GEOCHEMISTRY AND MINERALOGYOF SOILS AROUND ATOK, LIMPOPO PROVINCE, SOUTH AFRICA

by

KGOETJA ABRINAH RAMAKADI

DISSERTATION

Submitted in fulfilment of the requirements for the degree of

MASTER OF SCIENCE

in

GEOLOGY

in the

DEPARTMENT OF GEOLOGY AND MINING

FACULTY OF SCIENCE AND AGRICULTURE

(School of Physical and Mineral Sciences)

at the

UNIVERSITY OF LIMPOPO

Supervisor: Prof JN DUNLEVEY

Declaration

I declare that the dissertation hereby submitted to the University of Limpopo, for the Degree of Master of Science in Geology and Mining has not previously been submitted by me for a degree at this or any other university; I declare that this is my work and that all references contained herein have been duly acknowledged.

Signature:

Date: 2021/09/10

Pamakacli

Dedication

This study is dedicated to my late father Ramaseu Ramson Ramakadi and late sister Mmabagwe Rahab Ramakadi. To my father, you left me so early before you could reap the fruits of your labour, but I know that you are proud of the woman I have become. To my sister, I remember how we used to talk about the day of my graduation, how you always did my chores and take care of the baby so that I can write. Thank you for the love and encouragement you always given me. I love you both.

Acknowledgements

A research project of this magnitude depends on contributions from a wide range of people for its success. Firstly, I would like to express my wholehearted thanks to the Almighty God, the Enabler. Without His Will this dissertation would not have been possible.

I would like to take the opportunity to acknowledge the many people who have contributed in different ways to this report: I would like to sincerely thank my supervisor, Prof J.N Dunlevey, for his guidance, encouragement and support throughout this study, and especially for his confidence in me.

To my sister, Tselane Ramakadi, thank you for all the baby sitting duties when I went away for writing retreats.

To my mother, Lina Molatela Ramakadi, Siblings Selaelo, Lesiba, Masehwana, Makgomo, Tselane, and Mokgadi thank you for your understanding and encouragement in many ways.

To my husband, Lehlogonolo; I am most grateful for all your love and support - this helped me get through some difficult times in the course of this study. Thank you also for being so patient with me.

To my daughter, Omaatla, you make me want to be the best version of myself.

To my sister and mentor, Maropene Rapholo, thank you for believing in me and pushing me to be the best that you know I can be.

To my cousins Clodean and Mabatho Mothapo; your valuable assistance in correcting my research proposal and literature review is much appreciated.

To the Mining Qualifications Authority for their financial support during this study undertaken at the Department of Geology and Mining at the University of Limpopo.

To the Baroka ba Nkwana Community Engagement Committee thank you for your support and interest in this research.

Abstract

Mining activities for mineral resources over the years have, according to certain people, resulted in soil damage in the Atok area because of huge amounts of waste earth and rock that was brought to the surface, this waste often becomes toxic when it comes into contact with air and water. However, the geology of the area which is mafic in composition has caused major damage to the soil in the area as well. Due the removal process of desired mineral materials, soil textures have been destroyed, various nutrient cycles disturbed, and microbial communities altered, changing the vegetation and leading to the format of land in the area. Therefore, soil restoration of mining lands became a very important part of sustainable development strategies and also prescribed by law in South Africa. The geochemistry and mineralogy of soil samples taken from the area of Atok were studied using X-Ray Fluorescence (XRF) and physio-chemical parameter analysis. These methods are used for investigating the element and mineral associations and the distribution of heavy metals in these soils around the mine. The chemical and mineralogical data from soil and tailings were collected from each of the following areas around Atok: (Sefateng, Moonametsi, Mohlahlaneng, Sefateng Tailing Dam and Mafeo), the samples were collected at various depths; at each sampling points. The results of XRF analysis indicated that the soils are rich in MgO, CaO and Fe₂O₃ with minerals such as pyroxenes, plagioclase feldspar and occasional olivine being dominant. An excess of these minerals caused the soil to be infertile. The physio-chemical analysis showed that the soil texture is sandy, therefore this is the reason that the soil has low water holding capacity (27%) and low soil moisture (1.2%), the pH (8.50) and EC (<0.50 dS/m).

Keywords: Soil composition, chemical properties, heavy metal, contamination.

Table of Contents

CH.	APTER 1: OVERVIEW	1
1	. 1 Background	1
1	. 2 Introduction	1
1	. 3 Problem Statement	2
1	. 4 Motivation	2
1	. 5 Aims and Objectives	3
1	. 6 Objectives	3
1	. 7 Material and Methods	4
1	. 8 Data Analysis	4
1	. 9 Scientific Contribution of the study	4
1	.10 Ethical Considerations	5
1	.11 Organisation of the dissertation	5
1	.12 Conclusion	5
CH.	APTER 2: LITERATURE REVIEW	7
	.1 Introduction	
2	. 2 The Bushveld Igneous Complex	8
	2. 2.1 Geological setting of the Bushveld Igneous Complex	
	2. 2. 2. The Rustenburg Layered Suite	9
	2. 2. 3 The Eastern Bushveld Igneous Complex	11
2	. 3 Natural concentrations of trace elements in soils	
	2. 3. 1 Geochemical origin of trace elements in soils	12
	2. 3. 2 Pedogenic processes that translocate trace elements in soils	13
2	. 4 Behaviour of trace elements in soils	14
2	. 5 Natural and provoked mobilization of trace elements in soils and sediments	15
2	. 6 Trace element toxicity	16
2	. 7 Geochemical behaviour of certain trace elements	17
	2. 7. 1 Arsenic	17
	2. 7. 2 Cobalt	18
	2. 7. 3 Chromium	18
	2. 7. 4 Copper	19
	2. 7. 5 Nickel	19
	2. 7. 6 Lead	20
	2. 7. 7 Zinc	20
2	. 8 Limpopo Province as a Mining Province	21

	2. 9 Impact of mining activities on soil and the environment	21
	2. 10 Tailings disposal	23
	2. 10. 1 Environmental impact of mine tailings in South Africa	24
	2. 10. 2 Mine Soil Stockpiling	26
	2. 11 Enzyme Activities of the Soil	28
	2. 12 Acid mine drainage	30
	2. 13 Influence of mines on natural water resources	32
	2. 13. 1 Surface and ground water contamination by mining effluents	32
	2. 14 Rehabilitation of the land disturbed by mining activities	32
	2. 14. 1 Environmental rehabilitation measures	32
	2. 14. 2 Rehabilitation of mining activities	33
	2. 15 Techniques used for soil analysis	34
	2. 15. 1 X-Ray Fluorescence (XRF)	34
Cŀ	HAPTER 3: RESEARCH METHODOLOGY	35
	3. 1 Introduction	35
	3. 2 Description of the study area	35
	3. 3 Geology of the study area	37
	3. 3. 1 The Rustenburg Layered Suite	38
	3. 4 Description of the soil sampling procedures	39
	3. 5 Laboratory determination procedures	40
	3. 5. 1 Procedures for physio-chemical properties analysis	40
	3. 5. 1. 1 Soil Texture	41
	3. 5.1. 2 Water Holding Capacity	42
	3. 5. 1. 3 Moisture Content	44
	3. 5. 1. 4 Bulk Density	44
	3. 5. 1. 5 pH and Electrical Conductivity	45
	3. 5. 1. 6 Organic Carbon and Organic Matter	45
	3. 6 X-ray fluorescence analysis	45
Cŀ	HAPTER 4: RESULTS AND DISCUSSIONS	47
	4. 1 Introduction	47
	4. 2 Discussions of physical-chemical parameters	47
	4. 2. 1 Soil texture classes	47
	4. 2. 2 Water Holding Capacity	51
	4. 2. 3 Moisture content	51
	4 2 4 nH	51

4. 2. 5 Electrical Conductivity	52
4. 2. 6 Soil Organic Carbon	52
4. 2. 7 Soil Organic Matter	52
4. 2. 8 Available Phosphorus	53
4. 2. 9 Available Potassium	53
4. 2. 10 Bulk Density	54
4. 3 The X-Ray Fluorescence Results and discussion	54
CHAPTER 5: CONCLUSION AND RECOMMENDATIONS	63
5. 1 Introduction	63
5. 2 Recommendations	63
REFERENCES	64

List of Figures

Figure 2.1:	Speciation of trace elements in soil as a percentage of total conten			
	after Kabata-Pendias (1992)	15		
Figure 3.1:	The map of the study area	35		
Figure 3.2:	Location of the Atok area and Potlake Nature Reserve	36		
Figure 3.3:	Location map of the mines operating at BIC but Bokoni Platinum	Mine		
	is under Care and Maintenance with Crocodile River Fault (CRF),		
	Wonderkop Fault (WF) and Steelpoort Fault (SF) (Atlatsa Res	ource		
	Corporations, 2017)	37		
Figure 3.4:	A map showing sampling sites	38		
Figure 3.5:	Graph showing soil texture percentages	39		
Figure 3.6:	Image showing WHC procedure	40		
Figure 3.7:	The XRF Machine	43		
Figure 4.1:	Textural Triangle showing different textures of soil. Coloured do	ts		
	show the soil textures derived from the samples	46		
Figure 4.2:	A graphical illustration of concentration of MgO, CaO, Fe ₂ O ₃ and	d		
	Al ₂ O ₃	54		
Figure 4.3:	Graphical illustration of concentrations of P ₂ O ₅ , K ₂ O and Na ₂ O	55		
Figure 4.4:	Graphical illustration of concentrations of V, Cu, Zn and Ni	56		
Figure 4.5:	Graphical illustration of concentration of Cr	57		
Figure 4.6:	Graphical illustration of concentrations of Na ₂ O, K ₂ O and P ₂ O ₅	from		
	Potlake	58		
Figure 4.7:	Graphical illustration of concentrations of MgO, CaO, Fe $_2$ O $_3$ and	Al ₂ O ₃		
	of Potlake	59		
Figure 4.8:	Graphical illustration of concentration of Cr in Potlake	59		

List of Tables

Table 2.1:	Toxicity of some heavy metals (McBride 1994)	16
Table 3.1.:	WHC readings	41
Table 4.1:	Soil texture determination	45
Table 4.2:	Physio-chemical parameters results	47
Table 4.3:	XRF analysis results of the major metals as oxides	53
Table 4.4:	XRF analysis results of the control samples of Potlake Nature Re	serve
	(H Du Plessis, pers. Comm. 2019)	55

CHAPTER 1: OVERVIEW

1. 1 Background

South Africa accounts for approximately 80% of the world's platinum supplies, and the palladium production represents about 40% of the world's gross production. Platinum Group Minerals (PGMs) are concentrated in the 2 billion-year old Bushveld Igneous Complex, especially in limbs found in the Limpopo and North West Province (Hulbert and von Gruenewaldt, 1982). In South Africa's Bushveld Igneous Complex – PGM (Platinum Group Minerals) occurs in sufficient quantities to be economically extracted. However, the platinum mining process is labour and capital intensive as some 12 tons of ore must be extracted and processed to produce one troy ounce (31.135 g) of pure platinum (Africa Mining IQ, 2018).

