoerd, 1986).

The MGB primarily subsists of varying geological formations comparatively; Mulati Formation, Leydsdorp Formation, La France Formation, Weigel Formation, Maykop Formation, Rubbervale Formation and Rooiwater Complex. Despite the number of formations consisting the Murchison greenstone belt, this study directs its focus on the on the Weigel Formation (Abbol *et al* 1985; Anhaeusser & Maske, 1986; Bailie *et al*., 2007; Pearton, 1979). The Weigel Formation take up the inner core of the MGB and subsist of the following but not limited to quartz-chlorite schist, quartzite, quartz-muscovite schist, minor Banded Iron Formation (BIF) and conglomerate units, as well as mafic lavas and talc-chlorite schists incorporation with talcose and siliceous carbonate rocks (Abbol *et al* 1985; Anhaeusser & Maske, 1986; Pearton, 1979)

The Weigel Formation is partitioned into easily detectable lithological segments. The lower segment is composed most importantly of difference quartz-chlorite schist of whom significant quartz-muscovite schist units occur. The conspicuous spits kop bar is a possible correlation occurring to the west of Gravelott town (Abbol *et al* 1985; Anhaeusser & Maske, 1986; Johnson *et al*., 2006; Pearton, 1979). The upper unit of the Weigel Formation is a monotonous sequence of quartz-muscovite schists. The Weigel Formation which hosts the antimony line to the south, comprise chiefly of

difference quartz-chlorite schists. The country rock located north of antimony line comprises of collection interblended with quartz-chlorite schists (Abbol *et al.*, 1985; Johnson *et al.*, 2006; Verwoerd, 1986).

Seven different dikes are observable in the MGB. Amongst them are biotite dikes, carbonate-chlorite dikes, irregular "diabase" dikes, older "tarentaal" dikes, older dolerite dikes, younger tarentaal dikes and Karoo dolerite dikes (Abbol *et al* 1985; Anhaeusser & Maske, 1986; Pearton, 1979). The ore bodies exist as part of stibnite distribution correlated with quartz veining and as discrete restrained lenses of stibnite-bearing crystalline quartz-carbonate rocks which are generally variable in shape and size (Anhaeusser & Maske, 1986; Johnson *et al.*, 2006; Verwoerd, 1986). With consideration of vast significant mineralisation ahead of antimony line , the Alpha-Gravelotte mineralisation emanate the shape or arrangement of stibnite-rich reefs in rich of Carbonate-rich Complex and mineralogy is dominated by quartz, chlorite, talc, various carbonates, calcite, magnesite and siderite as well as minor sulphide minerals with some trace elements.   (Anhaeusser & Maske, 1986; van Deventer, 2016). See Figure 3.12 and Table 3.1 for more detail.

3.1.12 TJ-23-Phalaborwa Copper mine (PMC), Phalaborwa, Limpopo Province

Phalaborwa is the largest open-pit copper mine in Africa, as well as world class phosphate (Verwoerd & du Toit, 2006:291). It is located between grid reference 23° 58' 04.73" S and 31° 07' 28.47" E in Limpopo Province of South Africa (Vielreicher *et al.*, 2000). Foskor (JT10) mine is located in Phalaborwa, Limpopo Province of South Africa, between latitude 24° 00' 52.65" south and longitude 31° 08' 14.75" east of Phalaborwa's town. It is in close proximity with PMC and the two mines share the same climate and geology within the great Phalaborwa Complex. The only difference is that Forskor mine has an abundant of phosphate as compared to PMC that has copper as a primary mineral being mined.
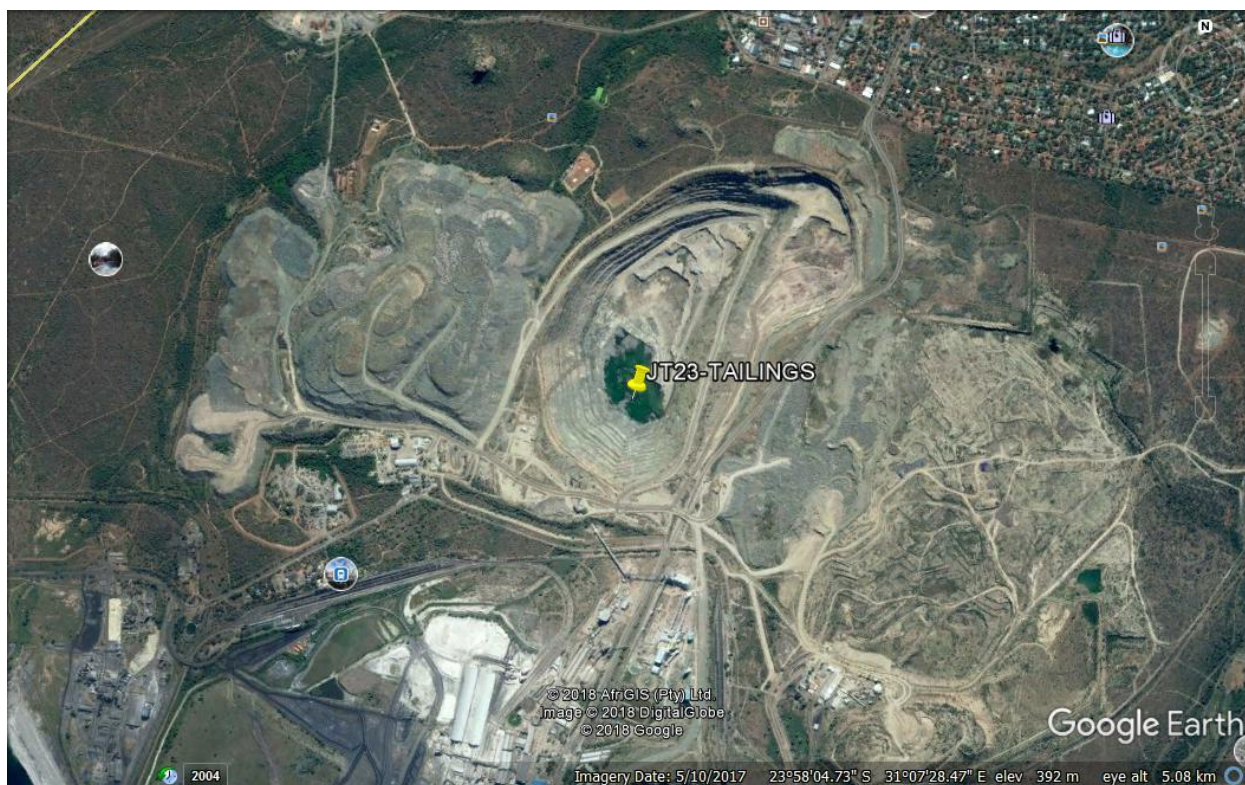
Figure 3. 13: **Map showing the locality of PMC and Forskor mine tailings (JT23) materials**

3.1.12.1 Climate of the area

Phalaborwa climatic condition is characterised to be local steppe. It receives a minimum amount of rainfall annually as compared to Barberton. The annual average temperature is 22.1°C and experiences the average annual rainfall of approximately 543 mm (https://en.climate-data.org/location/15344/). Chemical weatherings dominates slightly the disintegration process of the host rock and tailings material.

3.1.12.2 Geology and mineralogy of the study area

Phalaborwa Complex referred to be of economical significance is located south of the town of Phalaborwa in Limpopo Province, near the Kruger National Park. It extends 6.5 km north-south and 3.2 km east-west covering an area of about 16 km^2 (Hanekom, 1965). The mineralisation at Phalaborwa is ultimately associated with and hosted in an igneous intrusion and vast of the economically valuable minerals are contained by the Loolekop pipe (Johnson *et al.*, 2006; Vielreicher *et al.*, 2000).

The copper-bearing Loolekop carbonatite pipe was named after a hill that once existed within the area. Pegmatoids bodies and the Loolekop pipe contribute about 70% of the main ore body with a high content of phlogopite and apatite. The Loolekop pipe is ovally characterised by a dimension of about 1.4 km east-west and 0.8 km north-south.

The Loolekop pipe constitutes the copper ore deposit and it contains a minor amount of appetite, dolomite, chondrodite, olivine, phlogopite and biotite (Johnson *et al.*2006; Verwoerd, 1986). Johnson *et al.* (2006:291) documented that Phalaborwa Complex is alkaline and its alkalinity is due to the presence of phlogopite, apatite contents and carbonate bodies. Apart from copper mineralisation that painted the good name of the area in question, Phalaborwa Complex also contributes to one of the economic importance mineral resources which is phosphate. Phosphate occurs within the rock type called phoscorite also spelled foskorite. Phoscorite as described by Johnson *et al.* (2006) is roughly banded parallel to the boundaries of the pipe, individual bands consisting of continuous magnetite layers and parallel lines of magnetite crystals and clots. The final intrusive phase of the Phalaborwa Complex was a central, irregular body with innumerable off-shoots transgressing the earlier banding (Robb *et al.*, 2006; Krasnova *et al.*, 2004).

Phoscorite is plutonic ultramafic rocks comprising magnetite, apatite and one of the silicates forsterite and or phlogopite. Phoscorite is a coarse-grained, basic, ultrabasic rock composed of variably serpentinised olivine, magnetite, apatite, carbonates and phlogopite which decreases inwards the contact with bended carbonatite (Johnson *et al.*, 2006; Kransnova *et al.*, 2004; Vielreicher *et al.*, 2000). Apatite is the only phosphate ore minerals at Phalaborwa complex and occurs as a primary igneous phase in all rock types. Both the phoscorite and carbonatite host economic copper in chalcopyrite, bornite, cubanite and chalcocite, phosphorus in apatite and iron-oxide as magnetite mineralisation (Johnson *et al.*, 2006:291; Verwoerd, 1986)

Phoscorite is the principal host of baddeleyite and uranothorianite, blebs of bornite and chalcocite and the dominant sulphides in phoscorite and older carbonatite, whereas chalcopyrite and cubanite form veinlets along fractures in the transgressive

carbonatite. In addition, dolerite magmatism took place both before and after emplacement of the Phalaborwa Complex (Erickson, 1989; Johnson *et al.*, 2006). However, in terms of geology and mineralogy, phoscorite and carbonatite cannot be separated due to the fact that they both occur within Phalaborwa Complex in the Limpopo Province of South Africa. See Figure 3.13 and Table 3.1 for more detail.

3.1.13 TJ-24-Revolvervlei gold tailings, Barberton, Mpumalanga Province

It is situated within the Barberton area in Mpumalanga Province of South Africa, between latitude 25º 48' 45.83" south and longitude 30º 59' 25.64" north-east of Barberton town. See Figure 3.14 and Table 3.1 for more detail.

Figure 3. 14: **Google Earth Photograph showing the location of Revolvervlei gold mine tailings (JT24) materials in the Barberton area, Mpumalanga Province of South Africa**

3.1.13.1 Climate of the area

Barberton area is characterised by warm and temperate climate condition. It receives an annual rainfall of approximately 861 mm. The minimum rainfall is experienced

during winter seasons and high rainfall during the summer season. The high rainfall and tempratures control the chemical weathering process which is dominant in the disintegration of the host rock and tailings.

3.1.13.2 *Geology and mineralogy of the area*

Most of the World's gold mining has been from epigenetic hydrothermal deposits. Gold deposits of the Archaean greenstone belts (AGB) of the Rhodesian and Kaapvaal cratons Including the Barberton Mountain Land (BML) was believed to be initially present in mafic and ultramafic lavas and associated sediments and was mobilised and concentrated in dilatant zones during metamorphic events attendant upon granitic intrusions (Anhaeusser, 1986; Groves *et al.*, 1984; Saager, 1973; Viljoen *et al.*, 1969). Barberton Greenstone Belt (BGB) as one of the most explored granite-greenstone terrain in the world hosts a considerable amount of gold deposits and it comprises some of the unique and best-preserved lithologies world-wide, it is one of the three oldest and has served as a general working model of Archaean Greenstone geology around the globe (Brandl *et al.*, 2006).

Metamorphism in the Barberton Achaean Greenstone was influenced by three subdivisions of metamorphism namely the sea-floor, burial and dynamic metamorphism (Brandl *et al.*, 2006; Cloete, 1999; Ward, 2000). Mineralisation encompasses deposits of chrysotile, asbestos, barite, cinnabar, gold, haematite, magnesite, stibnite, talc and verdite (Brandl *et al.*, 2006; Viljoen, 1986; Ward, 1999).

The lithology and mineralogy of Barberton Achaean Greenstone comprises quartzite, mafic schist, shale and but not limited to banded iron formation, with quartz, quartz vein, pyrite and free gold contributing primary of dominants minerals (Brandl *et al.*, 2006; Diener, 2014; Enhaeusser, 1986; Van Deventer, 2016). Like on the other localities discussed, the mineral composition of in situ rocks play a contributing factor on the chemistry of mine tailings materials. See Figure 3.14 and Table 3.1 for more detail.

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3.1.14 TJ-25-Manganese mine tailings, Postmastburg, Northern Cape.

South Africa's is known to host about 80% of the world's high-grade manganese ore reserves. This manganese deposit called the Kalahari manganese field is located 700 Km south west of Johannesburg in the Northern Cape Province, between latitude 28° 22' 54.54" south and longitude 22° 56' 48.76" east of Postmasburg area. The district yield about 4 Mtpa (million tonnes per annum), mined mainly by two companies: Samancor and Assmang and it was originally established in 1935. These deposits occur in a deposit extending northwards over a distance of approximately 150 Km from just south of Postmasburg to as far as the Wessels and Black Rock mines north of Hotazel. (Tsikos & Moore, 1997; https://www.mining-technology.com/project/assmang/). See Figure 3.15 and Table 3.1 for more detail.
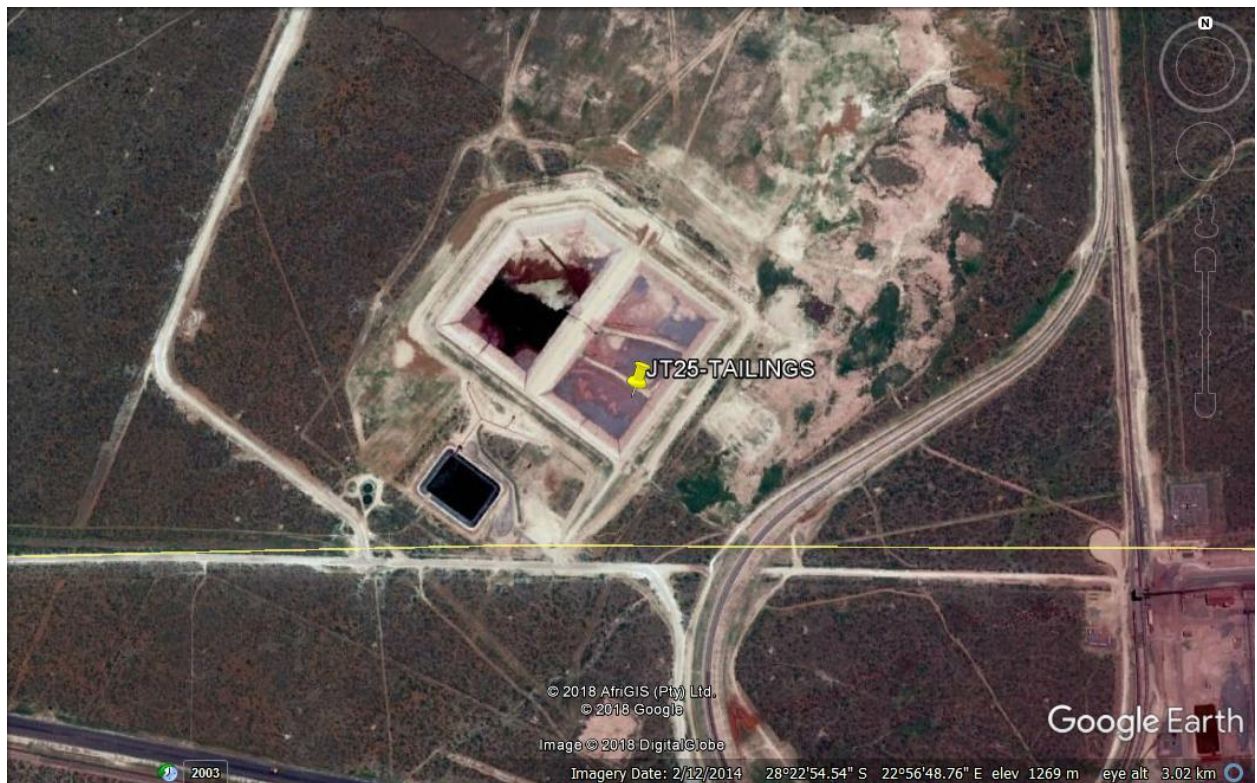
Figure 3. 15: **Map showing the location of Manganese mine tailings (JT25) in Northern Cape Province of South Africa**

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3.1.14.1   Climate of the area

Postmasburg normally receives about 241 of rain per year, with most rainfall occurring mainly summer. It receives the lowest rainfall (0mm) in July and the highest in March (57mm). The average temperatures range from 17°C in June to 32°C January during the day and become coldest during the night (www.saexplorer.co.za/south-Africa/postmasburg-climate.asp).   Physical weathering dominates the disintegration process and the chemical influence is restricted to the leachate of potential toxic elements.

3.1.14.2   Geology and mineralogy of the area

The Postmasburg manganese metallogenic belt starts from Sishen in the northern ends at the Postmasburg town It extends from South to North for 55km long and is about 5 to 10 km in width from east to west. The Postmasburg manganese metallogenic belt is divided into three ore belts: the east ore, west ore and south-west ore belt in the Wolhaarkop mining area. The regional strata mainly consist of Naraga's Formation of Campbellrand Subgroup of Proterozoic Transvaal Supergroup of Ghaap Group, Asbesberg Formation of the Asbestos Subgroup, Gamagara Formation of the Gamagara Subgroup of Postmasburg Group, Makganyane Formation, Ongeluk Formation, Fairfield Formation, Lorteri Formation, Groep Formation, Carboniferous Lucknor Formation and Quaternary system. Despite the existence of the above-mentioned Formation, the present study only directs its focus only on Griqualand west basin, Ghaap Groep and Gamagara Formation (Hartzer, 2000; Johnson *et al.*, 2006; Liao *et al.*, 2014).

Gamagara Formation is lithologically characterised by phyllite, shales, quartzite basal conglomerate in part of the layers, iron or manganese layers of about 300m thick. It is the thinner Formation within the Postmasburg Group of the Transvaal Supergroup. Gamagara Subgroup of Postmasburg Group of the Transvaal Supergroup is light yellow- grey thin sandy slate, outcrops thickness ranges from 15.18 m to 44.55 m width, is distributed in the western mining area, partly covered by

Quaternary sediments (i.e. Aeolian sand), presenting an uncomformable contact with strata underneath (Hartzer, 2000; Liao *et al.*, 2012; Moore *et al.*, 2001).

The Postmasburg Group in the Griqualand West basin consist of a conformable sheetlike sequence of diverse lithologies, commencing with a basal glacial diamictite, overlain by basaltic andesite lavas, Iron Formation and manganese, calcium-magnesium-carbonate. However, the unconformity in the Griqualand West basin is characterised by an overlying glacial unit and the lithology is dominated by chert, quartzite and shale (Erikson *et al.*, 2011; Grobbelaar and Beukes, 1986; Hartzer, 2000; Johnson *et al* 2006; Moore *et al.*, 2001). See Figure 3.15 and Table 3.1 for more detail.

3.2   METHODS AND PROCEDURES

A general description of the field and laboratory method used and all procedures followed throughout this research study has been outlined in this section.

3.2.1   Field measurements and sampling methods

Mine tailings materials of sixteen different sampling localities (as discussed in section 3.1 above) and ore bodies were sampled. All sample localities are in South Africa, but in different provinces. The oxidised top layer of each tailings site was identified and a representative area 400 m^2 was chosen to take the samples. All samples were taken from the oxidised top outer surface in 60 kg buckets. Tailings material was sampled using a manual auger as shown in Figure 3.16 and other hand tools such as shovel and pick

In most cases, the composite samples of 7 × 60 kg was taken mechanically at each site and transported to North-west University where it was thoroughly mixed, dried, sieved through a 2 mm sieve, mixed again and stored at ambient temperatures. Samples were stored in plastic bags and marked JT1 to JT25 for lab purposes (see Table 3.1).

Figure 3. 16: Photograph showing a manual auger (Daniell 2013)

3.2.2 Laboratory analysis

3.2.2.1   Tailing sample preparations

Tailings of varying mineralogical composition were sampled and taken to NWU laboratory for preparation and further analysis.

Samples were oven-dried for approximately 48 hours at a temperature of 40°C as outlined by Naveena *et al*. (2015:4610). All the dried samples were then exposed to sieve analysis (<2 mm fraction) to ensure a homogenous particle size. No

replications of analyses were done due to the composite sampling technique been used.

The research method employed to analyse the sixteen tailings samples are as thus:

- pH analysis in 1:2.5 solid : water solution
- EC and anions in the sentrifuged liquid of a saturated paste
- Excahgeable cations and CEC at pH 7 in a ammonium acetate solution
- ICP-MS method for total concentration of TE's in a total acid digestion solution (Cu, Zn, Mn, Pb, Cr, Co, Ni, Cd, U and As),
- Particle size distribution (PSD) by means of sieves and hydrometer methods

With these methods employed, potential environmental impacts of leach water for TSFs could be evaluated or determined.

3.2.2.2   *Physicochemical analysis of samples*

Samples were prepared and analysed for physicochemical analysis at Eco Analytica-laboratory (NWU). The purpose of oven drying is to remove moisture from tailings sample.

3.2.2.2.1   Particle size distribution (PSD)

Particle size distribution provides a clear understanding of the textural classification of soil (sand, silt and clay) as outlined in section 2.4.1 (Buol *et al.*, 2011; Eshel *et al.*, 2004; Isbell, 2016). In line with the aim of this study, PSD of tailings was accomplished by means of sieve analytical method. The sieves consist of the No.4 (largest) to No.1 sieve (smallest).Sieve assemblages is done with the No.4 sieve on top and the No.1 sieve on the bottom of the system sieves. The system is kept vibrating for the period of experiment. Particle are then distributed from the No.4 sieve (gravel texture) to No.1 sieve and the clay and silt fractions were determined by means of the hydrometer method. Tailing particle size fraction used for laboratory analysis was < 2 mm. Therefore, conclusion can be drawn with respect to the grading analyses.   Therefore after the percentage of sand, silt and clay were

determined soil texture was characterised by means of the USDA soil texture triangle (see chapter 4: results).

