

**Assessment of heavy metal contamination in soils around Krugersdorp
mining area, Johannesburg, South Africa.**

by

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Declaration

I, **Thabani Armstrong Mkhize** declare that:

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As the candidate's Supervisor I agree to the submission of this dissertation.

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Abstract

The mining industry remains a driving force of the South African economy, making a significant contribution to economic activity, job creation and foreign exchange earnings. However, in the process of mining and mineral production, millions of tons of waste are produced making this sector the potential source of air, soil and water pollution. There are more than 270 waste dumps known as tailing dams in the Witwatersrand Basin alone, covering 400 square kilometres in surface area (Oelofse et al., 2007, Rosner, 1999). Poor management of these tailing dams and waste rock dumps lead to uncontrolled release of acid mine drainage that in some cases cause soil degradation and water contamination around these sites. The aim of this study was to assess pollution levels of As, Cd, Cu, Cr, Pb, Hg, Ni and Zn in soils from the mining area of Krugersdorp and to compare them with the South African and international standards. The geo-accumulation index (I_{geo}), the single ecological risk factor (E_r), and potential risk index were calculated to assess the degree of contamination by these metals in soils.

Thirty one soil samples were collected from eleven different sites around the Krugersdorp area. Twenty three were collected from the Krugersdorp Game Reserve, four from private farmland, two from Mintails Gold Mine and two from Rand Uranium Mine. All collected samples were properly marked and identified by their sampling locations using a Global Positioning System (GPS). Samples were acid digested using microwave oven according to U.S EPA 3052B protocols and analysed for arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni) and zinc (Zn) with Inductively Coupled Plasma – Optical Emission Spectrometry technique (ICP-OES).

The concentration levels of heavy metals in soils were in the range of 4.1-155.5 mg/kg for As, 0.1-0.7 mg/kg for Cd, 13.4-119.1 mg/kg for Cu, 54.0-147.0 mg/kg for Cr, 0.02-1.36 mg/kg for Hg, 24.1-168.9 mg/kg for Ni, 5.5-82.5 mg/kg for Pb, and 12.5-641.0 mg/kg for Zn. Three sampled sites (KS7, KS8 and KS10) recorded high contamination levels by heavy metal compared with the relevant South African standard and other international standards. The geo-accumulation index assessment revealed that the soils vary between uncontaminated to the extreme pollution soil category. The ecological risk factor (E_r) mean values of As, Cd, Cr, Pb and Zn revealed low ecological risk to soils, while values for Cu and Hg indicated moderate ecological risk. Ni values indicate a considerable ecological risk. The potential ecological risk index (RI) values of three sites (KS1, KS5, and KS9) indicated low ecological risk. RI values for KS3, KS6 and KS11 showed that these sites posed moderate ecological risk. Considerable ecological risk was displayed by sites KS2, KS4 and KS8, while RI values of site KS7 and 10 displayed very high ecological risk. These results indicate that the anthropogenic mining activities have polluted the area with heavy metals. As a result a series of recommendation are forwarded in order to rehabilitate the quality of the soils affected.

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Abbreviations and Acronyms

AAS	Atomic Absorption Spectrometer
UN	United Nations
IOL	Independent Online
AMD	Acid Mine Drainage
GDP	Gross Domestic Product
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer.
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometer
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
GDACE	Gauteng Department of Agriculture, Conservation and Environment
USDA	United States Department of Agriculture
SSV	Soil Screening Value
DEA	Department of Environmental Affairs
MCLM	Mogale City Local Municipality
UNISA	University of South Africa
USEPA	United States Environmental Protection Agency
GPS	Global Positioning System
CRM	Certified Reference Material
IGCP	International Geoscience Programme
PTFE	Polytetrafluoroethylene
CCD	Charge - Coupled Device
UV	Ultraviolet

Chapter 1

1.1 Introduction

This chapter presents the background, the problem statement, area of study and motivation for the study. The aim and objectives are also outlined and lastly, the outline of the study is provided.

1.2 Background of the study

The term heavy metal is broadly used by researchers to denote chemical elements with metallic or semi-metallic (metalloids) properties that have been associated with contamination and potential toxicity or ecotoxicity (Duffus, 2002). Depending on their chemical and physical properties, metals are grouped as toxic, hazardous, trace, heavy or semi-metal (Roberts et al., 2005). Other researchers use the term to describe metals of high density or high atomic weight, wherever their source (Saif et al., 2017). Most authors refer to metals that are associated with contamination and potential toxicity as heavy metals (Duffus, 2002, Roberts et al., 2005). These metals occur naturally from the weathering of metal – containing rocks and volcanic eruptions, but have also been introduced to the environment by human activities such as mining and industrial emissions (Brevic and Burgess, 2013, McGrath et al., 1995). Several of these metals, including copper (Cu), iron (Fe), zinc (Zn), and calcium (Ca) are essential micronutrients for plants, animals and humans. However, cadmium (Cd) and mercury (Hg) have no known biological function or beneficial use and have caused concern about their potential health threat to humans and wildlife (He et al., 2005, Vrhovnik et al., 2013). Some of these metals and metalloids are significant pollutants and pose toxicity threat to both humans and animals even in small amounts. Heavy metals are non-biodegradable and persistent environmental pollutants which can accumulate to toxic levels. (Kumar et al., 2007).

Many heavy metals are natural components of the environment, however their presence in high concentration may pose environmental threat. Soil in particular, is not only regarded as a major sink for contaminants released into the environment by human activities, but also acts as a natural buffer controlling the movement and accumulation of chemical elements and substances in the environment (Kabata-Pendias and Pendias, 1985). Heavy metals coming from different sources may ultimately reach the surface soil, and their destiny relies on soil properties since these control the mobility, bioavailability, and residence time of contaminants (Eugenio et al., 2018). The persistence of contaminants in soil is much longer than in other components of the biosphere, and contamination of soil, especially by heavy metals appears to be virtually permanent (Kabata-Pendias and Pendias, 1985).

Environmental pollution by heavy metals is very common in areas of mining and on abandoned mine sites. Mining activity generate huge quantities of waste materials, which in most cases contain high concentration of toxic minerals containing elements such as arsenic, mercury, chromium, lead, and cadmium (Andras et al., 2012). According to Oelofse et al., in 2007, Rosner, T, 1999, South Africa has produced about 468 million tonnes of mineral waste per annum. Half of the 468 million tons produced come from gold mine waste, making it the largest producer of toxic waste. (Oelofse et al., 2007, Rosner, 1999) further mentioned that there are more than 270 waste dumps known as tailing waste facilities in the Witwatersrand Basin alone, covering 400 square kilometres of land. The tailing facilities contain waste rock, pyrite, and elevated heavy metals including radioactive uranium and are a main source of acid mine drainage (AMD) generation. Mountains of tailing dumps have also been a feature of the landscape in the area and have been discharging polluted water to the environment for decades (McCarthy, 2011).

In 2009, the Auditor general reported that there are 5906 officially listed abandoned mines, most of which are gold mines. The report further stated that out of the 5906 only 5 have been rehabilitated (Auditor-General, 2009). The mine, Blyvooruitzicht Gold is 80 kilometers west of Johannesburg, started operation in 1937 until 2013 when it shut down. Between 2007 and 2008, thousands of tons of pond tailing materials spilled from the mine on four occasions, some of the waste washings onto the nearby residential area (Olalde, 2015).

The location of a number of informal settlements near the tailing dumps therefore, are becoming a permanent environmental problem for the ecosystem and human health.

1.3 Statement of the problem

In South Africa, the first mine started operations in 1852 and since then this industrial sector has been the mainstay of the country's economy (Casey, 2019). South Africa is an important world producer of minerals and mineral products, and these products are sourced mostly from open-cast, underground, alluvial as well as offshore mining. "An estimated 7% direct contribution was made to GDP by mining in 2006 and R140 billion to South African exports in the same year, although when multipliers are accounted for the Gross Domestic Product contribution is closer to 40%" (UN, 2015). However, together with this economic development, mining caused a series of environmental and social problems in the country resulting in historical pollution in different areas. One of the areas that has sparked public interest is Krugersdorp. In recent years contamination of soil, air and water from historical mines has reached "catastrophic" levels according to non-governmental organisations. In particular, mining waste dumps on the surface as well as acid mine drainage from underground are sources of heavy metals polluting the soil, water and the air on which people and the communities are relying (Lieverink, 2019). In this context, this study aims to provide information on the level of heavy metals in soil from around Krugersdorp.

1.4 Rationale

There is not enough information on heavy metals loading in ecosystems around mine spoils and tailings dams in the Krugersdorp region in the Gauteng Province of South Africa. It is well documented that decades of alluvial gold mining has significantly changed the background levels of these elements in different environmental media, in a way that is adversely affecting the water resources, soil and food crops. The extent of pollution by heavy metals and the possible detrimental effects on the health of the nearby communities have not been documented. The present research is thus of critical importance in bridging these knowledge gaps as well as helping towards the development of practical solutions to the problems of heavy metal contamination from mining and the recommendation of appropriate land remediation strategies.

1.5 Aims and Objectives

The primary aim of this research is to report on the presence and toxicological and environmental risks of heavy metals in the mining area of Krugersdorp and to determine their level of concentration. To achieve this aim it was important to consider the following objectives:

- To measure heavy metal contents in different soils linked to different land uses in the vicinity of areas potentially affected by mining around Krugersdorp.
- To evaluate the contamination status of soils around Krugersdorp with respect to national and international guidelines.
- To study the release from mine sites and tailing dumps of heavy metals and their geochemical transportation.
- To assess the potential pollution and contamination of soils and the ecological and agricultural risks due to heavy metals in the soils in the Krugersdorp area.
- To recommend interventions for the management and improvement of potentially polluted soils.

1.6 Research Question

To achieve the aim and objectives, this study will attempt to answer the following research question:

To what extent is the soil in the Krugersdorp region contaminated by heavy metals from mining activities and what are the impacts of this contamination?

1.7 Methodological Approach

The study area is located in Krugersdorp, Mogale City on the West Rand, Gauteng Province, South Africa. A total of thirty-one samples were collected and sampling locations were recorded at each sampling point with GPS. The sampling was carried out in selected sites of four different locations namely: Krugersdorp Game Reserve (23 samples), smallholdings (4 samples), Rand Uranium Mine (2 samples), and Mintails Mogale Gold (2 samples). The samples were oven dried, crushed and prepared (including digestion). A blank was similarly

prepared without soil sample. The method of standard addition technique was used in the determination of amount of each element in the sample. Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) was then used to measure the concentration of eight elements (As, Cd, Cu, Cr, Hg, Pb, Ni and Zn). Standard reference material was also measured to have a check on the accuracy of the results.

In the second part of the study, the level of soil contamination assessment due to heavy metals was undertaken. This assessment was based on the chemical laboratory results obtained. The results obtained were then compared to national and international standards. The analysis of the risk of these elements in soils and implications for the surrounding communities and the terrestrial and aquatic ecosystems was undertaken. Implications for the contamination observed were discussed and recommendations for mitigation measures were forwarded.

1.8 Dissertation Outline

This dissertation is composed of six chapters and the contents of each chapter are briefly described below.

Chapter One Introduction and background: Consists of background of study, statement of the problem, rationale, research question, and aims and objectives of the study.

Chapter Two Literature review: Provides a comprehensive literature review that begins with an overview of different mining methods. This is followed by a brief discussion on mining activities and their environmental impacts, the sources of heavy metals pollutants and the behaviour of heavy metals in soils are also discussed. Finally, previous work on heavy metal in soils is covered and standards for heavy metal pollution are presented.

Chapter Three Study area: Gives a description of the study area and it is divided into six sections. These are location of study, climate, vegetation, geology, soils and hydrology features.

Chapter Four Methodology: Presents the key research methodologies and procedures used to conduct the study. Field sampling, sample preparation and the ICP-OES technique are fully outlined in this chapter. A justification of these methodologies and challenges encountered using these methods are presented. The methodology for analysing the contamination of soils is also included.

Chapter Five Results and discussion: Results for the soil elemental analysis and geo-accumulation index as well as risk assessment index are tabulated and discussed in this chapter. Implications for the surrounding communities and ecosystems are also discussed.

Chapter Six Conclusions and recommendations: The conclusions from the study are presented and recommendations based on these conclusions are also included.

Chapter 2

Literature Review

2.1 Introduction

The purpose of this chapter is to provide the theoretical framework to the study and introduce important concepts underpinning this research. As such this chapter presents an overview of different mining methods and how heavy metals are generated and transported to various environment media, with emphasis on soils. The impact of heavy metals on humans, wildlife and environment is also briefly discussed as well as standards used for heavy metal soil contamination. The chapter concludes with a brief background of the similar work done by other researchers on this topic.

2.2 Soils and Mining

Soil is an important part of the entire cycle of nature, it provides the base for vegetation and overall a habitat for microorganisms, plants and animals. It acts as a storage place for nutrients and it also serves a barrier to the migration of metals into neighbouring media (Schwedt, 2001). Together with air, water and radiation from the sun, soil provides for the growth of crops and trees which produce food, fibre for clothes, and shelter for vertebrates and invertebrates (Wild, 1993). Depending on the adopted appropriate mining technology and mining method, mining activity can cause significant environmental damage. Mining can result in the destruction of habitat, land degradation, ecosystem disruption and accumulation of toxic waste dumps in and around mining regions. Mining may as well cause the pollution of ground and surface waters with toxic chemicals and metals. Hence, the selected mining method should have minimum environmental and public health impact, because mining operations and the ecosystem are in direct relationship (Namin et al., 2011).

2.3 Overview of Mining Methods

Mining is regarded as the extraction of the ore from the earth in order to recover the valuable minerals (Warhurst and Noronha, 1999). Mining operations include, development, metallurgical extraction, and mineral processing. In the development stage, the deposit is open to gain access to the ore deposits. (Nilsson and Randhem, 2008). Mineral processing also known as beneficiation aims at improving the economic value of the ore by physically separating (grinding, crushing, flotation) and concentrating (solvent extraction, precipitation) the ore mineral(s). Finally, metallurgical extraction which produces a refined metal out of the mineral concentrate (Fashola et al., 2016). All three principal activities of the mining industry produce waste (solid, liquid or gaseous).

The key activities of the mine operation phase are illustrated in Figure 2.1

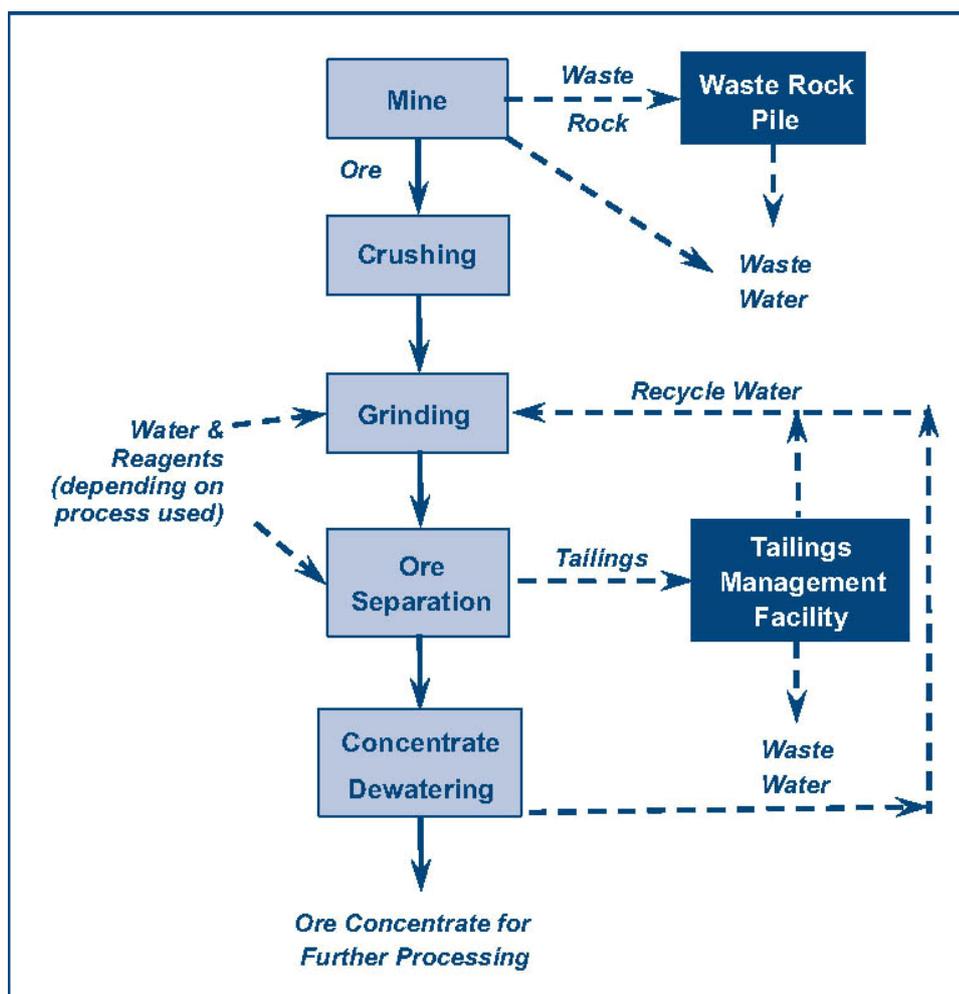


Figure 2.1: Typical Activities of the Mine Operations Phase (Oswer, 2012)

Mining is broadly divided into surface and underground mining, both of them have impacts on the surrounding soils and ecosystems depending on these soils (McLemore, 2008). The choice of mining method depends mainly on the type of the mineral deposit, safety and environmental concerns, and depth of the ore body (GDACE, 2008).

2.3.1 Surface Mining

Surface mining is used when the mineral is close to the surface of the earth. As the word suggests, surface mining involves digging the rock containing valuable mineral out from the surface leaving a hole or pit and high volume of material. The rocks are then blasted into smaller pieces using explosives, loaded onto huge trucks and taken away for further crushing and processing. Stripping, open-pit and quarrying are common surface mining techniques. Surface operations require large areas of land to use as waste dumps to store overburden products. (GDACE, 2008).

- Open pit mining: A surface pit is excavated using a sequence of horizontal benches. The barren rock material covering the ore body is drilled, loaded with explosives and blasted to break it up for removal. The whole ore body is mined with no overburden being put back into the void. The waste rock and waste from ore processing is dumped onto a surface waste dump (Darling, 2011).
- Quarrying: This is a kind of open pit mine from which rock for various purposes are excavated, including construction and road building. Depending on the type of rock, drill and blast techniques are also used.
- Strip mining: The method is commonly used when the ore body is very close to the surface, such as coal seams. Top soil is removed and blasted rocks (overburden) are removed to uncover the ore. Like other types of surface mining, strip mining has a disruptive effect on the environment (Marcus, 1997).

Figure 2.2 illustrates a typical open pit mining operation.



Figure 2.2: An open pit mine with benches (gettyimages.com/open-pit-mine).

2.3.2. Underground Mining

Sometimes the ore deposit is too deep for surface mining, then underground mining is considered. The structure of the mine depends upon the nature of the deposit (Manahan, 1994). Commonly, the ore will be drilled and

blasted, and then transported to the surface to be refined into a high-grade concentrate (Tatiya, 2005). Underground mines are divided into two type, hard rock and soft rock, depending on the type of rock the minerals are hosted in. Hard rock mining technique tend to be deep, and is used to excavate ore containing metals such as gold, silver, copper, iron, zinc, nickel, lead, and tin, also ores containing gems such as diamonds. Soft rock mines are predominantly coal, metalliferous shale, potash, and salt mines. In this case, the rock and the minerals are softer and easier to break up (Yang et al., 2018).

