Geochemical characterisation of gold tailings footprints on the Central Rand Goldfield

by

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DECLARATION

GEOCHEMICAL CHARACTERISATION OF GOLD TAILINGS FOOTPRINTS ON THE CENTRAL RAND GOLDFIELD

I declare that the above dissertation for MSc in Environmental Science at the University of South Africa (UNISA student no. 51878216) is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

____________________________
Khathutshelo E. Netshiongolwe

_______ Day of_______________ 20____ in____________________
DEDICATION

I dedicate this dissertation to:

My only beautiful wife Lufuno Love Netshiongolwe

My daughter Oritonda Charisma Netshiongolwe

My mother Tshisaphungo Netshiongolwe
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The undertaking of this dissertation has been one of the most significant academic challenges I have ever had to face. Without the support, patience and guidance of the under mentioned people, this study would not been completed. It is to them that I owe my deepest gratitude.

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ABSTRACT

Gold mining in the Witwatersrand Basin of South Africa has resulted in soil contamination due to the lack of sufficient environmental management plans for the tailings dumps and remnant footprints. Tailings reclamation as a strategy of reducing pollution in the Central Rand, for instance, has resulted in contamination of water systems by acid mine drainage (AMD). After removal of the tailings dumps, remnant material is left over on the tailings footprints and these contain significant amounts of pollutants that were initially in the tailings. Heavy rainfall during summer dissolves primary minerals and later in the dry season, secondary minerals are precipitated as efflorescent crusts on and nearby tailings dumps as well as footprints due to high evaporation. The efflorescent crusts can redissolve when it rains and form acidic, metal and sulphate-rich solutions due to their soluble characteristics.

This study aimed to characterise tailings footprints in areas targeted for human settlements and office spaces to assess their potential to release left over toxic elements such arsenic (As), lead (Pb), copper (Cu) and zinc (Zn). The approach to the study involved characterisation of oxidised and unoxidised tailings material and secondary precipitates on both tailings dumps and footprints. This involved determining the mineralogical composition using Powder X-ray Diffraction (PXRD). Dissolution and leaching studies were also conducted on the material followed by determination of constituent elements using inductively coupled plasma optical emission spectroscopy (ICP-OES) and sulphates using ion chromatography (IC). The leaching solutions used included rainwater; dilute sulphuric acid at pH of 3.0 (a common leachate in such acidic soils); as well as plant exudates such as oxalic and citric acids.

The leachate solutions were used to correlate the mineralogical composition of secondary precipitates and tailings footprints. Potential implications on humans following any accidental ingestion of the tailings or contaminated soils were assessed using gastric juices. The ecological risk factors and risk index together with the model to evaluate daily intake and different pathways to humans were used to assess the toxicity caused by exposure to contaminants in the materials. The experimental work was augmented by computer simulations based on geochemical
modelling (using the PHREEQC geochemical modelling code) to determine the speciation of elements (and thus their potential lability and bioavailability), dissolution and formation of secondary mineral precipitates in the tailings dumps and footprints. The findings of the PXRD study showed that the mineralogy of the tailings and footprints was dominated by quartz (SiO$_2$) and some minor minerals such as pyrite (FeS$_2$), pyrophylite (Al$_2$Si$_4$O$_{10}$(OH)$_2$), chlorite (Mg,Fe)$_3$(Si,Al)$_4$O$_{10}$), mica (K(Mg,Fe)$_3$AlSi$_3$O$_{10}$(F,OH)$_2$) while that of secondary precipitates was dominated by jarosite (KFe$_{3+}$3(OH)$_6$ (SO$_4$)$_2$), goethite (FeOOH), melanterite (FeSO$_4$.7H$_2$O) and gypsum (CaSO$_4$.2H$_2$O). Minerals obtained for the secondary precipitates were corroborated by geochemical modelling.

Leaching results using rainwater with pH ranges from 3.5 to 3.9 showed that trace elements are released very slowly from tailings dumps and footprints and in small concentrations during rainy seasons as follows: As (1.5 mg/L-4.5 mg/L), Pb (3.5 mg/L-5.5 mg/L), Cu (4 mg/L-4.8 mg/L) and Zn (23 mg/L-44 mg/L). The release and mobility of Cu, Pb, Zn and As occurs quite markedly when secondary precipitates dissolve, making the immediate impacted environment unfavourable for plant growth and any habits in the vicinity. This was substantiated by simulated dissolutions and assessment of the resulting elemental speciation that pointed to the elements being distributed in bioavailable forms, implying potential uptake by plants (such as vegetables that may be cultivated on such impacted soils).

The model was used to evaluate the daily intake and different exposure pathways and the results showed that children may daily intake 48.4 mg kg$^{-1}$ day$^{-1}$ and adults’ 32.8 mg kg$^{-1}$ day$^{-1}$. After 5 years (1825 days) of exposure more harm may be experienced and findings shows that kids are the most victims on these contaminated sites compared to adults. Both children and adults may absorb low levels of these toxic elements daily and after long time of exposure it may cause disease like cancer in their body which may lead to death. Pathways may be through inhalation and accidentally ingesting tailings soil that contain toxic elements. Drawing from the above findings, it will be important that tailings footprints that have been earmarked as land for development (residential or office space) be thoroughly assessed for potential release of toxic elements and high levels of acidity. Further reclamation aimed at reducing these hazards can then be implemented.
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LIST OF ACRONYMS AND SYMBOLS

AMD : Acid Mine Drainage
ARD : Acid Rock Drainage
CRG : Central Rand Goldfield
CRB : Central Rand Basin
DME : Department of Minerals and Energy
DWA : Department of Water Affairs
ERG : East Rand Goldfield
ERB : East Rand Basin
ERPM : East Rand Property Mine
GCRO : Gauteng City Region Observatory
GDARD : Gauteng Department of Agriculture and Rural Development
ICP-OES : Coupled plasma-optical emission spectroscopy
GTF : Gold tailings footprints
GPS : Global positioning system
PAF : Potential acid formation
PXRD : Powder X-ray diffraction
US EPA : United States of Environmental Protection Agency
WRG : West Rand Group
WRB : West Rand Basin
XRF : X-Ray Fluorescence
GLOSSARY OF TERMS

**Tailings dumps**: Mine waste products derived from mining activities after mineral processing.

**Tailings footprints**: Remnants left over after tailings dumps reclamation.

**Toxic elements**: Potential harmful elements leaching from tailings and footprints like Pb, As, Zn, and Cu to our natural environment.

**Dispersion**: Spatial distribution of toxic elements in different chemical forms in the environment.

**Reclamation**: The removal of tailings dumps to create land for development purposes on disturbed sites selected for land use.

**Toxicity**: High levels of toxic elements that have ability to impact environment and human health due to absorption of elevated concentrations of elements.

**Bioavailability**: Ability of plants to uptake toxic elements from the tailings footprints and also absorbed by humans as well as animals.

**Risk assessment**: Scientific/conceptual study of chemical properties of leaching elements on the environment.

**Statistical analysis**: Scientific tool applied for decisions making needed to be achieved.

**Geochemical Modelling**: It is a powerful tool used for characterizing tailings footprints, elemental speciation of leachates in environmental site contamination and predicting its impact.
CHAPTER ONE: INTRODUCTION

1.1. Background of the study

The Witwatersrand basin in South Africa is the world’s greatest goldfield. About 52,000 tons of gold were extracted from the gold-bearing conglomerate deposit in the basin. Gold mined in the Witwatersrand basin represented one third of gold produced compared to the gold mined around the world. The estimation has been done and according to the calculation of probability of ore reserve, about 30,000 tons of resources may still be recovered in the future (Conradie, 2000; Viljoen, 2009).

The first gold was discovered by Fred and Harry Struben in the quartz vein of the quartz pebble conglomerate in Witwatersrand basin. The panning of quartz veins in the area was reported and after gold was discovered, milling of quartz veins started and probably small volumes of quartz pebble conglomerate deposit was carried out by Fred and Harry Struben (Agangi et al., 2015). In the year 1886, George Harrison and George Walker discovered the gold bearing conglomerate deposit that was of economic importance. The rich auriferous conglomerate deposit was discovered in the Main Reef Leader at Langlaagte farm just west of Johannesburg, which was followed by rapid development in the Witwatersrand basin (Viljoen, 2009).

Main Reef Leader as it hosts the significant gold-bearing conglomerate deposit of the Witwatersrand basin, detail geological mapping was conducted along the Central Rand basin, and probably area covered was from 35 to 40 km. The mapping ranged from Durban Roodeport Deep mine in the western direction to the East Rand Property mine (ERPM) in the eastern side of Johannesburg. Different exploration techniques were implemented to find out the lateral variations of the Witwatersrand conglomerate deposit. Geophysical methods such as magnetic, gravity and seismic method was used to study the subsurface formations (Frimmel et al., 2005).

Findings showed that the Witwatersrand basin is a 6 km thick geological sequence formed in a sedimentological terrain comprised of thin sedimentary layers that stretch from east of Johannesburg in the north to the southern Free State in the south west and in outline that resembled a shallow elliptical dish (Viljoen, 2009; Dankert and Hein, 2010). The overlying Central Rand basin is dominantly composed of quartz-pebble conglomerate, quartzite, quartzwackes and some minor shale. The
Central Rand basin contains economic deposit that was rich in high gold mineralization and it is divided into lower Johannesburg and Turffontein Supergroup. Johannesburg and Turffontein Supergroup are comprised mainly of argillaceous clays and shale with occasional banded ironstone, a tillite and intercalated lava flow, while the upper part of the basin consists almost entirely of quartzite and conglomerates. It is estimated to have formed between 2.6 and 3.0 billion years ago (Viljoen, 2009; Guy, 2012).

Despite that many of older mines are now nearly exhausted, the Witwatersrand basin still produces most of South Africa’s gold and much of the total world output. Ag, Ir, As, Rn, Ni, Zn and many other radioactive materials like uranium are recovered as gold refining by products. Uranium minerals in the Witwatersrand conglomerate deposits are typically uraninite with lesser uranothorite and uranium is especially concentrated along the carbonaceous seams or carbon leaders (Zhao et al., 2006; Phillips and Powell, 2011; Guy et al., 2014; Phillips and Powell, 2015).

Mining activities in the Witwatersrand basin have resulted in large volumes of waste mainly in the form of slimes dams and sand dumps. Slimes dams consist of waste from the cyanidation process of gold while sand dumps consist of waste from the mercury amalgamation method which was used prior to the adoption of the cyanidation process (Tutu, 2008). Deep shaft mining currently occurs mainly in the West Rand Basin (WRB) of the Witwatersrand goldfields while in the East Rand Basin (ERB) and Central Rand Basin (CRB), a secondary method of mining in the form of tailings reprocessing is the major activity (Agangi et al., 2015).

Mining has played a significant role in the economic development of South Africa. After mines have closed in the CRB, it has left undesirable legacy. Mining is one of the biggest pollution contributors to soil and water systems, mine wastes as the main concern. According to Alakangas et al., (2010) retardation of sulphide oxidation in mine tailings due to exposure in atmospheric oxygen may change the quality of discharged effluents in the long term. Hydrogen ion activity of the tailings effluents may differ seasonally due to the local hydrological conditions. Trace elements may be released during sulphide oxidation where large quantities retained on tailings material left on the footprints by efflorescent crusts as secondary. The impacts of
mining on environment is not a short term crisis but has a long term implications and these may lead to environmental and human health impacts around the communities close to the mine waste dumps (Donkor et al., 2015).

Gold mining produces mine wastes consisting of milled and processed waste rocks that were dumped in large quantities in open areas, where environmental management plan was not implemented to prevent soil and water pollution caused by leaching toxic trace elements from the mine wastes. Mine pollution has resulted to environmental damage due to failure of mine waste dumps to be stabilized and sufficiently remediated (Getaner and Alemayehu, 2006). Mining in the CRB was identified as one of the human activities that negatively impacted the quality of the environment. It has resulted into destruction of natural environment and their impacts on the ecosystem were due to removal of soil, vegetation and the burial beneath waste disposal sites (Ogola et al., 2002).

Mine wastes are in a form of mining tailings, generated during ore mineral processing and waste rocks from blasted rock fragments to gain access to the economic ore deposit. Environmental impacts of mining affected physical/habitat destruction that resulted into loss of biodiversity and accumulation of toxic contaminants in different components of the ecosystem. Mine waste dump sites become a permanent toxicological problem in the ecosystem and human health (Donkor et al., 2015).

To respond to challenges that may affect soil and water quality after physical removal of mine dumps, this study was designed to characterise the tailings footprints in order to make assessment of various scenarios of pollutant release or its mobility as remnants material left on the tailings footprint may be secondary source of pollution. According to Heikkinen et al., (2009) primary factor that influences the effluent quality in tailings dumps is the chemical composition of mine wastes in which seepage quality was compared on the sulphide mineral tailings. The seepage pH and concentration of trace elements varied between the seepage points due to variation in the intensity of chemical weathering of mine dumps along the seepage flow paths.
1.2. Problem statement

Due to gold tailings reprocessing activities in the CRB, problems of dust and water pollution are quite common. Water pollution is mainly as a result of leaching of acidic plumes due to AMD resulting from the oxidation of residual pyrite and other sulphides in the waste ore. After reclamation of gold tailings dumps, remnants material are left on the tailings footprints and remaining tailing soil in the footprints may leach toxic trace elements on the topsoil horizon where plants extract nutrients (Rosner and van Schalkwyk, 2000).

Gauteng Department of Agriculture and Rural Development collected data which the findings shows that landscape in Gauteng province is covered by 374 mine residual areas (GDARD, 2012). An estimated 145 mine dumps remained and reclamation of tailings dumps is still going on in the Witwatersrand basin. Major concern is soil pollution caused by eroded waste material, the tailings footprint and polluted water (Tutu, 2008). For instance, soils below tailings dumps remain polluted even after the tailings have been removed and reprocessed (Camden-Smith and Tutu, 2014).

After physical removal of tailings dumps, the soils that they occupied may not be suitable for use as building sites (residential, office or industrial) or for recreational facilities owing to residual pollution. According to Heikkinen and Raisanen (2008) during acid mine drainage, elevated concentrations of trace elements, radionuclides and other pollutants are mobilized and dispersed into the surrounding environment. These tend to be retained in the soils due to adsorption and may be released slowly into groundwater over time (Tutu, 2011; Grover et al., 2016).

1.3. Justification

The characterisation of gold tailings footprints is significant, as after the reclamation of the gold tailings dams, some remnants materials are left on the top soil. Therefore the remaining tailings soil may be the secondary source of pollution and due to influence of leachability factors, the gold tailings footprints may leach toxic trace elements. When leachates enters soil and water medium through source-transport-trap mechanism may be the secondary source of pollution in soil and water systems and it may results into environmental and human health impacts on selected sites planned for developments after reclamation of the tailings dumps.
1.4. Aim and objectives

1.4.1. Main objective

This study aimed to characterise tailings footprints in areas targeted for human settlements and office spaces to assess their potential to release left over toxic element and this involved characterisation of oxidised and unoxidised tailings material and secondary precipitates on both tailings dumps and footprints. To this end, the central aim of this study was to determine a comprehensive geochemical characterisation of mine impacted sites in order to find out their mineralogical composition; acid generating potential materials and potential toxicity of trace elements that may cause human risks and deteriorate the environment.

1.4.2. Specific objective

This central aim was achieved by accomplishing the following objectives.

- Characterisation of the gold tailings dumps and footprints as sources of pollution.
- Assessment of various scenarios of pollutants release or mobilisation potential from tailings dumps and footprints.
- Assessment of potential toxicity using simulations based on geochemical modelling.

1.5. Hypothesis

This study is based on hypothesis that the tailings footprints in the CRG of the Witwatersrand basin after re-mining of the tailings dumps may be the secondary source of pollution in soils and water systems. Leaching of trace elements from tailings dumps depends on geochemical processes, pH and temperature. Therefore the experimental data may not be enough to understand the behavior or chemical forms of these contaminants. Geochemical models can be applied to understand the geochemical processes that lead to release, transport and dispersion of trace elements from both tailings dumps and footprints. Based on the modelling results, remediation of contaminated soil and water resources can be easily applied due to the fact that all sources of contaminants and their potential toxicity are clearly understood on the sites selected for developments.
CHAPTER TWO: LITERATURE REVIEW

This chapter aimed to provide detail information about the gold mine tailings, their sources of formation, mineralogy of the tailings, its geochemistry, and environmental impacts of tailings, leachates from the gold tailings dumps and footprints, the toxicity of the leachates from tailings footprints. Geochemical modelling was also introduced to clearly indicate the importance of modelling as a predictive tool in this study.

2.1. Tailings

Tailings are waste materials from mineral processing, which are composed of mixtures of crushed ore minerals and processed fluids from grinding mills, concentrators that are left after extraction of valuable minerals and economic metals from mine resources. The term “tailings” describes the waste product of several extractive mining activities including coal, gold, copper and uranium bearing commodities (Zhao et al., 2012). Gold mining in the CRB of the Witwatersrand basin resulted into higher tailings ratios when mining ceased in the basin.

Tailings are fine grained mine waste material remaining after the extraction of valuable minerals in hardrock mining and ore processing. Tailings are generated when mined ore is processed into fine sand particles through crushing, grinding and milling (Li et al., 2013). Ore mined is transported to the milling circuit where it is reduced into sand and silt sized particles, mixed with water and discharged as slurry to tailings. The economic minerals are separated from milled rock particles through physical and chemical processes in order to separate valuable minerals from unwanted materials (Kim, 2015).

Tailings are characterised into fine grained, typically silt size particle that range from 0.001 to 0.62 mm and solid material (remnant tailings material) left after the recovery of the metals and valuable minerals from economic ore deposit and the remaining fluids. The chemical and physical characteristics of tailings in terms of its composition are similar to sand and silt (Tutu, 2011). Their composition may differ depending on the economic geology of the ore deposit, as it may differ in terms of environment of formation. Remnants material left on the tailings footprint may have impacts on environmental and human health on sites where there is physical removal of mine dumps activities on locations selected for projects development.
Mine tailings accumulate amounts of toxic trace elements and may be leached out from the tailings dump and footprints. Geochemical processes in both tailings dump and footprints due to chemical reactions taking place results into AMD and release of toxic trace elements that may have impacts on environmental and human health. (Camden-Smith and Tutu 2014). The main concern is that after mining ceased and failure to implement proper environmental management plan, AMD pose a threat to soil and water quality due to rise of environmental critical level of groundwater that has filled the mine voids in abandoned mines in the Witwatersrand basin (Department of Water Affairs, 2012). The chemical composition of the gold mine tailings depends on the mineralogy of the ore deposits, the characteristics of processing fluids used from the processing plant (Zhao et al., 2012; AECOM, 2014).

### 2.2. Sources of tailings formation

In order to start with mine development, several factors such as location, morphology and geometry, depth, economic and environmental are significant to consider. It guides the mine planners to make a right choice on mining method to be implemented on that mine project development. Depending on mining method chosen and also on the size of the area where mine project will occur, project may show different ore extraction potentials and this will determine quantities of mine wastes dump (GDACE, 2008). The depth of economic ore deposit will determine whether surface or underground mining will be suitable to access the ore-deposit and brings profit.

Mined ore minerals are transported to the surface for mineral beneficiation. Ore minerals are crushed, grinded, washed, filtered and sorted into different particle sizes by gravity concentration. This is done to separate and concentrate valuable minerals from mine wastes (tailings and waste rocks), in order to remove impurities so that the economic ore minerals may further refined. Mineral processing serves to change concentrated valuable minerals to a useful chemical form (Nordstrom et al., 2015). For a mineral to change to a useful chemical form, high temperature or chemical reactions are applied to change mineral chemical composition. After extracting valuable minerals, processing plant discharges mine wastes as tailings and waste rocks (Zhao et al., 2012).
Tailings remain the main source AMD formation in the Witwatersrand basin and become the primary source of pollution for soil and groundwater. They are not vegetated and unlined, thus lead to dust pollution, soil contamination and as well both surface and groundwater (Camden-Smith and Tutu, 2014). Tailings in the Witwatersrand basin are located in urbanized area and also covered land used for agricultural activities. During mining, gold-bearing conglomerate was crushed and milled to separate gold from mine wastes by metallurgical techniques. The discharged slurry from the processing plant was then pumped through the pipe to the prepared dump sites, where it has formed tailings dump after fluids and water were allowed to evaporate (Nordstrom et al., 2015).

The tailings slurry mostly is pumped at high concentration in order to reduce the bulk of discharged mine waste material and transport cost. Pulp concentration in concentration in metallurgical plant by cyclones, classifiers, screens and filters are increased. The high volume or maximum concentration is limited by the pumping plant. Discharge of the slurry is through sub-aqueous and sub-aerial deposition. Sub-aqueous deposition is mostly in a form of uncontrolled discharge with the body of water (Name and Sheridan, 2014; Amos et al., 2015).

The tailings settle as soft sediments in the bottom, transported and dispersed to land suitable for dump site. Sub-aerial deposition is accompanied by slurry discharge from open ended pipe outlet. Sequence of discharge is cycled to allow slurry deposited layer dry up and this increases the density before the second slurry discharge (Netto et al., 2013).

2.3. Mineralogy of tailings

Abandoned tailings dump located in the CRB was studied. Due to reprocessing of tailings dump in the CRB, remnants materials are left on the tailings footprints. Oxidized and unoxidised tailings and effluent crust was sampled to find out the characterisation of the tailings dump and assessment of possible leachability of trace elements as source of secondary pollution on soil quality from the tailings footprints. Standard PXRD was used to assess the mineralogy of the tailings (Camden-Smith and Tutu 2014).
The PXRD pattern in both oxidised and unoxidised tailings samples clearly detected high concentration of quartz mineral, as quartz is highly resistant to chemical weathering. Quartz and other mineral phases such as Pyrophyllite (2 to 20 %), Chloritoid (3 to 19 %), Mica (4 to 12 %), Chlorite (4 to 11 %), Jarosite (2 to 3 %), Pyrite (1 to 3 %), Copiapite (4 to 11 %), Gypsum (~1 %), and Clay minerals commonly montmorillonite (~1 %) were detected by PXRD (Grover et al., 2016).

Therefore the mineralogical characterisation of the tailings dumps plays a significant role in the assessment of trace elements as pollutants to soil contamination. The presence of sulphide mineralisation in the tailings has a potential to react with rainwater and atmospheric oxygen and results into the formation of AMD. Acidic pH may influence the transport, effect and fate of chemical species from both tailings dumps and tailings footprints.

2.4. Geochemistry of tailings

Gold mining in the CRB of the Witwatersrand basin has resulted into formation efflorescent crusts on and nearby tailings dumps during dry seasons. Efflorescent crusts due to its soluble characteristic have an ability to generate acidity, metal and sulphate rich solutions during dissolution (Camden-Smith et al., 2014). Tailings dumps are the right sources that need to be investigated in order to make assessment on the leachability of trace elements as contaminants in both soil and water systems. Decanting acidic water resulted from oxidation of residual pyrite and other sulphide mineralisation from gold-bearing conglomerate deposit. AMD originate from complex geochemical and microbial processes (Tutu et al., 2008).

It is generated from tailings dumps and waste rocks. Decanting acidity to the natural ecosystem is primarily controlled by microbiological controls, depositional environment, acid and base balance of the mine wastes, lithology, mineralogy and hydrological conditions. Chemical weathering reactions occurs spontaneously on tailings dumps exposed to rainwater and atmospheric oxygen. The mineral phases in the tailings dumps and footprints are not in equilibrium with the oxidising environment, chemical reactions occur and minerals become transformed (Shabani et al., 2014; Nordstrom et al., 2015; Sun et al., 2015). Due to influence of microbial processes, reaction rates are accelerated and results into leaching of acidity and
trace elements as contaminants to the natural ecosystem. Pyrite is the common oxidised sulphide mineral. Pyrite reacts with atmospheric oxygen and water to produce ferrous iron, sulphate and acidity (Nordstrom, 2008; Maree et al., 2013; Gray and Vis, 2013; Wildenan et al., 2014).

The main environmental concerns associated with un-rehabilitated tailings dumps is the leaching of trace elements as secondary pollutants to soil and water systems. Tailings are transported through outlet pipes from the processing plants and discharged into the tailings impoundments. These results into the oxidation of sulphide minerals within the mine waste materials and leaching acidity influence the transport of trace elements from both tailings dumps and footprints to soil and water systems (Camden-Smith et al., 2015).

Tailings are finely ground left over waste materials from the mineral processing and the texture of tailings depends on the nature of the gold bearing ore deposit. Major factors that influence acid mine generation are sulphide minerals, water, oxygen, ferric iron, as well as bacteria to speed up the oxidation reaction on the tailings (Grover et al., 2015). Rainwater acts as a reactant or solvent and a medium for bacteria in the oxidation process, as well as oxidation products transporter. Mineral composition of gold-bearing conglomerate in the CRB is presented in Table 2.1.

**Table 2.1: Mineralogical composition of the gold-bearing conglomerate in the Central Rand goldfields (Pretorius, 1986; Grover et al., 2015)**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Abundance of mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz (primary and secondary quartz)</td>
<td>70-90 %</td>
</tr>
<tr>
<td>Muscovite and other phyllosilicates</td>
<td>10-30 %</td>
</tr>
<tr>
<td>Pyrites</td>
<td>3-5 %</td>
</tr>
<tr>
<td>Other sulphides</td>
<td>1-2 %</td>
</tr>
<tr>
<td>Grains of primary minerals</td>
<td>1-2 %</td>
</tr>
<tr>
<td>Uraniferous kerogen</td>
<td>1 %</td>
</tr>
<tr>
<td>Gold</td>
<td>~45 ppm in the Main reef</td>
</tr>
</tbody>
</table>
The major sulphide minerals in the mine waste materials are pyrite and pyrrhotite which are sulphur carriers in their chemical composition, and within the gangue, sulphide oxidation proceeds rapidly and is catalyzed by chemolithotrophic bacteria of the *Thiobacillus* group (Tutu, 2008). The Main reef was the main zone of gold mineralisation in the CRB. The gold bearing conglomerate deposit, when mined and processed, mine wastes pose a potential environmental hazard to the ecosystem and human health (Nordstrom *et al.*, 2015).

The exposure of fresh rocks surfaces during mining, as well as produced crushed and milled mine waste (tailings and waste rocks), subjected to chemical weathering processes, cause large scale environmental impact due to poor management of mine waste material after excavation (GDARD, 2012). The sulphide bearing mineralisation when oxidised at the surface has potential to produce acid rock drainage (ARD) and acidic pH influences leaching of trace elements from both tailings and waste rocks (Torres *et al.*, 2014).

The soil contamination threat in the area may cause geotechnical problems on the stability of the ground surface on the surrounding environment. Poor design of tailings dumps may lead to physical weathering of tailings material and trace elements may disperse in the nearby soils (Li *et al.*, 2013; Simate and Ndlovu 2014). The underground mining method, as was one of the common method used for mining in the CRB, generated large quantities of tailings dumps and waste rocks containing the targeted gold and uranium minerals in order to extract the desired quartz pebble conglomerate deposit (GDARD, 2012; Kim, 2015).