Bokoni Platinum mine is located on the north-eastern limb of the Bushveld Igneous Complex, to the north of and adjacent to the Ga-Phasha Project. The mining rates were approximately 80,000 tonnes per month (tpm), at an average grade of 4.3 g/t. (Aanooraq Resource Cooperation, 2010) The production was split between the Merensky and UG2 Reefs at 50,000 and 30,000 tpm respectively, and once processed, produces approximately 150 000ounces (4665 kg) per annum (Aanooraq Resource Cooperation, 2010). Bokoni was the only eastern limb operation with significant Merensky production, being high in platinum grade with a 2:1 platinum: palladium ratio and a high UG2 reserve grade of 5.36 g/t.

Mining and smelting operations are coincident with the most important local sources of environmental pollution by metals and metalloids (Ettler et al., 2014). In particular, soil systems can be affected by mining, or smelting-related dust particles containing metallic contaminants (Castillo et al., 2013; Candeias et al., 2014; Ettler et al., 2014).

1. 2 Introduction

Although mining activities can create a major burden on the environment, expansion and growth within the mining sector leads to the development and economic growth. Thus, whatever may be the amount of wealth generated from mining, it should not be

at the cost of environmental sacrifice leading to a serious public health risk and ecological imbalance (Goswami et al., 2008). The exploitation of minerals influences different environmental domains of the exploited areas affecting the air, water and soil, as well as socio-economic and cultural environment. In the present study, the soil samples were analysed to infer the impact of mining on the quality of soil in and around Atok.

1. 3 Problem Statement

Mining is an activity and occupation concerned with the extraction of minerals. The ever-increasing demand for minerals and energy as well as advancement in extraction techniques has increased the mining of minerals in South Africa (Whiteman, 1982; and Schobert, 1987). Mining activities have generated large amounts of unconfined waste in Atok. The environmental impacts of such waste, specifically mine tailings, generally results from their low pH, and high metal content. The impact of mining activities on the environment in arid and semi-arid regions such as Atok has received less attention than temperate regions. The erosion of mine tailings in Atok poses risks to surrounding areas in two ways:

- i. Airborne release of heavy metals particulates from tailing sites:
- ii. Soil contamination with potentially toxic metals and metalloids.

Although there has been prolonged and extensive mining in the Atok Region, no definitive study has been undertaken to establish the mineralogy or chemical composition of soils and establish the background levels of undesirable elements. It is therefore not possible to evaluate the effects or potential for negative impact of mine waste such as tailings dumps and slime dams and differentiate between areas of natural low productivity and polluted areas.

The findings of this study will be of assistance in examining the influence of past and future mining activities and the geology of the area on the soil by investigating heavy metal and Mg levels in the mine tailings, sediments and agricultural soils.

1. 4 Motivation

• The platinum mine at Atok was one of the largest PGM's and chromite mines in South Africa (Africa Mining IQ, 2018). Mining, ore dressing and disposal of the tailings provide obvious sources of heavy metal contamination to areas around the mine. When the mine went under care and maintenance in December 2017 the community lost a major source of income. The community has very little fertile land and it is commonly believed that the soil has been contaminated by the mining.

Therefore, the following considerations provided justification:

- Assessment and analysis of the soil composition to determine the reason for soil infertility.
- ii. The challenges of tailing dams as maintenance is critical for sustainability of mine land rehabilitation;
- iii. As part of potential rehabilitation plan, there is a need to continuously monitor and examine vegetation around tailing dams;
- iv. Sustainable management and storage of mine waste soils is critical to maintaining soil health.

1. 5 Aims and Objectives

The aim is to determine soil composition in Atok Region of Sekhukhune District, Limpopo Province of South Africa.

1. 6 Objectives

The main objectives are to:

- Determine the mineralogy, chemical and physical properties of soil in Atok Region.
- ii. Evaluate the concentration of potentially deleterious elements in the specific components of the soils in order to predict bio-availability and the potential impact of ground water quality.
- iii. Provide a baseline study for the development of research that relates geology and soil composition to rural development and health.

1. 7 Material and Methods

Soil samples were collected from different sites of the area to characterize their geochemical and mineralogical properties and establish their influence on soil fertility for agriculture.

The soil samples were air-dried and gently crushed to pass a 2.0 mm sieve prior to analyses. Soil pH was determined with a glass/calomel electrode in 1:1 the soil.

X-Ray Fluorescence (XRF) employed to establish the major and trace element composition. The PW2400 XRF and Epsilon 3 equipment in the Department of Geology and Mining (University of Limpopo) was used for the analyses.

1. 8 Data Analysis

All analytical and other data were analysed using standard statistical and geochemical methods with appropriate software packages such as: Microsoft Excel, ArcGIS and Omnion software.

1. 9 Scientific Contribution of the study

Soil mineralogy is recognized as being very important in influencing the retention capacity, bioavailability of heavy metals and their mobility in specific environments. Mineralogy and geochemistry are important soil information governing many physicochemical processes in soil and the bioavailability of elements. Therefore, by establishing the mineralogy and geochemistry of the soil, it is possible to deduce the factors that are influencing soil productivity in the area. Potential toxic and negative components, such as trace and heavy metals, can be identified and methods of remediation identified. There is a scarcity of literature regarding the study area, and this research contributes to the literature of the area and be applicable to other areas of the Bushveld Igneous Complex. As there is only minimal information available in the scientific literature publication of results and finding will be appropriate and an addition to developing future research.

Community Engagement - The Baroka ba Nkwana Community Engagement Committee of Atok wrote a letter to the Department of Physics and Geology requesting help with the assessment of the barren soil areas which they believe might be affected by the tailing dam next to the area. The project will give back to the community of Atok by analysing the soil and giving them recommendations of how they can rehabilitate the soil and productivity to the benefit of the community.

Research - The outcomes of the research are being published (Ramakadi and Dunlevey 2020), and will contribute to the scientific literature by providing understanding of soils developed on mafic igneous units in the Atok Area.

1.10 Ethical Considerations

No human or animal subjects' data were involved in the research.

1.11 Organisation of the dissertation

The dissertation is laid out as follows:

- i. Chapter 1 provides the introduction and background to the research problem and the objectives investigated in this study.
- ii. Chapter 2 reviews the literature on soil composition in a former mining areas, environmental impacts of tailing dams and rehabilitation strategies.
- iii. Chapter 3 presents the description of the study area, and the methodology used to collect and analyse data.
- iv. Chapter 4 presents results and a discussions of the data in Chapter 3.
- v. Chapter 5 presents the conclusions and recommendations.

1.12 Conclusion

As deducted from the background and the problem statement, the aim of this study is to determine soil composition in Atok Region of Sekhukhune District, Limpopo Province of South Africa the objectives laid out are to be dealt with in various chapters.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

South Africa accounts for approximately 80% of the world's platinum resources and the palladium production represents approximately 40% of the world's gross production (Africa Mining IQ, 2018). Platinum Group Metals are concentrated in South Africa's 2 billion-year old Bushveld Igneous Complex found in the Limpopo and North West Provinces (Africa Mining IQ, 2018). Platinum is found with other PGMs such as Palladium, Iridium, Osmium, Rhodium and Ruthenium. In South Africa's Bushveld Igneous Complex there is a limited number of other commercially valuable mineral deposits such as gold, copper and nickel. PGM occurs in quantities so that it is cost-effective to extract these metals exclusively.

Mining can result in degradation of soil physical properties, significant loss of organic matter and nutrients and hence diminishes soil productivity (Akala and Lal, 2001). Underground mining causes huge amounts of waste earth and rock to be brought to the surface. This waste material often becomes toxic when it comes into contact with air and water. Restoring the soil productivity and the establishment of sustainable vegetative cover are primary objectives of mine soil reclamation. In the process of open-cast mining, the area is first completely stripped of vegetation to remove overburden covering the reef. Soil loss is a regular occurrence at surface mines, especially older mines where soil management was not a priority at the onset of the mining operation (Zaccardelli et al., 2013). In some areas, soil was not even stripped prior to mining as it was not a requirement (Cogho, 2012). Adequate soil stripping, stockpiling and management of this material at an opencast mine is therefore of utmost importance. Without proper soil management, post-mining substrate might not only comprise soils but that might also limit the ability of the substrate to support a good vegetation cover (Mentis, 2006). Soil generation (paedogenesis) is a lengthy process that spans over several years (Strohmayer, 1999).

Therefore, it becomes imperative to review existing literature on:

- (i) The Bushveld Igneous Complex,
- (ii) The Limpopo Province as a Mining Province.

- (iii) Trace Elements,
- (iv) The impact of mining activities on soil and the environment,
- (v) Tailings disposal,
- (vi) The environmental impact of mine tailings,
- (vii) The mine soil stockpiling,
- (viii) The enzyme activities of the soil,
- (ix) The effects of contamination by wastewater from platinum mines,
- (x) The influence of mines on natural water resources,
- (xi) rehabilitation of the land disturbed by mining activities, Techniques used in determination of contaminants from mining effluents in soil.

2. 2 The Bushveld Igneous Complex

The unique geology of the Bushveld Igneous Complex has over decades attracted researchers from all over the world, resulting in the accumulation of a large body of knowledge and literature. Aspects that have received attention include the parental magmas of the Bushveld Igneous Complex (Davies et al., 1981; Sharpe, 1985), the formation of the chromitite layers (Cameron 1978, Kinnaird et al., 2002), and the fractionation processes that took place in the magma chamber (Barnes, 1986; Billhaus and Stumpfl, 1986, Eales et al., 1988). In addition, there are enigmatic features that are associated with the normal magmatic rocks of the Bushveld Igneous Complex. These features usually disrupt the rocks of the Bushveld Igneous Complex, and are useful in providing invaluable insight into the magmatic evolution.

A short overview of the stratigraphy of the Bushveld Igneous Complex is presented, followed by the regional geology of the eastern Bushveld Igneous Complex and lastly the local geology of the study area.

