Contamination of water, soil and plants by contaminants from gold mine tailings in Matjhabeng Local Municipality, South Africa

by

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PREFACE

This work that is presented in this thesis was carried out in the Faculty of Health and Environmental Sciences; Central University of Technology, Free State, with the supervision of Doctor Leana Esterhuizen and the co-supervision of Professor Annabel Fossey.

As the candidate's supervisors we agree that the student can proceed and submit the thesis.

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Professor Annabel Fossey	Doctor Leana Esterhuizen

DECLARATIONS

Declaration 1: Plagiarism

I, Gladys Nyoh Belle, identity number and student number , declare that:

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2. The thesis complies with the code of Academic Integrity, as well as other relevant policies, procedures, rules and regulations of the Central University of Technology, Free State.
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Declaration 2: Publications

One journal article has been published from this work in an accredited journal. The second article is under consideration for publication in SN Applied Sciences. The third manuscript has been written completely and will be submitted once an appropriate journal has been sourced. For each of the articles, I wrote the manuscripts, while the co-authors were involved in editing the manuscripts.

Article 1:

Title: Contamination of groundwater by potential harmful elements from gold mine tailings and the implications to human health: A case study in Welkom and Virginia, Free State Province, South Africa

Authors: Gladys Belle; Annabel Fossey; Leana Esterhuizena; Roshila Moodley
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Article 2:
Title: Contamination and seasonal variation of potential harmful elements in surface water and the pollution risk: A case study in Matjhabeng Mining area, South Africa

Authors: Gladys Belle; Annabel Fossey; Leana Esterhuizena; Roshila Moodley

Article 3:

Title: Soil pollution by contaminants from gold mine tailings and the impacts on environment and human health: A case study in Matjhabeng Local Municipality, Free State, South Africa

Authors: Gladys Belle; Annabel Fossey; Leana Esterhuizena; Roshila Moodley

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ABSTRACT

Mining of gold in Matjhabeng Local Municipality area (MLM), Free State, South Africa has produced numerous gold mine tailings, which contain a variety of contaminants. This study, investigated the extent of pollution of water bodies and soil by contaminants from gold mine tailings in the MLM area. The uptake of contaminants by plants, such as medicinal plant species, sweet thorn, as well as food crop species, maize, was also investigated. Surface water and soil were assessed at 15 sampling sites, and within five demarcated zones in uncultivated lands in terms of six physical properties, as well as 12 potential harmful elements (PHEs), while contamination in sweet thorn plants was assessed for the PHEs. The contamination of cultivated soil and maize seeds were studied from 12 sampling sites, and within four demarcated zones in cultivated lands in terms of the physical properties and the PHEs. Groundwater contamination was assessed from eight of the 12 sampling sites, and within three of the four zones, in terms of the physical water quality properties, the PHEs, as well as microbiological properties, since groundwater in the area is also used for drinking. Several environmental pollution risk indices, as well as health risk indices were quantified to determine the potential risk of the contamination of surface water and uncultivated soils by PHEs, as well as the health risk of ingesting the different PHEs in sweet thorn leaves samples, which is used for medicinal purposes. The results of this study revealed that the water, soil and plants in the MLM area have been severely contaminated by the contaminants from the gold mine tailings and of much concern is the contamination by the PHEs. The concentrations of As, Co, Cu, Fe, and Zn, were higher than the surface water quality limits, while Fe, Pb, Ca and Mg measured in groundwater exceeded the drinking water quality limits, with Pb and Fe found to be at toxic levels. The overall contamination of groundwater, revealed that majority of the groundwater in the study area is unsuitable for drinking, as confirmed by high Drinking Water Quality Indexes. On the other hand, the concentration of Cr, Cu, Zn and Fe also exceeded the limits and the background concentrations for uncultivated soils in South Africa, while the concentrations of Cu and Zn exceeded the permissible limits for cultivated soil, as well as the background concentrations in South Africa. Concentrations of Pb and Fe measured in leaves of sweet thorn exceeded the limits while the accumulation of Pb and Se in sweet thorn leaves were found in close to 20% of the sampling sites. However, with maize samples, only arsenic exceeded the limit as stipulated by the Australian Standards for Food Safety, at four sampling sites. The high level of contamination of water, soil and plants in the MLM area was also affirmed by the Geo-accumulation Index results for surface water. The Single Factor Pollution Index results indicated a high contamination by As, and exceptionally high contamination by Se for majority of the surface water samples. On the other hand, human health risk indices results indicated severe non-carcinogenic health risk of As, Pb, Co, Cu, Fe and Pb, from the ingestion of sweet thorn leaves for medicinal purposes with Hazard Index (HI) values > 1. The carcinogenic risk for As at 20% of the sampling sites, and at 40% of the sampling sites for Pb exceeded the 1×10^{-4} value as stipulated by the USEPA, which suggested a significant cancer risk to the local people in the MLM area. To ascertain the total pollution risk in the MLM area, a Combined Risk Index (*CRI*) was developed. The results of the *CRI* revealed that majority of the sampling sites in the MLM area have been contaminated by PHEs and therefore poses risk to the environment and human health. The general trend was that the level of contamination decreased away from Zone 1, in the downstream direction in relation to the prevailing wind in the area, with the least level of contamination registered at the control Zone 5, which was in the upstream wind direction. The overall environmental and health risks classification results for each of the 15 sampling sites for the uncultivated lands revealed three sites, S2, S7 and S9, as high risk areas in the MLM area. Additionally, five sites, S4, S5, S10, S11 and S15 were within the low risk category, while the remainder of the sites have been classified moderate risk areas. The findings from this study indicated that gold mine tailings, as well as mining activities are the major source of PHEs contamination in the MLM area. The results from this study provides scientific facts and evidences that can be used as a baseline for further research on remediation and measures to mitigate the level of contamination by PHEs in the MLM area.

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ABBREVIATIONS

AMD	Acid mine drainage
ANC	African National Congress
As	Arsenic
AS_2S_2	Realgar
As_2S_3	Orpiment
AWQUS	Aquatic Water Quality for Urban Streams limits
BAF	Bioaccumulation Factor
BGI	Biogeochemical Index
Ca	Calcium
$CaC0_3$	Calcium Carbonate
CCME	Canadian Council of Ministers of the Environment water quality limits
Cd	Cadmium
Cdeg	Degree of contamination
CDI	Chronic Daily Intake
cfu	Colony Forming Units
CN	Cyanide
Co	Cobalt
CR	Cancer Risk
Cr	Chromium
CRI (w + s)	Combine Risk Index for water and soil
CRM	Standard Reference Materials
CSF	Cancer slope factor
CSI	Contamination Security Index
Cu	Copper
$Cu, Fe_{12}Sb_4S_{13}$	Tetrahedrite
$CuFeS_2$	Chalcopyrite
CUT	Central University of Technology
DEA	Department of Environmental Affairs

DEC	Department of Environment and Conservation
DMR	Department of Mineral Resources
DNA	Deoxyribonucleic Acid
DO	Dissolved oxygen
E. coli	*Escherichia coli*
EC	Electrical conductivity
EDTA D1	Ethylenediaaminetetraacetic acid
EF	Enrichment Factor
EFF	Economic Freedom Fighter
EIA	Environmental Impact Assessment
EMPs	Environmental Management Plans
ExF	Exposure factor
FAO	Food and Agricultural Organisation
Fe	Iron
Fe (1-X) S	Pyrrhotite
FeAsS	Arsenopyrite
$FeCr_2O_4$	Chromate
FeS_2	Pyrite
(FeNi)S8	Pentlandite
g	Grams
GDP	Gross Domestic Product
Hg	Mercury
HI	Hazard Index
IHI	Index of Habitat Integrity
HNO_3	Nitric acid
HQ	Hazard Quotient
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
Igeo	Geo-accumulation Index
JSE	Johannesburg Stock Exchange
km	Kilometre

mCd	Modified degree of contamination
MCSA	Mineral Council South Africa
MEC	Multi-element contamination
MERMQ	Probability of toxicity
Mg	Magnesium
mg/L	Milligram per Littre
MGB	Migori Gold Belt
ml	Millilitre
MLM	Mathjabeng Local Municipality (MLM)
mm	Millimetre
Mn	Manganese
Mo	Molybdenum
MPN	Most Probable Number
mS/m	Millisiemens per meter
NEMA	National Environmental Management Act
NEPM	National Environmental Protection Measures
Ni	Nickel
NiAsS	Gersdorffite
NIPI	Numerow Integrated Pollution Index
NNE	North-northeast
NTU	Nephelometric turbidity units
NW	Northwest
°C	Degree Celsius
Pb	Lead
PC	Principal Components
PCA	Principal Component Analysis
PHEs	Potential Harmful Elements
Plave	Average Single Pollution Index
PIN	Background enrichment factor
Pisum	Sum of contamination

PIVector	Vector Modulus of Pollution Index
PLI	Pollution Load Index
PM	Particulate Matter
QAS	Quality Assessment Score
qi	Quality Rating
RfDo	Oral Reference Dose
RI	Potential ecological risk
SAHO	South African History Online
SANS	South African National Standard on drinking water
Se	Selenium
SE	Southeast
SFPI	Single Factor Pollution Index
SIi	Sub-Index of the ith property
SPSS	Statistical Package for Social Sciences
SSW	South-southwest
TEF	Toxicology Education Foundation
USEPA	United States Environmental Protection Agency
µm	Micro meter
µs/cm	Micro siemens
UV	Ultraviolet light
WB	Witwatersrand Basin
WHO	World Health Organisation
Wi	Relative Weight
WQI	Water Quality Index
WRC	Water Research Commission of South Africa
WWTP	Waste Water Treatment Plant
Zn	Zinc
ZnS	Sphalerite

Chapter 1

Introduction

1.1 Background to the study

Over the past century, mining has been the backbone of South Africa's economy. Gold mining brought about widespread employment, wealth, and contributed to the development of several sectors in the South African economy (Durand, 2012). These sectors include the development of infrastructure and the establishment of manufacturing and service industries (Durand, 2012; CMSA, 2014). The rapid growing gold mining industry brought South Africa to the forefront as one of the most industrialised countries in Africa. Gold mining developments resulted in the establishment of numerous settlements around the gold mining areas, which later developed into larger towns and cities. One of the first settlements that was established because of gold mining was the city of Johannesburg in the Gauteng Province, previously named Transvaal (Naicker et al., 2003; Durand, 2012). The city of Johannesburg is often referred to as "Egoli", meaning the Place of Gold (Durand, 2012).

Though gold mining is a major contributor to South Africa's Gross Domestic Product, these mining activities are responsible for extensive environmental pollution, as well as impacting the health of people living in this mining area (Wahl et al., 2013; Wu et al., 2014) The increasing rate of exploitation of gold, including the use of very sophisticated machineries to extract gold from the earth's crust, as well as the processing of gold ores, produces large quantities of waste by-products (Lottermoser, 2010; Kossoff et al., 2014). In most instances, a larger proportion of gold extracted end up as waste materials (Lottermoser, 2010; Muhammad et al., 2011; Ali et al., 2013; Kossoff et al., 2014; Ngure et al., 2014; Hao & Jiang, 2015; Egli et al., 2017). These gold mining waste by-products are collected and accumulated in tailings on the surface of the earth in the vicinity of a gold mine. Gold mining activities within the WB have produced about 400 km^2 of mine tailings, which constitute a potential source of pollution of the environment (Kamunda et al., 2016).

Gold mine tailings, also referred to as mine dumps, contain several contaminants. Some of the contaminants found in tailings originate from the gold-containing ore, whereas other contaminants are added to the tailings during the chemical separation of the gold from its ore (Lottermoser, 2010; Kossoff et al., 2014). Contaminants that originate from the gold-containing ore include the mineral pyrite (iron disulphide), an acid producing rock, as well as potential harmful elements (PHEs), such as mercury (Hg), arsenic (As), cadmium (Cd), and lead (Pb) (Etteieb et al., 2020). Mercury and cyanide (CN) can also be added to mine tailings during the chemical processing of gold ore (Nkuba et al., 2019). Gold-containing ore also contain small quantities of other PHEs, described as micro-elements. These micro-elements include cobalt (Co), copper (Cu), chromium (Cr), nickel (Ni), iron (Fe), manganese (Mn), molybdenum (Mo), selenium (Se) and zinc (Zn) (Hogstrand & Wood, 2010; Abdul-Wahab & Marikar, 2012).

Environmental contamination from gold mine tailing waste has been a global issue for decades. The contaminants contained in gold mine tailings may be dispersed into the environment by wind, rain-water run-off and surface water flow, which eventually results in the contamination of water, soil and air. Besides the contamination of the environment, plants can also be contaminated through the uptake of contaminants from the environment through their roots. Wind blows dust and particulate matter containing contaminants from gold mine tailings over long distances, which eventually settle on soil, water bodies and plant leaves within the vicinity of a gold mine tailings (Blight, 2007; Ojelede et al., 2012; Castillo et al., 2013; Stovern et al., 2016).

Apart from wind acting as a dispersal agent, rain and thunderstorms also generate large volumes of water, which flow as run-off over a gold mine tailing and pollute the environment in the vicinity of the tailing. When rainwater percolates through gold mine tailings, sulphur-bearing pyrite reacts with water and air to form sulphuric acid and ferrous sulphate (McCarthy, 2011; Kinna, 2016). The acid run-off further dissolves PHEs into ground or surface water bodies and the seepage of the acidic water into water bodies and soil is generally referred to as acid mine drainage (AMD) (Oelofse, 2008; McCarthy, 2011; Kinna, 2016). AMD has been described as one of the greatest environmental dangers in the mining industry that can cause severe damage to the environment (Akcil & Koldas, 2006; Oelofse, 2008; McCarthy, 2011).

Humans may be exposed to gold mine tailing contaminants that are present in water bodies, soil and air, as well as contaminants that have accumulated in plants and aquatic organisms through uptake (Islam et al., 2015; Shaheen et al., 2016). Humans become exposed, particularly to PHEs, when they consume contaminated drinking water, or when eating contaminated foods, medicinal plants, aquatic organisms and animals (Bermudez et al., 2011; Islam et al., 2015; Shaheen et al., 2016). Humans also become exposed to gold mine tailing contaminants when they inhale dust and particulate matter that contains these contaminants, or when swimming in water polluted by gold mine tailing contaminants (Davies & Mundalamo, 2010).

The accumulation of PHEs in human bodies in concentrations that are greater than the allowable concentration limits may cause severe health effects. In particular, Cd, Hg, Pb and As have been described by the World Health Organisation as human carcinogens of major public health concern (WHO, 2011; Kamunda et al., 2016). Ingestion of these PHEs in humans, even at trace levels, may result in death (Tchounwou et al., 2012; Kamunda et al., 2016; Zhou et al., 2016).

1.2 Problem statement

This study was conducted in the Mathjabeng Local Municipality (MLM) area in the Free State Province of South Africa. The MLM forms part of the Witwatersrand Basin (WB) and is located about 140 kilometres north east of Bloemfontein in the Free State Province. The MLM is surrounded by some of the largest gold fields in the Free State, with mining of gold and uranium being the dominant economic activities in the area. Extensive agricultural activities, such as food crop cultivation and livestock farming are also performed in this area. The gold mining activities in this area have produced numerous gold mine tailings, which may contain a variety of different contaminants. Such contaminants may cause widespread pollution of the diverse water bodies in the MLM area, including the dams, pans, streams and rivers in the area. The contaminants from the gold mine tailings may also contaminate the soil in the MLM area, particularly agricultural soil, which may further result in the contamination of food crops, as a result of the uptake of the contaminants from contaminated soil. The people living in the MLM areas are thus vulnerable to these harmful contaminants through the consumption of contaminated water and food plants, and through the inhalation of contaminated air.

1.3 Significance of the study

This study is the first of its kind, investigating the extent of gold mine tailing contamination of water bodies, soils and plants in the MLM area. Little is known about the extent of contamination of the different water bodies and soils in the vicinity of the gold mine tailings in the MLM area. In addition, the extent of the uptake of contaminants, particularly potential harmful elements (PHEs) by medicinal and food plants is also unknown. Since PHEs are toxic and can accumulate in organisms, and given the potential harmful effects of PHEs on the environment and human health, this multidisciplinary research explores the impact of PHEs from gold mine tailings on the environment, as well as the health of the local people in the MLM area.

The major significant findings of this study revealed extensive contamination of water, soil and plants with Cu, Fe and Zn, which exceeded the limits. Other PHEs including As, Co, Cr and Pb were in high concentrations in some instances. Exceptionally high concentrations of these PHEs were detected at the centre of MLM areas, which had many mine tailings, as well as mines. For the most, the level of contamination of the PHEs in soil and plants were found to decrease beyond the gold mine tailing areas, with the least level of contamination detected in the upstream wind direction to the mine tailings. This high level of contamination of water, soil and plants by the PHEs from the gold mine tailings have the potential to cause harmful effects, particularly to the environment, humans and animals that live in the area. Besides these findings, an environmental pollution index was developed specifically for pollution in mining areas. This novel Combined Risk Index for water and soil was used to describe the total pollution risk from the contamination of both surface water and soil by PHEs in the MLM area. The index can be used as a tool to obtain specific information about the extent of contamination of an area, as well as the risks posed by the different PHEs on the environment. The findings from this study also revealed a severe health risk from the ingestion of As, Pb, Cu and Fe in leaves of sweet thorn, which is used for medicinal purposes in the area.

The combined environmental pollution risks condition for surface water and soil, together with the health risk condition for each of the 15 sampling sites were used to describe the overall risk classification condition in the MLM area. The overall classification of the level of contamination at each of the 15 sampling sites revealed three sites, which are a high risk area in the MLM area. Therefore, the local people who reside in these areas are exposed to the high risk of the contamination by PHEs in the environment and are also at high risk from the ingestion of PHEs in sweet thorn leaves samples. Additionally, five sampling sites have been classified as low risk areas, while the remainder of the sites are classified as moderate risk areas. Based on the evidence and magnitude of contamination in the area, the results of the study, therefore, provides the basis on which mitigation measures could be introduced in the MLM study area.

1.4 Aim and objectives of the study

The overall aim of this study was to determine the extent of the contamination of water bodies and soil by contaminants from gold mine tailings in the MLM area, as well as the contamination of two plant species namely the medicinal plant species, sweet thorn (*Vachellia karroo*), and the food crop species, maize (*Zea maize*). In order to meet this aim, the following objectives were devised:

1. To scout the MLM study area and identify suitable sampling sites;
2. To determine the quality of surface water, measured in terms of their physical water quality properties, as well as the extent of PHEs contamination;
3. To determine the quality of groundwater, measured in terms of their physical and microbiological water quality properties, as well as the extent of PHEs contamination;
4. To determine the quality of uncultivated and cultivated soil, measured in terms of their physical properties, as well as the extent of PHEs contamination;
5. To assess the extent of PHEs contamination of sweet thorn and maize; and
6. To determine the overall gold mine tailing contamination of the study area, and evaluate the potential environmental risk and the health risk to the local people.

1.5 Research questions and sub-questions

To be able to study the level of contamination arising from the contamination of surface water and groundwater, as well as the contamination of soil and plants by contaminants from gold mine tailings the research aim of this study was restated as a research question in the following manner:

Main research question: To what extend does contaminants from gold mine tailings contaminate water bodies and soil in the MLM area, as well as the contamination of the sweet thorn and maize plants. To provide answers to the research problem that was investigated in this study, the overall research question was further partitioned into sub-questions in the following manner:

1. To what extent is surface water contaminated by physical water quality properties, as well as PHEs from the gold mine tailings in the MLM area?

2. To what extent is groundwater contaminated by physical water quality properties, as well as PHEs from gold mine tailings in the MLM area?
3. To what extent is soil contaminated by physical soil quality properties, as well as PHEs from gold mine tailings in the MLM area
4. To what extent is the sweet thorn plants and maize plants contaminated by PHEs from gold mine tailings in the MLM area?
5. To what extent is the sweet thorn plants and maize plants contaminated by PHEs from gold mine tailings in the MLM area?
6. What is the environmental pollution risk and the health risk of the contamination by PHEs from gold mine tailings in the MLM area?

1.6 Structure of the thesis

Chapter 1: Introduction

This chapter provides the background to the study, problem statement, the aim, the objectives for conducting the study, research questions, as well as the significance of the study.

Chapter 2: General literature review

This chapter reviews previous studies on environmental contamination of PHEs from gold mine tailings in relation to the following aspects; gold mining process, gold mine tailings, contaminants in gold mine tailings, transfer of contaminants from gold mine tailings, effects of contaminants from gold mine tailings on the environment and human health, assessment of PHEs from gold mine tailings and the remediation of contamination from gold mine tailings.

Chapter 3: Study design and study area

In this chapter, the research paradigm, study design, concepts of interest and development of variables have been presented. Sampling sites and zones have also been described, as well as the criteria for selection of the sampling sites, as well as the zones.

Chapter 4: Water quality of surface and groundwater

This chapter comprises of the contamination of surface water and groundwater in and around the gold mine tailings in the MLM area. The contamination of surface water and groundwater by physical and chemical water quality properties, as well as PHEs have been examined.

Chapter 5: Soil quality

In this chapter the contamination of uncultivated and the cultivated soil has been examined in terms of the physical properties, as well as contamination by PHEs in and around the gold mine tailings in the MLM area.

Chapter 6: Uptake of potential harmful elements in plants

In this chapter the contamination of sweet thorn and maize by PHEs has been assessed.

Chapter 7: Environmental pollution risk and health risk of contamination by PHEs from gold mine tailings in the MLM Area

This chapter comprises of the potential environmental pollution risk resulting from the environmental contamination by PHEs, as well as the health risk that may arise from the exposure to PHEs by humans in the environment. In this chapter, the procedure for the development of the Combined Pollution Risk Index, for the determination of the total pollution condition for each of the zones that were identified in this study has been described. The chapter also contains the overall environmental and health risk classification of each of the sampling sites in the MLM area.

Chapter 8: Overall discussion, conclusions and recommendations

This chapter provides the major findings of the study, in relation to the extent of contamination of water and soil by contaminants from gold mine tailings. The chapter also contains major findings regarding the uptake of contaminants from contaminated soil by sweet thorn and maize plant. Finally, the chapter integrates the findings from this study with previous knowledge, and proposes recommendations as well as implications for future research.

Chapter 2

Literature Review

2.1 Introduction

Mining is a major economy activity in South Africa, because of the many mineral resources such as gold, diamond, coal, platinum, uranium, chromium, manganese etc. Though contribution from the mining sector has been declining in recent years, according to the Department of Mineral Resources (DMR), South Africa still has 96% of the world reserves of Chrome, Manganese and gold, with gold reserves alone being estimated at about 6000 tons (DMR, 2017). In 2009 mining contributed 8.8 per cent directly and 10 per cent indirectly to the country's gross domestic product (GDP), sustained one million jobs and provided 10.5 billion rand as state income from corporate tax (van der Schyff, 2012). In 1887 the largest Stock Exchange market in Africa, the Johannesburg Stock Exchange (JSE) was established to fund the mining sector and two years later in 1889, the Chamber of Mines was established which later became the Mineral Council South Africa (MCSA) in May 2018. Trade unions were also established, such as the Federation of South Africa Trade Unions (1979), the National Union of Mine Workers (1983), and the Congress of South Africa Trade Unions (1985) to collectively bargain for better pay and good working conditions for mine workers (MCSA, 2019). The Mining Charter of 2002 came into effect in 2004 (Twala, 2018; MCSA, 2019). In 2010 a new Mining Charter was launched in South Africa to facilitate the transformation of the mining sector and to allocate 26% of mining assets to black South African (Twala, 2018). While the discovery and mining of gold and other minerals was a huge support to the South African economy, the exploration and mining of these resources was also a source of bloody conflicts and racial unrests. For example, the Anglo-Boer/South African war (1894-1902) was due to fight over the control of goldfields. On the other hand, since the creation of trade unions, their activities have never stopped, and at times ended up in bloody confrontation like the Marikana massacre of 16 August 2012.

2.1.1 Background to gold mining in South Africa

Gold mining in South Africa started as far back as the 18th century along the Witwatersrand basin (WB). The main gold bearing conglomerate was discovered by George Harrison along Langlaagte farm, but, prior to this discovery, some minor gold reefs had been discovered by Jan Gerrit Bantjes on the Vogelstruisfontein farm, as well as on the Wilgespruit farm by Fred Struben (Durand, 2012, Harrison, 2016; Krugger, 2018). Later in the 18th century, nine other farms were established as public digging, and according to information from South African History Online (SAHO), these farms today form the Central Rand, which include; Elandsfontein, Driefontein, Doornfontein, Turffontein, Rand-jieslaagte, Paardekraal, Vogelstuisfontein and Roodepoort (Durand, 2012, SAHO, 2016). Towards the end of the 18th century, individual miners, as well as small companies could no longer mine the gold in these area as the gold ore became difficult to extract, and as such there was need for specialised equipments to extract and to crush the gold ores (Durand, 2012, SAHO, 2016). Then after, commercial mining companies took over the mining of gold, and some of the major role players who owned gold mines in that era were William Knight, who had the first gold mining company called the Witwatersrand Gold Mining Company (SAHO, 2018). Goch also founded the George Goch Mining Company, as well as the Wemmer Gold Mining Company. As the rich gold deposits extended deeper into the earth's crust, the mining process was transformed from the opencast shallow pit to the underground mining process, using new techniques and sophisticated technology (Durand, 2012). The underground mining process has been improved in South Africa, and is still the best method used till date for extracting gold. After 120 years of mining on the Kaapvaal Craton, operations in the area reached depths of 4 km (MCSA, 2021).

As the gold deposits got depleted around the Central Rand and production cost was high, new mines were now opened along the periphery of the Witwatersrand, such as the Free State, Far West Rand and Evander (Durand, 2012; MCSA, 2021). From around the late 19th century, the large gold mines on the West Witwatersrand line were established, and towns like Carletonville and Klerksdorp became prominent (MCSA, 2021). For many years, the Witwatersrand Basin (WB) contains one of the largest gold deposits in the world and approximately 40% of global gold production came from this area (Manzi et al., 2013; MCSA, 2021). The WB, which is in the north eastern part of South Africa stretches through three provinces; from Johannesburg and Vereeniging in Gauteng to Potchefstroom and Klerksdorp in the North West and down to Welkom in the Free State (Hansen, 2015; MCSA, 2021). Many companies started mining gold at the Witwatersrand and the concentration of these mining companies attracted many migrant workers not only from different parts of South Africa but also from neighbouring countries and beyond (MCSA, 2019). The name “Egoli” or the city of Gold as Johannesburg is popularly known stems from the dominance of gold mining. The Big Hole in the Northern Cape is also a historical mining site in South Africa (Casey, 2019; MCSA, 2020; 2021). In 1946, gold was discovered in the Free State (MCSA, 2019) and the MLM where this study is focused has historically been a major mining district in the Free State Province. The towns of Welkom and Virginia were established near Odendaalrus to accommodate the growing mining companies.

In recent years gold mining is dominated by legally registered multinational companies who own most gold mines in South Africa. However, there are small artisanal miners who often mine gold illegally. The illegal mining of gold by individuals popularly referred to in South Africa as the “Nzamazamas” provide individual income to the miners but is also a constant death trap to these illegal miners. While most gold mine tailing are produced by the large multinational companies, the small but collective impacts of open cast mining by artisanal miners on the environment also needs careful investigation for possible regulation by the government.

The increasing rate of exploitation of gold in these areas, including the use of very sophisticated machineries to extract gold from the earth’s crust, as well as the processing of gold ores, has produced large quantities of waste or by-products. In most instances, a larger proportion of the gold ores extracted end up as waste materials, which are disposed on the surface of the earth forming gold mine tailings (Lottermoser, 2010; Muhammad et al., 2011; Ali et al., 2013; Kossoff et al., 2014; Ngure et al., 2014; Kossoff et al., 2014; Hao & Jiang, 2015; Egli et al., 2017). These gold mine tailings contain several contaminants, which have been described as the most important source of environmental pollution (Hoa & Jiang, 2015; Ngole-Jeme & Fantke, 2017). As a result of the toxic, persistent and non-biodegradable properties of these contaminants, the high levels of these contaminants in the environment may pose a serious health risk to humans who are exposed to these contaminants (Goretti et al., 2016; Ngole-Jeme & FantKe, 2017).

2.2 Gold mining process

The gold mining process begins with the extraction of gold ores from the earth’s crust. The extracted gold ores are then crushed into fine particle sizes to ease the process of separation of pure gold component from the ores (McCarthy, 2011; Abdul-Wahab & Marikar, 2012). Mercury amalgamation and the cyanide leaching processes have mostly been used in South Africa to extract pure gold from its ores (Naiker et al., 2003).

Mercury amalgam technique was first used in South Africa in 1886 when gold was discovered along the WB in South Africa (Naiker et al., 2003; Tutu et al., 2008; Durand, 2012). With the amalgamation process, mercury is applied unto the crushed gold ores. The mercury dissolves small gold particles from the ores to form an alloy of gold and mercury, which is described as mercury – gold amalgam. At the end of the process, the mercury – gold amalgam is distilled to recover the fine pure gold particles (Naiker et al., 2003; Abdul-Wahab & Marikar, 2012). Over the years, the mercury amalgam technique became unprofitable since mining operations became deeper and the acid producing rock called pyrite was also found to be associated with the gold ores (Fashola et al., 2016). However, mercury amalgam technique is still used by artisanal and small-scale gold miners in South Africa.

The mercury amalgamation process was later replaced by the cyanide leaching process since the cyanide leaching process was more profitable, as the process could extract 95% to 98% of gold from its ores (Naiker, et al., 2003; Tutu et al., 2008; Durand, 2012). With the cyanide leaching process, the gold is first dissolved from its ore using a cyanide solution, and then the dissolved gold is recovered from the cyanide solution by cementing with zinc or adsorption to activate carbon (Fashola et al, 2016). For low-grade ore, gold can be separated from its ore by a cyanide “heap leaching” process. With the cyanide heap leaching process, a solution containing cyanide is added to the finely crushed heap of gold ores which are placed on a plastic-lined pads. The cyanide dissolves the gold from the ore into the solution as it drips through the heap and the resulting solution is collected at the bottom of the pad, and the pure gold is chemically extracted (Fashola et al., 2016). A high pH is required in the leaching process, and because of the acidic condition produced, lime is usually added to the cyanide solution to adjust the pH (Tutu et al., 2008). However, when separating gold from high grade ore, the tank leaching process is used, in which crushed ore is mixed with cyanide solution in large tanks. The cyanide binds to the gold ions, and makes them soluble in water, thereby allowing separation from the ore. The cyanide leaching process remains the most suitable method used to extract gold from ores in South Africa, particularly in the Witwatersrand areas (Abdul-Wahab & Marikar, 2012).

2.2.1 Gold mine tailings

The extraction and processing of gold ores simultaneously produces enormous quantities of waste. These waste, which are described as tailings are generated as by-products from the processing of gold ores, which consist of mixtures of crushed rocks, chemicals for processing of gold ores and processing fluids from mills, as well as washeries that remain after the extraction of the pure gold (Lottermoser, 2010; Abdul-Wahab & Marikar , 2012; Kossoff et al., 2014; Fashola et al., 2016). The waste substances that are produced from when the gold ore is mined from the earth’s crust until when the ore is refined are often disposed on the surface of the earth close to a mine sites and the waste is collectively described as gold mine tailings (Abdul-Wahab & Marikar 2012; Kossoff et al., 2014).

2.2.2 Storage of gold mine tailings

As a result of environmental pollution associated with tailings, several tailings disposal options have been adopted by different gold mining companies in South Africa. In most instances, environmental pollution associated with mine tailings can be prevented if tailings are properly preserved. Mine tailings may be stored under water. This involves direct disposal of tailings into rivers, lakes or sea to prevent oxidation of pyrite, which may be present in the tailings (Edraki et al., 2014; Kossoff et al., 2014; Schoenberger, 2016). Tailings may also be stored in pits that were created during the extraction of gold ores from underground mining or stored behind dams that have been created with the use of mine waste (Edraki et al., 2014; Kossoff et al., 2014; Schoenberger, 2016). Although disposal of mine tailings in water, and behind dams, or in isolated impoundments has been a practice over the years, in most instances, these practices usually result in dam failures with devastating consequences (Kossoff et al., 2014).

2.2.3 Contaminants in gold mine tailings

Mine tailings are a very harsh sites containing a wide range of contaminants. These contaminants in mine tailings include high concentrations of acid producing rocks called pyrite, as well as a wide range of chemical elements, which are metallic in nature, as well as metalloids (Lottermoser, 2010; Doronila et al., 2014; Fashola et al., 2016; Fashola et al., 2020). The acid producing rock pyrite, as well as other metallic elements such as mercury (Hg), arsenic (As), cadmium (Cd), and lead (Pb), cobalt (Co), copper (Cu), chromium (Cr), nickel (Ni), iron (Fe), manganese (Mn), molybdenum (Mo), selenium (Se) and zinc (Zn) in mine tailings originate from the gold-containing ore (Etteieb et al., 2020; Okereafor et al., 2020; Tun et al., 2020). On the other hand, mercury and cyanide (CN) are added to mine tailings during the chemical processing of gold ore (Nkuba et al., 2019).

These metallic elements and metalloids in mine tailings have been described with different names in literature. The majority of authors have described these metallic elements/ metalloids in gold mine tailings as heavy metals (Tchounwou et al., 2012; Kamunda et al., 2016; Ali et al., 2019). Other authors described them simply as metals and metalloids (Ali et al., 2019; Ngole-Jeme et al., 2020), while some other authors classified them as potential harmful elements (Ngure et al., 2014). However, in this study, these chemical elements that are associated with the gold mine tailings have been described as potential harmful elements (PHEs), because of the likely harmful effects of these chemical elements on the environment, as well as on human health.

2.3 Environmental pollution by potential harmful elements from gold mine tailings

2.3.1 Classification of potential harmful elements

PHEs are described as metallic elements which occur naturally in the earth's crust and have a high density. However, in recent times, anthropogenic activities such as mining have released these PHEs in high concentrations into the environment. Some of these PHEs, such as As, Co, Cu, Cr, Ni, Pb and Zn, exists in trace concentrations in the ecosystem, as such they are referred to as trace metals (Kamunda et al, 2016). More so, based on the role of these PHEs to humans and other living organisms in the ecosystem, some of these trace metals are described as essential trace metals, since they are required for various physiological processes (WHO, 2011; Kamunda et al., 2016; Engwa et al., 2019; Okereafor et al., 2020). However, high concentrations of these essential trace metals such as Cu, Co, Fe, Ni, Cr, Se, Mn and Zn may still cause harm to living organisms (WHO, 2011; Ali et al., 2019; Engwa et al., 2019). Other trace metals such as Cd, Pb, Cr and As, do not have any important role to humans and other living organisms, and are described as non-essential trace metals. Such PHEs are toxic at trace levels and can cause severe acute and chronic toxicities to living organisms (Tchounwou et al., 2012; Kamunda et al, 2016; Ali et al., 2019; Engwa et al., 2019; Okereafor et al., 2020). The World Health Organisation has also classified these PHEs as carcinogens and chemicals of major public health concern (WHO, 2011).

2.3.2 Occurrence of potential harmful elements in the environment

Due to the persistent properties of these PHEs, their accumulation in the environment may eventually contaminate food chain, causing potential health risk to humans and other living organisms (Ali et al., 2019). Furthermore, the extent of toxicity of PHEs in the environment is also because of the occurrence or the form in which these PHEs are present in the environment (Fashola et al., 2019). The oxidation state of these metals determines their relative mobility, bioavailability and toxicity (Ebenebe et al., 2017).

Occurrence of arsenic

Arsenic has been considered as one of the most toxic heavy metals worldwide. Even at a very low level of exposure, arsenic is considered as a human carcinogen (Fashola et al., 2016). The environmental occurrence of As, shows a strong association with gold ores. Arsenic is mostly present with gold ores in sulphides, particularly pyrite (FeS_2), arsenopyrite (FeAsS), realgar (AS_2S_2) and Orpiment (As_2S_3) (Bowell et al., 2014; Fashola et al., 2016). Arsenic is widespread in the earth’s surface with the mean concentrations of about 2 mg/kg in the earth’s crust, but concentration of As in water is usually below 0.01 mg/kg (DEA, 2010). However, an extremely high concentration of As ranging between 2500 to 6420 mg/kg has been measured in mine tailings within the Myungbong gold mine area in Korea (Ko et al., 2003). The high concentration of As in the tailings within the area were a source of contamination of the environment in the vicinity of the gold mine tailings. A relatively low concentration level of As, which ranged between 0.7 to 3.3 mg/kg have been measured in a gold mine tailing in the vicinity of the Chirano Gold Mine in Ghana (Sey & Belford, 2019). Although the concentration of As in the tailings were below the FAO/WHO permissible limits, there is still a possibility that the As which is leached from the mine tailings into the environment, may accumulate along the food chain to cause potential harm to humans. Within the Krugersdorp mining area in South Africa, high concentrations of As in the order of 3.17mg/kg to 4.00 mg/kg were measured in gold mine tailings soil in the area (Ngole- Jeme & Fantke., 2017).

Occurrence of Cadmium

Cadmium has also been described as toxic trace metal to majority of the living organisms. Cadmium is mostly associated to the gold ores as an isometric trace element in sphalerite (ZnS). The concentration of Cd in the gold ore depends on the concentration of the sphalerite that is also present in the gold ore (Fashola et al., 2016). The background concentrations of Cd in soils usually range between 0.6 mg/kg to 2.7 mg/kg and for water, the concentration is not usually greater than 1ug/l (DEA, 2010). However, a high concentration of Cd in the order of 62.08 mg/kg were measured in a mine tailing within an abandoned mine site in Tunisia, which exceeded the standards for Cd in soils in Tunisia and Canada (Olobatoke & Mathuthu, 2016). Concentrations of Cd ranging between 20.9 mg/kg to 47.0 mg/kg have also been registered in a gold mine tailing soil in Buru Island of Maluku (Hindersah et al., 2020).

Occurrence of lead

Lead is another toxic trace metal, which is non-essential to living organisms. In gold mine tailings, when the sulphide concentration is high, Pb is present in the gold mine tailings as galena (PbS) (Babbou-Abdelmalek et al., 2011). Naturally, Pb is present in the earth’s crust in different oxidation states, but Pb (II) and lead-hydroxy complexes are the most stable forms. However, the ionic form, Pb (11) is the most reactive form (Fashola et al., 2016). Background concentrations of Pb in surface soils range from 3.0 to 65.8 mg/kg, while for surface waters less than 0.01 mg/l can be measured (DEA, 2010). However, a high mean concentration of 17.01 mg/kg has been measured for Pb in mine tailings dam in the vicinity of an old gold mine in Johannesburg South Africa(Olobatoke & Mathuthu, 2016). A very high concentration ranging from 121.9 mg/kg to 125 mg/kg was measured in an abandoned gold mine dump in Ekurhuleni Area in South Africa (Ngole- Jeme & Fantke, 2017).

Occurrence of Chromium

Chromium is a toxic PHEs that occurs in trace concentrations in the earth's crust. It exists in the earth's crust as chromate ($FeCr_2O_4$), having 70% of pure Cr_2O_3. Cr occurs in different oxidation states ranging from -2 to +6, of which Cr (111) and VI are the most stable forms. In natural environments, Cr occurs as trivalent chromium (Cr (III)) such as in fresh vegetables, fruits, meat, grains, and yeast and is often added to vitamins as a dietary supplement (DEA, 2010; Fashola et al., 2016). However, the hexavalent chromium is the most oxidized form, and potentially dangerous substance due to its high solubility and mobility, which allows it to infiltrate and pollute water and soil, as well as underlying groundwater. This form is usually found at contaminated sites (DEA, 2010; Fashola et al., 2016). The concentration of naturally occurring chromium in South African surface soils ranges from 5.8 to 353 mg/kg, but may be considerably higher in mineralised areas and even exceed 2,000 mg/kg (DEA, 2010).

Occurrence of zinc in the environment

Zinc belongs to the group of essential trace metals, which serves as nutrients for plants and animals, as well as for humans. Zinc is associated with gold ore bodies in the form of sphalerite (ZnS) which is often associated with galena (Fashola et al., 2016). The background concentrations of Zn in soils may range between 12 to 115 mg/kg, while the concentrations in water may be as a low as 0.015 mg/l (DEA, 2010). A high mean concentration of Zn of 58.19 ppm has been measured in a tailing dam in the vicinity of an old gold mine in Johannesburg in South Africa (Olobatoke & Mathuthu, 2016).

Occurrence of Copper

Copper is also an essential trace element, which is required for several physiological processes in plants, animals, as well as humans. Copper is widely distributed in sulphides, arsenites, chlorides and carbonates in gold ores, which includes chalcopyrite ($CuFeS_2$), as well as tetrahedrite ($Cu, Fe_{12}Sb_4S_{13}$) (Vikent'ev et al., 2006; Fashola et al., 2016). Copper can exist as Cu (II), which is the oxidised state, as well as Cu (I), which is the reduced state (Fashola et al., 2016). Concentrations of Cu in soils may range between 3 mg/kg and 117 mg/kg. However, concentrations of 20.21 mg/l have been measured in tailing soil in South Africa (Olobatoke & Mathuthu, 2016).

Occurrence of Nickel

Nickel has also been described as an essential trace metal, which is required for the normal functioning of living organisms. However, when ingested at a high concentration, it may result to certain adverse effects (Okereafor et al., 2020). The concentration of Ni may vary in different soils, and may range from 3.4 mg/kg to 159 mg/kg (DEA, 2010). In the earth's crusts Ni is associated with gold ore in the form of pyrrhotite (Fe(1-X) S), as well as pentlandite (FeNi)S8 and gersdorffite (NiAsS) (Fashola et al., 2016). Ni exist in the earth's crust in different oxidation states, which include -1, +1, +2, +3 and +4 states, with +2 state being the most dominant (Cempel & Nikel, 2006; Genchi et al., 2020).

2.3.3 Transfer of potential harmful elements from gold mine tailings to the environment

As a result of the exposure of mine tailings on the earth's surface, these pollutants present in the mine tailings may be released into the environment, thus causing environmental hazards. Mine tailings containing pollutants may be transferred to the environment by wind, rainwater run-off, infiltration and percolation of rain water into the soil and rocks, as well as groundwater flow (Boularbah et al., 2006; Djebbi et al., 2017; Bae et al., 2010; Wahl et al., 2013, Chen, 2015). Furthermore, in certain rare situations, tailing dam failures may cause pollutants from mine tailings to be transferred into the environment (Chen, 2015). These PHEs may ultimately enter water and soils and may later be passed along the food chain from where they indirectly cause harm to the environment and living organisms (Boularbah et al., 2006; Zhuang et al., 2009; Chen 2015; Djebbi et al., 2017).

2.3.4 Wind transport of potential harmful elements from gold mine tailings to the environment

Transport of particulate matter from mine tailings by wind may be considered as the dominant cause of movement of pollutants from mine tailings into the environment. Mine tailings are predisposed to wind erosion mostly because the mine tailings are elevated, when compared to adjacent lands in the vicinity. Moreover, wind can easily transport mine tailing particles because these tailings are usually bare and lack vegetation cover, particularly in the arid and semi-arid regions having dry climate (Ojelede et al., 2012; Stoven et al., 2016). Wind erosion of mine tailings may also arise as a result of the reprocessing of the mine tailings to recover gold that was remaining in the tailings during gold extraction (Naicker et al., 2003; Ojelede et al., 2012). Such erosion may vary from very large dust storms that can travel thousands of kilometres in the atmosphere to small local sources having very little effects and restricted to a region (Stoven et al., 2016). During windy conditions, particulate matter is transported from contaminated mine tailing sites and deposited in the vicinity of the mine tailings, as well as beyond the tailings (Blight, 2007; Castillo et al., 2013).

High concentrations of PHEs have been measured in dust particles that are transported by wind from mine tailings. The concentrations of these pollutants were observed to decrease with distance away from the tailings (Djebbi et al., 2017). High concentrations of PHEs with toxic properties including, cadmium (36 mg kg^{-1}), arsenic (24 mg kg^{-1}) and mercury (1.2 mg kg^{-1}) were measured in particles that were blown from an abandoned mine tailing in Hammam Zriba, in the Northern part of Tunisia. The concentrations of other PHEs that were measured in the study, such as Ba (5%) Sr (4%), S (7%), F (1%), Zn (0.8%) and Pb (0.2%), revealed higher concentration closer to the tailings site as compared with concentrations away from the tailings. Although concentrations of these pollutants measured decreased with distance away from the tailings, the concentrations of the PHEs measured beyond the tailings were also higher than the standard limits in the area (Djebbi et al., 2017). The high concentrations of the PHEs that were measured away from the tailings could have resulted from the presence of other pollution sources in the area, such as industrial activities and moving cars. In a similar study, high concentrations of lead (1616 ppm) and arsenic (1420 ppm) were measured in dust particles from the Iron King Mine tailings site in Dewey-Humboldt Arizona, which contaminated the environment beyond the mine tailings with high concentrations of lead and arsenic. Modelling of the dust particles transported from the mine tailings to the surrounding region confirmed that dust transport from mine tailings is the dominant cause of the spread of contaminants into the surrounding areas (Stoven et al., 2014). In South Africa and for more than a century, the WB has experienced severe dust storms, which originated from its numerous gold mine tailings within the area (Ojelede et al., 2012). Soils collected from gold mine tailings in the eastern and western mining areas of the WB contained high levels of dust particles containing pollutants, with particulate matter sizes smaller or equal to 5 µm and smaller or equal to 10 µm (≤PM5 and ≤PM10). Such particulate matter with diameter of 10 µm and bellow can easily be eroded by wind and can also settle relatively quickly, particularly particulate matter from recent mine tailings. This result suggested that wind erosion and transportation of dust from mine tailings was the main source of particulate matter in the atmosphere within the vicinity of the mine tailings in the Witwatersrand areas (Ojelede et al., 2012). These increasing emissions of fine particulate matter from the tailings into the atmosphere have greatly impacted on the health of humans who are residing in and around the vicinity of the mining areas (Ojelede et al., 2012).