There is a wide range of underground mining methods and a few are described in the following paragraphs.

- Longwall mining: In this method, mineral is mined in blocks. The immediate overburden is then allowed to subside, filling the void created by excavation. The main environmental concerns with this mining method relate to the lack of roof support following mining. The impacts include subsidence of the surface, causing damage to surface structures, and the subsequent dewatering of aquifers in this zone (Hamrin, 2008).
- Room and pillar mining: In this method, the ore is dug out and pillars are left in place to support the roof while the rooms are mined out. When the ore bed is completely extracted, these pillars can be reclaimed (Hamrin, 2008).
- Cut and fill mining: Method in which ore is removed in horizontal slices, starting from a bottom undercut and moving upwards. Ore is drilled, blasted and removed from the stope. The resulting void after ore has been removed, is backfilled with tailings. The fill serves to support the walls and provide a working platform for equipment when the next slice is mined (Hamrin, 2008).

From the impacts enumerated above it is obvious that surface and underground mining has important impacts for the soils in the mining area. Not only are soils affected directly by being removed, but the quality of the surrounding soils is also affected by the excavated waste rock dumped. In many cases these waste rocks contain heavy metals which are brought to the surface, exposed to oxidative chemical reactions and enter the ecosystem affecting in the end people in the area.

2.4 Mining and the Environment

Mining is a destructive industry, both surface and underground mining operations can have a severe environmental impact including air, water and soil pollution and effect on wildlife population that lives nearby due to the generation of heavy metals (Kitula, 2006). Mining change the natural topography of the area thus increasing the potential for soil erosion and reduced agricultural productivity (Wantzen and Mol, 2013). Mining may also have profound impact on nearby water sources. Pumping and discharging untreated mine waste water may introduce high levels of heavy metals and other toxic materials to surface waters and soils (Borrvalho, 2014).

Mining operation has been the backbone in the economic and social development in many countries for centuries (Aryee, 2001, Battellino, 2010). In many developing countries, mineral resources account for a significant proportion of economic revenue, in terms of export income. In South Africa, the mining sector remains one of the major contributors of export revenue and its importance to the economy cannot not be underestimated (Mangondo, 2006). However, mining operations have unintentionally disturbed the crucial environmental balance established by nature over a thousands of years. The extent and nature of impacts can be significant, not only during the operational period but also long after the mining activities have ceased. The negative impact by mining activities are related to the release of toxic materials from mine sites into the environmental media such as air, soil and water. Mine waste pose a great threat not just because of their volume, but because some of them may contain significant amounts of minerals that may impact negatively on local environment (Lottermoser, 2010).

Research has shown that mining activity considerably alters the background levels of these toxic materials in the various environmental media, in a way that is adversely affecting the resources of water, soil and food crops (Navarro et al., 2008, Lim et al., 2008, Naicker et al., 2003, Baruah and Khare, 2010). The extent of the impact varies widely, depending on the ore being mined, the kind of technology and extraction methods used in mining, the on-site processing of minerals, the method used to dispose of toxic waste material and the nature of the local environment (Bell and Genske, 2001).

Complete removal of unwanted material lying above the mineral deposit always occurs during surface mining, which affects the top soil, surface vegetation and surface water, disturbing all land use activities. If the mining operation extends to depths below the water table, it will eventually affect the near-surface groundwater (GDACE, 2008). The dust and particles from blasting and drilling operations, waste rock dumps, and land disturbed by mining are a significant source of air pollution (Squillace, 1990). Heavy vehicles used also result to elevated dust and noise pollutions.

Wildlife, domestic animals and humans often suffer severely as a result of surface mining and a resultant pollution. Some species that depend on plants and trees for food are either starved to death or forced to re-locate from the area of the mine itself. Many animal species fail to adapt to disruptions caused by mining activities (Squillace, 1990). Surface and underground mining also exposes nearby water bodies to toxic chemicals and heavy metals that can alter the pH and leach into the surrounding environment. Such pollution can severely upset the delicate balance of aquatic ecosystem, thereby lowering population density. In case where some species survive, hazardous materials can drastically reduce breeding and growth rates (Beder, 1996)

The largest environmental impacts of an underground mine typically fall into three categories: subsidence, groundwater, and atmospheric emission. Subsidence is defined as the sinking of surface above mine workings as a result of the material setting into the voids created by mineral extraction (Nieto, 2011). The uncontrolled release of mine water is of concern as the water is associated with elevated amounts of salts and toxic metals. Acid generating rock of multiple types of excavated ore, waste, or overlying strata may produce acid mine drainage, which is regarded as the principal source of pollution of the fresh water (Namin et al., 2011).

2.5 Heavy metals in contaminated soils.

The term “soil contamination” is often used by many communities as a synonym of soil pollution. The definition of the two terms has since been formalised. Contamination happens when the amount of a substance or chemical is elevated above the natural background level but is not necessarily harmful. While, soil pollution refers to the presence of a substance or chemical at above the background concentration, often due to human activities, and has an adverse effect on any non-targeted living organisms (Eugenio et al., 2018). In other words, all pollutants are contaminants, but not all contaminants are pollutants (Chapman, 2007).

Heavy metal contaminants are introduced into soil, water and air from both natural and anthropogenic sources. The main natural sources include rock weathering, volcanic eruptions and forest fires. While inputs from natural sources constitute a sizable amount of heavy metals in soils, the contribution from anthropogenic (man-made) sources for many heavy metals is several times that from natural sources (Adriano, 1986). The major man-made sources of heavy metal input to soils are from ferrous and non-ferrous metal mining, smelting metallurgical industries, industrial and municipal waste disposal, corruptions of metals in use, agriculture, fossil fuel combustion, and sport and leisure activities (Hooda, 2010). Mining activities stand out when it comes to heavy metal production and deposition, mainly due to the generation of huge quantities of residues rich in contaminants. During mining operations, substantial amounts of waste of all form (soil, water or air), is dumped or released into nearby land, resulting in soil. Studies of heavy metal distribution in ecosystems show that soil close to industrial and mining sites contain much greater levels of contaminants (Asio, 2009, Karbassi et al., 2014, Bempah and Ewusi, 2016, Ding et al., 2016).

2.5.1 Mine waste

The term “waste”, which is in common use, refers to material which has little or no commercial value. The soil and rocks which are the by-products of ore extraction and processing are considered to be waste materials. While quantities of waste materials produced are significantly high, not all waste is considered harmful. However, waste contains substantial amount of minerals, and if it is poor managed, it may pose a large risk to environment and health of local communities (Muller, 2009). Waste is generated in different stages of the mining process and it continues long after mining has stopped. During hard rock mining, extraction is the first

step in the production stage that involves removal of ore from earth to the surface, which results in in generation of large volume of solid waste. The characteristics and volume of waste material produced differs depending on the mineral being mined and the mining method used (Politis et al., 2017). Waste rock, tailings, and acid mine drainage stand out with the largest volume.

2.5.2 Waste Rock

Waste rock is a by-product for mining that is excavated for the purpose of reaching the ore and it contains minerals in concentrations considered too low to be extracted at a profit (Hasan et al., 2019). Waste rock is often stored in large dumps or heaps on the mine site to minimise transport (Servida et al., 2012). Waste rock dumps differ in chemical compositions and properties and are a product of blasting, crushing and grinding of mineral bearing rock. (Moyle and Causey, 2001). The concentration of minerals in the non-economical waste rock is often higher than the natural background which may pose significant human health hazards and environmental damage (Brown and Calas, 2011). Heavy metals in the waste rock can be mobilised through the natural weathering process as well as by leaching, facilitated by precipitation and water runoff. Heavy metals, available in the fine particles of the waste material can be dispersed around by wind blowing and water erosion, and the elements released will depend on the composition of the waste rock (Pathania, 2016).

2.5.3 Tailings

The extraction process is never efficient to reclaim all reusable reagents and chemicals. The unrecoverable and uneconomic metals, minerals, chemical reagents, and process water are discharged, usually as water-based slurry called tailings, to isolated impoundments. However, due to poor management practices, these impoundments frequently fail, releasing large amounts of tailings into natural environment (Kossoff et al., 2014, Mileusnic et al., 2014). Tailings often contain significant levels of toxic materials, and are generally considered an environment threat (Ritcey, 1989). The properties and chemical composition of tailings also depends on nature of the ore and the extraction method used (Fashola et al., 2016). The ore may be extracted from mineral using either chemicals or water and gravity. If chemical extraction is used, the mineral rock is ground into small particles. Hence, tailing particles will be very small (Eugenio et al., 2018).



Figure 2.3: A tailings storage facility at a gold mine (Muller, 2009)

2.5.4 Acid mine drainage (AMD)

Of the three forms of mine wastes, acid mine drainage is regarded as the single most serious environmental threat. The threat AMD poses stems from its nature, high acidity and elevated toxic metals (Oelofse and Turton, 2008). The acidic nature of AMD derives from water-mineral chemical interactions that occur in defunct underground mine workings and in rock waste piles, sand dumps and tailing dams on surface. When sulphur-bearing minerals, pyrite (FeS_2) in particular, in mine waste (tailings and waste rock) are exposed to oxygen and water, sulphuric acid is produced. The acid will then further dissolve metals and other contaminants from mined materials (Simate and Ndlovu, 2014, Name and Sheridan, 2014). AMD does not only pollute surface and groundwater, but also responsible for soil degradation, ecosystem and wildlife disruption. The growing concerns about AMD is about its persistence and potential environmental threat long after mining operation have ceased. (Oelofse and Turton, 2008).

Figure 2.4 illustrates surface water quality degradation.



Figure 2.4: Acid mine drainage in the West Rand, Gauteng (Coetzee et al., 2010)

2.6 Heavy metals and their effects

Metals are natural component of the environment. Their presence in soil does not suggest contamination. The amount of metals in uncontaminated soil is mainly influenced by the parent material from which the soil was formed (McLean and Bledsoe, 1992). However, due to mining activities natural concentrations are usually increased (see previous section) leading to widespread environmental impacts including health and impacts for the surrounding communities. The following sections present these impacts with reference to each heavy metal investigated in this study.

2.6.1 Arsenic (As)

Arsenic is a metalloid present naturally in soils in very low concentrations. Arsenic occurs in a variety of mineral bearing rock, the most common of which is arsenopyrite (FeSAs). It is recognised as a notorious poison and one of the world's environmental hazards. The discharge of arsenic-containing tailings, originating from gold mining activities are of concern as potential source of air, water and soil pollution (Sodhi et al., 2019). Arsenic can exist in different valency states (-3, 0, +3, +5). The inorganic trivalent and pentavalent are the most common forms. Trivalent is highly toxic while organic forms are less harmful to health. (Fashola et al., 2016). Arsenic is mainly transported in the environment by water. The anions arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}) are the

most common mobile forms of arsenic. Arsenic compounds are readily soluble, however, arsenic migration is limited due to the strongly adsorption to soils. The speciation determines the toxicity of the soluble arsenic. Sodium arsenate (Na_3AsO_4) and arsenic trioxide (As_2O_3) are most toxic (Kabata-Pendias and Pendias, 1985). The arsenic in soil is both additive and cumulative, which may lead to arsenic being taken up by plants to the edible parts. The extent of exposure results in a broad array of effects on human health, ranging from skin ailment to neurological effects, cancers of lung, liver and kidney, and thereby to death (Ravenscroft et al., 2009).

2.6.2 Mercury (Hg)

Mercury occurs in metamorphic and sedimentary rocks in low quantities. It also exists naturally in top soils through atmospheric depositions due to volatilisation of element mercury by soils and plants and its emission by volcanic activity (Brevic and Burgess, 2013). However, considerable amounts of mercury that are found in water, soils and streams are as a results of human activities, particularly, gold extraction (Fashola et al., 2016). Given the mobility of mercury in the environment and its ability to bioaccumulate in food chains, knowledge of the occurrence of mercury in various environmental media is critical to understanding.

Mercury exists in three forms in the environment, elemental, organic and inorganic, with each form having its profile of toxicity. (i) Elemental mercury vaporises at room temperature, so that increase in temperature increases the risk of inhalation (Langford and Ferner, 1999). (ii) Methylmercury is the most widespread form of organic mercury found in the environment. All forms of mercury are toxic to humans and virtually all other forms of life. The organic form is mobile and soluble in soil making it the most harmful to human health (Zahir et al., 2005). Humans are mainly exposed to his form of mercury through the diet. However, depending on concentration, air and water can contribute greatly to the intake (iii) Inorganic mercury compounds exist in two ionic forms, mercury (I) and mercury (II). The latter tends to be more stable in the environment, and therefore dominate. Inorganic mercury salts are more hazardous than elementary mercury if ingested orally, due to their water solubility (Langford and Ferner, 1999)

2.6.3 Cadmium (Cd)

Cadmium is a relatively rare metal and it is found in low concentrations in earth's crust and in soils (Kabata-Pendias and Pendias, 1985). The major sources of cadmium pollution come from industrial and municipal wastes. Bitala et al (2009) reported high concentration levels of cadmium in soil samples taken near the gold mine in Tanzania. Depending on the soil characteristics and soil acidity, cadmium is relatively soluble in water. It is therefore more mobile, bioavailable, and tend to bioaccumulate (Kabata-Pendias and Pendias, 1985). Cadmium is not known for any biological functions and the effects of its toxicity to humans and environment has been widely reported. The history of cadmium health effects goes as far back as 1950s where skeletal

damage (itai-itai, where Cd replaces calcium in the bone), a disease associated with cadmium poisoning was first reported in Japan. The exposure was as a result of water contaminated by cadmium used for irrigation of local rice fields. Cadmium is also known for disturbing enzyme activities in both plants and humans; damages to kidneys and, lungs (if inhaled). (Järup, 2003, Naja and Volesky, 2009, Wuana and Okieimen, 2011). The toxicity of cadmium to both humans and environments is attributed to its longevity and accumulation in human organs after eating contaminated food, and the fact that its toxicological properties may occur at low exposure levels (Wuana and Okieimen, 2011).

2.6.4 Lead (Pb)

Lead is one of the first metals used by man. Its natural content is inherited from the parent rock. It is usually found in nature as Pb (II) and it combines with other elements such as sulphur and oxygen in a variety of minerals. However, due to industrial activities, it is most likely to find elevated concentrations of this metal in surface soils. (Kabata-Pendias and Pendias, 1985). Through industrial emissions, car exhausts (when leaded petrol is used), mining and smelting, lead finds its way to air, water and surface soil. These activities may lead to accumulation, redistribution and sometimes transforming the metal to chemical forms that are more available and more toxic to man (Goyer, 1990). Lead is the least mobile when compared to other metals and this is supported by the relatively low concentration in natural soil solutions and the fact that lead is concentrated near the surface soil, very little moving down the soil profile. (Kabata-Pendias and Pendias, 1985). Although lead serves no biological benefit to humans, it is present in tissues and organs of all mammals (Förstner and Wittmann, 2012). Food and water are the pathways of human exposure. The absorption depends on factors such as age and physiological status. Once the metal is absorbed in the body, it is distributed to the soft tissues like kidney, liver, heart, brain and, the bulk of lead accumulates in the skeleton (Naja and Volesky, 2009). Lead, at high levels, can severely affect central nervous system. Lead poisoning in young children in particular may lead to mental retardation and semi or permanent brain damage (Naja and Volesky, 2009).

2.6.5 Chromium (Cr)

In nature, chromium occurs in minerals such as chromite, with oxidation states ranging from Cr (III) and Cr (VI). Chromium (VI) is relatively stable in air water, but it is reduced to the trivalent state, when it comes into contact with organic ligands in soil and water. As a result, this form of chromium dominates in soils (WHO, 1988, Shanker et al., 2005). On the other hand, Cr (III) is stable and relatively immobile in soil. The increase in chromium content in surface soil due to pollution from various sources, including gold mine tailings increases the risk of its bioavailability, biomobility and thus toxicity (Shanker et al., 2005, Abdul-Wahab and Marikar, 2012). Cr (III) plays an important role to humans in potentiating the action of insulin in carbohydrates, lipids and protein metabolism. However, chromium is a toxic nonessential element to plants. In

humans, environmental exposure to Cr (VI) - containing compounds may result in renal damage, allergy and asthma, nose ulcers, severe respiratory and neurological effects, depending on the exposure and the extent of the exposure (Tchounwou et al., 2012).

2.6.6 Nickel (Ni)

Nickel occurs naturally in various mineral forms and its concentration level in soil depends on the parent rocks and soil forming processes. Human activities have significantly increased nickel contents in soils through discharge of industrial and municipality waste. Application of some phosphate fertilizers are also important sources on nickel into the environment as pollutants (Kabata-Pendias and Pendias, 1985). Elevated nickel concentrations in mine wastes in South Africa and Tanzania were reported by (Matshusa et al., 2012; Bitala et al., 2009). Human exposure to nickel compounds occurs mainly through inhalation and ingestion. Large amounts consumption of fruits and vegetables grown in nickel-polluted soil may be acutely harmful to both humans and animals. The toxic effects of nickel result from its ability to replace other essential metals ions, such as Fe in proteins and enzymes (Orisakwe et al., 2012). Excessive exposure to nickel may produce pathological effects such as lung fibrosis and cancer of respiratory tract. (Cempel and Nickel, 2006)

2.6.7 Zinc (Zn)

Zinc occurs in abundance in the natural environment, not as zinc metal but in the divalent state Zn (II). The most common zinc ore mineral is sphalerite (ZnS) (Alloway, 2008). Zinc is an essential dietary nutrient with a vital role in the immune system and production of enzyme in the body. Its primary anthropogenic addition to the environment comes mine tailings, zinc production and processing, and the use of fertilisers. Sources of exposure and toxicity to zinc include ingestion, inhalation, and through skin (Wuana and Okieimen, 2011). In sediment and soils, zinc may form complex with other minerals depending on soil properties. The solubility of zinc in soil depends on these properties and consequently, its bioavailable form and potential toxicity to organism (Takáč et al., 2009).

2.6.8 Copper (Cu)

Copper is found naturally in the earth's crust in mafic and intermediate rocks. Copper forms several easily soluble minerals, of which sulphides are the most common and therefore, which makes it more mobile compared to heavy metals (Kabata-Pendias and Pendias, 1985). Copper is released to the environment due natural weathering of soil and emissions from industries and domestic waste disposals (WHO, 1998). Copper, just like Zinc is an essential element for plants, microorganisms, animals and humans. Man and animals rely on plants for the supply of copper, therefore adequate amount of copper in plants is essential. The deficiency of copper in plants can affect physiological processes and therefore plant production and in human it may result in

neurological dysfunction (Crichton, 2016). Copper ions are essential as co-factors by certain enzymes such as oxidases and hydroxylases, but are toxic when present in large amounts (Yruela, 2005).