After the excavation, mined waste material (tailings dumps and waste rocks) were transported to the processing plants and then gold bearing conglomerate deposit was crushed into finely ground tailings for processing with various chemicals and separating processes to extract the desired gold metal. Geochemical and mineral processing techniques applied in the processing plant to separate valuable minerals from gangue (unwanted sediments) and after that, waste material were dumped on the land dump sites selected for tailings and waste rocks disposal (Figure 2.1).

Gold mine wastes were generated in the CRG over the past years after mines have closed in the nineteen seventies. A large quantity of tailings dumps remains forming
a feature of the Witwatersrand landscape and is dominated by tailings and sand dumps with grade as low as 0.3 g/t of gold (DME, 1995; DME, 1998; Viljoen, 2009). The Witwatersrand basin covers area of 1600 km²; more than 270 gold tailings dams have covered approximately 400 to 500 km² on surface ground in the Witwatersrand basin. Tailings dumps are mostly not unlined and vegetated and this gives access to extensive source of dust, as well as soil and water contamination (Hallberg, 2010; Camden-Smith et al., 2015).

Therefore due to some environmental management plan implemented in the CRB as part of tailings rehabilitation or tailings management, tailings are removed in order to reduce acid generation in the environment, as the mineralogy of gold tailings dumps cause impacts on the soil and water quality. After the removal of tailings dumps in the CRB, the contaminated soil remains as a mark of gold tailings footprints (Camden-Smith et al., 2014).

Figure 2.1: Area covered by mine tailings dumps in the Central Rand Basin (GCRO by Kerry Bobbins, 2015)
Reclamation of mine residue areas was proposed by Gauteng Department of Agriculture and Rural Development (GDARD) in 2010. Remote sensing and geographical information system (GIS) techniques were used for identification of mine dumps and the delineation of mine complexes boundaries (collaboration of different types of mine activities and tailings dumps (Naumov, 2011). Therefore in order to conduct environmental risk assessments on areas covered by the tailings dumps and waste rocks, characterisation of waste rock dumps, tailings dams, tailings dumps and spillage sites are significant (Naumov, 2010; Osovetskiy, 2012).

After the reprocessing of the tailings dumps, remnants material are left on the tailings footprints and this lead to continuous changes in chemical speciation depending on the mineralogy of the tailings dumps (Nordstrom et al., 2015). Continuous changes may occur from tailings dumps to footprints after physical removal of the mine dumps. Therefore remediation on those sites selected for development purposes is significant after physical removal of tailings residue. Mine residue areas selected for development purposes are regarded as highly polluted and this has caused impacts on soil and water quality (GDARD, 2011; Grover et al., 2016).

2.5. Environmental impacts of tailings

The mining industry has been one of the catalysts in the economic growth in South Africa. Currently due to some abandoned gold mines in the Witwatersrand basin left without any environmental monitoring plans, mine waste materials (tailings and waste rocks) has left an extremely undesirable legacy known as acid mine drainage. Mining worldwide has been identified as one of major polluter on natural ecosystems. Due to its anthropogenic activities, it causes negative impacts on the quality of natural environment (Camden-Smith et al., 2014; GCRO, 2015).

Mine development results into the destruction of ecosystems through the stripping or removal of top soil and vegetation. Mine waste disposal is the main environmental concern on environmental pollution and quality. Mine wastes are categorised into mine tailings, generated from mineral ore processing and waste rocks produced from blasting of rocks to gain access to the economic ore deposit. The ore deposits are grinded, recovered for desired particle size and mine wastes are disposed as slurry, to tailings or retention pond (Zhao et al., 2012; Kim, 2015).
Mostly high percentage of original waste material discharged from mine processing plant may finally become tailings when low quality ore are used. Tailings dumps due to its geochemical changes pose a permanent toxicological problem for the surrounding ecosystems and human health to communities residing close to the mine dumps (Tutu, 2011). Tailings dumps have environmental negative impacts on soil, water and air. Tailings dumps are contaminated with trace elements and this pose a threat to soil and water systems. Toxic contaminants may be released from tailings to soil and water resources, influenced by geochemical processes occurring during rainy seasons (Camden-Smith et al., 2014). Physical and chemical properties of the tailings has major role in the leaching of trace elements to be dispersed and accumulated in plants and animals (Zhao et al., 2012).

Tailings contain many trace elements that may cause impacts on the ecosystem, as some are toxic contaminants in the soil. Contamination of soils and water by trace elements is the major environmental concern in the mine sites due to their toxicity, persistence and accumulation to plants and it also threatens the food security. Trace elements are main concern to soil pollution (Torres et al., 2014). Trace elements have tendency to accumulate in soil and they are not biodegradable. They are also ubiquitous in soils arising from natural and anthropogenic activities (Kim, 2015; Nordstrom et al., 2015).

Some trace elements at low concentrations have a significant role as nutrients from plants, animals and human health. Higher quantities of some trace elements on certain chemical form may also be toxic and harmful to human health. Cu and Zn are good examples; both are significant for normal metabolism and can be harmful in high quantities. Higher concentrations of Cu and Zn in human body become harmful and may damage human body. Trace elements such as Pb and As are toxic to human health and consumption of these trace elements may cause cancer, neutral and metabolic disorders (Li et al., 2013; Wei et al., 2013).

As is one of the toxic contaminants of drinking water worldwide and it causes cancer of the skin, lungs, urinary bladder and kidney. Pb has great concern as it can cause brain, liver and kidney damage in children and in adults it can damage the nerves. One of the most important environmental problems linked with talings dumps is acid
mine drainage, produced pyrite is oxidized and other sulphide mineralisation. Soil contamination due to leachates from the tailings dumps poses a threat to human health (Greany, 2005; GDACE, 2008; Jones et al., 2009). Plants may uptake accumulated trace elements from the soil, due to uptake of minor quantities to human body through food chain, it may affect their health. These toxic mine wastes (tailings and footprints) cause problems to the environment as well as residents close to the tailings dumps. Toxic contaminants leaching from tailings dumps may cause birth defects, diseases and even death to people residing to nearby tailings dumps (Viljoen, 2009; Nordstrom, 2011; Department of Water Affairs, 2012).

Tailings materials react with rainwater and atmospheric oxygen and these results into leaching of acidity known as acid mine drainage. Acidic pH dissolves trace elements and releases those toxic contaminants from the tailings to the natural environment. Acidity leaching from the abandoned mines and tailings dumps has an impact on the ecosystem (Viljoen, 2009). It contaminates soil and water system and this destroys the aquatic species and threatens the food security. Acid mine drainage is a naturally occurring process whereby sulphuric acid is produced when sulphide minerals like pyrite are exposed to air and water (Camden-Smith and Tutu, 2014).

When large quantities of rock containing sulphide minerals are excavated from an open cast or opened up in an underground mine, it reacts with water and oxygen to form sulphuric acid. When water reaches a certain level of acidity, a naturally occurring type of bacteria called *Thiobacillus ferroxidans* may be involved, accelerating the oxidation and acidification processes and leaching even more trace elements from the mine wastes. The acid will leach from the rock as long as its source rock is exposed to air and water and until the sulphides are leached out, process can last hundreds and even thousands of years (Amos et al., 2015; Torres et al., 2014; Grover et al., 2016).

Acidic water is carried off from the mine dump site by rainwater or surface drainage and deposited into nearby streams, dams and sources of groundwater. AMD severely degrades soil and water quality and it destroys aquatic life on the ecosystem (Zhao et al., 2012; Simate and Ndlovu 2014). The cycle involved in AMD formation from the source to the natural environment is shown in Fig. 2.2 and 2.3.
AMD is very toxic to the natural ecosystem and humans’ health to those residing close to the mine dumps. Major concern about AMD is the fact that it is very complex to deal with it. AMD is a dangerous environmental hazard as it does not cause impacts on water and the soil system only, but it also causes a harmful effect on the human health due to release of toxic contaminants from the tailings (Nordstrom et al., 2015). Common problems are experienced in communities living near currently operating mines or abandoned mines. Some trace elements such as Pb and Zn which are toxic and radioactive particles from mining operations are released into the surrounding environment by surface runoff to soil and water systems (Tutu et al., 2008; Kim, 2015; Torres et al., 2014).

Figure 2.2: Source, transport and trap mechanism of pollutants (INAP, 2009)

Figure 2.3: Run off and seepage from a gold tailings dump (Wikipedia, 2013)
The contamination caused by mine water chemistry affects vegetation and results in the negative production in the agricultural sector, as agricultural industry being badly affected by mine water pollution especially in surface and groundwater for irrigation or drinking purposes (Department of Water Affairs, 2012). Generation of AMD originates with the diffusion of oxygen into the mine waste material (tailings and waste rocks) composed of reactive sulphide mineralization, where it is consumed by oxidation of sulphide minerals (Figure 2.4).

![Figure 2.4: Sulphur oxidation and composition of mine waste material (WUC Report, 2009)](image)

The geochemical composition and discharge rate of acid mine drainage from mine waste material deposited on the site, is influenced by several factors such as climatic conditions, mineralogical composition or geochemistry of the mine waste material, as well as the depositional or geotechnical design of tailings impoundments and hydraulic properties of mine waste material (Valente and Leal Gomes, 2009; GDARD, 2011, GCRO, 2015). Since large masses of sulphide minerals are exposed quickly during mining and milling processes, the surrounding environment can often not attenuate the resulting low pH conditions. Trace elements that were once part of
the host rock are solubilized and exacerbate the deleterious effect of low pH on terrestrial and aquatic receptors (Nordstrom et al., 2015).

Therefore to prevent surface runoff some paddocks are designed prevent physical weathering of tailings dumps. Paddocks are designed reduce dispersion of trace elements to the nearby soil and water systems. Due to concentrations of some common trace elements like Cu, Pb, As, Zn, Cd, Al, Fe and Mn increases in water with low pH (Sracek et al., 2010; Camden-Smith and Tutu, 2014; Grover et al., 2016). Hydrogen ion activity increases in trace elements levels in water from sulphide rich mining environments and it is very common where surface or groundwater pH is depressed by acid generation from sulphide minerals.

Figure 2.5: Paddocking used to control surface water flow from reprocessing Activities (Wikipedia, 2013)

A mine waste (tailings and waste rocks) that contains sulphides have the potential to produce AMD. The initial stage of AMD formation is when exposed sulphide minerals such as pyrite from the tailings dumps and waste rocks react with oxygen and moisture content in mine dump sites (Figure. When FeS₂ is oxidised, releases Fe²⁺ ion and Fe²⁺ become extremely oxidized slowly (Zhao et al., 2012).
Oxidation of Fe$^{2+}$ results in the formation of Fe$^{3+}$ ion (Netto et al., 2013; Maree et al., 2013). When Fe$^{3+}$ reacts with water, Fe(OH)$_3$ is precipitated from tailings material. The precipitation of Fe(OH)$_3$ results in leaching of toxic elements such Pb, Zn, Cu and As due to acidity resulting from oxygenated waters reacting with sulphide mineral like pyrite that has potential to produce sulphuric acid (Simate and Ndlovu, 2014; Amos et al., 2015).

AMD occurs in coal and goal mining commodities due to presence of sulphide mineralisation. Geochemical reactions of mine waste (tailings and waste rocks) and rainwater through chemical weathering processes results in the generation of AMD around the tailings and waste rocks (Abrahim and Parker., 2008). It is influenced by oxidation and reduction reactions that occurs when tailings material react with water and atmospheric oxygen (Kim, 2015; Nordstrom et al., 2015; Grover et al., 2016).

**Table 2.2: Indicate sulphide minerals that have potential in AMD generation**

<table>
<thead>
<tr>
<th>Mineral phase</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>FeS$_2$</td>
</tr>
<tr>
<td>Marcasite</td>
<td>FeS$_2$</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Fe$_x$S$_x$</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Cu$_2$S</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS$_2$</td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>FeAsS</td>
</tr>
<tr>
<td>Cinnabar</td>
<td>HgS</td>
</tr>
</tbody>
</table>

Formation of AMD occurs after long time after mines have been abandoned; mine waste materials have been left exposed without any implementation of environmental management plan. In undisturbed natural systems, this oxidation process occurs at slow rates over geologic time periods (Name and Sheridan, 2014).
AMD is generated when mine waste containing metal sulphide minerals are oxidized. Sulphide minerals are found in the country rock associated with gold-bearing conglomerate in the CRB. Due to mining operations taking place, oxidation of these minerals and the formation of sulphuric acid are influenced by the chemical weathering processes (Figure 2.6). Mostly tailings and waste rocks are dumped in a high elevation slope, especially in valley impoundments; tailings remain saturated for a limited period of time during mining, and the presence of moisture and oxygen can change the soil and water pH to be acidic (Wei et al., 2013; Nordstrom et al., 2015).

After reprocessing of tailings dumps, remnant amounts of tailings materials are left on top of soil horizon after reclamation. The remnant tailing material left on the tailing footprints may lead to downward migration of toxic contaminants to the subsoil, which may lead to groundwater contamination (Figure 2.6).

Figure 2.6: The geochemical processes that led to AMD generation around the tailings impoundment (Tutu et al., 2008)
When pyrite is exposed to oxygen and water it is oxidized due to presence of moisture in tailings pore spaces and these results in releasing acidic water, sulphate, and soluble trace elements (equation 2.1). The acidity of water is typically expressed as logarithmic concentration of (H$^+$) concentration in water, commonly a pH of 2.3 to 4.5 represent highly acidic conditions on the natural environment.

The following oxidation and reduction reactions show the reaction phases of pyrite that leads to acid mine drainage (Boukhalfa and Chaguer, 2012):

\[
2\text{FeS}_2 (s) + 7\text{O}_2 (g) + 2\text{H}_2\text{O} (l) \rightarrow 2\text{Fe}^{2+} (aq) + 4\text{SO}_4^{2-} (aq) + 4\text{H}^+ (aq) \quad (2.1)
\]

Pyrite + oxygen+ water $\rightarrow$ ferrous ion + sulphate ion + acidity

Further oxidation of Fe$^{2+}$ takes place when sufficient oxygen is dissolved in the water or when water is exposed to sufficient atmospheric oxygen circulation (equation 2.2) (Boukhalfa and Chaguer, 2012).

\[
4\text{Fe}^{2+} (aq) + \text{O}_2 (g) + 4\text{H}^+ (aq) \rightarrow 4 \text{Fe}^{3+} (aq) + 2\text{H}_2\text{O} (l) \quad (2.2)
\]

Ferrous ion + oxygen + acidity $\rightarrow$ ferric ion + water

Fe$^{3+}$ can either precipitate as Fe(OH)$_3$ due to an increase in the amount of phase present as it is influenced by the positive number that led the reaction into the precipitation phase. A red-orange precipitate is mostly visible in waters affected by acid rock drainage, or it can be due to contact with pyrite mineral, and that will lead to a direct reaction with pyrite to produce more ferrous iron and acidity as shown in equations 2.3 and 2.4. Hydrolysis and precipitation of iron hydroxides will result in forming most of acid in this process. When hydrogen ion activity is less than about 3.5, Fe(OH)$_3$ will not be stable and Fe$^{3+}$ will be part of the remaining solution (equation 2.3) (Heikkinen et al., 2009; Li et al., 2013).

\[
\text{Fe}^{3+} (aq) + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 (s) + 3\text{H}^+ (aq) \quad (2.3)
\]

Ferric ion + water $\rightarrow$ ferric hydroxide + acidity

Fe$^{3+}$ was formed by oxidation of Fe$^{2+}$ and oxidation process that has occurred especially at low pH conditions, strongly accelerated by microbiological process, ferric iron will be the first oxidant (equation 2.3) of FeS$_2$. During microbiological
processes, the rate of oxidation of FeS$_2$ by Fe$^{3+}$ influence the rate of oxidation of Fe$^{2+}$ which descend rapidly with decreasing hydrogen ion activity (H$^+$) (Zhao et al., 2012; Nordstrom et al., 2015).

$$\text{FeS}_2 (s) + 14\text{Fe}^{3+} (aq) + 8\text{H}_2\text{O} (l) \rightarrow 15\text{Fe}^{2+} (aq) + 2\text{SO}_4^{2-} (aq) + 16\text{H}^+ (aq) \quad (2.4)$$

**Pyrite + ferric ion + water$\rightarrow$ferrous ion + sulphate ion + acidity**

When Fe$^{2+}$ is produced (equation 2.4) and sufficient dissolved oxygen is present, the cycle of reaction 2.2 and 2.3 will continue indefinitely. Without the presence of oxygen dissolved equation 2.4 will continue to completion and water will show elevated levels of ferrous iron. The rate of chemical reactions (equation 2.4, 2.3, and 2.4) can be significantly accelerated by bacteria, specifically Thiobacillus ferrooxidans. Another microbe, ferro-plasma acidarmanus, has been identified in the production of acidity in mine waters (Appelo et al., 2002; Bakatula et al., 2012). Hydrolysis reactions of mostly common metals form precipitates and that led to generation of H$^+$ (Appelo et al., 2002).

The following oxidation and reduction reactions show the reaction phases of chalcopyrite that leads to acid mine drainage. When CuFeS$_2$ is oxidised, Fe$^{2+}$ and SO$_4^{2-}$ are formed (equation 2.5), based on the reaction products formed, it was clearly observed that ferrous ions catalyzed the oxidation by dissolved oxygen in acidic condition. CuFeS$_2$ dissolution can also be influenced strongly by galvanic effects (Nordstrom et al., 2015; Torres et al., 2014).

$$2\text{CuFeS}_2 + 4\text{O}_2 \rightarrow 2\text{Cu}^{2+} + \text{Fe}^{2+} + \text{SO}_4^{2-} \quad (2.5)$$

**Chalcopyrite + oxygen$\rightarrow$cupric ion + ferrous ion + sulphate ion**

Due to interaction of Fe$^{2+}$ oxidation and ferrihydrate, hydrolysis will be the main influential on acid formation process (equation 2.6) (Boukhalfa and Chaguer, 2012).

$$2\text{CuFeS}_2 + 8.5\text{O}_2 + 5\text{H}_2\text{O} \rightarrow 2\text{Cu}^{2+} + 2\text{Fe(OH)}_3 + 4\text{SO}_4^{2-} + 4\text{H}^+ \quad (2.6)$$

**Chalcopyrite + oxygen+ water$\rightarrow$cupric ion + ferric hydroxide + sulphate + acidity**
The following oxidation and reduction reactions show the reaction phases of arsenopyrite that leads to acid mine drainage (Li et al., 2013):

Arsenopyrite is oxidized due to some exposure of tailing impoundments on the surrounding environment where mine waste disposal is taking place and due to some atmospheric oxygen circulation (McCarthy, 2006; Sracek et al., 2010), the following oxidation reaction takes place:

\[ 4\text{FeAsS} + 13\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}_2\text{AsO}_4^- + 4\text{H} \]  

(2.7)

**Arsenopyrite + oxygen + water→ ferrous ion + sulphate ion + dihydrogen arsenate ion + acidity**

After oxidation of \( \text{Fe}^{2+} \) and \( \text{Fe(OH)}_3 \) precipitation occurred, the overall oxidation reaction will be formed (equation 2.8) (McCarthy, 2011).

\[ \text{FeAsS} + 3.5 \text{O}_2 + 6\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + \text{SO}_4^{2-} + \text{H}_2\text{AsO}_4^- + 3\text{H}^+ \]  

(2.8)

**Arsenopyrite + oxygen + water→ ferric hydroxide + sulphate ion + dihydrogen arsenate ion + acidity**

The physical properties of AMD depend on the dissolved and precipitated metals from tailings and waste rocks. The reddish colour in AMD indicate the dominance of Fe precipitate as \( \text{Fe(OH)}_3 \), orange to yellow colour show the presence of \( \text{Fe}^{3+} \) in sediments, white colour indicate the presence of aluminium Al precipitated as \( \text{Al(OH)}_3 \) and dark colour also indicate the presence of Mn precipitated as Mn (OH₂).

The following issues are of potential environmental consideration:

- The presence of sulphide in the ore deposits is a source for concern for water pollution originating from both mine workings and residue deposits in the form of mine waste and tailings.
- Structural controls to ore deposits present potential access of weathering agents such as groundwater and atmospheric oxygen.
- The resulting dewatering of acid mine drainage and its disposal to environment around the mine including surface streams.
- Soil contamination caused by leaching of metals from the gold tailings dumps.
Some of the above concerns can be observed in Figures 2.4 and 2.5. Erosion of material from dumps and accidental spillages (Fig. 2.5) can contribute significantly to pollution in the immediate environment. Ideally, erosion and water flow can be controlled by use of paddocks (Fig. 2.5). However, seepage into groundwater and surrounding soils cannot be totally eliminated.

2.6. Leachates from tailings

The gold tailings dumps contain high concentrations of pyrite. Due to geochemical reactions occurring in the tailings, pyrite is oxidised when the tailings materials are exposed to moisture content and atmospheric oxygen. The products from reactants are ferro-sulphate ($\text{FeSO}_4$) and sulphuric acid ($\text{H}_2\text{SO}_4$) (Kim, 2015). Toxic contaminates are leached out when they dissolve from tailings material due to acidity formed during hydrolysis process when $\text{FeSO}_4$ reacts with rainwater to form strong acid, $\text{H}_2\text{SO}_4$. Oxidation processes makes the hydrogen ion activity to drop from 8.5 to 3.0 which is very acidic (Torres et al., 2014). The chemical reactions during geochemical processes in the tailings results in the release of toxic leachates to soil and water systems. AMD due to its acidic pH, release trace elements from the tailings dumps. Trace elements may dissolve at acidic conditions, are soluble at the very low pH (Camden-Smith and Tutu, 2014).

Leaching trace elements such as Pb, Zn, Cu, As, Ni and Cd can be mobilized in water, accumulated in soil and end up percolating to groundwater system. The soil horizons acts as pathways of acidic leachates when water percolates get contaminated and acidified (Grover et al., 2016). According to Sutton and Weirsbye (2008) if uranium concentration is very low, it remains in the mine wastes and due to its radioactive characteristics, it becomes a threat also to human health.

The disposal of mine wastes worldwide has become a serious concern. The nature of mining and mineral processing techniques utilized, generates large quantities of mine wastes (tailings and waste rocks) compared to those from both domestic and industrial discharges (Wildenan et al., 2014; Kim, 2015). Mine waste disposal is a serious problem due to their chemical characteristics, especially the mobility of trace elements (Bakatula et al., 2012). The crushed ore from the processing plant after extraction of desired metal is discharged as slurry and later become tailings dumps.
Pollution of environment by leachates from tailings is the main concern on the natural ecosystem, soil and water quality (Li et al., 2013; Marre et al., 2013; Camden-Smith et al., 2015; Kim, 2015; Nordstrom et al., 2015; Grover et al., 2016).

2.7. Leachability factors

Based to this study, leaching was defined as process at which rainwater infiltrates and percolates through the tailings pore spaces and dissolves trace elements from the tailings dumps. Leaching processes occurs when rainwater get into contact with the surface of tailings dumps and rainwater as a solvent penetrates or diffuses into the tailings. Therefore trace elements (solute) dissolve from the tailings dumps into acidic rainwater acting as a solvent. Trace elements diffuse through the mixture to the surface of the tailings and through that process, toxic contaminants are leached out to soil and water systems (Camden-Smith and Tutu, 2014; Grover et al., 2016).

Factors that influence the leachability of trace elements in response to chemical reactions to the environment are based on the stability of the tailings dumps, characteristics of the tailings and climate of the area that determine the availability of water at the surface and groundwater. Therefore there is a need to come up with strategies to adequately control seepage (Li et al., 2013). It can be done by taking note of hydraulic characteristics and geotechnical aspects of foundation design of tailings dumps. Use of clay layer and construction of drainage for preventing low permeability on the tailings that may cause seepage or affect the stability of the tailings dumps is significant (GDARD, 2011, Gray and vis, 2013; GCRO, 2015).

2.8. Toxicity of elements in tailings

Mining impacts on the environment occurs in all stages of mining, starting from exploration phase, mine development and waste dumps, and last stage of ore processing where tailings are discharged as slurry to the natural environment. Toxicity of the tailings dumps pose threat to environmental safety and land production. Safety on the environment and physical stability of the tailings to prevent leaching of toxic contaminants from the tailings must be part of the plan from the start of the mine development to control toxic leachates from the tailings (Tutu et al., 2008; Bakatula et al., 2012; Camden-Smith et al., 2013).
Mine tailings are the main concern on the environment, due to release of trace elements to soil and water systems. Abandoned mine tailings commonly contains elevated concentrations of toxic contaminants such as Cu, As, Zn, Pb, and Cd. These toxic contaminants may be released from tailings soil and water resources. Toxic contaminants may also be dispersed on the surrounding environment due to their mobility and solubility characteristics (Zhao et al., 2012; Camden-Smith et al., 2014; Amos et al., 2015; Grover et al., 2016).

Mineralogy of the tailings plays a significant on the toxicity expected to leach out from the tailings. Tailings dumps are mostly rich in sulphide minerals like FeAsS, FeS$_2$, PbS, CuFeS$_2$ and ZnS (Leite et al., 2013; Li et al., 2013; Kim, 2015). When tailings are exposed to atmospheric oxygen, geochemical processes such as redox reactions, dissolutions, precipitation and adsorption, release of toxic contaminants from the tailings occurs (Grover et al., 2016). The oxidation of sulphide minerals results in the release of trace elements to the surrounding soil and water systems. Toxicity of trace elements depend on its chemical speciation, thus why it is significant to understand the geochemistry of tailings to find out the dissolution and precipitation characteristics of different minerals in the tailings dumps (Ntsume and McCarthy, 2005; Nordstrom et al., 2015).

The release of toxic elements such as Cu, As, Zn, Pb and Cd may have impacts on environment and human health. Toxic contaminants may be up taken by plants, in acidic conditions they may dissolve and accumulated in soils and seep to groundwater systems (Tutu et al., 2008). Soil and water pollution caused by leachates from the tailings is a very serious pollution state that need control actions, especially suspension of land development, concern of human health, growth of animals and plants (Shabani et al., 2014; Amos et al., 2015; Torres et al., 2014).

Trace elements are present at low concentrations in soils, water and rocks, but due to mining processes high quantities that are toxic to environment and human health are leached out from both tailings and waste rocks (Bakatula et al., 2012; Sun et al., 2015; Amos et al., 2015). During mining these toxic contaminants are released in large quantities from mine wastes produced during mine development and ore processing. Toxicity of mine tailings has an impact on the natural ecosystems and in
areas where residents are surrounded by the mine dumps. Seepage and dust emissions from the mine wastes are the major concerns on the landscapes covered by the mine dumps (GDARD, 2012; Simate and Ndlovu 2014; Torres et al., 2014).