3.2.2.2.2 Humidity cell leaching test

For the purpose of this study, Humidity Cell apparatus was used to establish the overall rate of oxidation and to predict weathering (Figure 3.17). Tailings material from the 2 mm fraction was passed through a 150 µm screen to achieve the acceptable particles size in accordance to the standard requirements as prescribed by de Wet (2010). Geotextile of a perfect cut was placed at the bottom of the humidity cell to avoid creases and drainage holes which are present. The 1kg of tailings material was placed to each of the 16 humidity cells and spread carefully. 750 ml of distilled or de-ionised water was flushed on top of the 1 kg tailing sample already in each humidity cell. The samples were left to soak for approximately 2 hours. Then valves were opened for leaching to commence and continued for 24 hours. After 24 hours leaching was terminated and dry air was flushed through the cells for 3 consecutive days and then moist air (40º C) for another 3 days. The experiment continued for 10 weeks. After the water sample or leachate has been collected, 45 micro-millimeter filters were used to remove suspended solids. Therefore, by means of a Multi meter pH, EC, Salinity, sulphates and Redox potential measured immediately after 24 hours leach, and then leached samples were taken to Eco analytica laboratory (NWU) for trace elements analysis (Mphinyane, 2018; de Wet, 2010). Figure 3.17 below shows the photo of humidity cells assembled.
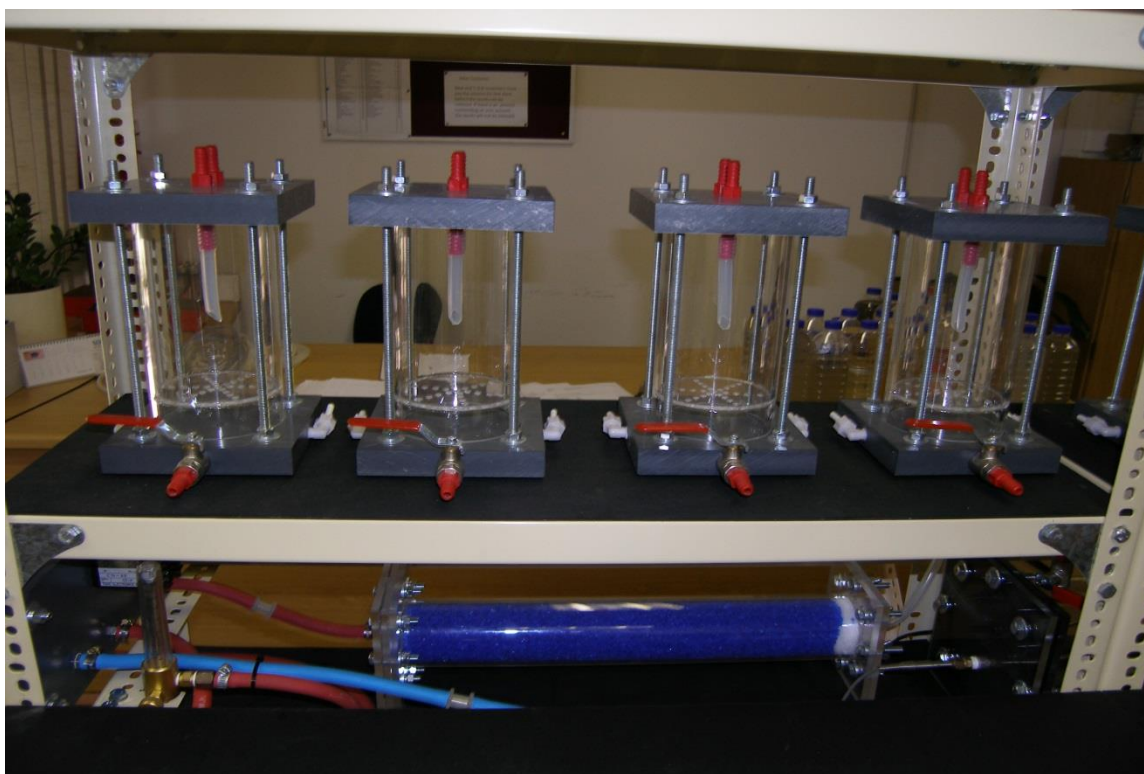
Figure 3. 17: **Photo illustration an assembled humidity cell (De Wet, 2010:10)**

The function of humidity cells are to predict the weathering of TSFs prior to determination of the kinetic behaviour of tailings material, and assess the risk of water and soil pollution arising from leaching of mine tailings materials (Shaw *et al*., 1998:211); cited from Mphinyane, 2018). Since it is a lag warp laboratory procedure it allows for significant conclusions on acid generation, transfer of TE's to the environment (soil, surface and groundwater). Comparative eminence of environmental cogent metallic elements and compounds of forthcoming water from the mine or rainwater infiltrating mine waste and eventually leach out. The most important merit of this leaching method is due to it's pliant in the test structure and allows for modification with respect to the type, size and frequency of materials to be analysed (Erguler *et al*., 2014; Hageman & Briggs, 2000; Parbhakar-Fox & Lottermoser, 2015; White *et al*., 1999).

Due to it's flexibility and wide application, the humidity cell procedure allows for the prediction of a long term weathering of TSFs and their negative impacts to soil, plants, surface and ground water (Barnes *et al*., 2015:2; Van der Sloot & Van

Zomeren, 2012:93; cited from Mphinyane, 2018). Amongst all the humidity cell test apparatus, the ASTM.D5744-96 standard methodology play a crucial role in predicting drainage chemistry even in the absence of acid generation (Hutt & Morin, 1999; cited from Mphinyane, 2018.

3.2.2.2.3 pH

Hannah multi-meters were used to determine the pH of the tailings sample. The pH meter was calibrated using buffer solutions of varying pH (4.01, 7.01 and 10.1) (Non-Affiliated Soil Analysis Work Committee, 1990; cited from Daniell, 2015:51). The oxidation-reduction potential (ORP) was also analysed with the same instrument but with a redox sensor. After analysis the pH meter was rinsed with distilled water to avoid contamination and then stored with the sensor immersed into KCL solution to prevent it from becoming dry. The pH procedure was done on a ratio 1:2.5 soil: water solution (i.e. 10 g soil and 25 ml of water).

3.2.2.2.4 Electrical conductivity (EC)

As it was explained in 2.4.2.2 EC is defined as a measure of the amount of salts presents in soil solution or its ability to conduct electric current and is measured by Milli-Siemens per meter (mS/m). Like pH, EC was measured using the Hanna multi-meter calibrated using the EC calibration standard (12.88 mS/m) as outlined by Daniell (2015:51: cited from Non- Affiliated Soil Analysis Work Committee, 1990). Electrical conductivity measurements were done on the water from a saturated paste. The EC value of about 6.1 mS/cm (610 mS/m) of tailings material marks the high risk (Daniell, 2015) for plants sensitive to saline conditions.

3.2.2.2.5 Total acid digestion of sample for total TEs in preparation for ICP-MS

Determining of TE's in tailings is one of the objectives in this research study. The ETHOS EASY MAXI-44 microwave acid digestion system was used based on the method described by Blust *et al.* (1988:389), Degger (2010:12) cited from Mphinyane (2018) and Geana *et al.* (2011:5214) as illustrated in Figure 3.18 bellow. This microwave is equipped with two 950 Watt magnetrons for a total of 1900 Watt. IT is

equipped with 44 TFM vessels having a volume of 100 ml holding up the very high throughput rotor.

These components make it perform simple digestion of leaching materials in varying tailings samples within the laboratory (Mphinyane, 2018). The microwave acid digestion was used in this case for determining the leaching behaviour of TE's from tailings material as shown in Figure 3.18 (Bettinelli *et al.*, 2000:290; Kingston & Walter, 1997:33; cited from Mphinyane, 2018).

Due to the procedural nature of microwave digestion system, the experiment was carried out according to the procedure described by Mphinyane (2018). Tailing samples were oven dried at a temperature of 60ºC for a period of 48 hours. The scale of 200mg samples and 10 ml HNO_3 was used according to the method procedure together with the Certified Reference Materials (CRM) weighed with same mass for every microwave digestion batch (Mphinyane, 2018). The 10 ml of HNO_3 was then added to a vessel with the use of plastic weighing boats (Mphinyane, 2018). Post digestion was then carried out according to the procedure explained by Mphinyane (2018).

Inductively coupled plasma mass spectrometry (ICP-MS) was then performed after digestion. ICP-MS is a one of the most attractive detection system and is routinely used in many diverse research fields such as environmental and earth sciences (Geana *et al.*, 2011:5213). The analytical set up and operation of this method was done by the certified lab technician as described by Mphinyane (2018).
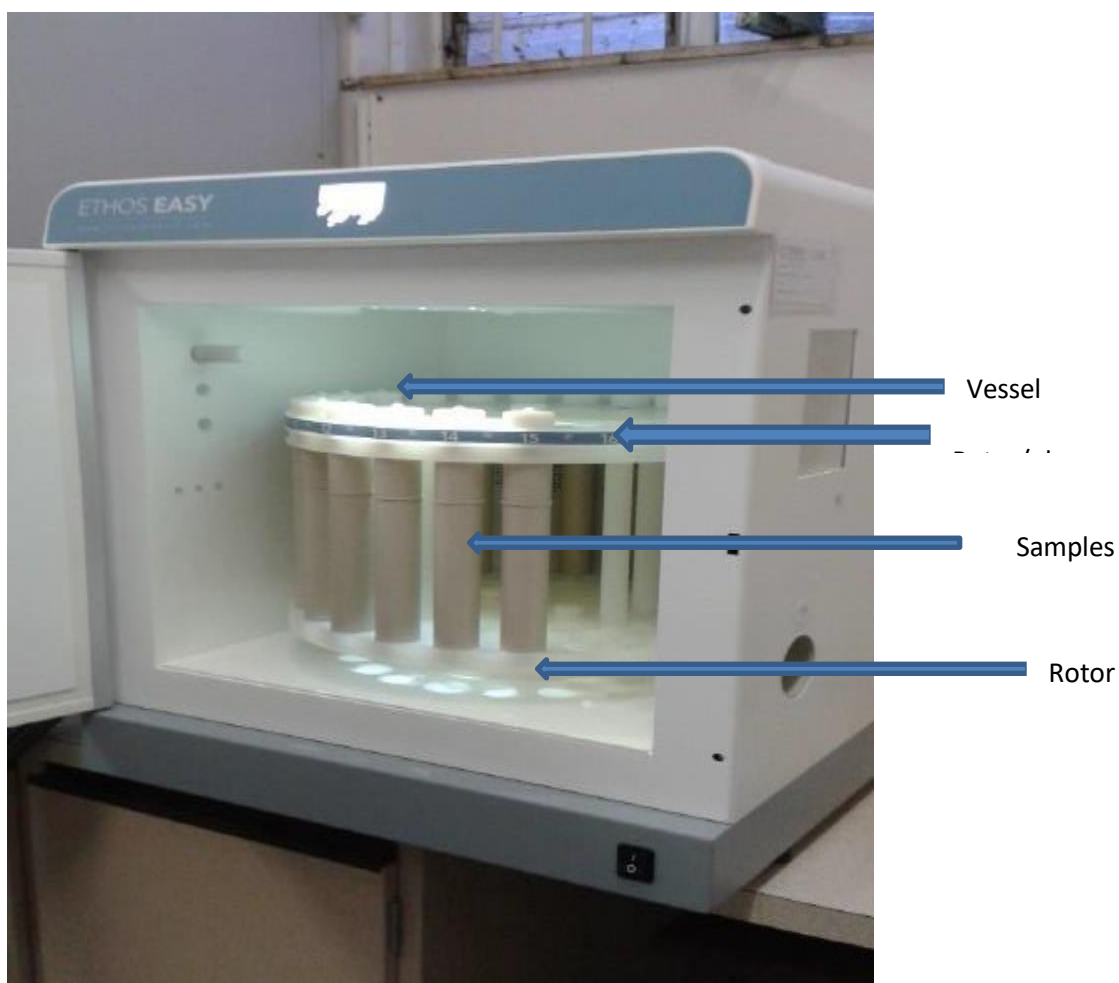
Figure 3. 18: The microwave oven interior. Photograph taken by Greying (2017), with permission, cited from Mphinyane (2018)

The addition of nitric acid for assimilation of Cu, Zn, Mn, Pb, Cr, Co, Ni, Cd, U and As prior to ICP-MS was done using the microwave digestion. As it was witnessed by Mphinyane (2018) it is enough to determine TEs concentration in tailings and leachate.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 RESULTS AND DISCUSSION

Chapter four of this research focuses on the presentation and discussion of analytical data or results. The research findings are presented in the form of graphs or figures and tables. Trace elements are generally found to be sources of water, soil and air pollution. These contaminants are emitted from different anthropogenic activities such as mining. Amongst them gold, copper and coal mining are considered the most common source of TEs of health concern, both animals and environmental health.

4.2 CHEMICAL PARAMETERS

A wide range of chemical parameters are studied in earth sciences. These parameters help to understand soil, water and plants quality for a variety of uses. Table 4.1 below shows the pH, EC and selected macro-elements results for all sixteen tailings samples.

Table 4. 1: Presentation of pH, EC and selected macro elements of all 16 tailings samples

Sample no.	Ca	Mg	K	Na	P	pH(H$_2$O)	EC
			(mg/kg)				*(mS/cm)*
TJ1	3026	822	471	4062	<0.01	7.66	61
TJ2	2421	223	871	1861	<0.01	10.12	1.1
TJ3	823	107	41.5	0.5	<0.01	2.55	16
TJ4	988	182	185	238	<0.01	7.51	5.1
TJ5	2144	180	115	86.0	<0.01	8.05	4.4
TJ6	267	24.0	37.0	7.5	<0.01	4.22	3.7
TJ9	3207	1478	37.5	281	<0.01	3.80	22
TJ10	921	208	63.0	28.0	<0.01	8.84	1.3
TJ12	3897	533	450	3819	<0.01	9.22	19
TJ15	4268	1033	44.5	935	29.2	3.57	17
TJ19	515	57.0	128	50.5	51.8	7.38	1.7
TJ20	2947	447	110	5.0	11.8	2.19	35
TJ22	254	1033	166	553	23.5	7.83	11
TJ23	2750	74.0	63.0	1.5	<0.01	9.01	0.50
TJ24	4490	1704	239	827	<0.01	8.53	19
TJ25	2073	172	53	159	4.5	9.01	1.7

Ca, calsium; Mg, magnesium; K, potassium; Na, sodium; H$_2$O, water; KCl, potassium chloride; EC, electrical conductivity (3.60 mS/cm are a threshold value)

4.2.1   pH

One of the chemical parameters used to assess soil and water quality is pH. Figure 4.1 below shows a variation in the pH of sixteen different tailings.
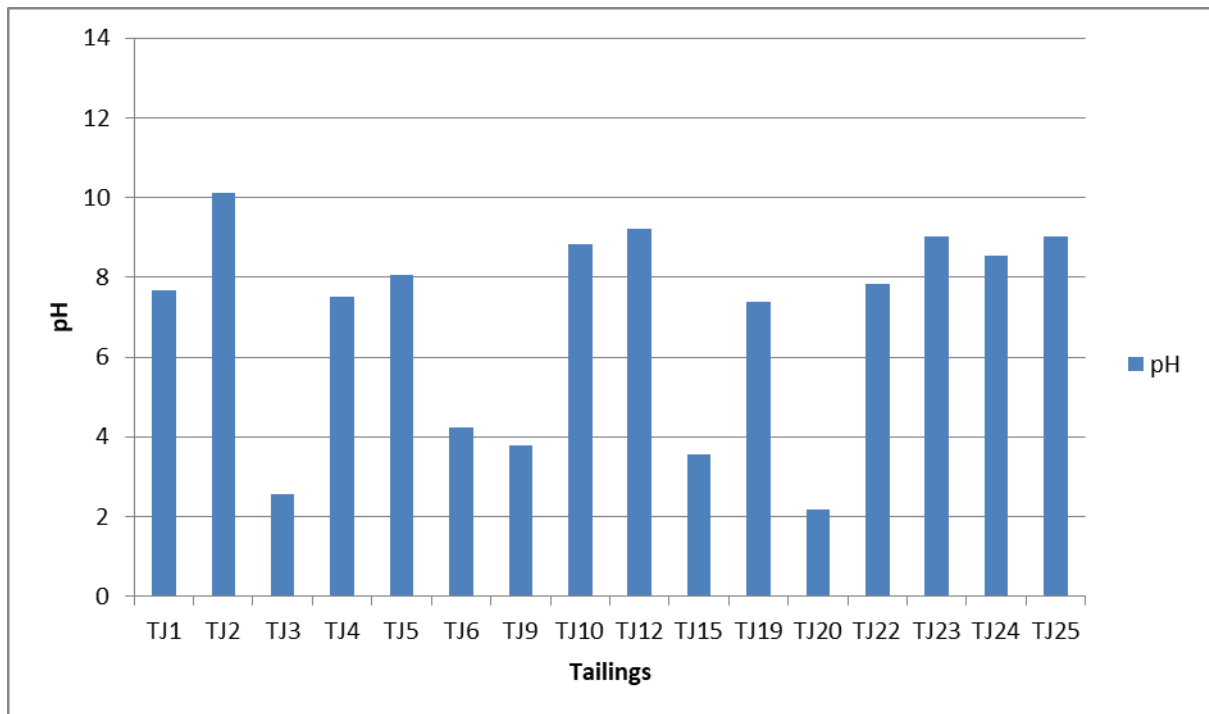
Figure 4. 1: pH-values for the different tailings materials in leachate

One of the crucial environmental factors affecting the solubility, leaching and uptake of nutrients in soil or any inorganic substance, is pH (Havlin *et al.*, 2016; Kirkham, 2006; Kumpiene *et al.*, 2008; Zayed & Terry, 2003). As it was discussed in *chapter two* and *chapter 3* of this research study, pH is described as the acidity and basic or alkalinity of soil (in this case the tailings) or solution (McCauley *et al.*, 2009; Oste *et al.*, 2002; Šlmek, & Cooper, 2002). The pH was done on a ratio of 1:2.5 tailings : water solution (10 g of tailings and 25 ml of water). As indicated in Table 4.1 and Figure 4.1, sample site TJ20= 2.19 (New Machavie), TJ3=2.55 (Witbank coal), TJ15= 3.59 (East rand gold mine), TJ9= 3.80 (Okiep copper mine) and TJ6= 4.24 (Aggeneys mine), the pH of the original tailings was very low (acidic). As a result of increased solubility due to low pH, high concentrations of TE's were mobilised and leached from tailings materials. Low pH poses a detrimental effect on plants nutrients availability. At pH below 5.5 the leachability of plant nutrients is too high as compared to pH of 5.5 to 7.0 ranges. As shown in Figure 4.1, sample site TJ3, TJ15, TJ9 and TJ6 in increasing order has pH range of less than 5.5. This pH range

implies that leaching of plant nutrients is faster than in other sites. The solubility and toxicity of TE's is also affected by a pH that is below 5.5.

4.2.2 Electrical conductivity (EC)

As discussed in Chapter 2 of this research study, EC is defined in terms of the concentration of soluble salts or ions in a water solution (Corwin & Lesch, 2003; Jungwirth & Tobias, 2001; Wilks, 2002). The higher the level of solubility of salts in growth mediums the greater the conductivity (Bernstein, 1975; Chen *et al.*, 2001;Ghoulam *et al.*, 2002; Parida & Das, 2005). Electrical conductivity is one of a few quality indicators that help to determine the moisture availability for crop yield purposes because the salts have a negative osmotic effect on the medium and therefore the salts are in constant competition for moisture. Some plants are more tolerant against certain EC values because of natural resistance to moisture deficiencies and all salts don't have the same EC at the same concentration. Therefore the negative effects of EC is correlated to dissolved salts content in tailings and the effect depends on the type of plants (Arshad & Martin, 2002; Bronick & Lal, 2005; Doran & Zeiss, 2000; Shukla *et al.*, 2006). The elevated EC at tailings sample TJ1, TJ3, TJ4, TJ5, TJ6, TJ9, TJ12, TJ15, TJ20, TJ22 and TJ24 as indicated on Table 4.1, respectively may be due to higher content of solubale salts in the host rock and tailings. Electrical conductivity of TJ1 and TJ20 respectively is greater than 2600 mS/m, therefore is regarded to be highly saline and potentially hazardous to crop production and vegetation cover. (Bianchi *et al.*, 2010; Howat, 2000; Yu *et al.*, 2015). These may negatively affect ecosystem health. Electrical conductivity has a detrimental effect on microbial activities and very much so in mine tailings (Schimmer 2017). Therefore it could be concluded that high EC values have negative effects on crop yield, crop suitability, plants nutrient availability and soil microorganism's activities. Low levels of EC at sample site TJ2, TJ10, TJ19, TJ23 and TJ25 respectively may be due to less amount of dissolved salts content in tailings.

4.2.3   Cations concentration (Ca, Mg, K and Na)

Macro elements are those chemical elements required in large quantities for the purpose of normal plant physiological processes. Figure 4.2, 4.3, 4.4 and 4.5 and Table 4.1 show a variation of plant available macro elements (Ca, Mg, K and Na) concentration in sixteen different types of tailings prior to leaching. In natural soils the plant available nutrients are not in equal concentrations present; the normal scenario is Ca>Mg>K. It is also the case with 16 tailings samples with the exception of TJ 22, the material from the antimony mine in which case the Mg is higher than the Ca. This may be due to a lack in Ca minerals in the host rock and or abundance Mg in the host rock. (FSSA, 2007) . It is also important to distinguish between plant avalailable and total cations. For plant growth and mine rehabilitation the plant availbale cations are more important to ensure a physiognomic balance in the plant tissue.
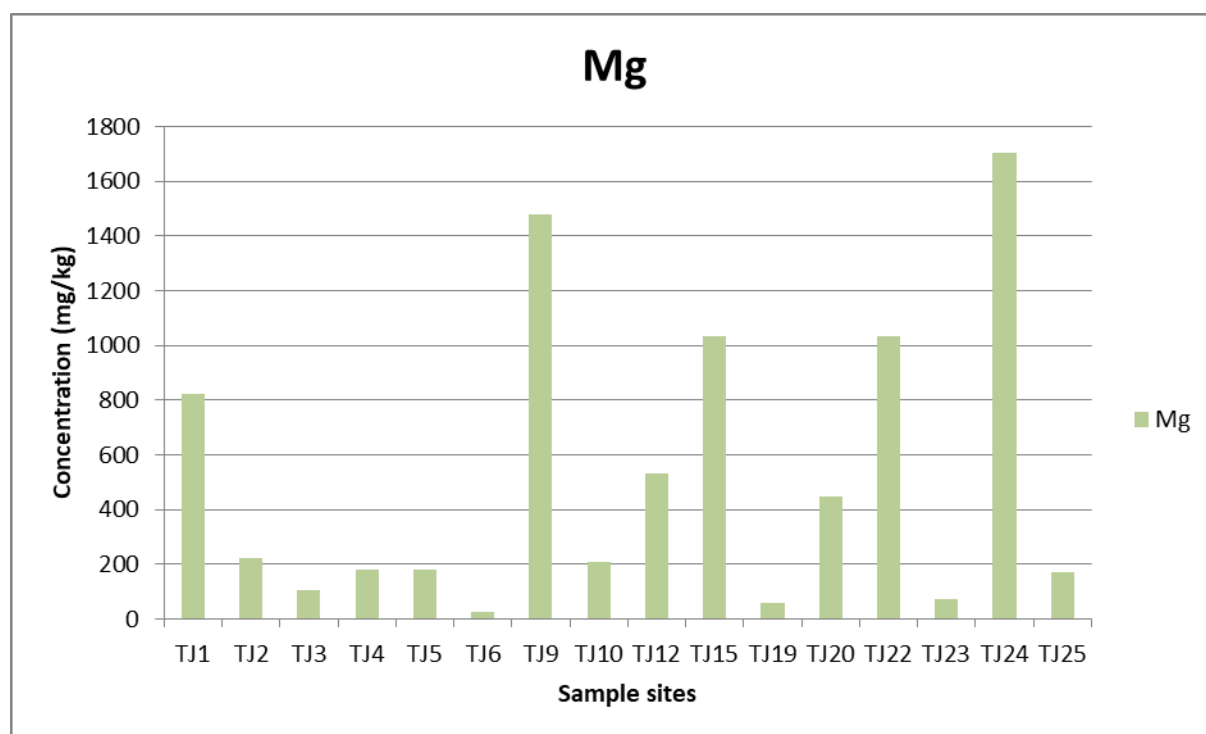
Figure 4. 2: **Total Mg cation concentration of different sample sites**