2. 2.1 Geological setting of the Bushveld Igneous Complex.

The Bushveld Igneous Complex was emplaced into the Kaapvaal Craton as a series of sheet-like intrusions injected into metasedimentary rocks of the Transvaal Supergroup in the Paleoproterozoic Era approximately 2.06 billion years ago (Scoates, and Friedman, 2008). The Bushveld Igneous Complex is endowed with an enormous mineral wealth, which includes platinum group elements (PGE) (Lee, 1986; Tredoux, 1986; von Gruenewaldt et al., 1986; Viljoen, 1998; Schurmann, 1998; Cawthorn, 199;) chromite (Cameron and Emerson 1959; Cameron, 1977; Schurmann et al., 1988),

titanium and vanadium, nickel, cobalt and gold (Klemm et al., 1985; Cawthorn and Molyneux, 1986). The rocks of the Bushveld Igneous Complex cover an area of about 65000km² (Cawthorn et al., 1999) and are subdivided into: the mafic/ultramafic rocks of the Rustenburg Layered Suite (RSL), the felsic rocks of the Rashoop Granophyre Suite, Lebowa Granite Suite (Hall, 1932; SACS, 1980; Tankard et al., 1982). Only the Rustenburg Layered Suite will be discussed as this is where the PGM's are concentrated and mining takes place. The rocks of the RLS outcrop in four major lobes or limbs, namely, the eastern, western, far western and the northern lobe. These lobes are composed of well-defined cyclic sequences of layered ultramafic/mafic rocks, which are geochemically and lithologically variable, reflecting the unique mixing and differentiation process that occurred in the magma (Kruger and Marsh, 1982; Maiers and Barnes, 1998; Cawthorn et al., 2006).

2. 2. The Rustenburg Layered Suite.

Hall (1932) and later SACS (1980) grouped the cyclic units of the Rustenburg Layered Suite (RLS) into five zones, namely, the Marginal Zone (MZ); Lower Zone (LZ); Critical Zone (CZ), Main Zone (MZ) and the Upper Zone (UZ). The development and succession of rocks is distinctly different across all five zones.

The Marginal Zone, ranges in thickness from 0-250 m (Teigler, 1990), is the lowest of the five zones and is composed of fine-grained, quench-textured rocks such as norites, olivine-rich cumulates and pyroxenites (Sharpe, 1981). The Marginal Zone has been interpreted as representing the relatively rapid crystallization of magmas, which are variably contaminated and differentiated relative to subsequent magmas of the RLS (Cawthorn et al., 2006).

The rocks of the Lower Zone are dominated largely by rocks that are composed of olivine and orthopyroxene, with subordinate chromite, clinopyroxene, plagioclase and biotite (Eales and Cawthorn, 1996). The main rock types are dunite, pyroxenite and harzburgite, with intermittent occurrences of norites (Cameron, 1978; Viljoen and Schurmann, 1998). The thickness of the Lower Zone sequence varies markedly and is largely influenced by topography and structure of the underlying meta-sediment sand basement rocks (Cawthorn et al., 2006), also in certain areas structural complexities in the floor have caused localized attenuation of the Lower Zone.

The Critical Zones has been extensively discussed in the literature (Cameron and Desborough, 1969; Cameron, 1980; Eales et al., 1988; Kruger, 2005; Cawthorn et al., 2006). The Critical Zone is made up mainly of cyclic units (Cameron, 1982; Eales and Reynolds, 1986), and is divided into a pyroxenite-dominated Lower Critical Zone, and a norite-anorthosite-dominated Upper Critical Zone, rocks have plagioclase as a cumulus phase (Cawthorn and Walraven, 1998). The deposits of economic interest in the Bushveld Igneous Complex are found in the Critical Zone (Cameron, 1980) and in the Platreef of the Northern Limb of the Bushveld Igneous Complex (Viljoen and Schurmann, 1998; Manyeruke et al., 2005). The Critical Zone is host to some of the world's largest deposits of Platinum Group Elements (Kinloch, 1982; Cawthorn, 1999) as well as vast chromite deposits (Vermaak, 1986, 1997). There are three groups of chromitite layers (Cousins and Ferringa, 1964) in the Critical Zone, namely, the Lower Group (LG), the Middle Group (MG) and the Upper Group (UG), with up to fifteen individual chromitite layers (Cousins and Ferringa, 1964), The Lower Group has up to seven chromitite layers (LG-1 to LG-7), the Middle Group has up to five chromitite layers (MG-0 to MG-4) and the Upper Group three chromitite layers (UG-1 to UG-3). The development and characteristics of the chromitite layers differ in the eastern and western lobes of the Bushveld Igneous Complex (Hatton and Von Gruenewaldt, 1985; Lee and Parry, 1988). The economic deposits of the Platinum Group Elements are hosted mainly by the UG-2 chromitite layer and Merensky Reef.

The Main Zone can be subdivided into five well-layered, mineralogically, and texturally different subzones denoted A to E (Nex, 1998). The stratigraphic sequence of the Main Zone is geochemically distinct from the underlying Critical Zone, with cumulates of the Main Zone having REE contents that are similar to the marginal rocks (Sharpe, 1981; Maier and Barnes, 1998). The Main Zone sequence is dominated by norites, pyroxenites, and gabbronorites with some anorthosites (Von Gruenewaldt, 1973; Eales and Cawthorn, 1996; Mitchel, 1996). Major rock forming minerals are plagioclase and calcium-poor clinopyroxene (Von Gruenewaldt and Weber-Diefenbach, 1977) and minor amounts of quartz, alkali-feldspar and apatite (Maier and Barnes, 1998). The thickness of the Main Zone varies in both the eastern and western limbs and can reach a thickness of up to 4 440 m, which makes it the thickest of the four zones of the Rustenburg Layered Suite. The Main Zone in both the eastern the western limb of the Bushveld Igneous Complex is considered to be barren of

economically exploitable deposits (Barnes and Maier, 2002), while in the northern limb of the Rustenburg Layered Suite in Mokopani, the presence of economic Cu-PGE mineralisation has been reported by McDonalds et al. (2017).

The Upper Zone has a cumulative thickness of up to 2 000 m and hosts between 25-30 magnetite layers (Tegner et al., 2006). The magnetite layers are associated with anorthosite, troctolite and ferrogabbros layers (Molyneaux, 1970; Von Gruenewaldt, 1973; Klemm et al., 1985; Reynolds, 1985). The three subzones identified are:

- i) The apatite-poor, high Ti-magnetite Subzone A
- ii) The apatite-rich, high Ti magnetite Subzone B
- iii) The apatite-poor, low Ti magnetite Subzone C

2. 2. 3 The Eastern Bushveld Igneous Complex

A comprehensive account of the geology of the eastern Bushveld Igneous Complex is given by Cameron and Emerson (1959), Cameron (1980), Scoon and Teigler (1995), and Scoon and Mitchell, (2011). The Eastern Bushveld Igneous Complex presents the most complete vertical profile of the Bushveld Igneous Complex, where the different zones can be seen at the outcrop scale (Cameron, 1978). The eastern Bushveld Igneous Complex has been subdivided into three sectors: the western, the central, and the southern sectors. Two major faults, the Wonderkop and the Steelpoort faults occur between the western and central sectors, and between the central and southern sectors. The Central Sector shows a large lithological variation and is divided into Clapham, Winterveld and the Jagdlust Sections (Cameron, 1977). The development and succession of rocks, especially the chromitite layers, differs significantly in each sector (Hatton and von Gruenewaldt, 1987), making it difficult to correlate the chromitite layers because not all the chromitite layers are equally well-developed in each sector (Hatton and von Gruenewaldt, 1986).

2. 3 Natural concentrations of trace elements in soils

Over ninety-nine per cent of the element content of the earth's crust is composed of the "major elements" which are O, Si, Al, Fe, Ca, Na, K, Mg, Ti and P. The remainder of the elements in the periodic table are trace elements as their concentrations in the earth's crust do not generally exceed 0,1 per cent (1000 mg/kg) (Alloway, 1995). Trace elements can also be referred to as micro-nutrients which are those elements essential for growth and development of organisms (e.g. Zn, Mn, Cu, Fe, Mo and B). However, a micro-nutrient in excessive quantity can be toxic, while non-essential exogenous metals, for example Cd and Hg, are toxic at virtually all concentrations. Heavy metals refer to metallic elements with an atomic weight greater than Fe (55,8 g/mol) or to an element with a density greater than 5,0 g/cm³ (Pierzynski et al., 1994). Although trace elements are ubiquitous in soil parent material, soils can be contaminated by trace elements due to anthropogenic activities. According to Alloway (1995), the major sources of anthropogenic trace elements inputs are: metalliferous mining and smelting; agricultural and horticultural material; sewage sludge; fossil fuel combustion; metallurgical industries (manufacture, use and disposal of metals); electronics (manufacture, use and disposal of electronic equipment); chemical and other manufacturing industries; waste disposal, warfare and military training.

2. 3. 1 Geochemical origin of trace elements in soils

Trace elements occur in rock forming minerals due to isomorphic substitution or by fixation on free structural sites. Isomorphic substitution refers to the replacement of one of the major elements by a trace element ion in the crystal lattice of the mineral at the time of crystallization. The substitution is governed by the ionic charge, ionic radius and electronegativity of the major element and the trace element replacing it. Complete substitution can only take place when there is a difference of less than 15 per cent in the ionic radii of the replacing ions and when the charge of the ions does not differ by more than one unit (Bohn et al., 1985). The natural concentration of trace elements in soils is a result of weathering that releases trace elements from their host minerals during soil formation (Kabata-Pendias, 1992). Soils represent a dynamic chemical system where mineral transformation occurs continuously. Weathering is the basic soil forming process and the degree of weathering that trace element containing primary minerals are subjected to, will influence the lithogenic metal content of soils (Kabata-Pendias; 1986). Weathering can be defined as the physical disintegration and chemical decomposition of rocks (Alloway, 1995). Singer and Munns (1992), describe physical weathering as the process which breaks down rocks to smaller particle sizes. Processes such as freezing and thawing, uneven heating, abrasion and shrinking and

swelling (due to wetting and drying) break large particles into smaller ones. Plant roots that grow into thin cracks, or the formation of salt crystals in cracks, can force joints or cracks open until the rock breaks. Chemical weathering is the process that changes minerals from their original composition to new minerals and chemical components that are stable and equilibrated in the particular soil environment in the presence of water (Kabata-Pendias, 1986). The rates at which these reactions take place are directly related to temperature and water availability, thus chemical weathering is more pronounced in the humid tropics than in cold and dry areas (Alloway, 1995). Water increases the rate of chemical weathering as water contains weathering agents (e.g. CO₂, O₂, organic acids such as humic and fulvic acid, SO₂ (aq), H₂SO₄ and HNO₃) in solution and transports these to chemically active sites on mineral surfaces.