2.3.5 Rain run-off transport of pollutants from gold mine tailings to the environment

During rainfall events, water infiltrate and percolates through mine tailings resulting in vertical and horizontal movements of water through the mine tailings, which in turn mobilises PHEs that are present in the mine tailing. The PHEs are leached from the tailings, and may contaminate surface water, groundwater and soils in the vicinity of the tailing. The water that infiltrates through mine tailings may also undergo reactions with pyrite present in the mine tailings. This results in oxidation of pyrite, which produces acids that mobilises the PHEs and cause the migration of PHEs through the mine tailings (Naicker et al., 2003; Akcil & Koldas, 2006;Tutu et al., 2008; McCarthy, 2011). Once these products from oxidation are released into the environment, they may cause serious negative impacts on the environment. For example, the Oxidation of pyrite within mine tailings in the Novo-Ursk mining area in Russia, as well as the Dabaoshan mining area of the Guangdong Province in China produced acid mine drainage (AMD), that precipitated pollutants such as Fe, Al, Cu, Zn, Pb, As, Se, Te, Hg and Cd from mine tailings (Jian-Min et al., 2007; Myagkaya et al., 2016).. The AMD containing pollutants that flowed from the mine tailings contaminated the water and soils in the surrounding areas. The acidity of UR River in the Novo-Ursk mining area reduced to 1.9 pH units with high concentrations of gold and silver, ranging between 0.4 to 1.2 ppb Au and 0.1 to 0.3 ppb Ag (Myagkaya et al., 2016). Paddy soils beyond the Dabaoshan mining area were also contaminated with high concentrations of toxic heavy metals, including Cu (567 mg kg^{-1}), Zn (1 140 mg kg^{-1}), Cd (2.48 mg kg^{-1}), and Pb (191 mg kg^{-1} (Jian-Min et al., 2007).

In the WB of South Africa, AMD and heavy metals produced from the gold mine tailings have also contaminated groundwater and streams beyond the mining area. Naicker et al. (2003) analysed the contamination of groundwater by heavy metals and acids arising from the oxidation of pyrite in the vicinity of the gold mine tailings and up to 10 km beyond the mine tailings (Naicker et al., 2003). The results reveal that acidic water from the mine tailings polluted the surface water within the surrounding area, particularly where the water table was close to the earth's surface. The acid mine drainage water, which flows from mine tailings into the environment are neutralised by adding limestone ($CaC0_3$) to increase the pH level of water (Akcil & Koldas; 2006; McCarthy, 2011). The limestone added reacts with sulphuric acid to produce sulphates salts. This raises the pH levels of the resulting effluent to acceptable concentrations that can be tolerated by humans who depend on the water beyond the mine tailing (Akcil & Koldas; 2006; McCarthy, 2011). AMD is a rising environmental and health problem in South Africa (Turton, 2012).

2.3.6 Dam failures as a transport medium of pollutants from mine tailings into environment

Tailings dam failure usually results when tailings lose their structural stability and materials that are released from the tailings constitute a mixture of liquids and solids that travel under much gravity. These environmental disasters often produce catastrophic effects on environment, as well as human health (Kossoff et al., 2014). The Fundão iron-ore tailings dam failure in 2015 caused the flow of sludge of about 62 million cubic meters from the mine tailings and contaminated vast area, including Bento Rodriques, which is situated in the state of Minas Gerais in Brazil (Neves et al., 2016). This disaster affected close to forty-one municipalities in the states of Minas causing the death of 19 people and leaving over 600 people homeless (Neves et al., 2016). The sludge also polluted the Rio Doce River in the area causing the death of fish and other aquatic organisms in the water (Neves et al., 2016). The Marriespruit dam failure in South Africa, which was caused by heavy rains that flooded mine dams in the area, resulted in severe environmental pollution (Davies, 2013). Since mine tailings contain toxic substances, safe methods must be used to design and construct these tailings dams, in order to prevent dam failure, or mitigate their impacts on water, soil, as well as human health.

2.4 Effects of potential harmful elements from gold mine tailings on the environment

Pollution of the environment by PHEs has received much attention over the years mainly because some of these PHEs are very persistent and can therefore accumulate in the environment and become highly toxic (Xu et al., 2016; Singh & Kumar, 2017). The accumulation of these PHEs in waters and soils poses a risk to the environment and human health (Cai et al., 2017).

2.4.1 Water pollution

Mine tailings contaminants have been described as the most prevalent source of pollution of surface and ground waters around the vicinity of the mine tailings. Water pollution from mine tailings contaminants has been a major problem worldwide, particularly in countries across, Asia, Australia, America, as well as Africa. Surface water is more susceptible to contamination because surface water is more exposed to the environment; they are accessible and are widely used for different activities (He, 2018). Surface water pollution may be transported beyond the mining area as a result of the flowing nature of water; thereby contamination is often spread beyond the source of pollution, such as mining areas (Ngure et al., 2014). Being one of the world's dominant gold producer, with a long history of mining and countless gold bearing reserves, China has over the years experienced severe water pollution problems due to the contamination of PHEs from gold mining (Zhang et al., 2017). Water quality assessment carried out in three natural reserves in Tianjin, China; Qilihai Natural Reserve, the DaShentang Reserve and the BinHai Wetland Reserve, using heavy metal pollution index and the human health risk index revealed contamination by Pb, As, Cd, Hg and Cr, with the concentrations of As and Pb exceeding the United State Environmental Protection Agency (US EPA) standards for marine water. The human health risk index determined for Qilihai Natural Reserve and the BinHai Wetland Reserve revealed that humans residing in the area were exposed to risk arising from the heavy metals pollution (Zhang et al., 2017). On the other hand, Gao (2017) also measured high concentrations of As and Hg in rivers in the vicinity of a gold mine in Mongolia, Northern China. The results of the study indicated that the concentration of heavy metals in the river decreased substantially with depth, as well as away from the gold mine, and were almost zero when measurements of these heavy metals were made in the Zhaosu River, which was further from the gold mine (Gao, 2017).

Water pollution by PHEs from mine tailings has also been a serious issue within countries in Australia. For example, gold mining processes within the Gold Ridge mine of Guadalcanal in South Australia caused the contamination of river courses, as well as sediments with high levels of As ranging between

0.087 mg/L to 377 mg/L, which were about 10 times higher than the sediment and water guidelines levels in the area. The contamination level in the river posed severe threats to aquatic organisms (Albert et al., 2017).

In countries in Africa, gold mining activities have caused severe pollution of rivers and streams, in the vicinity of the mining areas. Surface water within the Mari catchment in the Bétaré-Oya gold mining areas in Cameroon has been contaminated with high levels of Pb, Cd, Mn, Cr and Fe, exceeding the limits stipulated for safe drinking water by the World Health organisation (WHO) (Rakotondrabe et al., 2018). Thus, the surface water in the vicinity of the Bétaré-Oya gold mining area was no longer suitable for human consumption (Rakotondrabe et al., 2018).

Over the last few decades, there have been concerns on the impact of mining on water resources, mostly from small scale gold mining (Rakotondrable et al., 2018). The Gambia River in Senegal was contaminated with mercury (Hg), which is used to process gold by the artisanal small-scale gold miners in the Kedougou area. High levels of Hg of about 9.9 mgkg^{-1} were measured in the dry season in sediments within the vicinity, where the artisanal small-scale gold mining activities were practiced. The values exceeded the Sediment Quality Guidelines and the Probable effect concentration required for the Protection of Aquatic Life in Senegal (Niane et al., 2014). Moreover, the use of mercury to process gold by the artisanal small-scale gold miners has also resulted in the contamination of water in the vicinity of the Migori Gold Belt (MGB) in Kenya. High concentrations of Cd (1.5 to 10.5 μg l^{-1}), Pb (0.4 to13.1 μg l^{-1}), As (0.06 to 23.0 μg l^{-1}) and Hg (0.36 to 52.1 μg l^{-1}), higher than the maximum allowable levels (MAC) of the World Health Organization (WHO) and the Food and Agriculture Organisation (FAO) were measured in samples of water, from the area (Ngure et al., 2014). However, these heavy metals concentrations were observed to decrease at a reference site which was situated at approximately 70 km away from the mining site (Ngure et al., 2014). On the other hand, high concentrations of Hg in the order of 223 ng Hg L^{-1} and 2580 μg Hg kg^{-1} were measured in surface waters and sediments within the vicinity of the gold mine tailings in the Randfontein gold mining area in South Africa, resulting from artisanal mining activities (Lusilao-Makiese et al., 2013). Groundwater within the Krugersdorp Game Reserve, which is situated away from the Randfontein mining area were also observed to contain high Hg concentrations of about 223 ng Hg L^{-1} (Lusilao-Makiese, et al., 2013).

2.4.2 Effects of potential harmful elements on aquatic organisms

Accumulation of PHEs in water may pose a risk to aquatic organisms. Since aquatic organisms spend most of their life cycle in water, these aquatic organisms can take up these PHEs from polluted water and store them in some of their body tissues (Ali et al., 2013). Certain macro-invertebrates species that thrive in water contaminated by PHEs have been known to accumulate PHEs in their body tissues. For instance, cray fish, *Procambarus clarkii* collected from industrial polluted site, as well as from a reference site in Central Italy accumulated high concentrations of heavy metals including Cd (11.7 mg/kg), Cu (5.5mg/kg), Pb (3.6 mg/kg), Zn (1.0 mg/kg) in their hepatopancreas (Goretti et al., 2016). Even at lower concentrations of these heavy metals, Pb (4.34mg/kg), Cd (3.66 mg/kg), Zn (1.69mg/kg), Cu (0.87mg/kg) there was evidence of bioaccumulation of these heavy metals in some of the body tissues of the cray fish species. Therefore because of the heavy metals bioaccumulation in *Procambarus clarkia*, this species is used as a bioindicator for heavy metals pollution in freshwater ecosystems (Goretti et al., 2016). On the other hand, high concentrations of arsenic analysed in the waters along the Atlantic coastline in Nova Scotia, Canada, revealed that mollusc species accumulated arsenic in their soft-shell clam tissues (Doe et al., 2017). The bioavailability of arsenic in mollusc species at Seal Harbour was above the guidelines of the environmental quality in Canada (Doe et al., 2017).

Different fish species are capable of absorbing PHEs from contaminated water into their body tissues. In China, pollution of the upper Yangtze River with high levels of As, Cd, Cu, Hg, Zn and Pb caused fish species in the stream to accumulate As and Cd (Yi et al., 2017). However, the consumption of the contaminated fish species may not have caused any adverse health impacts to humans because the total target hazard quotient index that was computed suggested that the populations may not have been exposed to any carcinogenic health impacts (Yi et al., 2017). On the other hand, because of the heavy metal pollution of the water in vicinity of the Migori Gold Belt area in Kenya, certain fish species accumulated heavy metals in their body tissues. For example, the *Rastrineobola argentea*, stored heavy metals in their body tissues ranging between; Cd: (4.5 to 570 mg kg^{-1}), Pb: (5.9 to 619 mg kg^{-1}), As: (0.08 to 86.0 mg kg^{-1}), and Hg: (0.51 to 1830 mg kg^{-1}) (Ngure et al., 2014).

Heavy metals absorbed and stored in the tissues of aquatic organisms can be passed along the food chain, from one trophic level to the next. In most instances the concentration levels of the heavy metals in the tissues of the aquatic organisms increases as the metals are transferred from a lower trophic level to a higher trophic level, a condition that is described as bio-magnification (Ali et al., 2013). Oberholster et al. (2012) measured high concentrations of Al and Fe in different aquatic species along the food chain in Lake Loskop in South Africa. *Spirogyra fluviatilis* and *Spirogyra adanata* showed the highest concentration of Al (18,997.5 mg kg^{-1}) and Fe (22,054.2 mg kg^{-1}) in filamentous algae species, while the macro-invertebrate, *Gomphidae*, reflected the highest concentrations of Al (385.7 mg kg^{-1}) and Fe (1710.0 mg kg^{-1}). In addition, the bioaccumulation of Al and Fe in Mozambique tilapia, *Oreochromis mossambicus*, at levels of 2580 mg kg^{-1} for Al and 10,697 mg kg^{-1} for Fe, also supports the transfer of Al and Fe along the food chains.

2.4.3 Soil pollution

Pollution by PHEs arising from gold mine tailings has been the centre of research in most countries worldwide as soil are noted to be the major sinks for PHEs released into the environment (Masindi & Muedi, 2018). These PHEs released into the surrounding environments and their accumulation in the soil may have lasting detrimental effects on the environment. This assertion is supported by the fact that PHEs are non-degradable and may not be broken down by microbial or chemical processes, therefore, may remain in the soil over a long period, and affect soil properties like soil texture as well as the depletion of available nutrients in the soil (Ali et al., 2013; Ngure et al., 2014; Hao & Jiang, 2015). Within gold mining sites in Maldon, Victoria in Australia, high levels of As and toxic heavy metals such as Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn were measured in soils in the area. The results showed that these PHEs exceeded the standards stipulated by the Australian and Victorian average top soil levels, the health investigation levels set by the National Environmental Protection Measures (NEPM), as well as the Department of Environment and Conservation (DEC) of the State of Western Australia (Abraham et al., 2018). From the lists of toxic metals that were analysed, As and Hg were found to be very toxic, and therefore pose a risk to human health and aquatic ecosystems (Abraham et al., 2018). Within the vicinity of a tailing pond in Guangdong, China, the presence of high concentrations of PHEs in the tailing caused the transfer of the PHEs to the surrounding soils, causing a high concentration of Pb, Zn, Cu, Cd, Ni, and As in the paddy soil in the vicinity of the tailing dam, at concentrations, which exceeded the Chinees soil quality standards (Liang et al., 2017). In South Africa, high concentrations of As, ranging between 13.46 to 234.6 mg kg, that were higher than the South African soil quality standards, were measured in soils in the vicinity of an old gold mine tailing damp in Johannesburg, South Africa. The high concentration of As caused a reduction in the soil fertility in the area, and ultimately affected plant growth (Olobatoke & Mathuthu, 2016).

2.4.4 Effects of potential harmful elements on plants

The uptake of potential harmful elements from the soil by plants can be considered as one of the major sources of contamination of plants (Olowoyo et al., 2012). The absorption of these heavy metals and toxic substances by plants roots and their translocation and accumulation in stems and leaves is of serious environmental concern. This is because these potential harmful elements may not only affect the growth of plants, but could also bioaccumulate along the food chain and cause severe toxic effects to other living organisms in the food chain as well as human health problems (Olowoyo et al., 2012; Hao & Jiang, 2015).

The rate of uptake of these PHEs by plants from the soil, as well as their occurrences in crops can be influenced by several factors, including, soil pH, cation exchange capacity, organic matter content, soil texture, and interaction among the target element (Jung, 2008; Ebenebe et al., 2017). Soil pH is a vital factor, because it affects several biological, chemical, and physical soil properties, and has therefore been described as the "master soil variable" (Neina, 2019). When the soil pH is low, the solubility of heavy metals in the soil increases, as well as the mobility of the metals, which in turn increases the rate of uptake of heavy metals from the soil (Martin & Griswold, 2009) The uptake of Cd, Pb and Zn have been investigated in different plants species, including the alpine pennygrass (*Thlaspi caerulescens*) and results show an increasing rate of uptake of soluble fractions of these heavy metals with increasing pH conditions (Wang et al., 2019).

High concentrations of Zn at levels of up to 530 mg kg^{-1} were measured in shoots of a poisonous weed, *Zygophyllum fabago* and up to 390 mg kg^{-1} of lead were measured in *Helichrysum decumbens*, which were growing on a mine tailing in a semi-arid mining zone in southeast of Spain (Conesa et al., 2006). The detection of zinc and lead in the shoots of these native vegetables indicated the uptake of heavy metals by these plants species from contaminated tailing soils with high concentrations of lead ranging between 5000 to 8000 mg kg^{-1} and zinc ranging between 7600 to 12300 mg kg, $^{-1}$ (Conesa et al., 2006). Within the abandoned mining areas in Korea, rice plants growing in contaminated agricultural soils absorbed PHEs from the soils and were stored in the rice grains with levels of As (0.247 mg kg^{-1}), Cd (0.174 mg kg^{-1}), Cu (4.69 mg kg^{-1}), Pb (0.804 mg kg^{-1}) and Zn (16.8 mg kg^{-1}), exceeding the average limits stipulated by a number of scientific studies in most parts of the world (Kwon et al., 2016). On the other hand, within the Rongxi mining area in Chongqing, located southeast of China, heavy metals in the order of 323 to 8434 mg/kg for Mn, 0.42 to 1.24 mg/kg for Cd, 1.96 to 46.23 mg/kg for Cu, 3.90 to 105.84 mg/kg for Pb and 19.17 to 57.64 mg/kg for Zn, were detected in 37 species of plants growing in a highly contaminated soil. Even though these plants species were all growing in the same contaminated environment, some of the plants such as *Miscanthus sinensis* and *Stenoloma chusanum* absorbed high concentrations of these heavy metals in their roots and transferred only a small amount to their shoots (root accumulators). Other species such as *Polygonum lapathifolium* and *Phytolacca Americana* could accumulate high concentrations of the heavy metals in their shoots (shoot accumulators), whereas *Debregeasia orientalis, Boehmeria clidemioides* and *Artemisia annua* could only accumulate a comparatively lesser concentration of the heavy metals in their different parts (Hao & Jiang, 2015). Therefore, uptake, concentration and transfer of PHEs could differ from plant species to plant species.

In some African countries, studies have confirmed heavy metals uptake by medicinal plants from mining areas, which are a concern, as a result of direct human exposure through the consumption of such contaminated plants. Toxic heavy metals including arsenic (0.19 to 0.54µg g^{-1}), chromium (0.15 to 1.27 µg g^{-1}), lead (0.12 to 0.23 µg g^{-1}) and nickel (0.09 to 0.21 µg g^{-1}) were detected in a wide range of medicinal plants species that were growing in the Ngamiland metal mining District in Northern Botswana (Okatch et al., 2012). These medicinal plants have been used by traditional doctors in the area to treat diseases that are associated with HIV and AIDs (Okatch et al., 2012). The heavy metals absorbed by the medicinal plants from the metal polluted soils did not exceed the permissible limits as stipulated by the World Head Organisation (WHO, 2007) and may not pose any health implications to humans who consume the plants at the time of the study. However, because these toxic heavy metals are non-biodegradable and persistent, over time when these toxic heavy metals are consumed by humans, these heavy metals may accumulate in vital organs of the human body for years or decades, thereby causing serious health consequences (Olowoyo et al., 2012). In South Africa, trace metals studies for two medicinal plants species; *Datura stramonium* and *Amaranthus spinosus,* which were growing on a dump site in Pretoria was investigated. The concentrations of Fe in the plant species ranged from 17.35 to 78.65 µg/g; for Zn, 16.84 to 52.94 µg/g was measured; for Cu, it was 5.65 to 7.31 µg/g, while 0.51 to 1.98 µg/g was measured for Pb. The concentration range between 4.36 to 5.69 µg/g for Ni and for Mn, 18.20 to 33.56 µg/g were measured (Olowoyo et al., 2012). The concentrations of these trace metals measured in the medicinal plant species were also within the tolerable limit for safe human consumption, but over time, accumulation of these trace metals in the plant's species may also be detrimental to humans who consume the medicinal plants over time (Olowoyo et al., 2012).

Since mine tailing soils contain less plant nutrients but high concentrations of heavy metals and toxic substances, the soils are infertile and thus, may affect seeds germination and may not support healthy plant growth. Thus, only very resistant plants can survive in such conditions (Conesa et al., 2006; Chen, 2015; Shen et al., 2017). In a plant growth experiment in China, seeds that were grown in petri dishes containing increased concentrations (30 to 40%) of acidic mine tailings demonstrated retarded germination and growth rate whereas normal growth of seeds occurred in soils containing 5 to 10% of farmland soils and reduced concentration of the acidic mine tailings (Chen et al., 2015). Several plant growths experiments that have been performed in different countries worldwide, have also confirmed that germination and growth of selected plant species may be retarded when soils containing mine tailings are used as growth substrate (Dorolina et al., 2014; Alcantara et al., 2015; Cele & Maboeta, 2016).

2.4.5 Effects of potential harmful elements on human health and animals

Human health risk from consuming contaminated water, fruits, vegetables and food crops by PHEs have raised concerns worldwide on the safety of foods and health implications. For example, the health of humans was negatively impacted upon after the consumption of contaminated food crops grown in four villages around the Dabaoshan mine in South China. Food crops such as rice and taro that were grown in the mining area accumulated high concentrations of Cd and Pb whiles the concentrations of Cd, Pb and Zn in the vegetables exceeded the maximum permissible concentration in China (Zhuang et al., 2009). Human health risk assessment performed to estimate the health effects that might have resulted from the consumption of such contaminated food crops revealed the target hazard quotient (THQ) values for rice at the four sites with values ranging from 0.66 to 0.89 for Cu, 0.48 to 0.60 for Zn, 1.43 to 1.99 for Pb, and 2.61 to 6.25 for Cd. The daily intake (EDI) and THQs values for Cd and Pb of rice and vegetables was found to be higher than the FAO/WHO permissible limit, thus posing health risk to the local population (Zhuang et al., 2009). Waste produced from the Songchem silver and gold mine in Korea also caused contamination of water, soil, food crops and vegetables grown within the vicinity of the mine tailings (Lim et al., 2008). The levels of As, Cd, Pb and Zn detected in the samples were found to be higher than the permissible Korean levels (Lim et al., 2008). Due to such contamination of the soil, food crops and drinking water by the PHEs, people in the area showed higher incidences of cancer compared to the inhabitants in the surrounding areas. The carcinogenic risks of the people were found to be 2.7×10^{-3}, and above the allowable limit in Korea, indicating that out of every 1000 people in the vicinity, three were liable to suffer from cancer (Lim et al., 2008). A number of similar studies performed in Bangladesh and Nigeria also reported several human health effects from the consumption of heavy metals contaminated fruits, vegetables, as well food crops that were grown in soils contaminated with As and Pb (Islam et al., 2015; Kwon et al., 2016; Obiora et al., 2016). Using target hazard quotient and target carcinogenic risk, revealed that these contaminants were far above the maximum allowable concentration limits by the World Health Organisation and carcinogenic health risk were reported from sampled populations who consumed food with high concentrations of As and Pb (Islam et al., 2015; Kwon et al., 2016; Obiora et al., 2016). On the other hand, humans that were directly exposed to mercury from small scale gold mining activities in Sibutad, in Western Mindanao, were tested positive for blood mercury (Cortes-Maramba et al., 2006). Particularly, those that were directly exposed to mercury had higher mean blood total mercury and methylmercury compared to those humans that were indirectly exposed to the mercury levels (Cortes-Maramba et al., 2006).

2.5 Assessment of the potential harmful elements in gold mine tailings

Several approaches have been used by different researchers to assess the level of PHEs in different environmental media, including water, soil and plants. Environmental pollution risk indices have increasingly been utilised in several studies to assess the extent of contamination by PHEs in an environment, as well as the risks that may be caused by the contaminants in the environment (Wu et al., 2014; Fan & Wang, 2017; Kowalska et al., 2018). Different health risk assessment approaches have also been used to estimate the increased health risk of people because of the exposure to toxic pollutants in their environment (WHO, 2010; USEPA, 2016).

2.5.1 Environmental pollution risk assessments

Environmental pollution risk indices have been used to quantify the risk that may arise from the contamination of the environment by PHEs. These different environmental pollution risk indices can be classified broadly according to several criteria (Wu et al., 2014; Fan & Wang, 2017; Kowalska et al., 2018). Based on the type of contaminants measured, the different environmental pollution risk indices can be classified into two broad groups. One group measures the extent of environmental pollution for individual contaminants in the environment. These environmental pollution risk indices are the Geo-accumulation Index (Igeo), Enrichment Factor (EF), Single Pollution Index (SFPI), Contamination Factor (Cf), as well as the Biogeochemical Index (BGI). The second group are the complex environmental pollution risk indices, which are used to determine the level of contamination of the environment for more than one heavy metal or a sum of individual indices (Kowalska et al., 2018). These environmental pollution indices include Sum of contamination (Pisum), Nemerow Pollution Index (NIPI), Pollution Load Index (PLI), Average Single Pollution Index (PIave), Vector Modulus of Pollution Index (PIVector), Background enrichment factor (PIN), Multi-element contamination (MEC), Contamination Security Index (CSI), The probability of toxicity (MERMQ), Degree of contamination

(Cdeg), Potential ecological risk (RI), Modified degree of contamination (mCd) and Exposure factor (ExF) (Kowalska et al., 2018).

Environmental pollution risk indices could also be classified based on the pollution indicator of the index measured. In this category the different environmental pollution risk indices can be classified into six groups. In the first group the environmental pollution risk indices provide information about individual levels of pollution from each of the analysed heavy metals (Igeo, PI, Cf), while the second group determines the scale of total pollution (PIsum, PINemerow, PLI, PIave, mCd, PIVector, Cdeg, PIN and SCI). Additionally, the third group of environmental pollution indices provides the source of heavy metals (EF and MEC); while the fourth group measures the potential ecological risk of the heavy metals (RI and MERMQ). Furthermore, the fifth group of the environmental pollution risk provides information about the highest potential risk of heavy metal accumulation in an area (ExF); and the sixth group indicates the ability of the surface horizon to accumulate heavy metals (BGI) (Kowalska et al., 2018).

When considering the method of calculation, environmental pollution indices can be divided into three groups. These include:

i) environmental pollution indices that are based on the calculation of geochemical background values (EF, Igeo, PI, PIsum, PINemerow, PIavg, PIVector, PIN and PL);

ii) environmental pollution risk indices that are calculated based on data other than geochemical background values given in the literature (Cf, MEC, Cdeg, RI, MERMQ and CSI); and

iii) environmental pollution risk indices are calculated based on heavy metal content in the analysed soil profile but not in parent material (BGI, mCd and ExF).

A number of environmental pollution risk indices have been mostly used to determining the extent of contamination of environment by potential harmful elements. These environmental pollution risk indices included, the Enrichment Factor (EF), Geo-accumulation Index (Igeo), Single Factor Pollution Index (SFPI) and the Numerow Integrated Pollution Index (NIPI) (Fernandes & Nayak, 2013; Wu et al., 2014; Fan & Wang, 2017; Wang et al., 2019). The EF is used to compare the concentration of the measured PHEs in soils against the background or natural concentration of the PHE in the earth’s crust, to distinguish if the PHE is from a natural or anthropogenic sources (Xu et al., 2016; Mahlangeni et al., 2016). The soil is contaminated for a PHE if the concentration of the PHE is above the background levels (Wu et al., 2014). On the other hand, The Igeo is an alternative method that can be used to quantify the extent of anthropogenic contamination of water or soils by PHEs in relation to the background concentration of the PHE in the earth’s crust (Müller, 1969). The measured EF values indicated that the soils near New Union mine dump in Limpopo Province of South Africa have been moderately contaminated by As and Cd (Muzerengi, 2017). Similarly, the EF values, as well as the Igeo values revealed moderate contamination of sediments by Ni and Cu within two watersheds in Abiete-Toko gold district, in Southern Cameroon, while the Igeo values for As also revealed moderate to heavily and extreme contamination of soils in the vicinity of the Giyani Greenstone Belt, which contained abandoned mines and artisanal mining activities (Mandeng et al., 2019; Kapwata et al., 2020). The high contamination in the areas poses a risk to organisms in the environment, as well as the local people in the areas.

The extent of soil contamination by PHEs can further be assessed using the Single factor pollution index (SFPI), as well as the Nemerow integrated pollution index (NIPI). The SFPI is used to measure the pollution of individual PHEs in soils at the different sampling sites, while the NIPI determines the total pollution for the different PHEs that have been measured for the different sampling sites in an area (Yang et al., 2011; Zhao et al., 2015; Wang et al 2019).

2.5.2 Human health risk assessments

People are exposed to chemicals in the environment through three basic pathways, which include, inhalation of air, consumption of food or water, as well as through dermal contacts through skin. The health risk assessment is performed to estimate the probability of an adverse human health impact that may occur because of the environmental contamination by PHEs in an area. The process of the health risk assessment included, the hazard identification, exposure or the dose response assessment, toxicity assessment and the risk characterisation as prescribed by the Australian Environmental Health Council (enHealth, 2002); the World Health Organisation (WHO, 2010), as well as the South African Framework for the Management of Contaminated Land (DEA, 2010).

The hazard identification process focuses on identifying chemicals in an area, that have the potentials to cause health problems to humans who are exposed to these toxic chemicals in the environment. The hazard in an area consisted of the concentrations of the different PHEs that are measured in surface water, soils and in the sweet thorn plants. These PHEs are considered a hazard because the PHEs are a source of health risk to the local people. The exposure assessment is used to evaluate how much of the PHEs or the concentration of the PHEs that people are exposed to over a period of time, as well as the number of people who are exposed to this contamination. Exposure to PHEs may likely occur through three primary exposure pathways, which include ingestion, inhalation, and absorption through the skin (US. EPA, 2016; TEF, 2020). Risk characterisation information is used to illustrate how humans in a contaminated area have been affected by the PHEs in an environment. The risk characterisation is determined by assessing the potential carcinogenic and the non-carcinogenic health risk of the local people in a study area. Carcinogenic risk indicates the possibility of an individual to develop any type of cancer from lifetime exposure to the different carcinogenic PHEs, while the non-carcinogenic health risk that may arise from the consumption of contaminated food is determined by computing the Hazard quotient (HQ), which is a measure of the ratio of the concentration of CDI and the reference dose (RfD) (Chen et al., 2018; Gu et al., 2019). High hazard quotient values ($HQ > 1$)

were quantified from the contamination of soil samples by As (53.7), Cr (14.8), Ni (2.2), Zn (2.64) and Mn (1.67), as a result of the exposure of these metals by local people in the vicinity of the abandoned gold mine tailings in the Krugersdorp area, in South Africa. These high HQ values detected indicated a high non carcinogenic risk from the exposure of these PHEs by the local people in the area. High carcinogenic risk values above the acceptable value of 1×10^{-4} as stipulated by US EPA (2016) were quantified for As, 3×10^{-2} and Ni, 4×10^{-2} for children, and among adults, the values for As and Ni were 5×10^{-3} and 4×10^{-3} respectively. These high HI values that were quantified represented a high cancer risk from the intake of As and Ni by the local people, with a greater cancer risk from children being exposed to these PHEs (Ngole-Jeme & Fantke, 2017). On the other hand, the contamination of soils by heavy metals from gold mine tailings and mining activities in the Witwatersrand Gold Mining Basin, in South Africa have caused the local people in the area to a high risk of exposure to the heavy metals in the environment. High HI values of 2.13 were quantified for the adult population while 43.80 was quantified for children. These high HI values quantified for both the adult population and children, indicated that the local people in these areas are exposed to carcinogenic risk from the intake of cancer causing PHEs in the soils, with the risk of children being higher than for the adult population (Kamunda et al., 2016).

2.6 Measures to mitigate environmental pollution arising from mine tailings

Over the years, concerns have been raised worldwide on how to manage mine tailings because of their negative impacts on the environment and human health. Since PHEs released from mine tailings may have lethal effects on humans even at very low concentrations (Mahar et al., 2016), it is imperative for measures to be put in place to mitigate the impacts of pollution by PHEs on the environment and human health

2.6.1 Use of legislation and guidelines

A number of legislations have been put in place to facilitate the reduction of environmental pollution from mine tailings. Section 24 of the National Constitution of South Africa (1996) stipulates that everyone has the right to an environment that is not harmful to their health and well-being (Constitution of South Africa, 1996). Therefore, according to the National Constitution of South Africa, no one has the right to pollute the environment in the country. In instances where land owners carry out activities that cause pollution, it is expected that these land owners should put measures in place that will either eliminate the source of pollution, or remedy its effects (National Water Act, No. 108 of 1998). Additionally, according to the National Environmental Management Act (No. 107 of 1998), as well as the Mineral and Petroleum Resources Development Act (No. 28 of 2002) the costs of pollution remediation is the responsibility of the polluter; supporting the ‘polluter pays’ principle. Where more than one person is liable for the transgression, the charge must be assigned among the persons concerned according to the level to which each was responsible for the harm to the environment resulting from their respective activities (Van eeden & Durand, 2009).

Mine closure is now governed by a loose framework of acts working together with other regulations such as the requirement for Environmental Management Plans (Watson & Olalde, 2019). These acts include the Constitution of South Africa (1996), Mine Health and Safety Act (1996), National Environmental Management: Air Quality Act (2004), and Nuclear Energy Act (1999). Though these legislations are in place, evidence in South Africa in general, and in the West Rand and the Far East Rand in particular, have proven that none of the miming companies are operating according to an approved Environmental Management Plan in terms of the Mineral and Petroleum Resources Development Act (Durand, 2012).

2.6.2 Use of safe mine tailings waste disposal options

Massive environmental pollution originating from mine tailings, have prompted extensive research on different approaches to mitigate the level of environmental pollution arising from the mine tailings. Several strategies have been put in place, and some of them have provided effective results. One of the first approaches that have been used to reduce environmental pollution arising from mine tailings was the use of safe mine tailings disposal methods to reduce heavy metals pollution (Adiansyah et al., 2016). Based on this approach, mine tailings are disposed onto the surface of the earth or as mine backfill in the form of thickened paste. Water is withdrawn from the tailing before disposal, and such tailings are usually dense, and can therefore reduce the potential for acid mine drainage from the tailings. the other hand, mine tailings waste material is sometimes used as a feedstock to produce a valuable product (Edrika et al., 2014).

2.6.3 Use of remediation techniques of pollution from mine tailings

Recent technological innovations on the mitigation of environmental pollution arising from mine tailings focus on the ecological restoration of mine tailings. This process involves the use of plants, surface amendments and associated soil microbes to reduce the concentrations or toxic effects of contaminants on the environments (Ali et al., 2013; Zhang et al., 2014). The use of such biological and nature-based approaches to curb the problems of pollution of metals on the environment is described as phytoremediation. Phytoremediation measures to reduce pollution have been researched quite extensively in recent times (Ali et al., 2013; Doronila et al., 2014). The phytoremediation approaches are becoming attractive because, they are less expensive, friendly to the environment and aesthetically appealing. Plants used for phytoremediation are usually native plants such as trees, shrubs, and grass species, which are tolerant to the harsh conditions in the tailings environment and can grow and colonise these polluted sites easily. These plants can remove degrading or immobilizing harmful chemicals in the tailings (Conesa et al., 2010; Alcantara et al., 2015). Phytoextraction has been used as a phytoremediation option in which plants grown on a mine tailing substrate effectively extract large amounts of heavy metals from the soils and accumulate the metals into plant-parts above the ground, thereby stabilising the heavy metals in the soil (Alcantara et al., 2015). On the other hand, plants are grown on mine tailings to cover and stabilise pollutants in mine tailings waste, a procedure described as phytostabilisation (Ghosh & Singh, 2005). These plant species reduce the movement of heavy metals into the environment and restricts their uptake in plants (Ali et al., 2013). For example, an experiment was performed in a glasshouse using two drought resistant Australian native grass species; redgrass (*Bothriochloa macra*) and spider grass (*Enteropogon acicularis*) for the phytostabilisation of gold mine tailing soils containing high concentrations of sulphide and Arsenic (Ali et al., 2013). Although a decrease in leaf growth was detected, little As levels were determined in the leaves of the grass species. In addition, there was no correlation between the As that was present in the leaves and the As present in the soil. The plants therefore stabilised the pollutants in the mine waste, and thus restricted their movements into the grasses (Ali et al., 2013).

2.7 Discussion

With many minerals in the substratum of South Africa, mining becomes an important economic activity and a major contributor to the South African economy. Mining contributed R360.9 billion to South Africa's gross domestic product (GDP) during 2019, and up from R351 billion in 2018 (MCSA, 2020). While the Mineral Council South Africa reported an increase, the Statista (2020) reported a decrease from 351 billion in 2018 to 226.2 billion in 2019 (Statista, 2020). Despite these conflicting figures, one observes a steady decline in the contribution of mining to the GDP of South Africa since 2015 with a corresponding shading of mining jobs and rising labour unrests in the mining sector.

Gold mine tailings are the by-product from the gold mining process and poor disposal of these waste products can cause serious environmental pollution and degradation. The focus of this study is on gold mine tailings, which are not properly managed, and when disposed on land, the contaminants in the gold mine tailings are transferred to the environment in the vicinity of the mines, thereby causing surface water, ground water, soil and plant pollution. These mine tailings contain pollutants, particularly the PHEs, which have persistent properties, and their accumulation can cause both environmental pollutions, as well as pose human health risk when humans are exposed to the PHEs. These PHEs also have serious impact on aquatic organisms, soil organisms, animals and humans, as well as plants.

The high concentrations of PHEs in surface water in the vicinity of the gold mine tailings indicate a potential risk to aquatic organisms. When surface water is contaminated by As, fish and other aquatic organisms in streams may absorb the As into their cells and these may cause chronic and acute toxicity, including inhibition of growth and reproduction, immune system dysfunction and even death (Kumari et al., 2016). On the other hand, when fishes and other aquatic organisms are exposed to high concentrations of Zn ions, it may become lethal for such organisms (Hogstrand & Wood, 2010; Shah, 2017). However, high concentrations of Fe in the water may indirectly create a conducive condition for the growth of iron bacteria on the fish gills surfaces. This condition causes the bacteria on the fish gills surfaces to oxidise the soluble forms of iron (ferrous iron) to the insoluble iron (ferric oxide). Presence of insoluble iron on gills surfaces causes harm to gills, which in turn results in increased ammonia in blood plasma, as well as damage of kidney, liver, and spleen tissues (Slaninova et al., 2014). Even though copper is also an essential nutrient in living organisms, high concentrations of Cu in water can be absorbed in fish cells and may cause the reduction of growth and reproduction, as well as affect brain function and metabolism (USEPA, 2017). Additionally, chronic exposure of Zn ions to freshwater fish and aquatic organisms may be lethal for such organisms (Hogstrand & Wood, 2010; Shah, 2017).

The persistent properties of these PHEs are such that their accumulation in the environment may eventually contaminate food chain, causing potential risk to living organisms in the soil (Ali et al., 2019; Sey & Belford, 2019). Soil that has been contaminated by PHEs such as Pb, negatively impacts on the number, diversity and activity of soil organisms. This condition prevents the decomposition of soil organic matter, as well as nitrogen mineralisation processes (Chileshe et al., 2019). Contamination of soils by particularly Cr (V1) may cause harm to living organisms, by inducing phytotoxicity, which affects plant growth, decrease yields, reduce nutrient uptake, and slow down the process of photosynthesis (Oliveira, 2012; Singh et al., 2013; Shahid et al., 2017).

PHEs absorbed by plants from contaminated soils, affect other physiological processes in the plants. The uptake of Cd from soils by plants causes a reduction in the level of photosynthesis, protein synthesis levels, as well as damage to cell membrane, which ultimately retard plant growth (Okereafor et al., 2020). High concentrations of Pb in plants roots, shoots and leaves may result in Pb toxicity, which affects the growth and photosynthesis process, interference with vital enzymes, and thereby inhibiting seed germination (Okereafor et al., 2020). On the other hand, even though Zn is an essential plant nutrient, high concentrations of Zn in soils may impact on the growth of plants in the vicinity of mine tailings, resulting in poor shoot growth with symptoms such as stunted growth of shoots, curling and rolling of young leaves, death of leaf tips, as well as chlorosis (Long et al., 2011; Mishra et al., 2020). High concentrations of Ni above threshold values may impede plant growth, and cause other effects such as chlorosis, stunted root growth and brown interveinal necrosis (Cempel & Nikel, 2005).

For many decades, consumption of PHEs, such as Cd, Hg, Pb and As from contaminated water and foods have been associated with several dire health ailments. The WHO have described these PHEs as human carcinogens of major public health concern, in that they may be lethal even if ingested at trace levels (Abdul et al., 2015; Kamunda et al., 2016; Zhou et al., 2016). When humans consume drinking water contaminated by As, they are exposed to a higher risk of contracting skin cancer, skin lesions such as hyperkeratosis and pigmentation changes (Mandal, 2017). PHEs such as lead and cadmium may also cause neural and metabolic disorders and other diseases (Griswold & Martin 2009; Jaishankar et al., 2014). According to the EPA, Pb is a human carcinogen, which can affect all organs and systems of the human body (EPA, 2016). Prolonged exposure to Pb by humans may result in weakness in fingers, wrists ankles and anaemia. Moreover, high concentrations of lead levels can severely affect the brain and kidneys and may ultimately cause death (Ćwieląg-Drabek et al., 2020). Furthermore, in pregnant women, high levels of exposure to lead may cause miscarriage (Okereafor et al., 2020). The health risk of Cd on humans may range from mild to severe health risk. When humans are exposed to a lower concentration of Cd ingested in contaminated drinking water or food, they may suffer from mild symptoms such as nausea, vomiting, abdominal cramps and dyspnoea. However, where humans are exposed to a high level of Cd, they may suffer from severe symptoms such as pulmonary odema and even death in extreme cases (Singh & Kalamdhad, 2011). Additionally, when Cd is consumed over time, even at low concentrations, it may cause kidney diseases through gradual deposition of cadmium in the kidneys (Griswold & Martin, 2009). An increased intake of mercury can alter brain functions and lead to tumours and memory problems (Martin & Griswold, 2009; Jaishankar et al., 2014). Lead is also known to cause brain, liver and kidney damage in children, as well as nerve damage in adults (Jaishankar et al., 2014; Abushay et al., 2017). Moreover, increased intake of lead can result in miscarriages in pregnant women as well as damage of testis in males (Griswold & Martin, 2009; Khan, 2011). Worldwide, arsenic is a major contaminant of drinking water and has been implicated with cancer of the skin, lungs, urinary bladder and kidney (Martin & Griswold, 2009; Tchounwou et al., 2010; Jaishankar et al., 2014).

Even though Zn, Cu, and Ni are essential nutrient for growth of living organisms, the intake of high doses of these PHEs may have toxic effects on humans and other living organisms. The ingestion of toxic amounts of zinc contaminated food or drinking water by humans may result in abdominal pain, nausea, and vomiting. Additional effects include lethargy, anaemia, and dizziness (Plum et al., 2010). Furthermore, when high doses of Cu in contaminated food are ingested by human this may cause metal fumes fever, hair and skin discolorations, dermatitis, as well as respiratory tract diseases (Shah et al., 2013). On the other hand, when high concentrations of Ni are ingested in contaminated drinking water, and food, by humans and particularly by woman of child-bearing age, it may affect developmental effects on the offspring of females exposed during pregnancy (DEA, 2010). On the other hand, consumption of water, which has been contaminated with Ni may cause gastrointestinal disorders with symptoms such as nausea, abdominal cramps, diarrhoea and vomiting (Das et al., 2019).

To mitigate the impacts of mine tailing on the environment, animals and humans various options are available. These include the use of effective and efficient legislations including proper environmental impact assessment (EIA) and drafting of environmental management plans (EMPs) by the mining companies, safe mine-waste disposal techniques, biological and nature-based techniques. as well as the use of phytoremediation measures.

Chapter 3

Study Design and Sampling Sites

3.1 Introduction

In the Matjhabeng Local Municipality (MLM) area of the Lejweleputswa District Municipality there are numerous gold mine tailings, particularly within Welkom, Virginia and Allandrige area. These gold mine tailings are a source of pollution to the water bodies and the soils in the MLM area, as well as the plants which grow in the vicinity of the gold mine tailings. The focus of this study was to examine the extent of contamination by contaminants from gold mine tailings in water bodies and soil, as well as the uptake of these contaminants by plants of two species, the medicinal plant species, sweet thorn (*Vachellia karroo*), and a food crop, maize (*Zea maize*). The environmental pollution risk that may arise from the contamination of the environment by PHEs, as well as the health risk of the contaminant to the local people in the MLM area was also investigated. To achieve the research problem of this study, the following research question was answered:

Main research question: To what extend does contaminants from gold mine tailings contaminate water bodies and soil in the MLM area, as well as the contamination of the sweet thorn and maize plants? To address the main research question, this was the main objective that was measured.

Main aim: To determine the extent of the contamination of water bodies and soil by contaminants from gold mine tailings in the MLM area, as well as the contamination of sweet thorn and maize plant.