Toxic contaminants like Hg can be released from mine wastes directly to the atmosphere and it may evaporate at lower temperature. Once it is released to the atmosphere, it can be deposited to soils and water even far from the mine sites. Dust emissions from tailings may contain toxic elements such as Pb and Cd that may occur in that geological environment (Wei et al., 2013; Name and Sheridan 2014). Rainwater is the main agent of pollution in the tailings and as a solvent it may dissolve toxic contaminants from the tailings and leach those contaminants into soil and water system. Major sources of the trace elements are associated with AMD resulting from chemical reactions from mine waste (tailings and waste rocks) (Camden-Smith and Tutu, 2014; Kim, 2015; Nordstrom et al., 2015).

Toxicity of leached out trace elements is a very serious concern to human health. Hg is one of the toxic contaminants that may lead to central and peripheral nervous system problems in the human body. Health effects of Hg include personality changes, changes in vision, loss of muscle coordination and sensation. Danger of Hg to women is that, it can be passed through pregnancy and breast feed. Pb is neurotoxic and it damages the brain and nerve cells (US EPA, 2004; Li et al., 2013; Madzivire et al., 2014).

Children residing close to the tailings are in danger, elevated concentrations of Pb leaching from the mine wastes may affect the health and they may suffer from abnormal and reduce of physical growth, their intelligence and mental growth. It can also be passed to children through pregnancy and breast feeding. As can cause cancer of skin, liver, bladder and lungs (US EPA, 2004; Bakatula et al., 2012; Zhao et al., 2012; Madzivire et al., 2011).

It can be transported through dust emissions into the atmosphere and through breathing it may results into lung cancer. For environmental safety and human health, sites on nearby tailings dumps, environmental risk assessment must be conducted to prevent toxicity of trace elements from tailings that may cause health effects on communities close to the mine dumps (Bakatula et al., 2012).
2.9. PHREEQC geochemical modelling

PHREEQC geochemical modelling is a powerful tool used for characterising environmental site contaminations and predicting environmental impacts. Chemical reactions that occur on environment may affect soil and water quality. Mostly they occur at low temperatures (0-100 °C) at approximately atmospheric pressure (Nordstrom, 2008). Geochemical processes of interest include dissolution and precipitation; mixing of water bodies (dilution); redox reactions of constituents; speciation and complexation of inorganic and organic matter (Grover et al., 2016).

Computer modelling is applicable in order to understand the geochemical processes to interpret field data and laboratory experiments and making predictions on the behavior of chemical species in environmental system. Many concerns of pollution on the environment caused by mine waste disposal and chemical spillage and studying the behavior of toxic contaminants, geochemical models were used to anticipate pollution sources and impacts and implementation of strategies to minimise leaching of contaminants on the environment (Zhu and Anderson, 2002).

Geochemical models can be used to interpret and predict the geochemical reactions that may occur on the mine dumps and other chemical spillage. Therefore geochemical models can be constructed to optimise remediation effects, determining the significant parameters in the environmental systems and come up with solid plan to minimise leaching of toxic contaminants to the natural ecosystems (Zhu and Anderson, 2002; Charlton and Parkhurst, 2011).

Geochemical modelling utilises mass action and mass balance equations to model the above processes. It is subdivided into speciation-solubility models, reaction path models, forward and inverse models. Speciation-solubility models are utilised to determine the distribution of stable chemical species in the system and saturation state of different minerals within the modelling system (Grover et al., 2016). Forward modelling is used to calculate the composition of a solution after reaction or equilibrium. It is applicable in the performance test and design studies (Van der Sloot and Van Zomeren, 2012; Nordstrom and Campbell, 2014).

Thermodynamic models use equilibrium constraints and it is assumed to be valid for homogenous reactions where sufficient space time equilibrium is reached.
Heterogeneous reactions that are kinetically controlled are dissolution and precipitation of minerals and their adsorptive properties (Camden-Smith et al. 2014; Nordstrom and Campbell, 2014; Grover et al., 2016). Inverse modelling is commonly known as mass balance modelling. If mineralogy of the lithology and composition of water samples along the same flow path are known, inverse modelling can give a set of possible reaction that can transform a combination of initial water sample into a final composition. In the mass balance equations both thermodynamic and kinetic properties are considered (Crawford, 1999; Nordstrom, 2011; Grover et al., 2016).

Reaction path modelling tracks the reaction progress and in each step, the distribution of species and saturation indices is calculated. The equilibrium phase is maintained by the dissolution or precipitation of defined mineral phases. Reaction path models are utilised to determine the forward reaction processes and it occurs through titration, buffering, flushing and through kinetic reactions (Crawford, 1999; Zhu and Anderson, 2002; Nordstrom, 2011).

In this study PHREEQC geochemical modelling was used as predictive tool applied to understand the geochemical processes on the gold tailings footprints; AMD formations; bioavailability and risk assessment of trace elements leaching from the tailings footprints. Predictive modelling was utilised in order to get understanding of geochemical conditions in soils and it was helpful in the investigations of bioavailability and risk assessments of contaminated mine environments.

Geochemical modelling was used as tool for characterising environmental site contaminations and predicting environmental impacts (Zhu and Anderson, 2002). The predictive modelling was applied to gold tailings, acid mine drainage, bioavailability and risk assessment of toxic trace elements from the tailings footprints. Geochemical modelling is a crucial instrument to be utilised in order to get understanding of geochemical conditions in soils and it is helpful when investigating the bioavailability and risk assessments for contaminated environments (Zhu and Anderson, 2002; Parkhurst and Appelo, 2013). Geochemical models can help in the assessment of trace elements which are most bioavailable and harmful, especially the geochemical processes that controls the dissolution of trace elements in the tailing footprints (Zhu and Anderson, 2002).
PHREEQC interactive geochemical code is a computer programme designed to perform a wide variety of low-temperature aqueous geochemical calculations and it includes its capabilities to simulate dispersion, diffusion, stagnant zones in 1D-transport calculations, modelling of kinetic reactions with user-defined rate expressions, modelling formation or dissolution of ideal, multicomponent, binary solid solutions, modelling of fixed-volume gas phases in addition to fixed-pressure gas phases, to allow the number of surface or exchange sites to vary with the dissolution or precipitation of minerals and including isotope mole balances in inverse modeling calculations (Parkhurst and Appelo, 2013).

It can also be used as a speciation program to calculate saturation indices and the distribution of aqueous species. Modelling allows the concentration of an element to be adjusted to obtain equilibrium, specified saturation index or gas partial pressure with a specified phase. Solution compositions can be specified with a variety of concentration units, (Parkhurst and Appelo, 2013). PHREEQC interactive geochemical modelling code was used to determine the precipitation and dissolution reactions that could have occurred to produce a final solution from an initial solution or mixing of initial solutions, Inverse geochemical modelling use mass balance equations to identify the precipitation and dissolution geochemical processes or reactions taking place in the tailings footprints. Inverse modelling has an ability to construct geochemical models that allow transformation of initial solutions into final solutions (Parkhurst and Appelo, 2013; Camden-Smith and Tutu, 2014).

Due to its ability to identify the precipitation and dissolution of geochemical reactions, inverse geochemical modelling was used for correlating laboratory batch and sequential leaching studies. Migration of leachates from the tailings footprints precipitate minerals and leaching contaminants are accumulated in tailings ponds and paddocks. The transport, fate and speciation of toxic trace elements were taken into consideration to assess pollutants especially efflorescent crust formation and adsorption onto iron surfaces. Models were used to assess the mobility and migration of pollutants in the gold tailings footprint (Yibas et al., 2012).

To set up a geochemical model, information about the geological system was taken into consideration and conceptualisation of what chemical reactions are occurring
and what reactions are important to the questions seek to be answered. Geochemical model used is reaction path model as it covers the reaction and equilibrium phases. The choice of geochemical method was determined by samples to collected and what parameters to measure. Parameters that were taken into consideration during simulation reactions are dissolution and adsorption (Zhu and Anderson, 2002; Parkhurst and Appelo, 2013)

The purpose of modelling ranged from establishing a baseline geochemistry or background concentrations, predicting contaminant fate, transport and evaluating remedial alternatives (Camden-Smith et al., 2013). In order to model chemical reactions, geochemical properties of tailings footprints were taken into consideration. Sediment and mineral interactions requires knowledge of both chemical reactions and mineralogical compositions of the solid matrix (Figure 2.7). The purpose of collecting and analysing gold tailings footprints samples was to perform bench top leaching experiments and to use the results for geochemical modelling.

Figure 2.7: Conceptual model showing dispersion of toxic elements from gold tailings footprints
The significant amount of data from laboratory experiments and literature was used to put the benchmarks on this study. The data was used to conduct geochemical modelling simulations involving the oxidation of pyrite minerals from residual material left on the top soil horizon, dissolution of primary and secondary minerals, and mixing of various contaminant plumes resulting from mineral dissolution. The speciation of trace elements in the plumes emanating from the tailings footprints and the implications on the potential risk sites that may be used for office parks, industrial and residential stands.

The geochemical risk assessment was conducted with regard to speciation (chemical species); mineralogy of the gold tailings footprints, minerals such as carbonates, sulphide-bearing minerals, ferrihydrate and silica was noted in equilibrium conditions, influenced by its soluble characteristics in the natural environment (Tutu et al., 2008). Geochemical modelling as a predictive tool was used to determine the physical and chemical processes, the calculation of species distribution on aqueous solution, reaction paths in minerals and fluid mediums, and the solubility of mineral phases in solution.

Characterisation of gold tailings footprints was determined by the geologic characteristics i.e. ore mineralogy, geochemistry and host rock mineralogy because the primary ore and unwanted mine wastes are sources of toxic elements and release contaminants when primary and secondary minerals dissolves from the tailings dumps during chemical weathering (Masondo et al., 2011).

2.10. Environmental regulations

Constitution of the Republic of South Africa on the Bill of Rights (Sections 7-36) stated the rights of individual citizens. Fundamental principles concerning sustainable development and access to information were stated in Sections 24 and 32 that everyone has the right to live in an environment that is not harmful to his or her health or well-being; environment must be protected for the benefit of present and future generations through reasonable legislative and other measures that prevents pollution and ecological degradation; promote conservation; and secure ecologically sustainable development and use of natural resources while promoting justifiable economic and social development; have access to all information held by
the state or any information that is held by another person and is required for the protection or exercise of any of his or her rights.

The National Environmental Management Act (NEMA) 107 of 1998 has clearly stated the avoidance of ecosystems destruction and loss of biodiversity. It is also applicable to mining operations where natural ecosystems is disturbed and there is loss of biodiversity during mine development stages and through decanting of acidic water (AMD) and release of toxic elements from the mine wastes.


Environmental concerns related to mining activities, its negative impacts on the natural ecosystem are discovered after mine operation has closed. Many mine sites has been left un-rehabilitated; old shafts, tailings and waste rocks pose a serious threat to soil and water resources. When AMD decant to the surface it pollutes fresh water and threatens the food security as some trace elements may be accumulated in the soils (Camden-Smith and Tutu, 2014; Nordstrom et al., 2015).

2.11. Summary of the literature review

The output of this study came out with scientific investigations of geochemical processes that may occur after tailings dumps have been physically removed. Remnant tailings material are left on the tailing footprints and the soils that they occupied may or may not be suitable for use as building sites (residential, office or industrial) or for recreational facilities owing to residual pollution.

This was done by conducting a comprehensive geochemical characterisation of mine impacted sites, looking at the characterisation of the tailings dumps and footprints as sources of pollution and assessment of various scenarios of pollutant release or mobility potential from tailings dumps and tailings footprints. The assessment of potential toxicity using simulations based on geochemical modelling was used as predictive modelling tool in this study.
CHAPTER THREE: MATERIALS AND METHODS

This chapter presents the methods, procedures and equipment employed during the course of the study. The work is divided into five stages, namely: Literature review, reconnaissance survey, fieldwork, laboratory work and geochemical modeling.

3.1 Schematic procedures and stages of the project

![Flowchart of stages of work and types of activities that were undertaken]

Figure 3.1: Flowchart of stages of work and types of activities that were undertaken
3.1.1. Reconnaissance survey

Preliminary work was undertaken in the study area before the actual fieldwork was undertaken. The reconnaissance survey enables to precisely gain information about the study area, showing which areas to be sampled and why. Reconnaissance survey also helped to know the accessibility of the study area. The survey was undertaken in the CRG in order to find out the area covered by gold tailings and their impacts on the surrounding environment. The gold tailings footprints were the source target during mapping as it is of interest in this project investigation. In order to acquire data from the selected sites, different types of instruments such as digital camera, GPS, sampling shovel and tape measure were used. The reconnaissance survey also provided first-hand information and feel about the study area.

3.1.2. Fieldwork

This involved a snap survey of the study area (reconnaissance survey) undertaken by collecting preliminary data from the study area. The geology, pedology and vegetation around the study area were noted. The aim of conducting reconnaissance survey was to identify and mark out features of the study area onto a topography map. Fieldwork was undertaken by collecting the soil samples and gold tailings footprints samples along the zones of interest in the CRG. During the fieldwork, co-ordinates for all sampling points were noted and a topographic map was used as a reference.

3.2. The study area

3.2.1. Location of the study area

The study area of this research is located at CRG in the Witwatersrand basin, Gauteng Province in South Africa. CRG is located 24 km east of Johannesburg to 24 km west of the city. CRG forms part of the northern margin of the Witwatersrand Basin and is located at the middle zone, surrounded by ERG in the east direction and WRG in the west direction. The project study area stretches from Germiston to Roodepoort site, as an area of interest for the project investigation (Figure 3.2 and 3.3).
Figure 3.2: Location map of Central Rand Goldfields in the Witwatersrand Basin (McCarthy, 2006)

Figure 3.3: Map showing the lateral variation of the Central Rand Goldfield (Jurgo van Wyk, Department of Water Affairs, 2012)
3.2.2. Geology of the area

The geological sequence of the Witwatersrand basin is dominantly comprises of sediments that have been deposited from granitic greenstone basement. The Witwatersrand super group is about 7.5 km thick geological sequence of siliclastic sedimentary rocks and is divided into lower west rand and upper Central Rand (Viljoen, 2009). The WRG is divided into Lower Hospital hill, Middle Government and upper Jeppestown subgroups, which is dominantly composed of quartzite, shale, sandstone and thin beds of conglomerate and banded iron formation (Frimmel and Minter, 2002; Mason, 2005).

The lower sediments of the Witwatersrand basin were laid down before the compression by the tectonic activity, and prior to the deposition of the gold and uranium-rich conglomerates and sandstones of the CRG (Viljoen, 2009). The CRG stratigraphic layers were the world's largest gold producers and contain an estimated 82,000 tons of the metal at economically viable grades, were deposited between 3,074 and 2,714 Ma (Viljoen, 2009; England et al., 2002b; Tucker et al., 2016).

Stratigraphic deformation in the Witwatersrand basin during a period of compressive tectonism resulted in reworking of the CRG sediments. Concentration of gold and uranium to economic grades and hydrothermal remobilisation and concentration of the mineralisation occurred probably as a result of thermal metamorphism caused by the intrusion of the Bushveld Complex (Viljoen, 2009; Tucker et al., 2016).

Volcanic and sedimentary rocks of the Ventersdorp Super group which overlie the Witwatersrand Super group covered a large part of the Central Kaapvaal Craton and economic gold concentrations were experienced along parts of its basal contact with the Witwatersrand strata. The CRG is divided into Johannesburg and Turffontein subgroups, where Main Reef, South Reef, the Bird Reef, Kimberley Reef and Elsburg Reef were the zones of mineralisation. The highest grade and area of mineralised zone that was extensively mined was the Main Reef and South Reefs (Mphephu, 2001; Viljoen, 2009; Large et al., 2013).

The detail information was acquired in the lower Witwatersrand than in the upper Witwatersrand division and the reason was that the lower Witwatersrand division was exposed better on the surface, and the gold production on the CRG was from

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the upper Witwatersrand division. The greatest amount of gold on the CRG has been derived from reefs in the main reef leader. The main reef lies unconformable on the lower Witwatersrand division, at the base of the upper Witwatersrand division (Viljoen, 2009; Tucker et al., 2016). The main reef is divided into two components, the top part and the bottom part. The top part is divided into south reef, middle reef and main reef and the bottom part covers only the north reef (Law and Peter, 2005).

The south reef was found in a zone of thin reef lying 30m and it is the second one in terms gold production rate compared to the main reef. Main reef was the most target source of interest for gold mining in the CRG and due to the high grade of gold bearing mineralisation, it became the principal ore bearing reef (Viljoen, 2009). The south reef has the greatest lateral extent of all conglomerates and extends from eastwards to westwards direction beyond the boundaries of the CRG. The main reef as was the principal ore bearing commodity has been the most target during mining in the CRG (Drennan and Robb, 2006; Tucker et al., 2016).

The thickness of the main reef ranges from few centimetres to about 3m (Viljoen, 2009; Tucker et al., 2016). The main reef was the lowest compared to other major auriferous conglomerate and its thickness was up to 3.7m thick but was more commonly at thickness of about 1.5m and the diameter of the pebble was 5 cm and pebbles are poorly sorted (Viljoen, 2009; Tucker et al., 2016). The crucial source of gold in the CRG between Roodeport and Boksburg has been the banded pyritic quartzite. These rocks form infillings of erosion channels which has been cut in the shale, quartzite and conglomerate underlying the main reef. The channel material consists mainly of an assemblage of cross bedded quartzite, irregular conglomerates and sandy argillaceous layers (Viljoen, 2009; Fuchs et al., 2016).

3.2.3. Climate

The CRG is characterised by variety temperatures occurring in two distinct seasons in winter from April to August and in summer from September to March. During winter temperatures ranges from 10°C to 13 °C and winter months, especially from June to August are characterised by intermittent cold spells (Dyson and van Heerden, 2002). The summer temperatures varies from 24°C to 27 °C and much of the rainfall is received between the months of October to April and is characterised
by intense thunderstorms occurring mainly in the late afternoon and are accompanied by thunderstorms and lightning. The annual precipitation ranges from 500 mm to about 750 mm and evaporation is about 1600 mm/yr, meaning there is a water deficit in the area (Agricultural Research Council, 2003).

3.2.4. Topography and soil type

The topography of the CRG is characterised by the topographic terrain consisting of hills, ridges and undulating plains and no mountains in the area. The parent material, climate and geological history play a significant role in affecting soil properties on a larger spatio-temporal scale. However, the topography and land use may be the dominant factors of soil properties on the hill slope and small catchment. The topography of the area is generally flat and ranges from 1,460 to 1,760 m above the sea level (Agricultural Research Council, 2003).

The CRG lies in semi-desert latitude zone of almost no weathering and soil formation, due to the drop in precipitation and vegetation cover, and higher temperatures and evaporation rates. This leads to the lack of soil development in the area. This end up giving crisis on the lack of soil development in the area and variety of soil properties reveals the classification of soil, like the thickness, texture, structure and drainage which in turn shows the agricultural potential (Agricultural Research Council, 2003).

The soil is shallow on the high lying areas and contains the following soil types: shallow Mispah in dolomite, shallow Glenrosa in quartzite. In the low lying areas the soil is deep and the soil type is Hutton. The soil properties and their potential are as follows: Hutton is moderately from 600 to 1,200 mm deep, red in colour, structureless to weakly structured, sandy clay loam soils on hard to weathering rock and moderate in agricultural potential (Agricultural Research Council, 2003).

Glenrosa is shallow and ranges from 300 to 600 mm, grey to brown in colour, structureless, gravely loamy sand to sandy loam soils on weathered rock and low in agricultural potential. Mispah is shallow and ranges from 300 to 600 mm, yellow to brown in colour, structureless, sandy loam to sandy clay loam soils on mottled soft plinthite or weathered rock and low in agricultural potential. The Highveld covers the
majority of the plateau and is mostly 1,500 m above sea level. It is characterised by level or gently undulating grasslands (Agricultural Research Council, 2003).

3.2.5. Drainage pattern

The drainage pattern in the area is influenced by the geomorphology and climatic conditions in area. The mine development that was taking place in the central rand group have weakened geological strata, disrupted natural drainage patterns and transformed the natural environment. The semi-arid grasslands were converted to urban forest and mine waste material such as sediments have blocked the natural water ways. The northern part of the area forms the east-west watershed between the Crocodile River catchments in the north and the Klip River catchments in the south (Mphephu, 2001).

The Klipspruit River and the Natalspruit River both drain into the Klip River, which in turn flows into the Vaal River. The river drainage system is comprised of Vaal and orange rivers which rise almost on the eastern escarpment and flows across the country and discharge into the Atlantic Ocean. Limpopo and Olifants river networks are one of the major drainage systems which drain the northern portion of South Africa and discharges into the Indian Ocean (McCarthy, 2011).

The Vaal River supplies more water around the country not only on the Gauteng area but also in the mining sectors such as in Welkom and Sishen. Due to climate change in our country, climate cause the rainfall to decrease as evaporation is greater than rainfall in the area. The regions that experiences high rainfall in the eastern and central Highveld are major source of water for the Vaal river system, and this helps in the supply of water in the mining sectors in the Witwatersrand, as gold deposits lie within the Vaal river catchment (McCarthy, 2011).

3.2.6. Vegetation

The vegetation of the area is characterised by moderately undulating plains, Savannah grassland being the natural vegetation in the area. Mine development in the area has caused the modification of the original surface morphology of the area and the topography is gently undulated in Highveld terrain and no indigenous
vegetation remaining and in areas where there was mine development taking place; remain marked by open grass covered terrain (GPG, 2002).

3.3. Sampling

The soil and gold tailings footprints samples were sampled in the selected points and it has implications for subsequent testing for potential acid formation (PAF). The purpose of testing gold tailings footprints material was to classify tailings material, which in turn facilitates appropriate planning measures for the gold tailings footprints. Gold tailings footprints samples were selected to characterise the potential hazards with chemical aspects, including the mineralogy, pollutant release or mobilisation of trace elements and the acid potential of the soil. It is also crucial to identify and quantify low sulphide materials as well as alkaline materials. Descriptive views and geological cross sections has given a good understanding of the local geology which was used to show the spatial distribution of samples within the major rock units and major forms of mineral alteration (Figure 3.4).

![Figure 3.4: A Google Earth image showing the location of some tailings dumps close to residential and office areas in the Central Rand.](image)

Areas of interest for investigation sites were selected, and the sites for investigation was constructed, based on accessibility, safety and security of the exposed gold
tailings footprints. The study sites are located on the CRG in the Witwatersrand Supergroup. The selected study sites were chosen based on the geochemistry of mine waste or site characterisation, mining history in the basin, geological fieldwork conducted on the site, topography, drainage basin, plant species (vegetation) on the site and not forgetting the detail geological information in the Central Rand Basin (Figure 3.5 and Figure 3.6).

The solid samples collected from the selected sites of interest in this study was plotted to represent sampling points (Figure 3.6). The sampling protocols was consistent throughout for correlation of sampling points and sampling sites, procedures of sampling and sample preservation methods was briefly discussed. Two different tailings dumps were sampled during the course of this study. Sampling of reprocessed tailings dumps and abandoned tailings footprints in Germiston and near Roodeport were the main target for this study. Soil sampling on sites known to be impacted by mine dumps was conducted to determine the lateral variations and speciation of trace elements in abandoned tailings footprints (Figure 3.5 and 3.6).

Tailings material was sampled to determine the mineralogy of the tailings and to characterise the leachates that may be released from residual material left on the tailings after physical removal of the tailings dumps. To correlate the quantitative and qualitative of tailings composition both tailings and footprints materials were taken into consideration in order to characterise the tailings and toxic contaminants that may be released from the tailings footprints after physical removal of tailings dumps. Landscapes covered by tailings dumps were selected as suitable sites for development in the city of Johannesburg (GDARD, 2010).

Auger drilling was used as a method of tailings materials sampling during the fieldwork. This method was chosen in order to determine the chemical forms of tailings horizons. Tailings sampling in different tailings horizons was required for batch leaching to difference between yellow oxidised and grey unoxidised material and their potential to release trace elements to soil and water systems. Sampling on the tailings footprints was also conducted, where the outer later was removed to find out if residual material left on the talings footprints has potential to release trace
elements to soils. The tailings and soil samples were collected in a plastic bag and weight of each sample was 2 kg (Figure 3.5 and 3.6).

Figure 3.5: Google Earth image indicating all sites selected for solid samples collection from both tailings dumps and footprints

Figure 3.6: Tailings dumps (a) and (b) undergoing reprocessing in the Central Rand basin
Tailings footprints were sampled during dry and wet seasons. Therefore the major sampling points were clearly detailed in the Table 3.1 below.

**Table 3.1: Indicates the major sampling points collected in tailings footprints**

<table>
<thead>
<tr>
<th>Sample I.D</th>
<th>Depth</th>
<th>Weathering zone</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCR01</td>
<td>0-5 cm</td>
<td>subsoil</td>
<td>sandy clay</td>
</tr>
<tr>
<td>KCR02</td>
<td>5-10 cm</td>
<td>weathered</td>
<td>clay</td>
</tr>
<tr>
<td>KCR03</td>
<td>10-15 cm</td>
<td>weathered</td>
<td>clay</td>
</tr>
<tr>
<td>KCR04</td>
<td>15-20 cm</td>
<td>weathered</td>
<td>claystone + siltstone</td>
</tr>
<tr>
<td>KCR05</td>
<td>20-25 cm</td>
<td>weathered</td>
<td>sandstones</td>
</tr>
<tr>
<td>KCR06</td>
<td>25-30 cm</td>
<td>not weathered</td>
<td>sandstones + silt</td>
</tr>
</tbody>
</table>

The pH values obtained from the tailings ponds was averaged aligned with the depth to get clarity on the overall pH of tailings dumps and footprints. In the oxidation zone the pH was acidic (3.5-5.6) and in the reduction zone pH was properly 5.6 to 7.3 and this shows that pH in unoxidised zone is more or less neutral. The pH values in different depth was summarised in the Table 3.2 below.

**Table 3.2: pH values conducted on the tailings pond when efflorescent crusts precipitates and dissolves toxic elements to soil and water systems**

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-5 cm</td>
<td>3.5</td>
</tr>
<tr>
<td>5-10 cm</td>
<td>3.7</td>
</tr>
<tr>
<td>10-15 cm</td>
<td>4.2</td>
</tr>
<tr>
<td>15-20 cm</td>
<td>4.8</td>
</tr>
<tr>
<td>20-25 cm</td>
<td>5.6</td>
</tr>
<tr>
<td>25-30 cm</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Reprocessing of tailings dumps was conducted in 2004 and due to failure of implementing proper environmental management plan; reclaimed sites were abandoned without rehabilitation. Remnants material left on the tailings footprints resulted into leaching of trace elements into soil and water systems (Figure 3.6)
Figure 3.7: Indicates (a) efflorescent crusts on the surface near a tailings dump in the Central Rand. (b) different colourations of efflorescent crusts showing the different elements contained in them. The whitish crusts are predominantly gypsum; the yellow ones predominantly contain uranium; and the brownish ones contain mainly iron.

Leachates from both tailings dumps and footprints pose a threat to groundwater quality due to seepage taking place from abandoned tailings footprints. Unoxidised and oxidised tailings materials were sampled on and nearby the tailings dumps and efflorescent crust was sampled from the evaporated ponds (Figure 3.7 and 3.8).