Magnesium also occurs in primary and secondary minerals. It is essential for plants growth by being an essential element to plants or crops photosynthesis etc. (Barzegar *et al.*, 2002; Mulligan *et al.*, 2001; Zeng *et al.*, 2011). Figure 4.2 above shows variations in Mg concentrations of 16 different sample sites or tailings. As indicated above, Mg concentrations ranges between TJ24= 1704 mg/kg and TJ6= 24 mg/kg. The toxic effect of Mg is rare, but in excess it results in potassium deficiency causing damage to plants or crop leaves. Refer to Figure 4.2 and Table 4.1 (Parida & Das, 2005; Farooq *et al.*, 2009; Soetan *et al.*, 2010).
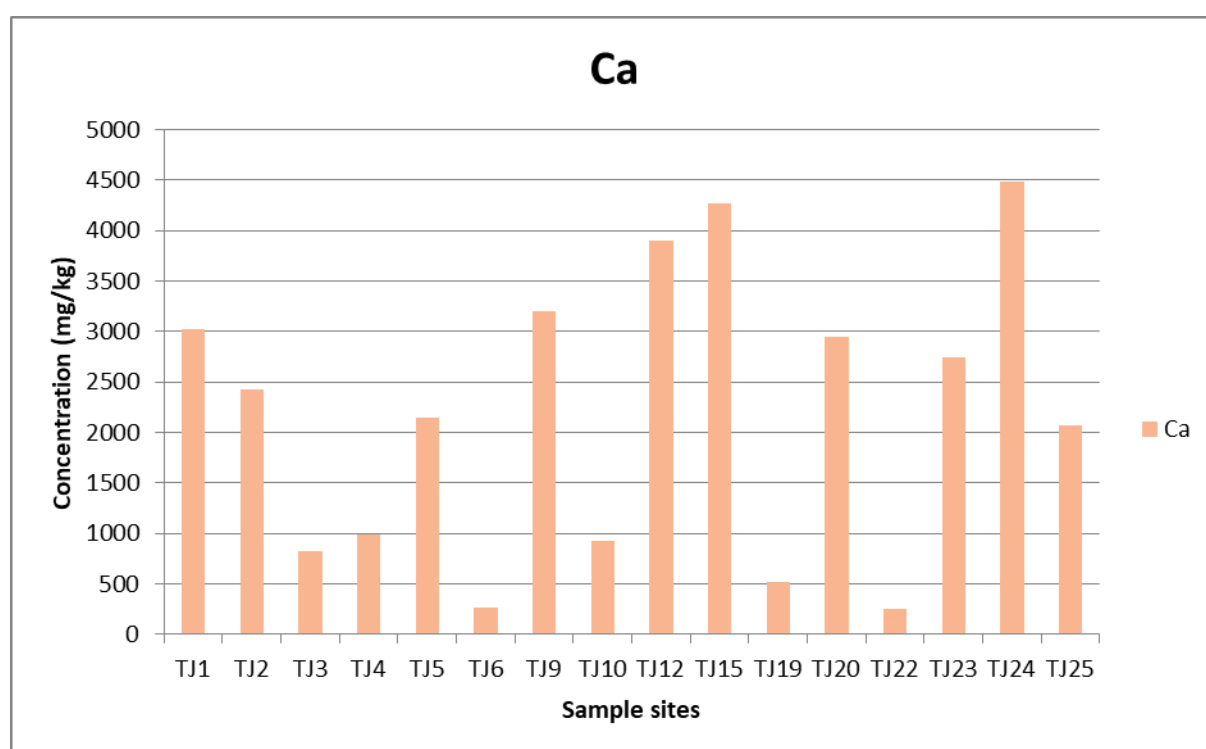
Figure 4. 3: **Total Ca cation concentration of different sample sites**

Calcium is an element occurring on earth in association with the primary or secondary minerals (limestone, shale etc) (Alloway, 2004; Mitchell, 2013; Skinner, 1993). It has an atomic number of 20 and found in group 2 of a periodic table. Calcium plays a crucial role on human health, animals and plant growth. However when Ca occur as a cation ion it becomes soluble and mobile. Bearing in mind that

Ca is considered the major cation, its deficiency depends on CEC and as a result it is in competition with other cations. However, pH controls the abundance of Ca in soil (Alloway, 2004; Mitchell, 2013; Skinner, 1993). At acidic condition, Ca availability is reduced and elevated at high pH. Despite that, Ca by its nature does not have any direct toxic effects. Figure 4.3 presents Ca variation of 16 different sample sites (tailings). Concentration variation of Ca as indicated in the above graph ranges between TJ24= 4490 mg/kg to TJ22= 254 mg/kg respectively. The highest Ca concentrations were due to high concentrations in the host rock and high CEC and elevated pH. The lowest Ca level was as a result of low pH and toxic levels of Al and Mn (Fertilizer Handbook, 2007: 85; Smith *et al.*, 2008). Refer to Figure 4.3 and Table 4.1.
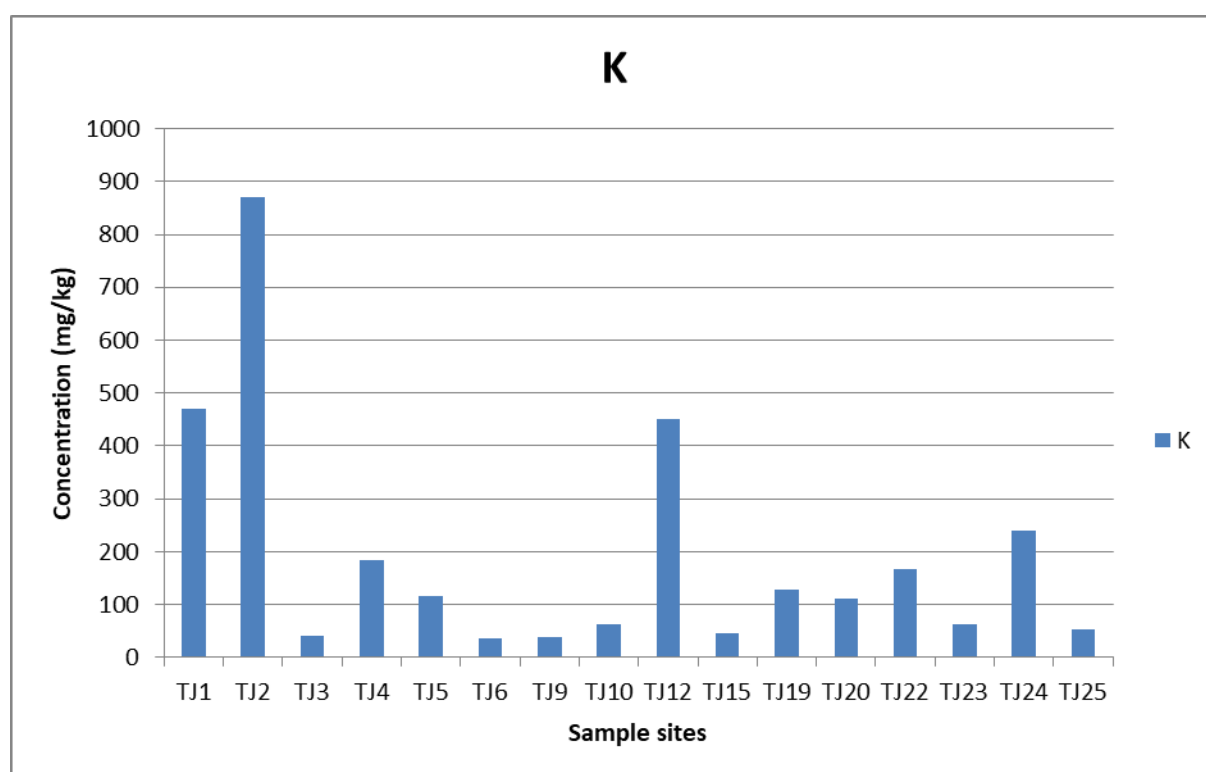
Figure 4. 4: **Total K cation concentration of different sample sites**

Potassium (K) is referred to as a chemical element found in group 1 of the periodic table and has an atomic number of 19. Potassium also occurs on earth or soils in association with primary and secondary minerals (Christistensen, 2001; Lützow *et*

al., 2006; Six *et al.*, 2004). It is one of the most essential macro element or plant nutrients in growth mediums. The role of K on plants or crops is for physiological and metabolic functions (Dudareva *et al.*, 2013; Fageria *et al.*, 1997; Mundree *et al.*, 2002). Figure 4.4 above shows a total variation of K concentration of 16 different sample sites or tailings. As indicated on the above graph, the total level of K in mg/kg ranges between TJ2= 871 mg/kg a nd TJ6= 37.0 mg/kg. Potassium has no direct toxicity; however in excess it may cause Mg deficiency. Potassium deficiencies limit a crop's ability to make use of N and are also related to a crop's resistance to disease. Refer to Figure 4.4 and Table 4.1.
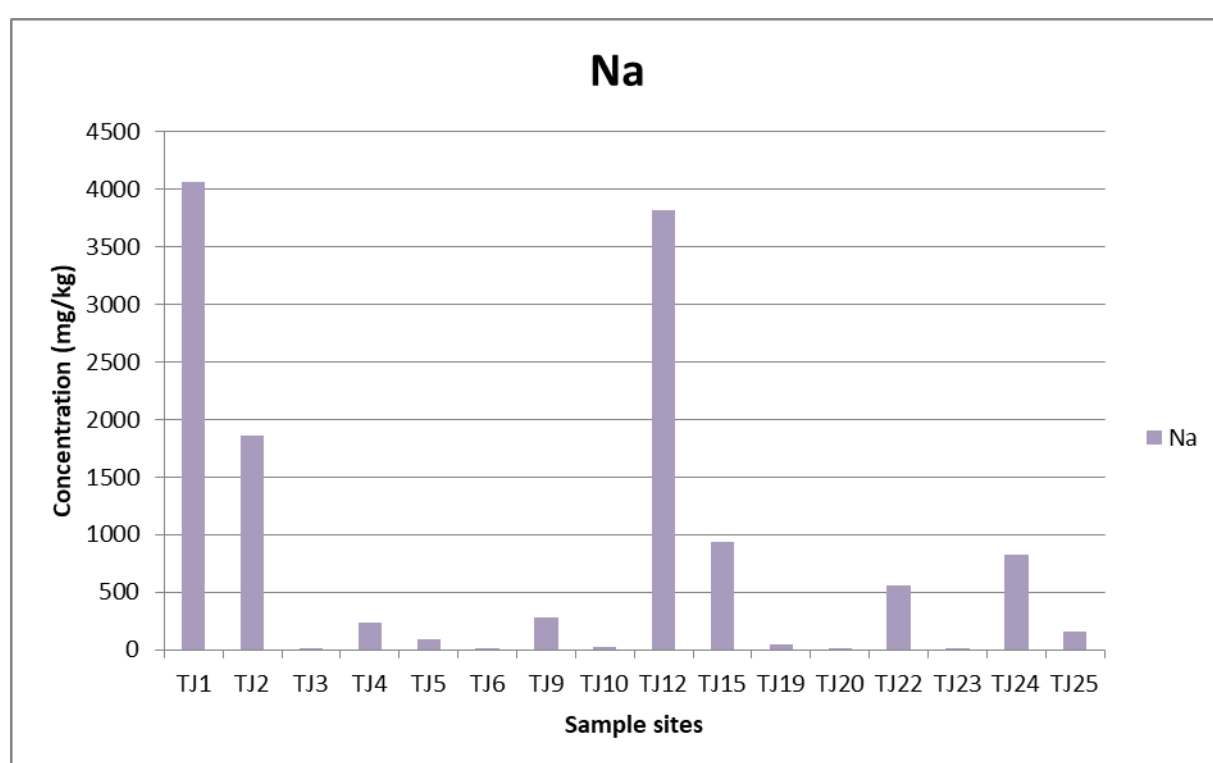
Figure 4. 5: **Total sodium cation concentration of different sample sites**

Sodium (Na) is an element found in group 1 of the periodic table and it has an atomic number of 11. Generally Na occurs as a compound of chloride (NaCl) on earth etc (Munns, 2002; Roland *et al.*, 1959; Shi *et al.*, 2009). On its solid form sodium is immobile and becomes adsorbed in soil. However its mobility (leachability) is increased immediately when in contact with water to form soil solution (Munns, 2002; Roland *et al.*, 1959; Shi *et al.*, 2009). Apart from other macro nutrients such as K^+,

Ca^{2+} and Mg^{2+}, Na$^+$ is the element with most negative on ecosystem (Bhausaheb, 2011; de Schamphelaere *et al.*, 2002; Gattward *et al.*, 2012) due to its association with soil erosion. Sodium at elevated concentration has indirect negative impact including but not limited to induced nutritional imbalances and impairment of soil physical quality i.e. dispersiveness and eventually erosion. Greater than 70 mg/l Na concentration in water becomes toxic depending on plants physiological strength (Gattward *et al.*, 2012; Hou *et al.*, 2007). Figure 4.5 and Table 4.1 present a variation of Na concentration in leached water of 16 varying tailings material. Sodium level in descending order was recorded at sample site TJ1= 4061 mg/kg, TJ12= 3819 mg/kg, TJ2= 1860 mg/kg, TJ15= 934 mg/kg, TJ24= 827 mg/kg, TJ22= 553 mg/kg, TJ9= 280 mg/kg and TJ4= 237 mg/kg. Sodium levels are very random in tailings and are a reflection of the extraction processes of the real ore from the host rock as well as to a lesser extent the specific primary minerals in the host rock.

4.2.4   Anion concentrations (mg/l)

Anion is defined as a negative charged ion and in this context it refers to negative charged bicarbonates, phosphates, chlorides, sulphates, nitrates etc as shown in Table 4.2 . Anions originates from the recovery process where the mines recover the real ore, ore from explosives. Oxidation pyrite act as a source of suphates and nitrate, bicarbonates originates from carbonates in the host rocks, chlorides from chloride minerals in the host rocks or from dispersive agents in the reduction plant and phosphates comes from the host rock or from dispersive agents in the reduction plants etc. Some of these types of chemical elements are required in small amount for healthier soil, water and plants. Table 4.2 below shows a variation of anions concentrations in sixteen different types of tailings.

As discussed in Chapter 2, anions are those molecules or elements exhibiting negative charge. (Goh & Lim, 2004; Keeney & Wildung, 1977; Summer et al., 1991). Diverse anion exist within the growth medium, however this study only focused on the following; PO4, SO4, NO3, NH4 and HCO3 respectively. Table 4.2 shows a variation in anions concentrations of 16 different tailings sample or sample sites. The highest level in descending order of phosphates was determined at sample site TJ1=

61.0 mg/l, TJ3= 37.8 mg/l and TJ9= 5.20 mg/l, whereas the lowest detected phosphate ion was < 0.01 mg/l.   According to Reta et al. (2018) elevated level of phosphates contaminates water sources (surface and ground water). Ideal P levels in natural growth mediums are 10-20 mg/kg. Sulphates on the other hand ranges between TJ20= 206930 (TJ 20: New Machavie) mg/l and TJ2= 14.7 mg/l respectively.

Table 4. 2: Presentation of anion concentration of 16 tailings samples

Total Anion Concentrations						
Sample no.	**PO_4** *mg/l*	**SO_4**	**NO_3**	**NH_4**	**Cl**	**HCO_3**
TJ1	61.0	3211	424	1.64	30598	30.5
TJ2	0.51	14.7	0.59	0.16	1.22	433
TJ3	37.8	33243	22.0	0.29	5.24	<0.01
TJ4	<0.01	3729	14.7	0.94	33.5	51.9
TJ5	<0.01	414	1646	0.60	287	51.9
TJ6	1.91	2826	24.0	1.70	33.7	0.00
TJ9	5.20	25831	76.3	3.68	2218	0.00
TJ10	0.47	391.09	135.24	1.28	58.37	101
TJ12	<0.01	7230	1843	0.32	2402	546
TJ15	<0.01	16132	933	44.3	675	<0.01
TJ19	<0.01	646	46.4	0.25	95.4	42.7
TJ20	<0.01	206930	100	0.00	24.2	<0.01
TJ22	<0.01	8075	632	0.16	516	45.8
TJ23	0.06	227	6.61	3.03	11.0	70.2
TJ24	<0.01	13339	1136	0.83	2630	39.7
TJ25	<0.01	83.2	137	<0.01	381	119

PO_4, Phosphate; SO_4, Sulphate; NO_3, Nitrates; NH_4, Ammonium; Cl, Chloride; HCO_3, Bicarbonate (Hydrocarbonate)

The soil screening value (SSV) of sulphates according to Nemwa (Act no. 59 of 2008) is 4000 mg/kg (mg/l). Above the SSV was observed at sample sites TJ20= 206930 mg/l, TJ3= 33243 mg/l, TJ9= 25831 mg/l, TJ15= 16132 mg/l, TJ24= 13339 mg/l, TJ22= 8075 mg/l and TJ12= 7230 mg/l as shown on Table 4.2 and the rests were below the SSV. As a result, remedial actions are recommended. A decrease in pH has an increasing effect on sulphates adsorption to a maximum adsorption level of pH. High level of sulphates in the environment may cause scaling pipes, may pose damage to surrounding vegetation, soil, may reduce surface and ground water quality, negatively affect building materials and in case of irrigation water, it may cause non-toxic stains on the leaves and fruits of trees. A decrease in ruminal metabolic activity in cattle is one of the effects caused by elevated sulphates (WHO, 2004:438-439). However there is a gap in literature with regard to level of sulphates in drinking water that can be toxic to human health. (WHO, 2004:438).

Nitrate is referred to as a form of inorganic nitrogen that occurs naturally in soil (Di & Cameron, 2002; Robertson & Groffman, 2007; Schulten & Schnitzer, 1997). However, in the tailings it could be a remnant from the explosives been used during the mining process. Nitrates (NO_3) were also analysed and the results range between TJ12= 1843 mg/l and TJ2= 0.59 mg/l as indicated on the table above (Table 4.2). The SSV in terms of Nemwa (Act 59 of 2008) is 120 mg/kg (mg/l). Most of the sites as projected on Table 4.2 are above the SSV1 and some are below. Above allowable level of nitrate in soil may affect plants growth or crop production and increases the risk of water quality reduction (ground and surface water). In addition, higher level of nitrates in soil can contaminate water supplies and create a potential health concern (Shrimali & Singh, 2001:351-359; Wakida & Lerner, 2005:3-16). Ground or surface water contamination may be via leaching or erosion. Soil texture (sandy, silt or clay) also play an important role on leaching of soil nitrate to either ground or surface water and the natural environment as whole. Remediation option such as reverse osmosis or ion exchange technology for water quality may be recommended. Standardised application of commercial fertilizers to on tailings or natural soils may also be recommended to minimise nitrates concentrations. Addition of commercial fertilizers may be recommended increase nitrate level in case where

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its deficiency is observed. The other nitrates are to the advantage for the plants to promote good growth.

During nitrification process in soil ammonium ion (NH_4^+) is converted to nitrates (NO_3^-) ion through the action of aerobic bacteria. Ammonium as a primary source of nitrogen (N) is sometimes utilised in the form of N by certain plants species or forest trees. Ammonium by its nature is a plant nutrients and it plays a crucial role in plants metabolic processes. Table 4.2 above shows a variation in ammonium concentration from 16 different tailing soils or sample sites. The concentration ranges between TJ20= 44.3 mg/l (mg.kg) and TJ15= <0.01 mg/l respectively. Addition of NH_4 is recommended for the entire sample site.

Chloride (Cl) is a chemical element found in group 7 of the periodic table and has an atomic number of 17. It also occurs in natural soils as plant nutrients in the form of chloride ion (Cl). Chloride as an important micronutrient it is absorbed by crops or plants in small amount. When occurring as a salt compound (KCl), Cl exhibit salinity and toxicity. Despite its toxic effects, chloride is essential for plant photosynthesis, osmotic adjustment and control plants diseases. According to Nemwa (Act 59 of 2008) the SSV of chloride (Cl) is 12 000 mg/kg (mg/l). Table 4.2 above shows a variation of Cl level of 16 different sample sites or tailings. Its concentration ranges between TJ1= 30598 mg/l (mg/kg) and TJ2= 1.22 mg/l (mg/kg) respectively. Above 70 mg/l of chloride concentration in water for agricultural purpose is safe for all types of plants species. However, Table 4.2 shows high concentration of Cl at sample site TJ1= 30598 mg/l, TJ24= 2630 mg/l, TJ12= 2402 mg/l, TJ9= 2218 mg/l, TJ15= 675 mg/l, TJ22= 516 mg/l, TJ25= 381 mg/l and TJ5= 287 mg/l in descending order. Above 350 mg/kg of Cl in irrigation water can result in severe effect on crops. However, for tailings to be declared contaminated for all land use the SSV for Cl concentration should be above 12000 mg/kg. From all 16 tailings only TJ1 has Cl concentration above the SSV and therefore it is declared unsafe. However,the rest of the tailings are safe. High Cl levels are most of the time associated with high Na levels if Table 4.1 and 4.2 are compared.

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Hydrogen carbonate or bicarbonate (HCO_3) is a product of the consumptions of hydrogen protons (H^+) by calcium carbonate ($CaCO_3$). Bicarbonate is an essential cause of soil salinity. When the HCO_3^- concentration in soil is high pH level tend to be reduced to approximately 7.5 to 6.7 a high level of HCO_3^- means high salinity, which has a negative effect on crops and plant growth or yield. Table 4.2 above gives an indication of HCO_3^- level in 16 different sample sites or tailings. The HCO_3^- level in soil or leached water ranges between 547 mg/kg (mg/l) and <0.01 mg/l. The highest levels in descending order were recorded at sample sites TJ12= 547 mg/l and TJ2= 433 mg/l respectively. The elevated level of Cl^- in plants includes but not limited to necrosis of leaf margins and tips, leaf drop and or leaf damage. This was due to the presence of carbonate rocks ($CaCO_3$). Remedial actions are recommended for these sites as well as an addition of carbonate nutrients in the form of lime is also recommended for lowest levels of HCO_3^- at different sample sites as indicated on Table 4.2 above.

4.2.5   Cation exchange capacity (CEC) in cmol (+)/kg

Cations exchange capacity influences the soil's ability to hold onto significant nutrients and makes a buffer against soil acidification.

Table 4. 3: **Presentation of CEC results for 16 different sample sites or tailings**

Sample	Ca	Mg	K	Na	CEC cmol/kg	S-value	Base saturation (%)	pH(H_2O)	ESP (%)
TJ1	15.1	6.77	1.21	17.7	8.39	40.7	485	7.66	210.5
TJ2	12.1	1.84	2.23	8.09	24.0	24.2	101	10.12	33.8
TJ3	4.11	0.880	0.11	0.00	7.70	5.09	66.1	2.55	0.00
TJ4	4.93	1.50	0.47	1.03	4.97	7.93	159	7.51	20.7
TJ5	10.7	1.48	0.29	0.37	6.90	12.9	186	8.05	5.4
TJ6	1.33	0.20	0.09	0.03	5.63	1.65	29.4	4.22	0.5
TJ9	16.0	12.2	0.10	1.22	7.89	29.5	374	3.80	14.5
TJ10	4.60	1.71	0.16	0.12	6.52	6.59	101	8.84	1.8
TJ12	19.5	4.38	1.15	16.6	37.0	41.6	113	9.22	44.9
TJ15	21.9	8.50	0.11	4.06	4.49	34.0	757	3.57	90.4
TJ19	2.57	0.47	0.33	0.22	4.68	3.59	76.7	7.38	4.7
TJ20	14.7	3.68	0.28	0.02	12.0	18.7	156	2.19	0.2
TJ22	1.27	8.50	0.43	2.40	7.51	12.6	168	7.83	32.0
TJ23	13.7	0.61	0.16	0.01	6.77	14.5	214	9.01	0.1
TJ24	22.4	14.0	0.61	3.60	11.5	40.64	353	8.53	31.3
TJ25	10.3	1.42	0.14	0.69	13.0	12.6	96.8	9.01	5.3
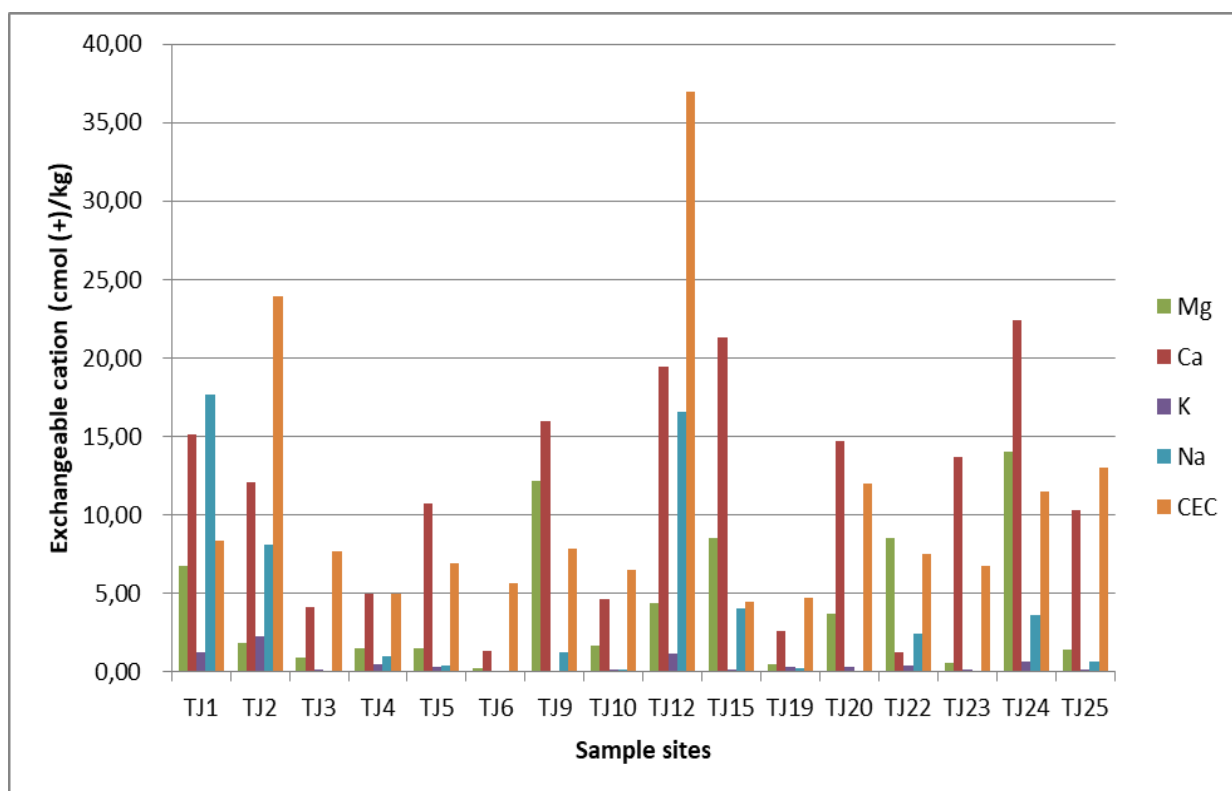
Figure 4. 6: **Exchangeable cations and cation exchange capacity (CEC) of different mine tailings**

Table 4.3 and Figure 4.6 above show a variation of CEC of sixteen different tailings samples.