3.1.1 Research paradigm

The contamination of water, soil, and plants by contaminants from gold mine tailings is considered as a real-world issue, which requires action through active intervention. Therefore, the post-positivist paradigm shaped the philosophical orientation of this research study (Mouton, 2001; Kawulich, 2012; Bertram & Christiansen, 2014; Okeke & Van Wyk, 2015). Unlike the positivists, the post-positivists claim that knowledge or reality exists, but they maintain that the world of knowledge cannot be known completely because of limitations on the part of the researcher (Kawulich, 2012). The post-positivist world view further holds that a researcher can discover reality within a certain realm of probability.

In line with the post-positivist viewpoint, this study was conducted in a natural setting of the gold mine tailings environment in the MLM area. Moreover, research questions were answered in this study by applying suitable methods, which include systematic sampling, careful measurements of relevant variables, the analysis, interpretation of results and finally drawing conclusions (Bertram & Christiansen, 2014; Van Wyk, 2016). On the other hand, the concentrations of the different contaminants from gold mine tailings that were assessed in water, soil, sweet thorn and maize plants were different for the various contaminants, as well as for the different sampling sites.

3.2 Conceptual framework

In this study, environmental contamination by contaminants from gold mine tailings was studied in terms of four main environmental polluting areas. The four environmental polluting areas included the contamination of surface water, groundwater, and soil, as well as the uptake of contaminants by plants from the contaminated soil. The contamination of surface water, groundwater, soils, and plants by contaminants from gold mine tailings constituted the dependent variables, which were measured in terms of several indicators of contamination, which formed the independent variables (Figure 3.1).

For surface water and groundwater, the indicators of contamination that were measured were the physical water quality properties, and the chemicals in the water. The physical water quality properties that were measured were the water temperature, pH, electrical conductivity (EC), dissolved oxygen (DO) and turbidity. On the other hand, the chemicals that were measured in the water are a group of metals or metalloids, which have the potential to cause harm to both the environment and human health when in excess. This category of chemicals has been described in this study as potential harmful elements (PHEs). The twelve PHEs were arsenic (As), cadmium (Cd), lead (Pb), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), selenium (Se), zinc (Zn), calcium (Ca) and magnesium (Mg). On the other hand, since the groundwater in the MLM area is used for domestic activities and for drinking, the microbiological quality, faecal coliforms and *Escherichia coli* (*E. coli*) were measured for groundwater. Furthermore, the extent of contamination of the different physical water quality properties, as well as the PHEs were determined for each groundwater sample by quantifying a Water Quality Index (WQI).

The contamination of soil and plants in the MLM area were also measured in terms of several indicators of contamination. The soil quality indicators of contamination that were measured included the physical soil quality properties, as well as the contamination by the 12 PHEs. The physical soil quality properties were the soil pH and the electrical conductivity in soil (EC). Similarly, the contamination of plants by the contaminants from the gold mine tailings was measured in terms of the 12 PHEs.

To be able to describe the risk of the different contaminants in the environment several environmental pollution and health risk indices were quantified. The measurements of the 12 PHEs that were measured in surface water, as well as in soil, were used to calculate the environmental pollution risk indices. These different environmental pollution indices were used to describe the environmental risk that may arise from the contamination by individual PHEs, as well as from the contamination by several PHEs, at a particular sampling site in the MLM area. Once the environmental pollution risk indices for the water and the soil were quantified, the environmental pollution indices were combined to develop a combined pollution index, called the Combined Index for water and soil. This Combined Index for water and soil was used to describe the extent of contamination by PHEs at each of the sampling sites in the MLM area, as well as the pollution condition at each of the five zones in the entire MLM area.

The local people of the MLM area are vulnerable to the contaminants in the water, soil, and plants in the area, they are therefore at risk of contracting several health complications. The health risk indices described the health risk that may arise from the ingestion of specific PHEs in an infusion of a sweet thorn leave sample, which has been collected from a particular sampling site. Therefore, different health risk indices were estimated to determine the risk to humans from the exposure of the PHEs in the environment in the MLM mining area.

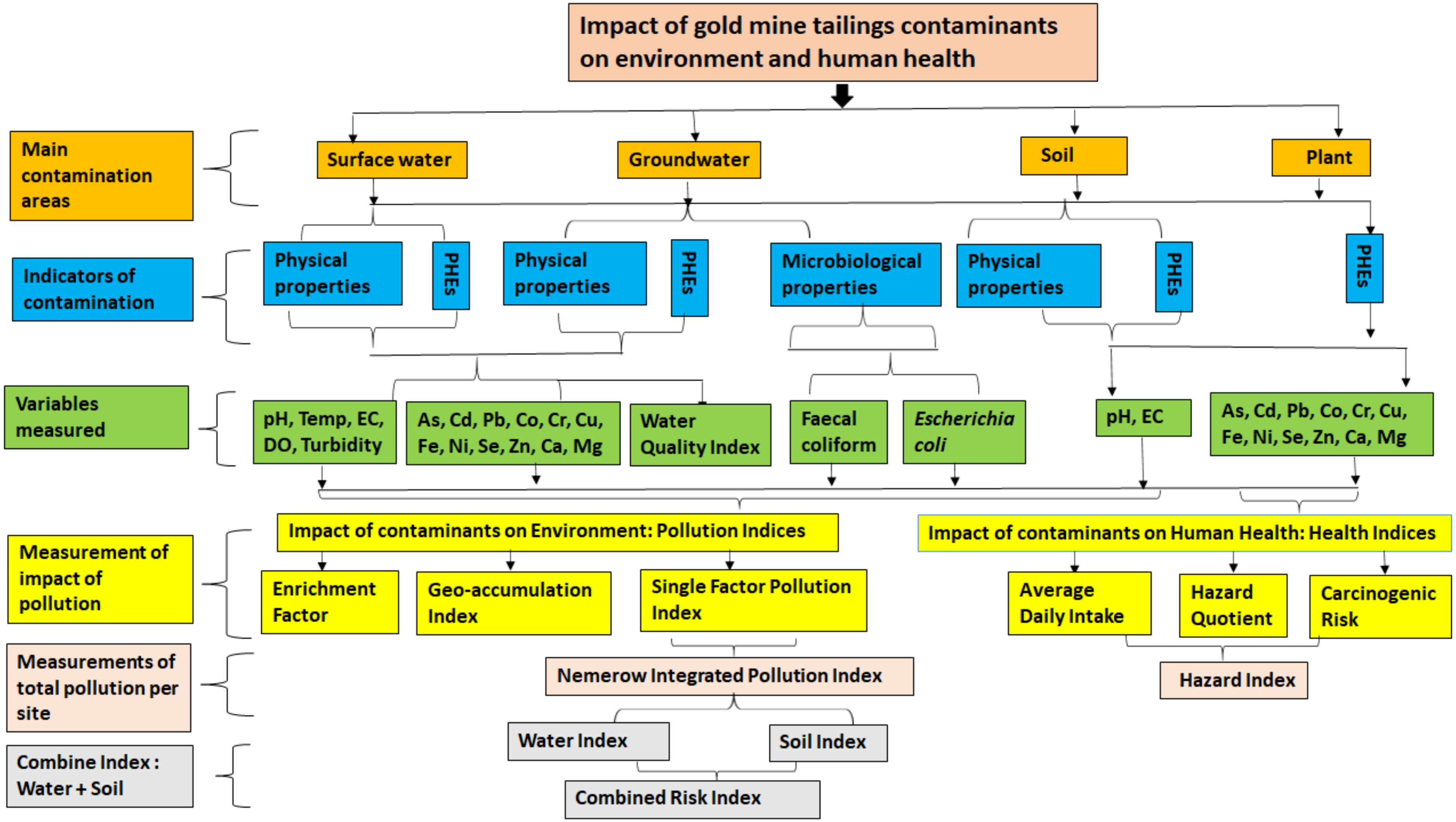

Figure 3.1 Conceptual framework of the study

3.3 Study design

To study the extent of contamination by PHEs in the MLM area, this study was partitioned into four broad investigations. Investigation one (1) was focused on contamination of water by contaminants from gold mine tailings; Investigation two (2) was based on the contamination of soil by contaminants from gold mine tailings; Investigation three (3) was focused on the contamination of plants; while Investigation four (4) assessed the pollution risk of gold mine tailings contaminants on the environment and human health.

For Investigation 1, the contamination of both the surface water and the ground water were evaluated. Surface water was assessed to determine the direct contamination by contaminants arising from gold mine tailings. Since some of the surface water bodies are at close proximity to the gold mine tailings, contaminants from the gold mine effluent may be transported into the surface water bodies by surface water run-off. The contamination of groundwater by contaminants from gold mine tailings within the MLM was assessed to determine if there existed some form of indirect contamination of groundwater by contaminants arising from surface water or soil. In addition, the contamination of groundwater by contaminants from gold mine tailings was assessed to determine if some form of filtering processes existed, which may reduce the level of contamination of groundwater as the water infiltrates through the soil layers (Keesstra et al., 2012).

The extent of contamination of soil in Investigation 2, was determined for uncultivated soil, as well as cultivated soil. The main reason for this decision was that soil that have been cultivated undergo some form of processing, such as tilling, addition of fertilisers and pesticides, which may affect the extent of contamination of cultivated soil by these contaminants.

Contamination of plants was determined in Investigation 3 for both plants that grow in the natural environment, as well as a cultivated food plant. Several criteria were used for the choice of a plant, which grow in the natural environment, as well as the cultivated food plant. The medicinal plant, sweet thorn, was selected for plants that thrive in a natural environment, since sweet thorn is used for several medicinal purposes and it is readily available in the MLM area. On the other hand, maize plant was the food crop that was selected, because maize plant is extensively cultivated in the MLM area and maize serves as a staple food, which is consumed by most households in the area. Additionally, the uptake of contaminants was analysed for both plants species that thrive in the natural and the cultivated environment, to ascertain if there could be differences in the rate of uptake of contaminants by the different plants species. The reason for this decision was mostly because, plants that grow within the natural environments develop adaptive mechanisms to survive within their surroundings, while cultivated plants thrive within artificial environments that has been created by humans.

As a result of the contamination of water, soil and plants by PHEs from gold mine tailings in the MLM area, Investigation 4 was studied to determine the risk that may arise from such contamination. The environmental pollution risk was quantified to determine the risk on the environment from the contamination by PHEs, while the health risk was assessed to determine the risk that may arise, when humans are exposed to PHEs in the MLM area.

Each of the three Investigations; 1, 2 and 3 were conducted in phases. These phases consisted of the scouting phase, data collection phase, measurements of variables phase, data analysis phase and the interpretation of results, discussion and conclusions phases. The description of each of these different phases for each investigation were presented in different results chapters. Investigation 1, was presented in Chapter 4, Investigation 2, was presented in Chapter 5 and Investigation 3 was presented in Chapter 6. On the other hand, Investigation 4, was presented in Chapter 7. The whole study design is represented graphically in Figure 3.2.

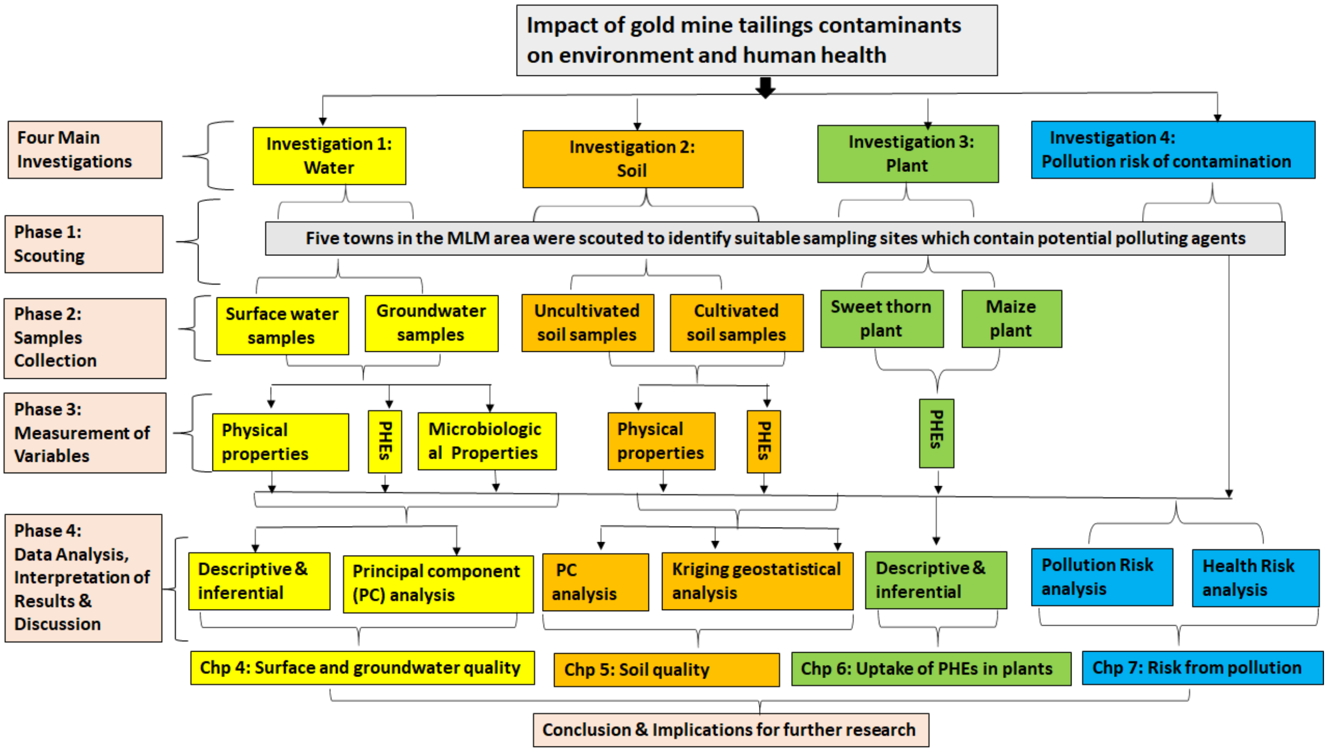

Figure 3.2 Flow diagram of the study design

3.3.1 Phase 1: Scouting

At the beginning of this study, the entire study area of the MLM area was scouted on two separate occasions. Scouting was performed to identify suitable sampling sites within the MLM area, which contained potential polluting agents. The presence of mine tailings and mines in an area were the most important criteria that were used in selecting the sampling sites. The presence of other polluting agents in the area, such as industries and agricultural activities were also considered in choosing the sites. Another factor that was considered in selecting the sampling sites was the presence of surface water or groundwater in an area. This was because for a sampling site to be selected, the sampling site should contain a water source, soil and sweet thorn or maize plants.

3.3.2 Phase 2: Data collection

Water samples, soil samples and plant samples were collected from each of the sampling site that was identified in the MLM area. The procedure that was followed was modified from (Chen et al., 2018), which specified that all the three samples, water, soil and plants, were to be collected within a vicinity of a particular sampling site, with similar conditions. The water, soil and plants samples were obtained from both the uncultivated lands in the MLM area, as well as the cultivated lands. Within the uncultivated lands, the water, soil and sweet thorn leaves samples were obtained from 15 sampling sites that had been identified. Within the uncultivated lands, water samples were collected from surface water, the soil samples were collected from uncultivated soils, while leaves samples of sweet thorn were collected from the same point from where the uncultivated soil samples had been collected. On the other hand, within the cultivated lands in the MLM area, cultivated soil and maize seeds samples were collected from 12 sampling sites that were identified within the cultivated maize farms. However, the groundwater samples were collected from boreholes at eight of the 12 sampling sites that were within the cultivated lands.

To cover the entire study area, as well as to obtain a large data set, some of the samples were collected in two seasons. Surface water samples, uncultivated soil samples, as well as sweet thorn leaves samples were collected in two seasons: during the warm summer season, as well as during the cold winter season. On the other hand, groundwater samples, cultivated soil samples and maize seeds were collected only during the cold winter season, since maize seeds mature during the winter season in the MLM area.

3.3.3 Phase 3: Measurement of variables

The level of contamination of contaminants from gold mine tailings in water, soil and sweet thorn leaves or maize seeds were measured using various indicators of pollution. The contamination of surface and ground water quality were measured in terms of the five physical properties and the 12

PHEs. In addition to these contaminants measured, two microorganisms were also analysed in groundwater samples. On the other hand, soil quality was analysed in terms of the two physical properties, as well as the 12 PHEs, while the extent of contamination of plants was measured in terms of the 12 PHEs. Therefore, the entire data set for this study consisted of eleven subdivisions. These subdivisions included;

- Physical water quality properties of surface water and PHEs in surface water;
- Physical properties of groundwater, microorganisms and PHEs in groundwater;
- Physical soil quality properties of uncultivated soil, as well as PHEs;
- Physical soil quality properties of cultivated soil, as well as PHEs;
- PHEs in medicinal plant; sweet thorn
- PHEs in a cultivated crop, maize plant.

3.3.4 Phase 4: Data analysis, interpretation of results and conclusion

The results were statistically analysed using the Statistical Package for Social Sciences (SPSS) Version 23. Statistical analysis including, descriptive and inferential statistics, Principal Component Analysis (PCA), Kriging geostatistical analysis, water quality index, pollution risk indices, as well as health risk indices were computed to generate the results in this study. The results obtained were interpreted and conclusions were drawn from the main findings of the research.

3.4 Study area

This study was conducted in and around the MLM area of the Lejweleputswa District Municipality. The MLM is situated in the north eastern part of the Free State Province, about 250 km South of Johannesburg and 140 km north east of Bloemfontein, which is the capital city of the Free State Province. The MLM is one of the most prominent gold mining areas in South Africa and contains some of the largest gold fields. Even though most of the gold mines in this area are no longer in operation, those still operating, particularly those in Welkom and Virginia, are owned and managed by Harmony Gold Mining Company. Some of the gold mines in the area include St Helena, Phakisa, Masimong no: 5, Brant no: 5 and President Steyn no: 4. The mining of gold in these areas have produced many gold mine tailings and some of these tailings are in close proximity to each other while others are in close proximity to human settlements. Besides, the extensive gold mining activities, there are many livestock and crop farms in the surrounding areas. The study area covered six towns in the MLM area, which included Welkom, Virginia, Allanridge, Hennenman, Odendaalsrus and Bronville. Parts of Bultfontein, which is close to Welkom were also included in the study area, even though the area was located slightly outside the borders of the MLM area (Figure 3.3).

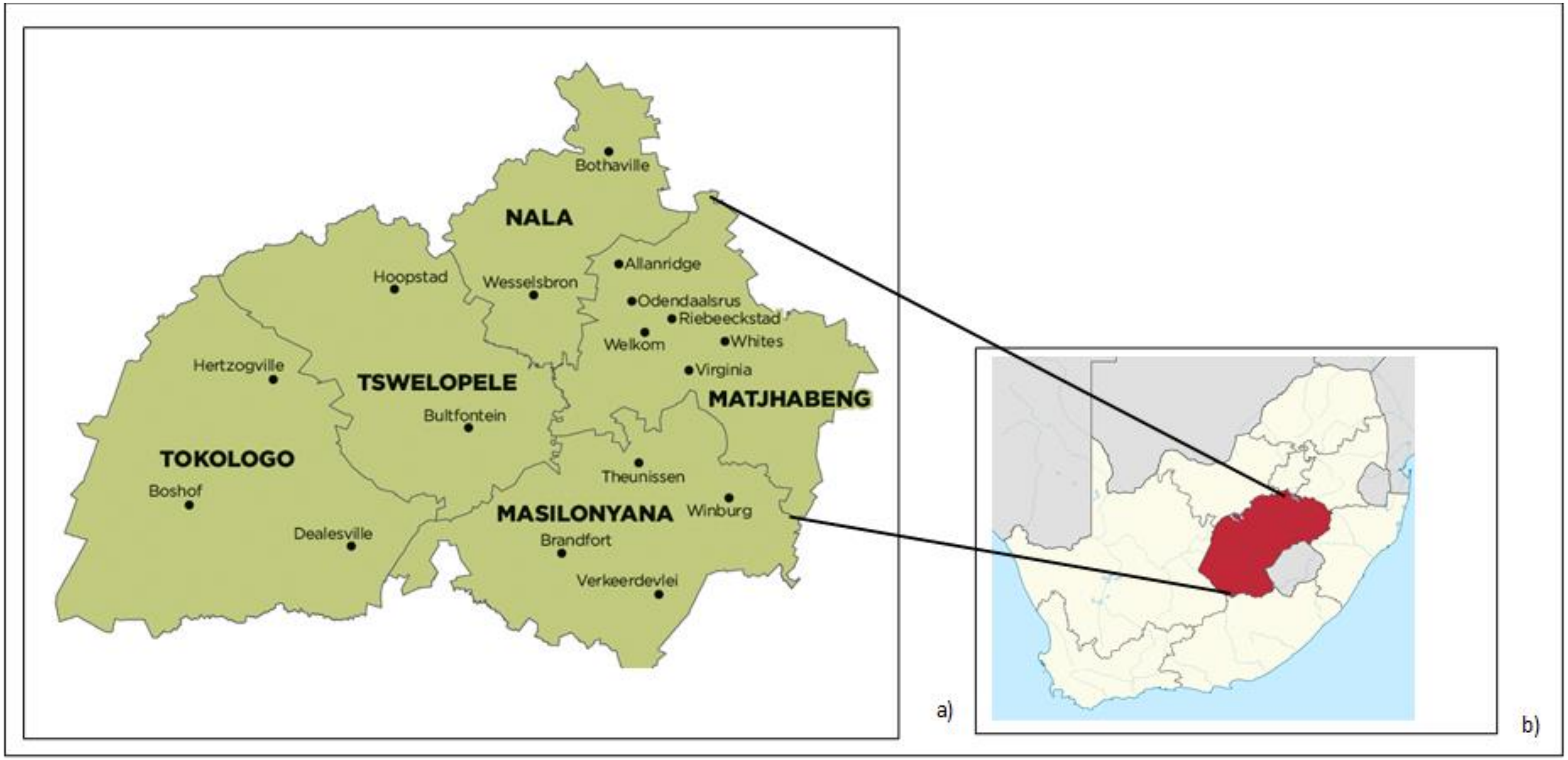

Figure 3.3 Location of study area in South Africa and the Free State a): Position of study area of Matjhabeng Local Municipality in Lejweleputswa District Municipality b): Position of Free State Province in South Africa

Source Google maps

The climate of the study area is associated with the Highveld. The average monthly summer temperature is about 17 ^{O}C while in winter, the average monthly temperatures drop to about 5 ^{O}C (Green Door Environmental, 2013). Most precipitation occurs in the summer months of the year with an annual average of 490 mm.

The geology of the study area consists of the Witwatersrand Supergroup, Ventersdorp Supergroup and Karoo Supergroup. These rocks are mostly composed of sedimentary rocks, which made up of shale, quartzite, and calcite (Green Door Environmental, 2013).

The natural soil in the area is composed of duplex soil with contrasting texture between soil horizons. The soil may be red, yellow, brown, dark, and grey soil based on subsurface colour (Green Door Environmental, 2013). The natural vegetation in the study area is grassland with two main subtypes: the Vaal-Vet Sandy Grassland and the Highveld Alluvial Grassland. The Vaal-Vet Grassland vegetation is found in most parts of the study area while the Highveld Alluvial Vegetation mostly occupies paths along streams and rivers. Most of the grassland in the area has been transformed, either because of agriculture, dam construction or overgrazing by cattle (Green Door Environmental, 2013).

The study area is situated within a relatively flat landscape. It is positioned at about 1260 metres above sea level with rolling plains and low hills (Green Door Environmental, 2013). The largest water catchment in the area is the Sand River, which flows to the south of Welkom and west of Virginia. The Sand River later joins the Vet River, which then flows into the Vaal River at Bloemhof Dam. The water bodies in the study area break into many pans. These pans collect run off water during the summer rainfall period and they eventually dry up during the dry winter period, therefore increasing the concentration of salt in the pans during winter (Green Door Environmental, 2013).

3.5 Identification of zones and sampling sites in the study area

3.5.1 Identification of zones and sampling sites within uncultivated lands

Five zones were selected within the uncultivated lands across the entire MLM area, from where sampling sites were selected. The location of the five zones was selected based on the presence or absence of mines and mine tailings in an area, anthropogenic activities, such as industries and agricultural activities, different distances beyond the mine tailings, as well as the prevailing wind direction in the area. To study the extent of contamination by the contaminants from gold mine tailings within the five zones, 15 uncultivated sampling sites were identified, from where the contamination of surface water, uncultivated soil, as well as the uptake of the contaminants by sweet thorn plants was investigated. The choice of a sampling site within the uncultivated lands was based on the presence of a surface water within an area. Therefore, each sampling site contained surface water, with uncultivated soil and sweet thorn plant in the vicinity of the surface water.

Zone 1 was in an area with many mine tailings, where majority of the gold mines are present, such as the Welkom Mines, Virginia Mines and Harmony. Therefore, Zone 1 was considered a reference zone, which was described in this study as the high density mine tailing zone. Furthermore, Zone 1 was at the centre of the MLM area, stretching along the northwest (NW) to the southeast (SE) direction from Odendaalsrus, through parts of Welkom, Bronville and Virginia. Seven sampling sites, including, S1, S2, S3, S4, S5, S6, and S7 were selected within Zone 1. The sampling sites that were positioned at the centre of Zone 1, (S1, S2, S7) are surrounded by mine tailings, as well as mines, while the sampling sites that were in the periphery (S3, S4, S5 and S6) are only partially surrounded by mine tailings and mines. Three sampling sites, S8, S9, and S10 were selected in Zone 2, which is in Virginia area and approximately 5 to 7 km beyond the high density mine tailings zone in Zone 1. Three sampling sites were also selected from Zone 3, which comprised of sampling sites S11, S12 and S13, and was located approximately 30 to 37 km beyond the high density mine tailings zone, covering parts of

Welkom and Bultfontein. Sampling sites within Zones 2 and 3 were selected in the downstream direction of the prevailing wind, which blows from the north-northeast (NNE) and slope in the south-southwest (SSW) direction in relation to the high density mine tailings zone. The prevailing wind direction was based on the Weather Statistics for wind direction and wind speed for Welkom Airport (2018).

For control purposes, a fourth and a fifth zone were chosen in the upstream wind direction in relation to the high density mine tailing zone. Zone 4 contained of a single sampling site, S14, which was situated in Hennenman, at approximately 10 to 12 km east of the high density mine tailings zone. This area did not contain any gold mining operations, as well as mine tailings at the time of this study. The only activities that were performed in the area, include farming for food crops and life stock rearing. Zone 5 also had a single sampling site, S15, which is positioned at about 10 to 12 km north from the high density mine tailings zone. The area contained a single mine and very few mine tailings. Figure 3.4 presents the 15 sampling sites that were selected within the uncultivated lands in the MLM area.

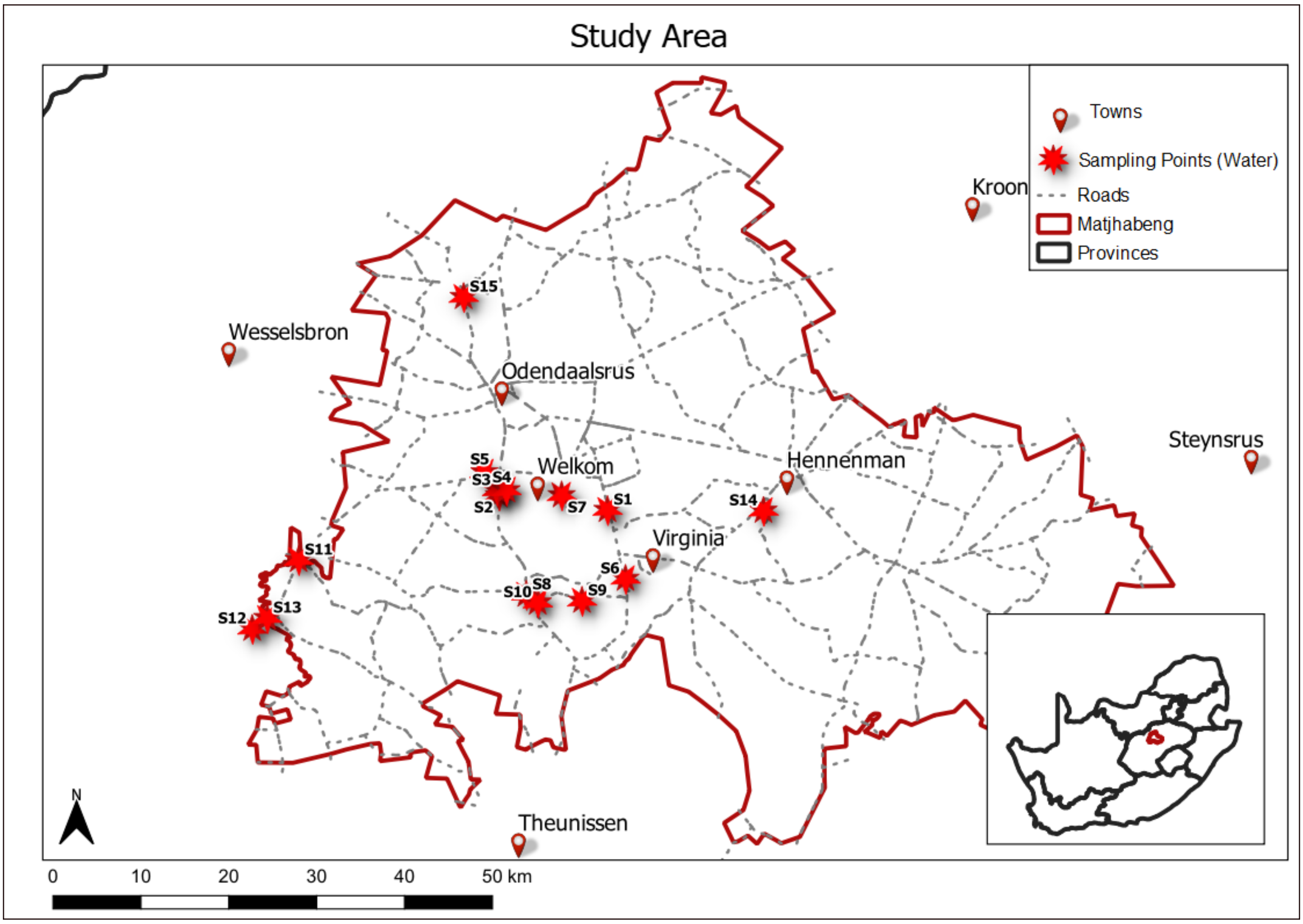

Figure 3.4 Study area of the Matjhabeng Local Municipality, showing the fifteen sampling sites within the uncultivated lands

Supplementary data were recorded at each of the 15 sampling sites that were positioned within the uncultivated lands in the MLM area. The data collected at each sampling site included a description of the sampling site, the surrounding human activities at each site, as well as the coordinates of the surface water sampling sites (Table 3.1). At each sampling site, coordinates were recorded for surface water only, since uncultivated soil and sweet thorn plants were positioned a few meters from the surface water.

Table 3.1 Sampling areas, references, description of areas and surrounding human activities.

Zones	Sampling sites	Description of locality	Potential polluting agents
Zone 1 - High-density mining area	**S1** (28.01895 °S, 026.81354 °E)	The sampling site is situated along the R73 highway in high density mine tailing zone in Bronville. The surface water at the site is a stream.	Pollutants in the area include Harmony mine, water treatment plant, landfill site, and a chicken farm. Cars driving along R73 are also a source of pollution.
	S2 (28.00199 °S, 026.68741°E)	Area is situated along R30 highway in Welkom, on the western side of St Helena; Welkom suburb. The surface water is a dam.	Cars moving along the R30 highway.
	S3 (27.99623 °S, 026.68496 °E)	On R30 highway in Welkom, and on the western side of St Helena; Welkom suburb. The surface water in the site is the Flamingo Pan.	Cars moving along the R30 highway.
	S4 (27.99614 °S, 026.69608 °E)	Along R30 highway in Welkom, on the western side of St Helena; Welkom suburb. Flamingo Lake is the surface water at the site.	A non- operational mine, mine tailing and waste rocks dumps are pollutants in the area, as well as St Helena and a Golf Course.
	S5 (27.97519 °S, 026.67041 °E)	Along the R710 highway, between Welkom and Odendaalsrus. A dam is the surface water in the area.	Tsepong mine is in the vicinity of the sampling site. Tailing and a waste dump are pollutants in the area including cars moving along the R710 highway.
	S6 (28.09896 °S, 026.83446 °E)	On the R73 highway, under the Sand River bridge in Virginia.	Virginia Mines, positioned within the northern part of the site, Sand River, as well as cars moving along the R73 highway are pollutant sources in the area. Other activities include Tikwe lodge, a conference centre.
	S7 (28.00191 °S, 026.76025 °E)	Witpan is in the vicinity of Welkom Centre, behind Welkom industrial area.	Industries, such as a non-operational Welkom Mine, WWTP, abattoir and Coca Cola brewery.
Zone 2 5 to 7 km beyond	**S8** (28.11.755 °S, 026.71919 °E)	Sand River, along the R30 highway, on the western side of Virginia.	Sand River in Virginia, as well as an informal settlement.
	S9 (28.12449 °S, 026.78390 °E)	The Pan is in a forested area in Virginia.	A WWTP and agricultural fields are in the area, as well as an informal settlement.
	S10 (28.12659 °S, 026.73249 °E)	The Sand River is in a forest area in Virginia, under a bridge	Agricultural activities are the dominant pollution source.
Zone 3 30 to 37 km beyond	**S11** (28.07710 °S, 026.45457 °E)	The site is between Welkom and Bulfontein, where the Sand River crosses the R710 highway.	A small farming settlement, agricultural activities, and cars that drive along the R710 highway.
	S12 (28.15707 °S, 026.40068 °E)	The site is along the R710 highway, between Welkom and Bulfontein and close to Groudkop Deport. The stream at the site is a man-made artificial stream.	Groudkop Deport., agricultural practises, as well as cars passing along the R710 highway are the dominant source of pollution in the area.
	S13 (28.14454 °S, 026.41808 °E)	The site is between Welkom and Bulfontein, where the Viet River crosses R710 highway	Agricultural practices in the area are performed in the locality, as well as cars that pass along the R710 highway.

Zone 4 - Control 10 km beyond	**S14** (28.01989 ^{O}S, 026.99482 ^{O}E)	The site is positioned inside a game lodge in Hennenman. The Reitspruit Dam is the surface water source in the area	Small farming settlement and a game lodge are the pollution sources.
Zone 5 - Control 10 to 12 km beyond	**S15** (27.77143 ^{O}S, 026.64635 ^{O}E)	The site is situated on R30 highway in Allanridge, north of the high-density tailings area. The stream in the area is the surface water source.	Target Gold Mine Shaft, waste rocks dump and Allanridge settlement are in the area. Cars that drive along the R30 highway are also a pollution source.

3.5.2 Identification of zones and sampling sites within the cultivated lands

Within the cultivated lands in the MLM area, four zones were selected to study the extent of contamination by contaminants from gold mine tailings in the MLM area. Within the four zones, 12 sampling sites were selected from where contamination of cultivated soil and maize seeds samples were determined. However, of the twelve sampling sites that were selected to study the contamination of cultivated soil and maize seeds, the contamination of groundwater was only studied from eight of the sampling sites and within three of the zones across the cultivated lands in the MLM area. The main reason was because some of the maize farms from where the cultivated soils and maize seeds samples were investigated did not contain boreholes.

Four different criteria were put in place for proper selection of the zones, within the cultivated lands, similar to the criteria for the selection of zones within the uncultivated lands. The criteria that were used for the selection of the different zones included, different distances beyond the mine tailings, anthropogenic activities, such as industries and agricultural activities, as well as the prevailing wind direction in the area.

Zone 1 was selected at about 5 km from the high density mine tailing zone, on the western side of Welkom. Five sampling sites, F1, F2, F3, F4 and F5 were selected within maize farms in Zone 1. Of all the sampling sites in Zone 1, boreholes were present at only sampling sites F2, F4 and F5, from where groundwater contamination was investigated. Zone 2, contained three sampling sites, F6, F7, F8, and were positioned at about 7 km to 10 km away from the high density mine tailing zone, occupying the western side of Virginia, as well as the southern border of the high density mine tailings zone. Each of the sampling site in Zone 2 contained a borehole, as well as a maize farm in the vicinity, from where the contamination of cultivated soil and maize seeds were assessed.

For control purposes, three sampling sites; F9, F10, F11 were selected in Zone 3. These sampling sites were positioned at about 10 km to 12 km, on the eastern side of the high density mine tailing zone and in the upstream wind direction. Two of the sampling sites within Zone 3, F9 and F10 also contained a borehole. Zone 3 did not contain any mine tailing or gold mines during the time of this study and therefore the prevailing wind that blows over the high density mine tailings zone may have negligible effects on the sampling site (Figure 3.5).

Zones 4 comprised of a single sampling site, F12 and was situated at about 30 km beyond the high density mine tailings zone, between Welkom and Bultfontein. This sampling site did not contain a borehole. Zones 1, 2, and 4 were in the downstream direction of the prevailing wind in relation to the high density mine tailings zone, while Zone 3 was positioned in the upstream wind direction in relation to the high density mine tailings zone.

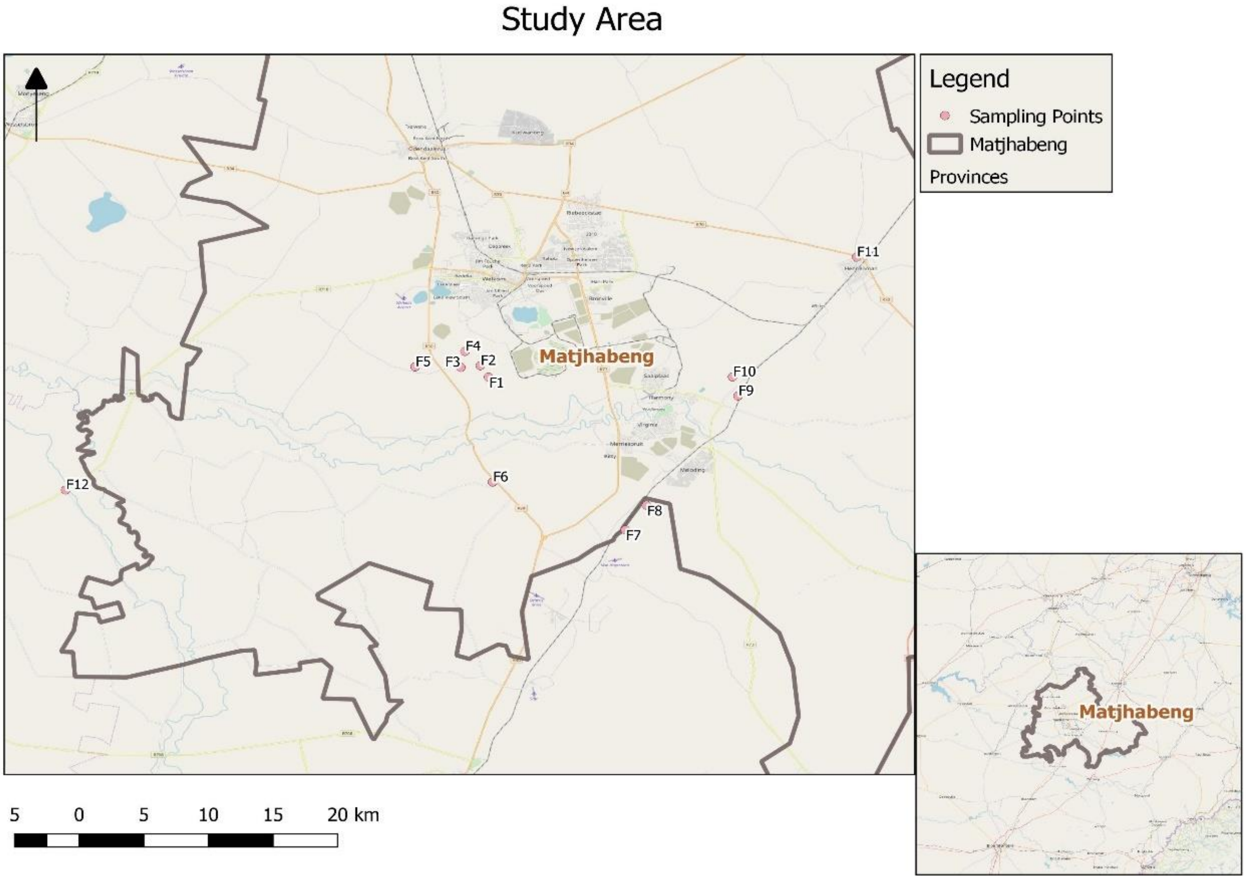

Figure 3.5 Study area of the Matjhabeng Local Municipality area showing the different twelve sampling sites with groundwater, cultivated soil and maize plant

Supplementary data were also recorded at each of the 12 sampling sites where the contamination of groundwater, cultivated soil, as well as maize seeds were investigated within the cultivated lands in the MLM area. These data included a description of the sampling sites and the surrounding human activities at each sampling site (Table 3.2).

Table 3.2 Sampling sites, references, description of sampling areas and surrounding human activities

Zone	Sampling sites	Description of locality	Potential polluting agents
Zone 1 5 km beyond the high-density tailing zone	**F1** (28.06367 ^{O}S 026.73369 ^{O}E)	Maize farming area, with cattle farming in the vicinity. Mine shaft located about 1 km from the farm, with mine tailings and mine rocks.	Mine shaft, mine tailings and mine rocks, as well as a cattle farm are the major contaminant in the area.
	F2 (28.05423 ^{O}S 026.72712 ^{O}E)	Maize farming area. A farmhouse located in the vicinity of the maize farm. There are no mines or tailings in the area.	Few farmhouses in the area
	F3 (2805563 ^{O}S 02671176 ^{O}E)	Extensive maize farm field. Presence of a workshop for repairing farming tools close to the maize farm	Farmhouses and a metal workshop, close to the farm for repairing farming tools.
	F4 (2804245 ^{O}S 02671506 ^{O}E)	Extensive maize farm on the western side Welkom, with newly deposited mine tailing, at close range to maize farm.	Mine tailings, as well as a cattle farm.
	F5 (2805520 ^{O}S 02667569 ^{O}E)	Maize farming area, with a shallow-open pan of muddy water opposite the farm. No mines or mine tailings present in the area.	Water that overflows from the shallow pan to the maize field.
Zone 2 7-10 km beyond	**F6** (2815089 ^{O}S 02673682 ^{O}E)	A maize farming area having few farming houses. A mine shaft is in the vicinity of the maize farm.	A mine shaft is in the vicinity of the site including few farming houses.
	F7 (2819056 ^{O}S 02684172 ^{O}E)	Large expanse of maize farm with a workshop for repairing tools on the farm premises.	A mine is in the vicinity of the site and a metal workshop
	F8 (2817008 ^{O}S 02685848 ^{O}E)	Within the maize farms, there is also a farmhouse.	Small farm community in the area
Zone 3 (control) 10–12 km beyond	**F9** (2807933 ^{O}E 02693070 ^{O}S)	Extensive maize farm along a road from Virginia to Hennenman. The area has few farmhouses.	Few farmhouses in the area, as well as cars moving along the road from Virginia to Hennenman.
	F10 (2806356 ^{O}E 02692637 ^{O}S)	Maize farm also located on the road from Virginia to Hennenman.	Few farmhouses in the area, as well as cars moving along the road from Virginia to Hennenman.
	F11 (2796411 ^{O}E 02702419 ^{O}S)	Small space of maize farm situated in the central part of Hennenman.	Residences and small businesses in Hennenman, as well as cars moving along the road.
Zone 4 30 Km beyond	**F12** (2815740 ^{O}E 02639968 ^{O}S)	A maize farm field along R710, between Welkom and Bulfontein and close to Groudkop Deport. Water in the area is an artificial stream, used for watering the maize fields.	The Groudkop Deport may be a pollution source in the area, as well as cars that move along R710.

Chapter 4

Water Quality of Surface and Groundwater

4.1 Introduction

The MLM area has a diversity of water sources. These include surface water bodies, such as lakes, streams, rivers, pans, and dams, as well as groundwater sources, such as boreholes. Some of the surface water bodies, as well as the groundwater sources are at a close proximity to the gold mine tailings in the area, and are therefore exposed to contaminants from the gold mine tailings. In particular, surface water bodies such as the Sand River, which is the largest water catchment in the MLM area, as well as Viet River, run through the MLM area, receiving contaminants, which are transported by run-off water from the gold mine tailings in the MLM area. Other surface water bodies in the area, such as the Flamingo Pan, the Flamingo Lake, the Witpan, as well as the Reitspruit dam are also exposed to the contaminants that are transported into the water by the run-off water. However, some of the dams in the area are mine dams, which are reservoir for the treated mine effluents from mines in the MLM area. The numerous gold mine tailings in the Matjhabeng Local Municipality (MLM) area, as well as the mining activities, may be responsible for the contamination of surface water bodies and groundwater in the area.