Rainwater is usually slightly acidic due to the presence of dissolved CO₂, or more acidic due to acid-rain forming agents. Rainwater lacks alkalinity and the slightly acidic rainwater is chemically aggressive and promotes weathering (Manahan, 1994). Typical chemical weathering reactions include: dissolution; hydration; dehydration; hydrolysis; oxidation; acid hydrolysis and complexation. These chemical weathering reactions are responsible for the conversion of rock forming minerals to soil minerals. According to White (1995), the rate at which chemical weathering of silicate minerals occur in the natural environment, depends on a number of factors, including mineral surface reactivity, the role of hydrologic heterogeneity on fluid residence times in soils, soil pH, vegetation and climate.

2. 3. 2 Pedogenic processes that translocate trace elements in soils

Paedogenesis is defined by Alloway (1995) as the process by which a thin surface layer of soil develops on weathered rock material, gradually increasing in thickness and undergoing differentiation to form a soil profile. The soil profile contains distinct layers (horizons) which differ, according to Jennings, Brink and Williams (1973), in moisture content, colour, consistency, structure, and texture. Soil formation is a function of climate, biological activity, topography, parent material and time (White, 1995).

Soil is a multicomponent system consisting of solid, liquid and gaseous phases as well as living organisms (Bohn et al., 1985). The solid phase is composed of inorganic

matter (primary and secondary soil minerals) and organic matter. The liquid phase or the soil solution is a water solution with a composition and reactivity defined by the properties of the incoming water and affected by fluxes of matter and energy originating from the soil solid phase, biological system and the atmosphere. The gaseous phase or the soil atmosphere is composed of the same gases as the atmosphere (CO₂, N₂ and O₂) as well as gases that arise from biological activity (Yaron et al., 1996). Natural translocation and accumulation of trace elements in soils are the result of soil processes which include leaching, gleying, podzolization, surface organic accumulation and ferralitisation (Thornton, 1999).

2. 4 Behaviour of trace elements in soils

According to Bourg (1995), the mobility of trace elements in soils depends on a complex network of interactions between aqueous and heterogeneous chemical reactions, as well as physical phenomena such as particle coagulation and flocculation. Bourg (1995), distinguished between soil chemical reactions that tend to increase trace element mobility in soils (e.g. dissolved inorganic and organic complexation) and reactions that delay trace element availability and transport (e.g. precipitation, adsorption, co-precipitation and sorption). The soil solution is the medium for these reactions, and the dynamic equilibria reactions which occur in soils (Lindsay 1979; Sparks 1995). Plants take up ions from the soil solution which can then be redistributed in the food chain. These ions are released back to the soil solution when the plants die and decompose. Ions in the soil solution can be sorbed on inorganic and organic soil components and these sorbed ions can be desorbed back to the soil solution. If the soil solution becomes over saturated with a certain ion, a mineral will precipitate, and a mineral will dissolve if the soil solution is under saturated with certain ions, until equilibrium is reached. Ions in the soil solution can be transported through the soil to the groundwater or ions can be removed through surface runoff. Upward movement of ions can occur through capillarity action, a process driven by evaporation and drying. Micro-organisms can remove ions from the soil solution. When these organisms die and the organic matter decomposes, ions are released into the soil solution (Thornton, 1999). Gases may be released to the soil atmosphere in soil pores or become dissolved in the soil solution.

2. 5 Natural and provoked mobilization of trace elements in soils and sediments

According to Kabata-Pendias (1992) the affinity of metals to the various soil components governs their mobility. Metals such as Cd and Zn that are generally more mobile, exist mainly as organically bound, exchangeable and water soluble species. Less mobile elements such as Pb, Ni and Cr are mainly bound in silicates or the residual fraction, while Cu and Mo occur predominately in organically bound or exchangeable soil fractions. The water soluble, organically bound and exchangeable soil fractions are the most mobile trace element occurrences in soils. Fig. 2.1 depicts the speciation of trace elements in soils. The mobility of metals in soils is strongly influenced by changing soil environmental conditions. According to Forstner and Kersten (1988) the solubility, mobility and bioavailability of particle bound metals can be increased by four main factors in terrestrial and aquatic environments:

- Lowering of pH. In general, most metal cations are most mobile under acid conditions with the exception of Mo that is more mobile under alkaline soil conditions.
- ii. Increased occurrence of natural or synthetic complexing agents which can form soluble metal complexes that will increase metal mobility.
- iii. Increasing salt concentrations result in an increase in competition for sorption sites on solid surfaces which increase the release of metals from sorption sites.

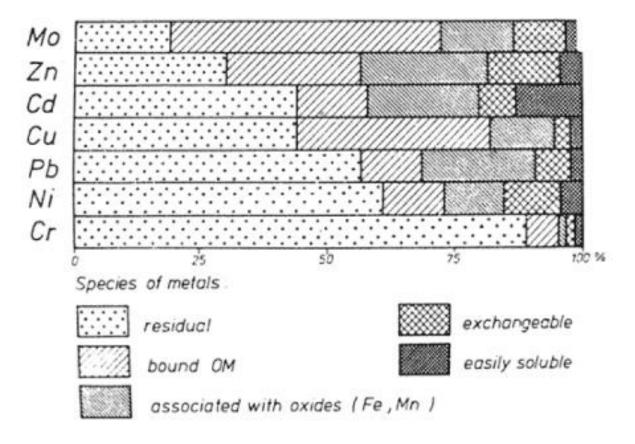


Figure 2.1: Speciation of trace elements in soil as a percentage of total content after Kabata-Pendias (1992).

2. 6 Trace element toxicity

At least 25 elements are considered essential to life; these include C, H, N, O and the macronutrients Na, K, Mg, S, P, CI, Si and Fe, of which the majority are metals. This trend also holds for the micro-nutrients, V, Cr, Mn, Fe, Co, Ni, Ca, Zn, Mo, Se, Fe. Trace elements or "heavy metals" refer to micro-nutrients and other non-essential elements that have low natural environmental concentrations. The micro-nutrients are essential to growth, but a micro-nutrient in excessive quantity can be toxic, while non-essential exogenous metals, for example Hg, are toxic at virtually all concentrations (Crounse et al., 1983). Any trace element can have an adverse effect on any organism if the dose is high enough. The biological function, phytotoxicity and mammalian toxicity character of some trace elements are presented in Table 2.1. According to McBride (1994) the elements listed in Table 2.1 that are more toxic to animals than plants (e.g. As and Pb) present the most insidious hazard to human health as these elements may accumulate in plants to concentrations that are toxic to animals or

humans even though the plants do not display any signs of phytotoxicity. The toxicity rating in Table 2.1 is dependent on the actual likelihood or frequency of toxicity in the natural environment. For example, Mn has a low toxicity to plants but Mn- induced phytotoxicity (commonly occurring as high Mn²⁺ concentrations) can develop in wet soils. In comparison, Cr and Pb have a higher phytotoxicity rating, but are usually very insoluble in soils so that these elements rarely induce toxicity.

Table 2.1: Toxicity of common heavy metals (after McBride 1994)

Elements	Phytotoxicity		Mammalian Toxicity
As	Medium-High	(5-20 ppm)	High
Со	Medium-High	(15-50 ppm)	Medium
Cr	Medium-High	(5-30 ppm)	Medium
Cu	Medium- High	(20-100 ppm)	Medium
Ni	Medium-High	(10-100 ppm)	Medium
Pb	Medium	(30-300 ppm)	High
Zn	Low-Medium	(100-400 ppm)	Low-Medium

2. 7 Geochemical behaviour of certain trace elements

2. 7. 1 Arsenic

The average arsenic concentrations in soils range between 2.20 and 25.00 ppm worldwide (McBride, 1994). Arsenic occurs in soils in the +3 and +5 oxidation state, although -3 and 0 oxidation states are possible in strongly reduced soils and sediments. Arsenate (+5) represents the oxidized state and occurs in aerobic soils, while arsenite (+3), which takes forms such as As(OH)₃ is stable in anaerobic soils. The chemical behaviour of arsenate is similar to that of phosphate in soils as it is likely to be adsorbed by Fe, Mn and Al oxides, noncrystalline aluminosilicates, and, to a lesser extent, layer silicates. Arsenate adsorbs most effectively at low pH values and has therefore a low mobility in acid soils with a high clay or oxide content. However, in neutral to alkaline soils, especially if the soils are sodic, As may be mobile in the form of soluble Na arsenate. The oxidation of arsenite to arsenate is promoted by the

presence of microbes and Mn oxides. Arsenite adsorbs less effectively in alkaline soils than in acid soils, adsorption being most effective in soil pH ranging from 7 to 9. If toxic soils are subjected to anaerobic conditions, both co-precipitated or adsorbed arsenate and arsenite can be released into the soil solution by the dissolution of Fe and Mn oxides. Desorbed arsenate is then reduced to arsenite which is eventually converted to insoluble forms, causing As mobility first to increase and then to decrease if anaerobic conditions are maintained. When soils remain anaerobic for long periods, sulphides, formed under reducing soil conditions, may co-precipitate As in its lower oxidation state. Volatile alkylarsene compounds may also form under these conditions causing, a loss of As to the atmosphere or to air-filled soil pores.

2. 7. 2 Cobalt

The average cobalt concentrations in soils range between 1.6 and 21.5 ppm worldwide (McBride 1994). Cobalt occurs in soils in the +2 and +3 oxidation state. Co²⁺ is the dominant form in the soil solution. Cobalt preferentially associates with Fe and Mn oxides due to sorption and co-precipitation. Cobalt is strongly sorbed on Mn-oxides where Co₂+is oxidized to CoH, which results in a low mobility of Co in oxidized soils. Cobalt is usually found in association with Mn-oxides in soils where Co can replace Mn in the oxide structure. Under neutral soil conditions cobalt is less mobile than under acid soil conditions due to increased sorption of Co on oxides, silicate clays, organic matter, and possibly the precipitation of Co(OH)₂ Under strongly reducing conditions, the precipitation of Co-sulphides may inhibit mobility.