As it was described in *chapter 2* of this research project, cation exchange capacity (CEC) is the adsorption capacity of organic or plant nutrient (cations) within the soil medium by negatively charged anions. The CEC of a soil or tailings are mainly a function of the secondary minerals in the host rock. Cations like Potassium ion (K^+), calcium ion (Ca^{2+}) and magnesium ion (Mg^{2+}) are of great importance to plants growth (Gattward *et al.*, 2012; Rajakaruna *et al.*, 2003; Ranjbar *et al.*, 2012). Sodium (Na^+), hydrogen ion, ammonium ion to mention few are also bioavailable as plants nutrients but in small amount Gattward *et al.,* 2012; Rajakaruna *et al.,* 2003; Ranjbar *et al.*, 2012). Figure 4.6 above present varying CEC capacity of 16 different sample sites. The CEC of sample site TJ12 (Samada mine tailings) and TJ2 (Cullinan diamond mine) in descending order is extremely high as compared to others. These elevated CEC was due to high content of clay minerals (smectite). However, sample

sites TJ4 (Kalgold), TJ15 (East rand gold) and TJ19 (Paardekraal) were recorded to have a CEC of below 5 cmol (+)/kg (see Table 4.3). The following were found to have the most suitable tailings material CEC, TJ1, TJ2, TJ3, TJ9, TJ12, TJ20, TJ22, TJ24 and TJ25.

The exchangeable sodium percentage (ESP) is the relative amount of Na^+ available on the soil and is given by percentage of total CEC. The varying ESP's of different TSF is given in Table 4.3. An ESP of <5% (safe), 5 to 10% (moderately erodible), 10 to 15% (highly erodible) and ESP> 15% (extremely erodible). As indicated in Table 4.3 the ESP of sample sites TJ1, TJ2, TJ4, TJ12, TJ15, TJ22 and TJ24 are extremely erodible. Wherein sample sites TJ9 is highly erodible, while TJ5 and TJ 25 are moderately erodible. However, the ESP of TJ3, TJ6, TJ10, TJ19, TJ20 and TJ23 is safe. (No erosion). Therefore, the risk of Na toxicity to the environment (soil, water and plants).

4.3 PARTICLE SIZE DISTRIBUTION (PSD)

With the use of D10, D30 and D60 the gradation of all sixteen tailings soil was determined. D10 means-10% finer, D30 means- 30 % finer and D60-means 60 % finer soil particles. The PSD tables and graphs are presented as Appendix.

Particle size distribution (PSD) as it was explained in 2.4.1.1 of this study is an essential soil property that classifies soil according to texture (sand, silt and clay). Appendix B-1 to B-15 below present PSD curves of 16 different sample sites (TJ1-TJ25). As illustrated in Appendix B-1 to B-15 most of the PSD curves of 16 different sample sites look alike, except for TJ5, TJ15, TJ20, TJ24 and TJ25. The behaviour of the curves is an indication of well graded, however the sorting is poor. This simply means the soil composed of particles of different sizes. As illustrated on Figure 4.7 the textural classification was achieved by means of USDA Soil Texture calculator (Daniel, 2015; Rorie, 2006; Shahri, 2016). From Figure 4.7 most of the sample sites indicated in red dots falls within the category of sand and loamy sand. An understanding of soil textural classification makes CEC to be easily understood. Sandy soil has a lower CEC as compared to clay. This is because it is poorly graded

which makes it to have a high standard of leaching (Daniels, 2015; Rorie, 2006; Shahri, 2016). Table 4.4 below provides a summary of textural classification of soil together with their percentages.
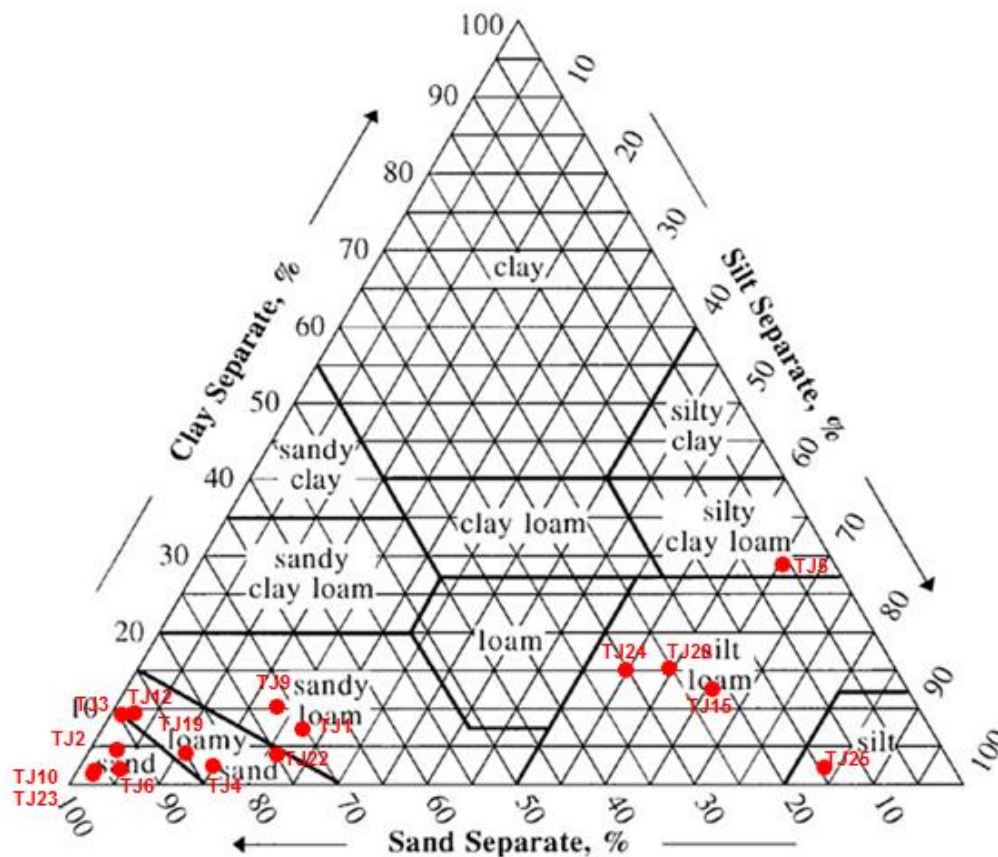
Figure 4. 7: **Triangle for soil textural classification of 16 different tailings or sample sites (Determined using USDA- NRCS, 2018)**

Figure 4.7 Indicates texture of different different tailings material. It describes the major physical property of soils. Texture is one of the factor that helps to predict the rate at which leaching take place (sand, silt and clay). Table 4.4 below provide a brief summary of soil textural classification of all 16 different tailings.

The grading analyses as shown in Table 4.4 and Appendix B was used to predict potential physical erosion. These discussions should be read with the Na levels in Table 4.3. Note the ESP values and potential chemical erosion of the tailings.

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Table 4. 4: **Brief summary of soil textural classification of 16 different tailings or sample sites**

Sample name	Texture	Sand %	Silt %	Clay %	Grading analysis
TJ1	Fine sandy loam	71.3	21.9	6.8	Well graded
TJ2	Coarse sand	93.5	2.5	4.1	Well graded
TJ3	Coarse sand	90.8	0.4	8.7	Well graded
TJ4	Loamy sand	83.8	14.2	2.0	Well graded
TJ5	Silty clay loam	6.8	64.7	28.5	Gap graded
TJ6	Fine sand	94.5	3.9	1.6	Gap graded
TJ9	Fine sandy loam	72.8	17.5	9.7	Well graded
TJ10	Sand	97.5	1.1	1.3	Poorly graded
TJ12	Loamy coarse sand	89.2	1.9	8.9	Well graded
TJ15	Silt loam	22.8	65.2	12.1	Well graded
TJ19	Loamy fine sand	86	10.4	3.7	Gap graded
TJ20	Silt loam	26.3	59.0	14.7	Well graded
TJ22	Loamy fine sand	75.9	20.7	3.4	Gap graded
TJ23	Sand	97.9	1.2	0.9	Poorly graded
TJ24	Silt loam	31.2	54.4	14.5	Well graded
TJ25	Silt	15.3	82.9	1.8	Gap graded

From Table 4.4 and Figure 4.7 the percentage of sand particles in tailing sample TJ5=6.8 %, TJ15=22.8 %, TJ20=26.3 %, TJ24=31.2 % and TJ25=15.2 % is lower as compared to other sites. Because of the ESP containing more than 15% of Na, the soil structure is prismatic. If Na occupies more than 15% of CEC, duplex properties and prismatic structure are likely to form. The production of crops on tailings with high Na content is limited by high pH, high ESP, poor water infiltration, inadequate

distribution of plant roots due to strong prismatic structure or poor soil grading (FAAS, 2007; Kay & Angers, 2001; Landon, 2014). See Table 4.4 and 4.3 for more details.

4.4   CONCENTRATIONS OF TRACE ELEMENTS IN 16 DIFFERENT TSF

Trace elements are elements such as Fe, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, Mo, Se and U, that normally occur at very low levels in the environment (Förstner & Wittmann, 2012 ; He *et al.,* 2005; Nagajyoti *et al.,* 2010). Table 4.5 and Figure 4.8 below show a variation in average leach-concentration (mg/kg) of selected TEs in sixteen different types of tailings. This variation in TEs concentrations is measured against the standard allowable values (SSV = soil screening values).

Table 4. 5: **Shows the average leach-concentrations of selected TEs from 16 different TSFs (ICP-MS)**

S/N	Sample number	Cr mg/kg	Mn mg/kg	Co mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	As mg/kg	Cd mg/kg	Pb mg/kg	U mg/kg
SSV		6,5	740	300	91	16	240	5,8	7,5	20	16
01	TJ1	0.059	0.180	0.045	0.019	0.032	0.113	0.000	17.9	0.116	0.209
02	TJ2	0.154	0.110	0.222	0.140	0.332	0.001	0.037	0.351	0.803	6.68
03	TJ3	1.12	20.9	34.9	172	105	151	20.7	0.108	0.517	10.0
04	TJ4	0.0148	0.548	0.123	0.522	0.058	0.319	0.021	0.016	0.177	0.733
05	TJ5	5.81E-	0.008	0.032	0.051	0.043	0.156	0.014	0.182	0.087	0.466
06	TJ6	0.000	10.36	5.31	14.3	0.005	0.830	0.087	1.45	0.036	3.97
07	TJ9	0.003	98.4	148	154	181	372	8.72	228	0.822	104
08	TJ10	0.000	0.091	0.142	0.165	0.724	0.995	0.316	0.493	0.258	0.375
09	TJ12	0.001	0.005	0.010	0.003	0.023	0.024	0.300	0.064	0.110	0.391
10	TJ15	0.147	133	15.8	22.8	6.38	192	0.040	47.2252	0.175	18.2
11	TJ19	5.98E-	0.031	0.005	0.055	0.143	0.380	1.37	0.030	0.028	1.51
12	TJ20	60.9	178	43.7	114	116	176	116	70.7	0.271	88.7

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13	**TJ22**	0.000	0.017	0.158	1.122	0.383	0.757	0.401	0.089	0.008	3.71
14	**TJ23**	0.000	0.004	0.003	0.190	0.003	0.460	0.066	0.067	0.025	0.006
15	**TJ24**	0.013	0.007	5.57	0.060	0.124	0.097	0.005	0.011	0.025	2.025
16	**TJ25**	6.72E-	0.013	0.163	0.522	0.253	0.488	0.155	0.114	0.199	0.913

The soil screening value (SSV1) used in this study is obtained from NEMWA (Act no. 59 of 2008). The SSV1 means soil quality values that are protective of both human health and ecotoxicological risk for multi-exposure pathways, inclusive of contaminant migration to the water resource (see Table 4.5.
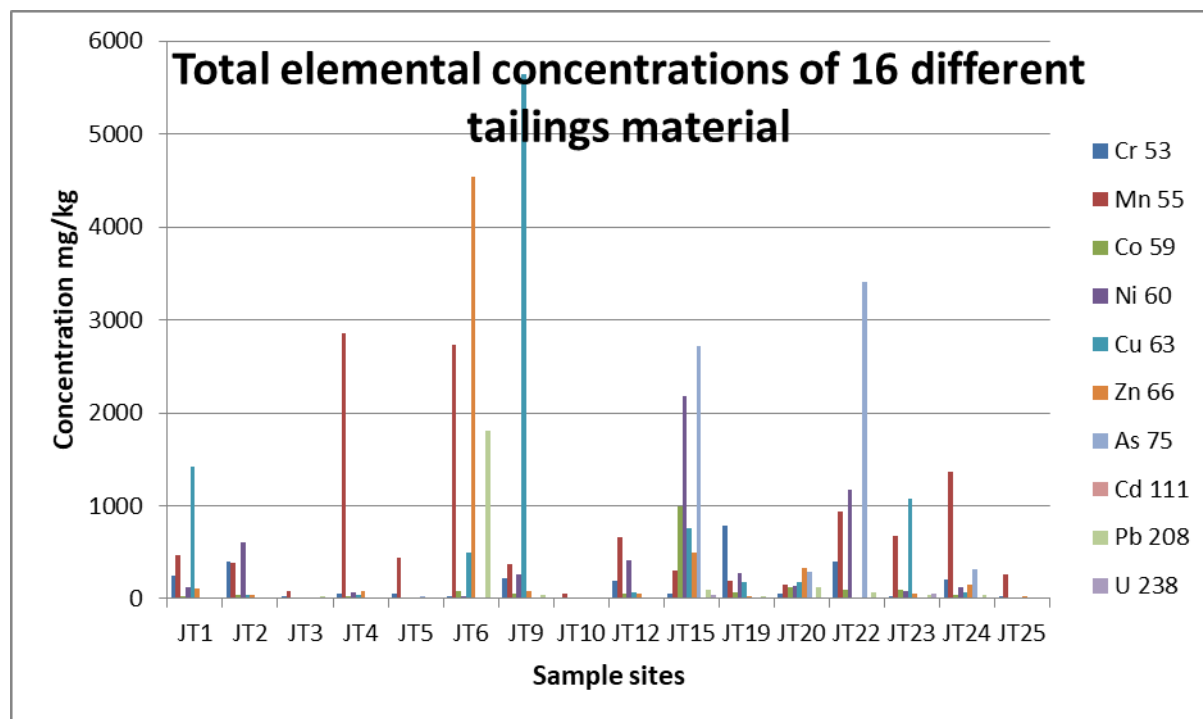
Figure 4. 8: **Variation of total TE concentrations of selected metals from 16 different tailings materials (sites)**

4.4.1   Uranium

As described in section *2.3.6* of this research study, U is a radioactive and chemo potential toxic element that occurs naturally within the earth's crust. Figure 4.9 below shows a variation in U concentrations (mg/kg) in sixteen varying tailings named TJ1 to TJ25 unevenly.
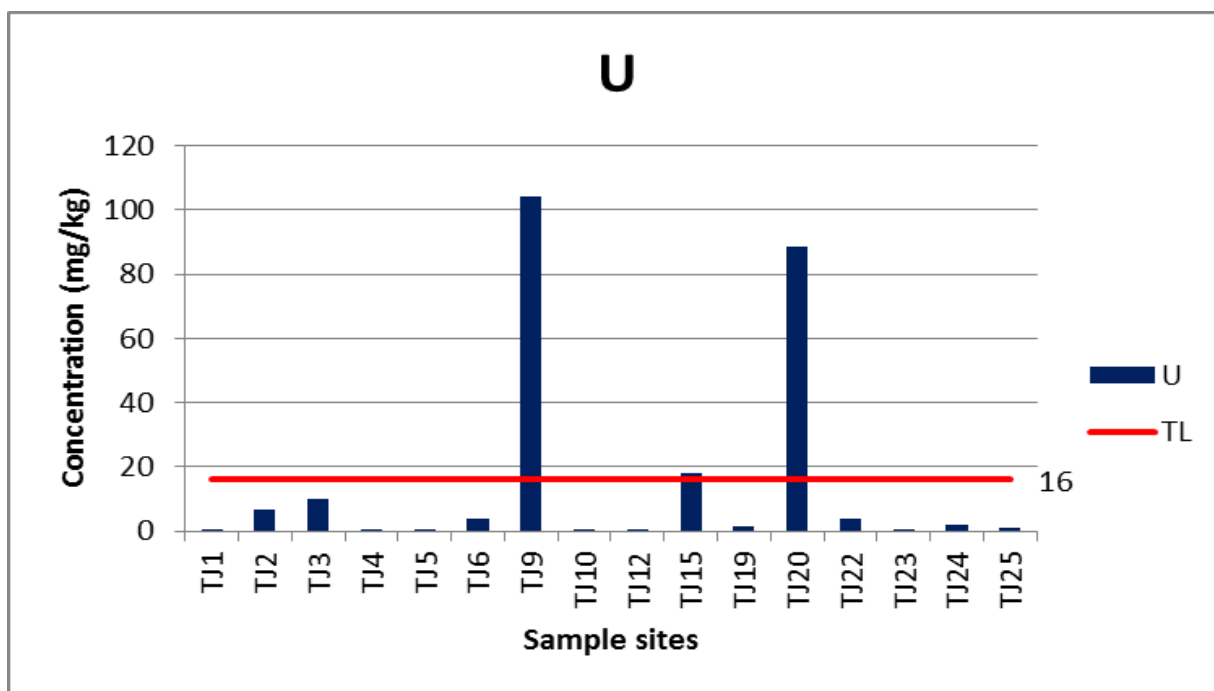
Figure 4. 9: **Variation of the concentration of Uranium at 16 different sites with TL threshold value of 16 mg/kg**

Uranium is a TE occurring in nature, as one of the most abundant metal on earth and in particular soil and sediments everywhere (Gadd, 2007; Garrett, 2000; Kabata-Pendias, 2010; Molinari and Snodgrass, 1990). Natural processes such as erosion, leaching and weathering together with anthropogenic activities like mining and processing contribute severely to the elevation of U concentration in soil and water environment (Alloway, 2013; Freedman, 1995; Förstner and Wittmann, 2012; Lenntech, 2004). Uranium threshold limit for land use is 16 mg/kg (Botha, 2015, Coetzee *et al*, 2006). Figure 4.9 above shows a variation in U concentration from 16 different mine tailings materials. The results indicate that U concentrations was above the threshold limit (16 mg/kg) at sample site TJ9=104 mg/kg (Okiep copper mine), TJ20=88.7 mg/kg (New Machavie gold mine) and TJ15=18.2 mg/kg (East Rand gold mine) and the lowest in ascending order was recorded at sample site TJ23=0.005 mg/kg (Phalaborwa copper mine), TJ1=0.209 mg/kg (Spektakelberg copper mine), TJ10=0.375 mg/kg (Foskor mine). Elevated U concentrations at sample site TJ9, TJ20 and TJ15 are due to the oxidation of sulphides minerals concentrated with U The migration of acid leachate with dissolved U and other trace

elements like As will contaminate the environment (soil and water). This acid condition is a result of the presence of sulphide minerals undergoing oxidation process. Low pH plays a primary role on mobilisation or leaching of U TE (Bolan *et al.*, 2014; Heasman *et al.*, 1997; Izquierdo & Querol, 2012; Kabata-Pendias, 2010).

4.4.2   Lead

As it was discussed in chapter 2 of this research study, Pb is a TE that is found in group 14 of the periodic table. Figure 29 below shows varying concentrations of Pb in sixteen different tailings in South Africa.
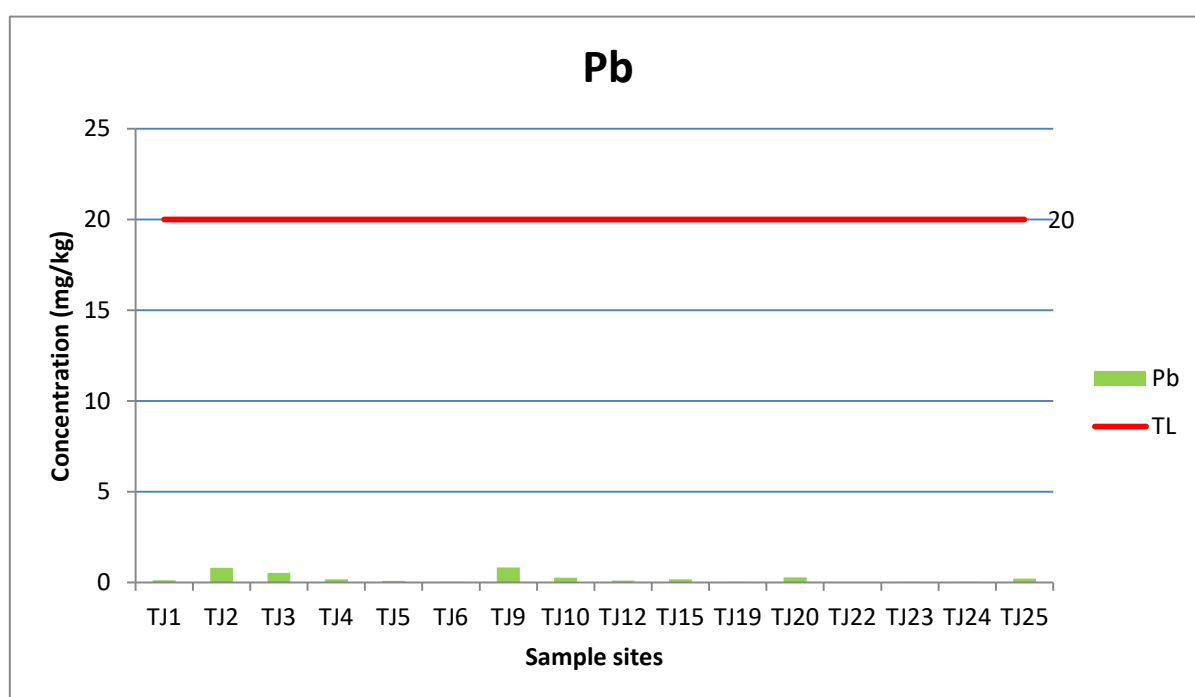
Figure 4. 10: Graph showing lead concentrations at 16 different tailings materials with TL threshold value of 20 mg/kg

The soil screening or threshold value of lead in soil is 20 mg/kg (NEMWA ACT. No 59 of 2008). Lead is a TE that is toxic to both plants and animals and it can degrade water quality (both surface and ground water quality) (Förstner and Wittmann, 2012; Kabata-Pendias, 2010; Nagajyoti *et al.*, 2010; Wong, 2003). Figure 4.10 above shows Pb concentration to be under the soil screening value. The greatest level of Pb determined was at sample site TJ9= 0.822, TJ2=0.803 mg/kg and TJ3=0.517 mg/kg. Taking in consideration that TJ1, TJ6 and TJ9 are from basemetal mines with

lead as a primary ore at TJ6, the lead content is very low. This is an indication that lead is not leached easily. The lower concentration of Pb in leached water from TSFs may be due to its low solubility and its higher ability to adsorb more specifically to other solid phases (Das *et al.*, 1997; Kabata-Pendias, 2010; Nkobane, 2014; Shukla *et al.*, 2002).