To determine the extent of contamination of surface water bodies, as well as the groundwater in the MLM area, water samples were collected from the different surface water and groundwater sampling sites and analysed for several water quality indicators of contamination. Surface water samples were collected from the fifteen sampling sites that were identified in the five zones, within the uncultivated lands, for both the hot summer and the cold winter seasons. For groundwater, the water samples were collected from eight of the sampling sites that were identified within the cultivated lands in the study area. Because, the boreholes that were chosen to collect the groundwater samples were those that were in the vicinity of a cultivated maize farm, therefore only eight boreholes sampling sites could be identified, for the collection of groundwater samples. Additionally, since groundwater samples had to be collected with cultivated soil and maize seeds samples, the groundwater samples could only be collected during the winter season, when maize seeds mature in the MLM area.

Several indicators were used to measure the extent of contamination of the surface water samples, as well as the groundwater samples. These indicators were the water pH, temperature, electrical conductivity (EC) and turbidity, as well as dissolved oxygen (DO). Chemicals in water, which are described as potential harmful elements, (PHEs) were also measured in the surface water and groundwater samples. The twelve PHEs were arsenic (As), cadmium (Cd), lead (Pb), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), selenium (Se), zinc (Zn), calcium (Ca) and magnesium (Mg). In addition, faecal coliform, and *Escherichia coli* (*E. coli*) were measured in groundwater since groundwater in the MLM area is used for drinking and other domestic purposes. Therefore, to determine the extent of contamination of the surface water bodies and groundwater by contaminants from goldmine tailings in the MLM area, the following research question was answered:

Sub Question: To what extent is the water contaminated by contaminants from gold mine tailings in the MLM area? To address this research question, these were the objectives that were measured:

Objective 2: To determine the quality of surface water, measured in terms of its physical water quality properties, as well as its PHE contamination.

Objective 3: To determine the quality of groundwater, measured in terms of its physical and microbiological water quality properties, as well as its PHE contamination.

4.2 Materials and methods

4.2.1 Collection of water samples

Water samples were collected according to the procedure described in the sampling guide of the quality of domestic water supplies, prescribed by the Water Research Commission of South Africa (WRC, 2003). At a sampling site, the surface water samples were collected either from a dam, lake, stream, river, or a pan, while groundwater samples were collected from a borehole tap. During the collection of water samples, protective clothing, such as boots and gloves, was worn as a precaution from being exposed to harmful pollutants in the water that may cause diseases. The surface water sampling sites were represented with the letters SW, which indicates surface water. Thus, sampling site number one was denoted as SW1, while sampling site fifteen was represented as SW15. For groundwater, the sampling sites were denoted with the letters GW, which represents groundwater. Thus, similarly to the labelling of the surface water samples, groundwater sample number one was represented as GW1.

Surface water samples were collected for the measurement of turbidity at each of the sampling sites, as well as for the measurement of the twelve PHEs in the laboratory. The surface water samples were collected in the following manner:

1. For the measurement of turbidity, water samples were collected in a 100 ml beaker from surface water that was approximately one metre from the embankment and 50 cm below the surface of the water.
2. For the measurement of PHEs, water samples were collected in a one litre bottle from the same area as for turbidity.
3. In instances where it was difficult to access the surface water at a sampling site, a rope was tied to a bucket that had been rinsed with distilled water, and lowered into the water to collect the water sample.
4. Water samples in the one litre bottle for the measurement of PHEs, were clearly labelled using a permanent marker with the site number, as well as the time and date of collection.

5. These sample bottles were then placed in a cooler box containing ice, after which they were transported to the Water Laboratory at the Central University of Technology (CUT), where the water samples were kept at 4 °C in the refrigerator until analysis.

At each groundwater sampling site, a water sample was collected from a borehole tap and then used for the measurement of turbidity, water pH, temperature, EC and DO. Groundwater samples were also collected for the measurement of PHEs, as well as for the presence of indicator microorganisms in water. The number of faecal coliform bacteria was counted to indicate the total bacterial load in the drinking water, as well as the number of *Escherichia coli* (*E. coli*) to determine the degree of pollution of the water from faecal matter (WHO, 2018).

The groundwater samples were collected in the following manner:

1. For the measurement of turbidity, water pH, temperature, EC and DO at a sampling site, water samples were collected in a 100 ml beaker from the borehole tap, while for the measurement of PHEs, water samples were collected in a one litre bottle.
2. Prior to the collection of a water sample destined for the measurement of the presence of the indicator microorganisms, the borehole tap was flamed, then opened, and allowed to run for at least three minutes, after which a water sample was collected in sterile 100 ml sampling bottle.
3. All sample bottles intended for the measurement of PHEs and microorganisms were clearly labelled with site number, time and date of collection and then placed in a cooler box containing ice.
4. These sample bottles were then transported to the Water Laboratory at the CUT, where the water samples were kept at 4 °C in the refrigerator until analysis.

4.2.2 Measurement of physical water quality properties

The physical water quality properties of turbidity, water pH, temperature, EC and DO were measured at each surface water and groundwater sampling sites. Turbidity was measured using a calibrated, battery operated Hach 2100Q turbidity meter and following the standard analytical procedures of the instrument in the following manner:

1. A surface water or groundwater sample from a collection bottle was poured into a clean Hach sample cell to the 10 ml mark.
2. The Hach 2100Q instrument was then switched on and its calibration verified by placing a clean sample cell containing a calibration solution of <100 nephelometric turbidity units (NTU) in the instrument's cell compartment.
3. After verifying the calibration of the instrument, the calibration sample cell was removed and replaced with a sample cell containing a water sample, which had been cleaned with a soft cloth to remove fingerprints and water marks.
4. The sample cell compartment was closed, the read button was pressed, and the turbidity reading recorded in NTU.

The water pH, temperature, EC and DO of the water samples were measured using a battery operated Hach HQd handheld meter, according to the analytical procedures of the instrument. These properties were measured directly in a surface water body by casting a measurement probe which is specific for a water quality property, into mid-stream water. After swirling the probe a few seconds, the water pH, temperature, EC or DO readings were recorded. For groundwater, the measurements of water pH, temperature, EC and DO were also obtained using the Hach HQd handheld meter. In contrast to surface water measurements, each of the specific probes was placed directly into a beaker containing a sample of groundwater.

4.2.3 Measurement of potential harmful elements

The twelve PHEs As, Cd, Pb, Co, Cr, Cu, Fe, Ni, Se, Zn, Ca and Mg were measured using the inductively coupled plasma optical emission spectroscopy (ICP-OES), for surface water, as well as for groundwater. The measurements were performed at the School of Chemistry and Physics, University of Kwa-Zulu Natal, Westville campus. Prior to elemental analysis, the water samples were digested using open vessel digestion in nitric acid (HNO_3). The procedure that was followed for the measurements of the PHEs, as well as the digestion procedures for the water samples were a modified process according to (Kisten et al., 2015).

The digestion of surface water and groundwater samples were performed to remove impurities from the water before measurement of the PHE content of a water sample with the ICP-OES. The procedure that was followed for the digestion process was as follows:

1. Five millilitres of water sample were added into a beaker containing 10 ml of HNO_3 solution.
2. The mixture was covered with a watch glass and left to digest at 80 ^{O}C on a hot plate in a fume cupboard until the water sample became clear, indicating that the digestion was complete.
3. Once the mixture was cold, it was filtered into a 25 ml volumetric flask using a 70 mm pore size filter paper.
4. The mixture was then diluted by adding double distilled water to the 25 ml mark.
5. Thereafter the diluted mixture was poured into a 50 ml polyethylene bottle for storage in the refrigerator until PHE analysis could be undertaken.
6. For quality control purposes, three digests were performed for each water sample.
7. To validate the digestion method, PHE standards were also prepared for each of the PHEs that were measured in this study.

After the digestion of the surface water and groundwater samples, the PHEs in the water samples were measured. The measurement of the 12 PHEs was performed using the ICP-EOS in the following manner:

1. Fifty millilitres of a digested water sample were transferred into a syringe and then filtered through a 0.4 µm pore filter paper.
2. The filtered water sample was then transferred into a 15 ml ICP-OES vial and labelled with site number.
3. The vial containing the water sample was placed in the ICP-OES for the measurement of the PHEs in the water sample.
4. The accuracy of the method for the determination of PHEs was measured using standard reference materials (CRM), White Clover (BCR 402), obtained from the Community Bureau of Reference of the Commission of the European Communities.

4.2.4 Measurement of microbiological properties

The number of faecal coliform bacteria and number of *E. coli* were counted using the Colilert 18/ Quanti-Tray method (ISO 9308-2:2012) according to the manufacturer's specifications (COLILERT QUANTI-TRAY®, IDEXX Laboratories, Inc., United States). The measurements were performed in the following manner:

1. Colilert 18 powder was poured into each water sample in the bottle, which was then shaken for a few minutes until the powder had dissolved.
2. The water sample containing the dissolved Colilert 18 medium powder was them poured into 97-wel Colilert 18 Quanti-TrayTM2000 tray and clearly labelled with the site name and number.
3. The 97-wel Colilert 18 Quanti-TrayTM2000 tray was then heat-sealed and incubated at 37 ºC for 20 hours.
4. If coliform bacteria were present in a water sample, the wells would appear yellow in natural light. In contrast, if *E. coli* were present in a water sample, the wells would fluoresce blue when placed under UV light.
5. The number of colony forming units (cfu) of faecal coliform bacteria and *E. coli* present in 100 ml of a water sample was determined using the Quanti-Tray®2000 Most Probable Number (MPN) table.

4.2.5 Measurement of overall groundwater quality

The drinking water quality of the groundwater samples was determined by computing a Water Quality Index (WQI) proposed by (Rakotondrabe et al., 2017) using the physical and chemical measurements of the groundwater samples. The drinking WQI proposed by Rakotondrabe et al. (2017) was most appropriate for use to compute the WQI in this study based on the fact that it only allowed for single set of measurement and it was also reatively easy to compute. A WQI integrates measurements of different water quality properties into a single value that describes the overall quality of the water at a particular sampling site (Kannel et al., 2007; Nikoo et al., 2011; Sharma et al., 2013). To compute the WQI, three physical water quality properties and the measurements of five PHEs were selected based on their impact to water quality and human health (Rakotondrable et al., 2017). The three physical water quality properties were turbidity, pH and EC. The five PHEs; Cu, Fe, Pb, Ca and Mg were selected because their concentrations were above the instrument detection limit at more than 50% of the sampling sites. Three main factors were computed in the determination of a WQI for a particular sampling site; relative weight (Wi), quality rating (qi) and sub-index of the ith property (SIi) according to the procedure of Rakotondrable et al. (2017).

For the calculation of W_i, weights ranging between 1 to 5, were assigned to each water quality property based on the impact of each property on water quality, as well as the harm that each of the water quality property may cause to human health. For example, a weight of two was assigned to a water quality property that may not have significant effect on water quality, as well as human health, but a weight of five was assigned when a water quality property can cause severe contamination to water and also cause critical health implications to humans (Table 4.1).

Table 4.1 Weights of water quality properties and standards

Property	**Weights**	**SANS 241** Drinking Water Standard
pH	3	≥ 5 and ≤ 9.7
EC (mS/m)	2	170
Turbidity (NTU)	3	≤ 5
Ca (mg/L)	2	(150 – 300)[1]
Mg (mg/L)	2	(150 – 300)[1]
Fe (mg/L)	3	0.3
Cu (mg/L)	3	2
Pb (mg/L)	5	0.01

[1] = World Health Organisation drinking water standard (WHO, 2018)

W_i was computed according to the equation below.

$$W_i = {}^{w_i}/_{\sum_{i=1}^{n} wi} \quad (1)$$

where, W_i is the relative weight, w_i *is* weight of each property, n is the number of properties

For the calculation of q_i, the concentration of each water quality property was divided by its limit according to the South African National Standard on drinking water (SANS 241, 2015) as the standard contained most of the water quality properties that were used in computing the WQI. But for Ca and Mg which did not have limits in SANS 241, the WHO (2018) drinking water limit was used. However, where the limit in SANS 241 and WHO was a range, the middle number was used.

$$q_i = \left(\frac{C_i}{S_i}\right) \times 100 \qquad (2)$$

where, q_i is quality rating, C_i is concentration of each water quality property and Si is the drinking water quality standard for each water quality property.

The product of the relative weights and the quality rating obtained for each water quality property is denoted by SI_i.

$$SI_i = W_i \times q_i \qquad (3)$$

where, SI_i is the sub-index of the i^{th} property, W_i is the relative weights and q_i represents the quality rating.

With the three factors in place, the drinking WQI was then calculated in the following manner:

$$WQI = \sum_{i=1}^{n} SI \qquad (4)$$

The calculated WQIs were interpreted according to five categories (Rakotondrable et al.,2017). Water with a WQI value < 50 was classified as excellent; water with a value ranging from 50 to 100 as good; water with a value ranging from > 100 to 200 as poor; water with a value ranging from > 200 to 300 as very poor water; and water with a value > 300 as extremely poor water.

4.2.6 Statistical analysis of water quality measurements

The Statistical Package for Social Sciences (SPSS) Version 23 was used to analyse the surface and groundwater quality measurements. Summary statistics were calculated for the physical water quality measurements, which included maximum, minimum, means and standard deviations. In addition, percentage compliance to the water quality limits were also calculated. Student's t-tests were also performed on the concentrations of the surface water quality measurements at 95% confidence interval, to ascertain if there were any seasonal differences between the measurements obtained for summer and winter. Additionally, Principal Component Analysis (PCA) was applied to compare the concentrations of the measured PHEs in surface water and their compositional relationship, to distinguish if these PHEs were from a similar source in the environment. This method of applying the PCA reduces complex measurements and presents the measurements into a simple manner by extracting new variables (principal components) from previous variables (metal concentration and site) (Wu et al., 2014).

4.2.7 Determination of quality assurance and quality control

Quality assurance procedures were applied to ensure that the measured results for surface and groundwater measurements were reliable. All instruments - the Hach 2100Q turbidity meter, Hach HQd hand-held meter probes for DO, pH, and electrical conductivity - were calibrated before measurements of on-site water quality properties. Double distilled water was used throughout the study to clean glassware, and the reagents that were used were of analytical grade. Reagent blank determinations were used to correct the instrument readings. For validation of the analytical procedure, standard reference materials (CRM), White Clover (BCR 402), obtained from the Community Bureau of Reference of the Commission of the European Communities was used. All samples were analysed in triplicates (n = 3).

4.3 Results of surface water quality

Measurements were recorded for the five physical water quality properties, as well as for the 12 PHEs during summer and winter seasons. To determine the level of compliance, the measurements of the physical water quality properties were compared to two sets of limits, for the protection of freshwater aquatic organisms in surface water. These limits were the Canadian Council of Ministers of the Environment water quality limits (CCME, 2008) and the Aquatic Water Quality for Urban Streams (AWQUS) limits (Belle et al., 2020). Similarly, the measurements of the PHEs were also compared to two different sets of water quality limits; the limit for the protection of freshwater aquatic organisms (CCME, 2008), and the limits for the protection of water resources, which are situated within contaminated lands, prepared by the South African Department of Environmental Affairs (DEA, 2010). The limits for the protection of water resources within contaminated lands were compiled to provide the set of criteria that can be used to identify and register contaminated lands sites in South Africa, as well as to assess the status and risk posed by contaminated lands on humans (DEA, 2010).

4.3.1 Physical properties

The measurements of water pH, temperature, EC, turbidity, as well as a DO were recorded for both sampling seasons. When the measurements were compared to the CCME (CCME, 2008) and the AWQUS limits (Belle et al., 2020), all the measurements of turbidity were non-compliant, besides one turbidity measurement, when compared to the measurements of water pH, temperature, EC and DO that showed fewer non-compliant measurements as indicated in Table 4.2. Overall, only two seasons of the water quality measurements were 100% compliant when compared to the two sets of surface water limits. These seasons were the winter season for temperature and the summer season for EC. When considering the measurements for EC, it was interesting to note that the EC measurements at eleven sampling sites for the winter season were substantially higher than the measurements of the summer season. This difference in seasonal measurements could be attributed to an increase in salts and ions in the water that were transported to the surface water through run-off during excessive rain on the day of water sampling.

Table 4.2 Results of the physical water quality properties of surface water for summer and winter

On-site properties		**pH**		**Temperature (°C)**		**EC (µs/cm)**		**Turbidity (NTU)**		**DO (mg/L)**	
CCME limit[1]		**6.5 – 9.0**		**-**		**≤1000**		**-**		**6.5 – 9.5**	
AWQUS limit[2]		**5.5 – 9.0**		**≥ 5 ≤ 25**		**≤1000**		**≤ 5.6**		**6.5 – 9.5**	
Site/Season	**Name**	**Summer**	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**
SW1	Stream	6.60	8.71	23.00	14.00	12.30	1036.00	18.50	9.51	6.80	7.53
SW2	Dam	7.69	8.85	23.70	14.50	7.60	1060.00	45.50	30.00	4.00	7.46
SW3	Flamingo pan	9.25	10.11	25.50	14.00	146.70	171.20	32.70	23.90	12.29	8.88
SW4	Flamingo Lake	8.66	9.58	24.30	14.40	32.10	28.30	16.40	14.80	7.32	9.11
SW5	Dam	4.00	4.32	23.70	14.60	100.60	78.80	7.70	1.08	7.68	8.53
SW6	Dam	8.18	8.64	24.60	14.20	200.00	241.00	168.00	57.60	18.92	10.40
SW7	Witpan	7.95	7.90	26.40	13.40	16.40	1407.00	24.70	14.90	6.78	4.07
SW8	Sand River	7.63	8.80	24.60	12.60	11.70	650.00	5.77	24.60	6.07	7.67
SW9	Stream	8.03	8.63	24.00	12.60	1.50	1557.00	175.00	150.00	7.37	9.32
SW10	Viet River	7.75	7.42	22.40	10.80	4.00	342.00	295.00	90.80	0.13	7.33
SW11	Sand River	7.74	9.08	24.60	12.83	13.10	1074.00	9.06	8.36	6.28	12.77
SW12	Rietspruit dam	8.21	8.24	23.90	11.40	4.50	467.00	107.00	52.10	6.80	8.23
SW13	Stream	7.71	8.03	24.50	13.00	14.30	1197.00	5.59	70.50	0.74	0.16
SW14	Pan	7.43	8.43	25.20	12.60	3.70	167.40	78.40	179.00	0.16	7.66
SW15	Sand River	8.43	9.12	25.50	10.40	25.20	1354.00	22.80	11.20	14.24	12.77
Maximum		9.25	10.11	26.40	14.60	200.00	1557.00	295.00	179.00	18.92	12.77
Minimum		4.00	4.32	22.40	10.80	1.50	28.30	5.77	1.08	0.13	0.16
Mean		7.68	8.39	24.39	13.02	39.58	722.04	67.47	49.22	7.04	8.13
Standard deviation		1.18	1.31	1.02	1.33	60.27	539.84	84.63	53.62	5.12	3.08
Percentage Compliance		87	67	73	100	100	53	0	0.06	40	67

[1]CCME = Canadian Council of Ministers of the Environment water quality limits; [2]AWQUS = Aquatic Water Quality for Urban Streams limits; SW = surface water samples; numbers in red represent measurements that exceeded the limits;

Student's t-tests were performed to ascertain if any seasonal effects existed for the physical water quality properties for the surface water samples. Highly significant differences could be established ($p \leq 0.05$) between the two sampling seasons for pH, temperature and EC. Table 4.3 shows the probability (*p*-Value) and the test statistics (t), as well as the confidence limits for the five surface water quality properties.

Table 4.3 Results of the Student's t-tests of seasonal variation for the physical properties of the surface water samples

PHEs	Mean Difference	95% Confidence Interval of the Difference		t	*p*-Value
		Lower	Upper		
pH	0.71	-1.05	- 0.36	- 4.39	0.001
Temperature	11.19	10.45	12.29	26.52	0.0001
EC	- 682.46	- 999.12	366.80	- 4.62	0.0001
Turbidity	18.25	- 20.31	56.81	1.01	0.327
DO	-1.09	- 3.43	1.25	- 0.99	0.337

PHEs = potential harmful elements; t = test statistic; *p* = probability at $p \leq 0.05$

4.3.2 Potential harmful elements

The measurements of the 12 PHEs were recorded for the 15 surface water sampling sites in the study area during the two sampling seasons. The concentrations of Cd, Cr and Pb were below the ICP-OES detection limits for surface water at all sampling sites. When viewing the concentrations for Ni, it could only be detected at a single water sample collected at SW4. On the other hand, when the PHEs measurements were compared to the CCME (2008) water quality limits for the protection of aquatic organisms, non-compliance was high for As and Co during the summer season, showing 73% and 93% non-compliance respectively (Table 4.4). More so, for the winter season, the one site for which Co was detected also exceeded the CCME (2008) water quality limits. In contrast to the CCME (2008) water quality limits, the concentrations of As and Co showed 100% compliance when compared to the permissible limit for the protection of water resources in contaminated lands as stipulated by the DEA (2010), for both the summer and the winter season. For measurements of Cu, 27% of the water samples revealed non-compliance to both the CCME (2008) limits and the DEA (2010) limits during the summer season. But for the winter season, the measurements of Cu showed 100% compliance to both limits. With the measurements of Fe, during the summer season, only three of the water samples from the 15 sampling sites revealed non-compliance to the CCME (2008) limits, while for the winter season, 67% of the measurements were non-compliant. More so, the single sampling site (SW5) where Zn was detected displayed non-compliance to the CCME (2008) limit during the summer season, while for the winter season, 53% of the Zn measurements exceeded the CCME (2008) limits. On the other hand, when the measurements of Zn were compared to the DEA (2010) limits, all the water samples for which Zn measurements were detected showed 100% compliance for both the summer and the winter seasons. However, although the concentrations of Se, Ca and Mg detected in surface water were extremely high, no surface water quality limits for the measured PHEs could be sourced, since their effects on the environment are negligible.

Table 4.4 Results of the mean concentrations (standard deviation) of potential harmful elements for the surface water samples for the 15 sampling sites for summer and winter

Metals			**As**	**Co**	**Cu**	**Fe**	**Ni**	**Se**	**Zn**	**Ca**	**Mg**
CCME limit[1]			**0.05**	**1.8**	**6.4**	**0.3**	**150**	**-**	**0.3**	**-**	**-**
DEA of SA limit[2]			**580**	**22000**	**16**	**-**	**1400**	**-**	**240**	**-**	**-**
Sites	**Names**	**Seasons**									
SW1	Stream	Summer	2.5 (0.12)	2.5 (0.12)	ND	ND	ND	35.0 (3.69)	ND	39000 (16)	13520 (10)
		Winter	ND	ND	1.5 (0.04)	ND	ND	11.3 (1.25)	0.07 (0.01)	1603 (14)	188 (5)
SW2	Dam	Summer	20.0 (0.69)	2.5 (0.36)	ND	ND	ND	42.5 (4.66)	ND	38025 (18)	11485 (5)
		Winter	ND	ND	1.5 (0.03)	ND	ND	28.5 (3.10)	0.3 (0.03)	1896 (7)	104 (3)
SW3	Flamingo pan	Summer	ND	2.5 (0.54)	ND	ND	ND	20.0 (2.30)	ND	36650 (15)	66875 (8)
		Winter	ND	ND	1.5 (0.04)	ND	ND	ND	ND	1937 (6)	4378 (11)
SW4	Flamingo Lake	Summer	17.5 (1.35)	2.5 (0.63)	ND	ND	4.6 (1.03)	30.0 (3.50)	ND	26200 (13)	23017.5 (5)
		Winter	ND	ND	1.5 (0.03)	2.7 (0.10)	ND	ND	ND	1078 (1)	829 (8)
SW5	Dam	Summer	0 (0)	22.5 (1.99)	60.0 (9.82)	ND	ND	32.5 (4.02)	5.4 (1.50)	250000 (23)	125600 (14)
		Winter	ND	2.5 (0.10)	2.9 (0.15)	ND	ND	12.0 (1.07)	12.6 (0.73)	10643 (29)	3326 (11)
SW6	Sand River	Summer	15.0 (1.59)	30.0 (1.58)	5.0 (1.53)	ND	ND	ND	ND	277500 (23)	92875 (14)
		Winter	ND	ND	1.5 (0.02)	0.04 (0.01)	ND	ND	ND	16567 (9)	6296 (7)
SW7	Witpan	Summer	5.0 (1.02)	2.5 (0.36)	2.5 (1.08)	ND	ND	15.0 (1.23)	ND	34675 (13)	11797 (10)
		Winter	ND	ND	1.5 (0.07)	ND	ND	14.5 (0.52)	2.6 (0.53)	3311 (7)	209 (3)
SW8	Sand River	Summer	0 (0)	2.5 (0.78)	25.0 (2.06)	ND	ND	ND	ND	32000 (16)	12985 (10)
		Winter	ND	ND	1.5 (0.02)	7.1 (0.05)	ND	ND	0.03 (0.01)	959 (6)	119 (8)
SW9	Pan	Summer	2.5 (0.58)	25 (1.72)	30.0 (3.98)	2780.0 (6)	ND	47.5 (3.21)	ND	14030 (11)	4915 (6)
		Winter	ND	ND	1.4 (0.02)	20.2 (3.97)	ND	11.0 (0.96)	0.7 (0.08)	189 (2)	ND

SW10	Sand River	Summer	5.0 (1.58)	2.5 (0.25)	ND	82.5 (3.00)	ND	42.5 (5.88)	ND	9890 (13)	3985 (5)
		Winter	ND	ND	1.45 (0.02)	15.4 (0.32)	ND	25.1 (0.50)	0.4 (0.02)	747 (4)	ND
SW11	Sand River	Summer	ND	ND	30.0 (4.00)	ND	ND	ND	ND	33050 (13)	10780 (6)
		Winter	ND	ND	1.46 (0.01)	3.2 (0.22)	ND	ND	0.5 (0.01)	1572 (7)	311 (3)
SW12	Man-made stream	Summer	12.5 (1.02)	5.0 (1.00)	ND	ND	ND	25.0 (2.7)	ND	10467.5 (13)	3595 (8)
		Winter	ND	ND	1.44 (0.01)	3.4 (0.53)	ND	15.6 (0.18)	0.6 (0.02)	1004 (3)	ND
SW13	Viet River	Summer	7.5 (0.54)	2.5 (1.04)	ND	ND	ND	ND	ND	44000 (14)	16030 (7)
		Winter	ND	ND	1.48 (0.03)	9.1 (0.01)	ND	12.9 (2.15)	0.2 (0.04)	1508 (3)	166 (3)
SW14	Dam	Summer	5.0 (0.23)	2.5 (0.06)	ND	1277.5 (5)	ND	27.5 (2.82)	ND	10270 (12)	4020 (3)
		Winter	ND	ND	1.47 (0.04)	20.8 (3.28)	ND	24.7 (1.41)	2.5 (0.29)	1,051 (5)	ND
SW15	Sand River	Summer	25.0 (1.07)	2.5 (0.09)	ND	ND	ND	20.1 (3.62)	ND	49875 (14)	32100 (10)
		Winter	ND	ND	1.49 (0.02)	5.6 (0.52)	ND	ND	0.4 (0.03)	1921 (8)	616 (3)

[1]CCME = Canadian Council of Ministers of the Environment water quality limits; [2]DEA of SA = limits for the protection of water resources within contaminated lands, stipulated by South African Department of Environmental Affairs South African; SW = surface water samples; numbers in red represents measurements that exceeded the limits; ND = Bellow instrument detection limit

Student’s t-tests were performed on the measurements of PHEs for summer and winter to ascertain if any significant differences existed for the two seasons. Highly significant differences ($p \leq 0.05$) could be established between the two sampling seasons for As, Cd, Pb, Cr, Cu, Fe, Se and Mg (Table 4.5).

Table 4.5 Results of the Student’s t-tests for seasonal variation of the potential harmful elements of the surface water samples

PHE	Mean		Mean Difference	95 % Confidence Interval of the Difference		*t*	*p*-Value
	Summer	**Winter**		**Lower**	**Upper**		
As	0.36	0.00	0.36	0.19	0.54	4.17	0.0001
Cd	- 27.84	0.00	-27.84	- 51.71	- 3.98	- 2.35	0.023
Pb	- 0.53	0.00	- 0.53	- 0.77	- 0.29	- 4.46	0.0001
Co	7.23	0.16	7.06	- 3.41	17.54	1.35	0.181
Cr	- 0.40	0.00	- 0.40	-0.59	- 0.22	- 4.38	0.0001
Cu	0.12	1.60	-1.48	-1.62	-1.33	-20.04	0.0001
Fe	-19.51	5.85	- 25.36	- 45.08	- 5.65	- 2.59	0.01
Ni	7.76	0.00	7.76	-12.13	27.65	0.786	0.43
Se	0.50	10.41	- 9.91	-12.95	- 6.86	- 6.56	0.001
Zn	9.21	1.43	7.78	-18.12	33.69	0.60	0.54
Ca	2837.64	3203.56	- 365.92	-1654.67	922.83	- 0.57	0.57
Mg	1734.69	1107.27	627.42	-17.20	1272.04	1.96	0.05

t = test statistic; *p* = Probability, indicating significance at $p \leq 0.05$

4.3.3 Sources of contamination of potential harmful elements in surface water

To determine if the measured PHEs in surface water were from a similar source in the environment, a multivariate PCA was performed on the measurements of the PHEs that could be detected. Since fewer measurements in the winter season were detectable with the ICP-OES, only the measurements that were recorded during the summer season were used for the multivariate PCA. The results of the multivariate PCA revealed four main principal components (PC) with eigenvalues equal or greater than one, and 91.47% of the total variance (Table 4.6). The minimum value of 0.6 was the list value, which a loading could have and be part of a PC list. The PC1 and PC2 were the major contributors to the total variance, with a cumulative variance of close to 70%, therefore, the PHEs in PC1 and PC2 may provide the highest level of contamination in the study area. The first principal component (PC1) showed relatively high loadings for the four PHEs Co, Cu, Ni, and Zn, and thus strongly suggests that these PHEs may have a common source of origin. Although Ca also falls within PC1, its source of origin may not be so strongly connected to the other four PHEs in PC1. The high loadings of Pb, Cr and Fe in PC2 further suggests that these PHEs may also have a common source of origin. Finally, the third principal component (PC3) had high loadings of Se, while As and Mg was within PC4. The separation of As from Mg in PC4 may suggest that As and Mg may have originated from different sources in the environment.

Table 4.6 Results of the principal components loading for the measurements of PHEs in surface water

PHE	**Component**			
	PC1	**PC2**	**PC3**	**PC4**
As	-0.219	-0.587	0.075	**0.663**
Pb	-0.077	**0.765**	-0.505	0.082
Co	**0.977**	-0.153	0.122	-0.032
Cr	-0.102	**0.952**	-0.240	0.020
Cu	**0.988**	-0.075	0.115	-0.043
Fe	-0.137	**0.790**	0.374	0.009
Ni	**0.992**	-0.057	0.059	-0.038
Se	0.192	-0.056	**0.945**	-0.017
Zn	**0.994**	-0.027	0.070	-0.034
Ca	**0.611**	-0.619	-0.175	0.084
Mg	0.032	0.145	-0.060	**0.940**
Eigen values	**4.853**	**2.607**	**1.407**	**1.196**
Percentage of total variance	**44.116**	**23.701**	**12.787**	**10.868**
Percentage of cumulative variance	**44.116**	**67.816**	**80.603**	**91.471**

PHE = potential harmful elements; PC = principal components

The corresponding scattered plots for the principal components loading for the measurements of the twelve PHEs in surface water are presented in Figure 4.1. The scattered plots confirmed the four main principal components for the measured PHEs, with the first and the second principal components demarcated in a circle.

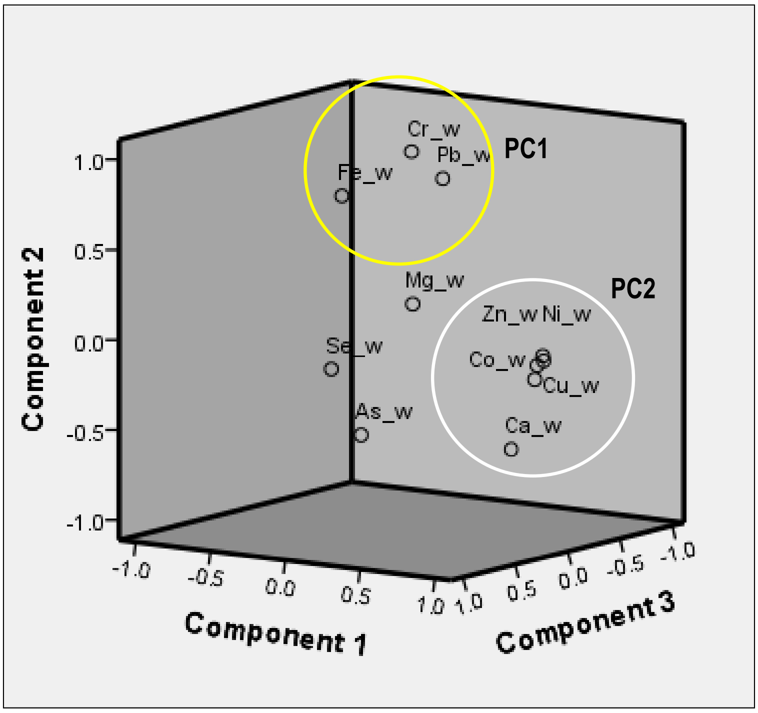

Figure 4.1 Principal component scartter plot in rotated space of the twelve potential harmful elements measured in surface water

4.3.4 Overall trend of the extent of contamination for the five zones

The overall trend of the extent of the contamination of surface water quality was assessed at the 15 sampling sites, within the five zones. The assessment took into account the arithmetic means of the different indicators of contamination of surface water that exceeded the surface water limits for particularly the summer seasons. The measurements that were recorded during the summer season were used to compute the overall trend in the level of contamination for the five zones. The findings did not reveal any obvious trend in the level of contamination of surface water by the contaminants from the gold mine tailings (Table 4.7). However, a higher level of contamination was detected for the control Zone 4 and Zone 5, which were positioned in the upstream wind direction in relation to the high-density mine tailing zone, when compared to the level of contamination for Zone 1, Zone 2, and Zone 3, which were positioned in the downstream wind direction in relation to the high-density zone (Table 4.7).

Table 4.7 Trend of concentration of potential harmful elements for the five zones

Zones/ Sampling sites		**Properties that exceeded the limits**									**Number of properties that exceeded the limits**
		pH	**Temp**	**Turbidity**	**Do**	**As**	**Co**	**Cu**	**Fe**	**Zn**	
Z1	SW1	-	-	x	-	x	x	-	-	-	xxx
	SW2	-	-	x	x	x	x	-	-	-	xxxx
	SW3	x	x	x	x	-	x	-	-	-	xxxxx
	SW4	-	-	x	-	x	x	-	-	-	xxxx
	SW5	x	-	x	-	-	x	x	-	x	xxxx
	SW6	-	-	x	x	x	x	-	-	-	xxxx
	SW7	-	x	x	-	x	x	-	-	-	xxx
Z2	SW8	-	-	x	x	-	x	x	-	-	xxxx
	SW9	-	-	x	-	x	x	x	x	-	xxxxx
	SW10	-	-	x	x	x	x	-	x	-	xxxx
Z3	SW11	-	-	x	x	-	-	x	-	-	xxx
	SW12	-	-	x	-	x	x	-	-	-	xxx
	SW13	-	-	x	x	x	x	-	-	-	xxxx
Z4	SW14	-	x	x	x	x	x	-	x	-	xxxxxx
Z5	SW15	-	x	x	x	x	x	-	-	-	xxxxx

Z = zones; SW = surface water samples

4.4 Results of groundwater quality

Measurements were recorded for temperature, pH, EC, turbidity, DO, faecal coliform, *E. coli*, as well as for 12 PHEs at the eight groundwater sampling sites during the winter season. Because the groundwater in the study area is used for domestic purposes, such as for drinking, the physical, and microbiological groundwater measurements, as well as the measurements for PHEs were therefore compared to drinking water quality standards, which were the World Head Organisation Drinking Water Standard, WHO (2018), as well as the South African National Standard on Drinking Water, SANS 241 (2015). Furthermore, a drinking Water Quality Index (WQI) was computed for each groundwater sample, using measurements of the groundwater quality properties to determine the overall quality of a water sample at each of the groundwater sampling site.

4.4.1 Physical and microbiological properties

Measurements were recorded for the five physical properties and the two microbiological properties of groundwater samples collected at the eight sampling sites during the winter season. Of the seven water quality properties, only pH and DO demonstrated 100% compliance when compared to the WHO (2018) and SANS 241 (2015) drinking water quality limits (Table 4.8). In contrast, the faecal coliform bacterial counts of the eight water samples were all non-compliant when compared to both the WHO (2018) and SANS 241 (2015) drinking water quality limits. On the other hand, the *E. coli* counts exceeded both the drinking water quality limits at half of the sampling sites, which is of great concern as the water is used for drinking purposes.

Table 4.8 Results of the physical and microbiological groundwater quality properties

Properties	**Physical**					**Microbiological**	
Limits	**pH**	**Temperature (°C)**	**EC (µs/cm)**	**Turbidity (NTU)**	**DO (mg/L)**	**Faecal coliform /100 ml**	***E. coli* /100 ml**
WHO limit[1]	**6.5 – 8.5**	**-**	**-**	**< 1**	**-**	**0**	**0**
SANS 241 limit[2]	**≥ 5 ≤ 9.7**	**-**	**≤ 1700**	**≤ 5**	**≤ 1200**	**0**	**0**
Sites							
GW1	6.8	19.4	1496	0.62	9.3	> 2420	6
GW2	6.8	17.2	372	2.3	1.5	> 2420	1
GW3	7.2	15.0	537	0.8	7.1	> 2420	0
GW4	7.7	15.2	1244	0.6	4.6	980	0
GW5	6.8	15.4	8940	0.8	8.1	> 2420	0
GW6	5.9	13.8	1738	0.3	7.7	1300	1
GW7	6.3	15.6	232	0.2	7.6	1203	1
GW8	6.7	17.2	952	0.2	6.6	1046	0
Minimum	5.95	13.8	232.00	0.27	1.59	980.00	0.00
Maximum	7.72	19.40	8940.00	2.33	9.38	2420.00	6.00
Mean	6.80	16.10	1938.88	0.76	6.62	1776.13	1.13
SD	0.53	1.75	2879.55	0.67	2.43	694.92	2.03
% compliance	100		75	88	100	0	50

[1]WHO = World Health Organisation; [2]SANS 241; South African National Standard on Drinking Water; GW = groundwater samples; numbers in red represent measurements that exceeded the limit of the test; > 2420 = measurement exceeds the limit of the test; SD = standard deviation

4.4.2 Potential harmful elements

Of the 12 PHEs studied, Cd, Co, Cr, Ni, Se and Zn were not detected in the water samples due to levels being below the instrument detection limit. Arsenic was only detected in the groundwater sample collected at site GW5. The level of arsenic in this groundwater sample exceeded the limits of both the WHO (2018) and SANS 241 (2015) drinking water quality limits (Table 4.9). The concentrations of all the measurements for Cu and Mg were within the specified limits. In contrast, the groundwater measurements of Fe were non-compliant to both the WHO and the SANS 241 drinking water limits for

63% of the groundwater samples. On the other hand, for Pd, all the groundwater samples, in which Pb was detected, exceeded the specified limits. Calcium was detectable in all the groundwater samples, of which 63% of the samples exceeded WHO drinking water quality limits.

Table 4.9 Results of the mean concentrations (standard deviation) of potential harmful elements for groundwater sampling sites for winter

PHE	As	Cu	Fe	Pb	Ca	Mg
WHO limit[1] (mg/L)	**≤ 0.01**	**≤ 2.00**	**< 1**	**≤ 0.01**	**150 - 300**	**150 - 300**
SANS 241 limit[2] (mg/L)	**≤ 0.01**	**≤ 2.00**	**≤ 2.00**	**≤ 0.01**	**-**	**-**
Site						
GW1	ND	0.03 (0.01)	3.07 (0.16)	ND	157.01 (1.85)	43.57 (0.30)
GW2	ND	0.03 (0.01)	ND	ND	305.23 (4.56)	127.14 (2.40)
GW3	ND	0.06 (0.02)	4.43 (0.04)	ND	66.65 (5.97)	16.80 (1.91)
GW4	ND	ND	2.33 (0.01)	0.45 (0.01)	152.53 (7.34)	22.16 (0.19)
GW5	0.02 (0.001)	0.22 (0.01)	2.87 (0.15)	ND	87.99 (1.57)	16.12 (0.32)
GW6	ND	ND	0.87 (0.10)	2.04 (0.06)	186.44 (3.89)	38.83 (0.13)
GW7	ND	ND	0.25 (0.02)	0.07 (0.01)	268.26 (1.83)	51.17 (0.22)
GW8	ND	ND	11.29 (0.28)	0.71 (0.02)	92.03 (3.71)	15.73 (0.49)

[1]WHO = World Health Organisation; [2]SANS 241; South African National Standard on Drinking Water; GW = groundwater samples; numbers in red = numbers that exceeded the limits

4.4.3 Water quality Index

The WQI values for drinking water was computed for the groundwater samples collected at the eight sampling sites to evaluate the overall drinking water quality of the water at each of the sampling site. The WQI values indicated that the drinking water quality of the groundwater was classified as good at only three of the sampling sites (Table 4.10). The drinking water quality of the groundwater at the remainder of the sampling sites was poor or very poor. When the different zones were considered, no explicit pattern could be established. However, the groundwater of one of the sampling sites in Zone 1 had the worst quality water (GW2). This site is located approximately 5 km from the high density mine tailing area. In contrast, the groundwater collected at sampling site GW8, which lies the furthest from the mine tailing area at about 7 km to 10 km, had the best quality water of all the groundwater samples.

Table 4.10 Results for the water quality indexes and water quality conditions for the water samples from the different sampling sites

Sites	Zones	Water source	WQI	Condition
GW1	Z1	Borehole	107.40	Poor water
GW2	Z1	Borehole	223.92	Very poor water
GW3	Z2	Borehole	62.24	Good water
GW4	Z2	Borehole	91.85	Good water
GW5	Z2	Borehole	196.33	Poor water
GW6	Z3	Borehole	106.88	Poor water
GW7	Z3	Borehole	113.90	Poor water
GW8	Z3	Borehole	56.70	Good water

WQI = water quality index; GW = groundwater samples; Z = zones

4.4.4 Overall trend of the extent of contamination for the three zones

The overall trend of the contamination of the different indicators of groundwater quality was assessed for the groundwater samples at the eight sampling sites, within the three zones. This assessment considered the quality of the various indicators of pollution that exceeded the limits in this study. Overall, there was no obvious trend that could be discerned for the level of contamination for the eight sampling sites, as well as for the three zones (Table 4.11).

Table 4.11 Overall trend of contamination of groundwater samples for the eight sampling sites, within the three zones

Zones/ Sampling sites		Property exceeding the limits									Number of exceeding properties
		EC	Turbidity	Faecal coliforms	*E. coli*	As	Fe	Pb	Ca	WQI	
Z1	GW1	-	-	x	x	-	x	-	x	x	5
	GW2	-	x	x	x	-	-	-	x	x	5
Z2	GW3	-	-	x	-	-	x	-	x	-	3
	GW4	-	-	x	-	-	x	x	x	-	4
	GW5	x	-	x	-	x	x	-	-	x	5
Z3	GW6	x	-	x	x	-	-	x	x	x	6
	GW7	-	-	x	x	-	-	x	x	x	5
	GW8	-	-	x	-	-	x	x	-	-	3

Z = zones; GW = groundwater sampling sites; WQI = water quality index; X = values which exceeded the limit

4.5 Discussion

Several water quality indicators were measured to ascertain the extent of contamination of surface water bodies and groundwater by contaminants from the gold mine tailings in the study area of the MLM area. The results revealed that several contaminants found in the surface water and groundwater samples could potentially have originated from the gold mine tailings. When considering the overall quality of the surface water samples from the different sampling sites for the different zones, it was observed that the level of contamination did not reflect any noticeable trend for the five zones, most probable because of the dilution effect in surface water (Loáiciga et al., 2015; Turunen et al., 2020) . Additionally, the reason for the absence of a noticeable trend in the level of contamination of surface water such as streams and rivers could be that surface water flows, and the contaminants in surface water are transported beyond the contamination source, which is the high density mine tailing zone in the MLM area. However, there was a higher level of contamination of the surface water bodies for the control Zone 4 and Zone 5. The high contamination in Zone 4 originated from the high density mine tailing zone, as polluted water is pumped from Sand River, which flows through the high density mine tailing zone and into the Reitspruit dam in Zone 4. The contamination of the surface water in Zone 5, may originate from the single mine in the vicinity, including the Target Gold Mine Shaft, as well as the waste rocks dump that is located in the vicinity of the sampling site GW15. In contrast, when the quality of the groundwater samples for the different zones were considered, the expectation that water samples from sampling sites beyond the mine tailings would present with lower levels of contamination, was not met. The most probable reason why there was no obvious trend in the level of contamination of the groundwater samples within the three zones could be attributed to the effect of filtering, which reduces the contaminants as the water seeps through the soil layers and into the groundwater (Keesstra et al., 2012).