2.7 Behavior of heavy metals in soils

The concentrations of elements in the Earth's crust and soils differ greatly between rock types, and because soil properties are influenced by their parent material, concentration in the soils also vary greatly. However, besides the geological parent material composition, the natural concentrations of trace elements present in soils depend other factors predominating during the process of soil formation (Sillanpaa, 1979). The mobility of heavy metals, their bioavailability and toxicity is determined by their chemical form (include free metal ions and metal complexes) in that particular environment (Giuliano et al., 2007, Singh et al., 2011). The biological activity, for example, toxicity or non-toxicity of an element can vary widely from compound to compound, and it is important to know if and how toxic forms are produced in the biological systems. Because of differences in the important physical properties of volatility and solubility for various chemical forms of an element, one or several may dominate physical exchanges in global geochemical cycles. Similarly, chemical properties may strongly affect rates of decomposition and rates of local transportation of various elements (Natusch and Hopke, 1983). Heavy metals may exist in soil environment in either the solid phase or the aqueous soil solution. In the solid phase they are immobile and harmless, while in aqueous phase are mobile and toxic (Ogundiran and Osibanjo, 2009). Once heavy metals are released into a particular environment, they are not necessarily confined to that condition. For instance, metals (in the soluble form) introduced to soil, may filter through the soil profile reaching the ground water or taken up and by plants, animals and man.

The potential risk of toxicity of heavy metals is not determined by the total metal concentration, but by the form that the metal is in (Wuana and Okieimen, 2011). For instance, the oxidation state of metal in soil may influence its toxicity, bioavailability and mobility. Metals such as Cr, Cu and As have more than one oxidation state, which can affect their behaviour in soil. For example, reduced Cr (III) is relatively immobile in soils and nontoxic while oxidised Cr (VI) is much more mobile and extremely toxic to humans. In the case of arsenic, trivalent (As (III)) is more toxic than pentavalent (As (V)) (Naja and Volesky, 2009). Again, Pb in the form of lead phosphate $Pb_3(PO_4)_2$ present no risk to the environment, however, lead nitrate $Pb(NO_3)_2$ is soluble and mobile in soil (McLean and Bledsoe, 1992). Table 2.1 presents the dominant soil species for the heavy metal pollutants considered in this research.

Table 2.1: Dominant soil species for soil metal pollutants (Eugenio et al., 2018)

Element	Chemical symbol	Dominant soil species
Arsenic	As	AsO_3^{2-} , AsO_4^{3-}
Cadmium	Cd	Cd^{2+}
Chromium	Cr	Cr^{3+} , CrO_4^{2-}
Copper	Cu	Cu^{2+}
Mercury	Hg	Hg^{2+} , $(\text{CH}_3)_2\text{Hg}$
Nickel	Ni	Ni^{2+}
Lead	Pb	Pb^{2+}
Zinc	Zn	Zn^{2+}

2.8 Pollution indices

Soil has been recognised as one of the vital environmental components for the survival of the human race. In recent years, there has been an increase in drive to formulate criteria to use to determine soil quality and to develop pollution indices (Nortcliff, 2002). Pollution indices are powerful tools and monitor for the overall assessment of the degree of soil contamination with heavy metals. The indices are used establish whether soil contamination with heavy metals is as a result of natural processes or human activities (Caeiro et al., 2005). The following two major indices were used in the study to assess the extent of pollution in the soil:

Geo-accumulation index (I_{geo}): This method is one of the first indices, formally developed by Muller in 1969, to assess metals in sediments and later improved by Hakanson in 1980 (Kowalska et al., 2018). Since then, this index has been used by many researchers (Huang et al., 2017, Barbieri et al., 2015, Li et al., 2014) to assess level of metal contamination in soils, The index compares current soil quality with background levels.

Potential ecological risk index: This method was developed by the Swedish scholar Lars Hakanson in 1980. This index is used to assess risk related to the accumulation of one or all determined metals in soil. The index also considers the ecological and environmental effects with toxicology of metals, giving a estimation of the potential risk of metal

2.9 Soil quality standards

The knowledge of background amount of metal is crucial for recognition and management of soil pollution. This kind of knowledge will shed light on reference values of uncontaminated soil that can be expected long before contamination by human activity, and yet this knowledge is not available in most countries. (Baize,

2000). Only by deciding on appropriate reference values is it possible to both to assess the possibility of contamination and to develop guidelines for maximum threshold levels of heavy metals in soils (Herselman, 2007).

Soil quality standards provide the permitted concentration limit of soil pollutant to indicate when changes in soil properties or qualities become harmful. This condition may lead to loss of soil productivity resulting from soil degradation (USDA, 2001). Declines in the quality of water and air are fairly easy to assess, water is normally evaluated in terms of suitable to drink and suitable to breathe with air. Whereas with soil, the decline in quality may not be easily noticed and or experienced immediately (Nortcliff, 2002). Another problem with soil is that changes in the external condition do not immediately change the soil. In most cases, soil is able to cushion the effects of potentially harmful conditions, at least to some threshold (Nortcliff, 2002).

2.9.1 Soil screening values

Soil Screening Values (SSVs) are general quality standards embraced by many countries to regulate the management of contaminated land (Duarte et al., 2017). They are normally expressed in the form of concentration baseline of contaminants, above which certain actions are recommended or enforced. The implications of exceeding the soil SSVs differ according to national regulatory frameworks. The term used to refer to “soil screening values” differ from country to country, so as the baseline values. Terms used range from “trigger values” to “reference values”, “target values”, “intervention values”, “clean up values”, “cut-off values”, and many others (Carlson, 2007). SSVs are used as initial screening tools to support the assessment of potential risks to soil quality and wildlife from the presence of chemicals.

In South Africa, a legislative framework exist to address most environmental needs. The National Framework for the Management of Contaminated Land (2010) is a tool and a reference providing standards and for the remediation activities in compliance with Section 7(2)(d) of the Waste Act (2008) pertaining to the remediation of contaminated land and soil quality. The framework is based on international standard and best practices (DEA, 2010). Soil Screening Values are listed in Table 2.2.

Table 2.2: Soil quality standards for Metals and Metalloids (mg/kg) of different countries:

Metals/metalloids	South Africa ¹ All land uses protective of the water resources	South Africa ¹ Informal residential	Netherlands ²	Australia ³	Canada ⁴
Arsenic (As)	5.8	23	29	20	12
Cadmium (Cd)	7.5	15	0.8	2	10
Chromium (Cr III)	46000	46000	-	-	-
Chromium (Cr VI)	6.5	6.5	100	50	64
Copper (Cu)	16	1100	36	100	63
Lead (Pb)	20	110	85	100	140
Mercury (Hg)	0.93	1.0	0.3	2	6.6
Nickel (Ni)	91	620	35	70	50
Zinc(Zn)	240	9200	140	200	200

1. Framework for the management of contaminated land 2010, Department of Environmental Affairs, Republic of South Africa.

2. Dutch Target and Intervention Values 2000, Ministry of Housing, Netherlands.

3. (Zarcinas et al., 2004)

4. (Provoost et al., 2006)

As can be noted from the above table, the soil quality standards for South Africa for informal residential use are on average higher for As, Cd, Cu, Ni and Zn and lower for Hg and Cr. When the protection of water resources (in a water stressed country like South Africa) is taken into account the local screening values are much lower as compared to the international ones for all heavy metals considered. This shows that no universal standards are possible for soils and each country adapts these standards for their own needs, reflecting the particularities of each country and the targets designed to be protect (humans and strategic resources).

2.10 Previous studies on heavy metals pollution due to mining

A number of authors and working groups, locally and internationally investigated the impact of mining activities on soil quality. A summary of the previous work and related studies conducted is presented below:

- The study on “Heavy metal contamination in the vicinity of the Daduk (gold, silver, lead and zinc) mine in Korea” was conducted by Lee, Chon and Jung (2001). The authors found significant levels of the elements in waters and sediments up to more the 3 km downstream from the mining site, especially cadmium and zinc. Enriched concentrations of heavy metals were also found in various plants grown in the vicinity of the mining area.

- Naicker, Cukrowska, and McCarthy (2002) did a study on "Acid mine drainage arising from gold mining activity in Johannesburg, South Africa". The study revealed that ground water, surface water and the soil within the mining district are heavily contaminated by heavy metals.
- Getaneh and Alemayehu (2006) conducted a study on "Metal contamination of the environment by pacer and primary gold mining in the Adola region of Southern Ethiopia". Their study showed that the sediments samples taken from the gold mining site had high levels of Ni, Cr, Cu, V, Zn, Pb and As.
- Navarro (2008) and others conducted a "Case study on abandoned mine sites in Spain as a source of contamination by heavy metals". Heavy metal content of lead, zinc, arsenic, iron and manganese were found very high and lower for cadmium.
- Lim and others (2008) conducted a study on "Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au–Ag mine in Korea". Samples of tailing and soil were collected around the mine site. Arsenic concentration and other heavy metals were found to be higher than the permissible level.
- "Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt" was conducted by Rashed (2010). The results reveal that the concentration of heavy metals such as chromium, zinc, lead manganese, mercury and silver in soil, decreases with the increase in the distance away from the tailing. The conclusion about the overall results, however, suggest that the soil and the plant near the gold mine tailings were highly toxic, such that plants and soil were not suitable for grazing or agriculture.
- Candeias (2011) and others conducted a study on "Soil contamination by potentially toxic elements around Aljustrel (Portugal) mining area." The authors found that a high concentration of toxic metals (mainly As, Cu, Cd, Zn and Pb) in soil samples were well above the values recommended for, European Union and Portugal.
- The study on "Assessment of agricultural soil contamination by potentially toxic metals dispersed from improperly disposed tailings (Kombat mine) in Namibia" was conducted by Mileusnic (2013) and others. Out of the seven elements analysed, copper and lead showed significantly high concentrations in soil.
- "A review of soil heavy metal pollution from selected mines in China" was conducted by Zhiyuan (2013) and others. The results obtained demonstrate that soils surrounding the mining areas are severely polluted by heavy metals (As, Cd, Cr Cu, Ni, Pb, Zn and Hg) emitted from mining activities. The authors concluded that the soil polluted by heavy metals pose a high carcinogenic and non-carcinogenic to the public, especially those living in the vicinity of the polluted region.

- Angelovicova and Fazekasova (2014) “Determined contamination of soil and water environment by heavy metals in a former mining area of Rudnany (Slovakia).” Very high, and well above limit values of copper and mercury were obtained in the sampled soils. Also, limit values for lead and zinc were exceeded at some localities.
- The study conducted by Ngure (2014) and others in Kenya on “Concentration levels of heavy metals from gold mining in Lake Victoria revealed high levels of Cd, Pb, As and Hg on soil samples”. After comparing reference soil samples taken 70 km from the mining area, researchers concluded that high levels of toxic elements are as a result of the mining activities.
- Jianbo (2015) and others conducted a study on “Distribution and migration of heavy metals in soils and crops affected by acid mine drainage in the area of Guangdong in China”. The data obtained showed that the local soils were heavily polluted with copper, cadmium and arsenic. The concentration of arsenic and lead in the rice grains, vegetable leaves, and sugarcane roots were found to be above permissible limits. The authors concluded that high levels of heavy metals in soil and crops suggests that the local soil is not suitable for cultivating the food crops.
- The study conducted by Mthunzi (2015) and others in Vanderbijlpark in South Africa on “Evaluation of heavy metal pollution in soil” revealed high level of lead (Pb). The study concluded that pollution in the area is mainly due to the anthropogenic activities and also that the concentration of the studied metals decreases with the distance from the industrial area.
- Olobatoke and Mathuthu (2016) conducted a study on “Heavy metals in soil in the tailing dam vicinity of an old gold mine in Johannesburg” and reported high values for the heavy metals in soil samples. According to the authors, Cr, Zn, As, Mn, Cu, Pb, Ni, Sr and Hg were all above South African Soil Quality Standard.
- The study conducted by Kamunda and others (2016) on “Health Risk Assessment of Heavy Metals in Soils from Witwatersrand Gold Mining Basin, South Africa” found that the concentration of both arsenic and chromium were far above the South African standard and other international countries.
- “Concentration and pollution assessment of heavy metals within surface sediments of the Raohe Basin, China” was conducted by Wei, J and others (2019). The obtained results show that the majority of metal values far exceeded their corresponding background values.
- The study conducted by Hwan and Yoonjin Lee (2020) on “Environmental pollution from heavy metals in soil and stream near an abandoned mine in Korea” The results obtained in the study showed high levels of As, Cu, Ni and Zn. Cd was found to be 6.0 time more than the soil counterplan in Korea.

The studies summarised in the previous paragraphs show that in different mining locations heavy metals pollution was of concern and in the majority of the case studies presented the standards for soils were exceeded. Different heavy metals had different concentrations in soils leading to different environmental impacts for nearby areas. The high levels of metals due to mining in plants, with consequences for agriculture, grazing and ecosystems need to be emphasised due to the serious toxicological effects which are extended beyond soils and impact different land uses and natural ecosystems.

2.11 Summary

This chapter discussed the literature on mining and soil contamination due to mining and heavy metals. The major heavy metals present on mining sites were discussed in detail as well as their impacts and standards. Previous studies on heavy metal contamination due to mining have been undertaken, locally and internationally, as presented in Section 2.8. However, no such study was performed in the Krugersdorp area and this research aims to fill that gap. Therefore, this research aims to provide this information. It is important for the Krugersdorp communities to know the impacts of living nearby historical mines and the heavy metal contamination load of soils due to these mines. This study should be seen as the first step towards mitigating potential impacts, aiming towards a healthier environment for the people and ecosystems in this area.

Chapter 3

Study area

3.1 Introduction

The aim of this chapter is to give a geographical and historical background to the area in which the research was undertaken. Therefore, this chapter presents the general impacts of mining in the larger West Rand area in which Krugersdrop is situated, as well as, the specific details in the area in which samples of soils were collected. In particular, details on the specific study area are included in terms of location, climate, vegetation, physiography, geology, soils and hydrology, as to give a better understanding of the sampling location and the associated interpretation of the results.

3.2 The West Rand – Historical perspective on mining and pollution in the area

The study area where samples were collected is situated in Krugersdrop which is part of West Rand District, South Africa. After more than hundred years of mining, the Witwatersrand goldfields (of which West Rand is part) region is left with tonnes of waste, known as tailings dumps, and network of abandoned mine shafts, which are gradually filling with water (Pratt, 2011). Most of these tailing dumps are from underground mining, however, some of them are also from surface mining, as the area has a long association with this activity. Krugersdorp, in Mogale City Local Municipality (MCLM) on the West Rand basin, came into existence in 1887 when gold was found in the area and, is essentially a mining town with a number of active and abandoned mines. Currently (2019), gold, manganese, and iron are all mined in the area, in surface and underground operations. Active underground mines keep water pumps going to prevent flooding. However, as the running cost escalate, mine cease to operate and owners will eventually shut down the pump and leave. The uncontrolled decant of the polluted water commences once the mine fill completely (McCarthy, 2011). The challenge with this water is that it is not localised and limited at the source, but may find its way to main water streams and be transported to distances places (Jamal et al., 1991). In addition, to the contaminated water transporting pollution (including heavy metals) also wind is transporting dust particle from mine waste dumps and with increased urbanisation these dumps are becoming inhabited by informal dwellers unaware of the possible contamination. This could have severe negative impacts on the surrounding communities and the wider environment. (Adler and Rascher, 2007). One such example is the case study investigated in the area.

In Krugersdorp, in the Gauteng province, Harmony Gold (now Rand Uranium) ceased operation, but pumps continued to operate to keep the water levels down until two years later (early 2002) when they were switched off. (Pratt, 2011). In August 2002, the West Rand basin sparked significant public interest following the news of acid mine water decant from this underground mine. *“A rising acid tide”* (Mail and Guardian, 12 April 2005); *“Acid river rocks the Cradle of Humankind”* (Independent online, 14 April 2005); and *“Krugersdorp basin polluted by acid water”* (News 24, 27 May 2014) were some of the headlines in the print media. This incident started when polluted water from this old mine shaft, began to flow out on to the surface, first through a borehole just before the Krugersdorp Game Reserve, and later through an old vent shaft pushed open by the force of water. The polluted water found its way into Tweelopiespruit river immediately upstream of the Krugersdorp Game Reserve (Oelofse and Turton, 2008). Concerns have also been raised by the downstream landowners and farmers in the area who rely entirely on groundwater for potable and business water use (Hobbs and Cobbing, 2007). There are also downstream impacts, in the Sterkfontein informal settlement and Krugersdorp Brickworks hostel dwellers who have little to no access to piped water, and are thus very vulnerable.

Figure 3.1 shows the uncontrolled decant of acid mine drainage from Mintails Mogale Gold property, near Krugersdorp.



Figure 3.1: Decant from an abandoned shaft (Turton, 2016)

Kagiso, the township of more than a quarter of a million residents located close to Krugersdorp, is a low-income settlement with limited access to facilities and services. Located in Krugersdorp, is the Tudor Shaft informal settlement with more than 197 families. The settlement was formed as a temporal shelter for people who became destitute after mining companies stopped their operations. It is built on the mine tailing soil and the land is contaminated by heavy metals due to the past mining activities (Krugersdorpnews, 2015, Njinga and Tshivhase,

2016). There is a strong possibility that the inhabitants are exposed to radiation and dust inhalation from the mine tailings (see figure 3.2). Fruits and vegetables grown on the land could be contaminated and pose a health risk. Wildlife population in the Krugersdorp Game Reserve rely heavily on water from the dams and vegetation for survival which could be contaminated by heavy metals and radioactive materials.



Figure 3.2

- A. Mining communities in the Witwatersrand goldfields are often built near, or on top of, tailings piles. Picture: Stephan du Toit, 2011
- B. Children from Tudor Shaft in Krugersdorp play amid sand that activists fear contains toxic levels of heavy metals. Picture: Paballo Thekiso

3.3 Location of study area

Krugersdorp (26° 6'0"S; 27° 46'0"E) is a small town with about 300 000 residences, located at the Western side of Gauteng Province of South Africa. Krugersdorp and other two local municipalities, Westonaria and Randfontein, were part of West Rand District Municipality. According to census 1996, the population growth is around 2.1 % a year and the rate of unemployment is close to 27 %. The place came into existence in 1887 when first after the discovery of first gold and it got its name after Paul Kruger. Mining has not stopped in the area although ore deposits are depleted. Krugersdorp has since been integrated with other small towns into greater Mogale City Local Municipality (MCLM).

Mogale City is diverse, with urban areas reflecting different levels of development and concentration of informal settlements in the other area. Mine dumps, which make up the boundary between the marginalised areas and former white areas are a threat. Over the years, these mine dumps have, altered the character of the landscape. The three broad geographical and sectorial segments in the city are: The urban region in the east, the rural smallholdings dominated by agriculture in the central zone and the natural habitat areas to the west. The

agricultural hub was formed to encourage small farming, where vegetables such as broccoli, lettuce, red cabbage, cauliflower and spinach may be produced and be sold to local market (Urban-Econ, 2010).

Figure 3.3 presents a simplified map of the study area (from where samples were collected) in the context of the larger Krugersdorp area. As can be seen from this map the main decant point from which acid mine drainage is originating as well as the open cast mining site and the slime dams are situated upstream and surface water as well as ground water is flowing from these mining areas towards the Krugersdorp Game Reserve and adjoining farms, as well as the boundaries of the Krugersdorp urban settlements. More details on the precise location of the sampling points are presented in Chapter 4.