Figure 3.8: Efflorescent crusts on the side of a tailings dump in the Central Rand. On dissolution, these increase the metal and sulphate concentrations in the adjacent ponds.
3.4. Characterisation of tailings

To determine the characteristics and chemical analysis of gold tailings, PXRD was used to determine the mineralogy of tailings and the efflorescent crust using a Bruker D2 phaser desktop diffractometer which was fitted with a cobalt X-ray source and a LynxEye 1-D detector. The PXRD pattern in both oxidised and unoxidised tailings samples clearly detected high concentration of quartz mineral, as quartz is highly resistant to chemical weathering. Quartz and other mineral phases such as Pyrophyllite (2 to 20 %), Chloritoid (3 to 19 %), Mica (4 to 12 %), Chlorite (4 to 11 %), Jarosite (2 to 3 %), Pyrite (1 to 3 %), Copiapite (4 to 11 %), Gypsum (~1 %), and Clay minerals commonly montmorillonite and kaolinite both (~1 %) were detected by PXRD (Zhou, 2004; Nengovhela et al., 2007; Grover et al., 2016).

The sampled tailings and soil samples, dissolved efflorescent crusts solutions and leachates solutions from tailings material left after reclamation on the tailings footprints were analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) for quantification of trace elements concentration. some collected samples in order to verify the quality of data, XRF analysis was utilised to analyse using acid digestion coupled with plasma atomic emission spectroscopy and the results correlated to show that the data collected is valid. The leachates were filtered using a 0.45 µm cellulose nitrate filter paper and geochemical parameters such as pH, electrical conductivity, redox potential and temperature were noted.

3.5. Leaching studies

A geochemical testing was undertaken, and it was generally performed on soil samples and gold tailings footprints samples to determine the current and potential long-term geochemical characteristics of the gold tailings footprints material. The following parameters for laboratory analysis were taken into consideration: Temperature, pH, colour, salinity, turbidity, conductivity and total dissolved solids. For laboratory analysis, leaching of toxic contaminants from gold tailings was undertaken using rainwater, citric acid, oxalic acid and sulphuric acid. Abandoned tailings and footprints in the Central Rand basin pose a serious threat on the environment and human health and this may lead to soil and water contamination (Rosner and van Schalkwyk, 2000; Tutu et al., 2008; Grover et al., 2016).
Pyrite is the common sulphide mineral found in the gold bearing conglomerate deposit. Heavy rain during summer seasons is highly experienced in the Gauteng province and this influences oxidation of pyrite when acid rain reacts with tailings materials. Hydrogen ion activity (pH) changes from alkaline and become acidic in the surrounding environment, the deterioration is influenced by acidic conditions that dissolves trace elements (Camden-Smith and Tutu, 2014; Grover et al., 2016).

Leachates from both tailings and footprints affect the both soil and water quality due to acidity leaching from the tailings that dissolves trace elements and transport them to the surrounding environment. Therefore in order to determine the dispersion of trace elements to the surrounding environments, tailings and soil samples were collected from the tailings dumps and footprints in order find out if residual material left on the footprints may be accumulated to topsoil horizons and up taken by plants.

3.5.1. Sample preparation

Tailings materials used in this study were collected in the abandoned mine tailings in the Central Rand Goldfields, Johannesburg. The tailings and soil samples were oven dried at 60 °C and the moisture content was determined. Mass of samples before and after drying was measured.

The mass differences on the samples were determined by the presence of moisture content before and after drying the samples. To relate the natural leaching system, dilute sulphuric acid, citric acid, oxalic acid and synthetic rainwater was prepared. Stock solution of concentrated sulphuric acid (96%) was diluted with de-ionised water to get a solution of 0.005 mol L\(^{-1}\).

Organic acids were prepared by dissolving an appropriate amount of acids in their powder form with de-ionised water. The solution of 0.05 mol L\(^{-1}\) of oxalic acid was prepared by dissolving 3.1675 g with 500ml of deionised water and 0.1 mol L\(^{-1}\) of citric acid solution was prepared by dissolving 10.507g with 500ml of deionised water. The synthetic rainwater was made by dissolving the compounds listed in Table 3.3 in 1 L of de-ionised water (Camden-Smith et al., 2013; Camden-Smith and Tutu, 2014; Camden-Smith et al., 2015).
Table 3.3: Composition of rainwater

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>5.615</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>1.740</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.014</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.554</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.572</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>1.201</td>
</tr>
</tbody>
</table>

The initial pH of the rainwater solution was 5.38. NaOH was added to adjust the pH to 6.55. Moisture content was determined as follows: Initial mass of tailings was 200.40 g, mass after drying = 172.92 g and hence the moisture content of the tailings is 27.480 g/200.40 g = 13.71% by weight. Dried samples were stored in the plastic bag and it was stored in cupboard to prevent external forces that may damage the samples before analysis. Before leaching, samples were crushed and ground into very fine texture (powder form) until colour of the ground sample is uniform.

3.5.2. Leaching experiments

40 g of the dried tailings was weight and transferred into 1 litre plastic beaker. The beaker was placed on the automated shaker. A solution of synthetic rainwater was added into the plastic beaker. A ratio of 1:10 (1 g soil: 10 mL solution) was used. While shaking 5mL of solutions were withdrawn in time intervals of 10 s, 50 s, 80 s, 110 s, 150 s, 300 s, 600 s, 900 s, 1800 s and 3600 s. The same procedure was followed with the solutions of sulphuric acid, citric acid and oxalic acid.

During the shaking of solution at time intervals 50 to 3600 (s), the leachates were centrifuged at 35 rpm for 10 minutes and solid particles were separated to solution and analysed by ICP-OES. In order to investigate the leaching of trace elements and total content of toxic contaminants in samples collected, samples were leached or digested respectively before analysis. Laboratory techniques used to handle the samples was through leaching, acid digestion, dissolution and precipitation methods in order to assess the chemical characteristics of tailings and footprints materials.
The leaching percentage of trace elements from tailings material may depend on the tailings matrix, pH, leaching solution and time it takes for trace elements to be released from the tailings materials. Acid digestion was utilised to determine the total concentration of elements that may be leached from the both tailings and footprints (Abiye, 2014). Batch and sequential extraction methods were used during leaching experiments. Batch leaching was employed in order to weigh portion of tailings material sample, adding volume of solution that may dissolve elements of interest.

Some elements may be leached from the tailings by rainwater and others by acid solutions. Samples are shaken for a period of time to allow mixture to occur and this is done to make tailings material to contact with the solution in order for the trace elements to be easily extracted from the mixture. Sequential extraction is not that quite different from the batch leaching, instead of getting rid of sample material from the first phase of leaching, through this technique same material are leached again using different chemical solution that may allow elements of interest to be leached out from the mixture, where the first solution failed to extract those elements from the mixture (Grover et al., 2016). After the experimental work, data was used for modelling in order to correlate the experimental data and modelling results.

### 3.6. Geochemical modelling approach

In order to simulate the dissolution and precipitation of minerals kinetics and thermodynamic data was used. Kinetics was based on the kinetic approach and additional parameters and thermodynamic approach was based on log K value already available in the PHREEQC database. Primary minerals are described as reactive once in mineral phases and they can dissolves only and secondary minerals like efflorescent crusts can both dissolve and precipitate. It is important to differentiate reactive and secondary minerals (Zhu and Anderson, 2002; Parkhurst and Appelo, 2013).

Primary or reactive minerals act as a source and redox reactions occur when contact with mineralogy of the unoxidised tailings materials. Secondary minerals releases toxic elements to soil and water systems through percolating and seeping of surface runoff to the top soil horizon. Primary or reactive minerals in the tailings dumps and footprints are pyrite, clay minerals (kaolinite and montmorillonite) and carbonates.
(calcite and dolomite). Secondary mineral that can both dissolve and precipitate are ferric hydroxide, carbonate (calcite) and gibbsite. Ion activity product (IAP) and saturation index (SI) are significant factors in determining the dissolution and precipitation of mineral phases (Zhu and Anderson, 2002). To have better understanding of these two process, dissolution can be regarded as forward reaction and precipitation as reverse reaction. Equilibrium constants can be calculated using the equations below (Zhu and Anderson, 2002):

\[
\text{Mineral} \rightleftharpoons C + D \tag{3.1}
\]

(\rightleftharpoons) indicates both forward reaction (dissolution) and reverse reaction (precipitation). Equilibrium constant is calculated as follows (Zhu and Anderson, 2002):

\[
K = [C]_{eq}[D]_{eq} \tag{3.2}
\]

(K) is the equilibrium constant

Measured activities on the equilibrium constant define the IAP and the saturation index is then defined by the following formulae (Zhu and Anderson, 2002):

\[
\text{SI} = \log \left[ \frac{\text{IAP}}{K} \right] \tag{3.3}
\]

Saturation index values differ depending on the behavior of reactants in the solutions. If saturation index (SI) is equal to zero (SI=0), indicates that the solution is saturated with the mineral. SI < 0 means that the solution is under saturated with the mineral and in this condition mineral dissolves (IAP<K). SI > 0 demonstrates that solution is supersaturated with a mineral and mineral precipitate under this condition (IAP>K). Geochemical model calculations are significant to determine the mineral phases (Zhu and Anderson, 2002; Parkhurst and Appelo, 2013).

Tailings samples used in the experimental data were in equilibrium with the solution (rainwater). Primary and secondary minerals were included in all calculations. Primary and secondary minerals included in the equilibrium phases of the geochemical model are pyrite, chalcopyrite, ferric hydroxide, goethite, gypsum, melanterite and jarosite. These minerals entered the model as equilibrium phased based on log K values, selected from the PHREEQC wateq4f database (Zhu and Anderson, 2002).
3.7. Data analysis and quality control

Data analysis discusses the analytical methods utilised to measure properties and mineralogy of the tailings samples collected from the sites of interest. Physiochemical properties like temperature, pH, redox reactions, moisture content and particle size distribution were determined in the collected samples. PXRD was used to identify the mineral composition of samples collected for analysis. In this study, Bruker D2 phaser desktop diffractometer fitted with a cobalt X-ray source and a LynxEye 1-D detector was used.

For data quality assurance, experimental data was used for geochemical modelling to make predictions on geochemical processes that may lead to releasing of trace elements from the tailings dumps. Geochemical models were constructed to get clarity on the chemical reactions, transport and fate of chemical species released from the tailings dumps and footprints (Grover et al., 2016). Models were constructed based on guidelines adapted from Zhu and Anderson (2002).

In order to simulate the dissolution and precipitation of minerals kinetics and thermodynamic data was used. Kinetics was based on the kinetic approach and additional parameters and thermodynamic approach was based on log K value already available in the PHREEQC database. Primary minerals are described as reactive once in mineral phases and they can dissolve only and secondary minerals like efflorescent crusts can both dissolve and precipitate. It is important to differentiate reactive and secondary minerals. Primary or reactive minerals act as a source and redox reactions occur when contact with mineralogy of the unoxidised tailings materials (Zhu and Anderson, 2002; Parkhurst and Appelo, 2013).

Secondary minerals releases toxic elements to soil and water systems through percolating and seeping of surface runoff to the top soil horizon. Primary or reactive minerals in the tailings dumps and footprints are pyrite, clay minerals (kaolinite and montmorillonite) and carbonates (calcite and dolomite). Secondary mineral that can both dissolve and precipitate are ferric hydroxide, carbonate (calcite) and gibbsite. Therefore in order to understand the geochemical reactions that influence leaching of toxic contaminants from the tailings, geochemical models were constructed. Experimental data obtained during laboratory analysis, it was examined using
A statistical test like student t-test. Speciation-solubility models were utilised in order to interpret the elemental distribution, leaching of trace elements to soil and water system. Reaction and transport models were used to determine the effect of tailings material when in contact with rainwater, redox reactions that influence the release of contaminants from both tailings and footprints. Leachates from the tailings are commonly released when they dissolve in rainwater and acidic solutions. Chemical reactions that take place once the trace elements are leached include dissolution, precipitation, adsorption, desorption, surface complexation, ion exchange and redox reactions.

It is significant to evaluate the transport, effect and fate of chemical species in the natural environment. Dissolution of minerals or oxidation-reduction reactions results in the generation of toxic contaminants from the tailings dumps and tailings footprints after physical removal of tailings to minimise leaching of trace elements from abandoned tailings dumps in the CRG. Lateral extent was determined in which toxic elements are released from the tailings dumps and footprints contaminating soil and water systems with accumulated toxic trace elements. Sampling techniques and procedures were presented and discussed in the sample collection. The analytical techniques have covered the sample preparation, composition, target elements including both analytical method and speciation analysis of targeted elements on the tailings dumps and footprints samples.

The statistical analysis of experimental data was performed for data analysis and the review of data inputs and statistical outputs for data validation was used for verification of whether data utilised was appropriate for data analysis and the statistical data results was reproducible. For comparability with the previous studies, according to Grover et al., (2016) elevated concentration of toxic elements like Cu, Pb, As and Zn were detected on samples collected on the tailings dumps and secondary precipitates and this has happened due to dissolution and precipitation of efflorescent crusts during wet and dry seasons. Tailings footprints data was analysed once all analytical data sets were available for data analysis. calculation of range, mean and cumulative frequency distribution of toxic elements, composition with sufficient data and some calculations for estimation of sampling variability based on replicate sample data was implemented.
CHAPTER FOUR: THE IMPACTS OF TAILINGS ON THE ENVIRONMENT

Toxic pollutants that are strongly bound on the matrix of the mine waste material are commonly not of great concern on the environment as they can be easily mobilised by rainwater in a short term. The once that are mobilised in a long term are of great concern as they pose a threat on the natural ecosystem. The dissolution and precipitation of secondary minerals are the main concern as they have potential to release toxic elements to soil and water systems. Trace elements are concentrated in the mine waste materials and leaching of toxic elements are major concerns on the environment.

Analytical methods like sequential extraction together with geochemical modelling was used to understand the geochemical processes associated with tailings dumps and footprints and chemical reactions that influence the leaching of toxic elements from tailings to the natural ecosystems. This chapter focuses on how released trace elements from abandoned tailings dumps and footprints have impact on the natural ecosystems. Trace elements that dissolve from tailings dumps and footprints in a form of secondary precipitates were also studied.

Tailings footprints may pose an environmental risk due to leachates emanating from remnant material left on the tailings footprints. This may be due to the fact that the mineralogy of the remnant material left on the tailings footprints is similar to that of the tailings dumps. Redox reactions occurs on the tailings materials and due to presence of sulphide mineralisation in the tailings dumps, rainwater reacts with tailings material exposed to atmospheric oxygen. When pH changes from neutral to acidic conditions, trace elements dissolves and released or easily mobilised by surface runoff during heavy rainfall events to soil and water systems.

4.1. Mineralogy of the tailings footprints

Abandoned tailings footprints located in the CRG were studied. Oxidised and unoxidised tailings material together with secondary (efflorescent crust) precipitates from the tailings was sampled. PXRD was used to investigate the mineral composition of the tailings materials. PXRD patterns to determine the percentage of different minerals in the residual materials left on the tailings footprints was detected from the collected samples. The PXRD patterns on the sampled residual materials
indicate that quartz is the dominants mineral in the remnants materials and this due to its resistivity to chemical weathering. Some minor minerals detected were pyrophyllite, mica, chlorite, jarosite and clay minerals. In other studies (Nengovhela et al., 2007; Tutu et al., 2008; Grover et al., 2016), assumptions that the oxidised section of tailings materials contains secondary sulphate minerals like jarosite and gypsum were made and this correlated with the secondary precipitates found in this study.

![X-ray diffractogram showing major and minor minerals in the tailings footprints.](image)

**Figure 4.1:** X-ray diffractogram showing major and minor minerals in the tailings footprints.

Therefore in order to verify whether that leaching data was valid, XRF analysis on other samples were analysed using acid digestion coupled with plasma atomic emission spectroscopy and the results from both instruments proved that the collected data is valid. Same toxic elements were detected by both instruments. The environmental risk assessment on the context of this study has been defined as a predicting technique in environmental pollution of top soil horizon on the gold tailings footprints caused by remnant residual deposits left on the soil, after tailings reclamation, as they pose a risk of adverse effects on the environment influenced by residual material left on the footprints (Rosner and van Schalkwyk, 2000; Grover et al., 2016).

Secondary precipitates from tailings dumps are influenced by evaporation, redox reaction, dilution, mixing and neutralisation. Efflorescent crust was identified as secondary precipitates from tailings dumps and footprints. Secondary precipitate
dissolves trace elements and lead to the mobility of toxic pollutants to soil and water systems. Gypsum and goethite were found as secondary precipitates in the tailings dumps. In this study pyrite, chalcopyrite and minor hematite were the common primary minerals in the tailings dumps and footprints on the selected sites. Due to high evaporation rate occurring on the tailings and footprints, secondary mineral phases like jarosite, goethite, melanterite and gypsum were commonly precipitated from both tailings dumps and footprints. Leachates from the tailings using different leachates solutions were detailed below.

4.2. The trace elements concentration in the solutions analysed with ICP-OES

The results for the trace elemental concentrations in solutions obtained from leaching with 0.1 mol L\(^{-1}\) of citric acid are presented in Figure 4.2. The detailed results are presented in Table A1 in the Appendix.

![Graph: Leaching trace elements with citric acid](image)

**Figure 4.2: Indicate the potential of citric acid to leach trace elements from the tailings materials**

The leachates showed elevated concentrations of Ca, S and Fe (slightly) compared to other elements. This trend correlated with the total concentrations that were observed in the material. Thus, the results point to a high likelihood of leaching of the above elements when the material is in contact with citric exudates, for instance. The
leached phases in this instance are acid-leachable and are likely to be sulphate salts of Ca (e.g. gypsum) and Fe (e.g. jarosite). Low concentrations of As, Pb, Cu and Zn released from tailings footprints may increase in time on top soil horizon. The concentrations were observed to increase with time, which is expected as the time of interaction between the solid and the leaching solution increased. The results for the trace elemental concentrations in solutions obtained from leaching with 0.05 mol L\textsuperscript{-1} of oxalic acid are presented in Figure 4.3. The detailed results are presented in Table A2 in the Appendix.

![Leaching of trace elements with oxalic acid](image)

**Figure 4.3: Indicate the potential of oxalic acid to leach trace elements from the tailings materials**

The leachates showed elevated concentrations of S, Fe, Zn and Ca (slightly) compared to other elements. This trend correlated with the total concentrations that were observed in the material. Thus, the results point to a high likelihood of leaching of the above elements when the material is in contact with oxalic exudates, for instance. The leached phases in this instance are acid-leachable and are likely to be sulphate salts of Ca (e.g. gypsum) and Fe (e.g. jarosite). Low concentrations of As, Pb and Cu released from tailings footprints may increase in time on top soil horizon. The concentrations were observed to increase with time, which is expected as the
time of interaction between the solid and the leaching solution increased. The results for the trace elemental concentrations in solutions obtained from leaching with 0.005 mol L$^{-1}$ of sulphuric acid are presented in Figure 4.4. The detailed results are presented in Table A3 in the Appendix.

**Figure 4.4: Indicate the potential of Sulphuric acid to leach trace elements from the tailings materials**

The leachates showed elevated concentrations of Ca, S, Fe and Zn (slightly) compared to other elements. This trend correlated with the total concentrations that were observed in the material. Thus, the results point to a high likelihood of leaching of the above elements when the material is in contact with dilute sulphuric acid exudates, for instance. The leached phases in this instance are acid-leachable and are likely to be sulphate salts of Ca (e.g. gypsum) and Fe (e.g. melanterite). Low concentrations of As, Pb and Cu released from tailings footprints may increase in time on top soil horizon. The concentrations were observed to increase with time, which is expected as the time of interaction between the solid and the leaching solution increased.
The results for the trace elemental concentrations in solutions obtained from leaching with 1 L of rainwater are presented in Figure 4.5. The detailed results are presented in Table A1 in the Appendix.

**Figure 4.5: Indicate the potential of rainwater to leach trace elements from the tailings materials**

The leachates showed elevated concentrations of K, S, Mg and Ca (slightly) compared to other elements. This trend correlated with the total concentrations that were observed in the material. Thus, the results point to a high likelihood of leaching of the above elements when the material is in contact with rainwater exudates, for instance. The leached phases in this instance are acid-leachable and are likely to be sulphate salts of Ca (e.g. gypsum) and Fe (e.g. goethite). Low concentrations of As, Zn, Pb and Cu released from tailings footprints may increase in time on top soil horizon. The concentrations were observed to increase with time, which is expected as the time of interaction between the solid and the leaching solution increased.

The leaching experiments results clearly indicate that different leachates may react to different leaching solutions on soil system, for instance Ca (sulphuric acid and oxalic acid), Mg (rainwater) and Zn (rainwater and sulphuric acid). In general, most trace elements were leached out with rainwater, except for Fe, S and Al. Fe and S
were leached with sulphuric acid, whereas, Al was leached out with oxalic acid. Secondary precipitates from tailings dumps and remnants materials left on the tailings footprints influence the release and mobilisation of toxic elements to soil and water systems. Quartz and other mineral phases like pyrophyllite, chloritoid, mica, chlorite, jarosite, pyrite, copiapite, gypsum, and clay minerals commonly montmorillonite and kaolinite both were detected by PXRD (Nengovhela et al., 2007; Grover et al., 2016). Therefore primary mineral like pyrite is the common sulphide mineral commonly detected on the mine dumps in the CRG. Secondary minerals are precipitated from the tailings dumps like jarosite (KFe$^{3+}$ 3(OH)$_6$ (SO$_4$)$_2$), goethite (FeOOH), melanterite (FeSO$_4$.7H$_2$O) and gypsum (CaSO$_4$.2H$_2$O). These secondary minerals (efflorescent crusts) are precipitated from tailings dumps and footprints, through dissolution and precipitation processes.

Jarosite has precipitated when sulphide mineral like FeS$_2$ as it is the common sulphide mineral found in the CRG was oxidised when it reacts with rainwater and atmospheric oxygen. Melanterite has precipitated as hydrogen iron sulphate from the decomposition of iron mineral (e.g. FeS$_2$) and goethite has formed when iron mineral (e.g. FeS$_2$) was oxidised during chemical weathering of tailings dumps. Precipitation of goethite was marked by the oxidation states when Fe$^{2+}$ changes to Fe$^{3+}$ and these redox reactions on the surface conditions influence the precipitation of goethite on the tailings dumps and remnants left on the tailings footprints. Gypsum precipitates are main source commonly source of Ca that bonds soil organic matter to clay mineral (e.g kaolinite and montmorillonite) in soils and support stability of soil aggregates.

The main concern on the tailings footprints is that precipitation of secondary minerals from remnants materials left on the footprints releases toxic elements like As and Pb very slowly at low pH and this affect the soil and water quality as these toxic elements are mobilised to the environment. Dissolution of efflorescent crust may results in the leaching of toxic contaminants in acidic conditions, discharged slowly to soils and water systems and evidence was observed by elevated concentrations of toxic elements discovered on the tailings ponds (Camden-Smith and Tutu, 2014).
Acidity is the main challenge in the area owing to the oxidation of remnant FeS$_2$ in the tailings and these results in mobilisation of trace elements and large quantities of secondary sulphate minerals. Trace elements like Cu, Zn, As and Pb are leached very slowly and may end up being accumulated in the soil and water systems and this pose a threat to environment. Therefore, the released and mobilised trace elements in this acid sulphate soils have impacts on this sites selected for development.

Toxic elements accumulated in the soil and water systems may affect the aquatic plants and animals. Impacts of the released and mobilised pollutants may depend on the volume of the acidity leaching and mobility of trace elements present, period of acid flows and regularity of its flows depending on whether acidic flows occurs seasonally or on-going processes. During summer seasons heavy rains and thunderstorms in the Gauteng province are experienced and due to poor stability of tailings dumps, surface runoff transport toxic elements to the surrounding environment (Figure 4.5).

Chemical weathering of tailings materials, redox reactions, trace elements are dissolved and dispersed in the surrounding environment and mostly are accumulated in the soil (Gitari, 2014; Gitari et al., 2013). Plants growing on these contaminated sites may absorb low concentrations of toxic elements daily to their rhizosphere and acidic conditions cause some plants species to deteriorate. The acidic conditions influences the leaching out of toxic elements like Cu, As, Zn and Pb which are threat to the soil and groundwater systems due to inflow and outflow of toxic elements from tailings footprints to groundwater storage (Coetzee et al., 2010; Anna et al., 2014).

Leaching of these toxic contaminants occurs very slowly and elevated concentrations of dissolved trace elements may be accumulated in the soil (Figure 4.5). The dissolution of primary (e.g pyrite) and secondary minerals (goethite and gypsum) occurs during summer seasons. Surface runoff and seepage occurs from the tailings dumps and footprints. Geochemical processes continues to take place on the tailings footprints and the pH changes from slightly acidic (pH 5.6) to acidic (pH 3.9) due to redox reactions occurring on the tailings material and this is influenced by oxidation of sulphide minerals commonly pyrite (Figure 4.5).
The acid sulphate soil was disturbed and oxidised and it generates large quantity of acidity. Jarosite as one of secondary precipitates it gives clear evidence that the tailings footprints are acid sulphate soils and environmental deterioration may indicate the acidity of the top soil horizon which restrains the growth of plants and crops. Efflorescent crusts on soil surfaces are by product of remnants material precipitated from the tailings dumps. Remediation plans must be implemented surrounding tailings footprints and the factors need to be considered are soil types, buffering capacity and pollutants contained within the soils (CSIR, 2009).

4.3. Statistical data evaluation
Statistical analysis was applied as a scientific technique for decisions making needed to be achieved. It has played a significant role in answering the objectives that this research seeks to address. It was used to analyse the results from the leaching experiments, and this was done by using student t-test (two sample t-tests). It was done to determine if the mean of the two data sets are statistically different and the main crucial factors are mean and the variance in a complex equation. Statistical t-test formula used for analysis is as follows (Smith et al., 2009):

\[ t = \frac{(\bar{x} - m)}{s_x} \]  

(4.1)

Where
- \( \bar{x} \): is the mean of the sample
- \( m \): is the population mean
- \( s_x \): is the standard error of the sample

To determine the statistical analysis, the two-sample t-test was conducted to allow statistically determination of differences in the levels of trace elements distributions, means and variances of datasets in Pb, As, Cu and Zn. After running a t-test in Microsoft excel, the probability (P-value) calculated from the datasets has given go ahead whether there is a difference between the levels of trace elements or there is no difference in their levels from both site.

The critical value has played a crucial role to determine the difference in distributions of two datasets. Critical value is 0.05 and if probability value is less than the critical value, it indicates that there is difference in levels of distributions. The probability (P-value)
value) of the dataset if it is greater than the critical value, indicate that there is no difference in the level of distributions.

Description of statistical analysis done using datasets was presented in the tables below, (Table 4.1, Table 4.2, Table 4.3, Table 4.4 and Table 4.5).

The probability values (P-value) calculated from datasets were clearly summarised in the following tables. The statistical analysis of Ca clearly gives confirmation that secondary precipitate like gypsum precipitated from the tailings dumps and footprints materials (Table 4.1). According to study conducted by Grover et al., 2016 secondary minerals like goethite, gypsum, melanterite and jarosite were also detected as precipitates.