Lead by its nature is non-essential to plants metabolism. Lead is highly toxic to physiology and morphology of plants (Botha, 2015:53; Kabata-Pendias, 2011:346; Nagatjyoti *et al.*, 2010: 207). Botha (2015:53) discussed that Pb toxicity is often a cumulative process in the environment, biota and humans. In this study there is no anticipated future soil and water contamination. This is because Pb is immobile under oxidising condition at low pH and during leaching very small amount of lead was detected in the leachate sample.

4.4.3   Arsenic

Arsenic is a TE found in group 15 of the periodic table as it was discussed in chapter 2 (2.3.4) of this study. Figure 4.11 below indicates variations of As concentration in sixteen different types of tailings.
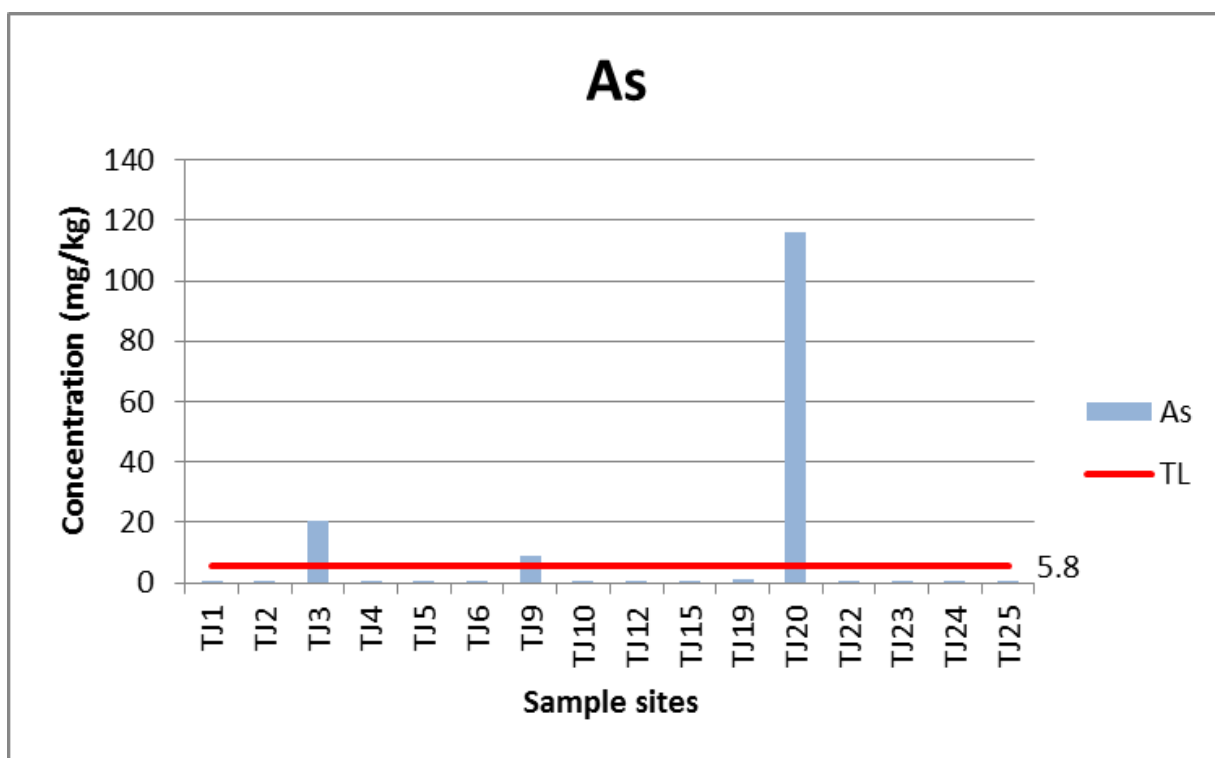
Figure 4. 11: **Variation of Arsenic concentrations at 16 different sites with TL threshold value of 5.8 mg/kg**

According to Centeno *et al.* (2007), Cicchella *et al.* (2008), Jomova *et al.* (2011) and Tchounwou *et al* (2012), arsenic (As) as one of TE's on earth is ubiquitous in soil due to human and geogenic activities. Figure 4.11 above shows a variation in As concentration from 16 different mine tailings. The SSV used in this study for As is 5.8 mg/kg. The graph above shows higher elevation of As concentration on sample site TJ20=116 mg/kg (New machavie gold mine), TJ3=20.7 mg/kg (Wit bank coal), TJ9=8.7 mg/kg (Okiep copper mine). An increased level of As at these three sample site is due to significant amount of oxidised sulphide minerals, leading to low pH and reduced redox potential resulting in an increase mobility through dissolution and leaching of metals oxides (Gambrell *at al.*, 1991; Goldberg, 2002; Smedley and Kinniburgh, 2002; Wuana and Okieimen, 2011). Dissolved calcium also influences the sorption of As metal in soil solution (Bauer & Blodau, 2006; Bradl, 2004;

Charlatchka & Cambier, 2000; Davis *et al.*, 1987). It is highly likely that arsenopyrite in the ore is the potential source of As in the leach water.

Arsenic concentrations in surface soil environment are normally considered to be due to the fact that leaching enables accumulation in the lower horizon, more especially for sandy soils (Botha, 2015:58; Kabata-Pendias, 2011: 354). Arsenic toxicity to plants is high, despite that plant-to-animal transfer is considered to be low (Botha, 2015:58; cited from Kabata-Pendias, 2011:360). Arsenic also has some health effects such as lungs, bladder and liver to mention few. However, De Wet (2017) focused on both human and animal health effects of As.

4.4.4 Manganese

Manganese is a TE that is found in group seven of the periodic table. Figure 4.12 below shows varying Mn concentrations in sixteen different types of tailings. The standard allowable Mn concentration used in this study is 740 mg/kg (SSV1).
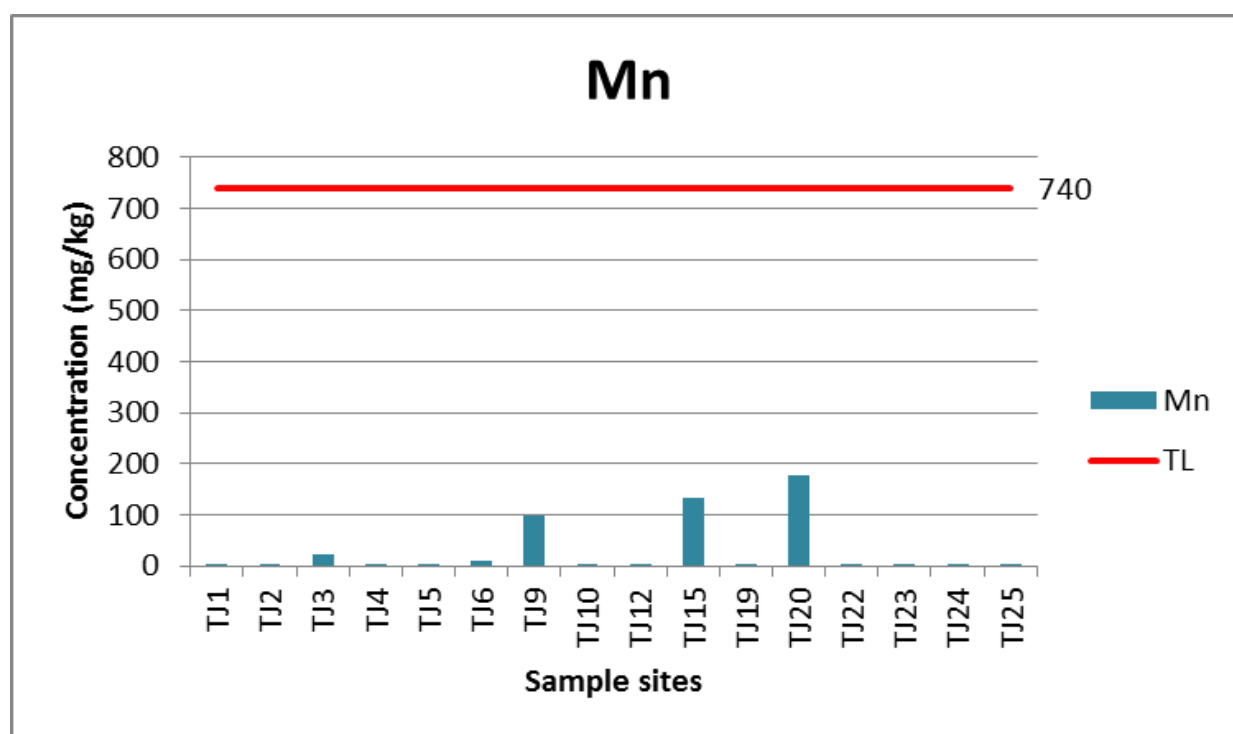
Figure 4. 12: Variation of manganese concentrations at 16 different sites with TL threshold value of 740 mg/kg

Manganese (Mn) is a TE's that naturally occurs in rocks, soils and or biota (Aydin *et al.*, 2010; He *et al.*, 2005; Kabata-Pendias & Mukherjee, 2007; Tebo *et al.*, 2005). Manganese like other TE's like Zn, Cu etc. is an essential micronutrient and contributes significantly to plant growth. However, above SSV for land use it becomes toxic. Almost all soils of South Africa contain Mn at low concentrations (Bell *et al.*, 2001; Post, 1999; Singh *et al.*, 2011). Figure 4.12 above shows a variation of Mn concentration at 16 different sample sites or tailings materials. The SSV for Mn concentration used in this study is 740 mg/kg. As illustrated on the graph above, Mn concentrations is below the threshold value. The highest Mn concentration was recorded in sample site TJ20=178 mg/kg (Wit bank coal) (Bell *et al.*, 2001; Coetzee *et al.*, 2002; Rashed, 2010; Sahoo *et al.*, 2016). The high Mn concentration at TJ20 as compared to other sample points is due to high content of organic matter, low pH (Johnson, 2003; Querol *et al.*, 2006; Redman *et al.*, 2002; Rodriguez *et al.*, 2009). Therefore, there is no Mn toxicity in all 16 sampling sites and no remediation or control measures are needed. It could be concluded that the Mn is not easiliy soluble.

4.4.5   Cobalt

Figure 4.13 below shows a variation in Co concentrations in sixteen different types of tailings, measured against the SSV1 of 300 mg/kg according to Nemwa act No 59 of 2008.
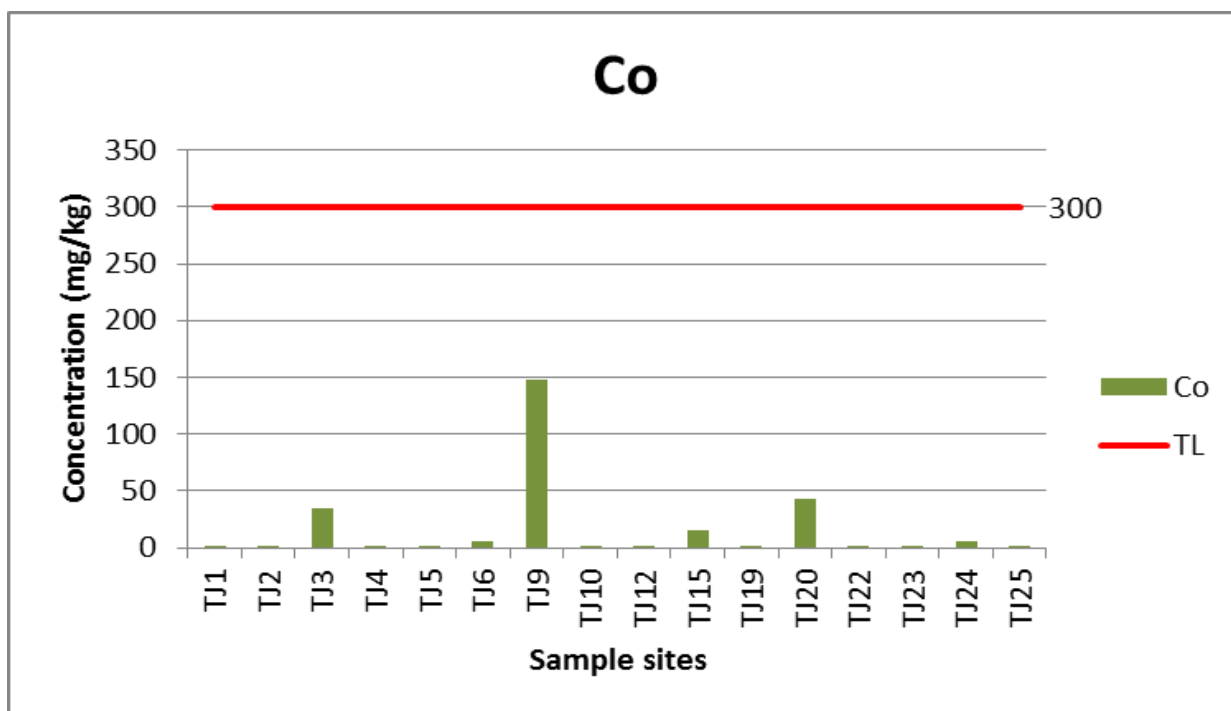
Figure 4. 13: **Variation of cobalt concentrations at 16 different sites with TL threshold value of 300 mg/kg**

Cobalt (Co) is a TE's that is essential to plants at allowable concentration (Fan *et al.*, 2007; Luo *et al.*, 2010; Robinson *et al.*, 1999; Sanders, 1983). Figure 4.13 above shows a variation of Co concentration at 16 different tailings sites. The SSV for Co used on this study is 300 mg/kg. Red horizontal line represents the threshold limit or SSV.

The higest level of Co concentration was observed tailing site TJ9=148 mg/kg (Okiep copper mine) and the lowest at sample site TJ23=0.003 mg/kg (Phalaborwa copper mine). The increase in Co concentration at soil sample TJ9 was due to decrease in pH=3.88. The low pH resulted in increased solubility of Co leading to increase mobility (Aery & Jagetiya, 2000; Grybos *et al.*, 2007; Harter & Naidu, 2001; Lange *et al.*, 2016). The lowest level of Co in tailings was due to high content of sulphate minerals and increased pH of up to nine at sample site TJ23.

Cobalt is present in soil solution at higher pH levels (Botha, 2015:45); Ma & Hooda, 2010:469). It is essential for microorganisms in nitrogen-fixation and may be of

importance to plants growth (Botha, 2015:46). Higher levels of Co in tailings may cause dermal, lung, cardiac, liver, kidney and immunological diseases to human health. At elevated stage, cobalt is also toxic to plants' growth and it may affect the plants' metabolism (Botha, 2015:46; cited from ATSDR, 2004a:18-19). However, Co concentrations at all 16 sample sites are below the SSV and as a result, Co do not pose any environmental impacts there. See Figure 4.13 above.

4.4.6   Chromium

Chromium is a TE that is found in group 6 of the periodic table. Figure 4.14 below shows a variation in Cr concentrations in sixteen different types of tailings measured against the SSV1 of 6.5 mg/kg according to Nemwa act No 59 of 2008. The threshold limit is indicated in red for TEs.
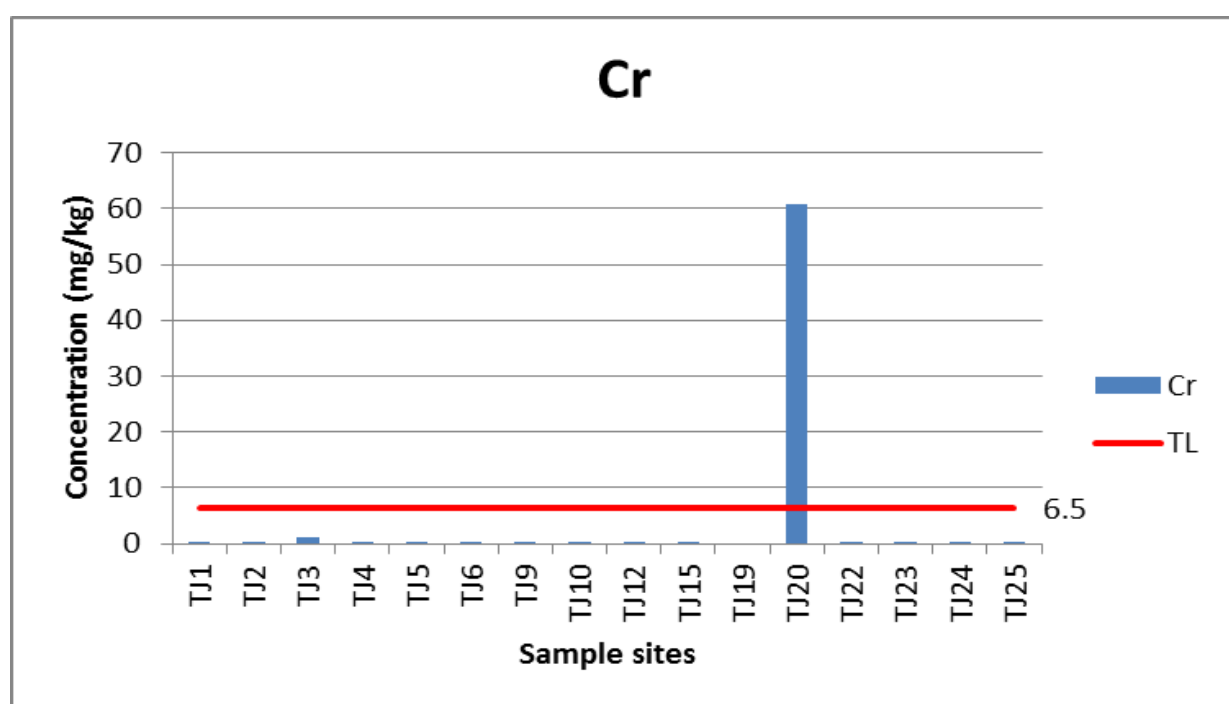
Figure 4. 14: **Variation of total chromium concentrations at 16 different sites with TL threshold value of 6.5 mg/kg**

Chromium (Cr) occurs naturally in varieties of oxidation states ranging from Cr (II) to Cr (VI) (Izbicki *et al.*, 2008; Kotaś & Stasicka, 2000; Nakayama & Bucks, 1981). Chromium (III) is essential for both human and animal's health. Chromium (VI) is highly toxic than Cr (III). Various Industrial and agricultural activities increases the concentrations of Cr in soil (Kabata-Pendias, 2010; Loska *et al.*, 2004; Nagajyoti *et al.*, 2010; Sharma *et al.*, 2007). The SSV for Cr (lll) concentrations used in this study is 6.5 kg/mg. Figure 4.14 above shows a variation in Cr concentration at different tailings sites. The highest level of Cr concentration was detected at sample site TJ20=60.9 mg/kg (New Machavie gold tailings) of which it has exceeded the Threshold value of 6.5 mg/kg as indicated on the graph above. This tailing is dominated by quartz, feldspar, pyrite, sphalerite, pyrrhotite, ilmenite, chalcopyrite and chromite minerals. Therefore, the presence of those minerals are evidence to the elevated Cr concentration at sample site TJ20.

4.4.7 Nickel

Nickel is a TE that is found in group 10 of the periodic table. Figure 4.15 below shows a variation in Ni concentration in sixteen different types of tailings. The recommended SSV1 used in this study for Ni concentrations is 91 mg/kg as outlined by Nemwa act No 59 of 2008.
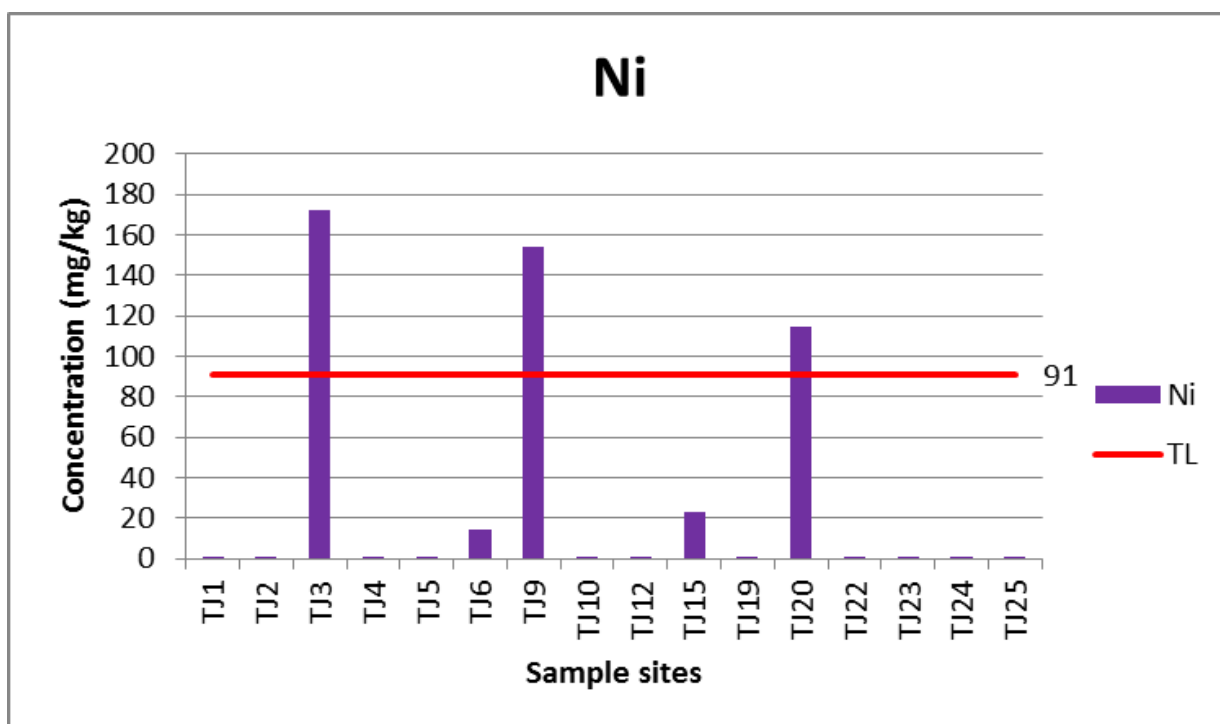
Figure 4. 15: **Variation of Nickel concentrations at 16 different sites with TL threshold value of 91 mg/kg**

Nickel is unessential for plants and has a severe negative impact on water quality (Förstner & Wittmann, 2012; Mishra *et al.,* 2008; Nagajyoti *et al.,* 2010; Sobukola *et al.,* 2010). Figure 4.15 above shows a variation of Ni concentrations at 16 different tailing sites. The SSV for Ni concentration used on this study is 91 mg/kg. Nickel concentrations above threshold limits were observed at sample sites TJ3=172 mg/kg (Witbank coal field), TJ9=154 mg/kg (Okiep copper mine) and TJ20=114 mg/kg (New Machavie gold tailings), While the lowest concentration was observed at sample site TJ12=0.003 mg/kg (Samada diamond mine). At concentration 15 mg/kg Ni pollution may be observed in rural soil. The increased in Ni concentration above the threshold limit as indicated on the graph above may be due to the mineralogy of the ore body. At low pH Ni is easily mobilised and leached. The lowest Ni concentration at sample site TJ12 was due to increased pH. Nickel deficiency may cause negative effects on plants metabolism, leaf and meristem chlorosis, reduced Fe uptake to mention few (Ahmad & Ashraf, 2012). Whereas higher level of Ni in tailings environment may cause seed germinability retardation in a variety of plants

and ground water quality (Ahmad & Ashraf, 2011; Harasim & Filipek, 2015: 526-527). However, only TJ3, TJ9 and TJ20 sample sites requires remediation since Ni concentrations is above the threshold limit (SSV1) according to Nemwa act No 59 of 2008. See Figure 4.15 above.