For the measurements of the physical properties, most of the surface water samples showed high levels of turbidity, which is often an expectation for surface water. Turbid water is mostly as a result of suspended particles, which include clay, silt, sand, leaves and twigs that end up in the surface water bodies, mostly through run-off and wind (Suthar et al., 2010; Rakotondrabe et al., 2017; Bhardwaj et al., 2018). The presence of high levels of suspended particles in surface water tends to block the passage of light, which in turn reduces the rate of photosynthesis in photosynthetic organisms living in the water (Bhardwaj et al., 2018). This reduction in photosynthesis ultimately reduces the amount of oxygen produced by these photosynthetic organisms (Bhardwaj et al., 2018). The low levels of dissolved oxygen in the surface water samples measured in this study could thus largely be attributed to the high levels of suspended particles in the water. Low levels of dissolved oxygen further cause a reduction in the growth of macrophytes and other aquatic plants and aquatic animals living in the water. When the levels of dissolved oxygen become too low to sustain aquatic life, organisms may die, which could lead to decomposition bacteria using up all available dissolved oxygen (Belle et al., 2020).

The assessment of the presence of PHEs in the surface water samples revealed that high concentrations, above the surface water limits were observed for the PHEs As, Co, Fe, Cu, and Zn, which are typical contaminants that are associated with gold ores and gold mine tailings and therefore, these PHEs may likely have originated from gold mine tailings (Liang et al., 2017; Chen et al., 2018; He et al., 2018). These results are similar to the results obtained in a study, in which a high concentration of As, Pb, Cd, Mn, Cr and Fe, above the limits were measured in surface water as a result of mining activities within the vicinity of the abandon mining areas (Ngure et al., 2014; Rakotondrabe et al., 2017; Bouzekri et al., 2020). The high concentrations of As, as well as Co detected in the surface water during the summer season may cause severe toxicity to aquatic organisms, as a result of the accumulation of these PHEs in cells of the organism, such as the liver cells and kidneys cells (Kumari et al., 2017; Shah, 2017). The uptake of As in cells of fish and other aquatic organisms may result in some form of chronic and acute toxicity, including inhibition of growth and reproduction, immune system dysfunction and ultimately death (Kumari et al., 2016). Chronic exposure of fish and aquatic organisms to Co, may cause different levels of enzyme activity changes in gill, liver, and muscle tissues, as well as haem oxidation and blockage of inorganic calcium channels, cytotoxicity and genotoxicity (Karthikeyan et al., 2019; Kosiorek and Wyszkowski, 2019 ; Sun et al., 2020). On the other hand, Fe, Cu and Zn are essential nutrients for growth of fish and other aquatic organisms. However, high concentrations of Fe in the water may indirectly affect fish in water, by creating a conducive environment for the proliferation of iron bacteria on the fish gills surfaces, which oxidises the soluble forms of iron (ferrous iron) to the insoluble iron (ferric oxide). The presence of insoluble iron on gills surfaces cause damage to gills, which in turn results in increased ammonia in blood plasma, as well as damage of kidney, liver, and spleen tissues (Slaninova et al., 2014). But high concentrations of Cu absorbed in fish cells may cause the reduction of growth and reproduction, as well as affect brain function and metabolism (U.S EPA, 2017). Additionally, chronic exposure of Zn ions to freshwater fish and aquatic organisms may be lethal for such organisms (Hogstrand & Wood, 2010; Shah, 2017).

The concentrations of the PHEs measured in the surface water samples collected during the summer season varied considerably when compared to the concentrations of PHEs measured in water samples collected during the cold winter season. The significant ($p \leq 0.05$) higher concentrations recorded for the measurements of As, Co, Se, Ca and Mg during the summer season could thus be as a result of the increased solubility, mobility and availability of these PHEs because of the higher summer temperature (Li et al., 2013).

The WQI, which describes the overall water quality as a single value, classified the groundwater quality as poor for majority of the sampling sites (Rakotondrabe et al., 2017). This is of major concern as the groundwater abstracted from the eight boreholes is used for domestic purposes, which includes drinking water. The poor water quality due to the high faecal coliform bacterial count, as well as the high *E. coli* count could impact on the health of the people since the groundwater is the only available domestic water source. The high faecal coliform bacterial count may cause diarrhoea, particularly in children, whilst abnormal levels of *E. coli* in the water may cause gastrointestinal diseases, such as, cholera, typhoid fever and dysentery (Fakhr et al., 2016; Mahmud et al., 2019).

Groundwater samples also presented with relatively high concentrations of PHEs. In particular, the concentrations of Fe and Pb in most of the water samples exceeded the prescribed limits, indicating the potential for metal toxicities due to these metals. These metals are typical contaminants associated with gold ores from mining activities and gold mine tailings, which could be the sources of contamination (Tutu et al., 2008; Jaishankar et al., 2014). When borehole water containing high levels of Fe, is used as drinking water, it could result in the production of hydrogen free radicals, which attack DNA, resulting in cellular damage, mutation and malignant transformations, which in turn, could cause a series of diseases (Jaishankar et al., 2014). Lead, on the other hand, is known to cause brain, liver, and kidney damage in children, as well as nerve damage in adults (Khan, 2011; Jaishankar et al., 2014; AbuShady et al., 2017). Moreover, an increased intake of Pb can result in miscarriages in pregnant women, as well as damage of testis in males (Griswold & Martin, 2009; Muhammad et al., 2011).

Chapter 5

Soil Quality

5.1 Introduction

Soil contamination by contaminants from the gold mine tailings in the Matjhabeng local municipality area (MLM) is a serious concern to both the environment and human health. Since some of these contaminants from the gold mine tailings are toxic and non-biodegradable, contamination of particularly agricultural soil may have detrimental effects on food production and human health (Tchounwou et al., 2012; Naveedullah et al., 2013). The extent to which the soils in the Matjhabeng Local Municipality (MLM) area have been contaminated was determined by analysing several soil quality indictors in both the uncultivated and the cultivated soils samples that were collected from the area. The uncultivated soil samples were collected from the 15 sampling sites in the same vicinity of the uncultivated lands, from where surface water samples had been collected, during summer and the winter season. Additionally, the 15 sampling sites from where the uncultivated soil samples were collected were within the five zones identified in the uncultivated lands in the study area. On the other hand, the cultivated soil samples were collected from the twelve sampling sites that were in the vicinity of the cultivated maize farms from where the groundwater samples had been collected. Additionally, the 12 sampling sites from where the cultivated soil samples were collected were within the four zones that were identified within the cultivated lands in the MLM area. Considering that the cultivated soil samples were to be collected at the same time with the groundwater and maize seeds samples, the cultivated soils could only be collected during the cold winter season, since maize seeds mature only during the winter season in the MLM area.

The soil quality of the uncultivated and the cultivated soil samples were assessed by measuring soil quality indicators, similar to surface water. Two physical soil quality properties were measured, which include soil pH and electrical conductivity, as well as the twelve PHEs, arsenic (As), cadmium (Cd), lead (Pb), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), selenium (Se), zinc (Zn), calcium (Ca) and magnesium (Mg). To determine the extent of contamination of soil by contaminants from goldmine tailings in the MLM area, the following research question was answered:

Sub Question: To what extent is the soil in the MLM area contaminated by contaminants from the gold mine tailings? To address this research question, the following objective was measured:

Objective 4: To determine the quality of uncultivated and the cultivated soil, measured in terms of the physical soil properties, as well as PHE contamination.

5.2 Materials and methods

5.2.1 Collection of soil samples

Soil samples were collected from the different sampling sites that were identified in the MLM area, following the modified sampling procedure by Chen et al. (2018). The uncultivated soil samples were collected at about five meters from the banks of the surface water from where the surface water samples had been collected within the uncultivated land in the MLM area for the two seasons. On the other hand, the cultivated soil samples were collected in a maize farm that was also close to the boreholes from where the groundwater samples were collected in winter. The uncultivated soil sampling sites were represented with the letters S, such that sampling site number one was denoted as S1 and the sampling site fifteen was denoted as S15. The cultivated soil sampling sites were represented with the letters, CS, which stands for cultivated soil. Therefore, similarly to the labelling of the uncultivated soil sampling sites, the cultivated sampling site number one was denoted as CS1.

The soils samples were collected for the measurement of both the physical soil quality properties and the PHEs. At a sampling site, the soil samples were collected in the following manner:

- A sharp wooden object was used to dig into the soil and 500 g of the soil samples were collected 15 cm beneath the soil.
- The soil samples were placed in a labelled self-sealing polyethylene bag to avoid soil moisture evaporation and oxidation with air, before transportation to the Water Laboratory at the Central University of Technology (CUT), awaiting the preparation of the soil samples.

5.2.2 Preparation of soil samples

The soil samples were prepared to convert the soil samples into fine powder before the soil samples could be used for analysis. The powdered soil samples were then used for the measurement of soil pH and the electrical conductivity (EC), as well as for the measurements of the PHEs in the soil samples.

The preparation of the soil samples, which involved, drying, grounding, and sieving of the soil samples were performed in following manner:

1. The soil samples were dried in an oven at 60 ^{O}C for 48 hours to remove moisture from the samples and for the soil samples to acquire a constant weight (Wong & Li, 2003).
2. The dried soil samples were ground in a porcelain mortar using a pestle, and then sieved through a 2 mm silicon handler stainless steel sieve and packaged into separate zip sealed plastic bags, which had been labelled with the site numbers.
3. The prepared soil samples were stored in an airtight container before transportation to the School of Chemistry and Physics, University of Kwa-Zulu Natal, Westville campus, for digestion and chemical analysis of the samples using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OEP).

5.2.3 Measurement of potential harmful elements

Before the measurement of PHEs in the soil samples, some of the powdered soil samples were digested in concentrated acids. However, the PHEs that existed in the soils samples in exchangeable form were extracted directly from the powdered soil samples using an extractant solution. The process of digestion of the soil samples releases the PHEs from the solid soil matrix directly into the concentrated acids, for easy measurement using the ICP-OES (Koki, 2015). These PHEs that were measured after they have been released into concentrated acids following the digestion of the soil samples are described as total PHEs. On the other hand, the other category of PHEs, which were extracted directly from the powdered soil samples using an extractant solution are described as the exchangeable PHEs.

Digestion of soil samples

The soil samples were digested in concentrated acids before analysing the samples for total PHEs to convert the solid soil samples into a solution. The digestion process that was followed was modified from the procedure of Kisten et al. (2015), in the following manner:

1. From each of the prepared soil samples, 0.25 g was weighed and placed into a 100 ml beaker, containing 10 ml of 70% HNO_3.
2. The mixture was allowed to pre-digest for 30 minutes, and then it was covered with a watch glass and digested on a hot plate in a fume cupboard until no traces of solid particles could be visible and the mixture became clear.
3. Once the digestion mixture became clear, a similar procedure like that of the digestion of water samples was followed. For quality control purposes, three digests were also performed for each soil sample. To validate the digestion method, PHE standards were also prepared for each of the PHEs that were measured in this study, similar to the digestion of water samples.

Extraction of exchangeable potential harmful elements in soil samples

The available PHEs that were present in the soil samples were measured to determine which of the PHEs in the soil samples existed in exchangeable form and can be absorbed by plants. The exchangeable PHEs were extracted using an extractant solution, which was prepared according to the modified procedure described by Moodley et al. (2012) as follows:

1. 38.542 g of the soil samples were measured, as well as 0.5 M Ammonium Acetate crystals and 37.225 g of 0.1 M Ethylenediaaminetetraacetic acid (EDTA D1 – sodium salt)
2. The substances were transferred into a one litre volumetric flask and were dissolved in distilled water.
3. 25 ml, of 96% Acetic acid solution was also added into the one litre volumetric flask and the mixture was diluted to the mark with double distilled water.

The prepared extractant solution was then used to extract the available exchangeable PHEs in the soil samples in the following manner:

1. 25 ml of the extractant solution was added to a 2.5 g of a soil sample in a 100 ml beaker, and then mixed.
2. The mixture was later covered with paraflim and transferred onto a shaker machine to shake for four hours.
3. The extractant solution was filtered to remove any particulate matter from the mixture using a 70 mm pore size filter paper. Then after, the filtrate was stored in labelled 50 ml plastic bottles in a refrigerator awaiting the ICP-OES analysis.

Once the digestion and the extraction of PHEs were completed, the ICP-OES measurements of both the total PHEs, as well as the exchangeable PHEs in the soil samples were measured using the ICP-OES. These PHEs, which include As, Cd, Pb, Co, Cr, Cu, Fe, Ni, Pb, Se, Zn, Ca and Mg, in the soil samples were measured following similar procedure as for the measurement of the PHEs in water samples.

5.2.4 Measurement of soil pH and electrical conductivity

The soil pH determines the level of acidity and alkalinity of the soil, which ultimately influences the EC of the soil. Soil pH and EC were measured for both the uncultivated and cultivated soil samples. The measurements were also performed in the School of Chemistry and Physics, University of Kwa-Zulu Natal, Westville campus. The soil pH, as well as the electrical conductivity of the soils samples were measured by preparing a mixture of soil and distilled water in a ratio of 1: 2.5 soil water mixtures in the following manner.

1. 10 g of each soil sample was measured into a 120 ml screw glass bottles. Thereafter, 25 ml of distilled water was added into each bottle.
2. The soil pH was then measured using a Mettler Delta 3510 pH meter while soil conductivity was measured using Accumet Conductivity Meter (Mahlangeni et al, 2016).

5.2.5 Statistical analysis of soil quality measurements

The Statistical Package for Social Sciences (SPSS) Version 23 was used to analyse the PHEs in soil, similar to the water quality measurements. Principal Component Analysis (PCA) was applied to compare the studied PHEs concentrations so as to determine environmental sources (Wu et al., 2014). The measurements of the PHEs in the uncultivated soil samples was further analysed using the Kriging geostatistical procedure to estimate the spatial distribution of the PHEs in soil, as well as the areas, which are prone to risk (Benndorf & Menz, 2014; Wu et al., 2014). Kriging geostatistical procedure is a GIS software that is used to analyse the PHEs to generate a spatial interpolation of the PHEs in the soil, according to Singh & Kumar. (2017). The spatial distribution maps provide a visual representation of the spatial distribution of PHEs in soil within the MLM area, including hotspot areas, which might present high risk to the environment and human health.

5.2.6 Determination of quality assurance and quality control

Quality assurance procedures were applied to ensure that the soil quality measurements results obtained were reliable as the case with surface and groundwater measurements. During the collection of the soil samples, only wooden objects were used to dig below the soil from where the soil samples were collected. Moreover, when the soil samples were prepared in the laboratory, and during digestion and the analysis of the samples, the laboratory utensils that were used were properly cleaned regularly with doubled distilled water. Additionally, all the samples were analysed in triplicates (n = 3) and the reagents that were used were of analytical grade. Furthermore, a standard reference material (CRM), White Clover (BCR 402), that was obtained from the Community Bureau of Reference of the Commission of the European Communities was used to validate the analytical procedure.

5.3 Results of soil quality of uncultivated soil

The measurements of the two physical soil quality properties, as well as the 12 PHEs were recorded for the 15 sampling sites during summer and winter seasons. The measurements for the PHEs were recorded for both the total PHEs present in the soil samples, as well as for the PHEs that are present in exchangeable form in the soil samples. For compliance purposes, the measurements of the total PHEs were compared to the two sets of guidelines for the protection of soil quality, as well as the background concentrations of PHEs in soils in South Africa. One of the guidelines for the protection of soil quality is a set of soil quality limits prescribed by different international bodies, such as the World Health Organisation (WHO), Food and Agricultural Organisation (FAO), as well as different European countries, which was compiled by Chiroma et al. (2014). The measurements of the total PHEs in the uncultivated soil samples were also compared to the limits for the protection of contaminated lands, prepared by the South African Department of Environmental Affairs (2010). These limits for the protection of contaminated lands were put together to provide the set of criteria that can be used to identify and register contaminated lands sites in South Africa, as well as to assess the status and risk posed by contaminated lands on humans (DEA, 2010). On the other hand, the measurements of the total PHEs were also compared to the background concentrations of PHEs in South Africa. The background concentrations were established to provide information about the natural concentration of PHEs in soils, which may be expected before the contamination of soils by anthropogenic activities (Herselman, 2007). Once the natural concentrations of PHEs in soils have been established, it becomes possible to determine the extent of anthropogenic contaminations (Batwa-ismail, 2018). The background concentrations of the PHEs in South African soils were obtained from a study conducted by Herselman (2007) on the concentration of selected trace metals of soils in South Africa.

5.3.1 Physical properties

Measurements were recorded for the two physical soil quality properties for summer and winter. Soil pH measurements ranged between strongly acidic to slightly alkaline pH conditions. The concentrations of the EC measurements were relatively similar across the 15 sampling sites for the two seasons. For compliance purposes, the soil pH measurements, as well as the EC measurements of the soil samples were compared to the Canadian soil quality guidelines for the protection of the environment and human health, for residential and parklands (Table 5.1). For the soil pH results, three, out of the 15 soil samples exceeded the pH limits for the summer season, while a single soil sample exceeded the limit in winter. On the other hand, exceptionally high EC measurements were recorded for the 15 soil samples for both the summer and the winter season, which indicates a high level of non-compliance to the soil quality limits. The was only one exception at sampling site S15 during the winter, where the EC measurement reflected compliance to the soil quality limit.

Table 5.1 Physical properties of uncultivated soil for summer and winter

Sampling sites	**pH**		**EC (µS cm)**	
Seasons	**Summer**	**Winter**	**Summer**	**Winter**
CCME limit	**4 - 8**		**20**	
S1	4.06 (0.01)	6.42 (0.02)	29.83 (0.21)	61.70 (0.26)
S2	5.73 (0.01)	7.01 (0.01)	47.27 (0.12)	41.20 (0.20)
S3	7.23 (0.01)	4.52 (0.02)	61.20 (0.20)	73.67 (0.25)
S4	6.82 (0.01)	6.76 (0.02)	59.73 (0.12)	55.37 (0.21)
S5	7.14 (0.02)	5.93 (0.01)	56.07 (0.15)	39.67 (0.25)
S6	4.38 (0.02)	5.97 (0.03)	37.73 (0.15)	41.73 (0.21)
S7	5.20 (0.01)	6.72 (0.02)	54.73 (0.21)	47.73 (0.12)
S8	5.64 (0.01)	5.64 (0.01)	52.80 (0.30)	81.73 (0.47)

S9	3.77 (0.01)	6.05 (0.01)	75.73 (0.15)	67.63 (0.38)
S10	5.70 (0.01)	7.27 (0.02)	58.70 (0.20)	49.50 (0.40)
S11	4.95 (0.03)	4.02 (0.02)	44.70 (0.20)	69.57 (0.21)
S12	3.02 (0.02)	7.08 (0.04)	34.07 (0.12)	51.50 (0.40)
S13	6.30 (0.02)	4.68 (0.03)	37.10 (0.10)	77.57 (0.40)
S14	3.17 (0.01)	5.12 (0.02)	54.87 (0.35)	59.47 (0.32)
S15	5.43 (0.02)	3.93 (0.03)	35.37 (0.21)	1.60 (0.36)

CCME = Canadian Council of Ministers of the Environment water quality limits; S = uncultivated soil samples

5.3.2 Potential harmful elements

The measurements were recorded for the total PHEs in the soil samples, as well as the PHEs that existed in exchangeable form in the soil samples, for summer and winter. Of the 12 PHEs that were analysed in the soil samples, all the total PHEs were detected in the soil samples during the hot summer season and all these PHEs were also found to exist in exchangeable form in the soil samples. For the winter season, seven of the PHEs were detected in the soil samples, including As, Cu, Fe, Cr, Zn, Ca, and Mg. Of the seven PHEs, only As, Cu, Fe, Ca, and Mg were found to exist in exchangeable form in the soil samples. The PHEs that were detected in the uncultivated soil samples in exchangeable form for both the summer and winter season are presented in Table S1 in Appendix A; supplementary data section of this document.

To determine the level of compliance, the measurements of the total PHEs were compared to the national and international limits for protection soils. With the exception of a single soil sample for Ni, high level of compliance was observed for As, Co, and Ni to both the DEA (2010) and the limits prescribed by different international bodies (Chiroma et al., 2014), for both seasons (Table 5.2). For Cd and Pb, compliance was also high, with only a single soil sample that exceeded the DEA (2010) limits during the summer season. On the other hand, when the measurements for Cd and Pb were compared to the limits prescribed by different international bodies for the protection of soils (Chiroma et al., 2014), non-compliance was detected for Cd only at two sites (S7 and S14) during the summer season, while the measurements for Pb displayed 100% compliance to the limit for both seasons. Some level of non-compliance was observed for Cr and Zn, with 40% of soil samples for Cr and 27% of the soil samples for Zn exceeding the DEA (2010), while three of the soil samples for Zn was higher than the limits prescribed by the different international bodies (Chiroma et al., 2014). In contrast, all the measurements for Cr and Zn displayed compliance to the limits prescribed by different international bodies (Chiroma et al., 2014) for both the summer and the winter season. On the other hand, exceptionally high level of non-compliance was registered for measurements of Cu and Fe when compared to the two sets of limits. All the measurements for Cu showed non-compliance to the DEA, 2010 limits for both the summer and the winter seasons but two of the measurements exceeded the limits prescribed by the different international bodies (Chiroma et al., 2014) for the summer season. Additionally, all the measurements for Fe, revealed 100% non-compliance when compared to the two soil quality limits. However, although the concentrations of Se, Ca and Mg detected were extremely high, similar to the measurements that were detected in surface water samples, no soil quality limits for the measured PHEs in soils could be sourced, since these PHEs may have negligible effects on the environment.

When the measurements of the PHEs were compared to the background concentrations of PHEs in South African soil (Herselman, 2007) non-compliance was exceptionally high for Cd and Cu, with all soil samples exceeding the background concentrations for both seasons. For Zn, 87% of the measurements were non-compliant for the summer season. But a single site for Pb and two sites for Ni exceeded the background values for soils in South Africa, but for Ni, 40% of the soil samples were non-compliant to the background concentrations of PHEs in South African soil (Herselman, 2007).

Table 5.2 Results of the mean concentrations (standard deviation) of potential harmful elements for uncultivated soil samples for the 15 sampling sites for summer and winter

PHEs		**As**	**Cd**	**Pb**	**Co**	**Cr**	**Cu**	**Fe**	**Ni**	**Se**	**Zn**	**Ca**	**Mg**
DEA of SA limit[1]		**5.8**	**7.5**	**20**	**300**	**6.5**	**16**	**-**	**91**	**-**	**240**	**-**	**-**
Limit[2]		**20**	**3**	**100**	**50**	**100**	**100**	**425.5**	**50**	**-**	**300**	**-**	**-**
SA Baseline Values[3]			**0.1**	**21.7**	**18**	**71.9**	**29.5**		**38.7**		**45.2**		
Sites	**Seasons**												
S1	S	1.6 (0.89)	1.4 (0.98)	6.5 (1.20)	30.6 (9.99)	17.0 (2.74)	45.4 (3.46)	7774 (10)	31.6 (4.65)	6.0 (1.25)	181 (13)	26620 (20)	2973 (15)
	W	ND	ND	ND	ND	5.3 (0.14)	97.6 (4.63)	11682 (13)	ND	ND	ND	6114 (7)	1343 (5)
S2	S	ND	0.6 (0.02)	14.9 (2.36)	9.9 (1.02)	ND	37.8 (8.52)	2327 (11)	5.2 (2.14)	1.1 (0.21)	271 (11)	11770 (28)	1632 (8)
	W	ND	ND	ND	ND	ND	42.5 (0.29)	1507 (8)	ND	ND	ND	678 (3)	161 (0.7)
S3	S	ND	0.4 (0.02)	1.7 (0.87)	2.6 (0.08)	ND	25.4 (4.56)	3973 (6)	ND	ND	66 (9)	13050 (21)	1314 (10)
	W	2.8 (0.05)	ND	ND	ND	12.7 (0.98)	69.9 (0.45)	19987 (10)	ND	ND	ND	9532 (11)	3929 (4)
S4	S	ND	1.0 (0.03)	5.0 (2.05)	7.5 (0.19)	2.2 (0.09)	37.3 (6.87)	5438 (6)	5.3 (2.45)	ND	42 (14)	80540 (31)	5333 (11)
	W	ND	ND	ND	ND	ND	52.6 (0.64)	13269 (6)	ND	ND	ND	4124 (4)	3388 (3)
S5	S	0.8 (0.26)	0.5 (0.05)	4.0 (1.36)	17.9 (3.54)	2.3 (0.23)	191.1 (11.20)	3013 (4)	39.8 (3.65)	3.3 (1.04)	178 (16)	20320 (30)	2616 (9)
	W	ND	ND	ND	ND	ND	83.9 (0.67)	11513 (13)	ND	ND	8 (0.5)	3155 (7)	1634 (2)
S6	S	3.1 (0.89)	1.3 (0.87)	5.4 (1.57)	44.5 (6.58)	0.8 (2.58)	97.4 (9.24)	4056 (11)	59.0 (6.65)	3.6 (1.54)	367 (15)	20800 (21)	1637 (13)
	W	ND	ND	ND	ND	ND	49.9 (0.16)	10737 (9)	ND	ND	ND	7264 (3)	1975 (0.8)
S7	S	4.0 (1.12)	7.6 (1.03)	32.4 (6.52)	16.3 (1.55)	23.8 (2.58)	184.0 (10.23)	16390 (14)	28.4 (4.52)	5.4 (1.87)	907 (10)	40180 (31)	1990 (11)
	W	ND	ND	ND	ND	ND	56.9 (0.21)	12998 (11)	ND	ND	ND	6262 (7)	2004 (6)

S8	S	2.2 (0.23)	0.3 (0.05)	6.2 (1.06)	25.3 (5.87)	ND	36.2 (2.58)	2636 (9)	29.5 (4.25)	1.4 (0.98)	47 (13)	9165 (25)	1226 (18)
	W	ND	ND	ND	ND	ND	53.4 (1.56)	11447 (16)	ND	ND	20 (1.5)	4294 (6)	1634 (0.5)
S9	S	1.1 (0.63)	2.1 (0.41)	7.5 (1.45)	26.1 (6.74)	16.3 (3.58)	45.8 (3.45)	9265 (16)	17.2 (3.58)	4.6 (1.54)	55 (9)	7646 (16)	1267 (16)
	W	3.6 (0.12)	ND	ND	ND	4.5 (0.14)	47.7 (0.45)	9832 (3)	ND	ND	ND	3437 (2)	972 (2.5)
S10	S	0.6 (0.04)	1.4 (0.54)	5.1 (1.08)	20.4 (5.65)	14.5 (2.98)	39.1 (6.21)	7803 (10)	19.0 (4.20)	1.9 (0.87)	74 (7)	18140 (14)	2099 (13)
	W	3.5 (0.23)	ND	ND	ND	ND	45.9 (0.20)	6619 (4)	ND	ND	ND	3031 (1)	1425 (2.7)
S11	S	0.5 (0.02)	0.2 (0.07)	2.5 (0.86)	9.6 (1.65)	ND	26.4 (5.64)	2104 (12)	4.6 (1.56)	0.9 (0.05)	46 (11)	5572 (6)	792 (7)
	W	ND	ND	ND	ND	ND	42.5 (0.57)	4698 (3)	ND	ND	ND	1247 (2)	777 (3)
S12	S	ND	0.2 (0.01)	3.6 (0.85)	8.4 (2.54)	ND	23.3 (8.88)	1912 (6)	ND	2.8 (0.98)	33 (11)	4418 (9)	799 (16)
	W	ND	ND	ND	ND	ND	40.9 (0.15)	4715 (7)	ND	ND	ND	450.8 (2)	233 (2)
S13	S	0.3 (0.05)	1.8 (0.07)	7.6 (1.88)	26.5 (8.20)	9.4 (1.58)	47.6 (9.41)	9512 (12)	21.4 (2.45)	1.4 (0.85)	58 (6)	23340 (16)	3389 (6)
	W	ND	ND	ND	ND	12.1 (0.42)	56.5 (0.39)	17199 (10)	ND	ND	ND	4814 (3)	3202 (6)
S14	S	0.2 (0.06)	4.2 (1.12)	15.8 (2.47)	11.8 (1.78)	31.0 (8.63)	89.8 (8.25)	15430 (15)	23.3 (3.65)	5.8 (1.54)	401 (16)	50790 (34)	4867 (5)
	W	2.2 (0.02)	ND	ND	ND	13.1 (0.14)	54.8 (0.59)	16544 (14)	ND	ND	21 (1)	46430 (13)	2987 (4)
S15	S	0.3 (0.10)	0.5 (0.02)	2.7 (1.08)	10.3 (1.49)	4.0 (1.08)	37.3 (6.98)	4047 (6)	9.1 (0.28)	1.2 (0.25)	135 (15)	4185 (10)	722 (7)
	W	0.81 (0.01)	ND	ND	ND	ND	50.9 (0.97)	5603 (13)	ND	ND	ND	523 (3)	422 (0.28)

[1]DEA of SA = limits for the protection of water resources within contaminated lands, stipulated by South African Department of Environmental Affairs of South Africa; [2] PHEs Limit = Chiroma et al. (2014); [3] SA Baseline Values = background concentrations of PHEs in South African soils; ND = bellow instrument detection limit; S = summer; W = winter; red colour = represents measurements that exceeded limits

Student’s t-tests were performed at 95% confidence interval on the concentrations of the measured PHEs in the uncultivated soil for summer and winter. The results indicated that highly significant differences ($p \leq 0.05$) existed for all the PHEs measured in the soils samples with Ca being the only exception (Table 5.3).

Table 5.3 Paired sample test of seasonal variation for potential harmful elements in uncultivated soil

PHEs	Means		Mean Difference	95% Confidence Interval of the Difference		t	*p*-Value
	Summer	Winter		Lower	Upper		
As	0.13	0.87	- 0.73	-1.31	- 0.161	- 2.58	0.013***
Cd	0.58	- 0.24	0.83	0.43	1.23	4.25	0.000***
Pb	58.86	- 0.25	59.11	19.57	98.66	3.01	0.004***
Co	6.69	- 0.10	6.79	3.73	9.85	4.47	0.000***
Cr	2.21	-3.89	6.11	2.60	9.62	3.51	0.001***
Cu	24.09	56.40	-32.30	- 45.082	-19.53	- 5.09	0.000***
Fe	2388.97	10496.74	- 8107.76	- 9822.93	- 6392.60	- 9.52	0.000***
Ni	7.18	- 0.10	7.28	3.404	11.17	3.78	0.000***
Se	0.80	- 0.321	1.12	0.53	1.72	3.83	0.000***
Zn	71.67	3.31	68.35	21.18	115.52	2.92	0.005**
Ca	8413.40	6967.02	1446.37	-3671.91	6564.66	0.57	0.572
Mg	816.39	1734.69	- 918.30	-1362.44	- 474.17	- 4.16	0.000***

PHEs = potential harmful elements; t = test statistics; *p* = Probability; ***, **, * indicates significance at 1%, 5% and 10% level, respectively

5.3.3 Spatial distribution of potential harmful elements in uncultivated soil

The spatial distribution of the PHEs provided a visual representation of the extent of contamination of the PHEs in uncultivated soil within the different sampling sites in the MLM area. The spatial distribution maps were prepared for the most important pollutants, which were Cd, Cr, Pb, As, Cu, and Zn and are known to cause pollution to the environment (Xu et al., 2013 ; Wu et al., 2014; Rakotondrabe et al., 2018). Since there were few measurements that were detected with the ICP-OES in the winter season, only the measurements that were recorded during the summer season were used to prepare the spatial distribution maps. Furthermore, it was important to prepare the spatial distribution maps for Fe and Se, which were abundant in the study area.

The contamination levels of the PHEs were unevenly distributed throughout the different sampling sites within the five zones in the study area. The spatial distribution maps showed highest levels of contamination for Cd, Cr, Pb, Fe and Se at sampling sites S1 and S7, which were centrally located within the high-density tailings area in Zone 1 (Figure 5.1). The remainder of the sampling sites that were peripherally located within the high density mine tailing zone, particularly sites S2, S3 and S4, did not reflect exceptionally high level of contamination for Cd, Cr, Pb, Fe and Se, compared to sampling sites S1 and S7. For the spatial distribution of the measurements of Cu, Zn and As, a slight variation existed in the spatial distribution. For the most, sampling sites S1, S6 and S7, within the high density mine tailing Zone 1, revealed highest level of contamination, but for the remainder of sampling sites (S2, S3, S4 and S5), the level of contamination was not very high. The levels of contamination for the PHEs were found to be decreasing in the downstream wind direction beyond the high density mine tailing Zone 1. The spatial distribution maps of Cd, Cr, Pb, Fe, Se, Cu, Zn and As for sites in Zone 2 (S8, S9 and S10), which were located within 5 km to 7 km beyond the high density mine tailing Zone 1 revealed low level of contamination compared to the high density mine tailing Zone 1. More so, lower concentrations of the PHEs were observed for sampling sites in Zone 3 (S11, S12, S13), which were positioned at 30 to 37 km from the high density mine tailing Zone 1, compared to the high density mine tailings Zone 1 and Zone 2. For the control sites, which were positioned in the upstream wind direction in relation to the high density tailing Zone 1, an exception was observed for the control site S14 in Zone 4, with a high level of contamination. On the other hand, the least level of contamination was registered for the control site S15 in Zone 5, which was positioned in the upwind direction north of the high-density tailing Zone 1.

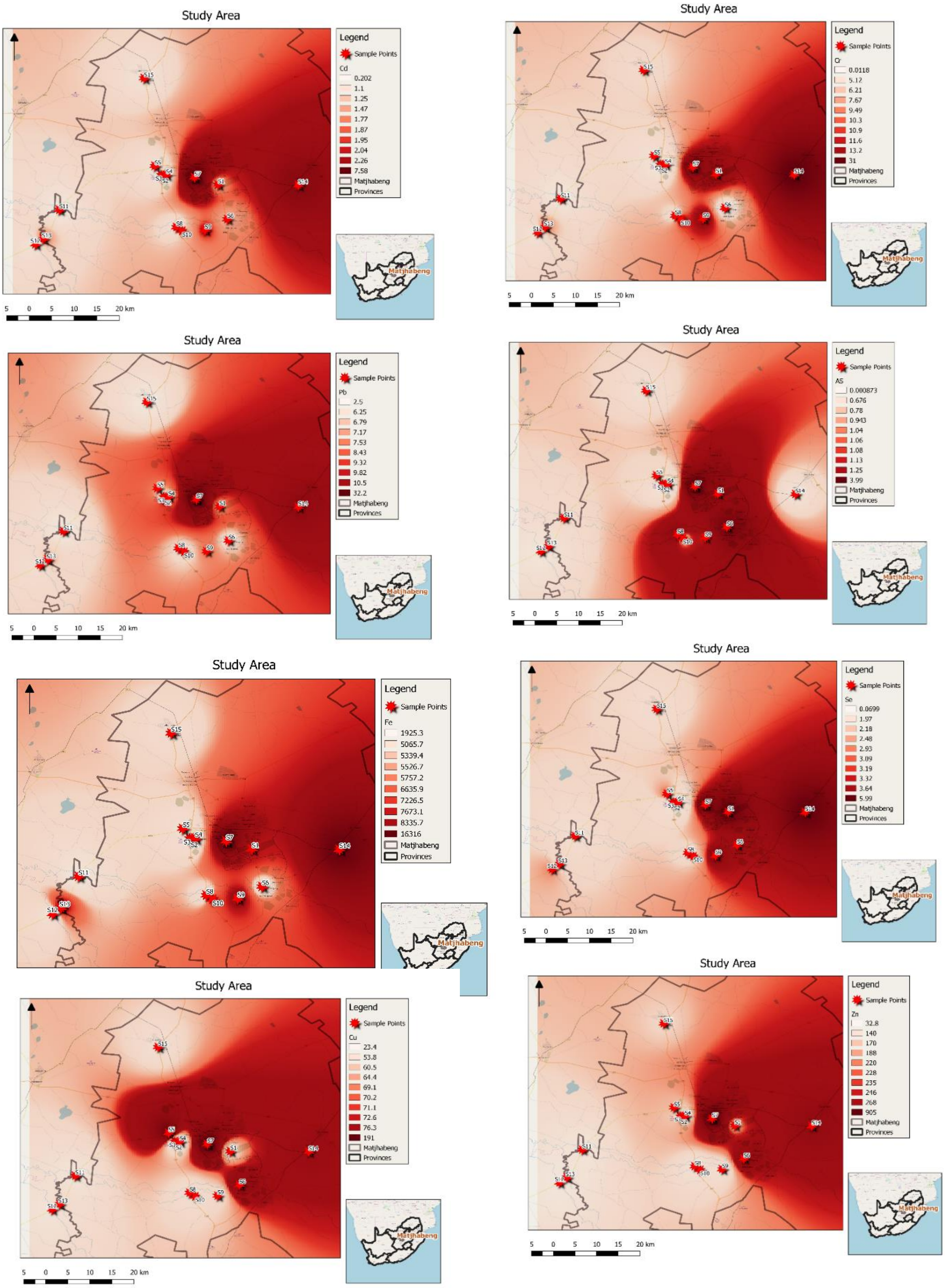

Figure 5.1 Spatial distribution of potential harmful elements in uncultivated soil for the 15 sampling sites within the five zones in the Matjhabeng Local Municipality area

5.3.4 Sources of contamination of potential harmful elements in uncultivated soil

Multivariate principal component analysis (PCA) was performed to determine if the PHEs detected in uncultivated soil were from a similar source in the environment. Similar to the spatial distribution maps that were prepared for the PHEs in uncultivated soils, few measurements were detectable with the ICP-OES in the winter season, therefore only the measurements that were recorded during the summer season were used for the multivariate PCA. The multivariate PCA results revealed three main principal components that account for 89% of the total variance with eigenvalues greater than 1 (Table 5.4). The minimum value of 0.5 was the list value a loading could have and be part of a principal component (PC) list. The first principal component revealed the major contribution to the total variance, indicating 65.6%. The high loadings of Cd, Pb, Cr, Fe and Zn, in the first principal component may indicate a similar source of pollution in the environment, such as mine tailings and mining activities in the area. The second principal component consists of As, Co, Ni and Se, and the separation of these PHEs might indicate a different origin in the environment, such as anthropogenic and natural sources. However, Cu appears to come from the same source as Cd, Pb, Cr, Fe, and Zn, as well as Co, Cr, Ni and Se, which suggest that Cu may originate from both anthropogenic activities such as mining and natural sources in the environment such as accumulated stocks of trash materials (Rakotondrable et al., 2018). The third principal component revealed high loadings of Ca and Mg, which may be added to the environment through weathering of rocks or when limestone reacts with acids from mine effluent (Naicker et al., 2003).

Table 5.4 Principal component loading for potential harmful elements in uncultivated soil

PHEs	Components		
	PC1	**PC2**	**PC3**
As	0.460	0.722	-0.389
Cd	0.920	0.237	0.272
Pb	0.920	0.237	0.272
Co	0.141	0.864	0.381
Cr	0.808	0.247	0.214
Cu	0.536	0.565	0.376
Fe	0.755	0.309	0.511
Ni	0.247	0.905	0.304
Se	0.544	0.658	0.096
Zn	0.813	0.356	0.207
Ca	0.398	0.133	0.859
Mg	0.300	0.263	0.902
Eigen values	**7.9**	**1.5**	**1.2**
Percentage of total variance	**65.6**	**12.9**	**10.0**
Percentage of cumulative variance	**65.6**	**78.5**	**88.5**

PHE = potential harmful elements; PC = principal components

The corresponding scattered plots for the principal components loading for the PHEs in uncultivated soil confirms the three main principal components for the PHEs. The clustering together of the PHEs in PC1 may also confirm that these PHEs are from a similar source in the environment. On the other hand, the scatering apart of the PHEs in PC2 may indicate that they originate from a different souce in the environment (Figure 5.2).

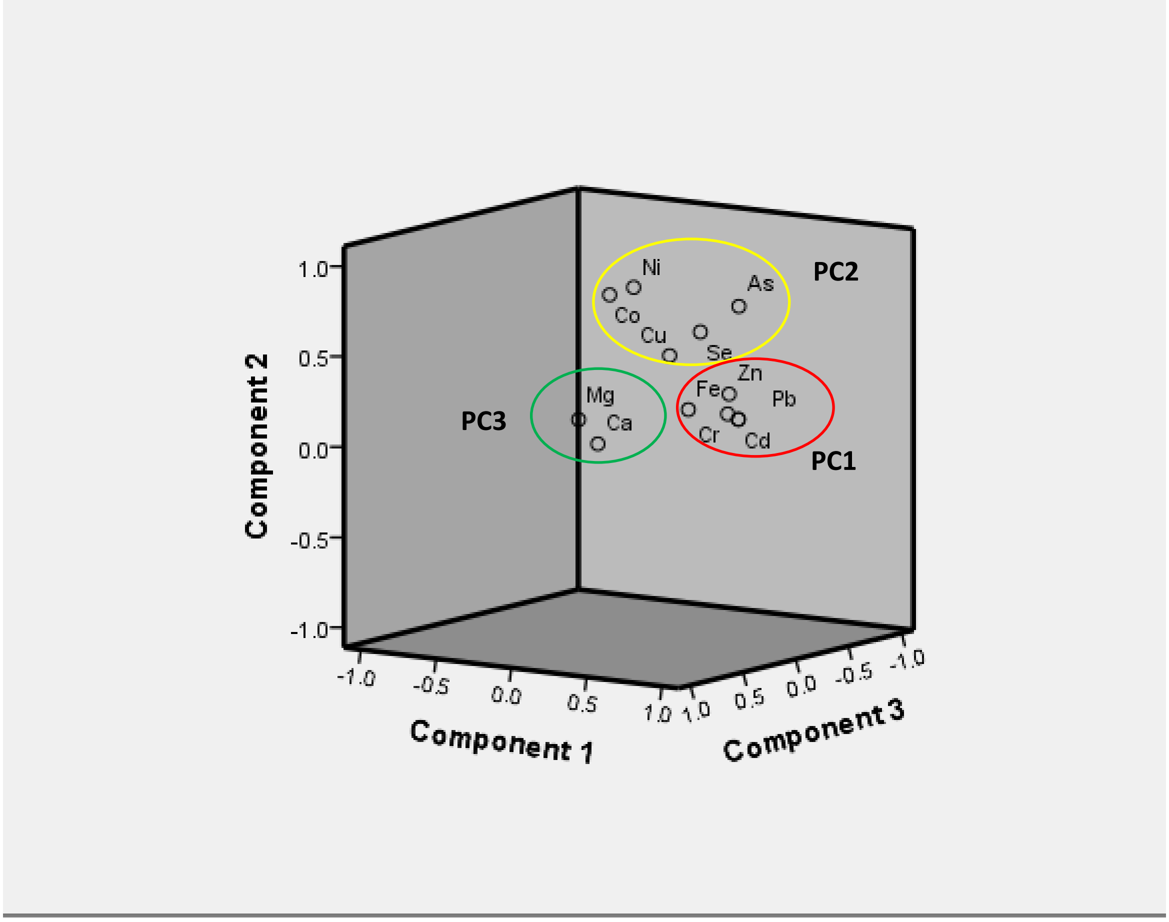

Figure 5.2 Principal component scartter plot in rotated space of the twelve potential harmful elements measured in uncultivated soil

5.3.5 Overall trend of the extent of contamination of PHEs for the five zones

The overall trend of the extent of the contamination of soil by PHEs was assessed at the 15 sampling sites, within the five zones. The assessment took into account the arithmetic means of the different indicators of contamination of surface water that exceeded the surface water limits for, particularly the summer seasons. This assessment took into account the measurements of the PHEs, which exceeded the soil quality limits for particularly the summer season, since few measurements were measured in the winter season. The results obtained for the overall trend of contamination of soil by PHEs results revealed a high level of contamination by the PHEs from the high density mine tailing Zone 1, as compared to Zone 2, and Zone 3, which were positioned in the downstream wind direction in relation to the high density mine tailing zone (Table 5.5). Additionally, there was also low level of contamination by PHEs for the control Zone 5. But for the control, Zone 4, which was positioned in the upstream wind direction in relation to the higher density mine tailing zone, a higher level of contamination for soil by PHEs was observed when compared to Zones 1, 2, 3 and 5.

Table 5.5 Trend of concentration of potential harmful elements for the five zones

Zones/ Sampling sites	**Properties that exceeded the limits**								**Number of properties that exceeded the limits**
		Cd	**Pb**	**Cr**	**Cu**	**Fe**	**Ni**	**Zn**	
Z1	S1	-	-	x	x	x	-	x	xxxx
	S2	-	-	-	x	x		-	xx
	S3	-	-	-	x	x		-	xx
	S4	-	-	-	x	x		-	xx
	S5	-	-	-	x	x		-	xx
	S6	-	-	-	x	x	x	x	xxxx
	S7	x	x	x	x	x	-	x	xxxxxx
Z2	S8	-	-	-	x	x	-	-	xx
	S9	-	-	x	x	x	-	-	xxx
	S10	-	-	x	x	x	-	-	xxx
Z3	S11	-	-	-	x	x	-	-	xx
	S12	-	-	-	x	x	-	-	xx
	S13	-	-	-	x	x	-	-	xx
Z4	S14	-	-	x	x	x	-	x	xxxx
Z5	S15	-	-	-	x	x	-	-	xx

Z = zones; S = uncultivated soil samples; X = values which exceeded the limit

5.4 Results of cultivated soil quality

Measurements were recorded for pH, EC and for the 12 PHEs that were measured in cultivated soils for the winter season. To determine the level of compliances, the pH and EC measurements were compared to limits for the protection of agricultural soils as prescribed by the CCME (2007). Similar to comparisons made for measurements of the PHEs in uncultivated soil, the measurements of the total PHEs in cultivated soil samples were also compared to two sets of soil quality limits for the protection of agricultural soils. These guidelines include the guidelines for the protection of agricultural soils as stipulated by CCME (2007), as well as the guidelines for the protection of agricultural soils, in South Africa (Herselman, 2007).