Table 4.1: Probability (“P-value”) of calcium datasets after statistical analysis

<table>
<thead>
<tr>
<th>Variable</th>
<th>Mean</th>
<th>Std Dev.</th>
<th>Std Err</th>
<th>Lower 95% CL</th>
<th>Upper 95% CL</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>156,750</td>
<td>76,013</td>
<td>26,875</td>
<td>93,202</td>
<td>220,298</td>
<td>8</td>
</tr>
<tr>
<td>Calcium</td>
<td>49,750</td>
<td>5,994</td>
<td>2,119</td>
<td>44,739</td>
<td>54,761</td>
<td>8</td>
</tr>
</tbody>
</table>

2-tailed t-Test

<table>
<thead>
<tr>
<th>Ho. Diff</th>
<th>Mean Diff.</th>
<th>SE Diff.</th>
<th>T</th>
<th>DF</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,000</td>
<td>107,000</td>
<td>24,860</td>
<td>4,304</td>
<td>7,000</td>
<td>0,004</td>
</tr>
</tbody>
</table>

Statistical analysis of As indicates that that the probability value is greater than the critical value and this concludes that As leaches very slowly from the tailings dumps due to influence of geochemical reactions and after long period of time, As may be highly accumulated in the soils (Table 4.2).

Acidity is the main challenge in the area owing to the oxidation of remnant FeS₂ in the tailings and these results in mobilisation of trace elements and large quantities of secondary sulphate minerals (Grover et al., 2016)
Table 4.2: Probability ("P-value") of As datasets after statistical analysis

<table>
<thead>
<tr>
<th>t-Test Result for Paired Datasets:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set 1 Range = As (A)</td>
</tr>
<tr>
<td>Set 2 Range = As (B)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Descriptive Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>As</td>
</tr>
<tr>
<td>As</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2-tailed t-Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho. Diff</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>0.000</td>
</tr>
</tbody>
</table>

Statistical analysis shows that the probability value is greater than the critical value, and brings conclusion that Cu is released slowly from the tailings dumps and footprints and after some quite time it may be highly accumulated in the soils. After conducting a statistical analysis of Cu the probability value was 0.065 which is above the critical value of 0.05 (Table 4.3).

The probability value of 0.065 indicates clear interpretation that it won’t be any difference in distribution as it supports the null hypothesis. Cu leach very slowly from both tailings dumps and footprints and after many years high concentration Cu may be accumulated in the surrounding environment and this pose a threat to environment and human health (Table 4.3).

For any project developments that may be implemented on the reclaimed mine site, environmental risk assessment, environmental monitoring and modelling should be conducted to investigate the dispersion of trace elements and their chemical form (Park et al., 2013).
Table 4.3: Probability (“P-value”) of Cu datasets after statistical analysis

<table>
<thead>
<tr>
<th>Descriptive Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Variable</strong></td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>Cu</td>
</tr>
</tbody>
</table>

2-tailed t-Test

<table>
<thead>
<tr>
<th>Ho. Diff</th>
<th>Mean Diff.</th>
<th>SE Diff.</th>
<th>T</th>
<th>DF</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,000</td>
<td>839,222</td>
<td>392,589</td>
<td>2,138</td>
<td>8,000</td>
<td>0,065</td>
</tr>
</tbody>
</table>

Statistical analysis of Pb indicates that the probability value is greater than the critical value. Pb is released very slowly in quite small concentration, after each and every year its concentration may increase and state of chemical form may be harmful to the natural ecosystems and human health (Table 4.4).

Table 4.4: Probability (“P-value”) of lead datasets after statistical analysis

<table>
<thead>
<tr>
<th>Descriptive Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Variable</strong></td>
</tr>
<tr>
<td>Lead</td>
</tr>
<tr>
<td>Lead</td>
</tr>
</tbody>
</table>

2-tailed t-Test

<table>
<thead>
<tr>
<th>Ho. Diff</th>
<th>Mean Diff.</th>
<th>SE Diff.</th>
<th>T</th>
<th>DF</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,000</td>
<td>937,625</td>
<td>429,740</td>
<td>2,182</td>
<td>7,000</td>
<td>0,065</td>
</tr>
</tbody>
</table>
Statistical analysis of Zn shows that the probability value is greater than the critical value and this clearly indicates that distribution levels of Zn elements it won't be quite different. Elevated concentration of Zn was released from both tailings dumps and footprints using leaching solutions like citric acid and oxalic acid and its concentrations may annually increases in the soil and water systems (Table 4.5).

Table 4.5: Probability (“P-value”) of Zn datasets after statistical analysis

<table>
<thead>
<tr>
<th>Variable</th>
<th>Mean</th>
<th>Std Dev.</th>
<th>Std Err</th>
<th>Lower95% CL</th>
<th>Upper95% CL</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>843,333</td>
<td>1178,060</td>
<td>392,687</td>
<td>-62,204</td>
<td>1748,870</td>
<td>9</td>
</tr>
<tr>
<td>Zn</td>
<td>30,889</td>
<td>51,229</td>
<td>17,076</td>
<td>-8,489</td>
<td>70,267</td>
<td>9</td>
</tr>
</tbody>
</table>

2-tailed t-Test

<table>
<thead>
<tr>
<th>Ho. Diff</th>
<th>Mean Diff.</th>
<th>SE Diff.</th>
<th>T</th>
<th>DF</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,000</td>
<td>812,444</td>
<td>376,189</td>
<td>2,160</td>
<td>8,000</td>
<td>0,063</td>
</tr>
</tbody>
</table>

Statistical t-test has played a crucial role in the determination of levels of distribution of toxic elements using the datasets to find out its probability value. Statistical analysis was done to find detail information about the probability of difference in distribution of toxic elements comparing the measured value. Leaching experiments was conducted to examine the extent to which solution chemistry of tailings footprints affect mineral dissolution (Grover et al., 2016).

The dissolution rates of measured average value from each set helped in assumption conditions representing dissolution rate. Sample A and B to all t-test were done to get findings about the differences of the two experimental conditions. The t-test was applied as technique to examine whether there is difference or not in the observed samples average in sample A and B. Statistical t-test and its corresponding probability (P-value) was taken into consideration for data analysis to be concluded (Reyment, 1999).
The P-value represents the probability of the results presented. Null hypothesis was applied when probability value is more than the critical value of 0.05 as it indicates that it won't be any difference in distributions and if the probability value is less the critical value of 0.05, it states that there may be a difference in distributions. After conducting a statistical analysis of As in Table 4.10, the probability value was 0.065 which is above the critical value of 0.05.

The probability value of 0.065 indicates clear interpretation that it won't be any difference in distribution as it supports the null hypothesis. As would be leached very slowly from tailings dumps and footprints and this pose a threat to soil and water systems. In acidic conditions As may dissolve and released to the soils and this pose a threat to food security and human health as elevated concentrations of trace elements may be accumulated in the soil systems (Equeenuddin et al., 2013).

The descriptive statististic and input range of As was indicated in figure 4.6 and presented in linear descriptive in Figure 4.7. The statistical analysis of toxic elements leaching from tailings dumps and footprints has correlated with the leaching experiments data and shows that trace elements may leach very slowly from the materials and elevated concentrations of leachates may be continuously released and mobilised to the natural environment (Ekemen Keskin et al., 2013).

Leaching results were correlated with the study conducted by Grover et al. (2016, unpublished), using sequential extraction procedure in oxidised tailings, the outcome showed that leachates released from the footprints is similar to the once found on the previous studies. Tailings footprints contained elevated concentration Al, Cu, Ca, Mg, Pb, Mn, As and Zn, which were mostly present in a readily soluble phases. These leachates were found to contain elevated sulphate concentrations and give clarity that dissolution of secondary precipitates releases toxic elements from secondary sulphate salts like gypsum and jarosite.
Statistics and input range of arsenic

Figure 4.6: Descriptive statististic and input range of As

Figure 4.7: Indicates linear descriptive of statistical analysis of As in both samples A and B

After conducting a statistical analysis of Pb in table 4.8, the probability value was 0.065 which is above the critical value of 0.05. The probability value of 0.065 indicates clear interpretation that there will be no difference in distribution as it support the null hypothesis.
The descriptive statistic and input range of lead was indicated in figure 4.8 and presented in linear descriptive in Figure 4.9.

Figure 4.8: Descriptive statistic and input range of Pb

Figure 4.9: Indicates linear descriptive of statistical analysis of Pb in both samples A and B

After conducting a statistical analysis Cu in table 4.7, the probability value was 0.065 which is above the critical value of 0.05. The probability value of 0.065 indicates
clear interpretation that it won’t be any difference in distribution as it support the null hypothesis. The descriptive statistic and input range of Cu was indicated in Figure 4.10 and presented in linear descriptive in Figure 4.11.

**Figure 4.10: Descriptive statistic and input range of Cu**

![Statistics and input range of copper](image)

**Figure 4.11: Indicates linear descriptive of statistical analysis of Cu in both samples A and B**

![Copper Concentration](image)
After conducting a statistical analysis of Zn in table 4.9, the probability value was 0.063 which is above the critical value of 0.05. The probability value of 0.063 indicates clear interpretation that it won’t be any difference in distribution as it supports the null hypothesis. The descriptive statistic and input range of Zn was indicated in Figure 4.12 and presented in linear descriptive in Figure 4.13.

Figure 4.12: Descriptive statistic and input range of Zn

Figure 4.13: linear descriptive of statistical analysis of Zn in samples A and B
Trace elements like Cu, Zn, Pb and As may be leached very slowly from both tailings dumps and footprints. Tailings footprints may be the source of secondary pollution in both soil and water systems. Therefore physical removal of tailings dumps to reclaim sites for development purposes is not enough, remnants material left on the tailings footprints when oxidised may be the secondary source of pollution. Leachates may be released very slowly to soil and water systems and this can deteriorate the environment due to mobility of trace elements in the natural ecosystems. Leaching elevated concentration of toxic elements has potential impacts on the environment.

In this study in order to determine the impacts of tailings dumps and footprints as primary and secondary sources of pollutants in soil and water systems, the analysis of variance (ANOVA) was conducted to assess the interaction between toxic elements and independent variables. Contamination factor and degree of contamination techniques proposed by Abrahim and Parker (2008) was applied in this study and this was based on the calculations of each pollutant, contamination factor (CF) was obtained by dividing the mean concentration of each trace element in soil by background value estimated from the collected samples on the reclaimed sites on abandoned mine sites.

Statistical analysis and data validation was done to determine the lateral extent of selected toxic elements in soil from tailings dumps and remnant material left on the footprints and investigating contaminant levels in soils in order to apply environmental monitoring and modelling techniques after tailings reclamation. The potential ecological risk factor and risk index (PERI) in order to determine the risk factors. PERI quantitatively defines the potential ecological risk of toxic pollutants in the tailings footprints samples (Power and McCarty, 2001; Abrahim and Parker 2008).

The ecological risk factors and risk index was defined in the equation 4.2 (Power and McCarty, 2001; Korobitsin and Chukanov, 2001):

\[
\text{PERI}_i = \sum_{i=1}^{7} \text{EF}_i = \sum_{i=1}^{7} \text{CF}_i \times \text{TF}
\]  
(4.2)
Where \( \text{PERI}_i \): represent potential ecological risk index for each sample

\( \text{EF}_i \): represent the monomial potential ecological risk factor

\( \text{CF}_i \): is the single contamination factor

\( \text{TF} \): is the trace elements toxic response factor of each element

Soil toxic response factors were computed for selected trace elements like Cu, Zn, As and Pb according to the toxicity factor requirements.

TF values obtained were: \( \text{As} = 4.5 < \text{Cu} = 4.8 < \text{Pb} = 5.5 < \text{Zn} = 44 \)

The risk factor estimated for each trace element potential pollution factor and potential ecological risk, has given clarity that both tailings dumps and footprints samples depth that As, Cu, Pb and Zn have low potential ecological risks, low risk in subsoil and only the topsoil are at very high risks as elevated concentration of toxic elements are accumulated in soil organic matter.

The PERI spatial distribution trace elements on the tailings footprints were classified with high ecological risks and it was summarised in the table below:

**Table 4.9: Median, minimum and maximum concentrations values of samples collected from the tailings footprints**

<table>
<thead>
<tr>
<th>Units</th>
<th>pH</th>
<th>Soil organic matter</th>
<th>As</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Top soil</strong></td>
<td>Median</td>
<td>4</td>
<td>13.8</td>
<td>4</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Min-Max</td>
<td>3.5-5.6</td>
<td>5.4-37.0</td>
<td>3-5</td>
<td>4-5</td>
<td>3-11</td>
</tr>
</tbody>
</table>

When comparing the ecological risk data obtained with world health organisation data, WHO data for selected elements was standardised as follows: Pb (0.01 mg/l), Cu (2.0 mg/l), As (0.01 mg/l and Zn (3.0 mg/l). Trace elements are released and mobilised slowly from the tailings footprints as follows: As (0.0045 mg/l), Pb (0.0055 mg/l), Cu (0.0048 mg/l) and Zn (0.044 mg/l). Elevated concentration of toxic elements leaching from tailings dumps and footprints have impacts on the environment and therefore tailings footprints may be the secondary source of pollutants. Some plants, vegetables and crops may extract these pollutants in soils.
CHAPTER FIVE: GEOCHEMICAL MODELLING SIMULATION REACTIONS FOR PREDICTING HUMAN IMPACTS OF THE TAILINGS

Geochemical modelling simulations involving the oxidation of pyrite mineral from residual material (mine wastes) left on the top soil horizon, dissolution of primary and secondary minerals, and mixing of various contaminant plumes resulting from mineral dissolution was done by reacting rainwater with minerals (primary and secondary minerals) as part of environmental risk assessment to find out the rate of leaching contaminants from the tailing footprints.

Risk assessment was conducted in order to find out what are the different health problems at different levels of exposure, how much of the pollutants people can take in during a time period and what is the extra risk of health problems in the exposed residents close to tailings dumps. To find out pathways of toxic contaminants to human body, synthetic solutions such as saliva juice, gastric juice and duodenum juice was used to predict how toxic elements are absorbed in gastrointestinal tract to blood system. The geochemical simulation reaction using synthetic saliva juice, gastric juice and duodenum juice was presented in graph form in order to find out the different reactivity of synthetic solution and duration of exposure assessment.

5.1. Reaction of rainwater with primary and secondary minerals

Rainwater reacted with primary and secondary minerals in the tailings footprints and the pH of rainwater was slightly acidic (pH 5.6) before any contact with the tailings footprints (Table 5.1 and Figure 4.9). After rainwater infiltrated into the pore spaces on the tailings footprints, chemical reactions started to take place as the reaction of rainwater and tailings footprints originated. The dissolution of primary and precipitated minerals occurred influenced by saturation process caused by heavy rain (Table 5.1).

Acidic pH in the tailings footprints has effect on the soil fertility on top soil horizon. Some plants do not grow well, soil organisms are reduced and trace elements like Mn and Al may dissolve and become toxic to plants species. Geochemical processes that are allowed to continue without any measures to control or monitor the situations on abandoned tailings dumps and footprints leach toxic elements that could affect soil and water systems (Cravotta et al., 2014).
Elevated concentrations of trace elements accumulated in the soils pose a threat to the natural environment and human health on the sites nearby the abandoned tailings dumps and footprints.

Table 5.1: Rainwater composition before reacting with mineral assemblages

<table>
<thead>
<tr>
<th>Elements</th>
<th>Molality</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>2.831e-03</td>
<td>2.831e-03</td>
</tr>
<tr>
<td>Ca</td>
<td>1.846e-04</td>
<td>1.846e-04</td>
</tr>
<tr>
<td>Cl</td>
<td>3.103e-04</td>
<td>3.103e-04</td>
</tr>
<tr>
<td>H (0)</td>
<td>2.282e-05</td>
<td>2.282e-05</td>
</tr>
<tr>
<td>K</td>
<td>7.672e-05</td>
<td>7.672e-05</td>
</tr>
<tr>
<td>Mg</td>
<td>2.879e-05</td>
<td>2.879e-05</td>
</tr>
<tr>
<td>N (-3)</td>
<td>1.356e-03</td>
<td>1.356e-03</td>
</tr>
<tr>
<td>N (5)</td>
<td>6.711e-05</td>
<td>6.711e-05</td>
</tr>
<tr>
<td>Na</td>
<td>1.566e-04</td>
<td>1.566e-04</td>
</tr>
<tr>
<td>S (6)</td>
<td>3.227e-05</td>
<td>3.227e-05</td>
</tr>
</tbody>
</table>

The tailings footprints contains a variety of sulphate-based salts and the most common salts found in the Central Rand goldfield are gypsum (CaSO₄.2H₂O), jarosite (KFe(SO₄)₂(OH)₆), melanterite (FeSO₄.7H₂O), copiapite (Fe,Mg) Fe₄(SO₄)₆(OH)₂·20H₂O), goslarite (ZnSO₄.7H₂O), and epsomite (MgSO₄.7H₂O) (Naicker et al., 2003; Tutu et al., 2008).

Rainwater solution was reacted with mineral assemblages occurring on the tailings dumps, next to tailings ponds and on tailings footprints. The tailings footprints sample was 200 g in total. The tailings footprints sample was composed of Chalcopyrite (30 g), Ferric hydroxide (20 g), Goethite (14 g), Gypsum (16 g), Jarosite (10 g), Melanterite (10 g), and Pyrite (100 g), (Figure 4.9 and Table 5.1).

Gold mining in the Central Rand has resulted in large quantities of tailing dumps, which have been deposited in a form of impoundments. Due to lack of proper environmental management plan in the area, leaching of toxic elements from the oxidised tailings has affected soil and water quality. The reprocessing of tailings
dumps in the basin as way of removing tailings impoundment that cause soil and water pollution in the area, some tailings dumps have been partially or completely reclaimed and through this process some residual material are left over the tailings footprints. Gold tailings footprints have been contaminated by AMD due to its lower pH. AMD is the source of all toxic elements leaching from both tailings and footprints.

The tailings footprints are threat to the natural environment and human health to the sites proposed for developments. Residual materials are oxidised and secondary minerals precipitate close to the tailings ponds. Mineral transformations during redox reactions have an influence in the release of toxic elements from both tailings dumps and footprints. Toxicity of leached trace elements depends on its chemical forms. Due to the precipitation of Fe(OH)$_3$, acidic pH makes the trace elements to be easily dissolved and released to the natural ecosystems and it affects biodiversity.

![Mineral phases](image)

**Figure 5.1**: Percentage of mineral phases on the tailings footprints

Mineralogic characterisation of gold tailings and footprints provided detail description about primary sources of leachates, identity of potential toxic elements and mobility of elements in the soil under acidic conditions as it influences mineral dissolution. The mineral phase assemblages (Figure 5.1) was used during simulation reactions, where it was reacted with rainwater solution and after chemical reactions the below
results was found (Table 5.2 and Table 5.3). Mineralogy of tailings footprints characterises the sources of toxic elements and acidity of soil on selected sites of this study. Abandoned tailings footprints in the Central Rand basin on both oxidised and unoxidised tailings material together with secondary precipitates was characterised in this study using PXRD. Mineralogical analysis by PXRD in this study shows that quartz is the dominant mineral and some minor minerals like pyrite, pyrophyllite, chlorite, jarosite and mica was detected by the instrument.

Textural analysis of tailings material showed that gold tailings dumps very fine to medium (>70% of the sample). Tailings material are characterised by sandy and clay texture. Clay minerals like kaolinite and montmorillonite were also detected from other studies (Tutu et al., 2003; Tutu et al., 2008; Grover et al., 2016). Mineral phases like jarosite, goethite, gypsum, and ferric hydroxide were also detected during geochemical modelling.

Tailings footprints as secondary source of pollution after physical removal of tailings was also characterised where leaching solutions such dilute sulphuric acid, citric acid, oxalic acid and synthetic rainwater were used to determine the potential leachability of toxic elements from tailings dumps and footprints. Geochemical analysis shows that trace elements are released very slowly from tailings dumps and footprints in very small quantity during rainy seasons (Figure 5.5 and Figure 5.6).

High evaporation rate results in the precipitation of secondary minerals like efflorescent crust. This accumulated salt on soil surface creates unfavourable environment for growth of plant diversity and it also affect soil fertility as top soil horizon rich in organic matter get washed away by surface runoff. When rainwater reacts with tailings and atmospheric oxygen redox reactions occurs and the pH of the natural environment changes and become acidic (Figure 4.15).

pH value of the contaminated tailings footprints ranges from 3.5 to 3.9 and it is acidic to strongly acidic. Topsoil horizon was mostly contaminated with elevated concentration of toxic elements like Pb, As, Cu and Zn. Due to high acidity in the topsoil, mobility of toxic elements from the tailings footprints resulted in permanent soil degradation. This creates a crisis in the land to be utilized for development purposes (Table 4.4).
Gauteng Department of Agriculture and Rural Development (GDARD) in the year 2009 conducted a conceptual study on reclamation of tailings dumps sites for development purposes. Mineralogy of tailings dumps and footprints has played a significant role in order to detect the primary minerals and composition of mine wastes (tailings and waste rocks). Tailings dumps are sources of trace elements released to soil and water systems and this occurs when trace elements under acidic conditions are dissolves during chemical weathering in rainy seasons.

Chemical reactions that occur during weathering of tailings dumps produce acidity and secondary minerals precipitates from the tailings dumps. Trace elements are dissolved and released to soil and water systems and commonly toxic pollutants are accumulated in soils and on the tailings ponds. Surface run-off, infiltration, percolation of dissolved solutions from tailings dumps and footprints controls the water chemistry of the drainage.

**Table 5.2: Mineral phase assemblages**

<table>
<thead>
<tr>
<th>Phase</th>
<th>SI</th>
<th>log IAP</th>
<th>log K (T, P)</th>
<th>Initial</th>
<th>Final</th>
<th>Delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>0.00</td>
<td>-35.27</td>
<td>-35.27</td>
<td>1.630e-01</td>
<td>1.63e-01</td>
<td>-4.34e-13</td>
</tr>
<tr>
<td>Fe (OH)_3 (a)</td>
<td>-5.90</td>
<td>-1.01</td>
<td>4.89</td>
<td>1.87e-01</td>
<td>0</td>
<td>-1.87e-01</td>
</tr>
<tr>
<td>Goethite</td>
<td>-0.00</td>
<td>-1.00</td>
<td>-1.00</td>
<td>1.57e-01</td>
<td>6.43e-02</td>
<td>-9.28e-02</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.00</td>
<td>-4.58</td>
<td>-4.58</td>
<td>9.30e-02</td>
<td>8.67e-02</td>
<td>-6.33e-03</td>
</tr>
<tr>
<td>Jarosite-K</td>
<td>-10.50-19.71</td>
<td>-9.21</td>
<td>1.90e-02</td>
<td>0</td>
<td>-1.90e-02</td>
<td></td>
</tr>
<tr>
<td>Melanterite</td>
<td>-0.41</td>
<td>-2.62</td>
<td>-2.21</td>
<td>3.60e-02</td>
<td>0</td>
<td>-3.60e-02</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.00</td>
<td>-18.48</td>
<td>-18.48</td>
<td>8.33e-01</td>
<td>5.23e-01</td>
<td>-3.10e-01</td>
</tr>
</tbody>
</table>

Due to reprocessing of tailings dumps in the CRG, large quantities of tailings are removed and remnants of material left on the top soil pose a threat on the soil and water quality. Vegetation cover such as small trees and grass growing on the contaminated soil may uptake toxic elements on the reclaimed sites, as toxic elements can percolates into the soil horizons. It may occur when vegetation absorbs toxic elements from the tailings footprints. The acidic conditions on the natural environment is due to exposure of tailings dumps to atmospheric oxygen.
during precipitation and chemical reactions taking place results in low pH and high loads of toxic elements such as Pb, Cu, Zn, As and SO$_4^{2-}$ (McCarthy, 2011).

Table 5.3: Solution composition after rainwater reacted with mineral phases

<table>
<thead>
<tr>
<th>Elements</th>
<th>Molality</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.756e-02</td>
<td>1.786e-02</td>
</tr>
<tr>
<td>Ca</td>
<td>6.434e-03</td>
<td>6.509e-03</td>
</tr>
<tr>
<td>Cl</td>
<td>3.067e-04</td>
<td>3.103e-04</td>
</tr>
<tr>
<td>Cu</td>
<td>4.291e-13</td>
<td>4.342e-13</td>
</tr>
<tr>
<td>Fe</td>
<td>6.744e-01</td>
<td>6.823e-01</td>
</tr>
<tr>
<td>K</td>
<td>1.885e-02</td>
<td>1.908e-02</td>
</tr>
<tr>
<td>Mg</td>
<td>2.846e-05</td>
<td>2.879e-05</td>
</tr>
<tr>
<td>Na</td>
<td>1.548e-04</td>
<td>1.566e-04</td>
</tr>
<tr>
<td>S</td>
<td>6.913e-01</td>
<td>6.995e-01</td>
</tr>
</tbody>
</table>

The low pH value of the soil influenced by leaching of toxic contaminants can lead to migration of precipitated toxic elements from efflorescent crust and increases the bioavailability and toxicity in the soil next to the tailings dumps where tailings footprints are left after reclamation. Heavy rainfall in the CRG during summer seasons, the oxygenated water accumulates in tailings ponds and paddocks at the top of the tailings dumps lead to runoff, infiltration and percolation of toxic elements in the soil, as it may be mobilised to groundwater system (Tutu et al., 2008, Camden-Smith and Tutu, 2014).

The chemical weathering on the tailings footprints and paddocks in the abandoned gold tailings dumps influences the mobility of toxic elements on the natural environment. Chemical weathering of sulphide minerals such as pyrite in the tailings results in acid mine drainage and the rate of acidity migration in the residual material depends on the solubility of minerals in the tailings dump, as it plays a huge role on how fast the toxic metals can leach out of the residual material left on the tailing footprints (Tutu et al., 2011; Grover et al., 2016).
The continuity of runoff on the tailing footprints and paddocks lead to geochemical reactions to occur as rainwater will react with residual material left on the tailing footprints. During chemical weathering the toxic contaminants from the tailing footprints migrate and percolate into groundwater formations (Yibas, 2012; Nordstrom 2011). The precipitation of Fe(OH)$_3$ influences high acidity resulting in the soil. pH of the soil is acidic and this makes the mobility, bioavailability and bioaccumulation of toxic elements easily on the soil (tailings footprints) in the selected sites (Tutu et al., 2008; Tutu et al., 2011).

During winter in the CRG, there is less rain compared to summer season, and this shows that precipitation of secondary minerals occur mostly during winter as it is a dry season in basin. The dissolution of primary and secondary minerals occurs during summer as there is more thunderstorms and heavy rain. When chemical reactions continues to take place on the tailings footprints, the pH has changed from slightly acidic (pH 5.6) to acidic (pH 3.9), the change in pH value is influenced by oxidation of sulphide minerals (Table 5.3).