4.4.8 Copper

Copper is a TE that is found in group 11 of the periodic table. Figure 4.16 below shows a variation in Cu concentration in sixteen different types of tailings measured against the SSV1 of 16 mg/kg outlined by Nemwa act No 59 of 2008 as indicated.
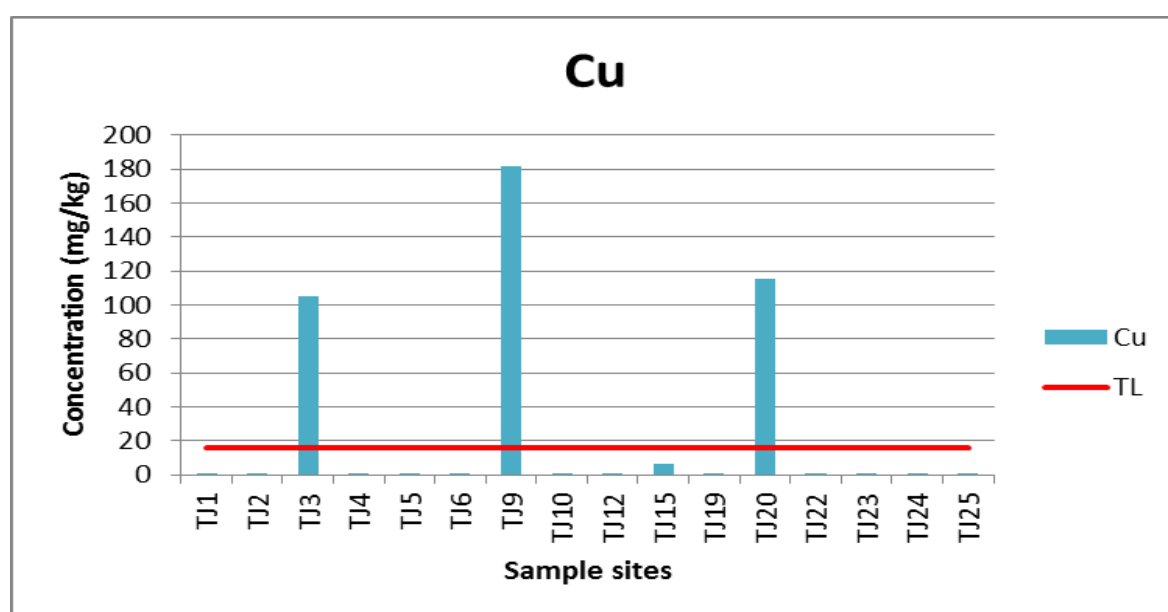
Figure 4. 16: Variation of copper concentrations at 16 different sites with TL threshold value of 16 mg/kg

Copper (Cu) like other TE occurs naturally in rocks and soils. It is transferred to the environment (soil, air and water) via human activities (Artiola, 2005; Bowen, 1985; Islam *et al.*, 2000; Wuana & Okieimen, 2011). Under certain environmental conditions such as low soil pH, Cu metal is mobile and bioavailable to living organism and become toxic to ecosystem health (Siegel, 2002; Vilante *et al.*, 2010; Wong, 2003; Wuana & Okieimen, 2011). Figure 4.16 above shows the concentrations of Cu metal from 16 different mine tailings facilities or sample sites.

The SSV for Cu concentration is 16 mg/kg and is indicated by a red horizontal line in the graph above. The vertical bars indicate an increase in Cu concentration. Above the threshold limit or soil screening value was observed at sample site TJ3=105 mg/kg (Witbank coal field), TJ9=181 mg/kg (Okiep copper mine) and TJ20=116 mg/kg (New Machavie gold mine). The lowest level of Cu leached was observed at soil sample TJ23= 0.003 mg/kg. The increased Cu concentration in leach water was due to dredged tailings materials. The mobilisation was influenced by a sudden change of redox condition. However low Cu concentration at sample site TJ23= 0.003 mg/kg can be due to that sampling was done on top of the tailings materials of which is richer in organic matter compared to the bottom part of the tailings.

Since Cu is essential for metabolism, plants growth and disease- resistance, its deficiencies can result in serious ramifications in the physiology of plants (Kabata-Pendials, 2011:262; Nagajyoti *et al.*, 2010:207; Cited from Botha, 2015:51). Copper is also toxic towards soil biota by means of affecting key microbial processes and may pose potential threats to plants (Basta *et al.*, 2005:57; Kosolapov *et al.*, 2004:403-404; Rooney *et al.*, 2006:726-729)

However at low level, Cu is important for microorganism (ATSDR, 2004; Botha, 201:51). See Figure 4.16 above.

4.4.9   Zinc

Zinc is a TE that is found in group 12 of the periodic table. Figure 4.17 below shows a variation in Zn concentrations in sixteen different types of tailings, measured against the SSV1 of 240 mg/kg as outlined by Nemwa act No 59 of 2008.

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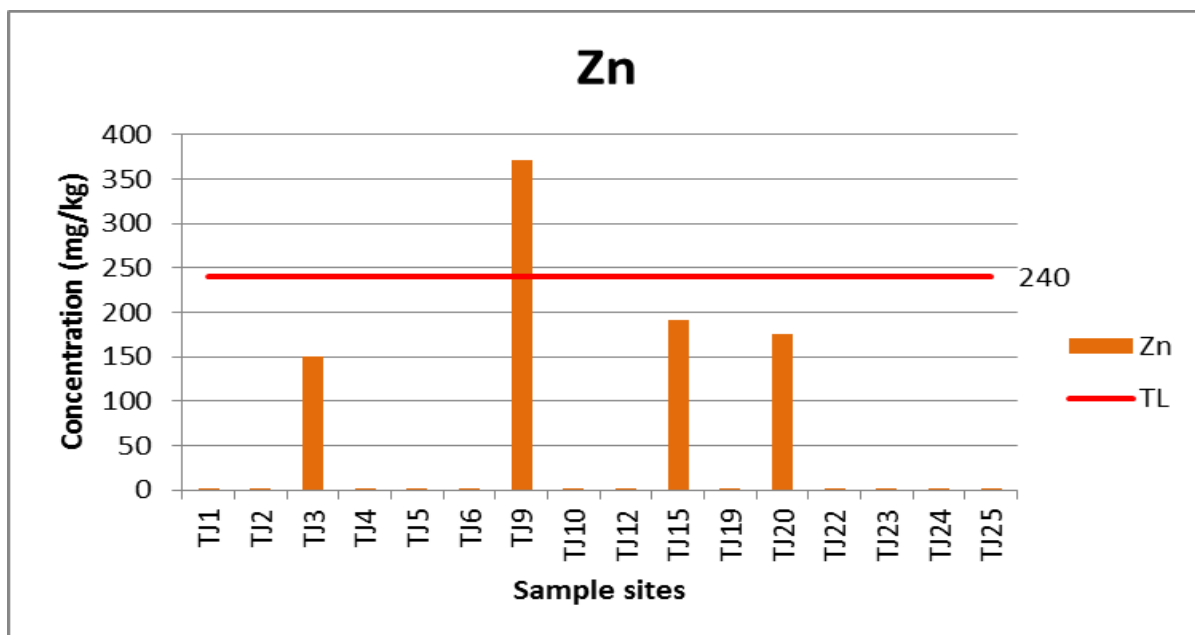
Figure 4. 17: **Variation of zinc concentrations at 16 different sites with TL threshold value of 240 mg/kg**

Zinc (Zn) similar to other TEs is one of the most crucial micronutrients for plants growth, animals and human health (Kabata-Pendias, 2010; Kabata-Pendias, 2007; McLaughlin *et al.*, 1999; Wuan & Okieimen, 2011). Figure 4.17 above shows a variation in Zn concentrations at 16 different tailing sites. The level of Zn in sample site TJ9= 372 mg/kg (Okiep copper mine which also have some Zn ore) was observed to be above the SSV=240 mg/kg. Red horizontal line indicated on the graph represents the SSV or threshold limit. Sample sites TJ3= 151 mg/kg (Witbank coal field), TJ15= 192 mg/kg (East rand gold mine) and TJ20= 176 mg/kg (New Machavie gold mine) on the graph also shows an elevated Zn concentrations; however the concentration is below the threshold limit or SSV of 240 mg/kg. Higher level of Zn leached at sample site JT9 was due to low pH of which has affected its solubility (Houben *et al.*, 2013:1454; Kabata-Pendias, 2010; Kumpiene *et al.*, 2008:221; Liu *et al.*, 2005:164). Zinc is an essential micronutrient for almost all fauna and flora (Chaney *et al.*, 2010:417; Kabata-Pendias, 2011:283; cited from Botha, 2015:55). Higher level of Zn metal in tailings can be toxic to plants by means

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of stunted growth and development and may pose a negative effect to human health (anaemia etc) via food chain (Kabata-Pendias, 2011:466; cite from Botha, 2015:56). It may also interfere with soil microorganisms, homeostasis of tailings together with synthesis and re-synthesis processes (He *et al.*, 2005:126-127; Khan *et al.*, 2000:198; Novak *et al.*, 2009:105-112). Remediation measures at sample site JT9 was recommended. See Figure 4.17 above.

4.4.10 Cadmium

Cadmium is a TE that is found in group 12 of the periodic table. Figure 4.18 below shows a variation in Cd concentration in sixteen different types of tailings, measured against the SSV1 of 7.5 as outlined by Nemwa act No 59 of 2008.
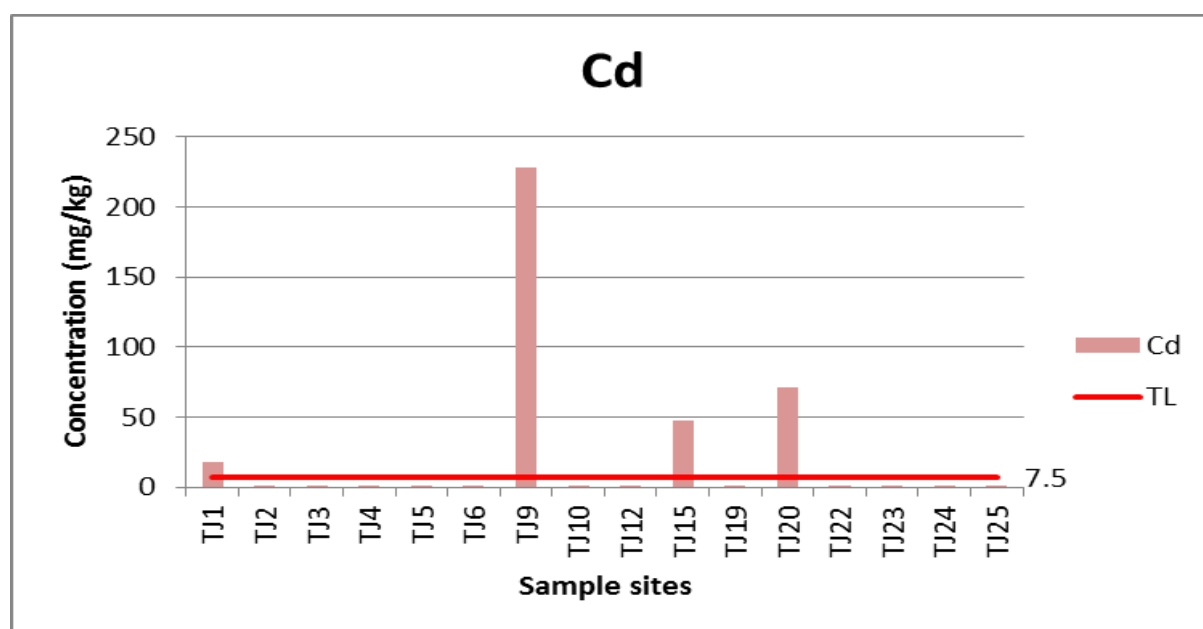

Figure 4. 18: **The variation of cadmium concentrations at 16 different sites with TL threshold value of 7.5 mg/kg**

Cadmium is a TE that can cause toxic effects even at low concentrations (Bernard, 2008; Duruibe *et al.,* 2007; Ercal *et al.*, 2001; Khan *et al.*, 2017). Figure 4.18 above shows Cd concentrations (mg/kg) from several different mine tailings materials or sample sites. The lowest Cd concentration of 0.011 mg/kg was recorded at sample site TJ24 (Revolvervlei gold tailings) and the highest was 228 mg/kg in sample site

TJ9 (Okiep copper mine). Cadmium concentration was found to be below the soil screening value in sample sites; TJ2, TJ3, TJ4, TJ5, TJ6, TJ10, TJ12, TJ19, TJ22, TJ23, TJ24 and TJ25. However, in sample sites TJ1, TJ9, TJ15 and TJ20 Cd was found to exceed the soil screening value or the threshold limit of 7.5 mg/kg for human health and ecotoxicological risk as indicated by a straight horizontal line on the above graph (NEMWA Act No. 59 of 2008). Above threshold limits means the site or soil is contaminated and therefore requires remediation measures. The higher level of Cd concentration at JT9 was due to acidic condition (pH <5.0) of tailing soil materials (Elliott *et al.*, 1986; Harrison *et al.*, 1981; Rodríguez *et al.*, 2009; Shu *et al.*, 2001). Lower pH increases the mobility or leaching of Cd in tailings, leading to higher concentrations of Cd on site JT9 (Basta *et al.*, 2001; Houben *et al.*, 2013; Schwab *et al., 2007)*. Furthermore, gold tailings are associated with sulphide minerals that plays a crucial role on acid production while in contact with water and oxygen leading to formation of acid mine drainage (Akcil & Koldas, 2006; Rios *et al.*, 2008; Simate & Ndlovu, 2014). Wherein the lower level of Cd concentration at sample site JT24 was influenced by increase in pH (pH>5.0) (Hudson-Edwards *et al.*, 2003; Kim & Kim, 2001; Mendez *et al.*, 2007; Mendez & Maier, 2008).

The solubility of Cd in tailings contributes to escalated levels of Cd concentration at TJ9 and all the sites where Cd is above the accepted soil screening value such as TJ1, TJ15 and TJ20 (Ewen *et al.*, 2009; Murata *et al.*, 2005; Zhang *et al.*, 2012). As a result Cd exposure may result in severe health impacts such as cancer and kidney damage to mention few (Bernard, 2008; Godt *et al.*, 2006; Johri *et al.*, 2010; Nordberg, 2004).

Cadmium concentrations also affect soil pH, microbial activities, plants growth and ionic strength to mention few (Brown *et al.*, 1994; Grant & Sheppard, 2008; Holmgren *et al.*, 1993; Zhang *et al* 2012). As it was explained by Kirkhan (2006:19-20), higher level of Cd is of great concern to the environment (soil, water and plants) (Kirkhan, 2006:20). This is because through food chain from soil to plants then to humans or animals, resulting in renal dysfunctional etc. However, this study only focuses on the environmental impacts of TEs and on static values only. See Figure 4.18 above.

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CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The research study uncovered that chemical and physical properties of tailings material contribute significantly to the leaching of TE's. The mineralogical composition of all sixteen tailing sites referenced to their original ore bodies provides a backgroung information on the occurrence of AMD. Humidity cell test results proved that all the tailing sites (TJ1-TJ25) are concentrated with TE's (U, Cr, Co, Ni, Pb, Cu, As, Mn, Zn and Cd) at varying level. The migration via leaching of TE's to the surrounding environment (soil, water and the to plants) are accelerated by low pH of less than 4.22. Nevertheless, this study proved that the rate at which TE's are leached and adsorbed depends on the type and content of the texture, chemical characteristics of the tailings. Furthermore, it was proven that the mineral composition for most of the tailings material consist of sulphides minerals and as a results they have potential to form AMD.

Variation in the level of TE's in tailings material is shown by Figure 4.8 to 4.18 respectively. Table 5.1 provide a summary of TE's which are observed to be above the threshold limit for certain specific tailings materials. As it is observed in Table 4.5 and 5.1 and or Figure 4.8 to 4.18, U, As, Cr, Ni, Cu, Zn and Cd are found to be above the threshold limit (SSV1) (Nemwa (Act no 59 of 2008). Soils, water and plants of the site where TE's exceeded the threshold limit are at risk of being contaminated. However, an indirect conclusion of the effects of TE's to plants is drawn based on the risk exposure of soils and water bodies to TE's contamination. This conclution was influenced by the complicated analytical procedures required for plant tissue material and lack of funds for direct analysis of plants to determine the potential effects of TE's to plants.

However, there is no doubt about the influence of physio-chemical-mineralogical characteristics on trace element concentrations in leach water and a subsequent effect on the environment in general.

From humidity cell test samples, only week 1, 3 and 10 were analysed and gradual decrease in TE's in all the samples is dipicted. See Appendix D: Table D-1 to D-3 For instance week1, 3 and 10 of Cu concentration at sample site TJ20 are: 202 mg/kg, 14.2 mg/kg and 6.25 mg/kg respectively. Therefore, this has proven that tailings material as a source are more concentrated with TE's as compared to receptors (soils and water). Finally the concentration and leaching of TE's from tailings materials is scientifically proven and the hypothesis successfully tested. The focus was only driven to leaching and not surficial processes.

Although statistical replicas were not tested, the hypothesis is accepted. No statistical analyses were done due to the replication of the composite sampling technique been used.

Table 5. 1: Summary of TEs above to SSV1, erosion potential and grading analysis

Tailings sample No	Specific analyses that do have a negative (or positive effect) on the ENVIRONMENT with special reference to SSV and water quality guidelines	Specific analysis that do have a negative impacts on chemical erosion potential	Grading analysis that do have an influence on physical erosion
JT 1	Cd is high	Extremely erodible	Well graded
JT 2		Extremely erodible	Well graded
JT 3	As too high, Ni is too high, Cu is too high	Low dispersiveness and low erosion potential	Well graded
JT 4		Extremely erodible	Well graded
JT 5	High clay content, excellent moisture retainer	Moderate erodible	Gap graded
JT 6	Extreme low clay, very low moisture retention and water holding capacity	Low erosion potential	Gap graded
JT 9	Radiation form uranium is high, As too high, Ni is too high, Cu is too high, Zn is too high, Cd is too high	Highly erodible	Well graded
JT 10		Low erosion potential	Poorly graded
JT 12		Extremely erodible	Well graded
JT 15	Radiation from U is high, Cd is too high	Extremely erodible	Well graded
JT 19		Low erosion potential	Gap graded
JT 20	Cr very high, As too high, Ni is high, U is too high, Cu is too high, Cd is too high.	Low erosion potential	Well graded
JT 22		Extremely erodible	Gap graded
JT 23		Low erosion potential	Poorly graded
JT 24		Extremely erodible	Well graded
JT25		Moderate erodible	Gap graded

Footnote: well graded gives a low to moderate physical erosion potential; poorly graded gives a moderate to high physical erosion and gap graded is in most cases medium to extreme erodible.

In the majority of the cases environmental rehabilitation is required to stabilise the tailings dams and prevent erosion and limit water infiltration and subsequent oxidation of the pyrite in depth or the release of sodium. The stabilisation is also required to prevent dispersion and erosion due to high sodium content.

Proper detail rehabilitation techniques are not described in this research because of the complicated nature and characteristics of the individual materials.

5.2 RECOMMENDATIONS

Recommendations for future research work are listed below:

- Detail sampling of plants and ground water needs to be conducted in oder to prove beyond reasonable measures whether plants and ground water of the surrounding investigated areas are affected by leaching of TE's.
- Phyto-remediation of sites contaminated by the TE's needs to be implemented as a means to rehabilitate the tailings.

Furthermore, attention should be given to the Uniformity index (I_u) and uniformity coefficient of the grading analyses with respect to correlations between permeability, bulk density and other soil chemical and physical properties.

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# APPENDIX A: TABLES SHOWING PSD RESULTS OF 16 TAILINGS SAMPLES

Appendix A: Table A-1: Presentation of PSD results for 16 sample sites.

| Sample	4.75 mm	Very coarse	Coarse	Medium-	Fine	Very fine	Silt	Clay
no.	%	sand	sand	sand	Sand	sand		
TJ1	0.0	1.0	1.2	7.9	35.1	26.1	21.9	6.8
TJ2	0.0	38.3	22.3	15.7	12.3	4.9	2.5	4.1
TJ3	0.0	35.1	25.8	19.7	7.9	2.3	0.4	8.7
TJ4	0.0	0.0	5.3	20.2	37.7	20.6	14.2	2.0
TJ5	0.0	0.0	0.1	0.2	0.8	5.7	64.7	28.5
TJ6	0.0	0.1	0.9	9.3	44.1	40.1	3.9	1.6
TJ9	0.0	1.8	1.6	5.7	36.6	27.1	17.5	9.7
TJ10	0.0	3.2	13.8	37.9	34.3	8.3	1.1	1.3
TJ12	0.0	26.4	20.4	19.3	16.3	6.8	1.9	8.9
TJ15	0.0	1.0	0.9	1.0	3.8	16.1	65.2	12.1
TJ19	0.0	0.3	0.5	7.7	45.4	32.1	10.4	3.7
TJ20	0.0	0.7	1.0	2.3	6.9	15.4	59.0	14.7
TJ22	0.0	0.0	0.1	4.3	40.3	31.2	20.7	3.4
TJ23	0.0	0.5	3.8	25.7	43.4	24.5	1.2	0.9
TJ24	0.0	1.9	1.7	1.6	6.3	19.7	54.4	14.5
TJ25	0.0	0.1	0.1	0.4	4.3	10.4	82.9	1.8