5.4.1 Physical properties of cultivated soil

Measurements of soil pH and EC were recorded for the 12 sampling sites during the cold winter season. Soil pH ranged between strongly acidic to weakly acidic condition (Table 5.6). When the measurements for the soil pH and EC were compared to the CCME (2007) guidelines for the protection of agricultural soils, 58% of the pH measurements were non-compliant to the limit, but in contrast, all the measurements for EC revealed compliance to the limit, indicating 100% compliance.

Table 5.6 Soil pH and electrical conductivity

Sampling sites	pH	EC (µs/cm)
CCME Limits	**6 - 8**	**2 ds/m 2000(µs/cm)**
CS1	4.94 (0.02)	72.43 (0.25)
CS2	6.75 (0.04)	77.27 (0.15)
CS3	5.34 (0.03)	59.13 (0.25)
CS4	5.95 (0.04)	56.53 (0.06)
CS5	5.79 (0.02)	51.37 (0.06)
CS6	6.02 (0.02)	61.43 (0.25)

CS7	6.26 (0.03)	65.53 (0.15)
CS8	4.95 (0.04)	57.67 (0.23)
CS9	5.05 (0.04)	66.70 (0.26)
CS10	6.15 (0.03)	41.60 (0.26)
CS11	6.34 (0.03)	47.70 (0.10)
CS12	4.08 (0.02)	89.33 (0.12)

CCME = Canadian Council of Ministers of the Environment water quality limits; CS = cultivated soil samples; Values in red are those that exceeded the limit

5.4.2 Potential harmful elements in cultivated soil

Measurements were recorded in winter for the total PHEs in the cultivated soil, as well as the PHEs that existed in exchangeable form for the 12 sampling sites, for the four zones. For the twelve PHEs that were measured in the cultivated soil samples, five of the concentrations of the PHEs, Cd, Co, Ni, Pb and Se, were below the instrument detection limit, while As, Cr, Cu, Fe, Zn, Ca and Mg were detected above the instrument detection limits. On the other hand, of the seven PHEs detected in cultivated soil samples, five of the PHEs were found to exist in exchangeable form, which included As, Cu, Fe, Ca and Mg. The PHEs that were detected in exchangeable form in the soil samples for the winter season are presented in Table S2 in Appendix A; supplementary data.

To determine the level of compliance, the measurements of the total PHEs in the uncultivated soil samples, were compared to the two sets of limits for the protection of agricultural soil. When the measurements were compared to the CCME (2007) limits for the protection of agricultural soil, compliance was high for As and Zn, with only a single sampling site for Zn showing non-compliance to the limit (Table 5.7). On the other hand, when the measurements were compared to the limits for protection of agricultural soils in South Africa (Herselman, 2007), compliance was high for Cr, with a single sampling site for Cu and Zn, showing non-compliance to the limit. High concentration was also measured for Fe, Ca and Mg, but there were no available limits for these PHEs for agricultural soils.

Table 5.7 Results of the mean concentrations (standard deviation) of potential harmful elements for cultivated soil sampling sites for winter

PHEs	**As**	**Cr**	**Cu**	**Fe**	**Zn**	**Ca**	**Mg**
CCME limit[1]	**12**	**-**	**63**	**-**	**250**	**-**	**-**
DEA of SA limit[2]	**-**	**80**	**100**	**-**	**185**	**-**	**-**
Sites							
CS1	2.66 (0.23)	7.98 (1.04)	96.02 (4.30)	5968.11 (7.35)	198.80 (3.19)	7618.64 (10.36)	388.73 (1.16)
CS2	2.78 (0.14)	18.38 (0.60)	101.11 (3.24)	8341.58 (12.79)	17.39 (3.60)	1013.07 (6.08)	645.37 (2.06)
CS3	2.50 (0.39)	10.88 (0.15)	94.77 (1.59)	7799.93 (15.11)	9.24 (0.33)	1065. 20 (7.98)	623.54 (2.06)
CS4	2.38 (0.35)	5.54 (0.29)	92.78 (1.25)	6596.62 (15.23)	0.13 (0.01)	334.30 (7.80)	499.39 (2.68)
CS5	3.53 (0.26)	3.67 (0.33)	88.70 (0.18)	6556.15 (7.24)	10.40 (1.10)	7597.27 (7.90)	1757.61 (6.10)
CS6	2.39 (0.37)	19.43 (1.85)	94.64 (0.14)	10170.95 (9.64)	13.67 (0.40)	935.79 (6.59)	827.85 (3.70)
CS7	1.36 (0.27)	23.35 (1.45)	91.25 (0.26)	9076.30 (12.49)	25.80 (1.12)	988.08 (9.78)	604.96 (6.09)
CS8	2.83 (0.06)	1.33 (0.44)	84.95 (0.32)	4151.51 (6.90)	5.47 (0.64)	359.46 (11.32)	225.91 (3.47)
CS9	3.49 (0.47)	14.61 (0.48)	84.78 (0.31)	5237.11 (10.04)	9.62 (0.06)	456.55 (7.53)	329.25 (0.35)
CS10	3.42 (0.09)	7.22 (1.04)	87.85 (0.34)	7044.24 (14.21)	21.63 (1.89)	948.27 (14.42)	524.05 (3.89)
CS11	4.81 (0.52)	15.31 (0.55)	97.52 (0.44)	1077.22 (13.83)	30.64 (0.79)	2005.55 (2.72)	1876.69 (8.37)
CS12	0.48 (0.03)	ND	86.34 (0.33)	4231.80 (13.77)	12.91 (1.64)	768.91 (8.46)	496.08 93.92)

PHEs = potential harmful elements; [1]CCME = Canadian Council of Ministers of the Environment water quality limits; [2]DEA of SA = limits for the protection of water resources within contaminated lands, stipulated by South African Department of Environmental Affairs South African; CS = cultivated soil samples; values in red represents measurements that exceeded the limits

5.5 Overall trend of the extent of contamination of potential harmful elements for the five zones

The overall trend of the extend of the contamination of the cultivated soil by the different contaminants were assessed at the 12 sampling sites, within the four zones, similar to the trend that were determined for the contamination of uncultivated soil. The assessment took into account the arithmetic means of the different indicators of contamination of the cultivated soil, which exceeded the soil quality limits for agricultural soils. Similar to the results obtained for the overall trend in the level of contamination for uncultivated soil, the overall trend for the contamination of cultivated soil results revealed a high level of contamination by the different contaminants for Zone 1, which was positioned at about 5 km from the high density mine tailing zone, as compared to Zone 2, and Zone 4, which were positioned in the downstream wind direction in relation to the high density mine tailing zone (Table 5.8). The control, Zone 3, which was positioned in the upstream wind direction in relation to the high density mine tailing zone, registered the lowest level of contamination for the uncultivated soil.

Table 5.8 Trend of concentration of potential harmful elements for the five zones

Zones/ Sampling sites	**Properties that exceeded the limits**				**Number of properties that exceeded the limits**
		pH	Cu	Zn	
Z1	CS1	x	x	x	xxx
	CS2	-	x	-	x
	CS3	x	x	-	xx
	CS4	x	x	-	xx
	CS5	x	x	-	xx
Z2	CS6	-	x	-	x
	CS7	-	x	-	x
	CS8	x	x	-	xx

Z3	CS9	x	x	-	xx
	CS10	-	x	-	x
	CS11	-	x	-	x
Z4	CS12	x	x	-	xx

Z = zones; CS = cultivated soil samples; X = values which exceeded the limit

5.6 Discussion

Different indicators of soil pollution were measured to determine the extent to which both the uncultivated and the cultivated soils in the MLM area have been contaminated by the contaminants that originate from the gold mine tailings in the area. The findings from this analysis have confirmed the presence of several contaminants in the uncultivated and cultivated soil samples, which may have originated from the gold mine tailings. When considering the level of contamination of the different contaminants for the five zones, the level of contamination, as well as the spatial distribution maps revealed high level of contamination for Zone 1, which contained numerous mine tailings, with the level of contamination decreasing beyond Zone 1, 2 and 3, particularly for uncultivated soil (Djebbi, et al., 2017; Gao, 2018). The possible reason could be that the mine tailings and the mining activities in the MLM area might be the dominant source of contamination to the soil in the area. Although a very high level of contamination was evident for the control, Zone 4, the contamination of soil in the area is from the Reitspruit dam in the vicinity of site, which has its origin from the high density mine tailing zone, in Zone 1. On the other hand, the high EC measurements in the soil samples could be attributed to ions from the different anthropogenic activities that is practiced in the surrounding environment, particularly the mine tailings and mining activities in the area (Luc Leroy et al., 2020).

The concentrations of PHEs also varied between the sampling sites within the different zones, particularly for the summer season. Highest concentrations of Cd, Pb, Cr, Cu, Fe, Ni and Zn, were detected at sampling sites S1, S3, S4, S6, and S7, which were located within the high density mine tailing zone in the study area. The high contamination of soils in the high density mine tailing zone with

Cd, Pb, Cr, Cu, Fe, Ni and Zn, is an indication that mine tailings and the mining activities are the major source of contamination of these PHEs. This outcome was supported by the PCA results that portrayed the clustering of these elements together in PC1, confirming that these PHEs are from a similar source in the environment, which could be the mine tailings and mining activities.

Majority of the soil samples, for the uncultivated and the cultivated soils indicated low levels of acidity, as well as exceptionally high EC measurements, which is an expectation for soils in the mining area. The low acidity in the soil within the MLM area may have resulted from the oxidation of pyrite in the mine tailings, which produces acids that are transported from the mine tailings and into the surrounding soils (Tutu, et al., 2008; McCarthy, 2011). The low acidity of the soils may affect soil microbes in the MLM area, particularly the bacterial communities in the area (Wu et al., 2017). This low pH of the soil reduces the abundance, as well as the composition and the diversity of soil microbes such as the bacterial community in soils in the area, which ultimately affects the soil productivity (Bhattarai, et al., 2015). Additionally, the transportation of acids from the mine tailings also mobilised PHEs and cause the migration of these PHEs through the mine tailings and into the soils in the area (Naicker, et al., 2003; Akcil & Koldas, 2006; Tutu et al., 2008; McCarthy, 2011).

Similarly, to surface water samples, the analysis of soils samples also revealed high concentrations of PHEs in the uncultivated soil samples, particularly during the summer season. Four of the PHEs including Cr, Cu, Fe and Zn were at high concentrations in uncultivated soil, above the soil quality limits and these PHEs may likely have originated from gold mine tailings (Wu et al., 2014; Hao and Jiang, 2015; Kwon et al., 2017; Bokar et al., 2020). The cultivated soil also contained high concentrations of Cu and Zn above the limits. These results were consistent to the results obtained in studies that were conducted within the Jiangxi, Chongqing and Tongling mining areas, in China (Xu et al., 2013; Wu et al., 2014; Hao & Jiang, 2015), as well as the in Korea (Kwon et al., 2017). Apart from Zn, Pb and Cd, concentrations of the majority of PHEs that were detected in uncultivated soil in this study, were lower when compared to results of a similar study conducted within the Witwatersrand Basin in the mining district in Johannesburg, South Africa (Kamunda et al., 2016).

The contamination of soils by these PHEs may also result in the loss of certain bacteria species in the soil, which are beneficial in the cycling of nutrients in the soil and therefore with the loss of these bacteria in soil, the functioning of the ecosystem may also be affected (Fashola et al., 2016). Contamination of chromium indicates a major threat to soil system. Cr (V1), is the most persistent and highly toxic form of Cr to biota. Even though Cr in soils predominantly accumulate in roots of plants, the limited transportation from soil to plants shoots may induce phytotoxicity by affecting plant growth, decrease yields, nutrient uptake, and photosynthesis (Oliveira, 2012; Singh et al., 2013; Shahid et al., 2017). On the other hand, toxicity of Cu in soils may damage plants roots, causing damage to root cuticle and a reduction in the growth of root hair, as well as reduce crop yields and quality of crops (Sheldon & Menzies, 2005; Adrees et al., 2015; Chiou & Hsu, 2019). Toxicity of soils by Fe may also reduce crop yields, particularly in rice plants (Sahrawat, 2006), while high Zn content in soils may affect growth of shoot (Long et al., 2011).

Higher concentrations of PHEs (80%) were measured during the hot summer seasons as compared to the cold winter seasons, with Cu and Fe being the only exceptions. Summer in the MLM area is the rainy season and with the high temperatures during this season, the dissolution of the PHEs and their mobility in the soil had to increase, thus enhancing their availability during the summer season (Li et al, 2013).

Chapter 6

Uptake of Potential Harmful Elements in Plants

6.1 Introduction

The Matjhabeng Local Municipality (MLM) area is a home to a diverse species of wild plants, as well as food crops, which are cultivated extensively in the area. Some of the wild plants that grow in the area, such as the sweet thorn plant are used for medicinal purposes by the local people, because these plants are readily available. The sweet thorn plant is widely distributed in the MLM area, as well as in other parts of South Africa. On the other hand, maize is one of the most important food crop that is cultivated extensively in the MLM area and it serves as a staple food for most people, particularly the poor (du Plessis, 2003). Maize is produced in large acres of land in the eastern and western side of the MLM area with some of the maize farms situated at less than one kilometre from a mine tailing or a mine, particularly in the western side of MLM area. There is therefore a high probability that the sweet thorn plants, as well as the maize plants that grow in the vicinity of the gold mine tailings in the MLM area, may absorb contaminants, which originate from the gold mine tailings and transport these contaminants into the stems, leaves and the seeds of these plants (Shaheen et al., 2016 ; Kwon et al., 2017; Adekiya et al., 2018).

The extent of contamination of the sweet thorn plants, as well as the maize plants by contaminants from the gold mine tailings was determined by analysing the leaves samples of sweet thorn, as well as maize seeds samples for indicators of contamination. The leaves of sweet thorn were collected from the same sampling sites, in the vicinity of the surface water bodies, from where surface water samples were also collected, as well as the uncultivated soil samples. The leaves samples of sweet thorn were collected for both the summer and the winter seasons, similar to collections that were made for surface water samples, as well as for the uncultivated soils samples. Maize seeds were collected from the same sampling sites in the vicinity where groundwater samples and cultivated soils were collected. Additionally, maize seeds were only collected during the cold winter season since maize seeds mature in winter in the MLM area.

The indicators of contamination that were analysed in sweet thorn leaves as well as maize seeds include the different potential harmful elements (PHEs) in the plant samples. The twelve PHEs included, arsenic (As), cadmium (Cd), lead (Pb), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), selenium (Se), zinc (Zn), calcium (Ca) and magnesium (Mg). To determine the extent of contamination of sweet thorn plants and maize plants by PHEs from goldmine tailings in the MLM area, the following research question was answered:

Sub Question: To what extent are the sweet thorn and maize plants in the MLM area contaminated by contaminants from gold mine tailings? To address the research question, the following objective was assessed:

Objective 5: To determine the extent of contamination of sweet thorn and maize plant, measured in terms of the PHE contamination.

6.2 Material and methods

6.2.1 Description of sweet thorn and maize plant

Sweet thorn plant

Sweet thorn is a legume that belongs to the pod-bearing family, Fabaceae. Scientifically the plant is described as *Vachellia karroo* and commonly known as “sweet thorn” and “white thorn”. In Sesotho the plant is described as “leoka”, “Soetdoring” in Afrikaans, “umuNga” in Zulu Xhosa, or “Mookana” in north Sotho and “Mooka” in Tswana (Taylor & Barker, 2012). Sweet thorn is a perennial plant and is widely distributed in all the provinces of South Africa, as well as in other parts of Southern Africa including

Namibia, Angola, Botswana, Zambia and Zimbabwe (Dingaan & Preez, 2018). The plant contains many white and paired thorns, which may grow up to about 20 cm in length (Figure 6.1). The flowers are yellow and are scented, with numerous fluffy heads about the size of a pea. The entire plant may vary from a thorny shrub to a tall tree depending on the climate, soil and other prevailing environmental conditions in the area (Taylor & Barker, 2012).

Sweet thorn plant has several uses, which range from medicinal, ecology to economic benefits. The bark, pods, seeds, leaves, and thorns are extremely useful to both humans and animals. For medicinal purposes, the bark, leaves, and gum are usually used as a remedy for diarrhoea and dysentery, wound bandages, eye treatments and cold remedies (Aubrey & Reynolds, 2002). On the other hand, in arid areas the sweet thorn is an indicator of water, both underground and in the surface. Different commercial products are obtained from the tree. For example, the pleasant tasting gum, which flows from wounds in the bark of the sweet thorn plant, is eaten by people and animals. Additionally, the bark is used for tanning leather and the inner bark can be used for making strong rope. The plant is also an excellent forage tree for game and livestock and game feed on the leaves, flowers, and pods. The flowers produce good quantity of nectar and pollen for bee-farming (Aubrey & Reynolds, 2002).

Figure 6.1 Photograph of a sweet thorn branch (*Vachellia karroo*)

Source PlantZAfrica.com

Maize plant

Maize is a cereal plant, which belongs to the grass family Poaceae. The plant is commonly called corn or Indian corn, and scientifically, the plant is called *Zea mays* (JW-Admin, 2017). Maize plant is an annual grass, which can grow for up to about 2 to 3 m in height and can only survive for one growing season. The plant is widely distributed in all the provinces of South Africa, and it is the most important grain crop produced in South Africa (du Plessis, 2003). The maize stem varies in height from less than 0,6 m to about 5,0 m in extreme cases, with a simple stem of nodes and internodes (Figure 6.2). A pair of large leaves extend from each internode and there may be about 8 to 21 leaves on one maize plant. The leaves may be linear or lance-like with obvious primary vein, and the leaves can grow from about 30 to 100 cm in length. The maize grains, or 'kernels', can be white, yellow, red, purple or black and are encased in husks, which may be up to about 30 to 1000 per ear (du Plessis, 2003).

Maize is the most important staple food to majority of the people in South Africa, particularly the poor. Maize forms a very important source of carbohydrates to human diet and is also high in energy and nutritional value (Tandzi & Mutengwa, 2020). It is rich in dietary fibre, Vitamins A, C and E, as well as other essential minerals (JW-Admin, 2017). Maize also forms an essential ingredient for animal feed production and it is also used to make other products, such as, biofuel, adhesives, clothing, and pharmaceutical tablets (du Plessis, 2003). The starch can also be converted into sweeteners and used in products such as soft drinks, sweets, bakery products and jams, while the oil from the embryo is used in cooking oils, margarine, and salad dressings (JW-Admin, 2017).

Figure 6.3 Maize (a) Maize plants (b) Matured maize seeds

Source Department of Agriculture, South Africa

6.2.2 Collection of plant samples

The leaves samples of sweet thorn and maize seeds were collected using a modified sampling procedure that was followed by Chen et al. (2018). At each of the 15 sampling sites, that were identified in the uncultivated lands in the MLM area, the leaves of sweet thorn were collected from a sweet thorn plant that was at about five meters from the banks of the surface water, from where the uncultivated soils were also collected. Maize seeds were also collected from all the 12 sampling sites within the cultivated maize farms, from where the cultivated soil samples had been collected.

The plant samples were collected in the following manner:

1. About 500 g of the leaves of sweet thorn plant were collected and were placed in separate labelled self-sealing polyethylene bags.
2. One cub of maize was collected from a maize plant and was placed in labelled zip sealed plastic bag.
3. The leaves samples of sweet thorn and the maize seeds were transported to the Water Laboratory at the Central University of Technology (CUT) awaiting the preparation of the plant samples.

The sampling sites from where sweet thorn leaves were collected were indicated with the letters, ST, which stands for sweet thorn. Thus, sampling site, one was indicated as ST1. Similar to the naming of the sampling sites for sweet thorn, the sampling sites from where maize seeds were collected were represented with the letters, MP, meaning maize plant. Thus, sampling site number one was denoted as MP1.

6.2.3 Preparation of plant samples

The leaves samples of sweet thorn, as well as the maize seeds were prepared to convert the samples into fine powder, before using the powdered samples for digestion and analysis of PHEs. As with the preparation of the soil samples, the plants samples were also prepared by drying, grounding, and sieving of the plant samples.

The preparation of the plant samples was also performed in the CUT Laboratory in following manner:

1. The leaves samples from each of the 15 sampling sites were washed in distilled water, to remove any surface metals
2. Then after, the leaves of sweet thorn, as well as maize seeds were placed in separate stainless-steel trails, and were dried in an oven at 60 ^{O}C for 48 hours.
3. The dried samples were ground in a porcelain mortar using a pestle, and then after, sieved through a 2 mm silicon handler stainless steel sieve.
4. The prepared samples were packaged into separate zip sealed plastic bags and stored in an airtight container before transportation to the School of Chemistry and Physics, University of Kwa-Zulu Natal, Westville campus for digestion and chemical analysis of the samples using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OEP).

6.2.4 Measurement of potential harmful elements

Prior to the determination of the 12 PHEs the prepared plant materials were first digested following a similar procedure as for the digestion of soil samples. After the digestion process the twelve PHEs including, As, Cd, Pb, Co, Cr, Cu, Fe, Ni, Se, Zn, Ca and Mg were measured in leaves samples of sweet thorn, as well as maize seeds samples using the ICP-OES, similar to the measurements for water samples, as well as for soil samples.

6.2.5 Determination of the bioaccumulation factor

The bioaccumulation factor was computed to determine the uptake of PHEs by the sweet thorn plants, as well as the maize plants from the contaminated soil and the accumulation of these PHEs in the leaves of plants. The BAF is a measure of the ratio of the concentration of the PHEs that have accumulated inside a plant and the concentration of the PHEs in the soil (Zhuang et al., 2009; Xu et al., 2013; Hu et al., 2014; Mahlangeni et al., 2016).

$$\text{BAF} = \left(\frac{Concentration\ of\ metal\ in\ plant}{Concentration\ of\ metal\ in\ soil}\right) \qquad (5)$$

The BAF values obtained for the different PHEs at each of the 12 sampling sites were interpreted as follows; The BAF value that was greater than one indicated that the plant can extract PHEs from the soil and accumulate the PHEs in parts above the ground, such as the stem and the leaves, but a value below one, indicates no form of accumulation of PHEs in the parts above the ground (Zhuang et al., 2009; Juárez-Santillán et al., 2010; Usman et al., 2019; Gebeyehu et al., 2020).

6.2.6 Determination of quality assurance and quality control

Quality control measures were followed to guarantee accurate results for the plants samples measurements. Before the drying of the plants leaves samples, the leaves were washed in distilled water to remove any surface metals. Additionally, a similar quality assurance procedure was followed for plant samples measurements as with the preparation of soil samples.

6.3 Results of uptake of potential harmful elements in sweet thorn

The measurements for the different PHEs in the leaves samples of sweet thorn were recorded for the 15 sampling sites, for both seasons. For all the 12 PHEs that were measured in sweet thorn leave samples, Cd and Cr were below the detection limits of the ICP-OES for both the summer and the winter season, even though Cd and Cr existed in exchangeable form in uncultivated soil, for the summer season. However, the measurements of As could only be detectable with the ICP-OES at two of the sampling sites in summer. Nickle was detected at a single sampling site, and the level exceeded the permissible limit for Ni, in an infusion prepared from the leave samples that is used for medicinal purposes (Shah et al., 2013). In addition, measurements of Pb, Co, Se and Zn were only detected in the leave samples during the summer season (Table 6.1). On the other hand, when the measurements that were detectable above the ICP-OES instrument detection limit were compared to the recommended limits for PHEs in an infusion made from a medicinal plant (Shah et al., 2013), high level of compliance was observed for Cu and Zn, indicating 100% compliance to the limits. For Pb, three of the samples exceeded the medicinal plants limits. On the other hand, the measurements for Fe indicated exceptionally high level of non-compliance, with 67% of the samples exceeded the limits for the summer season and 93% of the samples were non-compliant to the limit for the winter season. High concentrations of Se, Ca and Mg were detected in the leave samples of sweet thorn but there were no available medicinal plants limits for the measured PHEs, similar to the measurements that were made for surface water samples and soil samples.

Table 6.1 Results of the mean concentrations (standard deviation) of potential harmful elements for the sweet thorn samples for summer and winter

Metals		**As**	**Pb**	**Co**	**Cu**	**Fe**	**Ni**	**Se**	**Zn**	**Ca**	**Mg**
Limits[1]			**10**		**10**	**20**	**1.5**		**50**		
Sites	**Seasons**										
ST1	S	ND	0.3 (0.12)	0.3 (0.07)	1.4 (0.56)	ND	ND	2.2 (0.98)	1.8 (0.60)	10360 (11)	996 (5)
	W	ND	ND	ND	8.0 (0.31)	188 (13)	ND	ND	ND	3262 (6)	273 (4)
ST2	S	ND	4.5 (0.63)	0.4 (0.01)	2.6 (1.01)	135.8 (1)	4.9 (1.87)	0.5 (0.1)	13.4 (0.98)	6135 (17)	1247 (6)
	W	ND	ND	ND	5.6 (0.27)	377 (15)	ND	ND	ND	3138 (8)	254 (1)
ST3	S	ND	1.0 (0.00)	0.5 (0.09)	9.0 (1.79)	75 (2)	ND	ND	0.6 (0.30)	7699 (17)	2067 (6)
	W	ND	ND	ND	5.4 (0.14)	189 (6)	ND	ND	ND	5173 (15)	756 (4)
ST4	S	ND	0.4 (0.23)	0.2 (0.02)	2.2 (0.87)	30 (3)	ND	2.9 (0.69)	ND	8492 (12)	2061 (4)
	W	ND	ND	ND	3.8 (0.34)	268 (5)	ND	ND	ND	2836 (6)	425 (1)
ST5	S	0.1 (0.01)	ND	0.5 (0.02)	4.8 (0.23)	70 (4)	ND	3.0 (0.89)	11.2 (1.02)	10610 (12)	2117 (4)
	W	ND	ND	ND	6.7 (0.05)	284 (8)	ND	ND	ND	2212 (11)	243 (4)
ST6	S	0.4 (0.03)	3.8 (0.22)	0.4 (0.01)	5.7 (0.98)	9 (1)	ND	3.6 (0.58)	15.8 (2.58)	17490 (17)	2245 (2)
	W	ND	ND	ND	4.9 (0.16)	62 (4)	ND	ND	ND	2347 (10)	147 (6)
ST7	S	ND	2.9 (1.09)	0.2 (0.00)	3.7 (1.60)	ND	ND	ND	20.6 (1.38)	6703 (14)	2277 (2)
	W	ND	ND	ND	7.65 (0.20)	426 (3)	ND	ND	ND	3005 (1)	332 (3)
ST8	S	ND	0.9 (0.98)	0.5 (0.02)	3.2 (1.11)	493 (3)	ND	0.4 (0.0)	13.2 (1.06)	9090 (10)	852.5 (7)
	W	ND	ND	ND	6.9 (0.59)	103 (9)	ND	ND	ND	1601 (9)	124 (0.4)

ST9	S	ND	5.2 (1.02)	0.2 (0.03)	3.5 (1.22)	56 (6)	ND	0.9 (0.10)	ND	11990 (11)	1877 (4)
	W	ND	ND	ND	6.9 (0.05)	213 (6)	ND	ND	ND	1635 (3)	27 (0.04)
ST10	S	ND	ND	0.1 (0.00)	2.5 (1.05)	9 (3)	ND	1.3 (0.20)	7.6 (1.88)	6564 (1)	1490 (1)
	W	ND	ND	ND	4.9 (0.24)	9 (1)	ND	ND	ND	1972 (1)	282 (1)
ST11	S	ND	0.6 (0.62)	0.2 (0.01)	1.2 (0.06)	44 (5)	ND	ND	7.4 (0.58)	12530 (12)	1515 (2)
	W	ND	ND	ND	7.7 (0.28)	122 (4)	ND	ND	ND	3276 (6)	326 (1)
ST12	S	ND	ND	0.2 (0.02)	4.0 (0.36)	20 (2)	ND	ND	13.6 (1.54)	7373 (16)	1473 (2)
	W	ND	ND	ND	9.9 (0.27)	683 (21)	ND	ND	ND	3151 (11)	145 (5)
ST13	S	0.4 (0.02)	2.4 (1.02)	0.2 (0.02)	3.8 (1.20)	1 (1)	ND	0.8 (0.80)	27.5 (1.87)	5938 (11)	1096 (2)
	W	ND	ND	ND	9.7 (0.03)	1465 (12)	ND	ND	ND	2280 (3)	79 (0)
ST14	S	ND	1.5 (0.36)	0.3 (0.02)	3.4 (0.52)	25 (1)	ND	2.9 (1.36)	5.0 (0.25)	8084 (13)	951 (6)
	W	ND	ND	ND	4.87 (0.10)	433 (10)	ND	ND	ND	4016 (6)	154 (1)
ST15	S	ND	1.1 (0.28)	0.1 (0.01)	4.0 (0.54)	28 (3)	ND	0.2 (0.00)	2.0 (0.25)	6986 (16)	1309 (2)
	W	ND	ND	ND	6.9 (0.21)	395 (7)	ND	ND	ND	3693 (1)	732 (0)

[1] = Shah et al., 2013; ST = sweet thorn leaves samples; ND = below instrument detection limit

6.3.1 Bioaccumulation of potential harmful elements

The computed bioaccumulation factor (BAF) values of the different PHEs for sweet thorn leaves were recorded for the 15 sampling sites, for both seasons. BAF greater than one (BAF > 1) was only observed for Pb, Se, Ca and Mg (Table 6.2). However, a few sites showed BAF greater than two (BAF > 2) for Pb and Se at less than 20% of the sampling sites during the summer season, which indicates that at these sites the sweet thorn plant could absorb PHEs from contaminated soil and accumulated the PHEs in the leaves of the plants. But for the winter season, BAF greater than two were only detected for Ca at 20% of the sampling sites.

Table 6.12 Bioaccumulation factors in leaves of sweet thorn for summer and winter

Sites	**Seasons**	**As**	**Pb**	**Co**	Cu	Fe	**Ni**	**Se**	**Zn**	**Ca**	**Mg**
ST1	S	-	0.15	0.02	0.09	0.19	-	3.79	0.28	0.99	0.70
	W	-	-	-	0.13	0.01	-	-	-	0.37	0.08
ST2	S	-	2.99	0.04	0.07	0.06	0.94	9.55	0.05	0.52	0.76
	W	-	-	-	0.13	0.25	-	-	-	4.63	1.58
ST3	S	-	1.06	0.19	0.35	0.02	-	-	0.01	0.59	1.57
	W	-			0.08	0.01	-	-	-	0.54	0.19
ST4	S	-	0.08	0.03	0.06	0.01	-	-	-	0.11	0.39
	W	-	-		0.07	0.02		-	-	0.69	0.13
ST5	S	0.13	-	0.03	0.03	0.02	-	0.91	-	0.52	0.81
	W	-	-		0.08	0.02			-	0.70	0.15
ST6	S	-	0.41	0.01	0.11	0.01	-	3.25	0.01	1.67	1.81
	W	-	-	-	0.14	0.07	-	-	-	7.06	1.73
ST7	S	-	0.09	0.01	0.02	-	-	-	0.02	0.17	1.14
	W	-	-	-	0.13	0.03	-	-	-	0.48	0.17
ST8	S	0.13	2.56	0.01	0.06	0.00	-	1.00	0.04	0.84	1.37
	W	-	-	-	0.10	0.01	-	-	-	0.32	0.07
ST9	S	-	-	0.02	0.17	0.01	-	-	0.42	1.67	1.84
	W	-	-	-	0.43	0.14	-	-	-	6.99	0.62
ST10	S	1.33	-	0.01	0.08	0.00	-	0.57	0.47	0.25	0.32
	W	-	-	-	0.18	0.09	-	-	-	0.47	0.02
ST11	S	-	0.24	0.02	0.05	0.02	-	-	0.16	14.08	1.91
	W	-	-	-	0.18	0.03	-	-	-	2.63	0.42
ST12	S	-	0.09	0.03	0.04	0.00	-	0.50	0.01	0.16	0.20
	W	-	-	-	0.09	0.03	-	-	-	0.09	0.05
ST13	S	-	0.05	0.01	0.03	-	-	0.37	0.01	0.39	0.33
	W	-	-	-	0.08	0.02	-	-	-	0.53	0.20

ST14	S	-	1.36	0.01	0.08	0.01	-	0.20	-	1.57	1.48
	W	-	-	-	0.15	0.02	-	-	-	0.48	0.03
ST15	S	-	-	-	0.06	0.00	-	0.68	0.10	0.36	0.71
	W	-	-	-	0.11	0.00	-	-	-	0.65	0.20

St = sweet thorn leaves samples; BAF>1, red colour = indicates that the plant can extract potential harmful elements from the soil and accumulate them in parts above the ground

6.3.2 Overall trend of the extent of contamination of PHEs for the five zones

The overall trend of the extent of the contamination of sweet thorn leaves was assessed at the 15 sampling sites, within the five zones. In this assessment, the arithmetic means of the concentrations for the different PHEs that exceeded the limits for each of the sampling sites for the summer season were computed. The results of this assessment indicted a high level of uptake of PHEs by the sweet thorn plants, which grew within the high density mine tailing zone, in Zone 1, and the level of contamination decreased beyond Zone 1 (Table 6.3).

Table 6.3 Trend of concentration of potential harmful elements for the five zones

Zones/ Sampling sites		**Properties that exceeded the limits**			**Number of properties that exceeded the limits**
		Pb	**Fe**	**Ni**	
Z1	ST1	x	-	x	xx
	ST2	-	x	-	x
	ST3	-	x	-	x
	ST4	-	x	-	x
	ST5	-	x	-	x
	ST6	x	-	-	x
	ST7	-	-	-	-
Z2	ST8	-	-	-	-
	ST9	x	-	-	x
	ST10	-	-	-	-
Z3	ST11	-	-	-	-
	ST12	-	-	-	-
	ST13	-	-	-	-

Z4	ST14	-	-	-	-
Z5	ST15	-	-	-	-

Z = zones; ST = sweet thorn leaves samples; X = measurements that exceeded the limits

6.4 Results of uptake of potential harmful elements in maize plant

The extent of contamination of maize seeds by PHEs was registered for the 12 sampling sites in the MLM area in winter. Of the 12 PHEs analysed in maize seeds samples, measurements could only be detectable above the detection limit of the ICP-OES for As, Cu, Fe, Mg, Ca, while the concentrations of Cd, Pb, Co, Cr, Se and Zn, were below the instrument detection limit (Table 6.4). For compliance purposes, the measurements were compared to International guidelines for contaminants in food as stipulated by the World Head Organisation and the Food and Agricultural Organisation (FAO/WHO, 2015). For As, all the seven sampling sites which contained measurements that were above the instrument detection limit were non-compliant to the guidelines for contaminants in food (FAO/WHO, 2015). The International guidelines for contaminants in food did not contain limits for Cu, Fe, Ca and Mg, mostly because the concentration at which these elements are present in food samples may not impact human health (FAO/WHO, 2015).

Table 6.4 Mean concentrations (standard deviation) of potential harmful elements for maize seeds in winter

PHE	**As**	**Cu**	**Fe**	**Ca**	**Mg**
WHO/FAO limit	**0.1**				
MP1	1.60 (0.07)	3.07 (0.05)	31.47 (0.12)	907.77 (4.58)	1318.99 (7.94)
MP2	0.74 (0.02)	1.09 (0.01)	28.91 (0.51)	526.86 (4.80)	2167.31 (8.66)
MP3	1.16 (0.05)	4.73 (0.07)	22.29 (0.08)	106.95 (3.55)	1259.79 (7.15)
MP4	0.35 (0.04)	7.17 (0.06)	11.36 (0.08)	296.39 (2.21)	234.60 (5.490
MP5	ND	4.14 (0.01)	17.86 (0.05)	476.34 (6.74)	1089.06 (8.69)
MP6	ND	0.59 (0.01)	15.20 (0.07)	116.59 (2.97)	1152.26 (7.43)
MP7	0.59 (0.07)	1.95 (0.01)	6.42 (0.36)	106.48 (7.48)	578.32 (9.70)

MP8	ND	3.36 (0.11)	35.44 (0.47)	142.94 (3.21)	1494.92 (1.54)
MP9	1.15 (0.05)	1.58 (0.02)	41.58 (0.34)	153.53 (4.14)	1294.85 (7.79)
MP10	ND	6.38 (0.14)	9.25 (0.21)	16.98 (0.90)	1078.17 (1.57)
MP11	ND	8.68 (0.08)	37.35 (0.40)	71.84 (0.79)	1919.61 (6.34)
MP12	1.27 (0.13)	3.14 (0.04)	54.27 (0.17)	191.44 (0.03)	777 (4.91)

PHE potential harmful elements; WHO/FAO = World Head Organisation and the Food and Agricultural Organisation guidelines for contaminants in food; MP = maize plants samples

6.4.1 Bioaccumulation of potential harmful elements

Bioaccumulation factor (BAF) of potential harmful elements in maize seeds provided the extent to which maize plants extracted PHEs from the soils and accumulated the PHEs in maize seeds. Only a single site for As revealed bioaccumulation greater than 2, but the remainder of the sites indicated bioaccumulation below one, as well as for Cu, Fe and Ca, which indicated no form of accumulation for these PHEs from soil into the maize seeds (Table 6.5). However, bioaccumulation greater than two was observed for Mg at 50% of the sampling sites.

Table 6.5 Bioaccumulation factors in maize seeds

Sites	As	Cu	Fe	Ca	Mg
MP1	0.60	0.03	0.01	0.12	3.39
MP2	0.27	0.01	0.00	0.52	3.36
MP3	0.46	0.05	0.00	0.10	2.02
MP4	0.15	0.08	0.00	0.89	0.47
MP5	-	0.05	0.00	0.06	0.62
MP6	-	0.01	0.00	0.12	1.39
MP7	0.43	0.02	0.00	0.11	0.96
MP8	-	0.04	0.01	0.40	6.62
MP9	0.33	0.02	0.01	0.34	3.93
MP10	-	0.07	0.00	0.02	2.06
MP11	-	0.09	0.03	0.04	1.02
MP12	2.65	0.04	0.01	0.25	1.57

MP = maize plant samples; BAF>1, red colour = indicates that the plant can extract potential harmful elements from the soil and accumulate them in parts above the ground

6.4.2 Overall trend of the extent of contamination of PHEs for the five zones

The overall trend for the contamination by PHEs was determined for the 12 sampling sites, within the four zones that were situated within the cultivated maize farms. This assessment also considered the arithmetic mean of the concentrations of As that exceeded the limits for the different sampling sites for the summer season. The results revealed that the maize seeds that were grown at approximately 5 Km from the mine tailings absorbed a higher concentration of PHEs, which might have originated from the gold mine tailings area. But the level of contamination of the maize seeds reduces away from Zone 1, Zone 2 and Zone 3, as well as for the control, Zone 4 (Table 6.6).

Table 6.6 Overall trend of the extent of contamination of PHEs for the four zones

Zones/ Sampling sites		Property that exceeded the limits
		As
Z1	MP1	x
	MP2	x
	MP3	x
	MP4	x
	MP5	-
	MP6	-
	MP7	x
Z2	MP8	-
	MP9	x
	MP10	-
Z3	MP11	-
Z4	MP12	x

Z = zones; MP = maize plant; x = values that exceeded the limits

6.5 Discussion

The concentration of the PHEs was used as an indicator of pollution to assess the extent of contamination of sweet thorn leaves and maize seeds, because of the uptake of these contaminants by the plants from contaminated soil in the MLM area. The results revealed high level of contamination of sweet thorn leaves by high concentrations of Pb and Fe, which could probably have their source from mine tailings and mining activities in the area. However, at each of the five zones, the highest concentration of PHEs was absorbed by sweet thorn plants which grow in uncultivated soils at the sampling sites that were in the vicinity of the high density mine tailings zone. But the level of uptake of PHEs decreased for the sweet thorn plants, which grew in uncultivated soils within Zone 2 and Zone 3, as well as the control Zone 4 and Zone 5. A similar trend was also observed in the uptake level of PHEs by maize plants from cultivated soils in the MLM area. On the other hand, sweet thorn leaves accumulated high concentrations of Pb, Se and Ca in their leaves, which indicated that the concentration of these PHEs was greater in the plants leaves than in the soil. However, even though high BAFs was detected for Pb at a few of the sampling sites, absorption of Pb from the soil might not necessarily be the only source from which Pb might have been added unto the plants leaves. The reason could be because Pb levels in soils are mostly low, thus Pb contamination of plants and vegetable leaves mostly result from physical contamination of parts above the ground during field conditions (Xu et al., 2013). Therefore, Pb might have entered the plant leaves through the stomata as a result of aerial deposition from mining activities that are performed within the high-density tailings area, including other industrial activities such as paint industries found in the area (Ali & Al-Qahtani, 2012; Xu et al., 2013). The high bioaccumulation factor for Ca and Se detected in sweet thorn leaves, and Mg detected in maize seeds, might have resulted from the fact that these PHEs are essential micronutrients in plants, with no obvious toxicity effects, therefore bioaccumulation of these PHEs might have been required for growth and development of the plants (Mahlangeni et al., 2016; Batwa-ismail, 2018; Etteieb et al., 2020).

For the most, uptake of PHEs in sweet thorn and the accumulation of the PHEs in the leaves were lower in winter as compared to the summer season. This may be because of the fact that during warmer summer conditions, uptake of PHEs is faster as compared to cold winter conditions (Fritioff, et al., 2005). Furthermore, summer is also the season when sweet thorn plants flourish in the MLM study area.

Chapter 7

Environmental Pollution Risk and Health Risk of Contamination by PHEs from Gold Mine Tailings

7.1 Introduction

As a result of the extensive pollution of the environment in the Matjhabeng Local Municipality (MLM) area by particularly potential harmful elements (PHEs) from the goldmine tailings, it is important to understand the possible risks of such pollution on the environment in the area. Moreover, since people live in the MLM area and are exposed to the polluted environment, it is also essential to understand the risks on the health of the local people. It is also important to find different ways to describe the extent of pollution in the area based on the risk on the environment, as well as on the health of humans who reside in the area.

Several assessment approaches exist that can be used to evaluate the risks of the mine tailings contamination on the environment, as well as the risks of the contaminants on human health. One of the most widely used approaches involves the use of pollution risk indices (Wu et al., 2014; Zhao et al., 2015; Fan & Wang, 2017; Kowalska et al., 2018). Environmental pollution risk indices are a useful tool for the comprehensive evaluation of the level of contamination by contaminants in the environment (Wu et al., 2014; Zhao, et al., 2015; Fan & Wang, 2017; Kowalska et al., 2018). On the other hand, health risk indices have also been a valuable tool to estimate the nature and probability of adverse health risk on humans who may be exposed to chemicals in contaminated environment (Kacholi & Sahu, 2018).

To determine the environmental pollution risk in the MLM area, which may arise from the contamination of PHEs from the gold mine tailings, some of the most widely used environmental pollution risk indices were quantified. These environmental pollution risk indices included, the Enrichment Factor (EF), Geo-accumulation Index (Igeo), Single Factor Pollution Index (SFPI) and the Numerow Integrated Pollution

Index (NIPI) (Wu et al., 2014; Fan & Wang, 2017; Wang et al., 2019). The measurements of the PHEs for surface water, and the uncultivated soils were used in this study to quantify the different environmental pollution risk indices, because majority of the PHEs that were analysed were measured in the surface water and the uncultivated soil samples. The computed environmental pollution risk indices were used to quantify the extent of contamination in the MLM area as a result of the PHEs, as well as to determine the potential risk of the PHEs on the environment in the MLM area. Additionally, the environmental pollution risk indices were used to determine if the accumulation of the PHEs in the MLM area were caused by natural processes or as a result of anthropogenic activities in the area, particularly the gold mine tailings contaminants.

Similarly, different health risk indices have also been used to estimate the probability of an adverse human health risks that may arise from the exposure of a hazard in an environment. The hazard in the MLM area consisted of the concentrations of the different PHEs that were measured in surface water and soil in the area. These PHEs were considered a hazard because the PHEs are a source of health risk to the local people in the MLM area. The health risk indices that have mostly been computed in a health risk analysis include, Chronic Daily Intake (CDI), the Hazard Quotient (HQ), as well as the Hazard Index (HI) (Khan et al., 2013; Huang et al., 2013; Huang et al., 2014; He et al., 2018). Thus, the health risk analysis was therefore performed in this study to estimate how likely the exposure to the PHEs in the MLM area will cause health risks to the local people (WHO, 2010; U.S. EPA, 2016; Chen et al., 2018).