FeS$_2$ reacted with oxygenated rainwater in the tailings footprints, leaching of Fe$^{2+}$ and SO$_4^{2-}$ occurred (Table 5.4). After Fe$^{2+}$ was leached out, it reacted with oxygen and this resulted in the formation of Fe$^{3+}$. Due to the presence of moisture Fe$^{3+}$ will react with water to form Fe(OH)$_3$, (Mphephu, 2001). The acidic conditions influenced the leaching out of toxic elements like Cu, As, Zn and Pb which are threat to the soil quality and groundwater quality due to inflow and outflow of toxic elements from tailings footprints to groundwater storage (aquifer), (Rosner and van Schalkwyk, 2000, Mphephu, 2004; Tutu et al., 2008, Grover et al., 2016).

The pH of soil from the tailings footprints and water accumulated in the tailings ponds is extremely acidic due to leachates entering the mediums. The acidic conditions will affect the ecosystem and human health to residents residing next to the tailings dumps, (Rosner, 1998; Bakatula et al., 2012).

Children are particularly the once at high risk trace elements poisoning, are more likely to eat soil adhered on their hands and also in the toys. They have higher absorption of toxic trace elements from digestion system and higher haemoglobin sensitivity of toxic elements compared to adults digestive systems. Therefore after...
physical removal of tailings, remnants materials left on the tailings also pose potential health risks to humans and animals exposed to contaminated sites.

**Table 5.4: Distribution of species when rainwater reacted with minerals**

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (4)</td>
<td>1.765e-02</td>
</tr>
<tr>
<td>Ca</td>
<td>6.434e-03</td>
</tr>
<tr>
<td>Cl</td>
<td>3.067e-04</td>
</tr>
<tr>
<td>Cu (1)</td>
<td>3.482e-13</td>
</tr>
<tr>
<td>Cu (2)</td>
<td>8.093e-14</td>
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<tr>
<td>Fe (2)</td>
<td>6.744e-01</td>
</tr>
<tr>
<td>Fe (3)</td>
<td>2.421e-10</td>
</tr>
<tr>
<td>Mg</td>
<td>2.846e-05</td>
</tr>
<tr>
<td>N (-3)</td>
<td>3.730e-06</td>
</tr>
<tr>
<td>Na</td>
<td>1.548e-04</td>
</tr>
<tr>
<td>S (-2)</td>
<td>8.143e-12</td>
</tr>
<tr>
<td>S (6)</td>
<td>6.913e-01</td>
</tr>
</tbody>
</table>

The acidity leaching out of tailings footprints will impact the soil quality due to leaching of toxic elements from the gold tailings footprints. The grass and trees growing on the tailings footprints may absorb toxic elements and this pose a risk to cattle’s grazing on the tailings dumps (Figure 5.2). The acidic condition is influenced by remnant materials left on the tailings footprints after gold tailing dump removal and this result in soil contamination in the area (Rosner and van Schalkwyk, 2000; Oelofse *et al*., 2007; Camden-Smith and Tutu, 2014).

Toxic elements were introduced into soils from the tailings dumps and footprints as they are source of soil contamination. After physical removal of tailings dumps as a way of reducing threat on soil and ecosystem, the residual material left on the tailing footprints leaches some toxic elements like Cu, As, Zn and Pb on the top soil horizon, where they exist in different chemical forms (Tutu *et al*, 2003; Grover *et al*., 2016). The acidity caused by the leachates from the tailings footprints lead to soil
degradation and this affect the ecosystem and human health through food chain (Rosner and van Schalkwyk, 2000; Sutherland, 2000).

The pH of 3.5 to 3.9 was recorded and this was observed to be relatively low pH values as it was below 4. This was recorded to tailings dumps and also at some locations nearby the tailings ponds. The tailings footprints also attributed to the soil contamination due to leaching of toxic elements from remnant materials influenced by rapid oxidation of fresh portion exposed on the tailings dumps. The tailings footprints clearly shows the high level of soil contamination due to toxic elements released from the tailings dumps and adjacent ponds near active slimes dams and tailings spillages where tailings have been exposed for reprocessing (Tutu et al., 2008; Grover et al., 2016).

The lowest pH recorded was 3.5 on the tailings footprints and this was due to oxidation of remnant tailings left on a footprint, this resulted in acidification of the tailings ponds and this lead to contamination of our natural environment (Figure 3.8). This has occurred when toxic elements have an ability to enter different compartments of the food chain and availability in plant species. Plant species are crucial components in our natural environment, when these plants are growing on contaminated soils may absorb these toxic elements. Soil contamination pose a threat to human health as elevated concentrations of trace elements like Pb, As, Zn and Cu are accumulated in the soils and these may be absorbed in small quantities in their gastrointestinal tract to the blood vessels (US EPA, 1998).

The predictive modelling to find out pathways of transferability of toxic elements from tailing footprints to topsoil horizon was conducted to find out contamination influenced by toxic elements dispersion and organic contaminants. Stability of the tailings dumps is mostly affected by intensive surface runoff and it influences spatial distributions of trace elements on the environment. Leaching of trace elements is probably the most serious concern on abandoned tailings dumps and footprints and this pose a threat on soil quality and human health through direct contact or ingestion through food chain (Weiersbye, 2007; Suponik and Blanco, 2014).
Organic leaching solutions such as citric acid and oxalic acid were used to find out the bioavailability of toxic elements. The findings show that the tailings footprints contain elevated total concentrations of As, Pb, Cu and Zn in the crusts and plant species may absorb toxic elements from soil when soil is saturated. The mobility of the toxic elements and their availability in the tailing footprints plays a role in the transferability of toxic elements to the natural environment due to leachates released from the tailings dumps (Kirpichchikova et al., 2006; Sun et al., 2012).

Soil factors such as pH, Eh, clay content, organic matter, cation exchange capacity, nutrients balance, soil moisture, temperature and the concentrations of toxic elements in soil, have an influence on the bioaccessibility and bioavailability of toxic elements on plant species growing on the tailings footprints (Witkowski, 1998). Toxic elements are mostly absorbed faster by plant species (vegetables) such as lettuce, onion, spinach, cabbage and carrots (Biziuk, 2007; Strosnider et al., 2013).

The residential sites in the Central Rand basin (Roodepoort to Boksburg) that are located next to the tailing dumps may be affected by released leachates in the soil. During rainy seasons, run-off from the tailings footprints leads to leaching of toxic elements that have contaminated the soil (Pierzynski et al., 2000; Camden-Smith and Tutu, 2014). Contaminated tailings footprints due to its chemical characterisation affected the soil quality due to leachates from tailings and footprints on selected sites for development purposes. In terms of urban development and spaces that can be used for residential settlement, the toxicity of elements on the soil must be taken into consideration as it may affect their health.

The concentrations of leachates from the tailings footprints to the soil may increase due to acidification and interlinked system by organic acids formed in the rhizosphere by soil microorganism and plant roots (Hageman, 2007; Bakatula et al., 2012). The bioavailability and bioaccumulation of toxic elements was taken into consideration and characterisation of tailings footprints in areas targeted for human settlements and office spaces was assessed for their potential to release left over toxic elements like As, Pb, Cu and Zn.
Leaching of toxic elements would depend on the content of the elements and the contact of the host material (tailings and efflorescent crusts) with rainwater, dilute sulphuric acid (a common leachate in such acidic soils) as well as contact with plant exudates such as oxalic and citric acids, this latter scenario being possible in gardens put up on such impacted soils.

The leachate solutions were used to correlate the mineral composition of precipitates (efflorescent crusts) to the contaminants in the tailings dumps. Potential impact on humans following any accidental ingestion of the tailings or contaminated soils was assessed using gastric juices. The experimental work was augmented by simulations based on geochemical modelling to determine the speciation of elements (and thus potential lability and bioavailability), dissolution and formation of minerals. The results pointed to elevated total concentrations of As, Pb, Cu and Zn in the efflorescent crusts. These are essentially evaporite barriers that tend to concentrate leachates following evaporation.

Tailings, as the primary sources, were also found to contain significant concentrations of these elements (Camden-Smith and Tutu, 2014; Grover et al., 2016). Rainwater leachates of the crusts were found to contain high concentrations of the toxic elements, essentially signifying that these were solubilised on contact with rainwater (McLaughlin et al., 2000; Grover et al., 2016). Elevated concentrations of sulphates were obtained, implying that most of the elements precipitated as sulphates in the crusts (Table 5.3 and Figure 4.5).

Elevated concentrations of toxic elements were detected from the tailings footprints, and this was confirmed by statistical data evaluation. The statistical analysis of the experimental data has recorded elevated concentrations toxic elements and the following concentrations were detected: As (1.5 mg/L-4.5 mg/L), Pb (3.5 mg/L-5.5 mg/L), Cu (4 mg/L-4.8 mg/L) and Zn (0.023 mg/L-0.044 mg/L). These trace elements are released very slowly from the tailings dumps and footprints. Trace elements like As and Pb are major concern as they are not essential in human health even if they are released in low concentrations compared to Zn and Cu. Toxicity of trace elements are major concerns after physical removal of tailings dumps on the tailings footprints, due to their change in chemical forms.
When Fe$\text{S}_2$ is oxidised during the formation of AMD produces high $\text{SO}_4^{2-}$ as salts. The highest $\text{SO}_4^{2-}$ concentration recorded was 6872 mg/kg from the leachates on tailings footprints and this correlates with the lowest pH recorded in the study. Therefore in a nutshell, tailings footprints are characterised by sulphide mineralisation like chalcopyrite, pyrite, arsenopyrite, galena and sphalerite. Tailings footprints contains elevated concentrations of toxic elements such as Cu, Pb, Zn and As. High concentration of this toxic elements pose a threat to environment and human (Camden-Smith and Tutu, 2014; Grover et al., 2016).

The precipitation of ferric hydroxide generated acidity and buffers the hydrogen ion activity (pH) between 3.5 and 3.9 of the AMD. Due to acidic conditions, toxic elements like Zn, Pb, Cu and As leach from tailings footprints to topsoil horizon as the acidity increases the mobility and toxicity of elements. Fe(OH)$_3$ precipitation resulted to co-precipitation and adsorption of toxic elements in the mixture or solution during geochemical reactions. In the CRG, tailings dumps are the primary source of pollution since they are composed of elevated proportions of pyrite in their composition and residual material materials left on the tailings footprints pose a threat to environment due to its chemical characterisation (Tutu et al., 2008).

Acidity leaching from both efflorescent crusts and tailings footprints has elevated concentrations of As, Pb, Cu and Zn. Therefore these toxic elements are distributed from the tailings dumps to the topsoil horizon and due to its acidic conditions it may be mobilised to groundwater system. A high concentration of these toxic elements for both crust and tailings footprints contaminated the soil due to its chemical characterisation, when efflorescent crust dissolves it mobilises toxic elements to the soil (Tutu et al., 2008).

Tailings footprints contain elevated total concentrations of As, Pb, Cu and Zn in the crusts and plant species may absorb toxic elements from soil when soil is saturated (Farrell et al., 2010; Grover et al., 2016). Organic leaching solutions such as citric acid and oxalic acid were used to find out the bioavailability of toxic elements. Leachates from both crusts and tailings were detected whether these trace elements can be taken up by plants (Sun et al., 2001). The findings show that due to elevated concentrations of As, Pb, Cu and Zn, these trace elements may be taken up by
Plants may absorb As and high ranking concentrations may be present in food due to uptake of As by plants from the soil (Wuana et al., 2010). The concentrations of the dangerous inorganic As may be present in tailings ponds when tailings and efflorescent crusts dissolve during heavy rains, and this may affect also surface water quality (Boisson et al., 1999; Schmidt, 2003; Camden-Smith and Tutu, 2014).

When Cu is taken up by plants from soil, it does not break down in the natural environment and it can be accumulated in plants and animals when it is present in the soils. Only certain types of plants can survive to grow in Cu rich soils and this can results into destruction of plant diversity near Cu mine waste disposal sites. Elevated concentration of Cu may have effects upon plants when quantities of Cu are taken up by plants on rhizosphere soils. This pose a threat to sites that can be utilised possibly for gardening on the impacted soils by tailings dumps (Gao et al., 2003; Labanowski et al., 2008).

Presence of Cu depends upon the acidity of the soil and organic matter in influencing the proceedings of certain land use activities. High quantities of Cu in the soil on the abandoned tailings and footprints, animals such as cattles grazing on tailings dumps may absorb concentrations that may affect their health (Figure 5.2). Lead can be taken up by plants from the tailings footprints due to chemical reactions occurring on the soils and surface runoff to the tailings ponds. Pb cannot be broken down; it can only be converted to other chemical forms (elemental speciation) and it is accumulated in both soil and surface water (tailings ponds).

High ranking concentrations of Pb have effects on health due to lead poisoning (US DHHS, 1999; Labanowski et al., 2008). Soil quality is disturbed by lead intervention, especially possibly in gardens put up on such impacted soils. Elevated concentrations of toxic elements are accumulated in the soil and Pb is very toxic trace element. Pb accumulated in the soil through plant update may affect human health, when vegetables growing on the tailings footprints may absorb trace elements as nutrients from the soils (Rosen, 2002; Vassil et al., 1998).

Zn can be taken up by plants from soil contaminated by remnants material left on the tailings footprints and ends up in the environment. An elevated concentration of Zn
was found in soils contaminated by leachates from the tailings footprints. Plants can uptake Zn from the contaminated soil in the tailings footprints to their systems, when high quantities of Zn are accumulated in the soils. Soil was contaminated with elevated concentration of Zn due to leaching of toxic elements from both tailings dumps and footprints. Sites selected on the tailings footprints are contaminated with Zn, cattles grazing on the paddocks may absorb elevated concentrations of Zn that can damage their health (Labanowski et al., 2008; Vysloužilová et al., 2003).

Elevated concentration of Zn increased by the acidity of water on the tailings ponds. Dissolved trace elements accumulated in the soil can percolate and migrates to the groundwater system and pollute groundwater (Dold, 2003). Certain types of plants can survive in Zn-rich soils and this can be clearly visible by plant diversity next to the tailings dumps, only when elevated concentration of Zn is detected in high quantities becomes a threat to the environment and human (Martínez and Motto, 2000; Dold and Fontboté, 2002). Figure 5.2(a) clearly shows vegetation cover such as grass and trees growing on the paddocks and this may also pose a threat to cattle during grazing, as cattle's may uptake toxic elements from the grass. Cattles also drink from the Fleurhof Dam in the Central Rand and this dam receives drainage from the Florida Lake as well as from surrounding tailings dumps (Figure 5.2(b)).

![Figure 5.1: Indicate (a) cattle grazing on the paddocks of tailings dumps (b) drinking from the Fleurhof Dam in the Central Rand](image)

Due to acidic condition in the area, toxic elements may be released from the tailings footprints and plants growing on the tailings footprints may absorb these elements.
Plants roots extract Pb, Cu, Zn and As from the contaminated soil as nutrients and through food chain it may pass to human body through food consumption (GDACE, 2008; Wuana et al., 2010).

Therefore it is important to take note of the geochemistry of mine residue and mine water chemistry discharged on the natural environment, but in most residue deposits rainwater is the core agent of acid formation in oxygenated zones. Leaching out of trace elements through surface and groundwater flow resulted into degradation of soil quality, especially in the land use covered by tailings footprints (McCarthy, 2011). Landscape covered by gold tailings footprints has a huge space for future development (Reddy and Chinthamreddy, 2000; Camden-Smith, 2013).

Soil contaminated with toxic elements pose risks to land resource suitable for agricultural production and it affects food security due to bioavailability of toxic elements in the soil. The selected sites may not be suitable for practice for agricultural production due to soil contamination. Contaminated soils due to acidity of soil pH and released toxic elements like Pb, Cu, Zn and As from tailings footprints to the soil makes the sites not to be utilised for gardening as elevated trace elements are accumulated in soils (Vysloužilová et al., 2003).

The pH value clearly indicates that the hydrogen ion activity ranges from acidic to strongly acidic and this is an indication of poor soil quality. Acidic situation can lead to permanent soil degradation (Tandy et al., 2004; AECOM, 2014). The top soil horizon is the one containing the remnants material at a range of 25 to 45 cm depth and the contaminants leached out from the overlying tailings footprints represent the pollution source. Due to acidification continuously occurring on the tailings footprints, the top soil horizon remain highly acidified.

The migration of toxic elements from the tailings footprints may also pose threat on groundwater due to influence of geochemical processes and geological structures interaction on the underlying geology. The pathway or distribution of pollution plumes occurring on groundwater subsurface formations is due to geohydrological flow patterns (Bolan et al., 2008; Nordstrom, 2011; Nordstrom et al., 2015).
The probability of harm on the contaminated sites covered by mine wastes and reclaimed mine sites on the selected study sites, the assessment of risks posed by residual material on the tailings footprints was done in order to gather and interpret information collected on the sites. This was done to find out the characteristics of sources, pathways and receptors on the study sites and their threat on the human and the environment.

The characterisation of the geochemistry of the tailing footprints, soil properties and geochemical processes on the study sites was conducted to find out the characteristics of soil on the tailings footprints and contaminant fate and transport of toxic elements on the soil (Tutu et al., 2008; Grover et al., 2016). The geological structures of the subsurface formation located where the tailings dumps and waste rocks are deposited, may influence the migration of toxic elements from the tailings footprints to the groundwater system. The texture and grain size distribution influences the migration of toxic elements and the permeability of fluid in the medium depends on the sorting of the grains (TCTA, 2012).

Therefore it is crucial to take note of soil texture and grain size distribution during risk assessment and these influences the transport of toxic elements from the tailings footprints (Oelofse et al., 2007; Bakatula et al., 2012). The efflorescence crusts contribute to soil and water (tailings ponds) contamination due to dissolution of salts crust on the surface area. Dissolution of salts crust lowers pH, the leaching of contaminants in soluble phases increase the solute load (Tutu et al., 2011; Camden-Smith and Tutu., 2014).

The fate and transport of toxic elements in soil depends on the chemical form (elemental speciation) of the trace elements (England et al., 2001; Ahmad et al., 2009). Bioavailability, mobility, and toxicity of trace elements like Pb, Cu, Zn and As are controlled by geochemical reactions of these elements in soils and the spatial distribution of these toxic elements is determined by mineral precipitation and dissolution, ion exchange, adsorption, aqueous complexation, mobilisation and this lead to plant uptake of this toxic elements in the contaminated soil due to different chemical form or speciation of trace elements (Greany, 2005; Kirpichtchikova et al., 2006; Tutu et al., 2008; Xu et al., 2009).
Geochemical characterisation of gold tailings footprints has clearly set up detail description of tailings footprints characteristics on the selected sites. The experimental data and geochemical modelling simulations have described what is in the soils and the composition of the tailings footprints. Mineral composition of tailings in the CRG is characterised by pyrophyllite, chloritoid, mica, chlorite, jarosite, pyrite, gypsum and high quantity of quartz mineral as it is highly resistant to weathering. The finding shows that soil on the tailings footprints are contaminated with elevated concentrations of toxic elements like Pb, Cu, Zn and As and it affects the areas targeted for human settlements and office spaces (Pierzynski et al., 2000; Sun et al., 2001; Xu et al., 2008; GCRO, 2015).

The risk assessment of potential release left over toxic elements on the tailings footprints was properly conducted and due to toxicity of this leached out toxic elements; the evaluation of risk assessment conducted indicates that these trace elements pose a threat to the environment and human due to elevated concentrations of leachates from the tailings footprints (Schmidt, 2003; Falayi and Ntuli, 2014). The selected sites may be used for residential site, office parks and industrial sites (Figure 5.3 and Figure 5.4).

During urban development or infrastructure development, it is important for urban and regional planners to take note of acidity in the soil and leaching out of toxic elements from the tailings footprints on the selected sites. This will play a significant role in the choice of materials that will be used, as material used must be resistant to corrosion due to acidic pH of soil (Figueiredo and Da Silva, 2011). The presence of CaCO$_3$ from limestone in the soil can help to reduce the transport of toxic elements from tailings dumps and footprints to the soil. CaCO$_3$ can buffer the hydrogen ion activity (pH) from acidic to alkaline (Tutu et al., 2008).

When the pH is no longer acidic, the solubility and availability of toxic elements may decline due to change of pH on the soil. Mine residue areas proposed for development in the CRG after physical removal of tailings, residual materials left on the tailings footprints may be the secondary source of pollution. Selected sites may not be suitable for agricultural activities due to elevated concentrations of trace elements like As and Pb detected from the tailings footprints and these elements are not essential to human health (Figure 5.4).
Figure 5.2: Indicates the human settlement sites in the city of Johannesburg and surrounding townships (GDARD, 2009)

Figure 5.3: Indicates the reclamation of mine dumps sites for development purposes in the Central Rand (GDARD, 2009)
5.2. Reaction of saliva, gastric and duodenum juice with minerals

As part of this research investigation a conceptual model was constructed in order to find detail information about impacts of tailings footprints on human health to adults and children residing next to abandoned tailing dumps and footprints.

![Conceptual model showing pathways where toxic elements can enter the human body through ingestion.](image)

**Figure 5.4: Conceptual model showing pathways where toxic elements can enter the human body through ingestion.**

Children are the once particularly in danger of toxic elements poisoning. They can mostly ingest any non-food objects left on the ground and sucking of their finger with adhered tailings soil on their fingers unaware of danger of mine tailings on their health. After ingesting tailings soils, children are in danger as they can absorb high quantities of toxic elements due to their higher haemoglobin sensitivity of trace elements compared to adults (Labanowski et al., 2008). Therefore tailings dumps and footprints are major concern in the playgrounds and urban settlements on sites where children spend most of time playing on those abandoned tailings dumps and footprints (Farrell et al., 2010; Torres and Auleda, 2013).

Ingestion of soil and dust particles by children is commonly known as one of pathways of these toxic elements to human body. Accidental consumption of contaminated soil from the tailing footprints by children may result in acute poisoning and health risks may be less effective to adults than children. Young children may get soil on their hands when they are playing on sites exposed to soil contaminated with Pb, Cu, Zn and As. This may occur especially when children are busy playing on the ground and soil adhered on their fingers, may lead the dirty fingers...
accidentally put on their mouth and due to elevated concentration of toxic elements ingested; the human health may be affected by high consumption of toxic elements. The ingestion of medium amount of toxic elements from the tailings footprints every day for several years may cause long term health effects or risks, (Schmidt, 2003; US EPA, 2004; Rashed, 2010).

When children and adults accidentally ingest tailings soil, the salivary glands will secret the lubricating fluid (saliva). Saliva will react with the ingested tailings soil and consumed tailings soils containing those toxic elements from the tailings footprints may be less reactive. Contaminated soil consists of Pb, Cu, Zn and As and it may be ingested and descend through the muscular propulsion on the pharynx, where it will be transported through oesophagus to the stomach (Vysloužilová et al., 2003; Basta et al., 2005; Labanowski et al., 2008; Martens et al., 2008).

The chemical break down of ingested soil in the stomach may occur through acid and enzymes, the mechanical processing through muscular contraction may take place. After chemical break down in the stomach, the enzymatic digestion and absorption of water, organic substrates, vitamins, and ions will occur in the small intestine (duodenum) to the blood vessels (Greany, 2005; Figure 4.8).

Characterisation of soil on the tailings footprints provided an insight of toxic elements speciation and bioavailability of Pb, Zn, Cu and As in the contaminated soil. Tailings dumps as source of contamination, after reclamation of these tailings dumps remnants materials are left over the tailings footprints. The remediation plan of toxic elements on the contaminated soil would need knowledge of geochemistry of tailings dumps to understand the source of contamination, basic chemistry (environmental chemistry), and associated health risks of these toxic elements (Tandy et al., 2004).

Risk assessment is an applied scientific tool which helps in decision making to manage the contaminated sites. Mineral assemblages (Figure 5.1) were selected to determine the elemental speciation of the mineral composition of tailings footprints and reacted those selected mineral phases with different body fluids. Simulation reactions have showed distribution of species and their chemical forms (Table 5.5, Table 5.6 and Table 5.7). Saliva juice was reacted with mineral phases such as chalcopryte, ferric hydroxide, goethite, gypsum, jarosite, melanterite, and pyrite to
determine the speciation of elements (Table 5.5). Due to accidentally consumption it may be absorbed in high levels in their blood vessels and it may results into health effects in human depending on the duration of exposure on soil contaminated with toxic elements (Table 5.7).

Table 5.5: Solution composition after saliva juice reacted with mineral phases

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.710e-02</td>
</tr>
<tr>
<td>Ca</td>
<td>1.660e-01</td>
</tr>
<tr>
<td>Cl</td>
<td>3.017e-02</td>
</tr>
<tr>
<td>Cu</td>
<td>1.630e-01</td>
</tr>
<tr>
<td>Fe</td>
<td>1.304e+00</td>
</tr>
<tr>
<td>K</td>
<td>1.932e-01</td>
</tr>
<tr>
<td>N</td>
<td>1.006e-03</td>
</tr>
<tr>
<td>Na</td>
<td>2.213e-02</td>
</tr>
<tr>
<td>P</td>
<td>1.106e-02</td>
</tr>
<tr>
<td>S</td>
<td>1.305e+00</td>
</tr>
</tbody>
</table>

Saliva juice was reacted with mineral phases and the findings show that when tailings soil is ingested, reaction of saliva juice and mineral composition of tailings footprints is highly reactive and there are high levels of toxic elements that can be absorbed in blood vessels when ingested soil is swallowed to the stomach due to its high solubility (Table 5.5).

Therefore trace elements leaching from the tailings dumps and footprints can’t be ignored. Some trace elements like Cu and Zn are harmless in low levels, unfortunately other trace elements like As and Pb even at extremely low level is very harmful as they are not essential to human health. Elevated concentrations of toxic elements in human body may cause diseases such as cardiovascular disease and cancer (Table 5.5; Table 5.6; Table 5.7 and Table 5.8).
### Table 5.6: Distribution of species when saliva juice reacted with mineral phases

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (4)</td>
<td>1.668e-02</td>
</tr>
<tr>
<td>Ca</td>
<td>1.620e-01</td>
</tr>
<tr>
<td>Cl</td>
<td>2.944e-02</td>
</tr>
<tr>
<td>Cu (1)</td>
<td>9.627e-03</td>
</tr>
<tr>
<td>Cu (2)</td>
<td>1.494e-01</td>
</tr>
<tr>
<td>Fe (2)</td>
<td>1.202e+00</td>
</tr>
<tr>
<td>Fe (3)</td>
<td>7.024e-02</td>
</tr>
<tr>
<td>K</td>
<td>1.885e-01</td>
</tr>
<tr>
<td>N (-3)</td>
<td>7.096e-06</td>
</tr>
<tr>
<td>Na</td>
<td>2.159e-02</td>
</tr>
<tr>
<td>P</td>
<td>1.079e-02</td>
</tr>
<tr>
<td>S (-2)</td>
<td>4.905e-01</td>
</tr>
<tr>
<td>S (6)</td>
<td>7.826e-01</td>
</tr>
</tbody>
</table>

After reaction of reactants (saliva juice + minerals), products (mixed solution) due to its high solubility is swallowed to the stomach. Gastric juice has highly reacted with the first solution (saliva juice + minerals); stomach due to its acidic hydrogen ion activity and enzymes (electrolytes) may influence the speed up of reaction during digestion in a stomach (Table 5.7).