2. 7. 3 Chromium

The average Cr concentrations in soils range between 7 and 221 ppm worldwide. Chromium occurs in soils in the +3 (chromic) and +6 (chromate) oxidation state. CrH₂⁺ is the dominant form in the soil solution. The chromic cation is very immobile in soils as it complexes strongly with soil organic matter and sorbs even at relatively low pH values on oxides and silicate clays. In Fe-oxides, Cr³⁺ can replace Fe in the crystal lattice, and in higher soil pH conditions, Cr(OH)₃ precipitates, both processes reducing mobility. If the soil is not exceedingly acidic, the Cr⁺ form is very immobile in soils and thus the insoluble Cr²⁺ form dominates in most soil types, and it generally occurs as

insoluble hydroxides and oxides. The mobility and bioavailability of the chromate ion (CrOt) in soils is higher, as chromate is less strongly adsorbed by soil constituents. The chromate ion is very toxic and is stable at higher soil pH values, but generally most Cr⁶⁺ is spontaneously reduced to Cr²⁺under acid soil conditions in the presence of soil organic matter, as the organic material provides complexing groups which stabilise the chromic form. This reduction occurs more rapidly in acid soils than in alkaline soils.

2. 7. 4 Copper

The average Cu concentrations in soils range between 6.00 and 80.00 ppm worldwide (McBride 1994). Copper mainly occurs in soils as the divalent Cu²⁺ cation, although the reduction of Cu²⁺ (cupric) to Cu⁺ (cuprous) and CUD (metallic copper) can occur in reducing conditions, particularly when stabilizing halide or sulphide ions are present. Copper has a low mobility in reduced soils as the element is chalcophilic and forms insoluble minerals such as Cu₂S and CuS. In oxic soils, Cu²⁺ is also relatively immobile as copper is easily adsorbed on most colloidal soil material (e.g. Mn-, Fe- and Aloxides, silicate clays and humus). Adsorption increases with increasing soil pH. Above a pH of 6.00, precipitation of malachite or azurite may occur in soils with a sufficient Cu concentration. Organically bound Cu²⁺ is the least mobile of all organically bound divalent transition metals. Copper is rated to have a low mobility in near-neutral soils as the high-affinity of soil colloids for Cu²⁺ reduces the concentration of the element in the soil solution. In more alkaline soils, the mobility of copper may become significant due to the formation of soluble complexes of Cu²⁺ (hydroxy, carbonate and organic matter complexes) which are adsorbed to all lesser degree.

2. 7. 5 Nickel

The Average Ni concentrations in soils range between 4 and 55 ppm worldwide (McBride 1994). The Ni²⁺ oxidation state is the only stable form of nickel in the soil environment. The Ni²⁺ cation is comparable in geochemical behaviour with Cu²⁺, except that it is slightly less electronegative than Cu²⁺. However, nickel is several times more phytotoxic than Cu. Nickel is the smallest divalent transition metal cation and fits easily into octahedral sites of silicate clays and co-precipitates readily into Mn- and

Fe-oxides. Nickel also bonds preferentially with soil organic matter and bio accumulation of Ni in organic rich soils is pronounced. The mobility of Ni is rated as medium in acidic soils, but very low in neutral to alkaline soils, Ni sorption onto oxides, noncrystalline aluminosilicates and clay minerals increases above pH 6. Under reducing soil conditions Ni has a restricted mobility since Ni^{2 +} is incorporated into sulphides.

2. 7. 6 Lead

The average Pb concentrations in soils range between 10 and 84 ppm worldwide (McBride 1994). Lead exists principally in the Pb²⁺ oxidation state in soils. Lead is the least mobile heavy metal in soils, particularly under reducing or non-acid soil conditions. Lead is a strongly chalcophile element and is very immobile in reducing soil conditions as lead precipitates as insoluble sulphide compounds. In toxic soils, Pb solubility decreases with increasing pH, since at higher pH levels, complexation of Pb with organic matter, sorption of Pb on oxides and clays and precipitation of Pb carbonate, hydroxide or phosphates, are favoured. Manganese oxides in soils may also oxidize Pb²⁺ to the even less soluble Pb⁴⁺ ion which will further reduce the mobility of lead in oxic soils. Lead complexes strongly with soil organic matter and when introduced to soils, will bio-accumulate in organic rich topsoil. In alkaline soils however, the mobility of lead may be slightly increased due to formation of Pb-organic or Pb-hydroxy complexes.

2. 7. 7 Zinc

The Average Zn concentrations in soils between 17 and 125 ppm worldwide (McBride 1994). Zinc exists only in the Zn²⁺ oxidation state in soils. Zinc is the most mobile and soluble trace metal cation under acidic, oxic soil conditions, as Zn²⁺ is held in exchangeable forms on soil organic matter and clays. However, the mobility of zinc in neutral soils is significantly lower, since sorption on oxides and as well as complexation with soil organic matter, lowers the solubility of zinc. Zinc is not known to co-precipitate into octahedral sites of oxides and silicates. In alkaline soils, the mobility of zinc may increase since soluble Zn-organo and Zn-hydroxy anions may

form. If Zn is present in sufficient concentration, insoluble Zn-oxide, hydroxide or hydroxycarbonate precipitates will restrict the mobility of zinc. In anaerobic soils, the release of Zn²⁺ from dissolved Fe and Mn oxides may at first increase Zn mobility, but the mobility will finally be restricted by the precipitation of exceedingly insoluble ZnS (sphalerite).

2. 8 Limpopo Province as a Mining Province

Limpopo Province has a large number of mining industries due to the presence of numerous economic minerals. Atok area is renowned for its mining activities for PGMs, chrome, sulphites and gold production among others. Bokoni Platinum Mine, a member of Atlatsa Group, quarried. PGM bearing mineral ore in the area, which was a highly valued commodity in the metal industries for its wide application. According to 2008 economic data baseline survey report, the Mining Industries contribute approximately 60% of the national municipal district GDP (Municipality Draft IDP document 2012/17).

2. 9 Impact of mining activities on soil and the environment

Beside the socioeconomic benefits of mining, the activity poses huge threats to natural resources round the globe such as soil, water, air as well as aquatic and terrestrial animals including humans. For instance, Soil contamination in the vicinity of the Dabaoshan Mine, Guangdong Province, China was caused by a combination of Cu, Zn, Cd, and Pb, with tailings and acid mine drainage being the main pollution sources affecting soils (Maria and Azevedo, 2003). Contamination of the soil and water environment by heavy metals in the Former mining area of Rudňany (Slovakia) where high contents of heavy metals in soil and water result from long-term mining and smelting activities predominantly focused on copper and mercury production (Chibuike and Obiora, 2014). Therefore, water and wind pollution from mines and mine tailings pollute natural resources while damages by mining products such as pyrite (iron sulphite) occur when it oxidizes through bacterial action to produce sulphuric acid and leads to the production of acid mine drainage, which constitutes a hazardous product to the soil and the environment (Pierzynski et al., 2005). The discovery of more mineral reserves will lead to an intensification of mining activities in the near future and result

in continuous production of similar or other by-products that are hazardous to the soil. Most of by-products particularly heavy metals, are toxic to living organisms primarily due to their protein-binding capacity and hence ability to inhibit enzymes (Renella et al., 2003). The nature and degree of inhibition of soil enzymes by metals is strongly related to soil fertility (Perez-de-Mora et al., 2006). Metals have a varying impact on soil enzyme activity depending not only on their total concentration in the soil but also on their capacity to interact with enzyme protein (Schlüter, 1993).

Strip or surface mining can completely eliminate existing vegetation, destroy the genetic soil profile, displace or destroy wildlife and habitat, degrade air quality, alter land use, and to some extent permanently change the general topography of the area mined (Rule and Iwashchenko, 1998). The community of microorganisms and nutrient cycling processes are upset by the movement, storage, and redistribution of soil (Biester et al., 2002). Generally, soil disturbance alters or destroys many natural soil characteristics, and may reduce its productivity for agriculture or biodiversity (Schlüter, 1993). Strip mining leads to exposure of nearby streams to the dangers of acidification with sulphuric acid thereby causing subsoil infertility and stream pollution, which could lead to the killing of fish, plants and aquatic animals that are sensitive to drastic pH shifts (Boominathan and Doran, 2003).

Elevated concentrations of mining pollutants such as heavy metals in soils have been reported to produce adverse effects on microorganisms and microbial processes (Biester et al., 2002). Among soil microorganisms, mycorrhizal fungi are the only ones providing a direct link between soil and roots, and can therefore be of great importance in metal availability and toxicity to plants (Schlüter, 1993). An understanding of the various aspects of interaction between heavy metals and mycorrhizal fungi is therefore crucial particularly in soils with different kinds and levels of metal pollution. Such interactions include the effects of heavy metals on the occurrence of mycorrhizal fungi, heavy metal tolerance of these microorganisms, and their effect on the metal uptake and transfer of plants (Schlüter, 1993; Leyval et al., 1997). However, limited study of the mechanisms involved in metal tolerance, uptake and accumulation by mycorrhizal hyphae and endo- or ecto-mycorrhizae have been documented (Leyval et al., 1997).

Mining can contaminate soils over a large area. Agricultural activities near a mining project may be particularly affected. According to a study commissioned by the

European Union: mining operations routinely modify the surrounding landscape by exposing previously undisturbed earthen materials. Erosion of exposed soils, extracted mineral ores, tailings, and fine material in waste rock piles can result in substantial sediment loading to surface waters and drainage ways. In addition, spills and leaks of hazardous materials and the deposition of contaminated windblown dust can lead to soil contamination. Human health and environmental risks from soils generally fall into two categories:

- i) contaminated soil resulting from windblown dust,
- ii) soils contaminated from chemical spills and residues

The dust can pose significant environmental problems at some mines. The inherent toxicity of the dust depends upon the proximity of environmental receptors and type of ore being mined. High levels of arsenic, lead, and radionuclides in windblown dust usually pose the greatest risk. Soils contaminated from chemical spills and residues at mine sites may pose a direct contact risk when these materials are misused. The displacement of settled communities is a significant cause of resentment and conflict associated with large-scale mineral development. Entire communities may be uprooted and forced to relocate often into purpose-built settlements not necessarily of their own choosing. Besides losing their homes, communities may also lose their land, and thus their livelihoods. Community institutions and power relationships may also be disrupted. Displaced communities are often settled in areas without adequate resources or are left near the mine, where they may bear the brunt of pollution and contamination. Forced resettlement can be particularly disastrous for indigenous communities who have strong cultural and spiritual ties to the lands of their ancestors and who may find it difficult to survive when these are broken (International Institute for Environmental Development, 2002).