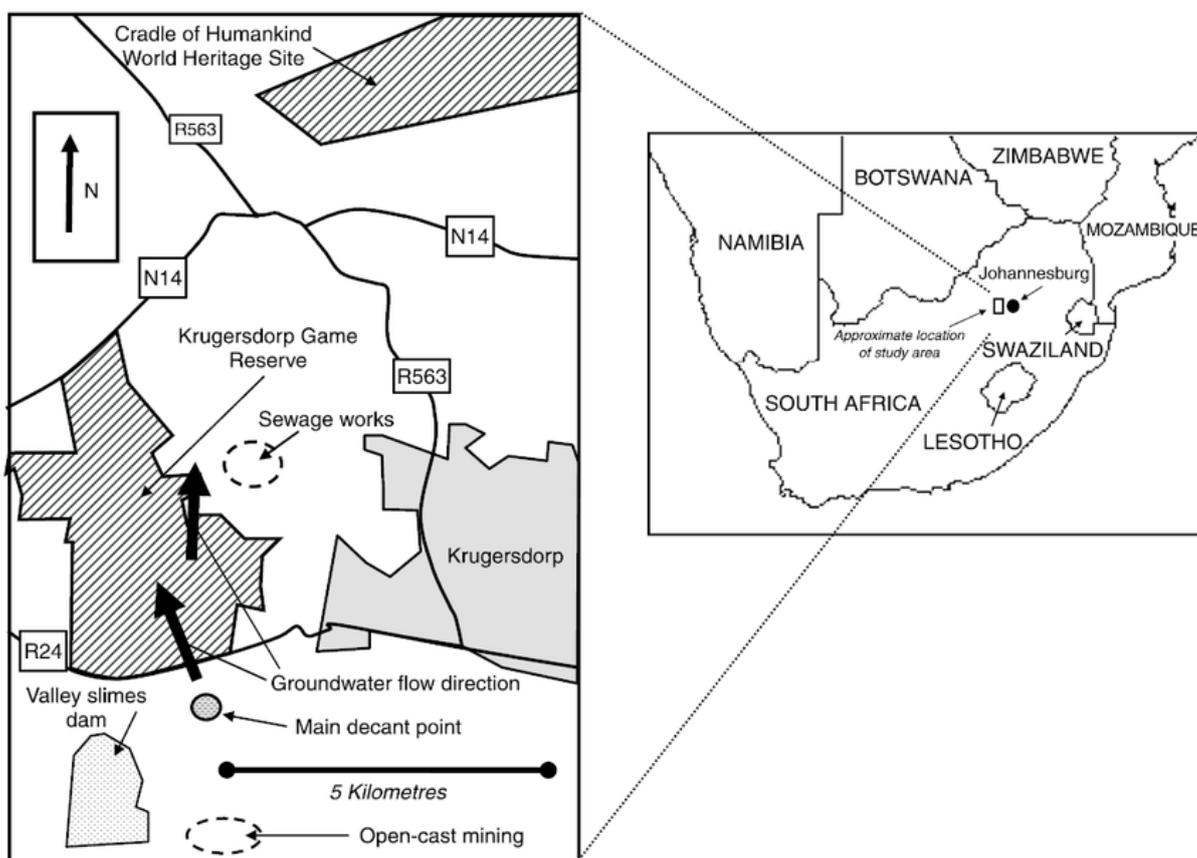


Figure 3.3: Sketch map of the study area.

3.4 Climate

The climate in Krugersdorp is sub-humid and warm. About 759 mm of precipitation falls annually. In winter there is much less rainfall than in summer, with most precipitation falling in January, averaging 142 mm. The driest month is August with only 7 mm of rainfall. The average annual temperature in Krugersdorp 15.6 °C; the

warmest month of the year being January with average of 20.1 °C. In June, the average temperature is 9.1 °C, is the lowest average temperature of the whole year.

3.5 Vegetation

Vegetation of the study area comprises generally flat or slightly undulating grassland- mainly grasses and shrubs, with few scattered small trees in places. Remnants of native vegetation, shrubby and thorn-tree species occur mainly on hilly ground where there has been no disturbance from mining, urbanisation or clearing for cultivation.

3.6 Geology

Geologically the study area can be classified under the Transvaal and the Witwatersrand Supergroups. The West Rand goldfield is hosted by rocks of the Witwatersrand Supergroup forming a syncline which plunges to the southeast. This Supergroup is directly linked to the mineral deposits found in the area. Stratigraphically lower strata of the West Rand Group surround the triangle of Central Rand Group rocks that are overlain in parts by younger strata of Ventersdorp and Transvaal Supergroups. These units overlay uncomfortably the Archaean basement which outcrops to the north and west of Mogale City. The geological feature of the Transvaal Supergroup is the band of dolomite, which gave rise to the local caves, and that is running through the study area. Therefore, the Transvaal Supergroup is dominated by dolomites and the Witwatersrand Supergroup conglomerates consists of quartz pebbles, typically 1-3 cm in diameter, set in a matrix of quartz sand. The matrix typically contains about 3 percent pyrite, and lesser amounts of a wide variety of other sulphide and oxide minerals, in addition to gold. Some 70 different ore minerals have been identified in the conglomerates, the most abundant of which, after pyrite, are uraninite (UO₂), brannerite (UO₃Ti₂O₄), arsenopyrite (FeAsS), cobaltite (CoAsS), galena (PbS), pyrrhotite (FeS), gersdorffite (NiAsS) and chromite (FeCr₂O₄) (Naicker et al., 2003). More details of the geological location of these two supergroups in relation to the sampling points for this study are included in Section 4.4 and in particular in Figure 4.4.

3.7 Soils

The soil of the study area are mainly reddish brown to red, and range in the texture from clayey silt through silty clay to loam. At very few sites, sandy clay was also encountered, but the sand content was always in small percent. The soils are mainly light textured and differ in depth from less than 400 mm to 1.2 m deep. Although Mogale city is earmarked as the agricultural hub in Gauteng, however, the area has not reach its full potential. Some of the areas with moderate or high potential soils for cultivation have been developed (such as the area immediately to the west of Krugersdorp), or lie within mining areas (Paterson, 2008).

3.8 Acid mine drainage (AMD) and the hydrology of the Krugersdorp Game Reserve area

Acid mine water drainage from the West Rand Mining basin first appeared in August 2002. Initial estimates of the decant volume ranged between 7 and 12 million litres per day (Cobbing et al., 2008). The acid mine drainage is collected and contained in various holding facilities, from where it is pumped to a treatment plant for neutralisation and iron removal. The Krugersdorp Game Reserve lies immediately downslope (see figure 3.3) of the location of acid mine drainage coming largely from the Mintails Gold mine settings. Other potential receptors of acid mine drainage include downstream land owners and local farmers that entirely rely on ground water for clean and business use. It is proper, therefore, that the hydrological environment which hosts mine water decant and is the potential recipient of acid mine drainage, is understood in regard to all potential impacts and contaminant migration pathways (Hobbs, 2015). This is required to formulate the most suitable management solution within the framework of technical, socio-economic and governance challenges faced by industry and regulators; hence the rationale for this current investigation.

3.9 Summary

In summary this chapter presents a historical and geographical perspective of the study area, and this perspective is needed to give background to the methodology (in particular sampling) and the interpretation of the results in this research. The study area has a lengthy history of mining (surface and underground) and pollution. With the increase in human population due to urbanisation, these problems are affecting more and more people and the ecosystems they depend upon. Therefore, the sampling and assessment of the level of heavy metals in soils in the area are important in order to assess the local situation and protect humans and local ecosystems and the following chapter presents the methods employed.

Chapter 4

Methodology

4.1 Introduction

This chapter gives background to the methodological framework for this study and the detailed research process followed. As such it presents the analytical instrument, analytical techniques and instrument parameters that were used in the study to generate reliable and reproducible data in terms of the concentration of heavy metals in the collected soil samples. Description of sampling locations in the study area discussed, and the detailed sampling procedures are also outlined. In the second part of this chapter the methodology used to assess the environmental risk, based on the amounts of the heavy metals, is presented. In particular the geo-accumulation index and the ecological risk index are discussed.

4.2 Overall Approach and theoretical background on analytical techniques

4.2.1 Overall research approach

To achieve the aims and objectives of this study and to answer the research question 2 research approaches were used in terms of methodology, namely a quantitative and a qualitative approach. The quantitative approach focused on the determination of the amounts of the metals and the qualitative approach focused on the analysis of these concentrations in the local geographical context and the determination of the risks involved with regard to these concentration and the land use where they occurred.

For qualitative analysis, geo-accumulation index was used to assess the extent of soil contamination with heavy metals in the area. This index helps to assess whether the soil contamination was on account of natural processes or human activities. The analytical technique (ICP-OES) and calibration curve (Standard addition) used for quantitative measurements were selected based on the literature and the history of the sample composition. The eight metals investigated were: arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc. A certified reference material (CRM) was also analysed to validate the analytical method and to assess the quality of the results.

The major steps in this research are listed as follows:

- (i) Undertaking the literature review which informed the entire study (the majority of the literature review is

presented in Chapter 2 and the literature review with regard to analytical technique is presented in Section (4.2.2)

- (ii) Collection of data in the form of samples from the study area (see Section 4.4),
- (ii) Laboratory work and chemical analysis of these samples and the determination of concentrations for heavy metals.
- (iv) Statistical analysis of metal concentrations obtained and the assessment of assumptions, limitations and uncertainty
- (v) Comparison of concentrations obtained with national and international standards and the evaluation of risks
- (vi) Analysis of the concentration of heavy metals by using the geo-accumulation index and the potential ecological risk index
- (vii) Drawing conclusions from results obtained and the writing of the dissertation.

The literature review is important as it informs the entire study and allows for analysis and conclusions to be drawn. Various information relating to the key concepts and the wider study area has been collected and critically reviewed. Sources used to obtain this information were journals, reports, newspapers, books and websites. Various search techniques have been employed to find these sources and search engines like Google Scholar and Science Direct were used. The keywords used in these searches were related to mining activities (internationally and in South Africa), heavy metals in soils, standards for these metals in soils for different land uses, international and national case studies of soil contaminated by metals and mining pollution in the Krugersdorp area and in South Africa in general. In addition to the searches on the concepts involved, other searches involving the methodology to be used were undertaken in order to understand and select appropriate techniques with regard to the analytical methods to be used. This literature review is presented in the following section as it informed the analytical methods used.

4.2.2 Scope and application of analytical techniques

Assessments of the environmental of soils may be done for different reasons according to B.J. Alloway (1995). These include the measurements of elementary contents which provide information about possible changes in soil constituents brought about elution, pollution, plant uptake or agricultural manipulation. The analysis may also be carried out to determine the amount of nutrients available to plants and hence the possibility of their uptake into the food chain of animals and man. The reliability of analytical results is very critical because of the growing interest in environmental pollution control with its heavy reliance on accurate data for enforcement, regulation, and litigation. Equally important is appropriate selection of instrument parameters and careful implementation of corresponding analytical procedures (Gaines, 2011).

The saying "The devil is in the details" best demonstrates the numerous decisions that the researcher will have to make when determining soil quality. Besides the often advanced analytical techniques, soils research also involves acquiring a representative sample, sample pre-treatment as well as compliance to quality control standards (Boone et al., 1999). In practice, each step in the analytical method may contain an error, which may affect reproducibility and accuracy of results.

4.2.3 Sampling and sample preparation

In any chemical analysis, acquiring a representative sample is a crucial step. Sampling is regarded as the most difficult step in the entire analytical process. The significance and accuracy of measurements can be limited by this step. The end product of the sampling step is a quantity of homogenous material weighing of a few grams and whose characteristics represent the entire population (Skoog et al., 1991). It is advisable to collect several sub-samples at each sample location, and then form a composite sample by combining equal portions of individual sub-samples (Darnley, 1995). The use of composite samples provides the advantage of increased representativeness of a measurement. This is based on the assumption that analysis of the composite samples produces a better estimate of the mean concentration. It is necessary to keep the samples into cold storage to prevent or minimise any chemical transformation in the soil (Boone et al., 1999).

The vast majority of analytical measurements are performed on solutions of the analyte. More often than not, one or more pre-treatment steps are necessary. For geochemical analysis, samples need to be fully decomposed by mixed acid digestion before instrumental analysis. This process, quite often requires heating the digestion solution using a hot plate (open vessel system) or a microwave oven (closed vessel system). Microwave digestion has become an increasingly popular technique to dissolve metals since the digestion process can be accomplished in few minutes, rather than the hours it takes with hot plate digestion. The difference in the two methods is that high temperatures and pressures are achieved when using closed vessel microwave unit. Further advantages of microwave digestion are that loss of volatile components of a sample is minimised and contamination by reagents is also drastically minimised since small amounts of reagents are required for digestion. The acid digestion is done to destroy the silicate structure of a siliceous material, thus rendering its cations free for analysis.

4.3 Analytical methods for heavy metals determination

Most techniques for elemental analysis of soil require that all elements are brought into solution before analysis. Several spectroscopic techniques are used for quantitative elemental analysis, but the common ones are flame and ICP spectrometers. Each of these techniques has its own advantages and disadvantages, therefore, a number of factors must be considered when selecting an instrument for analysis. In selecting a technique, the researcher must first define the objective of the analysis, also consider factors such as sample type, sample volume, metals

to be determined, detection limits, precision, accuracy, interference effects and speed of analysis. The instrument settings must be appropriate such that all parameters selected to fit the particular method.

The ICP-OES was used in this study because it offered several advantages, including the ability to measure a large number of elements simultaneously over a wide range of concentrations. This made it possible to determine both high and trace concentrations. The detection limits for most of these elements are generally in the parts per million range (Boss and Fredeen, 2004). Another major advantage, compared to ICP-MS, is that it is less costly and it can handle samples with high dissolved solids. Over the past two decades ICP has become the technique of choice for many researchers who need to measure metal contents in soils, sediments, plants and animal tissues. A study by (Chand and Prasad, 2012) in the analysis of Al, As, Cu, Co, Cr, Fe, Mn, Ni, Pb and Zn in sediments employed the method. (Wei and Yang, 2009), used ICP-OES for the analysis of Cd, Cr, Cu, Pb and Zn in urban soils, urban dusts and agricultural soil. Other researchers who employed the same analytical technique in the analysis of heavy metals include (Bettinelli et al., 2000) who studied Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in soils and sediments, (Nicholson et al., 2003) in their study of Cd, Cu, Cr, Pb, Ni and Zn, and (Bingöl et al., 2010) used the same technique in their study of As, Cd, Cu, Pb and Zn in soft drinks.

4.3.1 ICP-OES technique

ICP-OES finds widespread application as an analytical instrument for both qualitative and quantitative assessment of trace elements present in a sample. Major advantages the ICP-OES enjoys over other elemental analysis techniques include its ability to provide multi-element determinations on a single sample and the large concentration range over which the calibration curves are linear (Skoog et al., 1991). The ICP-OES principle is based on the ability of atoms and ions can absorb enough energy to move electrons from a ground to an excited states. When electrons or ions drop back to the ground state, energy as light (photons) is emitted at specific wavelengths. The amount of light emitted at each wavelength is measured and it is directly proportional to the amount of the element. Figure 4.1 shows a representation of the layout of a typical ICP-OES.

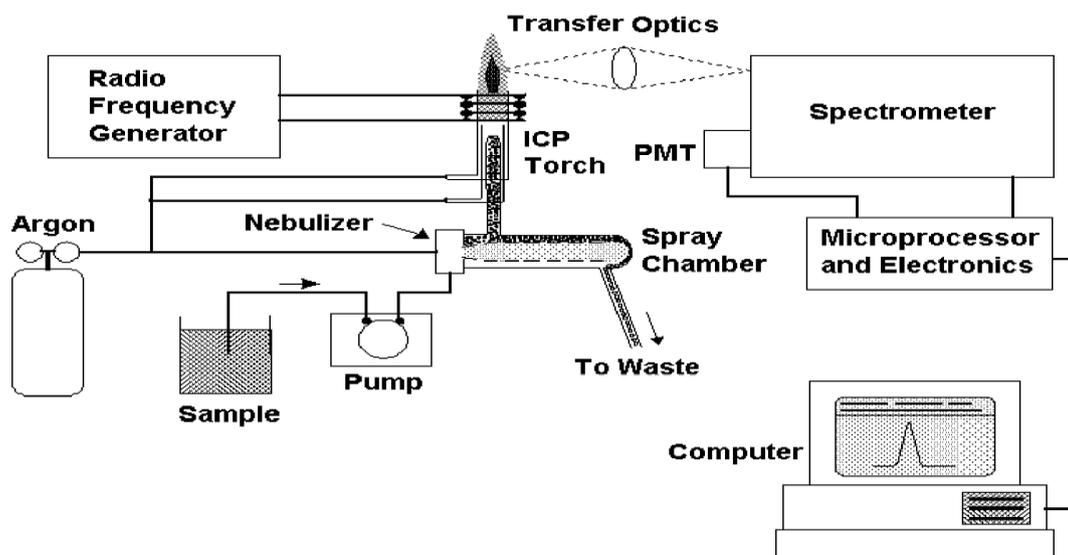


Figure 4.1: A typical ICP-OES instrument layout. Source courtesy of PerkinElmer - Concepts-of-ICP-OES-Booklet

Liquid and gas samples may be introduced directly into the instrument, while solids samples require acid digestion so that the analyte will be present in a solution. The solution containing analyte is aspirated into a nebuliser through a peristaltic pump attached to an automatic sampler. The nebuliser then converts the solution to an aerosol, a very fine sample droplets. The droplets are introduced into the central channel of the argon plasma torch which maintains high atomisation temperature of about 10 000 K. In the plasma torch, the solvent evaporate from the sample, leaving the sample as tiny salt particles. The salt particles are decomposed into discrete molecules, then dissociated into atoms. The excitation and ionisation processes then occur (Boss and Fredeen, 2004). Both the atomic and ionic excited states species may drop back to lower states after releasing light energy at wavelengths that are characteristic to their respective elements. The light intensity emitted by the atoms and ions of a particular element are then measured quantitatively. (Cazes, 2004).

As the excited or ionised atom relax and release a photon, one may or more be obtainable for detection. Based on the nature and sensitivity required, the researcher has to decide on the position of the monochromator entrance with reference to the plasma source. The three positions in which the instrument can be configured are radial, axial and dual view. In a radial design, the plasm is viewed from the side (vertical orientation), providing wide linear range. Axial view (horizontal orientation) offers excellent detection limits due to longer path length it provides. Dual view, provides both viewing options (Tatro, 2016).

ICP technique is relatively free from interferences compared to any of the commonly used flame-based spectroscopic techniques. However, spectral interferences have been found to be most prominent. Also, matrix effects associated with the chemical and physical differences between calibration standards and samples may

affect sample transport and nebulisation (Mokgalaka et al., 2001). The standard addition calibration technique can be used in ICP-OES to compensate for each of these effects.

The ICP-OES methodology used in any analysis will have several common features such as sample preparation, sample introduction, plasma view, method development, and data acquisition. The first decision to be made in developing ICP-OE method is, the elements to be determined. All subsequent procedures rely on this first decision. Next step is sample and standard preparation and it depends on the nature of the samples. Once samples are ready, the sample introduction procedure has to be determined. This step controls the amount of sample that reach plasma. This may increase the sensitivity or impact negatively on plasma stability depending on the nature of the sample. Plasma view is the next setting. There are three possible views to choose from depending on the sensitivity and detection limits: axial, radial or dual. The next step is method development using the computer software. At this point, decisions on the optimum operating conditions of the instrument required, including wavelength selection. The final step is data acquisition and processing. This step involves instrument calibration, emission measurement, integration time, and the number of integrations (Rury, 2016). Once the researcher is satisfied the instrument working conditions, analysis may begin. (Boss and Fredeen, 2004).