Due to high solubility of mineral phases, mixed solutions may be highly reactive and it is easy for toxic elements to be absorbed in the blood vessels. Gastric juice may be highly reactive with toxic elements like Pb, Pb, Cu and Zn. High reactivity of toxic elements in the stomach may results in elevated concentrations of toxic elements to be absorbed in the blood vessels and this pose a health risk to human. Digestion in the stomach plays a crucial role in order for digested material to be more soluble and absorbed in the human body (Table 5.8).
Table 5.7: Solution composition after gastric juice reacted with mineral phases

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.710e-02</td>
</tr>
<tr>
<td>Ca</td>
<td>8.378e-01</td>
</tr>
<tr>
<td>Cl</td>
<td>1.345e-01</td>
</tr>
<tr>
<td>Cu</td>
<td>8.330e-01</td>
</tr>
<tr>
<td>Fe</td>
<td>6.664e+00</td>
</tr>
<tr>
<td>K</td>
<td>8.742e-01</td>
</tr>
<tr>
<td>N</td>
<td>7.039e-03</td>
</tr>
<tr>
<td>Na</td>
<td>7.140e-02</td>
</tr>
<tr>
<td>P</td>
<td>1.307e-02</td>
</tr>
<tr>
<td>S</td>
<td>6.665e+00</td>
</tr>
</tbody>
</table>

Table 5.8: Distribution of species when gastric juice reacted with mineral phases

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (4)</td>
<td>8.051e-03</td>
</tr>
<tr>
<td>Ca</td>
<td>3.945e-01</td>
</tr>
<tr>
<td>Cl</td>
<td>6.336e-02</td>
</tr>
<tr>
<td>Cu (1)</td>
<td>2.451e-02</td>
</tr>
<tr>
<td>Cu (2)</td>
<td>3.677e-01</td>
</tr>
<tr>
<td>Fe (2)</td>
<td>2.955e+00</td>
</tr>
<tr>
<td>Fe (3)</td>
<td>1.826e-01</td>
</tr>
<tr>
<td>N (-3)</td>
<td>1.803e-05</td>
</tr>
<tr>
<td>Na</td>
<td>3.362e-02</td>
</tr>
<tr>
<td>P</td>
<td>6.157e-03</td>
</tr>
<tr>
<td>S (-2)</td>
<td>1.241e+00</td>
</tr>
<tr>
<td>S (6)</td>
<td>1.897e+00</td>
</tr>
</tbody>
</table>
Duodenum juice was reacted with the second solution (mixed solution) from the stomach and these resulted into high absorption of toxic elements like Pb, As, Cu and Zn in gastrointernal tract to blood system. The reaction of duodenum juice and mixed solution (from the stomach) due to high solubility of toxic elements in the solutions, it may results in high absorption of toxic elements and this may pose a threat to human depending on the level of absorption of those toxic elements (Table 5.9 and Table 5.10).

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.820e-01</td>
</tr>
<tr>
<td>Ca</td>
<td>8.378e-01</td>
</tr>
<tr>
<td>Cl</td>
<td>2.048e-01</td>
</tr>
<tr>
<td>Cu</td>
<td>8.330e-01</td>
</tr>
<tr>
<td>Fe</td>
<td>6.664e+00</td>
</tr>
<tr>
<td>K</td>
<td>8.742e-01</td>
</tr>
<tr>
<td>N</td>
<td>1.009e-02</td>
</tr>
<tr>
<td>Na</td>
<td>1.803e-01</td>
</tr>
<tr>
<td>P</td>
<td>1.328e-02</td>
</tr>
<tr>
<td>S</td>
<td>6.668e+00</td>
</tr>
</tbody>
</table>

Environmental pollution generated by abandoned tailings dumps and footprints is the major source of contaminants in both soil and water systems. Mine pollution is the main concern in both active and abandoned mines and geochemical reactions that occurs in the mine dumps is unpredictable as it happens naturally. Therefore lack information to the residents close to the mine dumps may lead to many deaths of people. Residents may be affected by the leachates and dust particles from abandoned tailings dumps and footprints (Bakatula et al., 2012). Thus why in this study environmental risk assessment was another concern after the physical removal of the tailings dumps, as residual materials are left on the tailings footprints and tailings materials left on the tailings may be a secondary source of pollution.
Table 5.10: Distribution of species when duodenum juice reacted with mineral phases

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (4)</td>
<td>5.816e-02</td>
</tr>
<tr>
<td>Ca</td>
<td>2.677e-01</td>
</tr>
<tr>
<td>Cl</td>
<td>6.544e-02</td>
</tr>
<tr>
<td>Cu (1)</td>
<td>2.210e-02</td>
</tr>
<tr>
<td>Cu (2)</td>
<td>2.441e-01</td>
</tr>
<tr>
<td>Fe (2)</td>
<td>2.009e+00</td>
</tr>
<tr>
<td>Fe (3)</td>
<td>1.203e-01</td>
</tr>
<tr>
<td>K</td>
<td>2.794e-01</td>
</tr>
<tr>
<td>N (-3)</td>
<td>1.561e-05</td>
</tr>
<tr>
<td>Na</td>
<td>5.762e-02</td>
</tr>
<tr>
<td>P</td>
<td>4.243e-03</td>
</tr>
<tr>
<td>S (-2)</td>
<td>8.414e-01</td>
</tr>
<tr>
<td>S (6)</td>
<td>1.290e+00</td>
</tr>
</tbody>
</table>

The assessment was to estimate the nature and probability of adverse health effects due to the exposed tailing dumps and footprints after the reclamation of tailings dumps next to human settlement sites and reclaimed site for developments purposes. Remnants material left over the tailings footprints on the top soil horizon may contaminate the soil and water systems on the selected sites. Health risks may be affected by dust inhalation and accidental ingestion of tailings soil, as topsoil contains toxic elements from the tailings footprints (Bose-O'Reilly et al., 2010).

Statistical data evaluation of experimental data has recorded the high elevation of toxic elements and the following concentrations were detected: As (1.5 mg/L-4.5 mg/L), Pb (3.5 mg/L-5.5 mg/L), Cu (4 mg/L-4.8 mg/L) and Zn (0.023 mg/L-0.044 mg/L). The evaluation of chronic daily intake of toxic elements from tailings footprints was done in order find out the health risks on residence close to the tailing dumps and reclaimed sites for development purposes. Elevated total concentrations of toxic elements like Pb, As, Cu and Zn detected from the tailings footprints pose a threat in
human, animals and plant biodiversity. Due to influence of redox reactions that occur on the residual material left on the tailings footprints, acidic pH in the tailings footprints makes the toxic elements to migrate and dispersed on the natural environment. The pathways of toxic elements through leaching from the tailings footprints and paddocks runoff lead to dispersion of these toxic contaminants in the soil and the natural environment (Basta et al., 2005; Bolan et al., 2008).

Leaching of toxic elements from the tailings and efflorescent crust pose a threat to soil and water resources. Paddocks runoff is highly influenced by heavy rains during summer seasons and the transported toxic elements are dispersed in soil and some are transported to Fleurhof Dam (Figure 5.2). Cattles drinking water from the Fleurhof Dam may be affected by elevated concentration of toxic elements leaching from the tailings and paddocks through surface runoff.

Tailings ponds adjacent to tailings dumps are also filled with contaminated mine water and this has health risks to children playing in mine contaminated water in a pond adjacent to tailings dumps (Figure 4.15). Due to the lack of knowledge on how mine tailings dumps may be harmful to their health, children plays in mine contaminated water in a pond adjacent to a tailings dumps. This is a clear indication that children are in a high risk of being affected by high consumption of toxic contaminants leaching from the tailing dumps compared to adults (Figure 5.6).

Geochemical cycle of toxic elements in contaminated soil from the tailings footprints pose a health risks on the selected sites for development purposes in areas where people reside next to the tailings dumps and reclaimed sites where tailings footprints can also leach toxic elements to the soil due to remnants material left over tailings footprints. Soils on the reclaimed sites for development purposes are accumulated with toxic elements like Pb, Cu, Zn and As from the tailings footprints.

Elevated concentrations of toxic elements from tailings dumps and footprints pose threat to human health and may cause diseases such as cardiovascular diseases and cancer (Vysloužilová et al., 2003; Labanowski et al., 2008). Therefore reclaimed sites may not be suitable for agricultural practices due elevated concentrations of As and Pb accumulated in the soils and plants may uptake this toxic elements as nutrients from the soils (Durand, 2012).
Figure 5.5: A newspaper clip shows children playing in mine contaminated water in a pond adjacent to a tailings dump (picture by James Oatway)

Toxicity of elements contaminating the soil depends on their rates of exposure, transferability from the tailings dumps to random environmental sites where elevated concentrations of direct exposure occur. The elemental speciation of toxic elements was found in the receiving environment and has increased the bioavailability of these elements in the soil. Children at an age of 1 to 5 years are the once in danger, as mostly they enjoy playing outdoors. The exposed tailings dumps or contaminated soil from tailings footprints and tailings ponds pose a health effect (risks) due to toxic elements leaching from the tailings dumps and footprints (Martínez and Motto, 2000; Rosen, 2002; Kirpichtchikova et al., 2006).

They may accidentally consume contaminated soil containing toxic elements from the tailings footprints and elevated concentration of toxic elements may be absorbed in their body in small concentration. After some days or years, the concentration of these toxic elements may be high as consumption of contaminated soil goes on (US EPA, 1993; US EPA, 2001; US EPA 2005a; US EPA 2005b; US EPA 2005c). Health risk assessment model for carcinogenic and non-carcinogenic species was conducted by applying US Environmental Protection Agency (US EPA) techniques.
US EPA model was used to evaluate the toxic elements contamination risks in human settlements and reclamation of mine dumps sites for development purposes close to the tailings dumps (tailing footprints).

Toxic elements detected from the tailings footprints after tailings dumps reclamation for developments purposes are Pb, Cu, Zn and As. The selected sites after reclamation of tailings dumps can be used for development purposes such as residential sites, offices and industrial sites. Risk assessment was done to find out the characterisation of tailings footprints and health risk of toxic elements is the main concern on the suggested sites for development purposes.

Accidental consumption of contaminated soil on the tailings footprints may results in toxic elements accumulation in their body at low levels and elevated concentrations may results into acute and chronic effects. Pb, Cu, Zn and As can be taken up plants possibly in gardens put up on such impacted soils. The above toxic elements can be absorbed into the body each day at low concentration through food chain. Toxicity of trace elements depends on the dose absorbed, route of exposure and duration of exposure (Vysloužilová et al., 2003).

Human settlements sites close to the tailings dumps and reclaimed site for development purposes, residents may have an idea of making small gardens where they will plant some vegetables such as onion, spinach, cabbage, and carrots as a way of food production for their family. Vegetables growing on the tailings footprints may absorb some toxic elements such Pb, Cu, Zn and As from the soil.

These toxic elements may be harmful to human health due to consumption elevated concentrations of elements through food chain. Soil contamination poses a health risk to humans and animals on our natural environment as a system through direct ingestion or contact with polluted soil (Schmidt, 2003; Farrell et al., 2010; McCarthy, 2011). This model was used to evaluate the daily intake and different exposure pathways for accidental consumption of contaminated soil on the gold tailing footprints (US EPA, 2004; Sánchez España and Diez Ercilla, 2008).

The following calculation formula was used to evaluate the chronic daily intake of toxic elements from contaminated soil on the tailing footprints:
Ingestion dose:

\[
\text{CDI}_{\text{ing}} \text{ (mg kg}^{-1} \text{ day}^{-1}) = \frac{C \text{ (mg kg}^{-1}) \times R_{\text{ing}} \times CF \times EF \times ED}{BW \times AT}
\]

- \(\text{CDI}_{\text{ing}}\): is a daily exposure amount of toxic elements, (mg kg\(^{-1}\) day\(^{-1}\))
- \(C\): mean concentration of toxic elements, (mg/kg)
- \(R_{\text{ing}}\): ingestion rate of soil, (mg/day)
- \(CF\): conversion factor, (kg/mg)
- \(EF\): exposure frequency, (days/year)
- \(ED\): exposure duration, (years)
- \(BW\): average body weight, (kg)
- \(AT\): average time (days). 365 * ED
- \(\text{CDI}\): chronic daily increase/intake

For risk assessment on this project, the following data was used to calculate the chronic daily intake (Table 5.11).

**Table 5.11: Shows the data used to calculate the chronic daily intake (exposure factors for dose model)**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Definition</th>
<th>Units</th>
<th>Adults</th>
<th>Children</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDI(_{\text{ing}})</td>
<td>is a daily exposure amount of toxic elements</td>
<td>mg kg(^{-1}) day(^{-1})</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>(C)</td>
<td>mean concentration of metals</td>
<td>mg/kg</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>(R_{\text{ing}})</td>
<td>ingestion rate of soil</td>
<td>mg/day</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>(CF)</td>
<td>conversion factor</td>
<td>kg/mg</td>
<td>1.00 \times 10^{-6}</td>
<td>1.00 \times 10^{-6}</td>
</tr>
<tr>
<td>(EF)</td>
<td>exposure frequency</td>
<td>days/year</td>
<td>240</td>
<td>240</td>
</tr>
<tr>
<td>(ED)</td>
<td>exposure duration</td>
<td>years</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>(BW)</td>
<td>average body weight</td>
<td>kg</td>
<td>50</td>
<td>14</td>
</tr>
<tr>
<td>(AT)</td>
<td>average time (365 * ED)</td>
<td>days</td>
<td>1825</td>
<td>1825</td>
</tr>
</tbody>
</table>

After calculating the daily exposure amount of toxic elements (CDI\(_{\text{ing}}\)) using information from above table (Table 4.24), the findings shows that young children
may accidentally ingest 48.4 mg kg\(^{-1}\) day\(^{-1}\) of contaminated soil and adult may also ingest 32.8 mg kg\(^{-1}\) day\(^{-1}\) of contaminated soil and this clearly indicates that residents nearby the tailings dumps are at high risk of being attacked by cardiovascular diseases and cancer caused due toxicity of elements leaching from both abandoned tailings dumps and footprints. People residing in the city of Johannesburg and surrounding townships close to the tailings dumps are the once in danger of health risks of toxic elements.

Elevated concentrations of toxic elements can results in various disorders (damage) due to oxidative stress (elemental speciation) of the absorbed toxic elements. These toxic elements are commonly found in the environment and diet. At low levels trace elements like Zn and Cu are essential for maintaining good health but elevated concentrations become toxic. As and Pb even at low levels are not essential for human health, therefore these are very toxic to human health. Trace elements toxicity can damage the functioning of the brain, lungs, kidney, liver, blood composition and it can lower energy levels. Level of toxicity of some toxic elements can exceed the background concentrations of the natural environment (Zhuang et al., 2005).

Leachates from the tailings dumps and footprints when concentrated surface water through runoff or chemical weathering during heavy rainfall seasons are transported from the original locations (dump sites) downstream to the residential sites. The slope of the landscape plays a significant role in the dispersion of toxic elements in the surrounding environment. Rainwater and wind are main agents of pollution from abandoned tailings dumps and footprints (Blowes et al., 2003).

Elevated concentration of toxic elements are accumulated in the soils and soil contamination in the area is major concern as accumulated toxic elements on top soil horizons may dissolve and seeps to the groundwater systems. after physical removal of tailings dumps as way of minimising impacts of environmental pollution caused by mine dumps, remnants material left on the tailings footprints leaches toxic elements to the soils which can be used for other project developments like building residential houses and creating land for agricultural activities that may boast the growth of South African economy (Figure 5.4).
Figure 5.6: This schematic diagram shows pathways of harmful metals to human body, the different types of body fluids and their composition in the gastrointestinal tract (Plumlee, 2006)

![Diagram showing pathways of harmful metals to human body](image)

Figure 5.7: Indicate health risks sites in the city of Johannesburg and surrounding townships close to the tailings dumps reclaimed for development purposes (Google Earth, 2016)

As and Pb are the most toxic elements detected as leachates from the tailings dumps and footprints. Chronic daily update of As was estimated to be 0.8-1.7 mg/kg
from the tailings footprints. Consumption of contaminated soil from the tailings footprints and feeding on vegetables growing on the tailings footprints may pose health risk to young children and adults residing on these contaminated sites due to As exposure from tailings dumps and footprints through food chain in both food and drinking water (US EPA 2005a; US EPA 2005b; US EPA 2005c).

Elevated concentrations of As leaching from the tailings dumps and water accumulated in the paddocks pose a threat to water quality in the Fleurhof Dam due through surface runoff from the tailings footprints and paddocks. Fishing in the Fleurhof Dam may pose a threat to health effect depending on the levels of As entering the dam and these can lead to elevated concentrations of As in fish to be high (Tandy et al., 2004; Tolonen et al., 2014).

When fish absorbs high levels of inorganic As may pose health risks to humans through food chain. Low levels of inorganic As can results in health effects such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. High levels uptake of inorganic As can results in cancer development such as skin cancer, lung cancer, liver cancer and lymphatic cancer. It may also cause infertility and miscarriages to women, heart disruptions and brain damage with both men and women (Greany, 2005).

As exists in different chemical form (elemental speciation) when it is dispersed in soil when it is released from the tailings footprints and this occurs in more than one oxidation state like As (V) and As (III). The oxidation states of As plays a significant role in the mobility, bioavailability, and toxicity of elements. Elemental speciation of trace element like As is bioavailable when it exposed to As rich waters and dermal contact with soluble compounds. Inorganic As is highly toxic compared to its organic form (US Department of Health and Human Services, 2013; Basta et al., 2005).

As to humans pose a health risk from low to high levels of absorption in human body through ingestion, inhalation and drinking water contaminated by As element. As poisonings may occur mainly in water and these results in predominant exposure accessibility to human system. As element due to presence of sulphide mineralisation on the processed mine wastes such as arsenopyrite, low quantities of As remains on the tailings dumps and footprints. Tailings footprint contains As.
leaching from both tailings dumps and footprints to the soil. Due to accidentally consumption by children and adults; it may be accumulated in tissues like in the skin, hair and nails (Zhuang et al., 2005; Bolan et al., 2008).

These may result in various clinical symptoms to human residing close to the tailings dumps due to lack of knowledge of how As pose health effects (risk) on their health. Residents close to the tailings dumps are at high risk as As can harm their skin, gastrointestinal organ, and can also results in lung cancers (USEPA, 2002). Elevated concentration of As (1.5 mg/L-4.5 mg/L) was leached out and in terms of frequency distributions, cumulative frequency shows that 10-11 % of As from the tailings footprints pose a health effects (risks) on humans staying close to the exposed tailings dumps and reclaimed sites for development purposes.

Health effect may depend on the time frame and levels of exposure (Table 4.25 and Figure 4.18). Accumulation of low and high levels of As in the human system; it may affect different systems such as cardiovascular, gastrointestinal and urinary systems.

Table 5.12: Frequency distribution of As into the human body through ingesting contaminated tailings footprints soil in the human body

<table>
<thead>
<tr>
<th>Frequency Distributions for: As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data Range: Sample A and B</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Frequency Distribution</th>
<th>A</th>
<th>N</th>
<th>Cum. N</th>
<th>%</th>
<th>Cum. %</th>
<th>B</th>
<th>N</th>
<th>%</th>
<th>Cum. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000</td>
<td>1,000</td>
<td>1</td>
<td>1</td>
<td>11,111</td>
<td>11,111</td>
<td>3,000</td>
<td>1</td>
<td>3,000</td>
<td>10,000</td>
</tr>
<tr>
<td>2,000</td>
<td>2,000</td>
<td>8</td>
<td>9</td>
<td>88,889</td>
<td>100,000</td>
<td>4,000</td>
<td>8</td>
<td>4,000</td>
<td>80,000</td>
</tr>
<tr>
<td>5,000</td>
<td>5,000</td>
<td>1</td>
<td>1</td>
<td>10</td>
<td>10</td>
<td>5,000</td>
<td>1</td>
<td>5,000</td>
<td>10,000</td>
</tr>
</tbody>
</table>
Elevated concentration for chronic daily update of Cu was estimated to be 3.6-4 mg/kg from the tailings footprints. Health risk (effects) of Cu can be through consumption of different kinds of food, in drinking water contaminated with Cu and dust particles through inhalation, (Vysloužilová et al., 2003). Elevated concentrations of 4 mg/L-4,8 mg/L of Cu were leached out from the tailings footprints.

Due to exposure of Cu from the tailings dumps and reclaimed sites for development purposes, high levels of Cu may be absorbed each day through eating vegetables growing in tailings footprints, drinking water contaminated with Cu and inhaling polluted air (dust particles) from the tailings dumps. Low levels of Cu are essential for human health but high levels of Cu may cause health problems. Slow adsorption reactions of Cu for days/years results in human health effects such as irritation of the nose, mouth and eyes and it causes headaches, stomach and intestinal irritation, dizziness and diarrhoea (Labanowski et al., 2008).

Cu is an essential element for both plants and animals for growth. In humans, it plays significant role in the production of blood haemoglobin, while in plants it helps in seed production, water regulation and disease resistance. High levels uptake of Cu may cause liver and kidney damage. Chronic poisoning of Cu may damage brain and this may lead to death (Turnlund et al., 1998). Elevated concentrations of 4 mg/L-4,8 mg/L of Cu were leached out from the tailings footprints and in terms of frequency distributions, cumulative frequency shows that 9-10 % of Cu from the
tailings footprints pose a health effects (risks) on humans staying close to the exposed tailings dump and reclaimed sites for development purposes (Table 4.26 and Figure 4.15). Cu may be distributed in different chemical forms (speciation of elements) and is mainly found as cuprous (Cu\(^+\)) or Cupric (Cu\(^{2+}\)). Cu soluble salts are very toxic compared to Cu in a metallic form as it has little toxicity compared to Cu precipitates. Cu toxicity may results into autosomal recessive disorder when Cu is accumulated in the liver and brain (Araya et al., 2003). It is important to assess the distribution and effects of toxic Cu elements in human health (Table 5.13 and Figure 5.10).

Table 5.13: Frequency distribution of Cu into the human body through ingesting contaminated tailings footprints soil in the human body

<table>
<thead>
<tr>
<th>Frequency Distributions for: Cu</th>
<th>Data Range: Sample A and B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency Distribution</td>
<td></td>
</tr>
<tr>
<td>A N  Cum. N</td>
<td>%  Cum. %</td>
</tr>
<tr>
<td>4,000  2  2</td>
<td>20,000</td>
</tr>
<tr>
<td>5,000  8  10</td>
<td>80,000</td>
</tr>
<tr>
<td>5,000  1  10</td>
<td>10,000</td>
</tr>
</tbody>
</table>

Figure 5.9: indicate frequency distribution of Cu in sample A and B
Elevated concentration for chronic daily update of Pb was estimated to be 2.7-10.5 mg/kg from the tailings footprints. High levels of Pb absorbed in human body may pose a health risks after uptake from vegetables growing on the contaminated soil, dust particles and drinking water contaminated with Pb. Pb is a toxic element, it can be accumulated in individual organisms and uptake through food consumption (Gao et al., 2003; Labanowski et al., 2008; Bhattacharyya and Gupta, 2008a).

Tailings footprints is characterised by toxic element like Pb as source of soil contamination on the reclaimed sites for development purposes. Health risks may be due to exposure of Pb from contaminated soil on the reclaimed sites through accidentally consumption of contaminated soil or inhalation of polluted air (dust particles) from the tailings footprints (Wuana et al., 2010; Cukrowska et al., 2013).

High levels of Pb in soil can results in uptake by plants and elevated concentrations of Pb may be accumulated in leafy vegetables (lettuce) and on the root crops such as carrots. Plants may uptake low levels of Pb from the tailings footprints and high levels of Pb may be accumulated through direct exposure (eating of tailings soil). Accidental consumption of contaminated soil is the main concern for young children as they are at high health risks of eating soil from the tailings footprints and pose threat to their health (Bhattacharyya and Gupta, 2011; Cukrowska et al., 2015). High levels of Pb in the soil pose a health risk of Pb poisoning through food consumption (ingestion) and Inhalation (Sun et al., 2001; Antwi-Agyei et al., 2009).

Elevated concentration of Pb may be accumulated in the brain and may results in Pb poisoning or even death. The Kidneys and central nervous system may also be affected by high levels of Pb consumption. Children are the once at high risk when they play outdoors on the contaminated soil, they may accidentally eat soil contaminated by leachates from tailings dumps. Health risks on children may be the impaired development, lower IQ, hyperactivity, and mental deterioration. Children under the age of 5 are the most victims on Pb exposure as their body, brain, and metabolism are still developing (Schaumberg, 2004; Rimstidt and Vaughan, 2014).

To adults health effect may be the decreased reaction time, loss of memory, nausea, anorexia, and weakness of the joints. Pb may seriously damage the brain, red blood cells, and kidneys. These may be determined by biological effects depending on the
duration of exposure and level of Pb consumption. Leaching of more SO$_4^{2-}$ makes the PbS to be stable in solid form (Pb$^{2+}$) in the soil matrix and it is a common reactive form of Pb (US Environmental Protection Agency, 2005c; Bolan et al., 2008).

High levels of Pb may be accumulated in human organs through uptake of food, especially in vegetables and fruits growing on the tailings footprints, water contaminated with leachates from the tailings and inhaling polluted air (dust particles). Pb dissolves very easily at low pH and bioavailable in dust particles and soluble compounds. Plant uptake of trace elements is generally the first step of their entry into the food chain. Uptake of toxic elements by plants depends on the fate and transport of elements from the soil (rhizospheric soils) to the plant root. Pb may pass through the membrane of epidermal cells and transported to the xylem. Toxic elements may be mobilised from leaves to storage tissues used such as seeds and fruits in the transport system (Bálintová and Singovszká, 2011; Abiye, 2014).

Elevated concentrations of 3.5 mg/L-5.5 mg/L of Pb were leached out from the tailings footprints and in terms of frequency distributions, cumulative frequency shows that 6-9% of Pb from the tailings footprints pose a health effects (risks) on humans staying close to the exposed tailings dump and reclaimed sites for development purposes.

Table 5.14: Frequency distribution of Pb into the human body through ingesting contaminated tailings footprints soil in the human body

<table>
<thead>
<tr>
<th>Frequency Distributions for: Pb</th>
<th>Data Range: Sample A and B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Frequency Distribution</strong></td>
<td></td>
</tr>
<tr>
<td>3,000</td>
<td>6</td>
</tr>
<tr>
<td>4,000</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Elevated concentration for chronic daily update of Zn was estimated to be 1.5-53.1 mg/kg from the tailings footprints. Zn is an essential element for human health (biological systems), it plays a significant role in many biochemical processes that support life and this includes the physiological duties in normal immune function, neurosensory function such as cognition and vision (US Environmental Protection Agency, 2005b). Low levels of Zn absorbed in the human body may result in loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores (Oteiza and Mackenzie, 2005). Zn is not harmful if taken orally and becomes harmful when acute poisoning is due to Zn exposure from primary source such as mine tailings dumps (Zhuang et al., 2005; Greany, 2005).