The accumulation of PHEs in water, soil, as well as plant, indicates the direct route through which PHEs can gain access into the human food chain. Exposure to PHEs may occur through three primary exposure pathways, which include ingestion, inhalation, and absorption through the skin (Cal/ EPA, 2001; U.S. EPA, 2016; TEF, 2020). The oral intake of PHEs in contaminated water or food samples has been considered as the most important entry route by which PHEs can enter into the human body, as opposed to inhalation and dermal contact (Muhammad et al., 2011; Huang et al., 2014). Therefore, the health risk indices were computed in this study to estimate the potential health risk that may arise from the consumption of PHEs in an infusion from sweet thorn leaves, which is used for medicinal purposes by the local people in the MLM area. Both the carcinogenic risk and the non-carcinogenic health risk were estimated as a result of the exposure to PHEs by the local people in the study area. Given the fact that very few PHEs measurements were detected in groundwater and maize seeds samples, the health risk that may arise from the consumption of PHEs in groundwater and maize seeds could not be estimated.

Several environmental pollution risk indices existed that have been used to determine the risk that may arise from the contamination by PHEs of either water or soil in a study area. The environmental pollution risk indices, which were computed in this study, were used to develop, and quantify a combined environmental pollution index specifically for mining areas. The novel environmental pollution index was described as the Combine Risk Index for water and soil ($CRI\ (w + s$). This novel index was developed to determine the total pollution risk of surface water and soil by PHEs from goldmine tailings at each of the sampling sites, as well as for each of the five zones that was identified in the MLM mining area. Although several environmental pollution indices existed that have been used to quantify the extent of contamination by PHEs in an environment, the existing indices only quantify the potential pollution risks resulting from the contamination of either water or soil (Ngure et al., 2014; Mohammadi et al., 2018; Fan & Wang, 2017). Additionally, these environmental pollution risks indices could only be used to quantify the contamination of either water or soil by the different PHEs for a single sampling site or provided the total environmental pollution risk of the different PHEs for different sampling sites in a study area (Wu et al., 2014; Zhao et al., 2015; Fan & Wang 2017). However, a composite environmental pollution risk index, which provides a comprehensive understanding of the total pollution risk arising from the contamination of both surface water and soil by PHEs in a study area, has not been developed. Though Huang et al. (2013) and Ahmed et al. (2015) calculated health risk indices at specific sampling sites or averaged the health risk indices for different sampling sites in a study area; and later Chen et al. (2018) developed an Integrated health risk index for an entire study area, their focus was not on the environment. The Combine Risk Index for water and soil was quantified from the pollution risk indices that were computed for both the surface water and soil sampling sites. Therefore, this approach advances the knowledge on the assessment of environmental pollution and human health risk, as a result of the contamination by PHEs from gold mine tailings.

The combined environmental pollution risks condition for surface water and soil, together with the health risk condition for each of the 15 sampling sites were used to describe the overall risk classification condition in the MLM area. Therefore, to determine the environmental risks of PHEs from gold mine tailings on the environment at the MLM area, as well as to estimate the health risk to the local people from the exposure of the different PHEs that are present in the environment, the following research question was answered:

Sub Question: What is the environmental pollution risk and the health risk of the contamination by PHEs from gold mine tailings in the MLM area? To address this research question, the following objective was measured:

Objective: To determine the potential risks of PHEs from gold mine tailings on the environment and on human health in the MLM area.

7.2 Materials and methods for environmental pollution risk indices

The different environmental pollution risk indices were quantified in this study to determine the risk that may arise from the contamination of surface water and the uncultivated soil samples by PHEs from the gold mine tailings in the MLM area. The Igeo, SFPI and the NIPI were quantified for the different PHEs that were analysed in the surface water samples. The EF could not be computed for the surface water samples since the concentrations for the reference element; Zn was below the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) detection limits for close to 90% of the surface water samples. More so, very few measurements of the different PHEs were detected during the winter season, therefore, the environmental pollution risk indices were quantified for the measurements of the PHEs that were detected in surface water and in the uncultivated soil samples for the summer season.

7.2.1 Determination of the Geo-accumulation Index

The Geo-accumulation Index (Igeo) was originally proposed by Müller (1969) to measure the contamination of metals in bottom sediments within the aquatic environments. Since Muller (1969) proposed the Igeo, the Index has been used by many researchers worldwide to measure the extent of enrichments by heavy metals in stream sediments, as well as the level of enrichments of heavy metals in soils from different anthropogenic activities (Guimarães et al., 2011; Nowrouzi & Pourkhabbaz, 2014; Abdulqaderismaeel & Kusag, 2015; Barbieri, 2016; Fan & Wang, 2017; Muzerengi, 2017; Adimalla & Wang, 2018). The Igeo was calculated as follows:

$$I_{geo} = Log^2\left(\frac{Cn}{1.5\ Bn}\right) \qquad (6)$$

Where:

C_n is the measured concentration of the element in the water or the soil sample;

Bn is the geochemical background value of the element in the earth's crust (Herselman et al., 2005); and the factor 1.5 is introduced to minimise possible variations in the background values due to lithological differences.

The calculated Igeo values for each PHEs for surface water and soils were classified using the seven modified descriptive quality classes devised by Müller (1969). The modified descriptive quality classes were based on the increasing Igeo values, which results from the increasing level of pollution by the PHEs from different anthropogenic activities at each of the sampling sites (Table 7.1). The highest class, which indicates the highest level of pollution, may indicate about a 100 fold enrichment factor above background values (Barbieri, 2016).

Table 7.1 Geo-accumulation Index classification with description of the seven quality classes of the level of pollution by PHEs for the different water or soil samples

Geo-accumulation Index classes	Igeo value	Description of the pollution level by PHES in water or soil
0	Igeo ≤ 0	PHEs at extremely low concentration indicating background concentration
1	0 < Igeo ≤ 1	PHEs at relatively low concentration, indicating a non-pollution condition
2	1 < Igeo ≤ 2	PHEs at low concentration
3	2 < Igeo ≤ 3	PHEs at moderate concentration
4	3 < Igeo ≤ 4	PHEs at significant concentration
5	4 < Igeo ≤ 5	PHEs at high concentration
6	5 > Igeo	PHEs at extremely high concentration

Igeo = Geo-accumulation Index; PHEs = potential harmful elements

7.2.2 Determination of the Enrichment Factor

The Enrichment Factor (EF) is an alternative index that is used to measure the magnitude of the contamination of PHEs in the soil. The EF is used to determine the origin of the different PHEs in soils, by comparing the measured concentration of the PHEs in soils against the background concentration of the PHEs in the earth's crust (Mahlangeni et al., 2016; Xu et al., 2016; Guo et al., 2017; Fan & Wang, 2017; Muzerengi, 2017; Gu et al., 2019). The soil is considered contaminated for a PHE if the concentration of the PHE in the soil is above the background levels. Therefore a high EF value above background values is an indication of an increased level of anthropogenic contamination (Wu et al., 2014). The EF was calculated using the formula, according to Hasan et al. (2013).

$$\mathrm{EF} = \left(\frac{\left(\frac{Metal}{zn}\right)sample}{\left(\frac{Metal}{zn}\right)background}\right) \tag{6}$$

Where:

$\left(\frac{Metal}{zn}\right) sample$ = the ratio between the concentration of the target element and Zn in the soil; and $\left(\frac{Metal}{zn}\right) background$ = the ratio between the concentration of the target element and Zn in the earth's crust.

The background concentration provides information about the natural concentration of the PHEs in soils, which may be expected before the onset of contamination of soils by anthropogenic activities. Once the natural concentrations of PHEs in soils have been established, it becomes possible to determine the extent of anthropogenic enrichments (Batwa-ismail, 2018). Thus, the background concentrations for PHEs in South African soils were obtained from a study conducted by Herselman (2007) on the concentration of selected trace metals in soils in South Africa. These background values (mgkg) were Cd (0.1), Cr (71.9), Ni (38.7), Pb (21.7), Zn (45.2), Cu (29.5), and Co (18). Since there were no background concentrations available for As and Se in South Africa, the metal composition estimates of the upper continental crust as determined by Rudnick (2014) were used for As and Se in this study. The metal composition estimates of the upper continental crust were (mgkg); Cd (0.09), Cr (92), Ni (47), Pb (17), Zn (67), Cu (28), Co (17.3), As (4.8), and Se (0. 09). Furthermore, to quantify the extent of the contamination of soils by the different PHEs, a reference element, (Zn) was used in this study since its background concentration is available in South Africa (Herselman et al., 2005; Mendiola et al., 2008).

The computed EF values were interpreted using the six modified categories formulated by Sutherland (2000). These categories were based on the level of enrichments of the PHEs at the different sampling sites (Table 7.2).

Table 7.2 Enrichment Factor classification with description of the six categories of the level of pollution by PHEs for the different water sampling sites

Enrichment Factor categories	EF value	Description of level of pollution by PHEs in water
1	EF ≤ 1	PHE at extremely low concentration indicating background contamination
2	1 > EF ≤ 2	PHEs at low concentration
3	2 > EF ≤ 5	PHEs at moderate concentration
4	5 > EF ≤ 20	PHEs at significant concentration
5	20 > EF ≤ 40	PHEs at a very high concentration
6	EF > 40	PHEs at an extremely high enrichment

EF = Enrichment Factor; PHEs = potential harmful elements

7.2.3 Determination of the Single Factor Pollution Index

The Single Factor Pollution Index (SFPI) measures the pollution condition of individual PHEs in water or in soils at the different sampling sites in a study area. The SFPI can further be used to determine which PHEs indicates the greatest pollution risk in soil within a study area (Kowalska et al., 2018).

The SFPI for each PHE was quantified using the formula according to Zhao et al. (2015).

$$P_i = \frac{Ci}{Si} \tag{7}$$

Where:

Pi is the Single Factor Pollution Index for each PHE that was measured at each sampling site;

Ci is the mean concentration of the PHEs in a soil sample; and

Si is the background concentration of the PHEs in the earth's crust.

The calculated SFPI values were classified using five modified categories according to Zhao et al. (2015). These five categories for which the SFPI values were classified against were based on the contamination level of the different PHEs in water or in soils at each sampling site (Table 7.3).

Table 7.3 Single Factor Pollution Index classification with description of the five categories of the level of pollution by PHEs for the different water or soil sampling sites

Single Factor Pollution Index categories	*PI* value	Description of the level of pollution by PHEs in water or soil
1	$Pi \leq 1$	PHEs at extremely low concentration, indicating a non-pollution condition
2	$1 > Pi < 2$	PHEs at low concentration level indicating a low level of pollution
3	$2 \geq Pi < 3$	PHEs at moderate concentration, indicating a moderate level of pollution
4	$3 \geq Pi < 5$	PHEs at high concentration, indicating a strong level of pollution
5	$Pi \geq 5$	PHEs at a very high concentration, indicating a very strong level of pollution

PI = Single Factor Pollution Index; PHEs = potential harmful elements

7.2.4 Determination of the Nemerow Integrated Pollution Index

The NIPI was used to measure the pollution condition of the total PHEs that were measured from the different sampling sites in the study area (Yang, et al., 2014; Zhao et al., 2015; Kowalska et al., 2018; Wang et al., 2019). To calculate the NIPI, the mean and maximum values of the SFPI were used according to Wang et al. (2019).

$$I = \frac{\sqrt{P_{i\,Max}^{2} + P_{i\,Ave}^{2}}}{2} \qquad (8)$$

Where:

I is Nemerow integrated pollution index at location I;

PI_{Max} denotes the maximum SFPI values; and

PI_{Ave} represents the average values of SFPI for each PHE.

Once the NIPI values have been calculated for each sampling site, they were then classified according to five environmental quality categories (Yang et al., 2014; Zhoa et al., 2015). These five modified categories were based upon the level of PHE pollution at a particular site (Table 7.4).

Table 7.4 Nemerow Integrated Pollution Index classification with description of the five categories of the pollution condition for the total concentrations of PHEs in each water or soil sampling site

Nemerow Integrated Pollution Index categories	I value	Description of the collective pollution level for the different PHEs for water or soil
1	$I \leq 0.7$	PHEs at extremely low concentration, indicating safe level
2	$0.7 < I \leq 1.0$	PHEs at relatively low concentration, indicating warning line pollution level
3	$1.0 < I \leq 2.0$	PHEs at low concentration, indicating low pollution level
4	$2.0 < I \leq 3.0$	PHEs at moderate concentration indicating moderate pollution level
5	$I > 3.0$	PHEs at high concentration, indicating a heavy pollution level

I = Nemerow Integrated Pollution Index at location I; PHEs = potential harmful elements

7.2.5 Determination of the combined environmental pollution risk index

The combined environmental pollution risk that may arise from the contamination of both the surface water and soil by PHEs from goldmine tailings in the entire MLM area was determined by quantifying a combined environmental pollution risk index for water and soil. The new index, the Combine Risk Index (CRI) for water (w) and soil (s) takes into account the combined pollution condition of surface water and soil by PHEs from gold mine tailings at each of the 15 sampling sites in the MLM area. The Combined Risk Index for water and soil; CRI ($w + s$) was computed from the NIPI values that were quantified for each of the different sampling sites for surface water and soils in the following manner:

Calculation of the Combined Risk Index (CRI) for water (w) and soil (s): To quantify the CRI (w + s) at each of the surface water or soils sampling sites the $NIPI$ values that were calculated for surface water and for soil were combined to obtain a Combined Risk Index for both water and soil.

$$CRI\ (w+s) = \sum_{i=0}^{n} I_i(w) + I_i(s) \tag{9}$$

Where:

CRI (w + s) is the Combine Risk Index for water and soil;

while I (w) and I (s) is the Nemerow Pollution Index at location i, which specifies the total pollution condition for all the PHEs that were quantified at each of the 15 sampling sites for either surface water (w) or in soil (s).

The computed CRI (w + s) values were classified using five pollution categories. These pollution categories were modified from the Water Quality Index (WQI) classification condition for drinking water quality according to Rakotondrable et al. (2017) (Table 7.5).

Table 7.5 Combined Risk Index classification with description of the five categories of the level of pollution by PHEs for the combined pollution risk condition of water and soil at the different sampling sites

Combined Risk Index Classes	***CRI* (*w* + *s*) values**	**Combined pollution risk condition for each site**	**Classification of zones**
1	$CRI \leq 10$	PHEs at extremely low concentration, indicating safe level	Green zone
2	$10 < CRI \leq 50$	PHEs at a low concentration, indicating a low level of pollution	Blue zone
3	$50 < CRI \leq 100$	PHEs at moderate concentration, indicating moderate pollution level	Yellow zone
4	$100 < CRI \leq 200$	PHEs at high concentration, indicating a high pollution level	Purple zone
5	$CRI > 200$	PHEs at extremely high concentration, indicating a high pollution level	Red zone

CRI = Combined Pollution Index; w = water; s = soil

7.3 Materials and methods for health risk indices

The human health risk indices were computed in this study to estimate the probability of an adverse human health risk from the exposure to PHEs in the environment in the MLM area. Since different PHEs may have different health risks in human bodies, the potential health risk of the different PHEs can be determined by quantifying the non-carcinogenic health risk, as well as carcinogenic health risk of the PHEs to humans (Chen et al., 2018; He et al., 2018). Therefore, the potential non-carcinogenic health risk, as well as the carcinogenic health risk to the local people who are exposed to the PHEs in the MLM area were quantified to determine the health risk that may arise from the ingestion of PHEs in an infusion made from sweet thorn leaves, which is used for medicinal purposes in the MLM area (Muhammad et al., 2011; Huang et al., 2014).

7.3.1 Determination of the non-carcinogenic health risk

The non-carcinogenic health risk was quantified in this study to determine the health risk of the local people from the exposure to PHEs that have the potential to cause a non-cancer effect. The non-carcinogenic health risk was determined by computing the Hazard quotient (HQ), for each of the individual PHEs, including Co, Cu, Fe and Zn. However, since As and Pb may also pose certain non-carcinogenic health risk to humans as a result of the ingestion of the PHEs in and infusion of sweet thorn leaves, the HQ was also computed for As and Pb in this study.

Hazard quotient

The HQ is defined as a measure of the ratio of the average daily intake (ADI) of the estimated amount of a PHEs, to the oral reference dose (RfDo) (WHO, 2010; Kamunda et al., 2016; Chen et al., 2018; Gu et al., 2019). In determining the HQ, there is a postulation, that, if the ratio of ADI of PHEs is equal or less than the RfDo, then the risk of a PHEs to human health will be minimum, but when ADI is above the RFDo, it may pose human health risk (Javed & Usmani, 2016). To calculate the HQ, the ADI of the

PHEs that can be ingested with a contaminated infusion of a sweet thorn leave per kilogram of body weight per day was first calculated.

Average daily intake of PHEs

The ADI of PHEs by the local people in the MLM area was determined by estimating the ADI of the PHEs that is ingested in an infusion of sweet thorn leaves per day. The ADI was computed on the fresh weight basis from the consumption of an infusion of sweet thorn leaves in the following manner:

$$ADI = \frac{C_{metal} \times W_{plant}}{BW} \tag{10}$$

Where:

ADI is the "Average Daily Intake" of PHEs in contaminated infusion of sweet thorn leaves;

C_{metal} (mg/kg) is the concentration of PHEs in contaminated leaves of sweet thorn;

W_{plant} (L per day) represents the daily average consumption of medicinal plants extracts; and

BW is the average body weight for an adult, which was considered to be 70 Kg in this study (Zhuang et al., 2009; Chen, et al., 2014; Huang et al., 2014).

The average daily consumption of an infusion made from leaves of sweet thorn was assumed to be 0.75 L. This value was computed from the daily average consumption of a medicinal plant infusion for medicinal purposes by an adult, which is assumed to be 2 to 4 cups (470 ml to 940 ml) per day (Ausbrooks, 2019). Therefore, the middle number between 470 ml to 940 ml, which was 705 ml (0.75 L) was considered as the average daily consumption of an infusion made from leaves of sweet thorn in the study area.

The computed values of the ADI of PHEs that were computed in this study were interpreted in the following manner: If the ratio of ADI of PHEs to its RfDo was equal to or less than the RfDo, then the risk will be negligible. But if the ratio of ADI of PHEs to its RfDo was > 1 to 5 times the RfDo then risk will be low, while if the ratio of ADI of PHEs to its RfDo was > 5 to 10 times the RfDo, then the risk will be moderate. However, if the ratio of ADI of PHEs to its RfDo was > 10 times the RfDo, then the risk will be high, indicating potential health hazard to the public (Javed & Usman, 2016).

Once ADI was determined, the non-carcinogenic health risk that may arise from the consumption of PHEs in an infusion of sweet thorn leaves samples was determined by computing the HQ in the following manner:

$$\text{HQ} = \frac{ADI}{RfDo} \tag{11}$$

Where:

HQ is the Hazard Quotient;

ADI is the Average Daily Intake of PHEs per day; and

RfDo is the oral reference dose.

The RfDo values (mg/kg/day) that were used to calculate the HQ for the adult population were obtained from the South Africa's Framework for the protection of contaminated lands, as stipulated by Department of Environmental Affairs of South Africa (DEA, 2010). The RfDo values obtained were (Mg kg); As = 0.003; Cd = 0, 0005; Cr = 0.003; Co = 0.01; Cu = 0.037; Pb = 0.0036; Zn = 0.3; Ni = 0.02. The DEA (2010) has not established an RfDo for Fe, therefore the RfDo value used for Fe was = 0.7 and it was obtained from Javed & Usmani. (2016).

The HQ values quantified for the different PHEs were interpreted in the following manner: HQ values less than one (< 1) represented no risk of pollutants but HQ values greater than one (> 1) indicted high risk of pollutant with long term health effects (Xu et al., 2013; Singh & Kumar, 2017; Gu et al., 2019).

7.3.2 Determination of the Hazard Index

The HI was used to measure the combined potential non-carcinogenic health risks posed by the exposure to more than one PHEs in a sample (Chen et al., 2018; Gu et al., 2019). HI was determined by quantifying the cumulative probability of the HQ values for the different PHEs that were detected in sweet thorn leaves samples at a sampling site, including As, Pb, Co, Cu, Fe and Zn. Therefore, the greater the risk factors that were considered, the greater is the probability for a human health risk.

$$HI_i = \sum HQ_i = \frac{ADI_1}{RfDo_1} + \frac{ADI_2}{RfDo_2} + \frac{ADI_i}{RfDo_i} \qquad (11)$$

Where:

HI = Is the Hazard Index for exposure to PHEs 1 through i;

i = represented the HQ of each PHE;

HQ = Hazard quotient for the ith PHEs.

The HI values obtained for the different PHEs were interpreted similar to the HQ values: HI values less than one (< 1) represented no risk of pollutants but HI values greater than one (> 1) indicted high risk of pollutant with long term health effects (Xu et al., 2013; Singh & Kumar, 2017; Gu et al., 2019).

7.3.3 Determination of carcinogenic health risk

Carcinogenic health risk indicates the probability of an individual to develop any type of cancer from lifetime exposure to the different carcinogenic PHEs. For a PHEs which can cause cancer, there is the general assumption that there is no concentration to which humans are exposed to these PHEs which is considered safe, or without risk (Cal/ EPA, 2001; U.S. EPA, 2016). Even at very low exposure, there is increased risk of cancer. The cancer health risk was determined by calculating the excess lifetime cancer risk associated with the estimated exposure to As an Pb, according to equation 11 (Adimalla & Wang., 2018).

$$Cancer\ risk\ (CR) = ADI \times CSF \tag{12}$$

Where:

Cancer risk is the probability that an individual will develop cancer from the exposure to a potential carcinogenic PHEs;

ADI (mg/kg/day) is the average daily intake of the PHEs that can be ingested per kilogram of body weight per day;

and CSF (mg/kg/day) is the cancer slope factor for the PHEs. The carcinogenic risk could only be quantified for As and Pb, which was detected in sweet thorn leaves sample and has a cancer slope factor value. The CSF value for As (1.50) and Pb (0.0085) was obtained from Kamunda et al. (2016).

The carcinogenic risk values that were computed in this study were classified as follows: When Cancer risk is $< 1 \times 10^{-6}$, the carcinogenic risks to human health can be considered as negligible and therefore is not considered to pose a significant health risk. More so, if Cancer risk range between $1 \times 10^{-4} <$ Risk $< 1 \times 10^{-6}$, the risks is generally considered as an acceptable range. But Cancer risk $> 1 \times 10^{-4}$ is unacceptable and presents a high risk for the development of cancer (Fan & Wang, 2017).

7.3.4 Re-classification of the Hazard Index values for the different sampling sites

A re-classification of the health risk that may arise from the ingestion of the different PHEs in sweet thorn leaves samples was performed using a five-health risk class classification system. The health risk classes were modified from the 26-point scoring system of the Index of Habitat Integrity according to Dallas (2005). In this study, an HI score of zero denotes that there is little or no health risk of PHEs from the intake of sweet thorn leaves for medicinal purposes in the MLM area. Additionally, an HI score between 1 to ≤ 6 was indicative of a comparatively low health risk, while and HI score of > 6 to ≤ 10 signified a moderate risk. However, HI values from 10 to ≥ 20 revealed that there is a high risk from the intake of sweet thorn leaves samples in the area (Table 7.6).

Table 7.6 Categories for the re-classification of the Hazard Index values for the different sampling sites

Hazard Index classes	*HI* values	Health risk condition
1	$HI \leq 0$	No health risk
2	$0 < HI \leq 1$	Low health risk
3	$1 < HI \leq 6$	Moderate health risk
4	$6 < HI \leq 10$	High health risk
5	$10 < HI \geq 20$	Extremely high health risk

HI = Hazard Index

7.4 Determination of the overall classification of the environmental pollution risk condition and health risk condition at each site

A qualitative assessment of the environmental pollution risk condition and health risk condition for all the different sampling sites was undertaken to ascertain the overall risk condition at each of the sampling site, as a result of the exposure to the different PHEs by the local people in the entire MLM area. This assessment considered the combined environmental pollution risk condition as a result of the contamination of both the surface water and soil by PHEs from goldmine tailings, as well as the health risk condition that may arise from the ingestion of PHEs from sweet thorn leaves in the MLM area. This assessment was undertaken by calculating a Quality Assessment Score (QAS) for the combined environmental pollution risk condition, as well as the health risk condition at each of the sampling sites in the following manner:

1. For each of the pollution indicators that were accessed, a qualitative assessment was performed, by scoring the environmental pollution risk condition, as well as the health risk condition for each sampling site with a rating scale ranging from one to five.
2. A score of five was indicative of an extremely high pollution level at a site, with an extremely high health risk from the exposure of PHEs in the area. More so, a scale of 4 was indicative of a high level of pollution, as well as a high health risk condition, while a scale of 3 represented a moderate pollution risk and a moderate health risk of contamination. Furthermore, where the pollution condition and the health risk condition were relatively lower at a particular site, as compared to the rest of the sampling sites, a scale of 2 was used to represent the state of pollution and health risk at the site. But a scale of one indicated a good quality site where there was a negligible environmental pollution risk or a negligible health risk, from the exposure to the contamination.
3. After the different indicators of pollution categories were scored, all the values for a particular site were then summed to provide the composite score. This QAS was then used to classify the overall risk level at each sampling site (Table 7.7).

Table 7.7 Classification of the overall environmental and health risk condition for each sampling site

Quality Assessment Score classes	**QAS values**	**Classification of the overall environmental and health risk condition for each sampling site**	**Classification of each site**
1	QAS ≤ 5	Relatively low risk	Green area
2	6 ≥ QAS ≤ 7	Moderate risk	Yellow area
3	8 ≥ QAS ≤ 10	High risk area	Red area

QAS = Quality Assessment Score

7.5 Results of environmental pollution risk indices for surface water

The environmental pollution risk indices values were computed for the measurements of the four PHEs, which were detected in some of the surface water samples during the summer season and which has a geochemical background value for elements in the earth’s crust in South Africa. The Igeo, SFPI and NIPI values that were computed provided the risk of contamination for surface water by the PHEs from gold mine tailings. The EF could not be computed for surface water since the element Zn, which is used in the calculation of the index, was below the instrument detection limit for close to 98% of the surface water samples.

7.5.1 Geo-accumulation Index

When the Igeo values were calculated for As, Co, Cu and Se that were present in the water samples, some variations were observed in the concentrations of the computed Igeo values. The Igeo values for Cu could be calculated at only 40% of the water samples, but for As, Co and Se, the Igeo values were computed for majority of the water samples (Table 7.8). The Igeo results for Co and Cu revealed that these PHEs were at extremely low concentrations (Igeo ≤ 0) in the water samples, which is an indication that the contamination was at background levels an did not reflect anthropogenic interference. For As, of the twelve water samples for which the Igeo values were calculated, the results revealed that the concentration of As in the water sample was low (1 < Igeo ≤ 2) for four of the water samples, which may indicate minimal anthropogenic contributions. In contrast to Co, Cu and As, the Igeo values for Se revealed extremely high concentrations (Igeo > 5) of Se in the water samples, which may indicate contamination from anthropogenic activities in the MLM area.

Table 7.8 Geo-accumulative Index values of the level of pollution by PHEs for the different surface water sampling site

Geo-accumulative Index **(Igeo)**				
Sites	**As**	**Co**	**Cu**	**Se**
S1	-1.5	-	-	-
S2	1.47	-3.43	-	8.30
S3	-	-3.43	-	7.21
S4	1.28	-3.43	-	7.80
S5	-	-0.26	0.44	7.91
S6	1.06	0.15	-3.15	-
S7	-0.53	-3.43	-4.15	6.80
S8	-	-3.43	-0.82	-
S9	-1.53	-0.11	-0.56	8.46

S10	-0.53	-3.43	-	8.30
S11	-	-	-0.56	-
S12	0.80	-2.43	-	7.53
S13	0.06	-3.43	-	-
S14	-0.53	-3.43	-	7.67
S15	1.80	-3.43	-	7.22

Igeo values in red = values above background levels, indicating different levels of anthropogenic interference

7.5.2 Single Factor Pollution Index

The SFPI results indicated variations in the pollution condition for each of the four PHEs that were detected at each of the different surface water sampling sites. The SFPI results for Co and Cu revealed that these PHEs were at extremely low concentrations (Pi < 1) at close to 80% of the water samples, indicating that the contamination was at background levels and therefore a non-pollution condition (Table 7.9). But a low concentration of Co (1 > Pi < 2) was evident for 20% of the water samples, while less than 15% of the water samples showed low concentration of Cu, which indicates a low contamination by Cu, as well as a moderate contamination for a single water sample (2 ≥ Pi < 3). When considering As, the SFPI results revealed a low concentration of As at 27% of the water samples, which showed that there was no form of anthropogenic interference (Pi < 1). A moderate concentration (2 ≥ Pi < 3) of As was evident for a single sample while a high concentration (3 ≥ Pi < 5) was evident for three of the surface waters samples. However, a very high concentration (Pi ≥ 5) by As was registered at a single water sampling site from where the surface water sample had been collected (Table 7.9). Conversely, very high (Pi ≥ 5) SFPI results were detected for Se at 80% of the water samples, which indicated a very high level of Se contamination of surface water, which may arise from anthropogenic activities.

Table 7.9 Single Factor Pollution Index of the level of pollution by PHEs for the different surface water sampling sites

	Single Factor Pollution Index (PI)			
Sites	**As**	**Co**	**Cu**	**Se**
S1	0.52	0.14	0.00	388.89
S2	4.17	0.14	0.00	472.22
S3	0.00	0.14	0.00	222.22
S4	3.65	0.14	0.00	333.33
S5	0.00	1.25	2.03	361.11
S6	3.13	1.67	0.17	0.00
S7	1.04	0.14	0.08	166.67
S8	0.00	0.14	0.85	0.00
S9	0.52	1.39	1.02	527.78
S10	1.04	0.14	0.00	472.22
S11	0.00	0.00	1.02	0.00
S12	2.60	0.28	0.00	277.78
S13	1.56	0.14	0.00	0.00
S14	1.04	0.14	0.00	305.56
S15	5.21	0.14	0.00	223.33

PI values in red = increasing pollution condition of individual PHEs above background conditions

7.5.3 Nemerow Integrated Pollution Index

The NIPI results provided the total pollution condition for the four PHEs that were detected at each of the surface water samples. The NIPI results revealed that for 27% of the water samples the total PHEs were at extremely low concentrations, which indicates a safety pollution level (Table 7.10). The safe pollution condition at these sites may indicate that even though there might be some form of contamination from different anthropogenic activities at these sites, the contamination levels by the PHEs are at an extremely low level, which may not pose health risk to humans in the area. However, for the remainder of the 73% of the water samples, the total PHEs were at a high concentration, which indicates a high level of PHEs accumulation in the area. The high level of PHEs condition observed for the water samples, which were collected from the different sampling sites were extremely higher than the heavy pollution level category (I > 3) used by other researchers to classify the pollution condition in an area (Zhoa et al., 2015). Though the pollution level was very high for the 73% of the water samples, in particular, the pollution condition was exceptionally high for the first two water samples, which were collected from sampling sites SW1 and SW2 that were positioned at the high density mine tailing Zone 1.

Table 7.10 Nemerow Integrated Pollution Index of the total contamination by PHEs for the different surface water sampling site

Nemerow Integrated Pollution Index (I)		
Sites	**I value**	**Description of the collective pollution level for the different PHEs**
S1	200.45	PHEs at high concentration, indicating a heavy pollution level
S2	243.51	PHEs at high concentration, indicating a heavy pollution level
S3	27.80	PHEs at high concentration, indicating a heavy pollution level
S4	42.14	PHEs at high concentration, indicating a heavy pollution level
S5	45.55	PHEs at high concentration, indicating a heavy pollution level
S6	0.62	PHEs at extremely low concentration, indicating safe level
S7	39.11	PHEs at high concentration, indicating a heavy pollution level
S8	0.12	PHEs at extremely low concentration, indicating safe level
S9	66.34	PHEs at high concentration, indicating a heavy pollution level
S10	59.18	PHEs at high concentration, indicating a heavy pollution level
S11	0.13	PHEs at extremely low concentration, indicating safe level
S12	143.25	PHEs at high concentration, indicating a heavy pollution level
S13	0.21	PHEs at extremely low concentration, indicating safe level
S14	38.35	PHEs at high concentration, indicating a heavy pollution level
S15	28.70	PHEs at high concentration, indicating a heavy pollution level

7.6 Results of environmental pollution risk indices for uncultivated soil

The different environmental pollution risk indices values were computed for the measurements of the nine PHEs that were detected from the 15 uncultivated soil samples during summer. The EF, Igeo, SFPI, as well as the NIPI were computed to estimate the environmental risk that might arise from the contamination of soil by the different PHEs in the MLM area.

7.6.1 Geo-accumulation Index

The Igeo results indicated the extent of enrichment of soils by the different PHEs that were measured in the soil samples from the different sampling sites. The Igeo values for As, Pb and Co, revealed that these PHEs are at extremely low concentrations (Igeo < 0) in soils in the MLM area. These results indicated that the contamination of soils by As, Pb and Co is at background levels, and does not reflect contamination from the different anthropogenic activities that are practiced in the MLM area (Table 7.11). For Cr, Cu and Ni, the Igeo results revealed that the PHEs were at a low concentration for more than 60% of the soil samples, which indicated low levels of contamination of soils by the PHEs. A low concentration (1 < Igeo ≤ 2) of Cu was evident for two of the soil samples, while for a single soil sample there was a moderate concentration (2 < Igeo ≤ 3) of Cu and Cr, which indicated that the soil was moderately contaminated by the PHEs. In addition, there was a significant concentration of Ni for one soil sample (3 < Igeo ≤ 4), as well as a high concentration (4 < Igeo ≤ 5) for another soil sample. On the other hand, a low concentration of Zn was evident at 33% of the soil samples while two of the soil samples revealed a moderate concentration by Zn, with a significant concentration level for a single soil sample. For Cd, the Igeo results of two of the soil samples revealed a relatively low concentration of Cd, while 33% of the soil samples presented with low concentration by Cd, and another 33% revealed a significant concentration of Cd for the soil samples. More so, there was a high concentration (4 < Igeo ≤ 5) of Cd for a single soil sample, while an extremely high concentration (Igeo > 5) of Cd was also evident for another soil sample. The Igeo results further revealed a moderate concentration of Se at only a single sampling site. However, four of the soil samples presented with a significant concentration level by Se, while two of the soil samples indicated a high concentration of Se. An extremely high concentration of Se was also evident for close to 27% of the soil samples.

Table 7.11 Geo-accumulative Index values of the level of pollution by PHEs for the different soil sampling sites

	Geo-accumulative Index (Igeo)								
Sites	**As**	**Pb**	**Co**	**Cr**	**Cu**	**Ni**	**Cd**	**Se**	**Zn**
S1	- 2.17	-2.32	0.18	- 2.82	0.04	- 0.88	3.22	5.47	1.42
S2	-	-1.13	-1.45	-	- 0.23	- 3.48	2.00	3.03	2.00
S3	-	- 4.26	- 3.38	-	- 0.80	-	1.42	-	- 0.04
S4	-	- 2.70	-1.85	- 5.77	- 0.25	- 3.45	2.74	-	- 0.68
S5	- 3.17	- 3.02	- 5.70	2.11	- 0.54	4.61	1.74	-	1.39
S6	-1.22	- 2.59	0.72	- 7.23	1.14	0.02	3.12	4.74	2.44
S7	- 0.85	- 0.01	- 0.73	- 2.33	2.06	-1.03	5.66	5.32	3.74
S8	-1.71	- 2.39	- 0.09	-	- 0.29	- 0.98	1.00	3.37	- 0.52
S9	- 2.71	- 2.12	0.18	- 2.82	0.04	- 0.88	3.81	5.47	- 0.30
S10	- 3.58	- 2.67	- 0.40	- 3.05	-0.18	-1.61	3.22	3.81	0.12
S11	- 3.85	- 3.70	-1.49	-	- 0.75	- 3.66	0.42	2.74	0.55
S12	-	- 3.18	-1.68	-	- 0.93	-	0.42	4.37	-1.05
S13	- 4.58	- 2.10	- 0.03	0.11	-1.44	3.37	3.58	-	- 0.22
S14	- 5.17	-1.04	-1.19	-1.95	1.02	-1.32	4.81	5.43	2.58
S15	- 4.58	- 3.59	-1.39	- 4.91	- 0.25	- 2.67	1.74	3.15	1.00

Igeo values in red = values above background levels, indicating different levels of anthropogenic interference

7.6.2 Enrichment Factor

The extent of the contamination of the soils in the MLM area was also determined by computing the EF values for the eight PHEs that were detected in the uncultivated soils samples. The EF results for As, Pb, Cr and Ni reflected that these PHEs are at extremely low concentrations (EF ≤ 1) in the soil samples, which indicates background concentrations. Therefore, from the EF results, the contamination of soils by As, Pb, Cr and Ni might not have originated from anthropogenic activities that are practiced in the MLM area (Table 7.12). Additionally, a low concentration level (1 > EF ≤ 2) was observed for Co and Cu for a few soil samples, while the majority of the soil samples showed no form of contamination that may arise from anthropogenic activities. Conversely a moderate concentration (2 > EF ≤ 5) was computed for Cd for 40% of the soil samples, with significant concentration (5 > EF ≤ 20) for close to 27% of the soil samples. For Se also, a moderate to significant concentrations were registered for 27% and 60% of the soil samples, respectively, with an extremely high concentration level of Se for two of the soil samples (EF > 40).

Table 7.12 Enrichment Factor values of the level of pollution by PHEs for the different soil sampling sites

	Enrichment Factor (EF)							
Sites	**As**	**Pb**	**Co**	**Cr**	**Cu**	**Ni**	**Cd**	**Se**
S1	0.08	0.07	0.42	0.06	0.38	0.20	3.50	16.66
S2	-	0.11	0.09	-	0.21	0.02	1.00	2.04
S3	-	0.05	0.10	-	0.59	-	2.74	-
S4	-	0.25	0.45	0.03	1.35	0.15	10.69	-
S5	0.04	0.05	0.25	0.01	1.64	0.26	1.27	9.30
S6	0.08	0.03	0.30	0.00	0.41	0.19	1.60	4.93
S7	0.04	0.07	0.05	0.02	0.31	0.04	3.79	2.99
S8	0.44	0.27	1.35	-	1.18	0.73	2.87	14.90
S9	0.19	0.28	1.19	0.19	1.28	0.37	17.26	42.00
S10	0.08	0.14	0.69	0.12	0.81	0.30	8.57	12.93

S11	0.10	0.11	0.52	-	0.88	0.12	1.96	9.78
S12	-	0.23	0.65	-	1.09	-	2.76	43.00
S13	0.05	0.27	1.14	0.10	1.25	0.43	13.98	12.08
S14	0.00	0.08	0.07	0.05	0.34	0.07	4.67	7.16
S15	0.02	0.04	0.19	0.02	0.42	0.08	1.67	4.46

EF values in red = increased level of enrichments above background levels, which indicates different levels of anthropogenic interference

7.6.3 Single Factor Pollution Index

The SFPI results indicated variations in the level of pollution for the nine PHEs in soils at the 15 uncultivated soil sampling sites. The SFPI results indicated that As, Pb, Cr and Ni, were at extremely low concentrations ($Pi \leq 1$) in the soil samples, and did not reveal anthropogenic interferences. The only exception was a single soil sample for Pb and two soil samples for Ni, which reflected a low concentration of Ni ($1 > Pi < 2$) that might have originated from anthropogenic activities. More so, the was low concentration of soils by Co for 33% of the soil samples, while majority of the soil samples did not show any contamination by Co, which might have originated from anthropogenic activities (Table 7.13). Furthermore, there was low concentration of Cu for 53% of the soil samples, as well as 40% of the soil samples for Zn. Additionally, the concentration of Cu was high ($3 \geq Pi < 5$) for less than 20% of the soil samples, as well as for close to 27% of the soil samples for Zn, which indicated a high contamination by the PHEs. On the other hand, 70% of the soil samples tested indicated a very high ($Pi \geq 5$) concentration for Cd while all the soil samples from where Se had been measured registered a very high concentration of Se, which specified a very high contamination of soil by Se from anthropogenic activities in the MLM area.

Table 7.13 Single Factor Pollution Index values of the level of pollution by PHEs for the different soil sampling sites

Single Factor Pollution Index (*PI*)									
Sites	**As**	**Pb**	**Co**	**Cr**	**Cu**	**NI**	**Cd**	**Se**	**Zn**
S1	0.33	0.30	1.70	0.24	1.54	0.82	14.00	66.67	4.00
S2	-	0.69	0.55	-	1.28	0.13	6.00	12.22	5.99
S3	-	0.08	0.14	-	0.86	-	4.00	-	1.46
S4	-	0.23	0.42	0.03	1.26	0.14	10.00	-	0.94
S5	0.17	0.18	0.99	0.03	6.48	1.03	5.00	36.67	3.94
S6	0.65	0.25	2.47	0.01	3.30	1.52	13.00	40.00	8.11
S7	0.83	1.49	0.91	0.33	6.24	0.73	76.00	60.00	20.07
S8	0.46	0.29	1.41	-	1.23	0.76	3.00	15.56	1.04
S9	0.23	0.35	1.45	0.23	1.55	0.44	21.00	51.11	1.22
S10	0.13	0.24	1.13	0.20	1.33	0.49	14.00	21.11	1.63
S11	0.10	0.12	0.53	-	0.89	0.12	2.00	10.00	1.02
S12	-	0.17	0.47	-	0.79	-	2.00	31.11	0.72
S13	0.06	0.35	1.47	0.13	1.61	0.55	18.00	15.56	1.29
S14	0.04	0.73	0.66	0.43	3.04	0.60	42.00	64.44	9.00
S15	0.06	0.12	0.57	0.06	1.26	0.24	5.00	13.33	2.99

PI values in red = indicates increasing pollution condition of individual PHEs above background conditions

7.6.4 Nemerow Integrated Pollution Index

The NIPI results provided the total level of contamination for the different PHEs that were detected in the soil samples at each of the uncultivated soil sampling sites. The NIPI results revealed that the PHEs were at extremely low concentration only two of the soil samples, which suggested that the two sites belonged to the safety pollution level ($I \leq 0.7$). On the other hand, the PHEs were at high concentrations for the remaining 87% of the soil samples, which indicated a heavy pollution ($I > 3.0$) by the different PHEs (Table 7.14).

Table 7.14 Nemerow Integrated Pollution Index showing total contamination level by PHEs for the different soil sampling site

Nemerow Integrated Pollution Index (*I*)		
Sites	***I* value**	**Description of the collective pollution level for the different PHEs**
S1	33.70	PHEs at high concentration, indicating a heavy pollution level
S2	6.40	PHEs at high concentration, indicating a heavy pollution level
S3	0.65	PHEs at high concentration, indicating a heavy pollution level
S4	0.93	PHEs at high concentration, indicating a heavy pollution level
S5	18.58	PHEs at high concentration, indicating a heavy pollution level
S6	20.37	PHEs at extremely low concentration, indicating safe level
S7	31.40	PHEs at high concentration, indicating a heavy pollution level
S8	7.92	PHEs at extremely low concentration, indicating safe level
S9	25.92	PHEs at high concentration, indicating a heavy pollution level
S10	10.79	PHEs at high concentration, indicating a heavy pollution level
S11	5.08	PHEs at extremely low concentration, indicating safe level
S12	15.83	PHEs at high concentration, indicating a heavy pollution level
S13	8.06	PHEs at extremely low concentration, indicating safe level
S14	32.91	PHEs at high concentration, indicating a heavy pollution level
S15	6.79	PHEs at high concentration, indicating a heavy pollution level

7.6.5 Combined environmental pollution risk index

The combined environmental pollution risk resulting from the contamination of both surface water and soil by PHEs from gold mine tailings were determined by quantifying the Combined Risk Index values for each of the 15 sampling sites in this study. The Combined Risk Index values for both water and soil; $CRI\ (w + s)$ results revealed that a higher level of contamination by PHEs originated from surface water when compared to the contamination of soils in the study area. For each of the sampling sites, there were variations in the level of contamination for the $CRI\ (w + s)$ values that were quantified for both surface water and soil (Table 7.15). Although a considerable concentration of the PHEs were registered for each of the different sampling sites, the level of contamination by the PHEs was still at safe levels ($CRI \leq 10$) for close to 20% of the sampling sites, while a low concentration ($10 < CRI \leq 50$) of PHEs was evident at close to 40% of the sampling sites. The low concentration of the PHEs that were registered at 40% of the sampling sites may indicate a relatively low level of contamination by PHEs at the sites. However, there was a moderate concentration ($50 < CRI \leq 100$) of the PHEs at 33% of the sampling sites, with a high concentration level of the PHEs at a single sampling site. In contrast, the concentration of the PHEs was exceptionally high ($CRI > 200$) for the first two sampling sites that were positioned at the high density mine tailing Zone 1, which indicate a high level of contamination by PHEs in the area.