4.3.2 Interferences

By definition, an interference is anything that causes change in the intensity of analyte signal. The unexpected interferences may therefore have negative impact to the accuracy of a determination. While all techniques suffer from interferences to some extent, latest instruments however, are designed to minimise interferences (Boss and Fredeen, 2004)

Interferences in elemental analysis are classified as: chemical, physical and spectral. *Chemical interferences* occur when a species is present in the sample matrix that affects the atomization or ionisation of the analyte. Chemical interferences are rare in ICP due to the efficiency of atomisation in the high temperature plasma. *Physical interferences* are as a result of changes in sample physical properties (matrix, density, viscosity) which affect nebulisation process. Physical interferences effects can be overcome by diluting the sample or matrix matching. Standard addition calibration technique is preferred when the sample matrix is completely unknown. Finally, *Spectral interferences* are occur when emission from a species not being analysed overlaps with the emission for the element of interest leading to false results. This can be solved by choosing a different analytical wavelength for the element(s) of interest (Cazes, 2004, Dunnivant and Ginsbach, 2009)

4.3.3 Analytical Wavelength (line)

Selecting an optimal line for each element can be a long and tedious process, however, modern ICP instruments are equipped with a software that makes the task easy and fast. The choice is based on the desired quality of the

results in terms of precision and accuracy (Gaines P.R, 2011). There are several measures to consider when selecting analytical wavelengths. Firstly, it is recommended to select more than one wavelength for each element of interest. Second, if a wide range of concentrations is expected to be encountered in the samples, a high sensitivity wavelength might be chosen along with a low sensitivity wavelength. Third, the wavelength selected must be free from spectral interferences (Ticová et al., 2019, Rury, 2016)

4.3.4 Calibration standard preparation

ICP-OES standards preparation is carried out by dissolving either high purity metals or salts using high purity acids and then diluting to obtain the required concentrations. When preparing multi-element standards from salts, the researcher must ensure that the physical properties of salts are almost the same. Wide range of good quality standards may be purchased from different suppliers which may be diluted as per requirement.

4.3.5 Quality control and quality assurance.

The data acquired is meaningless unless measures have been taken to verify the credibility of the analytical method. The appropriate approach to validate the method is to use suitable reference material. A reference material is a purchased sample that has been tested and given a certified concentration of the analyte with uncertainty. The accuracy and bias of the method is validated by comparing the measured analyte content with the certified (true) value. The composition and concentration of the selected reference material should be a match and the matrices be alike (Geboy and Engle, 2011).

4.3.6 Standard addition technique

The underlying analytical problem with soil analysis is matrix interference which may cause deviations of results from expected content of analyte in a sample, thus, eliminating or overcoming the matrix influence is necessary (Gaines, 2011, Sadler et al., 1997). Method of standard addition is useful when matrix affects the analyte signal (Alloway, 1995). In this method, the sample is spiked known quantities of standard, and the increase in signal is due to the standard. The method of standard addition is widely used in spectroscopy to obtain the results that are more accurate than those obtained using calibration curves (Heltai et al., 2019, Soubhia et al., 2017). The use of this method can overcome a number of method and sample related interferences since the analyte and calibration standards are measured under identical conditions.

A standard addition method may take different forms. One of the most common forms involves addition of several equal volume aliquots of sample to volumetric flasks. Increasing concentrations of the metal analyte of interest are pipetted into each flask beginning at zero. Each solution is then diluted the mark before measurement. Thus, each flask has equal volumes of sample, and a linear increase of known analyte added starting at zero addition in the “blank” flask and ending at the highest analyte concentration. In this case, the standard is subjected to the same environment as the analyte. Instrument measurements are then made on each

of these solutions and corrected to any blank response to yield a net instrument response. In spectrophotometric calibration curve, a plot of instrument response S (measured absorbances) as a function of volume of standards added V_s (or concentration) is a straight line of the form $S = mV_s + b$. Such a standard addition plot is shown in Figure 4.2

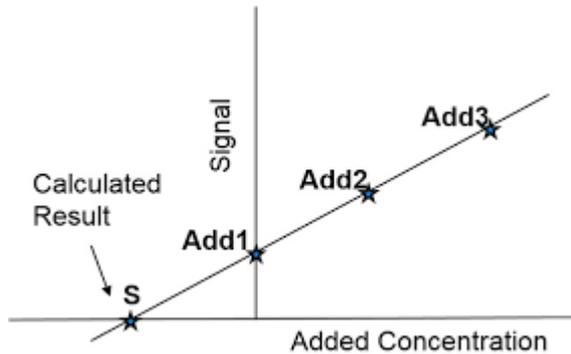


Figure 4.2: Typical standard addition plot.

A least-squares analysis can be used to determine the slope of the line, m and y-intercept, b , the concentration of the analyte can then be calculated or may be determined by extrapolation, and therefore a linear response in the appropriate concentration range is crucial for attain accurate results. The amount of each element is calculated in mg/kg or % mass/mass using the formula below.

$$C_x = \frac{bc_s}{mV_x} \quad (\text{Equation 4.1})$$

Where C_s = Conc. of standard

V_x = Volume of unknown

C_x = Conc. of unknown

4.4 Soil Sampling

The choice of sampling sites and approaches (sampling and handling) were mainly based on the aim of the study, the accessibility to the areas of interest, the proximity from the possible pollution sources and environmental hot spots. A total of thirty one composite soil samples (Table 4.1 and Figure 4.3) were collected. Twenty three samples were collected from the Krugersdorp Game Reserve, four samples from private farmland, and two samples each from Mintails Gold and Rand Uranium underground mines. At each sampling location, a square of 10 meter x 10 meter was established and four samples from each corner (where possible) were

obtained. A 1metre x 1metre pit, at a depth of 40 cm was dug using a shovel, hoe and pick. A 20 L plastic bucket was used to thoroughly mix the soil representing each sampled location. Approximately 250 g composite sample was obtained and carefully packed in a labelled brown paper envelopes, in accordance with IGCP 259 recommendations (Darnley, 1995). All collected samples were appropriately labelled with the sampling locations and identified using a Global Positioning System. Their precise sampling points and sample identities are listed in table 4.1. All samples were taken to the laboratory for further treatment and analysis. The samples were kept in the refrigerator to minimise degradation.



Figure 4.3:

- A. Showing a 1meter x 1meter pit dug to a depth of 40 centimeters
- B. Collected sample is placed in a pre-labelled kraft paper envelope.

Table 4.1: Presents the precise geographical coordinates of the sampling points and their sample identity.

Sample Identity	Latitude	Longitude	Sample Area
KS1A	26° 05'74.5"S	27° 70'94.4"E	Krugersdorp Game Reserve
KS1B	26° 05'72.7"S	27° 70'94.9"E	
KS1C	26° 05'78.3"S	27° 70'92.3"E	
KS1D	26° 05'79.8"S	27° 70'91.2"E	
KS2A	26° 07'55.0"S	27° 70'90.2"E	Krugersdorp Game Reserve
KS2B	26° 07'54.0"S	27° 70'91.7"E	
KS2C	26° 07'57.7"S	27° 70'86.9"E	
KS2D	26° 07'58.8"S	27° 70'85.6"E	
KS3A	26° 08'90.4"S	27° 72'25.6"E	Krugersdorp Game Reserve
KS3B	26° 08'89.2"S	27° 72'27.0"E	
KS3C	26° 08'94.1"S	27° 72'23.4"E	
KS3D	26° 08'95.3"S	27° 72'22.1"E	
KS4A	26° 05'23.0"S	27° 70'62.0"E	Krugersdorp Private Farmland
KS4B	26° 05'24.7"S	27° 70'61.5"E	
KS5A	26° 07'25.3"S	27° 09'70.5"E	Krugersdorp Private Farmland
KS5B	26° 07'17.1"S	27° 69'10.5"E	
KS6A	26° 14'72.7"S	27° 71'66.2"E	Rand Uranium Mine
KS6B	26° 14'72.9"S	27° 71'64.2"E	
KS7A	26° 11'66.0"S	27° 73'12.9"E	Mintails Gold Mine
KS7B	26° 11'65.2"S	27° 73'10.9"E	
KS8A	26° 07'62.4"S	27° 69'95.3"E	Krugersdorp Game Reserve
KS8B	26° 07'63.4"S	27° 69'96.9"E	
KS9A	26° 06'21.1"S	27° 71'07.6"E	Krugersdorp Game Reserve
KS9B	26° 06'23.0"S	27° 71'13.2"E	
KS9C	26° 06'23.0"S	27° 71'13.2"E	
KS9D	26° 06'3.0"S	27° 71'13.2"E	
KS10A	26° 08'45.9"S	27° 70'81.3"E	Krugersdorp Game Reserve
KS11A	26° 08'70.2"S	27° 72'15.4"E	Krugersdorp Game Reserve
KS11B	26° 08'71.6"S	27° 72'14.6"E	
KS11C	26° 08'69.4"S	27° 72'20.0"E	
KS11D	26° 08'70.9"S	27° 72'21.8"E	

Figure 4.4 presents a map of the study area in relation to the local geology and rivers. As can be seen most of the sampling points were located in the Malmani geological areas and these are dominated by dolomites formations. Three of the sampling points (KS6, KS7 and KS11) are above Witwatersrand Supergroup geological strata characterised by quartzite formations linked to the occurrence of mineral deposits and mining activities. The geology of an area is important for the natural, background metal concentration in the soils above and this in turn is important for the calculation of the geo-accumulation index (see Section 4.7.1).

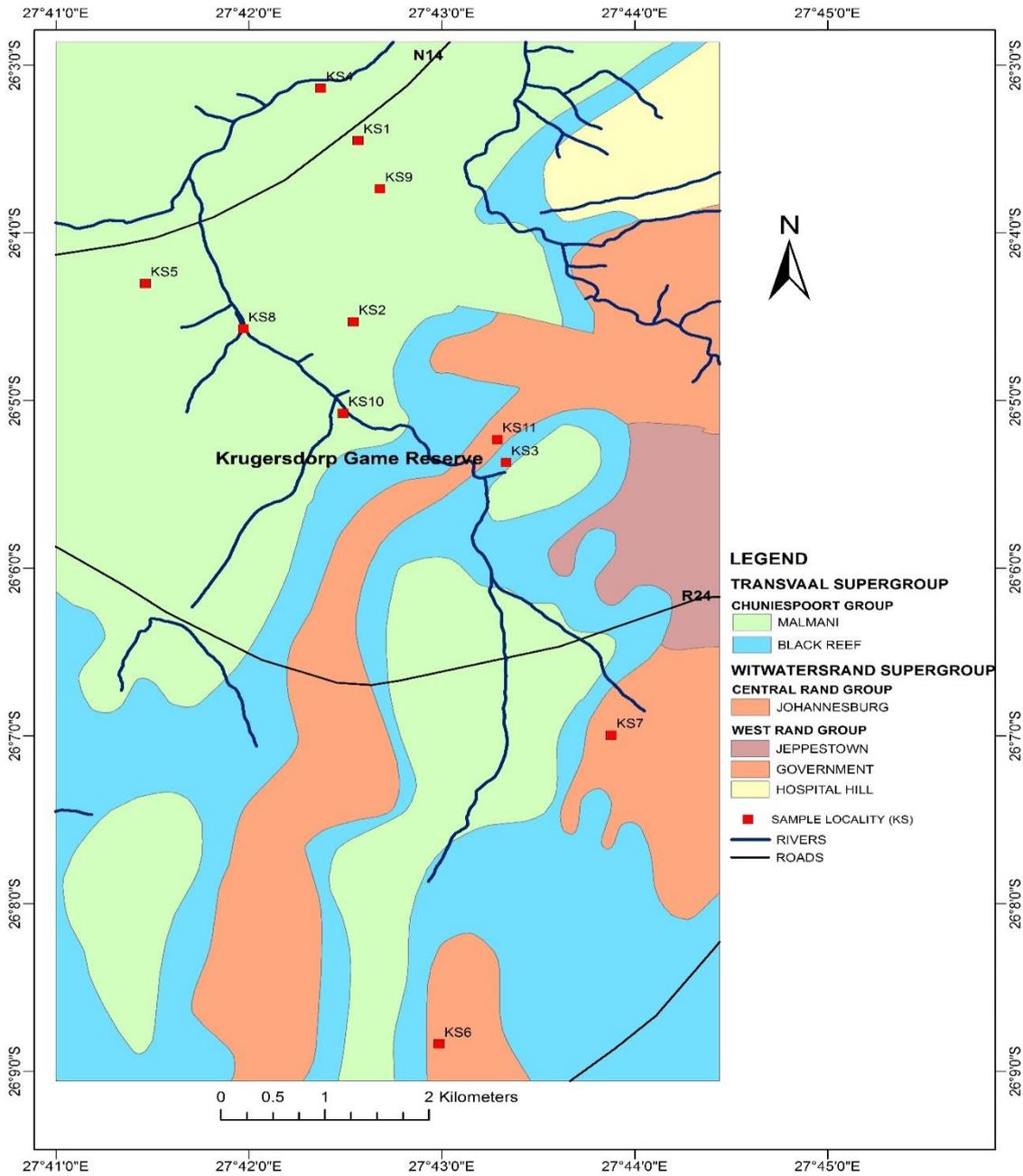


Figure 4.4: The map showing the sampling locations.

4.5 Analytical Methods

4.5.1 Sample Treatment

When soil samples reached the laboratory, they were spread out on a brown paper. Lumps were then broken down using a small hammer and small stones and other non-soil ingredients were hand-picked from each sample. Samples were oven dried at 35°C overnight. The particle size of the dried sample was reduced to pass through a 12-mesh (2 mm) sieve using mortar and pestle. The grinding and sieving procedures also help to homogenise the sample mixture. Precautions were taken to prevent cross contamination during the two procedures by thoroughly cleaning the equipment. The fine, representative subsamples were taken and stored in a clean glass vials and kept in desiccators until digestion and chemical analyses.

4.5.2 Microwave acid digestion

The microwave digestion of soil samples was carried out according to U.S EPA 3052B protocols using an Anton Paar Multiwave 3000 Microwave Digestion System. The purpose of this method is to achieve a complete sample dissolution and with appropriate choice of acid combinations, this is achievable for most matrices. Approximately 1.0 g of each dried and homogenised soil sample was accurately weighed and transferred directly into the PTFE–TFM digestion vessel liners. 12 mL concentrated nitric acid (60% HNO₃, Supelco Ultrapur), 4 mL concentrated hydrochloric acid (30% HCl, Supelco Ultrapur) and 6 mL concentrated hydrofluoric acid (48% HF, Supelco Ultrapur) were added to digestion vessels. The addition of HF helps to break down silicates and minerals in soils and for refractory elements. The smallest possible volume of HF, however, should be used since its corrosive nature may have negative impact on the instrumental and glassware used in the sample preparation step (Sandroni and Smith, 2002).

Each of the sixteen vessels was marked with the sample number. The vessels were sealed and placed into the rotor 6MF100 for microwave digestion. The microwave unit was programmed according to the manufacturer's recommended specification that was similar with the U.S EPA 3052B method. After digestion, the digests were cooled, uncapped and vented in a fume hood. Whatman filter paper No. 41 was used to filter the solution obtained before transferring quantitatively into 100 mL volumetric flasks and filled up to the mark with MilliQ water. The diluted samples were then transferred into plastic bottles for storage until time for analysis. One vessel contained only the acids with no sample was prepared as analytical blank (to monitor reagents contamination) and another contained Certified Reference Material (CRM), DS10 which was treated similarly to the samples. Water and concentrated nitric acid were used to clean the reaction vessels.

Table 4.2: Operation Conditions of Anton Paar Microwave Digester**Steps**

Step	Temperature (°C)	Power (W)	Time
Power ramp		1300	0.500
Power hold		1300	35.00
Cooling	70	0	0.00

Limits

Max. Pressure increase rate	0.3 bar/s
Max. Pressure	40.0 bar
Max. Microwave Power	1300 W
IR Temperature Limit	210 °C
Internal Temperature Limit	240 °C

4.6 Experimental Methodology**4.6.1 Standard Preparation**

10.0 µg/mL (ppm) PerkinElmer multi-element calibration standard (Lot No. CL2-29MKBY1) was used as the stock standard for preparing working standards. 20.00 mL of this standard was pipetted into 100.00 mL volumetric flask and dilute to the mark with MilliQ water to make 2.0 ppm standard solution.

4.6.2 Standard addition Technique

Using a micro-pipette with disposable tips, 500 µL (0.5 mL) of digested soil sample were pipetted into four different 25.00 mL volumetric flasks (previously cleaned with 5% nitric acid) labelled 0, 1, 2 and 3. Exactly 0.00, 200.00, 300.00 and 400.00 µL of the 2.0 ppm standard solution were added to each flask. After dilution to volume with MilliQ, measurements were then made on the ICP-OES spectrometer. Both the sample blank and CRM were also treated and analysed in the same manner.

Table 4.3: Sample preparation

Solution Number	Volume of Sample in mL	Volume of 2 ppm Standard added in mL	Total volume in mL
1	0.5	0.0	25
2	0.5	0.2	25
3	0.5	0.3	25
4	0.5	0.4	25

4.6.3 Instrumentation

All quantification procedures were performed on a simultaneous Agilent 710-ES axial ICP-OES with CCD detector, providing lowest possible detection limits. ICP Expert II software version 1.0 with MultiCal feature was used for instrument operations. The MultiCal feature allows extended linear dynamic range. Auto-sampler was used for sample introduction. Instrument parameters such as proper wavelength selection, sample aerosol formation from the nebuliser, plasma temperature, and emission viewing mode were carefully optimised. The operating parameters of the system are listed in Table 4.3.

Table 4.4: ICP-OES operating parameters

Parameter	Instrument Operating Condition
Power	1.50 KW
Plasma flow	15 L/min
Auxiliary flow	1.50 L/min
Nebulizer flow	0.75 L/min
Pump rate	15 rpm
Replicates	4
Replicate read time	10 sec
Stabilisation delay time	15 sec
Sample uptake delay time	30 sec

4.6.4 Analytical Wavelengths Used

Wavelength calibration for each element was done by aspirating the multi-element standard solution. Based on the quality of emission produced by each element of interest in the solution, a decision was made. The decision was based on the guidelines mentioned on section 4.3.3 of this chapter. The selected analytical wavelengths are listed in appendix A.

4.7 Soil contamination assessment

A soil contamination assessment was performed by comparing heavy metals concentrations determined (by following the methodology from the previous sections) to the concentrations of individual metals and the soil standards (i.e. soil screening values) presented in the literature review (see Section 2.9.1). Through this comparison it was possible to evaluate the degree of contamination for each sampling point and for each metal considered. However, this direct comparison only provided partial information because it cannot provide details about the origins of these heavy metals (i.e. if they originate from rock parent material or if they have been transported into the soil sampled by water action). It also cannot provide details about the cumulative

contamination plume Therefore, the geo-accumulation index (single) was used as well as the ecological risk index (complex).