Zn is distributed commonly in acidic conditions especially in acidic mine waters as Zn$^{2+}$ and ZnOH+ form in neutral water. Zn compounds are soluble in water and consumption of very high levels of Zn can damage the pancreas and disturb the protein metabolism and cause arteriosclerosis. Zn salts such as Zn phosphate may affect several organs due to uptake of Zn through accidental consumption of tailings soil and water contaminated with Zn. Very high levels of Zn may also result in a variety of chronic effects in the gastrointestinal, hematological and respiratory systems along with alterations in the cardiovascular and neurological systems of humans (US Environmental Protection Agency, 2005a; Maret and Sandstead, 2006).
Zn salts are corrosive and ingestion can result in injury to the mouth, throat and stomach. The effects may be seen by symptoms include burning of the mouth and pharynx with vomiting and later be accompanied by erosive pharyngitis, esophagitis, and gastritis. Stomach pains and diarrhea are symptoms of Zn poisoning, in most cases vomiting, chest tightness, nausea, coldness, coma and death can occur from pulmonary edema and liver damage (Cai et al., 2005; Basta et al., 2005).

Although Zn is needed for human diet, high levels of Zn can also results in eminent health problems such as stomach cramps, skin irritations, vomiting and anaemia (US Department of Health and Human Services, 2003). Elevated concentrations of 23 mg/L-44 mg/L of Zn were leached out from the tailings footprints and in terms of frequency distributions, cumulative frequency shows that 3-10% of Zn from the tailings footprints pose a health effects (risks) on humans staying close to the exposed tailings dump and reclaimed sites for development purposes. High level of consumption for many years may results in a chronic illness that may lead to death (Table 5.15 and Figure 5.12).

Table 5.15: Frequency distribution of Zn into the human body through ingesting contaminated tailings footprints soil in the human body

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
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<td>60,000</td>
<td>60,000</td>
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<tr>
<td></td>
<td>2,000</td>
<td>5</td>
<td>7</td>
<td>50,000</td>
<td>70,000</td>
<td>3,000</td>
<td>1</td>
<td>7</td>
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<td>8</td>
<td>10,000</td>
<td>80,000</td>
<td>28,000</td>
<td>1</td>
<td>8</td>
<td>10,000</td>
<td>80,000</td>
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<tr>
<td></td>
<td>7,000</td>
<td>1</td>
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<td>10</td>
<td>10,000</td>
<td>100,000</td>
<td>137,000</td>
<td>1</td>
<td>10</td>
<td>10,000</td>
<td>100,000</td>
</tr>
</tbody>
</table>
Gauteng Premier in 2009 identified provincial priorities to implement strategies to find out available sites for development purposes. Due to large quantity of tailings dumps covering the landscape in the Central Rand basin, Department of Agriculture and Rural Development’s (GDARD) responded to the Premier’s call for the implementation of government priorities and feasibility study for the reclamation of sites covered by tailings dumps were identified (GDARD, 2009).

Tailings dumps reclamation is currently taking place in many landscapes covered by tailings in the Central Rand basin. After reclamation of tailings dumps for development purposes in the basin, remnant material is left over on the tailings footprints and these contain significant amounts of pollutants (Pb, Cu, Zn and As) that were initially in the tailings. Remnant material pose a threat to soil and water quality as it may leach to the subsoil and this is due to oxidation of remnants material left over the tailings footprints creating acidification (low pH) and influences the mobility of toxic elements to the groundwater system (Johnson and Hallberg, 2005; Tutu et al., 2008; McCarthy, 2011; Zhang, 2011).

Lack of implementation of environmental management plans on the tailings dumps after mineral processing, poor vegetation cover may results in dispersion of toxic elements by wind and water. Agents of toxic contaminants (water and wind) increase the probability of human exposure through accidental consumption of contaminants from the soil and inhalation of polluted air (wind-blown dust). Due to poorly vegetated
zones in flat surfaces, these zones are characterized by increased rainfall recharge and this may result in the mobility of toxic elements to groundwater and leaching of elements reducing the soil fertility (Rosner, 2000; Naicker et al., 2003).

Tailings footprints are characterised by elevated concentrations of toxic elements like Pb, Cu, Zn and As. Leaching of toxic elements from the tailings footprints contaminated the soil and this pose a threat to environment or health risk due to high levels of toxic elements in the soil. This is a clear indication that sites reclaimed have the potential to disperse toxic elements surrounding selected sites (land) that can be utilised for development purposes (Goga, 2011; Chatain et al., 2013).

Summary of all descriptive statistics of leachates from the tailings footprints to soil was expressed in mg/L in the Table 5.16 below.

**Table 5.16: Describes the statistical concentration of trace elements leaching in the tailings footprints (units in mg/L)**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Standard deviations</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>3,000</td>
<td>5,000</td>
<td>4,000</td>
<td>0.471</td>
<td>4,000</td>
</tr>
<tr>
<td>Pb</td>
<td>3,000</td>
<td>11,000</td>
<td>4.667</td>
<td>3.080</td>
<td>3.000</td>
</tr>
<tr>
<td>Cu</td>
<td>3,000</td>
<td>5,000</td>
<td>4,000</td>
<td>0.471</td>
<td>4,000</td>
</tr>
<tr>
<td>Zn</td>
<td>2,000</td>
<td>137,000</td>
<td>28,000</td>
<td>49.162</td>
<td>2.000</td>
</tr>
</tbody>
</table>

The release of toxic elements from both tailings dumps and footprints pose potential health risks. Tailings dumps and footprints were chosen as primary and secondary sources of toxic pollutants to soil and water systems (Bernd, 2003). The main aim of statistical analysis and data validation was to determine the lateral extent of selected toxic elements in soil medium from tailings dumps and remnants material left on the tailings footprints and find out contaminant levels in soils if are enough to be monitored even after tailings reclamation (Bowell., 2000; Cormier., 2011).

In 2015 Gauteng City Region Observatory (GCRO) collected the datasets of the location of the proposed mega-housing projects in high control zone within and outside the City of Johannesburg. Some sites planned for projects development were selected on the reclaimed mine dumps areas. In this study only three sites were selected to conduct a comprehensive geochemical characterisation of mine
impacted sites to determine the characterisation of the gold tailings dumps and footprints as sources of pollution.

Planned housing development sites based on selected areas for this study, site A was estimated to have 7473-11000 house units, site B was estimated to have 11001-15000 house units and site C was estimated to have 15001-22366 house units (GCRO, 2015). Due to assessments of various scenarios of pollutants release or mobilization potential from tailings dumps and footprints using simulations based on geochemical modelling, elevated concentrations of potential toxicity of leachates from tailings dumps and footprints like Pb, Cu, Zn and As were found as threat on the environment and human health in this study.

Toxic elements from contaminated tailing footprints may be absorbed by plants growing on the tailings footprints. Vegetation cover is characterised by grass and trees in most tailings dumps, due to uptake of toxic elements by plants, elements may be absorbed or accumulated in the grass growing on the paddocks and cattles feeding on grass (pasture) on the selected sites may absorb elevated concentrations of toxic elements from the plants growing on the tailings footprints (Sun et al., 2001; Hattingh and van Deventer, 2004; Strosnider et al., 2013; Sheridan et al., 2013).

Dissolution of toxic elements during chemical weathering may contaminate water in the Fleurhof Dam as tailings paddocks runoff during heavy rainfall seasons may distribute toxic elements to the surrounding streams and this may results in elevated concentrations of elements to be accumulated in Fleurhof Dam (Figure 4.10).

Planting vegetables on the tailing footprints may also pose a risk to human health as some vegetables may uptake toxic elements from the soil and through food consumption their health may be affected by elevated concentrations of toxic elements uptake by vegetables from the soil (Vysložilová et al., 2003; Stanton, 2008; Wang et al., 2012; Wildeman et al., 2014). The outcome of this investigation shows that the topsoil horizon is highly acidified and pH value ranges from 3.5 to 3.9.

Tailings footprints contain high levels of toxic contaminants which lead to soil degradation. This has resulted after tailings reclamation in the selected hot spots and elevated concentrations of toxic elements like Pb, As, Cu and Zn pose threat on soil
and water quality (Grover et al., 2016). pH ranges from 3.5 to 3.9 and this strongly indicate that top soil acidified probably from acidic to strongly acidic due to oxidation of remnant material left on the tailing footprints and this influences the migration of toxic elements. The migration of contaminants may pose risks (effects) on environment and human health (Wang, 2010; Morgan, 2013; Simsek et al., 2014).

The bioavailability of toxic contaminants like Cu, As, Pb and Zn in plants would be due to mobility of elements in acidic conditions, gold tailings and footprints are the source of leachates to the soil. Leaching of toxic elements depend on the content of the elements and the contact of the host material (tailings and efflorescent crusts) with rainwater, dilute sulphuric acid (a common leachate in such acidic soils) as well as contact with plant exudates such as oxalic and citric acids, this latter scenario being possible in gardens put up on such impacted soils. Leaching experiments has clearly indicated that gold tailing footprints contains elevated concentrations of toxic contaminants such as Pb, As, Cu and Zn that are harmful to the environment and human health (Masindi et al., 2014a; Dukic et al., 2015a; Dukic et al., 2015b).

The geochemical simulation reactions were conducted in order to find out the rate at which toxic elements are migrating from the tailings footprints. The acidic conditions in the area influenced the migration of toxic contaminants such as Pb, As, Cu and Zn in the soil (Chen et al., 2013). The predictive simulation reactions have shown that the topsoil is acidified with the oxidation of remnant material left on the tailing footprints and this has totally affected the soil quality in the area. Leaching contaminants from the tailing footprints may have effects on environment and human health on the residents next to the tailing dumps (Loch, 2000; Cheng et al., 2009).

Acidification of topsoil horizon due to residual left on the tailing footprints during reclamation has resulted to environmental pollution (soil and water systems) on the selected sites for development purposes. Dispersion of toxic contaminants has permanently degraded the soil and this may have effect on sites planned for developments like human settlement sites (residential, township and informal settlements), due to bioavailability of toxic elements in the soil, it pose a health risk to residents occupying land close to the tailings dumps (López et al., 2010; Zhang et al., 2013; Papassiopi et al., 2014).
Dissolution of efflorescent crust on the side of the tailings dumps increases the mobility of elements and sulphate concentration in the adjacent ponds close to the tailings dumps. The main important factors that play a huge role on dissolution reaction are hydrogen ion activity of soil and its oxidation state. Cu levels ranging from 1.5 to 4.5 mg/kg can destroy plant root growing on contaminated sites. Lead has low level of mobility in soil and is mostly accumulated within the topsoil (Oliver, 1997; Koglin et al., 2010). The bioavailability of toxic contaminants is influenced by its mobility and solubility that results into migration of toxic contaminants.

There are wide ranges of toxic elements in the tailings dumps and footprints which are major concern on environmental and human health. Acidic pH and elevated concentration of trace elements caused by AMD are released and mobilised in soil and water systems. Chemical weathering of tailings dumps and footprints release acid and elevated concentration of Cu, Zn, Pb and As through surface run-off and may also seep to the groundwater systems. These acidic water transport high load of dissolved toxic elements at low pH, commonly Cu, Zn and Fe as they are easily soluble in acidic conditions (GDACE, 2008; Masindi et al., 2014b).

Tailings footprints on the selected sites due to its characteristics (leaching of toxic elements) contaminated the soil planned for developments purposes and the toxicity of elements such as Cu, Zn, As and Pb pose a risk to environment and human health, residents on the planned mega housing projects may inhale dust particles or accidentally ingest contaminated soil (Aremu, 2008; Masindi et al., 2015).

Children are the most at high risk as they enjoy playing outdoors. Due to the lack of knowledge children may accidentally eat soil contaminated with leachates from the tailings dumps and footprints. Elevated concentrations of toxic elements discovered from the tailing footprints like Pb, As, Zn and Cu may be absorbed into their body. Effects of these toxic contaminants on human body indicate that tailings footprints are very dangerous to children and adults if they can ingest soil or drinking water containing these toxic contaminants (Martínez and Motto, 2000; Jeleni et al., 2012).

Toxicity of elements may results into the soil degradation and soil contaminated cannot be useful for ecological purposes unless some remediation plans are implemented (Rodríguez et al., 2009). The dissolution of efflorescent crust releases
toxic elements to tailings ponds and this affect soil quality. During heavy rainfall discharged water from the tailings ponds due to surface runoff, elevated concentration of toxic elements and high loads of sulphate concentrations may affect water quality of Fleurhof Dam.

Tailings ponds may be filled with water containing high levels of iron and other toxic elements (Ríos et al., 2008). After tailings dumps reclamation some remnants materials are left over the tailings footprints, this pose risk to environment and human health due to elevated concentrations of toxic elements leaching from tailings and footprints (GDARD, 2009). Gauteng City Region Observatory (GCRO) in 2015 proposed locations of planned mega housing projects in the Central Rand and due to lack of available space for development purposes, reclamation of tailings dumps were the priority to create enough space for developments. Mineralisation of tailings and footprints on the selected sites was dominated by the pyrite content and low levels of Cu, Pb, Zn and As.

Therefore the long term pollution on the tailings footprints can be influenced by the geochemical processes like geo-environmental characteristics, water balance and mineral solubility (Diehl et al., 2008). Based on the health risk assessment to determine the ingestion dose, shows that the tailings footprints pose risks to human health on sites close to the tailings dumps (Wissmeier and Barry, 2010). Findings shows that elevated concentrations of trace elements like Pb and As are released very slowly at low levels when rainwater contact with the tailings materials and released toxic elements are mobilised and accumulated in the soils.

Children are the once at high risk compared to adults. Therefore when they are playing on the tailings dumps and footprints may ingest tailings soil or possibly inhale dust particles that contain these toxic elements on the remnants material left after reclamation. Environmental monitoring and modelling should be considered even after reclamation of the tailings dumps as in this study tailings footprints was found to contain elevated concentration of Cu, Zn, As and Pb (Dietrich et al., 2004; Ndasi, 2004; Wright et al., 2014). Low levels of toxic elements like As and Pb as they are not essential to human body may cause impacts on human health and it may cause diseases like cancer which may lead to death (Lottermoser, 2007).
CHAPTER SIX: CONCLUSIONS AND RECOMMENDATIONS

In this chapter, the research findings came up with the following conclusions and recommendations:

6.1. Conclusions

The findings of research have satisfied its objectives. Characterisation of tailings dumps and footprints and the extent to which toxic elements can be dispersed from gold tailings and footprints in the Central Rand goldfield has been examined. The potential impacts of toxic contaminants on the environment and human health has been predicted.

This study came up with the following conclusions based on the findings investigated:

- Mineralogical analysis by PXRD in this study shows that quartz is the dominant mineral and some minor minerals like pyrite, pyrophylite, chlorite, jarosite and mica was detected. Textural analysis of tailings material showed that gold tailings dumps are very fine to medium (>70% of the sample). Tailings material are characterised by sandy and clay texture. Clay minerals like kaolinite and montmorillonite were also detected. Mineral phases like jarosite, goethite, gypsum, and ferric hydroxide were also detected during geochemical modelling.

- The outcome of this study has shown that tailings footprints have potential to release trace elements to the surrounding natural environment. Rainwater in the leaching of trace elements and sulphates in oxidised tailings show that during rainy seasons most trace elements are dispersed to soils and this was clearly observed on leaching experiments to determine the host of trace elements that could be released by rainwater.

- Geochemical processes were successfully simulated using computer modelling (PHREEQC geochemical modelling code) in order to complement the analytical results. The initial and final leachate solutions were analysed to find out which mineral phase's influences the release of toxic elements in the leaching process.

- Geochemical analysis shows that trace elements are released very slowly from tailings dumps and footprints in very small quantity during rainy seasons. pH
value of the contaminated tailings footprints ranges from 3.5 to 3.9 and it is acidic to strongly acidic. Topsoil horizon was mostly contaminated with elevated concentration of toxic elements like Pb, As, Cu and Zn.

- Due to high acidity in the topsoil, mobility of toxic elements from the tailings footprints resulted in permanent soil degradation. The residual material left on the gold tailing footprints after reclamation can be the future source of acid mine drainage if they are not taken into consideration after tailings dumps reprocessing.

- Tailings footprints are secondary source of toxic elements in the topsoil horizon as dissolution of efflorescent crust results into migration of contaminants to soil and water systems. Pollution of surface water may contaminate water in the Fleurhof Dam and this dam is a source of water for drinking to cattle’s grazing on that site.

- The bioavailability of toxic contaminants such as Cu, As, Pb and Zn was detected in gold tailings footprints and soil. Leaching experiments has clearly indicated that gold tailings footprints contain toxic contaminants like Pb, As, Cu and Zn that are harmful to the environment and human health.

- Tailings footprints contain toxic contaminants like Pb and As which are not essential to human body. Tailings footprints contaminated the soil and the selected sites may affects human health as residents may inhale dust or accidentally ingest contaminated soil and children are the most in high risk.

- The pH value (3.5-3.9) clearly indicate that the hydrogen ion activity ranges from acidic to strongly acidic and this is an indication of poor soil quality, as acidic situation can permanently degrade soil. Due to acidic condition in the area, the toxic elements may be leached out of the gold tailings footprints, where plants growing in the tailings footprints can absorb leached out element.

- When plants roots extract toxic elements from the contaminated soil, it may pass to human body through food consumption. Elevated concentrations of toxic elements in the tailings footprints and soil may be accumulated in the grazing cattle’s in the area, especially through the ingestion of grass and drinking water from Fleurhof Dam.
The spatial distribution of toxic elements within gold tailings footprints clearly indicated a good stratigraphic correlation with the surface evidence of mining history and mineralogical characteristics of the Central Rand goldfield. Heavy rainfall during summer seasons and wind are the major transporting agents for toxic elements from gold tailings and footprints into the surrounding environment.

The findings of this investigation have clearly found that mining activities that was practiced in the Central Rand goldfield has negatively affected the soil quality and ecosystem. Elevated concentrations of Cu, Pb, Zn and As pose a risk to human health especially residences close to the tailings dumps are at high risk.

6.2. Recommendations

According to the findings of this study, residual material left on the gold tailings footprints had polluted the soil and the surrounding environment. Vegetation cover such as grass must also be investigated so whether have the ability to bio-accumulate toxic elements which are harmful to animals through grazing.

For the fact that the area is not protected, the available land in this area is mostly covered by grass, and cattle’s are grazing on the grass growing on the tailings paddocks. It would be good to protect the area maybe by making a fence around the tailings paddocks to prevent animals from grazing within and around the tailings dumps and footprints. Grass growing on the paddocks reduces migration of toxic elements into the surrounding environment.

Tailings ponds must also be protected as during heavy rain, they are filled with more water, children find opportunities of swimming in this toxic water, which is very dangerous to their health as the may consume acidic soil or contaminated water from the tailings dumps and footprints. The results of this study have noted the leaching of elevated concentrations of toxic contaminants like Pb, As, Cu and Zn. The potential risks that Pb, As, Cu and Zn poses on soil and human health have been predicted. For future investigations urine and blood testing in cattle’s and human beings should be taken into consideration.
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APPENDICES

Table A1: Concentrations of metals leached with Citric acid

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Al</th>
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<th>K</th>
<th>Mg</th>
<th>Mn</th>
<th>Ca</th>
<th>Zn</th>
<th>Fe</th>
<th>Cu</th>
<th>Co</th>
<th>Cr</th>
<th>Au</th>
<th>S</th>
<th>P</th>
<th>Pb</th>
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<td>101.7</td>
<td>1.5</td>
<td>48.8</td>
<td>2.9</td>
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<td>1.9</td>
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Table A5: Frequency distribution of As into the human body through ingesting contaminated tailings footprints soil in the human body

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Table A6: Frequency distribution of Cu into the human body through ingesting contaminated tailings footprints soil in the human body

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Table A7: Frequency distribution of Pb into the human body through ingesting contaminated tailings footprints soil in the human body

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<td>N</td>
</tr>
<tr>
<td>3,000</td>
<td>6</td>
</tr>
<tr>
<td>4,000</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>9,000</td>
</tr>
<tr>
<td></td>
<td>11,000</td>
</tr>
</tbody>
</table>
Table A8: Frequency distribution of Zn into the human body through ingesting contaminated tailings footprints soil in the human body

<table>
<thead>
<tr>
<th>Frequency Distribution: Zn</th>
<th>Data Range: Sample A and B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1,000</td>
<td>2</td>
</tr>
<tr>
<td>2,000</td>
<td>5</td>
</tr>
<tr>
<td>6,000</td>
<td>1</td>
</tr>
<tr>
<td>7,000</td>
<td>1</td>
</tr>
<tr>
<td>95,000</td>
<td>1</td>
</tr>
</tbody>
</table>

Table A9: Descriptive statistics and input range of As

<table>
<thead>
<tr>
<th>Descriptive Statistics for: As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Range = As sample A and B</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>Mean</td>
</tr>
<tr>
<td>Median</td>
</tr>
<tr>
<td>Mode</td>
</tr>
<tr>
<td>Std Error</td>
</tr>
<tr>
<td>Std Dev.</td>
</tr>
<tr>
<td>Variance</td>
</tr>
<tr>
<td>Coeff. Var.</td>
</tr>
<tr>
<td>25th Percentile</td>
</tr>
<tr>
<td>75th Percentile</td>
</tr>
<tr>
<td>Sum</td>
</tr>
<tr>
<td>Minimum</td>
</tr>
<tr>
<td>Maximum</td>
</tr>
<tr>
<td>Range</td>
</tr>
<tr>
<td>Count</td>
</tr>
</tbody>
</table>
### Table A10: Descriptive statistics and input range of Pb

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean</strong></td>
<td>3,333</td>
<td>4,667</td>
</tr>
<tr>
<td><strong>Median</strong></td>
<td>3,000</td>
<td>3,000</td>
</tr>
<tr>
<td><strong>Std Error</strong></td>
<td>0,167</td>
<td>1,027</td>
</tr>
<tr>
<td><strong>Std Dev.</strong></td>
<td>0,500</td>
<td>3,082</td>
</tr>
<tr>
<td><strong>Variance</strong></td>
<td>0,250</td>
<td>9,500</td>
</tr>
<tr>
<td><strong>Coeff. Var.</strong></td>
<td>15,000</td>
<td>66,047</td>
</tr>
<tr>
<td><strong>25th Percentile</strong></td>
<td>3,000</td>
<td>3,000</td>
</tr>
<tr>
<td><strong>75th Percentile</strong></td>
<td>4,000</td>
<td>6,500</td>
</tr>
<tr>
<td><strong>Minimum</strong></td>
<td>3,000</td>
<td>3,000</td>
</tr>
<tr>
<td><strong>Maximum</strong></td>
<td>4,000</td>
<td>11,000</td>
</tr>
<tr>
<td><strong>Range</strong></td>
<td>1,000</td>
<td>8,000</td>
</tr>
<tr>
<td><strong>Count</strong></td>
<td>9,000</td>
<td>9,000</td>
</tr>
</tbody>
</table>

### Table A11: Descriptive statistics and input range of Cu

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean</strong></td>
<td>4,800</td>
<td>4,000</td>
</tr>
<tr>
<td><strong>Median</strong></td>
<td>5,000</td>
<td>4,000</td>
</tr>
<tr>
<td><strong>Std Error</strong></td>
<td>0,133</td>
<td>0,149</td>
</tr>
<tr>
<td><strong>Std Dev.</strong></td>
<td>0,422</td>
<td>0,471</td>
</tr>
<tr>
<td><strong>Variance</strong></td>
<td>0,178</td>
<td>0,222</td>
</tr>
<tr>
<td><strong>Coeff. Var.</strong></td>
<td>8,784</td>
<td>11,785</td>
</tr>
<tr>
<td><strong>25th Percentile</strong></td>
<td>4,750</td>
<td>4,000</td>
</tr>
<tr>
<td><strong>75th Percentile</strong></td>
<td>5,000</td>
<td>4,000</td>
</tr>
<tr>
<td><strong>Minimum</strong></td>
<td>4,000</td>
<td>3,000</td>
</tr>
<tr>
<td><strong>Maximum</strong></td>
<td>5,000</td>
<td>5,000</td>
</tr>
<tr>
<td><strong>Range</strong></td>
<td>1,000</td>
<td>2,000</td>
</tr>
<tr>
<td><strong>Count</strong></td>
<td>10,000</td>
<td>10,000</td>
</tr>
</tbody>
</table>
Table A12: Descriptive statistics and input range of Zn

<table>
<thead>
<tr>
<th>Descriptive Statistics for: Zn</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Range = Zn sample A and B</td>
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<td></td>
</tr>
<tr>
<td>Mean</td>
<td>12,000</td>
<td>28,000</td>
</tr>
<tr>
<td>Median</td>
<td>2,000</td>
<td>2,000</td>
</tr>
<tr>
<td>Std Error</td>
<td>9,245</td>
<td>15,544</td>
</tr>
<tr>
<td>Std Dev.</td>
<td>29,235</td>
<td>49,155</td>
</tr>
<tr>
<td>Variance</td>
<td>854,667</td>
<td>2416,222</td>
</tr>
<tr>
<td>Coeff. Var.</td>
<td>243,622</td>
<td>175,554</td>
</tr>
<tr>
<td>25th Percentile</td>
<td>1,750</td>
<td>2,000</td>
</tr>
<tr>
<td>75th Percentile</td>
<td>6,250</td>
<td>46,000</td>
</tr>
<tr>
<td>Minimum</td>
<td>1,000</td>
<td>2,000</td>
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<tr>
<td>Maximum</td>
<td>95,000</td>
<td>137,000</td>
</tr>
<tr>
<td>Range</td>
<td>94,000</td>
<td>135,000</td>
</tr>
<tr>
<td>Count</td>
<td>10,000</td>
<td>10,000</td>
</tr>
</tbody>
</table>

Figure A1: Indicate (a) cattle grazing on the paddocks of tailings dumps (b) drinking from the Fleurhof Dam in the Central Rand
Figure A2: Indicates (a) efflorescent crusts on the surface near a tailings dump in the Central Rand. (b) different colourations of efflorescent crusts showing the different elements contained in them. The whitish crusts are predominantly gypsum; the yellow ones predominantly contain uranium; and the brownish ones contain mainly iron.

Figure A3: A newspaper clip shows children playing in mine contaminated water in a pond adjacent to a tailings dump (picture by James Oatway)
Figure A4: indicate frequency distribution of As in sample A and B

Figure A5: Indicates linear descriptive of statistical analysis of As in both samples A and B
Figure A6: indicate frequency distribution of Cu in sample A and B

Figure A7: Indicates linear descriptive of statistical analysis of Cu in both samples A and B
Figure A8: indicate frequency distribution of Pb in sample A and B

Figure A9: Indicates linear descriptive of statistical analysis of Pb in both samples A and B
Figure A10: Indicate frequency distribution of Zn in sample A and B

Figure A11: Indicates linear descriptive of statistical analysis of Zn in both samples A and B