Appendix A Table A-2: Presentation of PSD results of all 16 tailings samples

Sample	4.75mm	Very coarse	Coarse	Medium-	Fine	Very fine	Silt	Clay
no.	%	sand	Sand	sand	sand	sand		
TJ1	100.0	100.0	99.0	97.8	89.9	54.8	28.7	6.8
TJ2	100.0	100.0	61.7	39.4	23.7	11.4	6.5	4.1
TJ3	100.0	100.0	64.9	39.0	19.3	11.4	9.0	8.7
TJ4	100.0	100.0	100.0	94.7	74.5	36.8	16.2	2.0
TJ5	100.0	100.0	100.0	99.9	99.6	98.9	93.2	28.5
TJ6	100.0	100.0	99.9	99.0	89.7	45.6	5.5	1.6
TJ9	100.0	100.0	98.2	96.6	90.9	54.3	27.2	9.7
TJ10	100.0	100.0	96.8	83.0	45.1	10.7	2.4	1.3
TJ12	100.0	100.0	73.6	53.2	33.9	17.6	10.8	8.9
TJ15	100.0	100.0	99.0	98.2	97.2	93.4	77.3	12.1
TJ19	100.0	100.0	99.7	99.2	91.6	46.2	14.0	3.7
TJ20	100.0	100.0	99.3	98.3	96.1	89.2	73.8	14.7
TJ22	100.0	100.0	99.9	99.8	95.5	55.2	24.0	3.3
TJ23	100.0	100.0	99.5	95.7	69.9	26.6	2.0	0.8
TJ24	100.0	100.0	98.1	96.4	94.8	88.5	68.8	14.5
TJ25	100.0	100.0	99.9	99.8	99.4	95.1	84.7	1.8
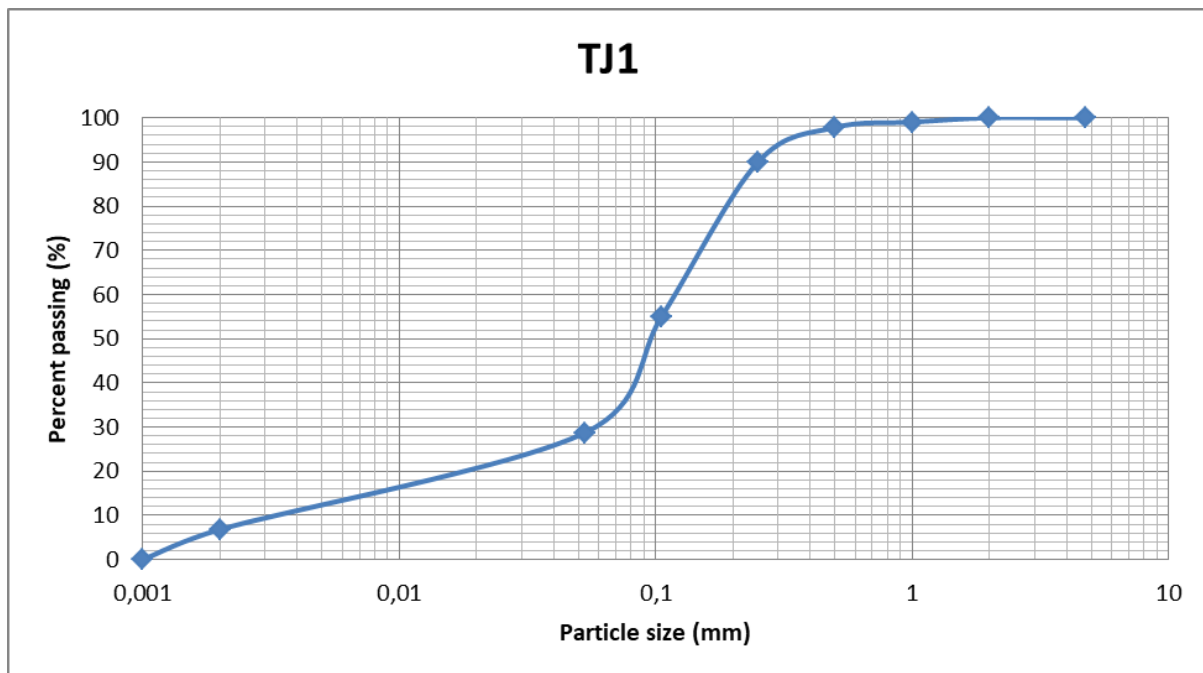
B-1: Graph showing PSD of tailing sample TJ1
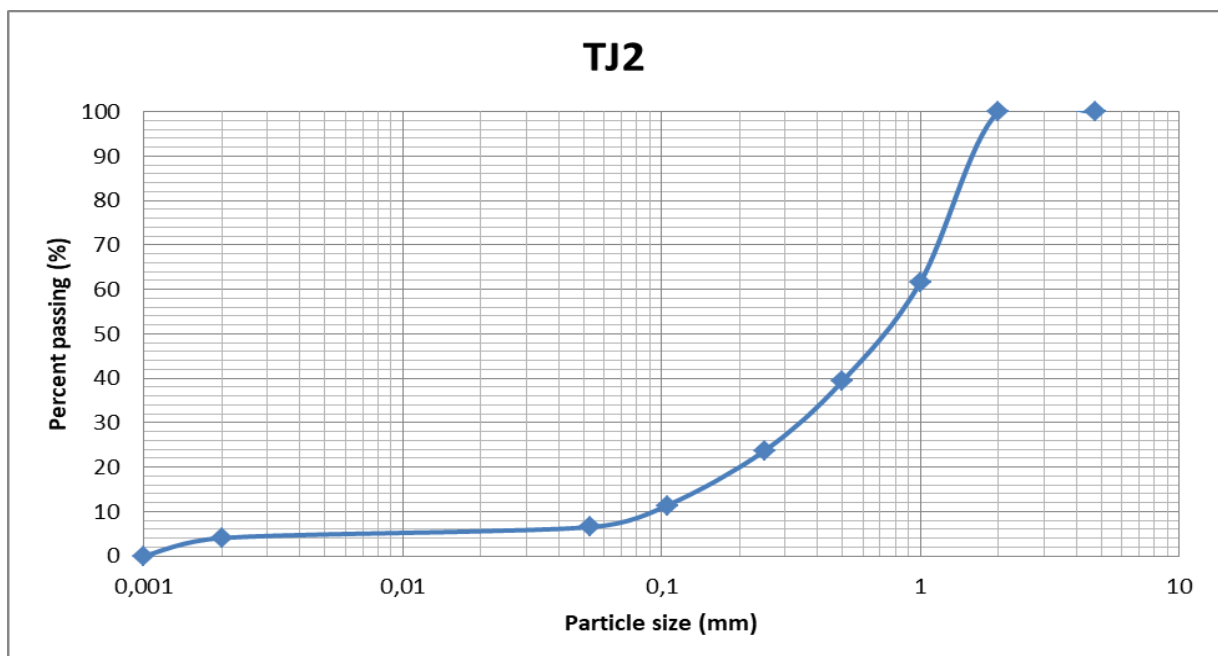
B-2: Graph showing PSD of tailing sample TJ2
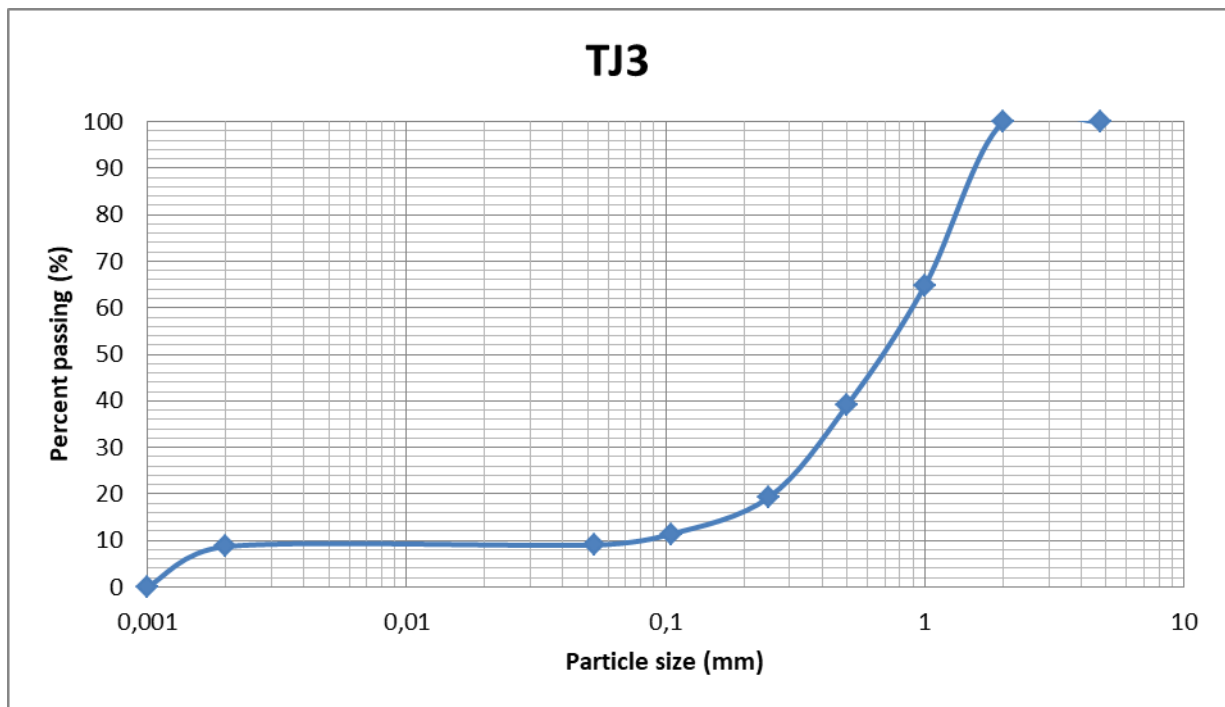
B-3: Graph showing PSD of tailing sample TJ3

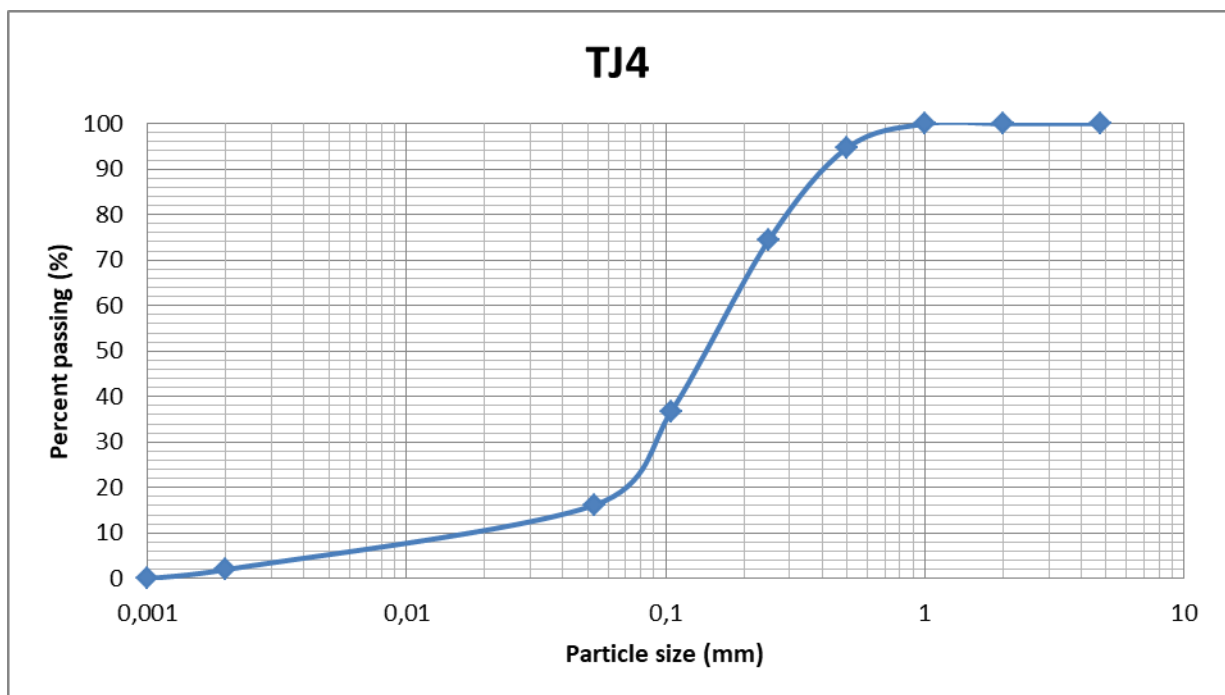**B-4:** Graph showing PSD of tailing sample TJ4

B-5: Graph showing PSD of tailing sample JT5

B-6: Graph showing PSD of tailing sample TJ6

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B-7: Graph showing PSD of tailing sample TJ9

B-8: Graph showing PSD tailing sample TJ10

179

B-9: Graph showing PSD tailings sample TJ12

B-10: Graph showing PSD of tailing sample TJ15

180

B-11: Graph showing PSD of tailing sample TJ19
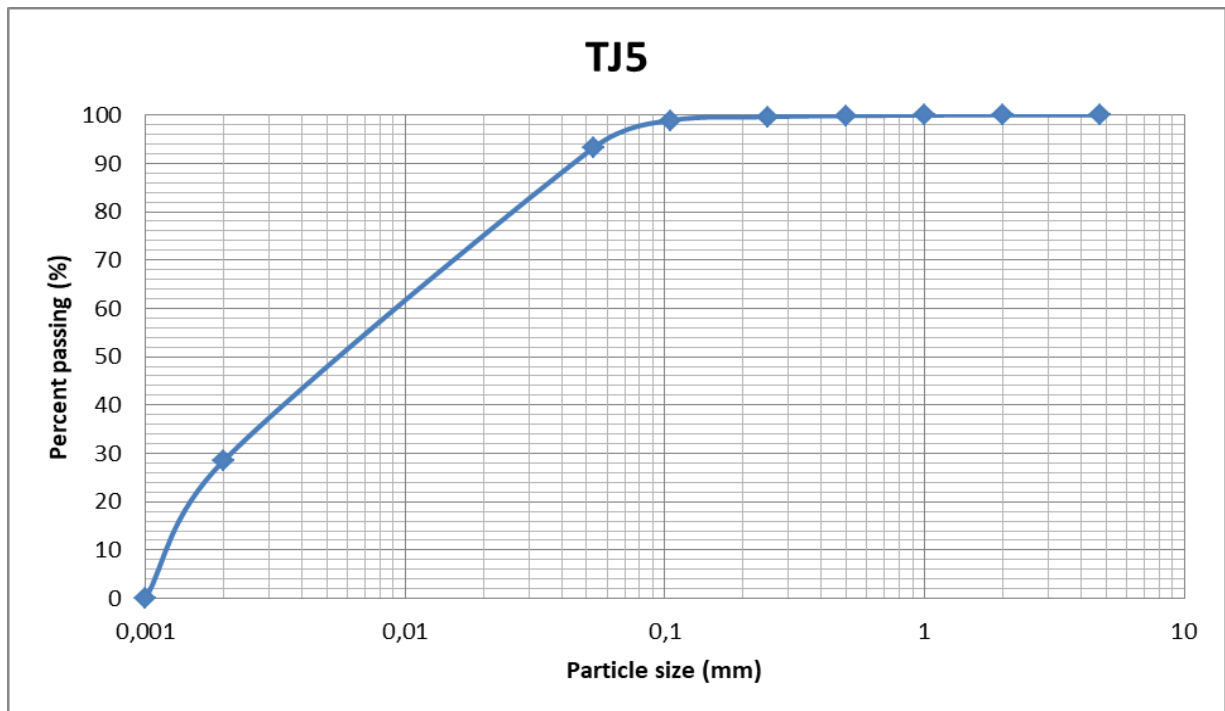