4.7.1 Geo-accumulation Index

The indices were explained in details in section 2.8 of chapter 2. The assessment of metal contamination levels in soil using these indices requires the knowledge of their natural contents in that particular area. Background concentration of heavy metals in the earth’s crust was used as a reference value implicating pre industrial environment. Background concentrations from South Africa (Herselman, 2007) and Dutch background concentrations were used (VROM, 2000). South African background values were preferred, however for Hg and As Dutch values had to be used because there are no South African values in the literature. This is consistent with other studies in the field (Dao et al., 2010, Darko et al., 2017, Al-Wabel et al., 2017).

In this method, levels of metal pollution are assessed (Table 4.5) based on the increasing numerical values of the index. It is calculated using the following formula:

$$I_{geo} = \log_2 [C_n / 1.5B_n] \quad \text{(Equation 4.2)}$$

where:

C_n = measured concentration of metal in soil

B_n = background value for a metal

The factor 1.5 is used to compensate for possible variations in the background values and small anthropogenic influences.

Table 4.5 presents the degree of metal contamination in soils as defined by Muller (1969). As can be seen from this table the soil quality ranges from uncontaminated to extremely contaminated and 7 levels have been defined.

Table 4.5: The degree of metal contamination (Muller, 1969).

I_{geo} Class	I_{geo} Value	Soil quality
0	<0	uncontaminated
1	0-1	uncontaminated to moderately contaminated
2	1-2	moderately contaminated
3	2-3	moderately to heavily contaminated
4	3-4	heavily contaminated
5	4-5	heavily to extremely contaminated
6	>5	extremely contaminated

4.7.2 Potential Ecological Risk Index

The potential ecological risk index method also developed by Hakanson was used in this study to evaluate the potential harm of heavy metals in soils. Countless number of authors have used this method to assess pollution in soils (Barbieri et al., 2015, Weissmannová and Pavlovský, 2017, Kowalska et al., 2018). Using this method, the risk posed by a single element may be assessed (ecological risk factor (E_r)) and also the risk posed by multiple elements (potential ecological risk index (RI)). The following equations are used to calculate the risk:

$$C_f = C_n / C_o \quad (\text{Equation 4.3})$$

$$E_r = T_r \times C_f \quad (\text{Equation 4.4})$$

$$RI = \sum E_r = \sum T_r \times C_f \quad (\text{Equation 4.5})$$

Where T_r is the toxic response factor for each given pollutant,

C_f is the contamination factor for each heavy metal,

C_n is the measured level of each heavy metal in the sediment,

C_o is the background level of each heavy metal,

E_r is the potential ecological risk index,

RI is the sum of all risk factors.

The toxic response factors as calculated by Hakanson (1980) and background values are shown in Table 4.6.

Classes of the heavy metal pollution ecological risk factor and index are detailed in Table 4.7

Table 4.6: Background values and toxic response factors

Metal	As	Cd	Cu	Cr	Hg	Pb	Ni	Zn
Background value (mg/kg)	20	0.62	2.98	5.82	0.15	2.99	3.43	12.0
Toxic response factor	10	30	5	2	40	5	5	1

Table 4.7: Hakanson ecological risk for metal pollution and classes

E_r	Ecological risk of single metal	RI	Ecological risk of environment
$E_r < 40$	low risk	$RI < 150$	low risk
$40 \leq E_r < 80$	moderate risk	$150 \leq RI < 300$	moderate risk
$80 \leq E_r < 160$	considerable risk	$300 \leq RI < 600$	considerable risk
$160 \leq E_r < 320$	high risk	$RI \geq 600$	very high risk
$E_r \geq 320$	very high risk		

4.8 Assumptions, limitations and uncertainties

In conducting this study a series assumptions were made. The first assumption is that soil sampling was done such that portions taken were a true representative of the entire area being investigated. It is also assumed that all precautions taken during sample transportation, preservation and processing were enough to avoid deterioration of soil quality and cross contamination. The use of microwave digester for sample dissolution helped to minimise sample loss through volatilisation. The third assumption involves the instrumental technique. ICP-OES, like any other technique, is vulnerable to systematic errors that may lead to analyte determination with false negatives and positives, non-detection, and over estimation. (Taylor, 2001). The accuracy of the developed method was verified by using a certified reference material. The standard addition method was used as a calibration technique to overcome matrix (often associated with soils) soil that would otherwise give rise to bias results. This calibration method requires that the curve be linear (conforms to Beer's law) for an acceptable extrapolation such as that shown in in figure 4.2 may be possible.

The basis of studying the distribution of a sample of measurements is finding the position of a central value about which the measurements are distributed. As a measure of location, the mean concentrations were calculated to provide an indication of whereabouts the data is situated. The standard deviations were also calculated to indicate the scattering of values around the mean. The higher the dispersion the greater the standard deviation.

The background concentrations used in the study are national averages and the assumption is that they are similar to the study area.

4.9 Summary

This chapter presents the methodology undertaken in order to derive the results which are at the basis of the conclusions for this study. In a first step a detailed literature review was undertaken which informed all the other steps in this study. This was followed by data collection in the form of a sampling campaign in the Krugersdorp area. Careful consideration was given to the location of sampling points. Once the soil samples have been collected they have been transported and stored in the laboratory where the chemical analysis took place to establish concentration of a range of heavy metals. The instrumentation and the methods involved in this process have been described and limitations and uncertainties identified. Once an average concentration for each metal has been established a soil contamination assessment has been performed by direct comparison with existing soil standards and by calculating a geo-accumulation index and an ecological risk index. This analysis allowed for the classification of the soils sampled and for discussions, conclusions and recommendations to be made. This approach is believed to be appropriate in order to achieve the aims and objectives of the study as presented in Chapter 1.

Chapter 5

Results and Discussions

5.1 Introduction

In this chapter the levels of heavy metals in the soil samples collected are reported and compared with the South African and other international standards. In addition, the geo-accumulation index was used to establish the extent of metal contamination and the ecological risk index to ascertain the level of risk posed by the metals. The soil samples were classified and the health and ecological risks were discussed.

5.2. Heavy metal concentrations in soil samples

The mean and standard deviation of amounts of all eight metals (As, Cd, Cu, Cr, Hg, Pb, Ni and Zn) are summarised in Table 5.1 below and the whole dataset used for statistical analyses is presented in Appendix C. The concentration of metals were computed applying the method outlined in section 4.3.6. The concentration of each element in the certified reference standard are also shown in table 5.1. The concentrations obtained and the concentrations supplied in the reference sheet are in good agreement confirming suitability of both analytical and digestion methods.

Table 5.1: Summary of metal concentrations in soil samples

Means ± standard deviation of metals concentrations (mg/kg) in soils from eleven locations in Krugersdorp									
Sample location	Sample identity	As	Cd	Cu	Cr	Hg	Ni	Pb	Zn
Game Reserve	KS1	5.8±0.78	0.1±0.0	13.4±2.98	54±13.80	0.03±0.008	24.1±5.58	5.2±0.82	17.8±3.77
	KS2	6.2±1.92	0.2±0.19	28.9±10.63	61.3±8.42	0.16±0.24	168.9±186.48	13.0±3.77	93.5±86.04
	KS3	7.2±0.48	0.1±0.0	44.0±3.55	113±0.97	0.04±0.005	56.3±5.51	8.6±2.17	41±15.43
	KS8	15.5±1.91	0.55±0.21	85.7±8.06	88±11.31	0.23±0.01	93.8±23.19	16.5±76.87	509±321.73
	KS9	4.1±0.72	0.1±0.0	20.1±2.81	74.3±11.76	0.03±0.009	29.8±1.73	6.0±2.02	18±2.22
	KS10	15.9±(n/a)	0.7±(n/a)	93.2±(n/a)	113±(n/a)	1.36±(n/a)	117.6±(n/a)	79.6±(n/a)	446±(n/a)
	KS11	8.0±3.0	0.1±0.0	30.3±19.65	147±96.65	0.04±0.008	31.3±17.59	6.5±2.45	22±11.43
Farmland	KS4	5.0±1.98	0.29±0.30	21.7±11.52	92±11.31	0.04±0.007	148.2±176.63	9.7±3.82	107±134.35
Farmland	KS5	3.8±0.49	0.1±0.0	18.1±2.83	101±8.48	0.02±0.00	20.7±1.48	7.6±2.33	12.5±0.71
Rand Uranium Mine	KS6	4.0±1.48	0.1±0.0	16.1±3.39	86±18.36	0.02±0.007	45.6±22.48	18.7±4.31	23.5±12.02
Mintails Gold Mine	KS7	155.5±20.93	0.55±0.35	119.1±5.37	104±22.63	0.3±0.04	92.2±7.64	82.5±13.86	641±690.14
Certified Reference Standard	CRS	44.3	2.6	153.9	54.0	0.29	74.0	152.7	360.0
	Expected	43.7	2.48	154.61	54.6	0.289	74.6	150.55	352.9

The mean concentration of the studied metals were compared with the South African, Dutch, Australian and Canadian soil standards (i.e. soil screening values) and a discussion for each heavy metal investigated is presented in the following sections.

5.2.1 Arsenic contents in soils

As presented in the Table 5.1, the average concentration of arsenic (As) has been determined for every sampling point (see Figure 4.4 for geographical location) together with the standard deviation for the average. Figure 5.1 summarises these concentrations and presents their relative values in relation to the soil standards (see Section 2.9.1 and Table 2.1) for different countries.

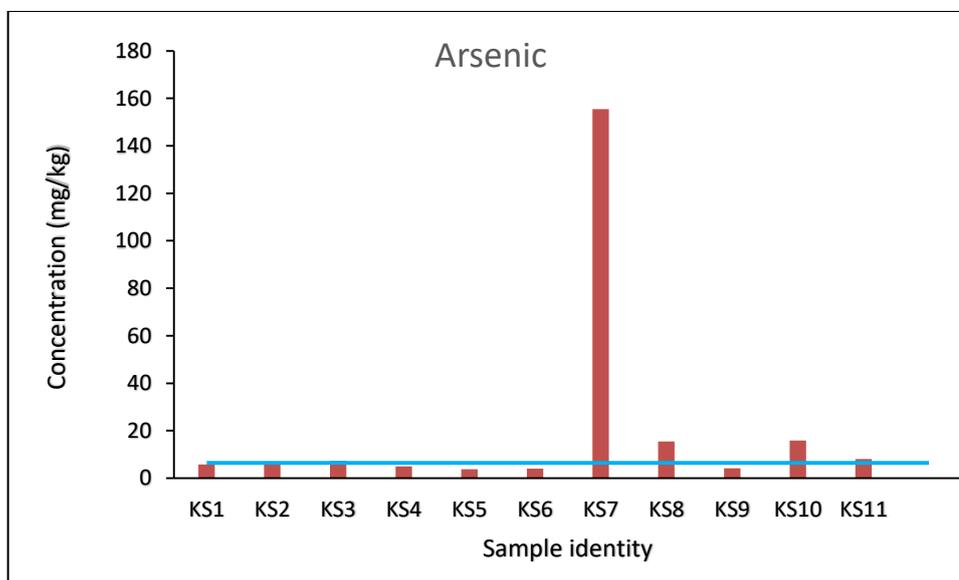


Figure 5.1: Arsenic bar chart

Taking into account the South African standard for all land uses protective of water resources the As concentrations are notably exceeded for sites KS7 (Mintails Gold Mine), KS8 (Game Reserve) and KS10 (Game Reserve). This South African screening value for As for all land uses protective of water resources is 5.8 mg/kg (DEA, 2010) and some of the sites sampled exhibit As concentration around or above this limit, meaning that they have the potential to leak As pollution to groundwater and the river downstream

The mean concentration of site KS7 was 155 mg/kg, the highest at all examined sites and this concentration should be attributed to the mining activity in this particular area. The Mintails Gold Mine is an active underground mine and the samples analysed were collected (with permission) from the tailing dumps situated in the vicinity of this mine. This concentration level is far above the South African, Canadian, Dutch and

Australian standards. These results agree with those seen in literature (Zhiyuan et al., 2013, Navarro et al., 2008, Olobatoke and Mathuthu, 2016) who reported extremely high arsenic contents for soils taken within the mining area. However, with proper management including restricted access to the areas, the risks of direct exposure can be reduced but the risk of wider pollution outside the mining area due to water and wind transport still exists.

Sites, KS8 and KS10 (both inside the Krugersdorp Game Reserve) recorded 15.5 and 15.9 mg/kg respectively and are higher than the Canadian standard, but within the South African standard. These two sites are in a protected area but in the proximity of the river and downstream from mining activities (open cast as well as underground mining and associated decanter – see Figures 3.1 and 4.4). Therefore, although within a protected area where mining did not take place, the proximity to opencast mining and underground mining (4-5 km from the Mintails Gold Mine and directly downstream) did cause pollution downstream either from acid mine drainage from the upstream decanter or from sediments transported from the open cast mine and/or the mine tailings from the gold mine. Other sites sampled which have similar geological substrate (namely the Transvaal Supergroup formations) do not exhibit elevated concentrations of As. As presented in Section 2.6.1, in the literature review, As is not very mobile and in the environment is mainly transported by water and the soluble forms of this heavy metal have the highest toxicity potential. As concentration is also cumulative in soils (see Section 2.6.1) and As is taken up from the soil by plants and can be passed to animals by ingestion. Therefore, the fauna and flora of the Krugersdorp Game Reserve might be affected in time due to bioaccumulation. This needs to be further investigated and was beyond the scope of this study. All the other samples collected from within the Krugersdorp Game Reserve, but further away from the river, have As concentrations within national and international standards and, therefore, pose lower risk to fauna and flora.

Sites KS4 and KS5 were on farmland and although the concentration of As in these two sites is within the soil standards considered, attention should be paid to this trend due to the bioaccumulation ability for this heavy metal. Huang et al. (2006) showed that As soil concentrations between 1.29 and 25.28 mg/kg bioaccumulations in crops occurs. Crops such as rice, radish, spinach, celery and onions accumulate more As than others. The values measured for sites KS4 and KS5 are within the range from literature and, therefore, more investigations are needed to the type of local crops and their bioaccumulation potential.

5.2.2 Cadmium concentrations in the soils samples

Figure 5.2 presents the cadmium (Cd) concentrations of the soils sampled in relation to the national and international standards for this heavy metal. None of the sites sampled exhibit concentrations above the national and international standards. Furthermore, the South African screening value for Cd for all land uses protective of water resources is 7.5 mg/kg (DEA, 2010) and only the sample from KS10 is close to this value (7.0 mg/kg). It has to be noted that the difference between standards between countries for this heavy metal is much larger with the South African standards (including for all land uses protective of water resources) on the upper scale of these international standards.

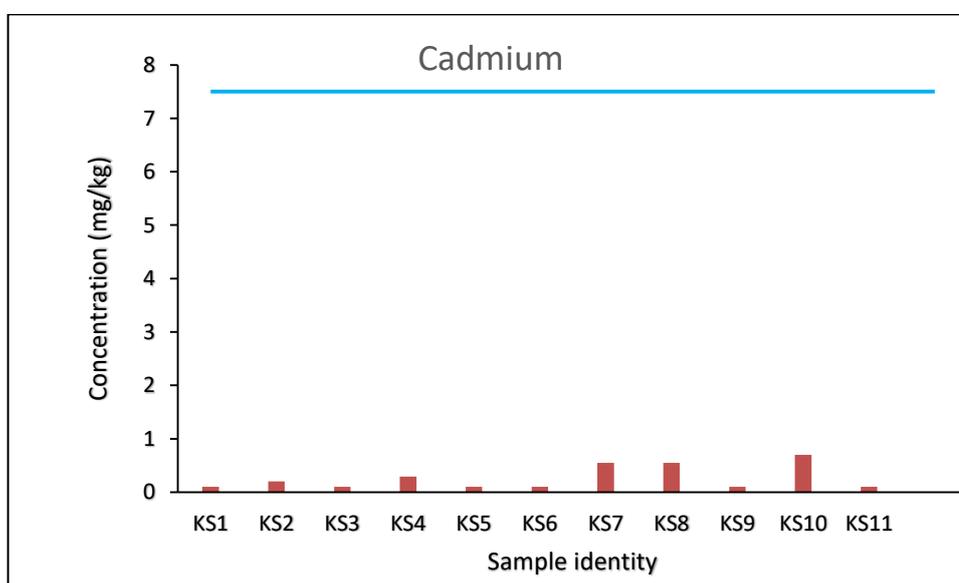


Figure 5.2: Cadmium bar chart

As can be observed from Figure 5.2 and Table 5.1 the highest Cd concentrations are on sites KS7 (Mintail Gold Mine), KS8 and KS10 (both sites in the Krugersdrop Game Reserve, next to the river). This suggests that water plays a role in transporting Cd from the mine to the sampling sites downstream and that accumulation occurs in the soils next to the river. Other sites sampled which have similar geological substrate (namely the Transvaal Supergroup formations) do not exhibit elevated concentrations of Cd. Site KS4 which is also closed to a downstream river from the Mintail mine, but at a greater distance exhibits only a slight elevation for this heavy metal. As different Cd compounds have different toxicities and these are related to the solubility of the compounds as well as the characteristics and the pH of the soils (see Section 2.6.3 in the literature review)

further study is needed to assess the detail impacts to fauna and flora in the game reserve due to bioaccumulation. However, in the literature Cd is considered bio-persistent (Wuana and Okieimen, 2011).

5.2.3 Copper concentrations in the soils samples

Figure 5.3 presents the copper (Cu) concentrations of the soils sampled in relation to the international standards considered for this metal. The South African standard for this metal is 1100 mg/kg and out of scale compared to the other international standards. However, the South African screening value for Cu for all land uses protective of water resources is 16 mg/kg (DEA, 2010) and all the sites with the exception of KS1 exhibit concentrations above this level, meaning that Cu can be potentially leached to groundwater and into the nearby river. KS10 All sites are having concentrations within the South African standard for informal settlements for this metal. However, this standard is very high as compared to the other international standards and needs to be investigated further.

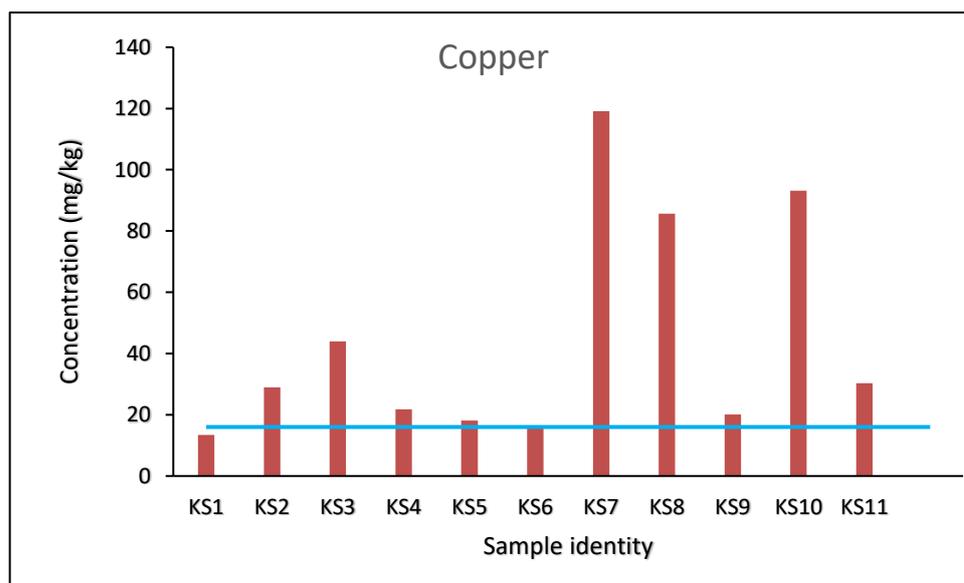


Figure 5.3: Copper bar chart

From Figure 5.3 and Table 5.1 the same pattern occurs with Cu as with Cd and As with the three sites (KS7, KS8 and KS10) showing elevated levels. Therefore, a similar explanation with regard to water transport of this metal originating from the mine upstream is hypothesised. Copper element is a necessity for living organisms (see Section 2.6.8 in the literature review), however, at increased concentrations it can become toxic and it also has the potential to accumulate in small quantities in crops (Toth et al., 2016). If such crops are consumed over an extended period of time it has the potential to affect humans. Fortunately, the two farmland samples show

Cu concentrations below the level at which it is considered problematic (100 mg/kg) in terms of agricultural use (Toth et al, 2016).