2. 10 Tailings disposal

Even high-grade mineral ores consist mostly entirely of non-metallic materials and often contain undesired toxic metals (such as cadmium, lead, and arsenic). Therefore, the beneficiation process generates high-volumes of waste called 'tailings,' the residue

of an ore that remains after it has been milled and the desired metals have been extracted (e.g., with cyanide (gold) or sulphuric acid (copper)). If a mining project involves the extraction of a few hundred million metric tons of mineral ore, then the mine project will generate a similar quantity of tailings.

Tailings disposal options includes:

- i. the use of a wet tailings impoundment facility or 'tailings pond';
- ii. dewatering and disposal of dry tailings as backfill;

The first option (a tailings pond) is by far the most commonly used option, but the second option (dry tailings disposal) is, in most circumstances, the environmentally-preferable option.

Before the adoption of environmental laws and standards, many mining companies simply dumped tailings in the nearest convenient location, often nearby rivers and streams. Some of the worst environmental consequences of mining have been associated with the open dumping of tailings, a practice now nearly universally rejected.

2. 10. 1 Environmental impact of mine tailings in South Africa

Although mine tailings may have a potential economic value, they also pose a threat to the environment. Mine tailings tend to include minerals that contain heavy metals, and during weathering these heavy metals may be leached into the groundwater. Toxic elements such as arsenic and lead may be found in tailings and transported to the nearby areas to pose as an environmental hazard. Mine tailings are known to be associated with heavy metal pollution in water and soil (Baath, 1989). The quality of soil is compromised by heavy metal contamination whereby the high concentrations of heavy metals alter soil properties such as pH, colour and fertility. Microbiological activity can also be affected due to an increase in heavy metals in the soil (Baath, 1989). The soil that is most likely to be affected is the one closest to the tailings site since material from tailings can be easily transported to the environment (Barkouch and Pineau, 2015).

There are two main transporting agents which carry heavy metals from the tailings to the environment,

- i) Indented water (run-off and acid mine drainage),
- ii) wind.

When water interacts with sulphides from tailings it forms acidic water which dissolves heavy metals. If there are aquifers at shallow depths, the acid water may contaminate the groundwater resource. Heavy rain may also promote the transport of components from tailings because of the high influx of surface run off. Surface run-off can erode particles, transporting them to different environments. This displaces solid material from the tailings with ease since the particle size ranges from course to fine and these are readily entrained during run-off.

In a study of a number of mine tailings dams in the South Africa, Marsden (1986) concluded that tailings dams of 20 years and older, have an oxidised zone where leachable sulphate (and associated low pH water and other toxic substances) are virtually absent. This conclusion is supported by the fact that grass and other vegetation grows on many discard dumps. Using hand auger and test pit, the thickness of this zone was established to be ~10 m in sand dumps and 2 - 3 m in slimes dams. (Marsden 1986). Blight and du Preez (1997) studied the escape of acid and soluble salt pollution from decommissioned mine tailings dams and confirmed the presence of the oxidised tailings zone on the surface of slimes dams. The rate of formation of this zone is greater than the rate of erosion from the dam, and consequently they predict that little pollution enters the environment as a result of physical redistribution of tailings. However, when erosion gullies that cut through the oxidised zone, are develop on the sides of some tailings dams, acid leachate can escape much more easily from the tailings impoundments. Marsden (1986) found that sulphate concentrations in soils surrounding mine tailings deposits, where tailings had been allowed to wash onto adjacent land, were on average 0.05 per cent (maximum of 0.25 per cent) enhanced. Rosner et al. (1998) summarised the results of research on the environmental effects of South African mine tailings. Trace element concentrations in water and sediments were analysed in the 1970's and it was found that elevated concentrations of Co, Cu, Fe, Mn, Ni and Zn are present in stream systems affected by Acid Mine Drainage (AMD) (Forstner and Wittmann, 1976). Funke (1985) concluded that slimes dams contributed approximately 2 per cent of the total salt load. Marsden (1986) concluded that mine dumps older than 20 years make no significant contribution to the current pollution load on aquatic systems, as these tailings dams are often depleted in sulphur

bearing minerals in the oxidised zone. Evans (1990) found trace element pollution caused by AMD generation in a wetland adjacent to a tailings dam, both Candeias et al. (2013) and Castillo et al. (2014) reported mining related heavy metal contamination. Verhagen and Taussig-Duthe (1993) attributed elevated sulphate and metals (Ni, Cu, Fe) concentrations in both, surface and groundwater systems in the Gauteng Region to AMD from tailings dams. Znatowicz (1993) found high concentrations of toxic metals (e.g. As, Cd, Ti, V and U) in water and sediment samples downstream from a tailings dam.

Coetzee (1995) detected significant radiometric anomalies in selected drainage systems of the Gauteng Province and attributed these to AMD from tailings dams. Michelsen, (1996) stated that seepage released from various waste deposits such as mine dumps was identified as the most significant pollution source with regard to the deterioration of water quality in Gauteng. Rosner (1996) found significant concentrations of As, Cr, Ni, Pb, V and Zn in the oxidized zone of a number of gold mine tailings dams in Gauteng.

2. 10. 2 Mine Soil Stockpiling

Stockpiling is a necessary part of civil engineering and mining operations, involving the removal of topsoil (the A- and B-horizon of the soil). The topsoil is usually removed with heavy equipment and then stored in large, piles for the duration of the civil engineering or mining project. When the project is complete, the soil is re-spread to allow for the establishment of vegetation. The storage period for stockpiled soil ranges from a few months to several years. The depth of the stockpile and the length of time it is stored affect the quality of the soil (Strohmayer, 1999). Soil takes centuries to develop from parent material and organic matter. In a study of soil development of six sites where surface mines existed between 5 and 64 years, the depth of the newly developed soil horizon in the 5-year-old site was 3 cm compared to 35 cm in the 55-year-old site (Strohmayer, 1999). If stockpiled soil is reapplied quickly after mining, with little compaction from mechanical traction, the production potential of vegetation on the stockpile remains high (Thomas and Jansen, 1985).

In the process of open-cast coal mining, topsoil is removed and stockpiled for future use. Stockpiled topsoil becomes highly degraded the moment this long-term structure

is disturbed. Several studies conducted (Fresquez and Aldon, 1984 and Harris and Birch, 1989; and Strohmayer, 1999) reveal that timeframe can lead to damage of most soil properties. The damage starts when topsoil is initially stripped from the ground. Changes that occur in soil include change in physical, chemical and biological properties, and loss or reduction of viable plant remnants and seeds (Strohmayer, 1999). For stockpiled soil to meet its goals of rehabilitation post mining-closure, quantification of soil physical and chemical properties that affect soil quality and crop production is necessary. Soil properties such as soil structure, microbial population and nitrogen can change rapidly when the soil is disturbed (Lad and Samant, 2015). The natural process of soil development can take hundreds of years and stockpiled topsoil can becomes highly degraded the moment the structure is disturbed (Birch et al., 1989). This time frame is when topsoil is initially stripped from the ground. Changes that occur in soil include increased bulk density, decreased water holding capacity, chemical changes, reduced nutrient cycling, reduced microbial activity, and loss or reduction of viable plant remnants and seeds (Harris and Birch, 1989).

Soils are in practice stockpiled in three categories according to their clay content, topsoil and subsoil, and not grouped together as commonly prescribed in the soil guidelines of a mine (New Hope Group, 2014). The A and B horizons are usually stripped and stockpiled together, diluting the fertility status of the soil (Cobârzan, 2008) and increase fertility requirements post-closure. Mentis (2006) also described this impact as an effect of soil disturbance when bringing the subsoil, saprolite and fragmented rock to the surface. These components then form part of the mixture with topsoil that is used for the top layer on a post-mining surface. The result is that the mixture often cannot support plant life. Therefore, for good rehabilitation results to reestablish plant life, the contamination of soil, especially when bulk volume soil stripping is practised on a site, should be minimized or prevented (COM and CRA, 2007).

Several researches on stockpiled soils were conducted in other countries addressing challenges and problems faced in those respective countries. Ghose (1989) conducted a study that focused on the effect of open mining on soil fertility in India's largest opencast coal project Eastern Coalfields Ltd. The study indicated that, for every million tonne of coal extracted by surface mining, approximately 4ha of surface area is disturbed. Harris and Birch (1989) noted that when soil stockpiles are more than a meter deep, chemical effects such as accumulation of ammonium and anaerobic

conditions occurred in the topsoil at the base of the pile. Other detrimental biological effects include absence of propagules and decrease in viability of buried seeds.

A study conducted in Wales and New Zealand by Williamson and Johnson (1994) reported that the soil pH and the mineral content of stockpiled soils are not affected, as long as the soil is not stored for long periods of time in deep stockpiles. The same study reported that soil biology of stockpiled topsoil is restored quickly once the soil is re-spread. Abdul-Kareem and McRae (1984) stated that, although there is a clear evidence of the effects due to storage and earthmoving equipment, the extent of deterioration of soil in stockpiles resulting from the equipment and storage has been greatly overestimated. The authors further indicated that there is no reason why soils should not continue to be stockpiled, although greater care must be given to minimize compaction and mixing of topsoil with subsoil.

A study conducted by Zelikman and Carmina (2013) demonstrated the possibility of using ground spectral-based approaches for digital quantification of some soil properties using the non-destructive NIRs (Near InfraRed) procedures. The study was also able to predict, soil moisture, hygroscopic water, carbonates and specific surface area at a reasonable level down the profile based on the spectral library containing laboratory and field in-situ collected spectra. Labovitz et al. (1983) demonstrated that the metal content in the soil changed the leaf reflectance, especially in those parts of the spectrum used for chlorophyll content and leaf water absorption, and that variation in trace metal content was associated with leaf reflectance. Schellekens et al. (2005) conducted a study that focused on changes of the leaf reflectance spectrum due to metal-induced stress from copper deposits.

2. 11 Enzyme Activities of the Soil

Enzyme activity in a soil property that is dominantly chemical in nature, but has a direct biological origin. Since soil enzyme activities are very sensitive to pollution, enzymes have been suggested as potential indicator or monitoring tools to assess soil quality and health. Enzyme activities can effectively reflect the biological status of the soil (Sisa, 1993). Dick et al. (1996) suggested that soil enzyme analyses could be a good indicator of soil quality, because:

- they are strongly linked to important soil properties such as organic matter, microbial activity or biomass,
- ii) they have the tendency to change earlier than other soil properties, and
- iii) they involve relatively simple methods as compared to other parameter assessment of soil quality.
- iv) The enzyme activity depends on the contents of the organic and mineral colloids, metal types and chemical properties (Kucharski and Wyszkowska, 2004).