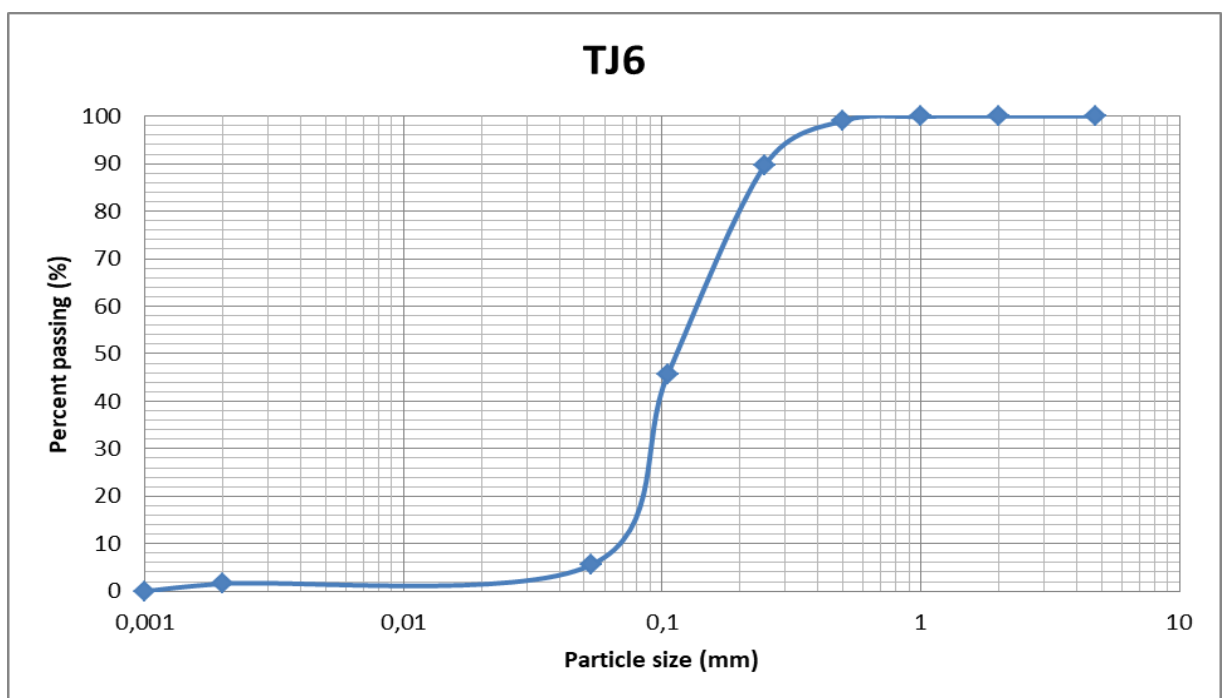**B-12:** Graph showing PSD of tailing sample TJ20
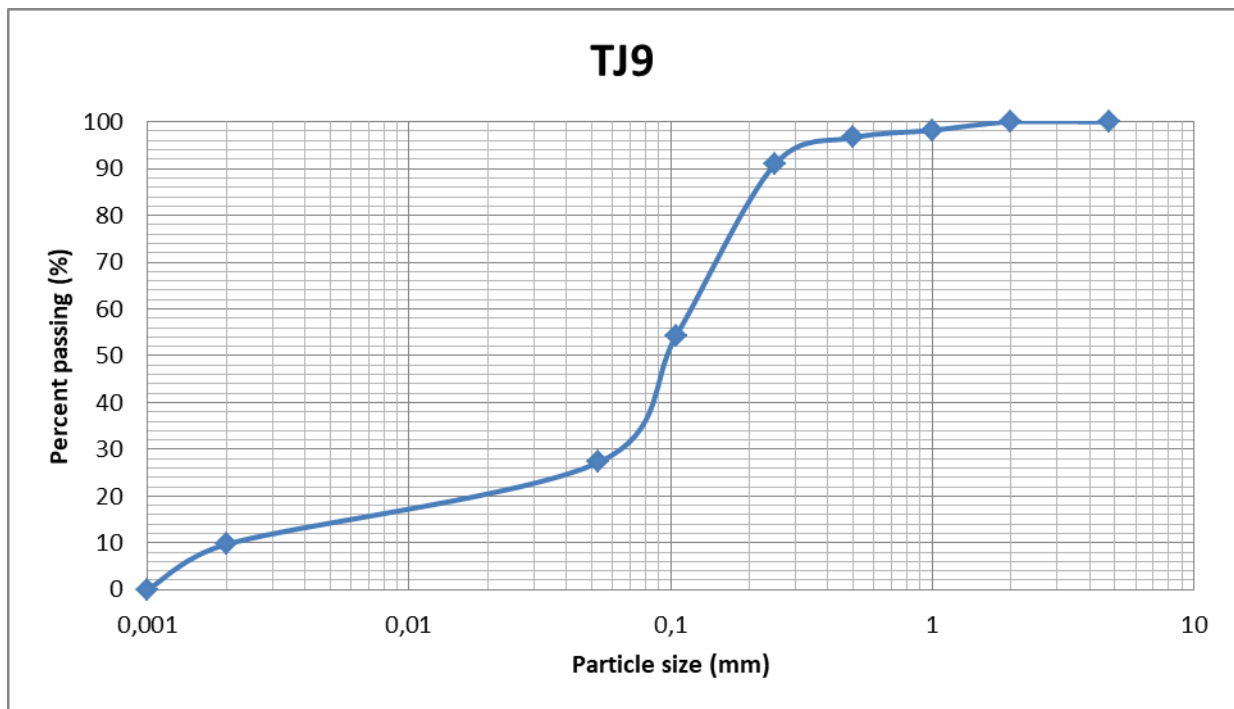
B-13: Graph showing PSD of tailing sample TJ22
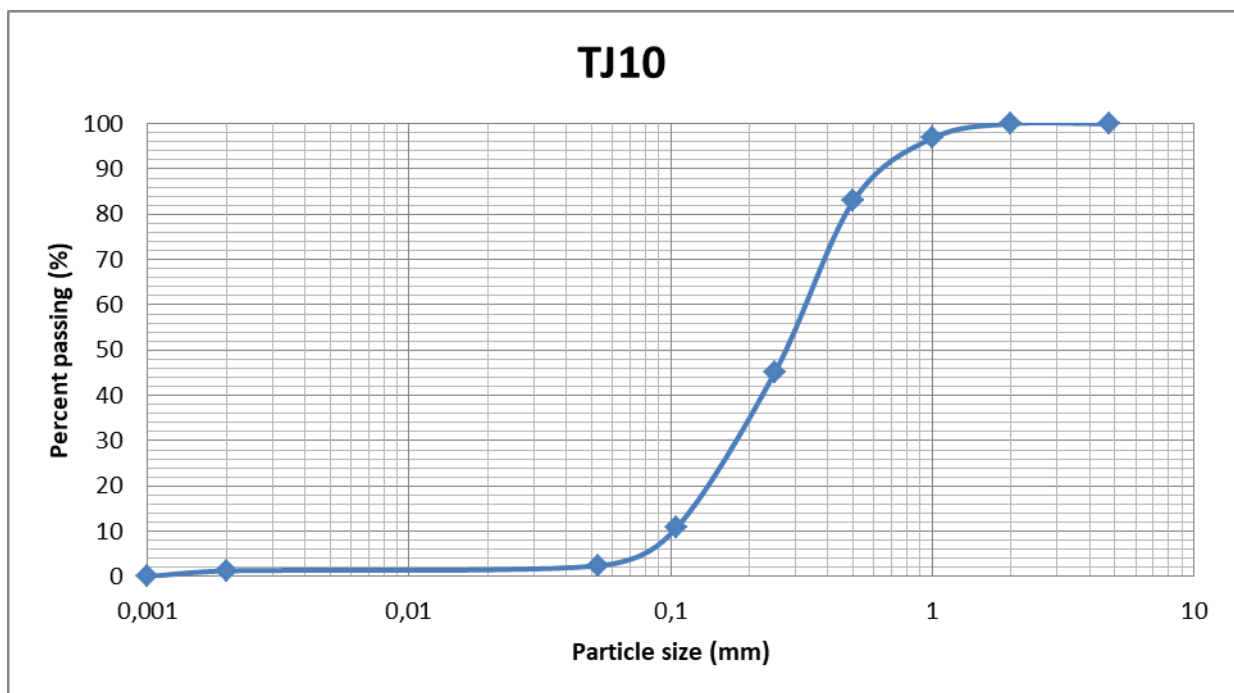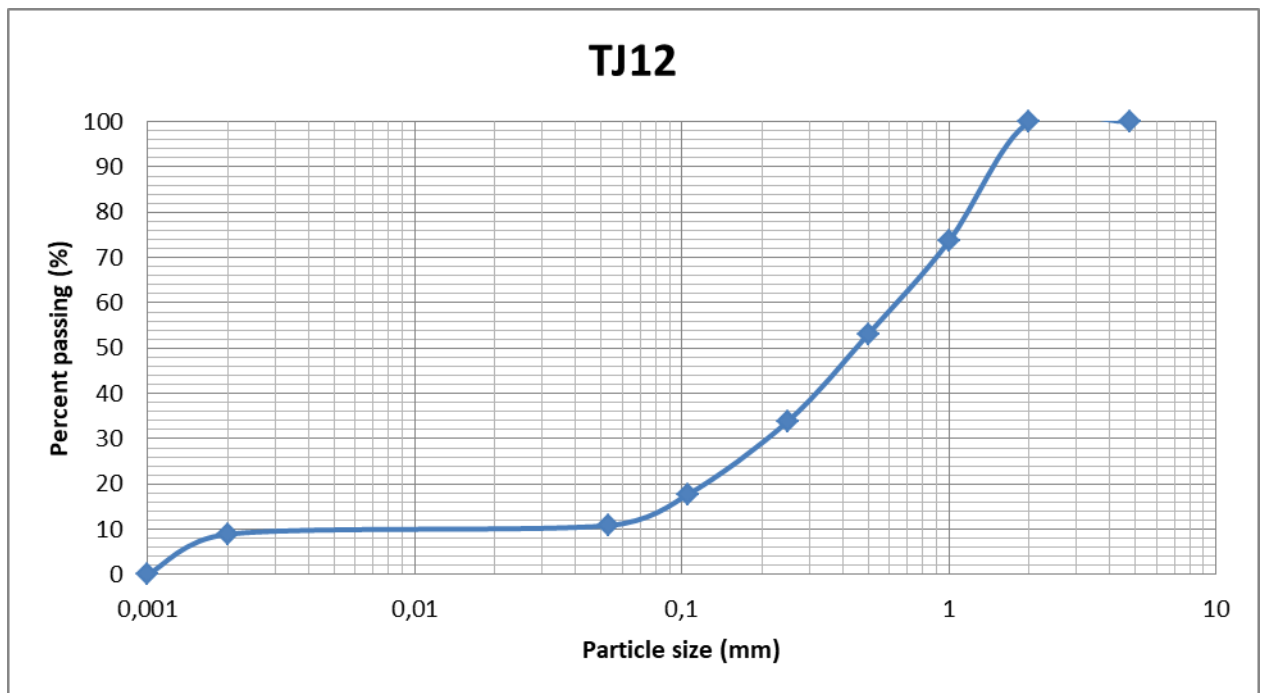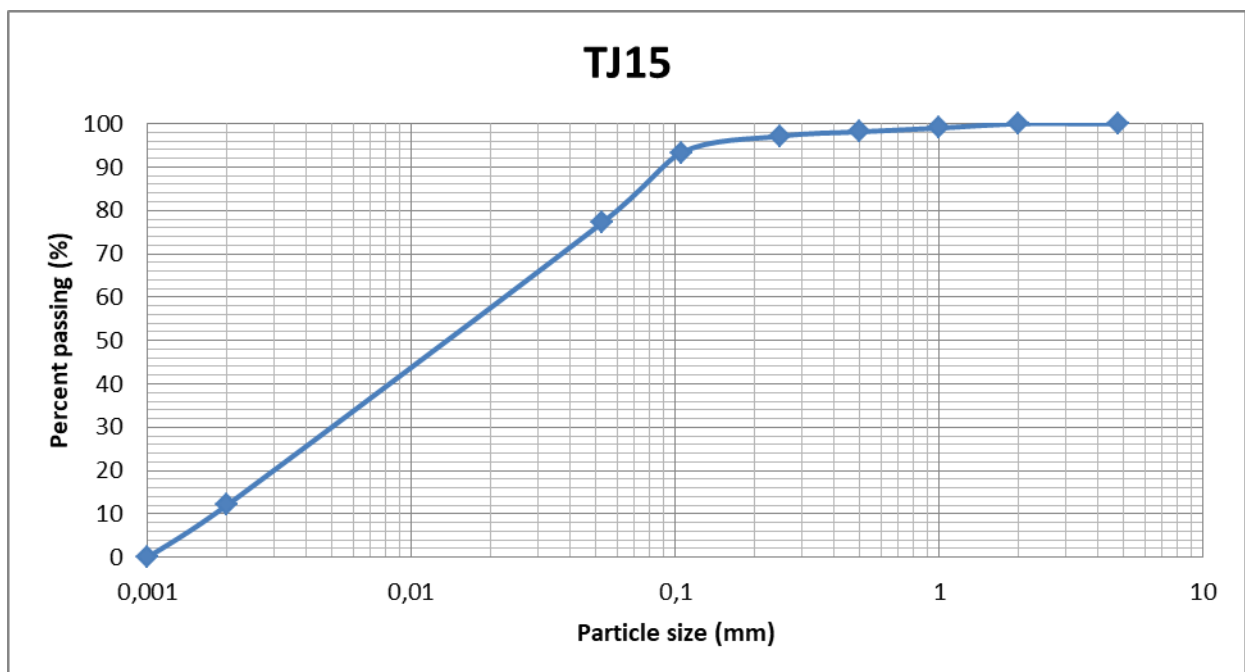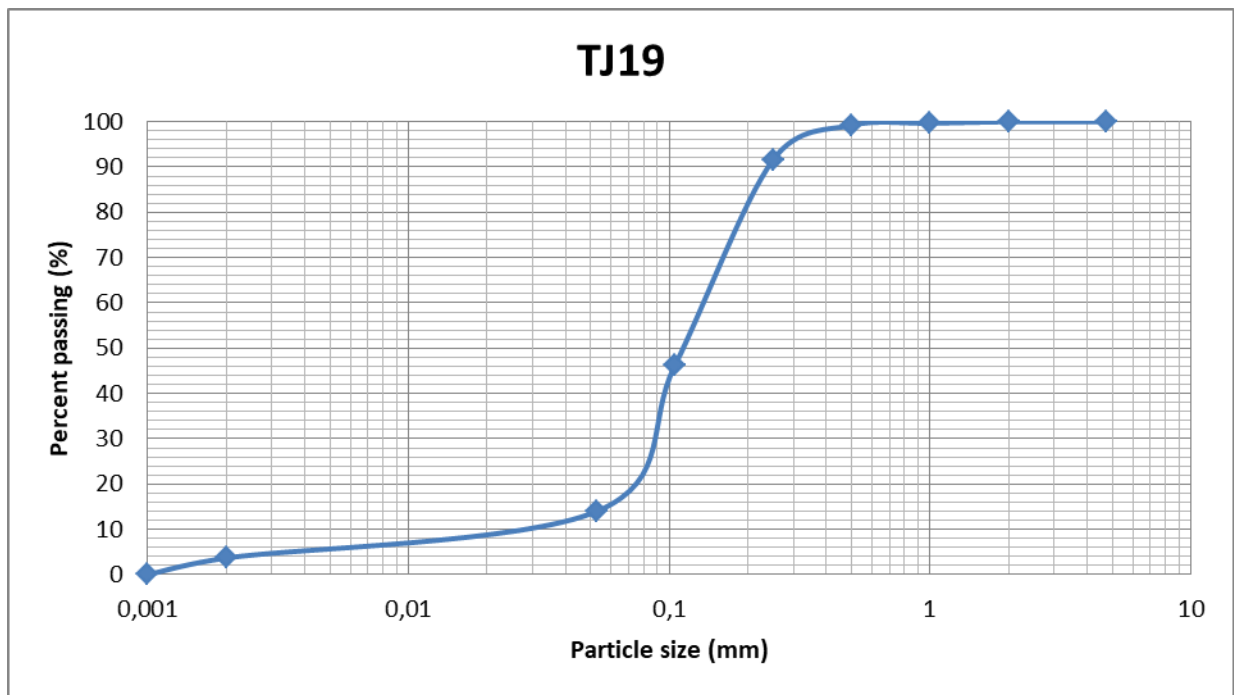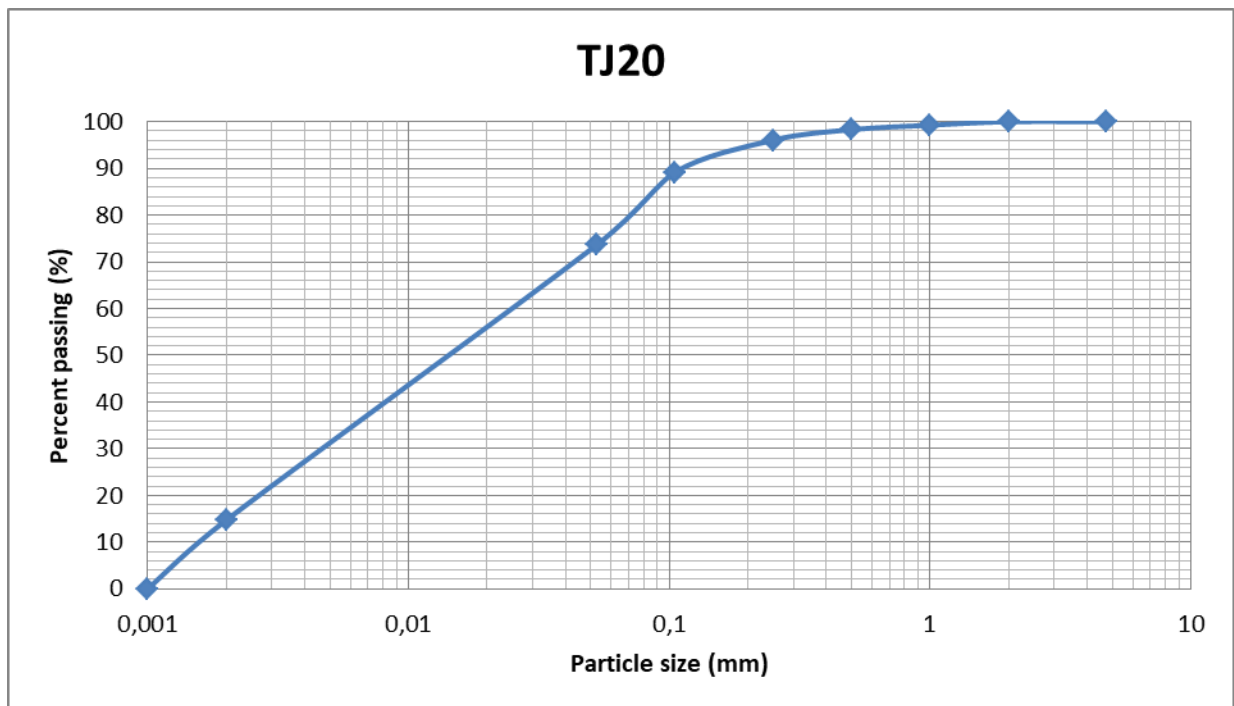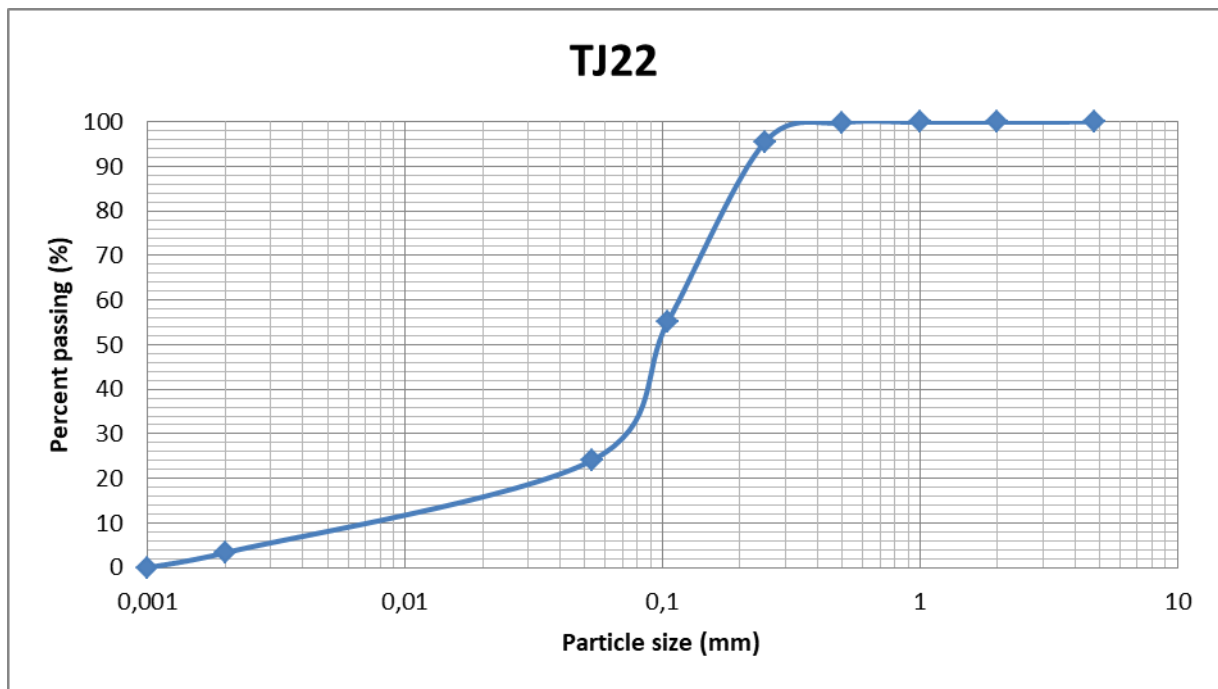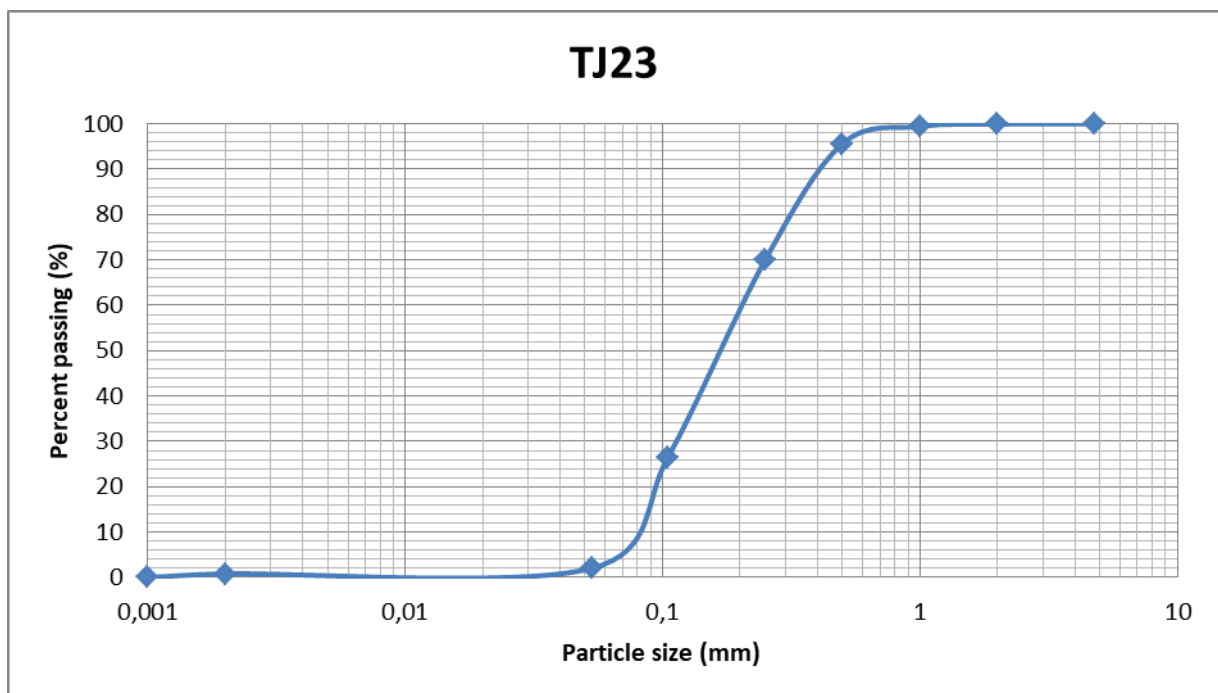

B-14: Graph showing PSD tailing sample TJ23
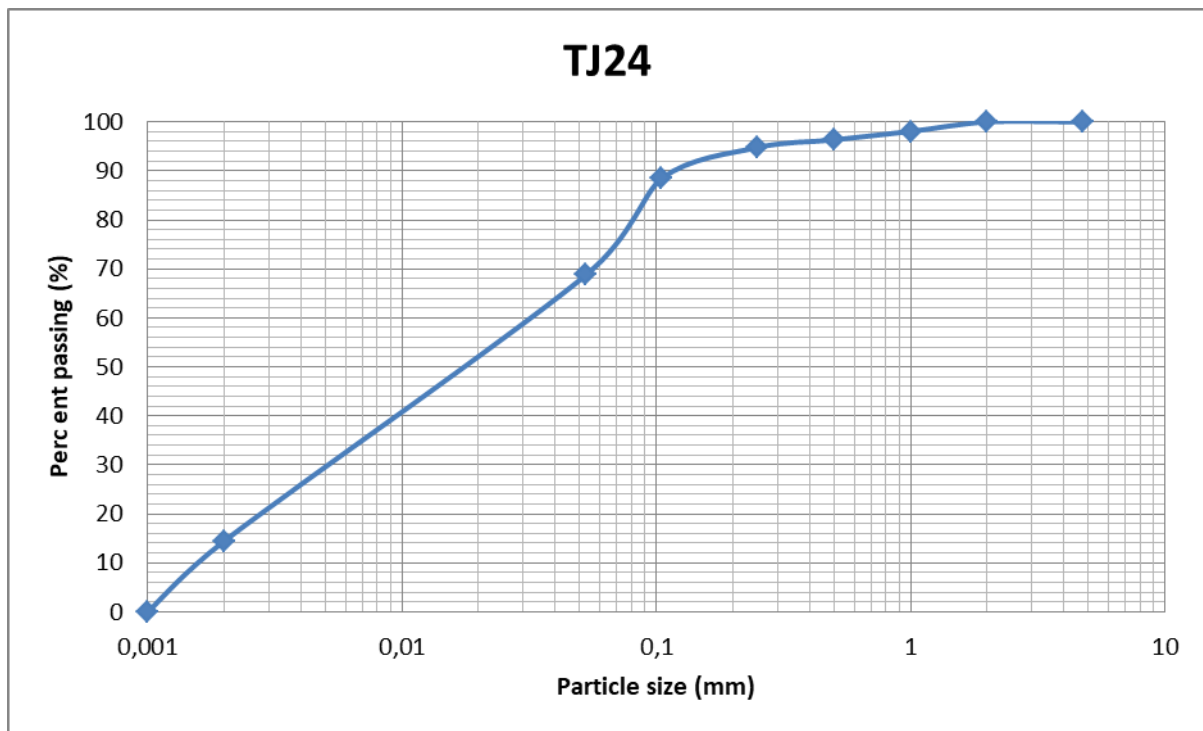
B-15: Graph showing PSD tailing sample TJ24

Appendix C: Table showing TE's against the SSV1(Baseline ICP-MS)

	SSV1	TJ1	TJ2	TJ3	TJ4	TJ5	TJ6	TJ9	TJ10	TJ12	TJ15	TJ19	TJ20	TJ22	TJ23	TJ24	JT25
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
As	5.8	1.45	1.77	3.35	17.67	26.68	4.69	1.09	1.40	1.93	2712.5	0.40	290.25	3405	6.10	318.25	7.88
Cd	7.5	0.08	0.11	0.10	0.28	0.03	14.77	0.64	0.01	0.09	1.07	0.24	2.07	0.07	0.11	0.59	0.06
Co	300	26.03	46.25	6.44	21.64	8.12	83.03	53.75	6.33	50.48	987.5	61.88	125.58	92.25	99.48	44.68	3.66
Cr	46000	247.22	398	26.55	59.43	48.95	28	216.63	19.41	186.65	53.85	787.75	48.53	400.25	25.25	211.9	26.18
Cu	16	1419.25	35.2	10.22	46.23	13.48	502.25	5642.5	13.59	63.92	754	182.7	174.83	10.22	1074.25	73.9	5.01
Mn	740	462	390.5	86.45	2862.5	435	2737.5	377	54.2	668.5	307	192.05	154.38	941.25	671.5	1363.5	258
Ni	91	121.55	607.75	11.32	73.65	14.53	30.7	266.5	16.67	412.75	2184.5	270.75	140.1	1168.25	78.25	122.13	7.48
Pb	20	7.84	9.23	23.96	4.34	5.61	1805	37.55	2.35	4.47	102.58	32.28	118.28	65.25	43.03	44.38	3.08
U	16	3.60	0.83	1.266	0.39	0.56	1.22	6.038	0.81	0.76	42.25	0.18	14.40	0.07	57.93	0.15	0.30
Zn	240	112.38	45.78	7.70	84.92	6.23	4540	88.45	7.51	49.63	493	32.27	334.5	18.16	56.75	152.45	21.76

Appendix D: Table D-1: Leach concentration of week one for all the TSF

	JT1	JT2	JT3	JT4	JT5	JT6	JT9	JT10	JT12	JT15	JT19	JT20	JT22	JT23	JT24	JT
As	1.447	0.001	0.695	0.004	0.004	0.004	0.095	0.004	0.006	1.077	0.006	337.200	13.670	0.004	0.017	0.
Cd	0.014	0.000	0.000	0.000	0.000	0.214	1.466	0.000	0.000	0.506	0.000	1.461	0.000	0.000	0.000	0.
Co	0.012	0.103	2.247	0.027	0.003	4.409	79.610	0.009	0.003	155.700	0.003	54.820	0.146	0.003	2.490	0.
Cr	0.147	0.617	0.296	0.009	0.000	0.000	0.007	0.000	0.002	0.079	0.000	29.560	0.004	0.000	0.028	0.
Cu	0.453	0.117	10.750	0.027	0.006	0.027	10230.000	0.098	0.014	48.140	0.262	202.100	0.039	0.029	0.092	0.
Mn	0.831	0.429	18.100	15.690	0.034	283.700	371.100	0.049	0.032	406.800	0.059	274.800	0.160	0.030	0.095	0.
Ni	0.024	0.850	19.460	0.384	0.007	4.390	409.800	0.027	0.014	497.900	0.150	160.400	13.110	0.148	0.074	0.
Pb	0.009	0.074	0.124	0.008	0.005	0.657	0.309	0.006	0.005	0.180	0.009	0.321	0.005	0.011	0.011	0.
U	0.008	0.055	0.127	0.003	0.003	0.048	6.294	0.003	0.003	7.700	0.003	12.770	0.003	0.003	0.003	0.
Zn	0.127	0.000	11.610	0.271	0.001	37.700	328.900	0.075	0.012	944.300	0.123	589.000	0.138	0.261	0.148	0.

	JT1	JT2	JT3	JT4	JT5	JT6	JT9	JT10	JT12	JT15	JT19	JT20	JT22	JT23	JT24	JT25
As	4.44E-05	0.001	0.031	0.004	0.005	0.004	0.005	0.004	0.012	0.643	0.004	2.855	8.544	0.004	0.007	0.007
Cd	0.032	0.001	1.24E-05	5.44E-05	5.97E-05	0.022	3.89E-05	6.83E-05	6.33E-05	2.71E-05	6.91E-05	0.019	6.83E-05	7.23E-05	6.82E-05	6.57E-05
Co	0.004	0.022	0.017	0.003	0.002	0.392	0.100	0.002	0.007	0.442	0.002	0.959	0.012	0.002	0.003	0.003
Cr	0.009	0.078	0.011	1.84E-05	1.4E-05	4.3E-05	4.76E-05	6.18E-06	0.006	2.77E-05	4.91E-05	0.411	1.49E-05	4.28E-05	2.09E-05	3.47E-05
Cu	0.043	0.035	7.473	0.002	0.003	0.011	40.53	0.010	0.017	0.651	0.052	6.253	0.002	0.018	1.85	0.006
Mn	0.048	-0.028	0.148	1.471	0.010	25.28	0.504	0.008	0.046	0.465	0.003	4.917	0.020	0.006	0.072	0.009
Ni	0.065	0.042	1.236	0.055	0.009	0.67	1.17	0.005	0.080	2.129	0.021	2.753	0.107	0.008	0.017	0.0217
Pb	0.011	0.053	0.227	0.010	0.010	2.458	0.056	0.010	0.012	0.059	0.010	0.083	0.014	0.017	0.018	0.010
U	0.007	0.054	0.009	0.003	0.003	0.005	0.039	0.003	0.003	0.216	0.003	0.175	0.003	0.003	0.003	0.003
Zn	0.036	0.002	23.24	0.018	0.027	9.195	1.775	0.026	0.037	2.033	0.056	21.9	0.032	0.030	0.081	0.021

Appendix D: Table D-3: Leach-concentrations of week three for all the TSF's

	TJ1	TJ2	TJ3	TJ4	TJ5	TJ6	TJ9	TJ10	TJ12	TJ15	TJ19	TJ20	TJ22	TJ23	TJ24	TJ25
As	6.57E-05	0.001	0.462	0.004	0.006	0.003	0.005	0.005	0.006	0.317	0.005	10.49	9.984	0.004	0.005	0.009
Cd	0.003	0.001	0.000	5.59E-05	5.96E-05	0.022	0.001	6.49E-05	2.61E-05	0.026	6.6E-05	0.068	0.000	7.35E-05	6.82E-05	5.4E-05
Co	0.004	0.093	0.941	0.011	0.003	0.766	0.448	0.002	0.003	8.124	0.002	2.625	0.020	0.002	0.003	0.003
Cr	0.012	0.533	0.140	8.65E-06	2.46E-05	5.62E-05	4.71E-05	2.63E-05	4.54E-07	6.55E-06	1.45E-05	1.185	2.66E-05	4.76E-05	1.23E-05	2.28E-05
Cu	0.061	0.147	23.5	0.016	0.002	0.011	67.03	0.028	0.013	3.076	0.052	14.17	0.006	0.017	0.013	0.010
Mn	0.167	0.424	8.474	10.21	0.154	56.94	2.083	0.0147	0.018	19.56	0.023	13.21	0.021	0.006	0.040	0.019
Ni	0.066	0.776	7.789	0.282	0.008	3.605	3.517	0.009	0.025	28.92	0.049	16.46	0.303	0.012	0.038	0.024
Pb	0.005	0.074	0.198	0.009	0.005	1.334	0.025	0.007	0.019	0.052	0.010	0.111	0.020	0.010	0.012	0.018
U	0.013	0.056	0.103	0.003	0.003	0.005	0.032	0.003	0.003	0.342	0.003	0.509	0.003	0.003	0.003	0.003
Zn	0.016	0.000	23.17	0.020	0.058	5.351	4.262	0.024	0.051	55.71	0.370	44.12	0.067	0.167	0.104	0.069