5.2.4 Chromium concentrations in soil samples

All examined sites show extremely high levels of chromium (Cr) concentration, far exceeding the South African and Australian standards. KS3, 10, 11, 5, and 7 are all above the Dutch standard. Only KS1 and 2 are below the Canadian standard (see Figure 5.4). These results follow a similar trend to the studies conducted by (Kamunda et al., 2016, Getaneh and Alemayehu, 2006). It has to be noted that the South African standard for this metal is set for hexavalent Cr (Cr VI) as this is the most toxic form (see Section 2.6.5 in the literature review) and represents the worst case scenario with regard to this metal. The South African screening value for Cr (III) is 46 000 mg/kg and for Cr (VI) it is 6.5 mg/kg for all land uses protective of water resources (DEA, 2010). For this research the value for Cr (VI) was used as it is the most sensitive, protecting water resources. In terms of this standard, in a worst case scenario, all sites investigated have the potential to pollute the groundwater and nearby rivers with regards to Cr. As all sites have elevated Cr concentrations and there is not a marked difference between the mining sites and other land uses it appears that high levels for this metal are the normal local background and are related to the geology of the area which gave rise to the soils investigated.

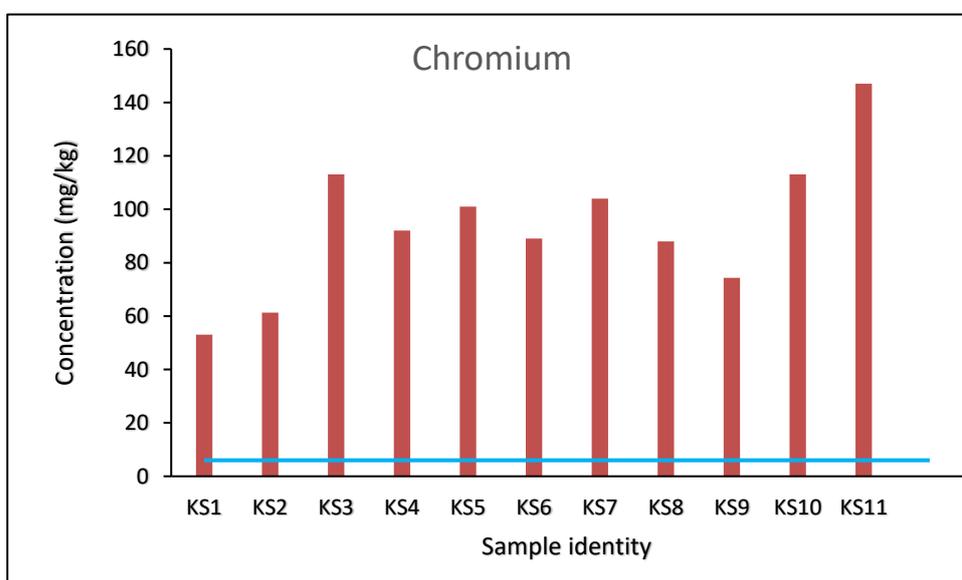


Figure 5.4: Chromium bar chart

The EU threshold for overall elemental Cr for agricultural use is 100 mg/kg (Toth et al, 2016). Therefore, since from all land uses from all sites the agricultural use has the highest potential for bioaccumulation for humans, it is of concern that the two sites KS4 and KS5 are having levels around this threshold as this means that Cr might enter the human food chain through the crops from these two sites. More study is required to determine exactly the type of Cr present in the samples as the trivalent Cr is less mobile in soils and mainly the hexavalent form has high mobility and toxicity associated (see Section 2.6.5), but the total Cr for these two sites.

5.2.5 Mercury concentrations in soil samples

All examined sites recorded low mercury (Hg) concentration levels except for KS10 (Game reserve) and Figure 5.5 illustrates these values in relation to the national and international soil standards. The Hg concentration at site KS10 is above the South African and Dutch standards and much higher as the concentration from the mining operations upstream. The high level of mercury at this site is of environmental and human health concern. Therefore, it seems that local geological conditions and/or accumulation are the cause for these elevated levels and more investigations are needed. It also seems that the form of Hg from site KS10 is not very mobile in terms of water mobility as the KS4 site which is downstream doesn't show elevated concentrations for this heavy metal.

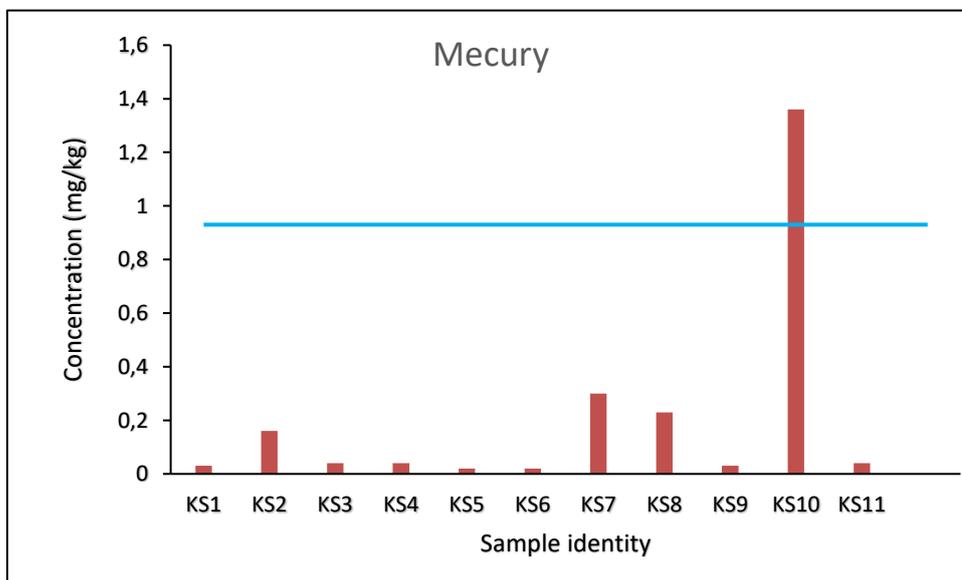


Figure 5.5: Mercury bar chart

The EU threshold for overall elemental Hg for agricultural use is 0.5 mg/kg (Toth et al, 2016) and the concentration for the two samples from farmland are way below that, meaning that Hg in the crops at these sites is not a risk for human consumption.

5.2.6 Nickel concentrations in soil samples

Nickel (Ni) concentration recorded are above the contamination level suggested by all four countries with the exception of sites KS1, KS5, KS9 and KS11 (see Figure 5.6). The South African screening value for Ni for all land uses protective of water resources is 91 mg/kg (DEA, 2010) and in terms of this value five sites (KS2, KS8, KS10, KS4 and KS7) have the potential to pollute waterbodies downstream. It is interesting to note that while the trend is similar with other metals reported above, KS2 (168.9 mg/kg) and KS4 (148.2 mg/kg) have also recorded very high concentrations for Ni. Ni is essential only at small doses and at elevated levels exhibits serious toxicity (Wuana and Okieimen, 2011), for people and ecosystems as summarised in Section 2.6.6.

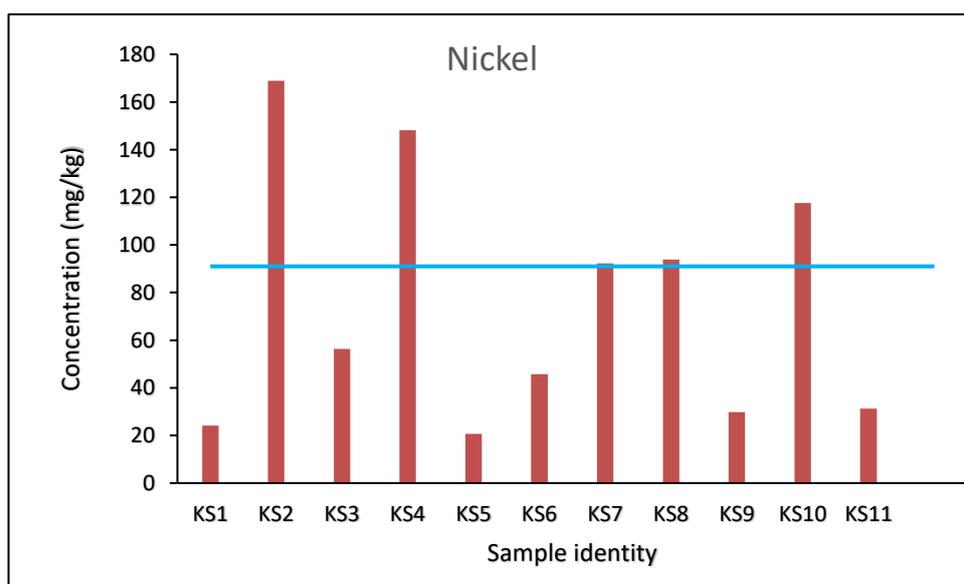


Figure 5.6: Nickel bar chart

High concentrations of Ni as shown in Figure 5.6 are considered serious pollution and are of great concern. They seem to be related to mining activities and water as a vehicle of pollution transport, as the Mintail mine site and all three sites next to the downstream rivers show elevated concentrations. In fact the river sites are having elevated levels as compared to the mine site (KS7) hinting at accumulation of this heavy metal in soils at KS8 and KS10 downstream of the mine. The contamination at site KS4 might be due to water transporting

this metal from KS7 but also due to contamination of the other tributary of this river (see map in Figure 4.4). More research is needed on the pollution transmission and accumulation of Ni in the local environment. Other sites of the same geological substrate (Transvaal Subgroup) have lower soil concentration of Ni showing that the elevated levels are not due to a natural Ni background concentration in these soils.

The EU threshold for elemental Ni for agricultural use is 50 mg/kg (Toth et al, 2016) and the concentration for sample KS4 (farmland) is almost triple that value, highlighting a very high risk of crop contamination by Ni at this location. In fact at this concentration the EU recommends soil remediation in order to be able to use this soil for agricultural purposes (Toth et al, 2016).

5.2.7 Lead concentrations in soil samples

The concentration levels of lead (Pb) are below the standards set by the four countries (see Figure 5.7), however, a few sites are above the South African screening value for Pb for all land uses protective of water resources, which is 20 mg/kg (DEA, 2010). Lead pollution of soils may pose a serious risk to animals and humans living in the vicinity of the mine. Therefore, according to this screen value, sites KS7 (Mintail mine) and KS10 (game reserve downstream) have the potential to leak Pb in the nearby river. The two farmland (KS4 and KS5) samples show Pb concentrations way below the level at which it is considered problematic (60 mg/kg) in terms of agricultural use (Toth et al, 2016). A study conducted in China confirmed that consumption of rice and vegetables cultivated on lead-contaminated soils resulted in a high daily intake of the toxic metal (Zhuang *et al.* 2009). In general, plants do not take up and accumulate lead easily and it needs high concentrations of this metal in soils in order to have moderate uptake by plants (Wuana and Okieimen, 2011).

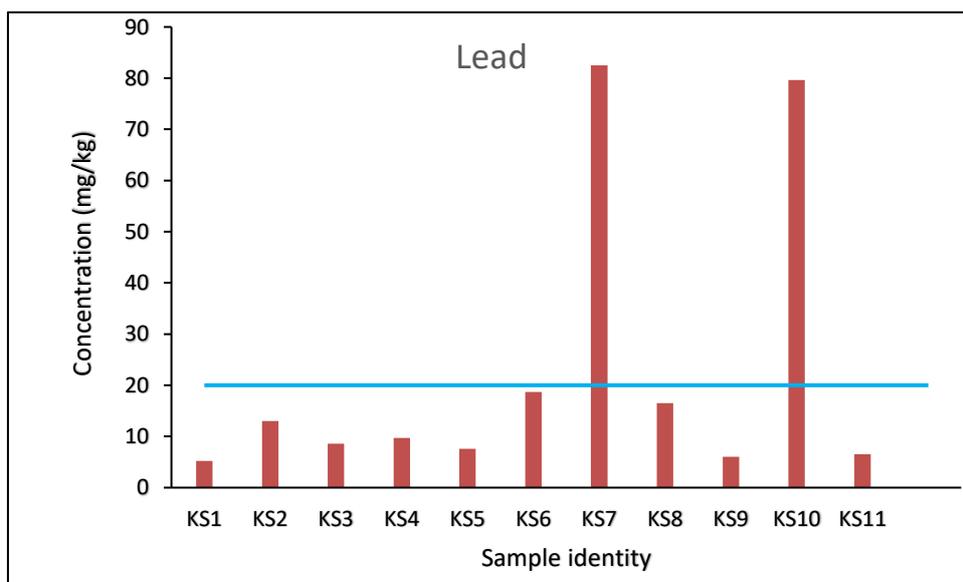


Figure 5.7: Lead bar chart

As seen in Figure 5.7, even though Pb concentrations are below national and international soil standards for most of the sites, again sites KS7 (mine), KS10 and KS8 (game reserve) show higher levels for this heavy metal as compared to the other sites. This is the same pattern as for other metals where water transport of pollutants and subsequent accumulation in soils near to the contaminated river was considered as possible explanation of why elevated levels are measures in a protected area close to a mine and linked by a river.

5.2.8 Zinc concentrations in soil samples

The concentration level of zinc (Zn) is significantly lower than the South African standard, but at sites, KS7, KS8 and KS10 concentrations are far above the standards of the other three international countries. Figure 5.8 presents the concentrations for the individual sites in relation to the local and international standards. In this figure the same pattern as explained for Pb in the previous section can be observed. The South African standard of 9200 mg/kg is way higher compared to the international standards and needs to be investigated. However, the South African screening value for Zn for all land uses protective of water resources, is 240 mg/kg (DEA, 2010) and is comparable to the other international standards. By using this screening value it can be observed that sites KS7, KS10 and KS8 have the potential to leak Zn in the nearby river. Zn is an essential mineral for humans, fauna and flora, however, toxicity and bioaccumulation is possible for this metal. In particular, accumulation in soils, interference with soil ecosystems (i.e. it is toxic to earthworms), accumulations in plants and leaching to groundwater have been observed (Wuana and Okieimen, 2011). All these effects are probable for the three sites in the area that exhibit high contents of Zn and further investigations are needed.

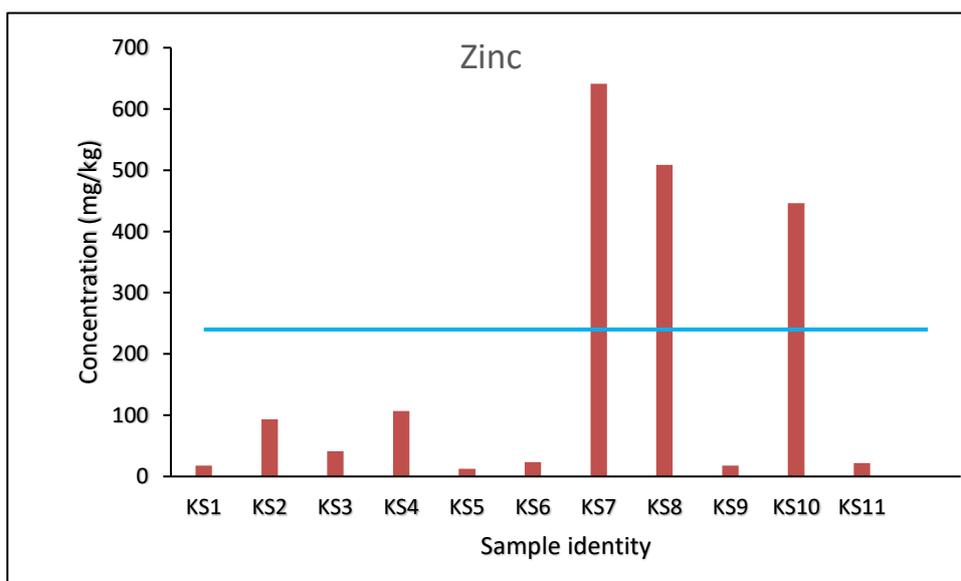


Figure 5.8: Zinc bar chart

The EU threshold for overall elemental Zn for agricultural land use is 200 mg/kg (Toth et al., 2016) and the concentration for the two samples from farmland are below that, meaning that Zn in the crops at these sites is not a risk for human consumption.

5.2.9 Overall discussion of metal concentrations in the soil samples

Three sites KS7 (Mintails Gold Mine), KS10 and KS8 (both within Krugerdporp Game Reserve) show consistent high contents of As, Cu, Cr, Ni, Pb and Zn. These results agree with many other local and international studies which confirm elevated levels for these heavy metals due to mining (these have been included in Section 2.10). For most of these metals the amounts in soils decreases with the increase of the distance from mine operations and mine tailings (KS7) and this is in agreement with Olobatoke and Mathuthu (2016) for another South African case study. The KS7 site is situated on a tailing dump from the underground mining of gold and is the most polluted site investigated. This site is situated upstream from sites KS10 and KS8 that are in the immediate vicinity of the Tweelopiespruit River showing that water transport was a key factor for the transport of heavy metals resulting from mining. The decant of millions of liters of contaminated water into the Tweelopiespruit River and the larger environment, as mentioned in the case study, seems to have played a role as high levels of heavy metals were detected next to the river in a protected area that historically had no mining. Water transport of pollutants and subsequent accumulation in soils near to the contaminated river was considered as the most likely explanation of why elevated levels are measures in a protected area close to a mine and linked by a river. This explanation is also substantiated by the fact that for many of these metals, the concentrations on site KS10 which upstream and closest to the mine is higher as compared to site KS8 that is a few kilometre further downstream.

Soils contaminated with metals as in the case of the study area, can pose direct and indirect risks for humans and the ecosystems that depend on them. Directly, metal contamination has negative effects in terms of the health of the soils' ecosystems and the plants that depend on these soils (natural vegetation and possible crops). Indirectly, these metals enter the food chain of animals and people. In general, the concentration level of the metals investigated did not exceed the South African and international standards in the study area with the exception of three sites (KS7, KS10 and KS8). It has to be noted that some of the South African standards are high compared to international ones and for Zn, Ni and Co the South African screening values protective of water resources are more stringent and closer to the international soil standards.

In the analysis presented in the previous sections of this chapter only effects of individual metals have been discussed, however by having a number of contaminants on a single site a synergistic, cumulative effect is expected to take place. Such an effect was observed by Wallace and Romney (1977) with regard to a few crop plants and a mixture of heavy metals caused greater toxicity as compared to individual metals at the same

concentration. Furthermore, Uwizeyimana et al. (2017) reported synergistic effects of heavy metals together with pesticides. This would be relevant for the two farmland sites if pesticides were applied. However, Gzik et al. (2003) have shown that in the Rustenburg area of South Africa ecosystems and biological communities have adapted to high metal contents from mining in the soils investigated, however bioaccumulation in crops is considered problematic.