Soil enzyme activities are very sensitive to both natural and anthropogenic disturbances and show a quick response to the induced changes (Dirk, 1997; Kumar et al., 2013). A study conducted by Fresquez et al. (1985) shows that soil stockpiling affected enzyme activity. Therefore, enzyme activities can be considered as effective indicators of soil quality changes resulting from soil stockpiling. Soil enzymes play a fundamental role in establishing biogeochemical cycles and facilitate the development of plant cover. The soil enzyme is an important aspect of the below-ground processes and give insight into the relative changes in below-ground system functioning as a plant community develops over time (Tabatabai et al., 2010). Enzyme activity in soil results from the activity of accumulated enzymes and from enzymatic activity of proliferating microorganisms (Kiss et al., 1975).

The enzymes mainly originate from soil microorganisms, which can indicate microbial activities in soil environment. Soil enzymes play an important role in organic matter decomposition and nutrient cycling. The activity of enzymes is affected by abiotic conditions (e.g. temperature, moisture, soil pH, and oxygen content), by the chemical structure of the organic matter and by its location in the soil strata (Deng and Tabatabai, 1994; and Pavel et al., 2004). Several studies show that soil enzyme activity data can be used as the foundation for the development of conceptual models that provide a more comprehensive understanding of key biochemical processes linking microbial populations and nutrient dynamics (Sinsabaugh and Moorhead, 1994; Schimel and Weintraub, 2003; Akca and Namli, 2015).

The enzymes catalyse all biochemical reactions and are an integral part of nutrient cycling in the soil. Soil enzymes are believed to be primarily of microbial origin but also originate from plants and animals (Deng, and Tabatabai, 1994). They are usually

associated with viable proliferating cells, but enzymes can be extracted from both living and dead cells. Soil enzymes are considered to be indicative measures of soil fertility and bioremediation activities due to the fact that they participate in elemental cycling (Dick et al., 1996). Many studies have also suggested that soil enzymes can be used as indices of soil contamination, soil fertility and soil health (Albiach et al., 1992; Giusquiani et al., 1994; Saviozzi et al., 2001). Soil enzyme activity is variable with substrate supply (Degens, 1998), providing useful linkage between microbial community composition and carbon processing (Waldrop et al., 2000) and is sensitive indicators to detect the changes occurring in soils (Gonzalez et al., 2007).

The criteria for choosing enzyme activities as biomarker to assess soil quality is based on their sensitivity to soil management practices, importance in nutrient cycling, organic matter decomposition and bioremediation activities. Among the parameters related to the biochemical and microbiological state of the soil, the most important are the indicators of the soil microbial activity. Principally different enzymatic activities that are specifically related to the cycles of nitrogen (N), phosphorus (P), and carbon (C) (urease, phosphatase, and β-glucosidase, respectively) (Bandick and Dick, 1999).

Since enzyme activity is linked to several ecosystem processes including soil formation, organic matter transformation and bioremediation activities. It is therefore, important to understand the different physical-chemical factors affecting the enzyme activities (Kujur et al., 2012). Given the importance of enzymes in the maintenance of soil quality, the present study was initiated to assess the impact of different soil amendments on enzyme activity, and to illustrate if soil enzyme activities can be used as indices for soil quality and health.

2. 12 Acid mine drainage

The impact of mining on the environment varies greatly, depending on the methods employed to exploit the mineral deposit, the type and extent of the mineral resources, pollution control, the waste management and proper reclamation. Acid mining drainage is probably the most severe environmental problem that occurs on mine sites. Acid Mine Drainage (AMD) happens where mineral and coal deposits contain sulphide minerals. When waste rock containing sulphides is exposed to air, these minerals are oxidized, releasing sulphuric acid (Economopoulos, 1993). The process

is accelerated by bacteria such as Thiobacillus ferrooxidans (highly acidophilic with pH 1.5 to 2.0) that obtain energy from the oxidation reaction (Weeks and Wan, 2000). The release of acid can cause the pH of surface water and groundwater to become very low. Under these acidic conditions, metal concentrations in water can become very high due to the dissolution of elements from waste rock (Álvaro-Fuentes et al., 2002). The generated acid leaches and releases heavy metals such as lead, zinc, copper, arsenic, selenium, mercury and cadmium into the environment. High concentrations of iron and aluminium are also common in acid sulphate waters (Bigham et al., 1996). In acid sulphate drainage waters and leachate solutions from mine waste tailings and soils, solubility appears to be controlled by a variety of basic aluminium/iron oxides, oxy-hydroxides and sulphate phases (Karathanasis et al., 1988; Monterroso et al., 1994). Acidic water from mine sites often kills vegetation, and may cause fish deaths in rivers. Of the chemicals used to process ores, cyanide may be the most problematic due to its toxicity and the complexity of its chemical behaviour in groundwater (Economopoulos, 1993). Cyanide degrades rapidly into nontoxic chemical compounds when exposed to air and sunlight, but in groundwater it may persist for long periods with little or no degradation (Aslibekian and Moles, 2000; Aslibekian et al., 1999). Cyanide in the subsurface can react with minerals in soil and rock to form a wide range of metal cyanide complexes, many of which are very toxic (Weeks and Wan, 2000).

The uncontrolled release of acid mine drainage (AMD) is perhaps the most serious impact that mining can have on the environment (Ferguson and Erickson, 1988). In addition to low pH (i.e. high acidity) acid mine drainage often contains dissolved trace elements in toxic concentrations. The high acidity of mine drainage arises from the rapid oxidation of sulphide minerals. AMD may occur anywhere where sulphide minerals are exposed at the earth's surface (e.g. road cuts or quarries), but metal mines where economically recoverable metals often occur in ore bodies of concentrated metal sulphides (e.g. pyrite, FeS₂; chalcopyrite, CuFeS₂ or sphalerite, ZnS) are the primary source of AMD. The generation of AMD is controlled by a series of factors that may be categorized as primary, secondary, tertiary and downstream factors (Ferguson and Erickson, 1988). Primary factors are those directly involved in the acid production process. Secondary factors control the consumption or alteration of the products of the acid generation reactions. The tertiary factors are the physical

aspects of the waste material or mine site that influence the acid production, AMD migration and consumption. Downstream factors control the precipitation of Fe and other metals in rivers and streams into which AMD is discharged. These factors control the quality (including trace element content) of AMD affected water that emanate from a site (Ferguson and Erickson, 1988).

2. 13 Influence of mines on natural water resources

The type of waste water contamination produced by a mining operation depends to a large extent on the nature of the mineralization and the chemicals used to extract or concentrate minerals from the ore.

2. 13. 1 Surface and ground water contamination by mining effluents

Heavy metal pollution is caused when metals such as arsenic, cobalt, copper, cadmium, lead, silver and zinc contained in excavated rock or exposed in a mine come into contact with water. Metals are leached out and carried downstream (Shandro et al., 2011). Although metals can become mobile in neutral pH conditions, leaching is accelerated in the low pH conditions (Gee, 1999). Processing chemicals pollution occurs when chemical agents such as cyanide or sulphuric acid (used by mining companies to separate the target mineral from the ore) spill, leak, or are leached from the mine site into nearby water bodies (McClure and Schneider, 2001). These chemicals can be highly toxic to both humans and wildlife.

2. 14 Rehabilitation of the land disturbed by mining activities

2. 14. 1 Environmental rehabilitation measures

Rehabilitation is, as pointed out above, the restoration of a disturbed area that has been degraded as a result of activities such as mining, road construction or waste disposal, to a land use in conformity with the original land use before the activity started. This also includes aesthetical considerations, so that a disturbed area will not appear significantly different to the natural environment. Rehabilitation includes the

development of management strategies to restore and maintain physical, chemical and biological ecosystem processes in degraded environments.

2. 14. 2 Rehabilitation of mining activities

Mining is one of the activities that can have a severe impact on all states of the environment. The Minerals Act (No. 50 of 1991) requires that an Environmental Management Programme Report (EMPR) containing rehabilitation plans be submitted and approved by the authorities before any mining activity can start, and that finances be set aside for this purpose. EMPRs are reports containing elements of Environmental Impact Assessments (EIAs) plus Environmental Management Programmes (EMPs) for the various stages in the life cycle of a mine. The EIA addresses all the impacts (positive and negative) on the fauna and flora, water (both surface and ground), air, soil and also on the society as a whole. A public participation process is undertaken, in which interested and affected parties (I&APs) are consulted and are provided with an opportunity to express their concerns.

Rehabilitation methods include the vegetation of mine dumps to blend in with existing vegetation, the reduction of storm water run-off and prevention of water pollution, and the backfilling of excavations, for example by making use of waste material during the mining process (Cobârzan, 2008). The main aim of rehabilitation is to restore the land to a potential similar to what it had before the activity started. The landscape must also be visibly acceptable that its excavations must be backfilled and visible structures, such as mine dumps, must be effectively camouflaged. Trees can be used to conceal visible structures and shrubs and grass can be used to blend the structures in with the environment and to prevent dust problems. Mine dumps typically consist of clay or hard rocks, which are unsuited for the establishment of vegetation. Therefore, topsoil is normally placed on the dumps to establish new vegetation on mine dumps. The slopes of the mine dumps must be altered so that they are not too steep, as steep slopes enhance erosion and have poor water retention which is not conducive to revegetation.

Another important reason to use vegetation that is similar to the existing vegetation in the area is that the new vegetation will be able to exist in the natural environment, after irrigation of the site has halted. For example, plants requiring high rainfall will grow in an area where there is low annual rainfall. The timing that planting of vegetation takes place for rehabilitation purposes is also important. Planting should not take place during the dry season. Although irrigation can enable the plants survive; this can be lengthy and costly exercise. The Environmental Management Programme Reports (EMPRs) outline how all the negative impacts can be prevented or minimised. Rehabilitation plans should be clearly outlined, and should include the method of payment for rehabilitation, as no EMPR will be approved without any financial provision for rehabilitation.

2. 15 Techniques used for soil analysis

2. 15. 1 X-Ray Fluorescence (XRF)

XRF is a physical phenomenon involving the interaction of X-Rays with matter. When high energy X-Rays strikes an atom, electrons are dislodging from the inner orbitals making structure unstable. The unoccupied positions in the lower orbital are promptly filled by electrons from an outer shell which have higher energy than the electron being replaced. The excess energy is released in the form of X-Rays of a characteristic energy level. Since the electronic energy levels for each element are different, the energy of X-Ray fluorescence peak can be correlated to a specific element and the intensity to the concentration of that element. X-Ray Fluorescence Spectroscopy (XRFS) is an elemental analysis technique applicable for element coverage from sodium to uranium in various matrices that typically requires minimal sample preparation.