Table 7.15 Combined Risk Index for water and soil and the pollution condition classification for each of the sampling site

Zones	Site	*NIPI (w)*	*NIPI (s)*	Combined Risk Index *CRI* (*w* + *s*)	Description of the pollution risk condition for each site
Zone 1	S1	200.45	33.70	234.15	Extremely high pollution level
	S2	243.51	6.40	249.91	Extremely high pollution level
	S3	27.80	0.65	28.45	Low level of pollution
	S4	42.14	0.93	43.07	Low level of pollution
	S5	45.55	18.58	64.13	Moderate pollution level
	S6	0.62	20.37	20.99	Low level of pollution

	S7	39.11	31.40	70.51	Moderate pollution level
Zone 2	S8	0.12	7.92	8.04	Safe level
	S9	66.34	25.92	92.26	Moderate pollution level
	S10	59.18	10.79	69.97	Moderate pollution level
Zone 3	S11	0.13	5.08	5.21	Safe level
	S12	143.25	15.83	159.08	High pollution level
	S13	0.21	8.08	8.29	Safe level
Zone 4	S14	38.35	32.91	71.26	Moderate pollution level
Zone 5	S15	28.70	6.79	35.49	Low level of pollution

NIPI = Nemerow Integrated Pollution Index; *W* = water; *S* = soil

The means of the Combined Risk Index results that were computed for each of the five zones in the entire MLM area indicated that there was a level of risk as a result of the contamination by PHEs in all the five zones (Figure 7.1). The highest risk of pollution by PHEs was observed in Zone 1, which was in the high density mine tailing zone, the major pollutant area in the MLM area. The pollution risk from the contamination of both the surface water and soil by PHEs decreased beyond Zone 1. The least contamination level was observed at the control Zone 5, which was positioned in the upstream wind direction in relation to the high density mine tailing Zone 1. However, for the control Zone 4 the expectation that the contamination level will be low was not met, even though Zone 4 was in the upstream wind direction to the prevailing wind in relation to the major pollution area in Zone 1. The major contributor to the pollution in Zone 4 was an artificial dam in the area, which originated from the mine tailings and mining areas in Zone 1, which are the major pollutants in the MLM area.

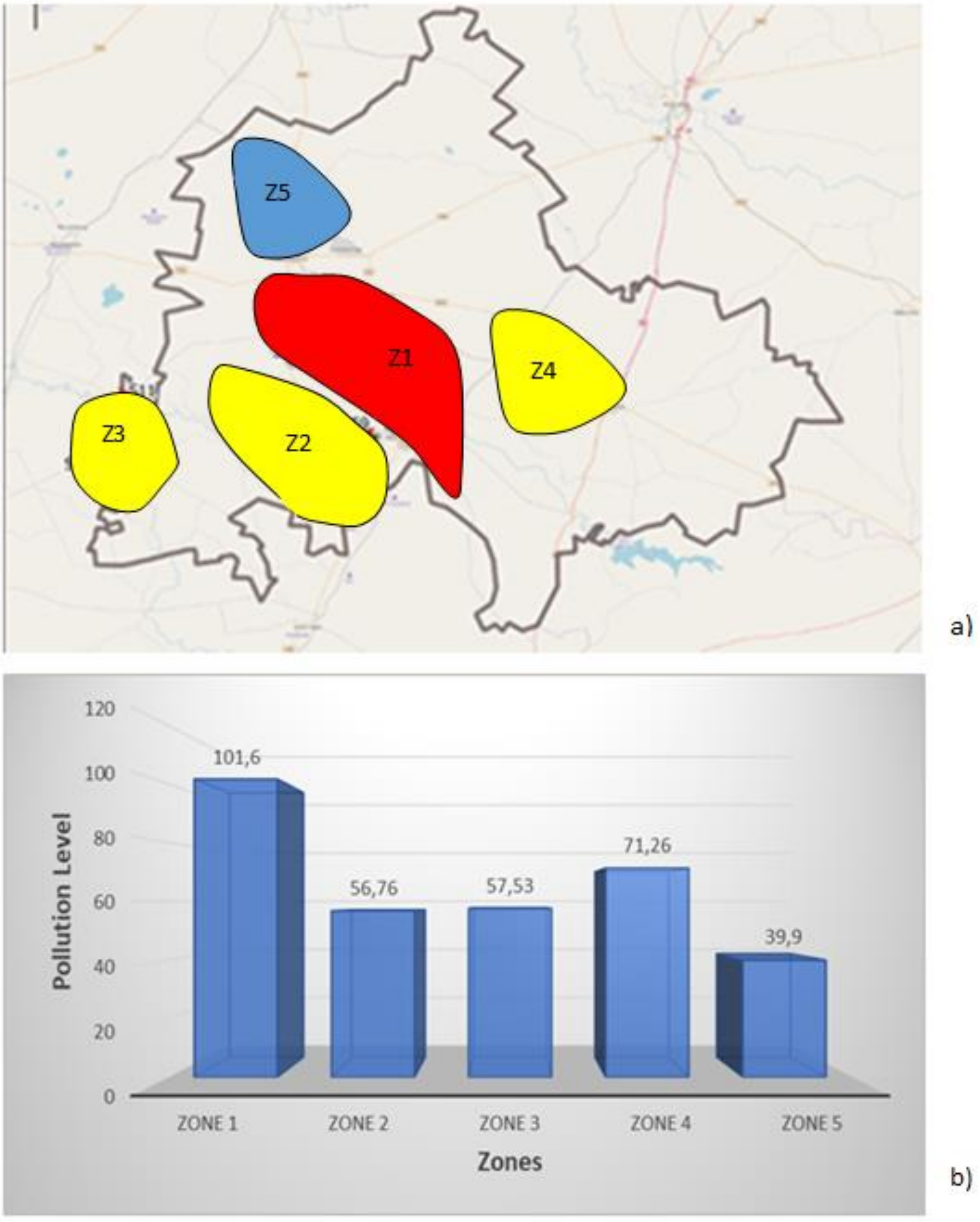

Figure 7.1 Combined pollution condition for water and soil for each of the five zones (a): position of the zones in study area (b): representation of the combined pollution condition

7.7 Results of human health risk indices

Several health risk indicators were quantified to determine the health risk that may arise from the intake of PHEs in an infusion of sweet thorn leaves samples by the local people in the MLM area. Both the non-carcinogenic and the carcinogenic health risks from the ingestion of PHEs in sweet thorn leaves were estimated.

7.7.1 Non-carcinogenic health risk

To determine the non-carcinogenic risk that may arise from the intake of individual PHEs, the HQ values were computed for the six PHEs that were identified in the sweet thorn leaves samples. The ADI values were first estimated since in quantifying the HQ Index, an estimation of the average daily intake of each PHE was required.

Average Daily Intake

The ADI values that were computed for the six PHEs specified the estimated concentration of each of the PHEs that can be ingested by humans in an infusion made from sweet thorn leaves. The ratio of the ADI computed for Co and Zn were less than or equal to their RfDo values for these PHEs, which indicates a negligible adverse health risk from ingesting these PHEs (Table 7.16). More so, the ADI ratio for Cu for 47% of the sweet thorn leaves samples, as well as 20% of the sw horn leaves samples for Fe, were 1 to 2 times higher than their corresponding RfDo values, which indicates a low risk from the intake of the PHEs by the local people. But for a single sweet thorn leave sample for Fe, indicated an ADI value above 5, which represents a low risk to the local people. However, the ratio of the ADI was more than 10 times higher than the RfDo value at two of the three sweet thorn leave samples from were As had been detected, as well as at three of the sweet thorn leaves samples for Pb. The high ADI values that were registered for some of the sweet thorn leaves samples for As and Pb, which were above their RfDo values indicated a high health risk of ingesting these PHEs from an infusion of sweet thorn leaves samples.

Table 7.16 Average daily intake of potential harmful elements in sweet thorn leaves

			Average Daily Intake (ADI)			
Sites	**As**	**Pb**	**Co**	**Cu**	**Fe**	**Zn**
S1	-	0.003	0.003	0.015	0.000	0.019
S2	-	0.048	0.004	0.028	1.455	0.144
S3	-	0.011	0.005	0.096	0.804	0.006
S4	-	0.004	0.002	0.024	0.321	0.000
S5	0.100	0.000	0.005	0.051	0.750	0.120
S6	0.400	0.041	0.004	0.061	0.096	0.169
S7	-	0.031	0.002	0.040	0.000	0.221
S8	-	0.010	0.005	0.034	5.282	0.141
S9	-	0.056	0.002	0.038	0.600	0.000
S10	-	0.000	0.001	0.027	0.096	0.081
S11	-	0.006	0.002	0.013	0.471	0.079
S12	-	0.000	0.002	0.043	0.214	0.146
S13	0.400	0.026	0.002	0.041	0.011	0.295
S14	-	0.016	0.003	0.036	0.000	0.054
S15	-	0.012	0.001	0.043	0.300	0.021

ADI values in red = ADI of PHEs above its RfDo values

Hazard Quotient

The HQ values provided the non-carcinogenic risk that may arise from the intake of individual PHEs. The HQ values were computed for As for only three of the sweet thorn leaves samples, where measurements were above the instrument detection limits. However, for Pb, Co, Cu, Fe, and Zn, the HQ values were quantified for all the 15 sweet thorn leaves samples (Table 7.17). The HQ values for Co and Zn, where below one, which indicated that there was no risk from the intake of these PHEs in an infusion made from sweet thorn leaves samples. For As, the HQ values for two of the sweet thorn leaf samples were above one, which poses a risk of ingestion of As in an infusion of sweet thorn leaves samples. For Cu, 53% of the sweet thorn leave samples had HQ > 1, but for Fe, the HQ values were more than one for only 26% of the sweet thorn leaves samples. The HQ values were higher for Pb, when compared to the remainder of the PHEs. The high HQ values for Pb, which were greater than one was detected at 73% of the sweet thorn leaves samples, which indicated a potential non-carcinogenic risk to humans when the leaves are used for medicinal purposes.

Table 7.17 Hazard quotient values of each potential harmful element for sweet thorn leaves samples for the 15 sampling sites

	Hazard Quotient (HQ)					
Sites	**As**	**Pb**	**Co**	**Cu**	**Fe**	**Zn**
ST1		0.89	0.32	0.41	0.000	0.06
ST2		13.39	0.43	0.75	2.079	0.48
ST3		2.98	0.54	2.61	1.148	0.02
ST4		1.19	0.21	0.64	0.459	0.00
ST5	0.36	0.00	0.54	1.39	1.071	0.40
ST6	1.43	11.31	0.43	1.65	0.138	0.56
ST7		8.63	0.21	1.07	0.000	0.74
ST8		2.68	0.54	0.93	7.546	0.47
ST9		15.48	0.21	1.01	0.857	0.00
ST10		0.00	0.11	0.72	0.138	0.27
ST11		1.79	0.21	0.35	0.673	0.26
ST12		0.00	0.21	1.16	0.306	0.49
ST13	1.43	7.14	0.21	1.10	0.015	0.98
ST14		4.46	0.32	0.98	0.000	0.18
ST15		3.27	0.11	1.16	0.429	0.07

HQ values red = HQ>1 = indicted high risk of pollutant with long term health effects

7.7.2 Hazard Index

The HI values specified the sum of the different HQ values that were computed for As, Pb, Co, Cu, Fe and Zn. The HI results for all the sweet thorn leaves samples were above the recommended limit of HI = 1 (Table 7.18). These results indicated that there was a potential non-carcinogenic health risk from the ingestion of these PHEs in an infusion of sweet thorn leaves samples collected from all the sampling sites. Even though the non-carcinogenic risk was higher than the recommended limit of HI = 1 for the 15 sweet thorn leaves samples, the HI results for particularly 40% of the samples were above 10. This high HI values of the sweet thon leaves samples indicated a higher non cancer risk to the local people in the MLM area from the ingestion of the different PHEs that were detected in sweet thorn leaves samples at each of the sampling sites.

Table 7.18 Hazard Index values of potential harmful elements for the sweet thorn leave samples for the 15 sampling sites

Site	Hazard Index (*HI*)	Description of the health risk condition
S1	1.68	High risk of pollution with long term health effects
S2	17.13	High risk of pollution with long term health effects
S3	7.29	High risk of pollution with long term health effects
S4	2.50	High risk of pollution with long term health effects
S5	3.75	High risk of pollution with long term health effects
S6	15.52	High risk of pollution with long term health effects
S7	10.65	High risk of pollution with long term health effects
S8	12.16	High risk of pollution with long term health effects
S9	17.56	High risk of pollution with long term health effects
S10	1.24	High risk of pollution with long term health effects
S11	3.29	High risk of pollution with long term health effects
S12	2.16	High risk of pollution with long term health effects
S13	10.88	High risk of pollution with long term health effects
S14	5.95	High risk of pollution with long term health effects
S15	5.04	High risk of pollution with long term health effects

7.7.3 Carcinogenic health risk

The cancer risk that could arise from the consumption of As and Pb in sweet thorn leaves by the local people of the MLM area were computed for the 15 sweet thorn leaves samples. The cancer risk values for As for the three sweet thorn leaves samples, as well as for 40% of the sweet thorn leaves samples for Pb exceeded the acceptable tolerable risk value of 1×10^{-4} as stipulated by the United states Environmental Protection Agency (U.S. EPA, 2010). These results suggested a significant cancer health risk to the local people in the MLM area because of ingestion of As, and Pb in and infusion made from sweet thorn leaves (Table 7.19).

Table 7.19 Carcinogenic health risk indices for As and Pb in sweet thorn leaves

Sampling sites	**Cancer health risk**		
	As	**Pb**	**Description of the cancer health risk condition**
S1	-	2.7×10^{-5}	Negligible health risk
S2	-	4.1×10^{-4}	Unacceptable and presents a high risk for the development of cancer
S3	-	9.1×10^{-5}	Negligible health risk
S4	-	3.6×10^{-5}	Negligible health risk
S5	1.6×10^{-3}	-	Unacceptable and presents a high risk for the development of cancer
S6	6.4×10^{-3}	3.4×10^{-4}	Unacceptable and presents a high risk for the development of cancer
S7	-	2.6×10^{-4}	Unacceptable and presents a high risk for the development of cancer
S8	-	8.2×10^{-5}	Negligible health risk
S9	-	4.7×10^{-4}	Unacceptable and presents a high risk for the development of cancer
S10	-	-	-
S11	-	$5.5 \times 10^{--5}$	Negligible health risk
S12	-	-	-
S13	6.4×10^{-3}	2.1×10^{-4}	Unacceptable and presents a high risk for the development of cancer
S14	-	1.3×10^{-4}	Unacceptable and presents a high risk for the development of cancer
S15	-	1.0×10^{-4}	Negligible health risk

7.7.4 Re-classification of the health risk indices for the different sampling sites

The different categories that were used to classify the health risk indices revealed variations in the health risk conditions from the ingestion of PHEs in the sweet thorn leaves samples. The health risk conditions that may arise from the ingestion of the total PHEs in a sweet thorn leaf samples, revealed that none of the re-classified HI results was within the no health risk category (Table 7.20). Three of the samples that were collected from sampling sites in Zone 1 and one sample each in Zone 2 and Zone 3 were in the low health risk category. The single sweet thorn leave samples in Zone 4 and Zone 5 were in the moderate health risk category. However, there was an extremely high health risk that could arise from the ingestion of PHEs in sweet thorn leaves at 20% of the sampling sites in Zone 1, as well as for 13% of the sites in Zone 2 and a single site in Zone 3. These results indicated that there was a potential non-carcinogenic health risk from the ingestion of these PHEs in an infusion of sweet thorn leaves samples collected from all the sampling sites.

Table 7.20 Health Risk Index values and health risk condition for the different sampling sites

Sampling sites	Health Risk Index values	Health risk condition
S1	1.68	Low health risk
S2	17.13	Extremely high health risk
S3	7.29	High health risk
S4	2.50	Low health rusk
S5	3.75	Low health risk
S6	15.52	Extremely high health risk
S7	10.65	Extremely high health risk
S8	12.16	Extremely high health risk
S9	17.56	Extremely high health risk
S10	1.24	Low health risk
S11	3.29	Low health risk
S12	2.16	Low health risk

S13	10.88	Extremely high health risk
S14	5.95	Moderate risk
S15	5.04	Moderate risk

7.8 Overall classification of the environmental pollution risk and health risk at each of the sampling site

The results of the overall risk level evaluation at each of the sampling sites in the MLM area indicated that there was some level of environmental pollution risk, as well as a health risk from the exposure of the different PHEs from the different sampling sites. However, at some of the sampling sites the risk was less but for other sampling sites, the risk level was significantly high.

In all the 15 sampling sites in the MLM area for which the overall risk level was evaluated, only 33% of the sites can be regarded as a relatively low risk area. Two sampling sites in Zone 1, (S4 and S5), which presented with a low risk of pollution, could be attributed to the fact that these sites were located at the peripheries of the high density mine tailing Zone 1 and the sites were only partially surrounded by mines and mine tailings (Table 7.21). On the other hand, the relatively low risk condition at sampling sites S10 in Zone 2 and S11 in Zone 3 may be attributed to the fact that these sites are positioned away from the high density mine tailing Zone 1. In addition, the sites are positioned in a forested area with few anthropogenic activities and thus limited pollution possibilities. Thus, people living in the vicinity of sampling sites S4. S5. S10 and S11 may not be at a high risk of pollution in the environment, as well as health risk of contracting diseases as a result of ingestion of PHEs in sweet thorn leaves. Furthermore, the control site S15 in Zone 5, was also classified as a comparatively low risk area, in which the environmental pollution condition is low and the health risk from the exposure of the pollution is moderate. The relatively low environmental condition risk at sampling site S15 may be attributed to the fact that this site was positioned at about 10 km to 12 km north of the high density mine tailings zone, with only a single waste rock dump and a mine in the vicinity of this sampling site. Also, the site was positioned after the sources of pollution in the area and therefore the effect of the prevailing wind blowing over the pollutant sources and unto the sampling site was negligible.

Some 47% of the sampling sites in the MLM area were also viewed as moderate risk areas. Out of the 47% of the sampling sites; S1, S3 and S6 are positioned in Zone 1. For sampling site S1, the level of the environmental pollution risk was extremely high, probably because of the pollution from Harmony mine, water treatment plant and a landfill site in the vicinity of the site. However, the health risk from the exposure to the pollution in the area was low. Most probably, the low health risk at S1 could be because the physical conditions in the soil in the area did not allow for easy uptake of PHEs by sweet thorn plants from the soil in the area and thus accounting for the low health risk condition from the ingestion of PHEs at the site. Sampling sites S3 and S6, which were also viewed as a moderate risk area in Zone 1, could result from the fact that these sites were positioned at the peripheral regions of the mine tailings and mines in the MLM area. The fact that these sites were only peripherally surrounded by mines and mine tailings led to low environmental pollution. However, the health risk from the exposure to the pollution in the area was high to extremely high. Most probably the conditions in the soil in the area were suitable for the uptake of the PHEs from the soil by the sweet thorn plants in the area.

Sampling sites S8 in Zone 2, S12 and S13 in Zone 3, as well as S14 in Zone 4 were viewed as a moderate risk area. The safe level for the environmental pollution at sites S8 and S11 may be attributed to the fact that these sites were positioned at about 5 to 7 km and 30 to 37 km respectively, from the high density mine tailing zone. Thus, the effect of the pollution by the mine tailings was less at these sites. Similar to sampling sites S3 and S6, the low environmental pollution risk condition and a high health risk of exposure to pollution at sites S8 and S11 could also arise from the fact that the soil in the area was suitable for the uptake of the PHEs by the sweet thorn plants in the area. Sampling site S14 was described as a moderate pollution area, in which the environmental pollution risk and health risk conditions were moderate. The surface water at this site was the major contributor to the moderate pollution condition at the site. The artificial dam at sampling site S14 is channelled from the high density tailing zone. The dam usually overflows its banks and into surrounding soils. Therefore, the moderate health risk in the area might also have resulted from the uptake of contaminants from the contaminated soil in the area.

Only three sites (S2, S7 and S9) out of the 15 sampling sites in this study area can be described as high risks areas. For sampling site S2 and S7, the high risk in the area could be attributed to the fact that these sites were situated at the centre of the high density mine tailing zone, and the sites were completely surrounded by mine tailings and mines in the area. Additionally, for sampling site S2, the high risk of pollution condition at this site could also be attributed to the disposal of sewage from St Helena settlement into the dam at the site. For Site S7, the high-risk condition in the area may be attributed to industrial activities in the area, such as non-operational Welkom Mine, WWTP, abattoir and Coca Cola brewery. When considering sampling site S9, the high pollution risk at this site may also be attributed to the contamination of surface water in the area, which was constantly polluted by WWTP effluent in the vicinity of the sampling site.

Table 7.21 Overall classification of the environmental pollution risk condition and health risk condition classification at each sampling site

Zones	Site	Environmental pollution risk condition for each site	Health risk condition for each site	Rating scale of pollution indicators	Sampling site risk level evaluation in MLM area
Zone 1	S1	Extremely high pollution level	Low health risk	XXXXX + XX = 7	Moderate risk area
	S2	Extremely high pollution level	Extremely high health risk	XXXXX + XXXXX = 10	High risk area
	S3	Low level of pollution	High health risk	XX + XXXX = 6	Moderate risk area
	S4	Low level of pollution	Low health rusk	XX + XX = 4	Relatively low risk area
	S5	Moderate pollution level	Low health risk	XXX + XX = 5	Relatively low risk area
	S6	Low level of pollution	Extremely high health risk	XX + XXXXX = 7	Moderate risk area
	S7	Moderate pollution level	Extremely high health risk	XXX + XXXXX = 8	High risk area
Zone 2	S8	Safe level	Extremely high health risk	X + XXXXX = 6	Moderate risk area
	S9	Moderate pollution level	Extremely high health risk	XXX + XXXXX = 8	High risk
	S10	Moderate pollution level	Low health risk	XXX + XX = 5	Relatively low risk area
Zone 3	S11	Safe level	Low health risk	X + XX = 3	Relatively low risk area
	S12	High pollution level	Low health risk	XXXX + XX = 6	Moderate risk area
	S13	Safe level	Extremely high health risk	X + XXXXX = 6	Moderate risk area
Zone 4	S14	Moderate pollution level	Moderate risk	XXX + XXX = 6	Moderate risk area
Zone 5	S15	Low level of pollution	Moderate risk	XX + XXX = 5	Relatively low risk area

X = pollution indicators

7.9 Discussion

Several pollution risk indices were quantified to ascertain the environmental pollution risk condition, as well as the health risk condition that may arise from the contamination of surface water and soils by PHEs, arising from gold mine tailings in the MLM area. The environmental pollution risk indices that were computed were then used to develop the Combined Risk Index for water and soil; $CRI\ (w + s)$, which was used to describe the total pollution condition for both the surface water and the soil for the different sampling sites, as well as for the five zones in the MLM mining area. On the other hand, the health risk that may arise from the contamination of PHEs from gold mine tailings in the MLM area was determined by estimating the non-carcinogenic, as well as the carcinogenic health risk from the consumption of PHEs from an infusion made from sweet thorn leaves for medicinal purposes.

The results of the overall classification of the sampling sites identified three sites, S2, S7 and S9, as high risk areas and therefore humans who are residing in the areas may be exposed to the contamination in the environment and they may also be at risk of contracting diseases as a result of ingestion of PHEs in sweet thorn leaves. However, five of the sampling sites (S4, S5, S10, S11 and S15) were classified as low risk areas and therefore the people who are living in the area may not be exposed to a very high level of contamination in the environment, as well as health risk from the consumption of PHEs from an infusion made from sweet thorn leaves for medicinal purposes.

When considering the overall level of contamination for the surface water and soil samples for the 15 sampling sites in the MLM area, as well as for the five zones, the $CRI\ (w + s)$ results indicated highest level of contamination for Zone 1, which was positioned within the high density mine tailing zone with major pollutants in the MLM area. The level of contamination decreased beyond Zone 1, with control Zone 5 registering the least level of contamination. The most probable reason for this observation could be that the mine tailings, as well as the mining activities are the main source of contamination in the MLM area.

The pollution risk indices results confirmed heavy pollution of surface water by Se in the MLM area, as well as a heavy pollution of soil by Cu and Zn, with an exceptionally heavy pollution of soil by Cd and Se in the MLM area. Contamination of surface water by Se in the MLM area may cause developmental deformities of larval stages of certain aquatic organisms, as well as mortality in extreme cases of contamination. On the other hand the contamination of soils in the MLM area by high concentrations of Cu may result in reduced chlorophyll content in plants, biomass and the gaseous exchange, which may ultimately result in the reduction of plant growth within the area (Saleem et al., 2020). Additionally high Zn levels in the soil may be toxic to plants that grow in the area, and can cause the blockage of xylem, prevent photosynthesis through alteration of electron transport with symptoms such as stunted growth of shoots, curling and rolling of young leaves, death of leaf tips and chlorosis (Mishra et al., 2020). On the other hand, Cd is a non-essential element that may affect plant growth and development by causing phytotoxicity, decrease nutrient uptake and prevent photosynthesis (Shahid et al., 2017).

The results of the health risk indices confirm a potential non-carcinogenic health risk and a carcinogenic health risk from the ingestion of an infusion made from sweet thorn leaves that is used for medicinal purposes. The hazard index values computed suggested that if local people consume an infusion made from sweet thorn leaves in the MLM area, they could suffer from severe health risk of As, Pb, Cu and Fe. The ingestion of As in sweet thorn leaves samples which is used for medicinal purposes, may cause immediate symptoms of acute arsenic poisoning, including vomiting, abdominal pain and diarrhoea from a long-term exposure to high levels of inorganic arsenic, which are usually observed in the skin, including pigmentation changes, skin lesions and hard patches on the palms and soles of the feet (WHO, 2018). Long-term ingestion of arsenic by the local people in the MLM area may also result in adverse health effects, including developmental effects, diabetes, pulmonary disease, and cardiovascular disease. Additionally, when Pb is consumed in the sweet thorn leaves samples, it may result in lead poisoning to the local people. Lead poisoning may result in further health complications including oxidative stress and DNA damage in human body, which may contribute to, anaemia, colic, headache, brain damage and even the central nervous system disorder (Akram et., 2019). Lead is also carcinogenic and can cause damage to the cardiovascular system, as well as organs, such as the kidney, brain and the gastrointestinal tracts (Meena et al., 2020). On the other hand, the ingestion of Cu in sweet thorn leaves may cause metal fumes fever, hair and skin discolorations, dermatitis, as well as respiratory tract diseases to the local people in the area (Shah et al., 2013). The high doses of Cu in the human bodies may result in the development of diseases such as Alzheimer and Parkinson diseases, as well as Wilson and Menke diseases (Huat et al., 2019; Pohanka, 2019). In addition, the intake of high doses of Fe from an infusion of sweet thorn leaves may result in iron overload to the local people in the MLM area.

Chapter 8

Overall Discussion, Conclusions and Recommendations

8.1 Introduction

The Matjhabeng Local Municipality area represents the centre of gold mining activities in the Free State Province, as a result of the extensive gold deposits in the area. The MLM area was chosen for this study because of the mining activities that has been practiced in the area for centuries, and these mining activities have resulted in the production of several gold mine tailings whose impacts on the environment and possible health risk on humans needed to be properly investigated. Of much concern is that, these gold mine tailings contain numerous toxic contaminants and most often, the gold mine tailings are very close to water bodies, agricultural fields and human settlements in the area. Therefore, these gold mine tailings pose a risk to the environment and the health of humans who are exposed to these contaminants in the MLM area. To determine the extent to which the contaminants from the gold mine tailings in the MLM area have contaminated surface water, groundwater, and soils in the area, as well as the plants which grow in the area, several indicators of contamination were assessed. The physical properties of water were measured for surface water and groundwater samples, as well as the physical properties of soil samples. Additionally, the concentration of potential harmful elements (PHEs) was measured in surface water, groundwater, soils, as well as in plants samples. These measurements of the different PHEs were then used to compute several pollution risk indices, which described the environmental risk as a result of the contamination by PHEs in the MLM area, as well as the health risk on humans from the exposure to the different PHEs in the area. This is the first of such a study in the MLM area, and in addition, a multidimensional approach was adopted to assess the extent of contamination of water, soil and plants by PHEs, as well as the possible environmental and health risk resulting from the contamination of PHEs in the area. Furthermore, the pollution risk indices that were quantified in this study were used to develop the Combined Risk Index for both water and soil, which was used to quantify the overall pollution risk from the contamination of both water and soil by PHEs at each of the five demarcated zones in the study area.

8.2 The environmental risk of contamination by contaminants from gold mine tailings for the different zones in the Matjhabeng Local Municipality Area

The findings from this study have revealed that the surface water, groundwater and the soils in the MLM area have been severely contaminated by several gold mine tailings contaminants. Besides, the sweet thorn and maize plants, which grow in the area have also absorbed these contaminants from the soil and transferred them to their leaves and seeds.

The variation in the contamination of the gold mine tailings contaminants were assessed for the different zones. For surface water there was no obvious trend that was detected in the level of contamination for the five zones, within the uncultivated land in the MLM area. The most probable reason is that most of the surface water that was studied was flowing waters, therefore the assimilative capacity of the water was evident. As the water flowed with high flow velocity and turbulence, there was bound to be some form of mixing and dilution of the contaminants in the water. Similar studies also observed this trend (Farhadian et al., 2015; Monfared et al., 2017; Turunen et al., 2020). However, a relatively higher contamination was observed for the control Zone 4 and Zone 5, which were positioned in the upstream wind direction in relation to the high density mine tailings zone, when compared to the level of contamination for Zones 1, Zone 2 and Zone 3, which were positioned in the downstream wind direction in relation to the high density mine tailings zone. Even though the level of contamination was highest for Zone 4, the source of contamination was from the high density mine tailings zone, since the contaminated Reitspruit dam water in Zone 4, is channelled from the Sand River, which has been contaminated by the mining activities in the high density mine tailings zone. On the other hand, the high level of contamination for Zone 5 may have its source from the Target Gold Mine Shaft, which is in the vicinity of Zone 5. The overall trend in the level of contamination for groundwater could not also be discerned, most probably because of the filtering effect of contaminants by the soil before the contaminants reach the groundwater level (Keesstra et al., 2012; EPA, 2015).

An obvious trend in the level of contamination for the five zones was observed for the uncultivated and the cultivated soils. The uncultivated soils within Zone 1 showed the highest contamination of the different contaminants, which may originate from the gold mine tailings in the high density mine tailing zone. This observed trend is supported in the reviewed literature (Djebbi et al., 2017; Gao, 2018; Lu et al., 2019). The level of contamination of the uncultivated soils decreased with distance beyond Zone 1, Zone 2 and Zone 3, which were positioned in the downstream wind direction in relation to the high density mine tailing zone. The spatial distribution of the PHEs in uncultivated soils in the MLM area, also indicated highest level of contamination of PHEs for Zone 1, with a decrease in the contamination beyond Zone 1. The possible reason could be that the mine tailings and the mining activities in the MLM area may be the dominant source of contamination to the soil in the area. Similar to the observed level of contamination for surface water, a high level of contamination of soil was also evident for the control, Zone 4, which also originated from the Reitspruit dam. In the same trend, the sweet thorn plants that are growing in Zone 1, also absorbed a higher concentration of PHEs from the uncultivated soils in the area, as such the highest level of contamination by PHEs was registered in Zone 1. The levels of uptake of the PHEs from the contaminated soils were lower for Zone 2 and Zone 3, as compared to Zone 1. This result concurred with the results of a similar study obtained by Jung (2008), as well as Huang et al. (2020). Therefore, humans who reside in the vicinity of Zone 1 and Zone 4, are exposed to the higher contaminations by contaminants in the area, which may cause several health risks. For example, when the local people use the sweet thorn plants for medicinal purposes, they may suffer from several health complications.

For the cultivated soils also, a high level of contamination by the different contaminants in the area were detected in Zone 1, which was positioned at about 5 km from the high density mine tailing zone, as compared to Zone 2, and Zone 4, which were positioned in the downstream wind direction in relation to the high density mine tailing zone. This finding is supported in literature from similar studies in other countries (Ngure et al., 2014; Djebbi, et al., 2017; Gao, 2018; Lu et al., 2019). The least contamination for the cultivated soil was registered in the control, Zone 3, which was positioned in the upstream wind direction in relation to the high density mine tailing zone. A similar trend was also observed for the uptake of PHEs from the cultivated soils within the different zones by maize plants, where maize plants that are growing closest to Zone 1 were more contaminated. As one moved away from the Zone 1, the rate at which the plants absorbed PHEs from the soil was lower as observed for Zone 2, Zone 3, as well as for the control zone for maize plants in the vicinity of Zone 4 (Jung, 2008; Huang et al., 2020).

The Combined Risk Index results resulting from the contamination of both surface water and soils by PHEs for the different zones concurred with the results obtained for the trend in the level of contamination for the different zones. Overall, the trend observed was that the risk of contamination decreased from Zone 1, Zone 2 and Zone 3, which were positioned in the downstream wind direction of the prevailing wind in relation to the high density mine tailing zone in the MLM area. The least risk level of contamination by contaminants from the gold mine tailings in the MLM area was observed for Zone 5, which was in the upstream direction to the prevailing wind in relation to the major pollution area in Zone 1. However, the total pollution risk of contamination was considerably higher for the control Zone 4. These results revealed that even though the total contamination of both water and soil in the MLM area by PHEs may also arise from other sources, such as weathering of parent materials, as well as anthropogenic sources, such as agriculture, waste water discharges from industries, as well as waste water treatment plants (WWTP), however, the contamination arising from the gold mine tailings and the mining activities are the major sources of contamination in the MLM area.

8.3 Human health risk of contamination by potential harmful elements

The different health risk indices that were computed confirm a potential non-carcinogenic health risk, as well as a carcinogenic health risk from the ingestion of an infusion made from sweet thorn leaves that is used for medicinal purposes by the local people in the MLM area. The hazard index values computed suggested that if local people consume an infusion made from sweet thorn leaves in the MLM area, they could suffer from severe health risk of As, Pb, Cu and Fe, which was similar to the results obtained from literature (Kamunda et al., 2016; Ngole-Jeme & Fantke, 2017; Kacholi & Sahu. 2018). The carcinogenic risk results for As and Pb at some of the sampling sites confirmed a probability of contracting cancer when sweet thorn leaves are ingested by the local people in the MLM area for medicinal purposes. Similarly, the carcinogenic risk values from ingesting As and Cd in food crops within Isiagwu, in Ebony state in Nigeria suggested a risk of contracting cancer over a life time period (Onyedikachi et al., 2018).

8.4 Overall risk classification of the different sampling sites in the Matjhabeng Local Municipality area

The overall environmental and health risks classification for each of the 15 sampling sites revealed three sites, which are of high health risks category in the MLM area. These sites included S1 and S7 in Zone 1, as well as S9 in Zone 2. People living in these areas are therefore exposed to a high risk of environmental pollution, as well as high health risk of contracting diseases from the ingestion of PHEs from sweet thorn leaves samples. On the other hand, seven of the sampling sites, including S1, S3, S6, S8, S12, S13, S14, are considered moderate risk areas, in which humans who reside in these areas will be exposed to a moderate level of contamination from the environment, as well as a moderate risk of contracting diseases from the ingestion of PHEs in sweet thorn leaves samples. Conversely, five of the sampling sites (S4, S5, S10, S11, S15) have been classified as a relatively low risk areas, where humans in the communities will only be exposed to low levels of contamination from the environment with a low health risk from ingesting PHEs in sweet thorn leaves.

8.5 Conclusions and recommendation for further research

Overall, the results obtained from this study have revealed that the surface water, groundwater, the soils, as well as the plants in the MLM area have been contaminated by PHEs from gold mine tailings. Although there are other sources of contamination by PHEs in the MLM area, the gold mine tailings, as well as mining activities could represent the most important source of PHEs contamination in the MLM area. Such contamination poses a risk to the environment, as well as the local people who are exposed to the contaminants in the area. Therefore, remediation measures need to be implemented by implicated stakeholders like the mining companies, as well as the local authorities to improve the quality of the surface water, groundwater and soil in the MLM area. This will prevent further deterioration of both the water quality, and soil quality, as well as prevent the uptake of contaminants, by particularly medicinal and food plants in the area. All these measures will in turn reduce the potential effect that the water and food may have on human health. This research provides essential evidence of environmental pollution, the potential environmental, as well as health risks of contamination by PHEs, and may act as the basis for remediation to mitigate the level of contamination in the MLM area.

Recommendation for further research

Based on the evidence and magnitude of the contamination in the MLM area, the results of this study laid the foundation for further research. These recommendations which also form the limitations of this study had to exist mainly because of the magnitude of the existing study, time, as well as the cost that would have been involved. Therefore, the following three areas are recommended for further studies.

1. The contamination of air by PHEs could not be included in this study, which would have been included in quantifying the Combined Risk Index to obtain a complete circle of contamination of PHEs in surface water, soil and air in the study area. Such a study will complement this multidimensional baseline study in the MLM area
2. The best sustainable and cost-effective mitigation measures to reduce the level of pollution could not also be included in the study. There is need for a research that will evaluate the various remediation options given the local context, carry out an effective Cost-benefit analysis and make scientifically supported remediation option or a combination of options.
3. A fuller soil characterisation using dimensionality reduction could not be included in this study to enrich the Principal Components Analysis assessment presented in this study. This has a wider application for bioaccumulation and toxicity studies in water and soil and their effects on the uptake of minerals by plants from soil.
4. Analysis of soil samples from the mine tailings itself could add more value to this study. The level of contamination of the mine tailings soils could not be measured as it was a challenge to get authorisation from the mining companies in the area to access the mine waste dumps that form the mine tailings.

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List of Appendices

Appendix A- Supplementary Data for Chapter 4

Table S1 Results of the mean concentrations (standard deviation) of exchangeable metal concentrations for uncultivated soil samples for the 15 sampling sites for summer and winter

Site/Metals	Seasons	As	Cd	Pb	Co	Cr	Cu	Fe	Ni	Se	Zn	Ca	Mg
S1	S	0.5 (0.13)	0.3 ± 0.05	0.7 ± 0.04	2.8 ± 0.03	ND	3.5 ± 1.98	1066 ± 10	ND	0.1 ± 0.01	8.1 ± 1.05	956.4 ± 10	502.8 ± 4
	W	ND	ND	ND	ND	ND	18.81 ± 0.53	3234 ± 9	ND	ND	ND	446 ± 18	661 ± 5
S2	S	ND	0.1 ± 0.02	0.2 ± 0.01	0.4 ± 0.01	ND	0.1 ± 0.01	1449 ± 7	ND	ND	ND	872.7 ± 9	202.5 ± 6
	W	ND	ND	ND	ND	ND	20.13 ± 0.28	393 ± 8	ND	ND	ND	10.9 ± 0.7	218 ± 1
S3	S	ND	0.4 ± 0.04	1.5 ± 0.78	1.8 ± 0.05	ND	2.8 ± 0.87	1930 ± 10	ND	ND	16.5 ± 1.99	953.6 ± 7	676.5 ± 14
	W	0.51 (0.02)	ND	ND	ND	ND	25.08 ± 0.12	7136 ± 58	ND	ND	ND	320 ± 2.5	1566 ± 13
S4	S	ND	0.1 ± 0	0.4 ± 0.25	2.1 ± 0.18	ND	8.6 ± 1.54	578 ± 10	ND	ND	25.2 ± 2.32	6937 ± 8	2262 ± 6
	W	ND	ND	ND	ND	ND	17.66 ± 0.08	3255 ± 53	ND	ND	ND	73.5 ± 1.7	1026 ± 10
S5	S	ND	0.1 ± 0.06	1.7 ± 0.87	1.5 ± 0.16	ND	0.1 ± 0.06	432.9 ± 9	ND	ND	29.2 ± 6.31	701.6 ± 10	301.6 ± 8
	W	0.34 (0.03)	ND	ND	ND	ND	24.93 ± 0.27	2762 ± 23	ND	ND	ND	51.9 ± 0.7	580 ± 6
S6	S	ND	ND	0.3 ± 0	2.1 ± 0.17	ND	1.5 ± 0.26	373.9 ± 9	ND	ND	25.6 ± 5.65	266.4 ± 3	291.1 ± 7
	W	0.20 (0.04)	ND	ND	ND	ND	17.96 ± 0.08	1431 ± 21	ND	ND	ND	2.9 ± 0.3	279 ± 2
S7	S	1.1 (0.60)	2.5 ± 1.02	4.5 ± 2.70	5.4 ± 1.01	21.2 ± 3.85	41.4 ± 2.87	8340 ± 5	7.3 ± 2.47	ND	460.7 ± 18.98	6507 ± 8	1457 ± 13
	W	ND	ND	ND	ND	ND	18.04 ± 0.13	2528 ± 28	ND	ND	ND	99.7 ± 1.4	564 ± 3

S8	S	1.5 (0.32)	0.7 ± 0.06	3.4 ± 0.32	7 ± 1.26	ND	8.7 ± 1.67	4041 ± 8	3.4 ± 1.08	ND	64.8 ± 6.98	2154 ± 17	658.4 ± 2
	W	ND	ND	ND	ND	ND	17.98 ± 0.31	2648 ± 42	ND	ND	ND	163 ± 4.3	669 ± 10
S9	S	ND	ND	ND	0.9 ± 0.01	ND	1.3 ± 0.09	545.9 ± 10	ND	1.3 ± 0.36	13.1 ± 2.09	541 ± 13	215.8 ± 5
S10	W	ND	ND	ND	ND	ND	14.86 ± 0.15	974 ± 7	ND	ND	ND	ND	203 ± 1
	S	ND	0.2 ± 0.05	2.2 ± 0.58	6.1 ± 1.52	ND	6.2 ± 1.06	9512 ± 12	3.6 ± 1.20	ND	15.5 ± 1.87	3134 ± 19	1897 ± 10
	W	0.14 (0.01)	ND	ND	ND	ND	17.67 ± 0.12	3394 ± 19	ND	ND	ND	65.5 ± 1.0	797 ± 1
S11	S	ND	0.1 ± 0.01	0.3 ± 0.03	1.8 ± 0.87	ND	2.2 ± 0.87	566 ± 8	ND	ND	2.7 ± 0.58	5572 ± 6	341.4 ± 9
	W	ND	ND	ND	ND	ND	14.84 ± 0.13	798 ± 38	ND	ND	ND	11.0 ± 0.5	301 ± 6
S12	S	ND	2.9 ± 1.07	2.7 ± 0.57	4.2 ± 1.44	4.9 ± 2.02	11.6 ± 1.36	13990 ± 15	10.5 ± 3.69	ND	94.7 ± 10.78	5506 ± 16	2291 ± 10
	W	1.13 (0.28)	ND	ND	ND	ND	17.30 ± 0.04	3089 ± 58	ND	ND	ND	857 ± 15.9	702 ± 5
S13	S	ND	0.4 ± 0.03	2.5 ± 0.98	5.4 ± 0.98	ND	9.1 ± 0.47	1414 ± 11	7.8 ± 2.54	ND	35 ± 6.57	1824 ± 13	1033 ± 10
	W	0.55 (0.15)	ND	ND	ND	ND	28.01 ± 0.11	2745 ± 15	ND	ND	ND	173 ± 2.3	508 ± 3
S14	S	ND	1.6 ± 0.78	1.6 ± 0.45	7.4 ± 0.68	0.6 ± 0.05	10.6 ± 2.54	7385 ± 12	2.8 ± 1.06	ND	25.9 ± 3.68	1558 ± 12	774.7 ± 12
	W	ND	ND	ND	ND	ND	17.13 ± 0.08	2401 ± 16	ND	ND	ND	65.5 ± 0.4	393 ± 2
S15	S	ND	0.2 ± 0.08	0.9 ± 0.08	6.6 ± 1.45	ND	5.3 ± 0.19	719 ± 9	3.8 ± 1.25	ND	16.9 ± 2.58	3238 ± 13	1610 ± 14
	W	ND	ND	ND	ND	ND	16.27 ± 0.28	1502 ± 11	ND	ND	ND	47.1 ± 0.5	496 ± 4

Table S2 Results of the mean concentrations (standard deviation) of exchangeable metal concentrations for cultivated soil samples for the 15 sampling sites for summer and winter

Sampling sites	As	Cu	Fe	Ca	Mg
CS1	0.43 (0.02)	27.53 (0.76)	115.80 (3.10)	444.87 (2.04)	38.51 (0.33)
CS2	0.39 (0.05)	26.7 (0.12)	446.47 (3.95)	25.47 (2.02)	40.59 (0.43)
CS3	0.30 (0.08)	37.47 (0.90)	765.47 (5.19)	159.13 (4.01)	41.15 (1.80)
CS4	0.18 (0.03)	27.27 (0.31)	595.67 (5.95)	116.80 (1.11)	40.33 (0.86)
CS5	0.07 (0.04)	26.87 (0.31)	589.33 (4.23)	415.47 (4.31)	49.46 (2.31)
CS6	0.12 (0.02)	27.00 (0.20)	712.80 (6.88)	173.13 (1.42)	41.82 (1.20)
CS7	0.22 (0.05)	36.87 (0.50)	77.20 (3.82)	152.87 (2.53)	40.36 (1.06)
CS8	0.25 (0.07)	26.53 (0.31)	185.53 (2.19)	107.40 (2.23)	37.63 (0.39)
CS9	0.28 (0.02)	26.73 (0.12)	435.00 (4.04)	134.33 (3.36)	38.99 (0.37)
CS10	0.32 (0.01)	37.67 (0.31)	884.13 (3.10)	46.47 (1.30)	42.18 (1.28)
CS11	0.19 (0.01)	27.40 (0.53)	618.93 (2.89)	63.27 (2.60)	48.21 (2.48)
CS12	0.15 (0.01)	26.60 (0.20)	296.13 (1.42)	165.27 (1.17)	39.99 (0.82)