The two sites used for agriculture (KS4 and KS5) show high amounts of Co, Cr and Ni and the potential of crop contamination by metals (depending on the crop). This is of great concern as bioaccumulation and synergistic effects are also possible once contaminated crops enter the food chain. These two sampling sites are situated on commercial farms and crops are rotated. The crops of the commercial farms where soils were sampled, were mainly vegetables grown for human consumption (i.e. broccoli, cabbage, cauliflower and spinach) and there is a direct risk that these heavy metals are entering the human food chain. In particular for Ni these sites should be remediated as per EU guidelines.

5.3 Ecological risk assessment

5.3.1 Index of Geo-accumulation

Average I_{geo} values for the eight metals for each sampled site is given in Table 5.2 and levels of metal contamination are given in Table 4.4. I_{geo} is clearly inconsistent and implies that soil around the Krugersdorp area range from uncontaminated to extremely contaminated. The results indicate that soil of this area are not contaminated by arsenic, cadmium and mercury, except for KS7 and KS10 that are moderately contaminated by arsenic and mercury respectively. All sites show moderate to extreme chromium contamination soil status. The I_{geo} values for copper indicate that sites KS3, KS8 and KS10 are moderate to extremely contaminated by copper and the other sites are uncontaminated to moderately contaminated. Site, KS2 is extremely contaminated by nickel, while the other sites are moderately to extremely contaminated. Most sites are between uncontaminated to moderately contaminated by lead except for KS7 and KS10 that are moderately to extremely contaminated. The I_{geo} values of sites KS7, KS8 and KS10 show that the sites are moderately to extremely by zinc and the other sites are uncontaminated to moderately contaminated.

Table 5.2

Geo-accumulation index for the metals from the eleven studied sites									
Sample location	Sample	As	Cd	Cu	Cr	Hg	Ni	Pb	Zn
Game Reserve	KS1	-2.91	-3.18	1.58	2.63	-3.91	2.23	0.21	-0.01
	KS2	-2.81	-2.18	2.69	2.81	-1.49	5.03	1.53	2.37
	KS3	-2.59	-3.18	3.30	3.69	-3.49	3.45	0.93	1.19
	KS8	-1.49	-0.76	4.26	3.33	-0.97	4.19	1.87	4.82
	KS9	-3.41	-3.18	2.17	3.09	-3.84	2.53	0.42	0.01
	KS10	-1.45	-0.41	4.38	3.69	1.59	4.51	4.15	4.63
	KS11	-2.44	-3.18	2.76	4.70	-3.49	2.60	0.53	0.29
Farmland	KS4	-3.12	-1.69	2.16	3.40	-3.49	4.85	1.11	2.57
Farmland	KS5	-3.52	-3.18	2.02	3.53	-4.49	2.01	0.76	-0.53
Rand Uranium mine	KS6	-3.44	-3.18	1.85	3.30	-4.49	3.14	2.06	0.39
Mintails Gold mine	KS7	1.84	-0.76	4.73	3.57	-0.58	4.16	4.20	5.15

	Extremely contaminated
	Moderately/Extremely contaminated
	Moderately contaminated
	Uncontaminated/moderately contaminated
	Uncontaminated

5.3.2 Ecological risk and potential ecological risk index

The calculations of single ecological risk values (E_r) and the potential ecological risk index of metals in soils were done using equations 2 - 4, parameters listed in table 5.3 and concentrations in table 5.1. The results are presented in Table 5.4. The ecological risk (E_r) values of As, Cd, Cr, Pb and Zn were all lower than 40, which indicated that they pose low ecological risk to the environment. The mean values for Cu and Hg indicated moderate ecological risk ($40 \leq E_r < 80$) and that for Ni indicated a considerable ecological risk ($80 \leq E_r < 160$). Sites KS2, KS4, KS7 and KS10 recorded such high values for metals such as Ni (246.2), Ni (216.03), Cu (200.0) and Hg (362.8) respectively. These values indicated high ecological risk ($160 \leq E_r < 320$) for both Ni and Cu, and very high ecological risk for Hg ($E_r \geq 320$). The potential ecological risk index (RI) values of three sites (KS1, KS5, and KS9) were less than 150, indicating low ecological risk. RI values for KS3, KS6 and KS11 sites posed moderate ecological risk ($150 \leq RI < 300$). Considerable ecological risk ($300 \leq RI < 600$) was displayed by sites KS2, KS4 and KS8, while RI values of site KS7 and 10 were greater than 600 posing very high ecological risk.

Table 5.3: Background values and toxic response factors

Metal	As	Cd	Cu	Cr	Hg	Pb	Ni	Zn
Background value (mg/kg)	20	0.62	2.98	5.82	0.15	2.99	3.43	12.0
Toxic response factor	10	30	5	2	40	5	5	1

Table 5.4 Ecological risk values (E_r) and the potential ecological risk index (RI) of heavy metals in soil.

Sample id	Ecological risk values, E_r								RI	Risk level
	As	Cd	Cu	Cr	Hg	Pb	Ni	Zn		
KS1	2.90	4.80	22.50	18.46	8.00	8.70	35.15	1.48	101.99	low risk
KS2	3.10	9.60	48.50	21.06	42.80	21.75	246.2	7.79	400.8	considerable risk
KS3	3.60	4.80	73.80	38.82	10.80	14.40	82.06	3.42	230.14	moderate risk
KS4	2.50	14.10	36.40	31.62	10.80	16.20	216.03	8.92	336.59	considerable risk
KS5	1.90	4.80	30.35	34.70	5.20	12.70	30.17	1.04	120.84	low risk
KS6	2.00	4.80	27.00	29.56	5.20	31.25	66.47	1.96	168.22	moderate risk
KS7	77.50	26.70	200.0	35.74	80.00	137.9	134.4	53.42	745.66	very high risk
KS8	7.70	26.70	143.8	30.24	74.80	27.60	136.73	42.42	489.96	considerable risk
KS9	2.00	4.80	33.70	25.54	8.00	10.00	43.45	1.50	128.99	low risk
KS10	7.90	33.90	156.35	38.82	362.8	133.1	171.43	37.17	941.47	very high risk
KS11	4.00	4.80	50.85	50.52	10.80	18.85	45.60	1.83	187.25	moderate risk
Mean	10.46	12.71	74.84	32.28	56.29	39.31	109.79	14.63		

5.3.3 Comparison of indexes and individual overall results

The discussion of individual heavy metal concentrations in the soil sampled show that sites KS7, KS8 and KS10 have highest contamination levels by most metals. However, when considering the indexes used the geo-accumulation index only detects site KS7 as extremely contaminated by Zn. The ecological risk index detects site KS7 and KS10 as very high risk and KS8 as considerable risk. From the individual heavy metal concentration results presented in Section 5.2 and the indexes presented in Section 5.3 it is clear that there is a

discrepancy between the calculated risk due to soil pollution by heavy metals due to mining. In particular the risk from contamination of land used for agriculture and growing crops for human consumption is not reflected for all metals investigated. Such an example is As for both the geo-accumulation index and the ecological risk value. Both of these two indexes do not signal the bio-accumulation potential of As in crops as assessed by Huang et al. (2006). Therefore, indexes like these should be used with caution in particular when applied to agricultural land. It has to be noted that these indexes have not been developed to target agricultural land and, the development of an index for this type of land use is necessary to allow for better assessment of combined soil pollution due to heavy metals.

5.4 Summary of results

In this chapter, the average concentrations and standard deviation of heavy metals in each site are presented. The mean concentrations were compared to South African, Australian and Canadian soil screening values. Graphs are also presented using values South African standard for all land uses protective of the water resource as a limit. Soil ecological risk assessment was performed using geo-accumulation index (I_{geo}) and ecological risk (E_r) to assess the risk posed by each metal and also potential ecological risk index (RI) which assesses the risk posed by each entire site.

Chapter 6

Conclusions and Recommendations

6.1 Introduction

The conclusions and recommendations for this study are presented in this chapter. As such, it summarises the results of this research and it highlights the key findings. Recommendations for further studies as well as for addressing contamination of investigated soils are also made.

6.2 Conclusions

South Africa has many active and abandoned mining sites and in the literature there are numerous investigations showing that soils contamination by metal in mining areas is of concern. In this context, this study aimed to quantify the level of soil contamination due to eight metals (As, Cd, Cr, Cu, Pb, Hg, Ni and Zn) and to assess the risks to nearby ecosystems and agricultural land. The study area (Krugersdorp) had a historical pollution incident where contaminated mine water flowed into the headwaters of the Tweelopiespruit river, which flows through the Krugersdorp Game Reserve, hence the study. After the decant of millions of liters of contaminated water into the environment as mentioned in the case study, significant amounts of heavy metal and high contamination levels were expected from the examined area. Three sites recorded high concentration levels that exceed South Africa standard. KS7 (Mintail Gold Mine) recorded high levels of arsenic, chromium and zinc and is considered the source of pollution. KS10 and KS8 (Game Reserve) downstream the river recorded high levels of arsenic, chromium, mercury and zinc. These results show that the areas within the mine vicinity and the point decant (upstream the Krugersdorp Game reserve) are polluted. The results also show that the pollution levels are lower at the other sites sampled which means contamination is most likely transported by water and the river is a vehicle for metals contamination. Along the river the level of pollution decreases with increased distance from the mine.

Ecological risk index indicated that sites, KS7 and KS10 pose very high risk to the environment which is in agreement with the results of the geo-accumulation index and sites, KS2, KS4 and KS8 pose considerable risk. It is important to note that sites KS2, KS4, KS8 and KS10 were in the proximity of the contaminated Tweelopiespruit river with KS10 and KS8 being the closest geographically. These results further suggest that the elevated metal concentrations at these sites is associated with spillages of acid mine drainage water into rivers as well as transport from mine dumps tailings and that soils are contaminated via these pathways.

The results also show that the geo-accumulation index and the ecological risk index should be used with caution when applied to agricultural soils as they do not detect the bio-accumulation potential of certain metals (e.g. arsenic in this study). In particular contamination of the agricultural soil Ni was at the level requiring remediation according the European Union standards for soil decontamination. Therefore, the use of crops from these contaminated soils should be further investigated as it could pose a direct risk to human health.

The results obtained in this study address all the aims and objectives as set out in the introduction of this dissertation. The levels of heavy metals concentration in soils from game reserve, farmland and mines around Krugersdorp are reported. Also, toxicological and environmental risks of these metals are highlighted.

6.3 Recommendations

6.3.1 Recommendations from this investigation and further studies.

1. Decontamination of agricultural land or change in land use so that human health is not at risk. This is particularly valid for nickel and the farmland sites investigated. Local bioaccumulation in crops from arsenic in soils should also be further researched as literature shows this kind of potential for the farmland sites sampled.
2. More investigation into the risk for humans of ingesting crops contaminated with heavy metals in particular nickel and arsenic.
3. There is a great need to establish background amountss of trace elements and heavy metals in the Krugersdorp area for recognition and management of soil pollution as well as deficiencies for plants and humans. This kind of information will give the researchers an idea of natural range in concentration prior to human activity.
4. For future studies, investigations of soil and ground water from nearby informal settlements will have to be made to establish the level of heavy metal contamination. Multiple pathways and exposures need to be taken into account for the inhabitants as they will ingest contaminated food and will be exposed to contaminated air (dust particles), water and soil. The standards for informal settlements for soil contamination should be revised taking into consideration these multiple exposures and pathways, as they are much higher as compared international standards and standards for other land uses.
5. Fauna and flora from the Game Reserve as well as crops from Farmlands in the area will have to be investigated for actual heavy metal uptake.

6.3.2 Recommendations for better management of soil pollution due to heavy metals from mining.

1. The minister of Minerals and Energy must enforce the following recommendations of section 43 of the Mineral and Petroleum Resources Development Act, 2002:
 - (i) The globally accepted “polluter pays” principle.
 - (ii) Rehabilitation, management and remediation of any negative environmental impacts to a sustainable usable condition before the closure certificate is issued to the mining permit holder.
2. Government should make funds available for researchers to monitor and assess toxic chemicals in areas around active and abandoned mines. This would assist to establish the levels of contamination in these areas and thus proper remedial actions and rehabilitation procedures.
3. The government and mining industries should form partnership and invest in developing mine water treatment technologies.

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List of appendices

Appendix A

Analytical wavelengths

Element	Wavelength (nm)
Arsenic (As)	193.691
Cadmium (Cd)	214.439
Chromium (Cr)	205.557
Copper (Cu)	324.747
Mercury (Hg)	194.164
Nickel (Ni)	231.602
Lead (Pb)	220.350
Zinc (Zn)	206.200

Appendix B
Analytical Data

		As	Cd	Cu	Cr	Hg	Ni	Pb	Zn
KS1	A	6.8	< 0.1	15.8	64	0.03	29.5	5.0	23
	B	5.2	< 0.1	11.8	47	0.03	24.0	4.8	15
	C	6.1	< 0.1	16.0	67	0.04	26.3	6.4	18
	D	5.2	< 0.1	10.0	38	0.02	16.4	4.6	15
KS2	A	4.1	0.1	16.0	52.0	0.03	38.5	7.5	25
	B	5.6	0.1	29.5	71.0	0.04	91.1	15.1	54
	C	6.5	0.2	27.9	65.0	0.07	97.1	15.8	79
	D	8.7	0.5	42.0	57.0	0.50	444.8	13.5	216
KS3	A	6.5	< 0.1	40.6	107	0.04	49.3	6.3	25
	B	7.4	< 0.1	43.1	101	0.03	61.4	7.1	30
	C	7.3	< 0.1	43.4	123	0.04	54.5	10.2	54
	D	7.6	< 0.1	49.0	122	0.04	59.9	10.6	54
KS4	A	6.4	0.5	29.8	100	0.04	273.1	12.4	202
	B	3.6	0.07	13.5	84	0.03	23.2	7.0	12.0
KS5	A	4.0	< 0.1	20.1	107	0.02	21.7	9.2	13.0
	B	3.3	< 0.1	16.1	95	0.02	19.6	5.9	12.0
KS6	A	5.0	< 0.1	18.5	99.0	0.01	29.7	12.4	15.0
	B	2.9	< 0.1	13.7	73.0	0.02	61.5	6.3	32.0
KS7	A	140.7	0.3	122.9	88.0	0.33	86.8	72.7	153
	B	170.3	0.8	115.3	120.0	0.27	97.6	92.3	1129
KS8	A	16.8	0.7	80.0	96	0.22	110.2	18.4	736
	B	14.1	0.4	91.4	80	0.24	77.4	14.6	281
KS9	A	4.7	< 0.1	18.6	69	0.03	29.5	7.0	19
	B	4.7	< 0.1	17.6	64	0.04	27.5	8.2	21
	C	3.9	< 0.1	20.0	73	0.04	30.4	5.2	16
	D	3.2	< 0.1	24.0	91	0.02	31.6	3.6	17

KS10	A	15.9	0.7	93.2	113	1.36	117.6	79.6	446
KS11	A	11.5	< 0.1	18.8	79	0.04	19.8	6.3	16
	B	7.6	< 0.1	11.1	49	0.03	13.9	3.6	10
	C	4.2	< 0.1	36.0	227	0.04	39.6	6.6	26
	D	8.5	< 0.1	55.3	233	0.05	51.9	9.6	36

Appendix C

Summary of minimum, maximum, mean and standard deviation (SD) of soils

		As	Cd	Cu	Cr	Hg	Ni	Pb	Zn
KS1	Min	5.2	0.1	10.0	38	0.02	16.4	4.6	15
	Max	6.8	0.1	16.0	67	0.04	29.5	6.4	23
	Mean	5.8	0.1	13.4	54.0	0.03	24.1	5.2	17.8
	SD	0.78	0.0	2.98	13.8	0.008	5.58	0.82	3.77
KS2	Min	4.1	0.1	16.0	52.0	0.03	38.5	7.5	25.0
	Max	8.7	0.5	42.0	71.0	0.50	444.8	13.5	216.0
	Mean	6.2	0.2	28.9	61.3	0.16	168.9	13.0	93.5
	SD	1.92	0.19	10.63	8.42	0.24	186.48	3.77	86.04
KS3	Min	6.5	0.1	40.6	101	0.03	49.3	6.3	25.0
	Max	7.6	0.1	49.0	123	0.04	61.4	10.6	54.0
	Mean	7.2	0.1	44.0	113	0.035	56.3	8.6	41.0
	SD	0.48	0.0	3.55	0.97	0.005	5.51	2.17	15.43
KS4	Min	3.6	0.07	13.5	84.0	0.03	23.3	7.0	12.0
	Max	6.4	0.5	29.8	100.0	0.04	273.1	12.4	202.0
	Mean	5.0	0.29	21.7	92.0	0.04	148.2	9.7	107.0
	SD	1.98	0.30	11.52	11.31	0.007	176.63	3.82	134.35

KS5	Min	3.3	0.1	16.1	95.0	0.02	19.6	5.9	12.0
	Max	4.0	0.1	20.1	107.0	0.02	21.7	9.2	13.0
	Mean	3.8	0.1	18.1	101	0.02	20.7	7.6	12.5
	SD	0.49	0.0	2.83	8.48	0.00	1.48	2.33	0.71
KS6	Min	2.9	0.1	13.7	73.3	0.01	29.7	6.3	15.0
	Max	5.0	0.1	18.5	99.0	0.02	61.5	12.4	32.0
	Mean	4.0	0.1	16.1	86.0	0.02	45.6	18.7	23.5
	SD	1.48	0.0	3.39	18.36	0.007	22.48	4.31	12.02
KS7	Min	140.7	0.3	115.3	88.0	0.27	86.8	72.7	153
	Max	170.3	0.8	115.3	120.0	0.33	97.6	92.3	1129
	Mean	155.5	0.55	238.2	104.0	0.3	92.2	82.5	641
	SD	20.93	0.35	5.37	22.63	0.04	7.64	13.86	690.14
KS8	Min	14.1	0.4	80.0	80.0	0.22	77.4	14.6	281
	Max	16.8	0.7	91.4	96.0	0.24	110.2	18.4	736
	Mean	15.5	0.55	85.7	88.0	0.23	93.8	16.5	509
	SD	1.91	0.21	8.06	11.31	0.01	23.19	76.87	321.73
KS9	Min	3.2	0.1	17.6	64.0	0.03	27.5	3.6	16.0
	Max	4.7	0.1	24.0	91.0	0.04	31.6	8.2	21.0
	Mean	4.1	0.1	20.1	74.3	0.03	29.8	6.0	18.0
	SD	0.72	0.0	2.81	11.76	0.009	1.73	2.02	2.22

KS10	Min	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	Max	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	Mean	15.9	0.7	93.2	113.0	1.36	117.6	79.6	446.0
	SD	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
KS11	Min	4.2	0.1	11.1	49.0	0.03	13.9	3.6	10.0
	Max	11.5	0.1	55.3	233.0	0.05	51.9	9.6	36.0
	Mean	8.0	0.1	30.0	147.0	0.04	31.3	6.5	22.0
	SD	3.0	0.0	19.65	96.65	0.008	17.59	2.45	11.43