CHAPTER 3: RESEARCH METHODOLOGY

3. 1 Introduction

This chapter outlines the methods used to collect samples and to analyse the data. It gives details of the background of the study area, description of the sampling procedures and laboratory procedures. In order to achieve the research objectives a number of methods were used. Data was collected through sampling and analysis.

3. 2 Description of the study area

The villages of the Atok group are located on the Critical Zone of the eastern Bushveld Igneous Complex and at (24°18′48″ S and 29° 55′ 30″ E) in Sekhukhune District, Limpopo Province of South Africa (Fig. 3.1). The towns of Polokwane and Burgersfort are located approximately 80 km and 70 km, to the north-north east and west-south west and 113 km from Mokopane respectively The area is serviced by a R37 tarred road between Polokwane and Burgersfort (Fig. 3.2). The areas are a host to Bokoni Platinum Mine which had four shafts operating (three underground and one open cast) but presently the mined is under 'Care and Maintenance' status. Atok is within what is general considered the summer rainfall with an average annual rainfall ranges between 300 mm and 500 mm, most of which occurs between November and March (Saviozzi et al., 2001). The climate of the area is considered as temperate, with moderate winter temperatures and warm to hot in the summers. Annual day temperatures vary between 20°C and 30°C in summer; and although winter night temperatures may occasionally fall below 10°C, winter day temperatures are normally in the mid-20s°C (Saviozzi et al., 2001; H. du Plessis pers. comm. 2019).

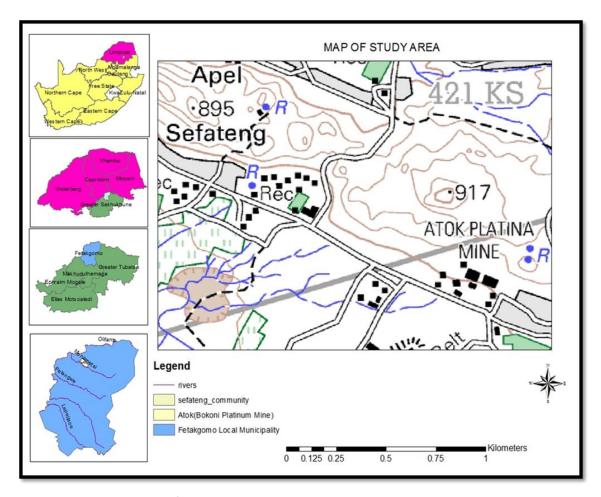


Figure 3.1. The map of the study area

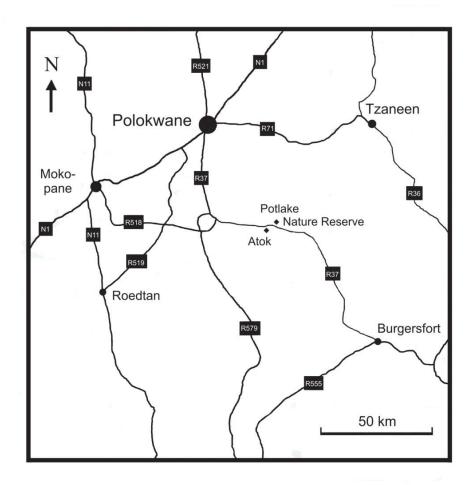


Figure 3.2: Location of the Atok area and Potlake Nature Reserve
3. 3 Geology of the study area

The Bushveld Igneous Complex was intruded into the Kaapvaal Craton and was intruded into the metasedimentary rocks of the Transvaal Supergroup in the Paleoproterozoic ~2.06 Ba (Scoates and Friedman, 2008). It is endowed with an enormous mineral wealth, which includes platinum group elements (PGE) (von Gruenewaldt et al., 1986; Lee and Tredoux, 1986; Viljoen and Schurmann, 1998; Cawthorn, 1999); chromite (Cameron and Emerson 1959; Cameron, 1977; Schurmann et al., 1988), titanium, vanadium copper and cobalt (Klemm et al., 1985; Cawthorn and Molyneux, 1986). The rocks of the Bushveld Igneous Complex cover an area of about 65 000km² (Tankard et al., 1982) and are subdivided into: the mafic/ultramafic rocks of the Rustenburg Layered Suite (RSL), the felsic rocks of the Rashoop Granophyre Suite, and Lebowa Granite Suites (Hall, 1932; SACS, 1980; Tankard et al., 1982). Only the Rustenburg Layered Suite will be discussed, as these

are the only units in the Atok area. The rocks of the RLS outcrop in each of the four major lobes or limbs, namely, the eastern, western, far western and the northern lobe. Each of these lobes contains a well-defined cyclic sequences of layered ultramafic/mafic rocks, which are geochemically and lithologically variable, reflecting the unique mixing and differentiation process that occurred in the basic magmas (Kruger and Marsh, 1982; Maiers and Barnes, 1998; Cawthorn et al., 2006).

3. 3. 1 The Rustenburg Layered Suite

Hall (1932) and later SACS (1980) grouped divided the cyclic units of the Rustenburg Layered Suite into five zones, namely, the Marginal Zone (MZ); Lower Zone (LZ); Critical Zone (CZ), Main Zone (MZ) and the Upper Zone (UZ). The development and succession of rocks is distinctly different across all five zones. However, only geology of the Critical Zone is discussed as this is the only unit relevant to this study.

Due to the extensive economic potential the Critical Zones has been extensively discussed in the literature (Cameron, 1980; Cameron and Desborough, 1969; Cawthorn et al., 2006; Eales et al., 1988; Kruger, 2005). The Critical Zone is composed mainly of cyclic units (Cameron, 1982; Eales and Reynolds, 1986), and is divided into a pyroxenite-dominated Lower Critical Zone, and a norite-anorthosite-dominated Upper Critical Zone, whose rocks have plagioclase as a cumulus phase (Cawthorn and Walraven, 1998). Nearly all deposits of economic interest in the Bushveld Igneous Complex are restricted to the Critical Zone (Cameron, 1980), except for the magnetiterich layers which occur in the Upper Zone (Klemm et al., 1985) and the PGE's in the Platreef of the Northern Limb of the Bushveld Igneous Complex (Viljoen and Schurmann, 1998; Manyeruke et al., 2005). The Critical Zone is host to some of the world's largest deposits of Platinum Group Elements (Kinloch, 1982; Cawthorn, 1999;) as well as vast chromite deposits (Vermaak, 1986, 1997). There are three groups of chromitite layers (Cousins and Ferringa, 1964) in the Critical Zone, namely, the Lower Group (LG), the Middle Group (MG) and the Upper Group (UG), with a total of up to fifteen individual chromitite layers (Cousins and Ferringa, 1964). The Lower Group has up to seven chromitite layers (LG-1 to LG-7); the Middle Group has up to five chromitite layers (MG-0 to MG-4) and the Upper Group has up to three chromitite layers (UG-1 to UG-3). The development and characteristics of the chromitite layers differ in both

the eastern and western lobes of the Bushveld Igneous Complex (Hatton and Von Gruenewaldt, 1985; Lee and Parry, 1988). The Platinum Group Elements are hosted mainly by the UG-2 chromitite layer and Merensky Reef. Fig. 3.2.3 indicates the Bushveld Igneous Complex.

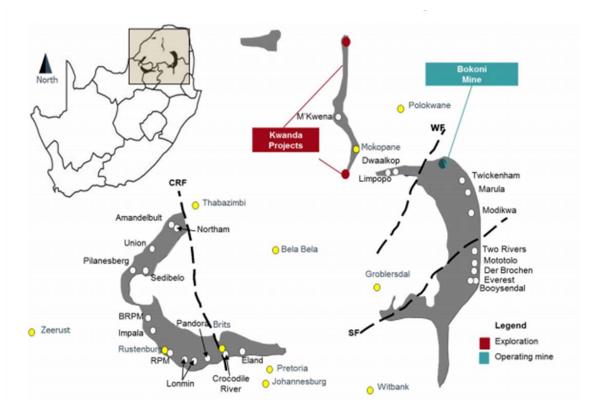


Figure 3.3: Location map of the mines operating at BIC but Bokoni Platinum Mine is under care and maintenance with Crocodile River Fault (CRF), Wonderlop Fault (WF) and Steelpoort Fault (SF) (After Atlatsa Resource Corporations, 2017).

Additional soil samples that serve as control were similarly collected from undisturbed Potlake Nature Reserve for the purpose of comparison. The Potlake Nature Reserve is located in the Sekhukhune district of Limpopo Province, South Africa. The reserve is situated some 8 km east-north east of Atok (approximately 80 km from Polokwane and Burgersfort), directly adjacent to the R37 and within Dilokong Spatial Development Initiative (Fig. 3.2).

3. 4 Description of the soil sampling procedures

A total of eighteen (18) soil samples representing three (3) from each village around the mines were randomly taken at three different points on each village using a soil auger at 0 - 15, 15 - 30 and 30 - 45 cm depth (Fig. 3.3) indicates the sampling sites. All soil samples were air-dried to eliminate any moisture that may be present between the soil particles which may add oxygen content of the data, then the samples were sieved through a 2.0 mm sieve (Hutchison, 1974). These samples were crushed to fine powder using the ring mill pulveriser to make them homogenous. In order to minimize any errors that may be caused by crushing, the ring mill was cleaned before crushing a new sample to prevents any contamination of the samples. The crushed and powdered samples were placed in 32 mm diameter aluminium sample cups and pressed at 20 tons for X-Ray Fluorescence (XRF) analysis (Hutchison, 1974).



Figure 3.4: A map showing sampling sites

3. 5 Laboratory determination procedures

3. 5. 1 Procedures for physio-chemical properties analysis

Soil samples collected were subjected to selected physical and chemical determinations which are pH, Electrical Conductivity (EC), Bulk Density, Moisture

Content, Water Holding Capacity, Organic Carbon, Organic Matter, Soil Texture and XRF analysis. These parameters assist in understanding of the soil undergoing analysis. For the purpose of comparisons, results for the concentration of the different heavy metals obtained will be compared with those from unpolluted soil samples obtained from Potlake Nature Reserve (Fig. 3.2) by as well as the standard permissible pollutant limits values obtained from literature.

3. 5. 1. 1 Soil Texture

To establish the Soil Texture, the Settling methods was used; 100g of soil samples were poured in six 200ml beakers and 150ml of distilled water was added and stirred using a spatula. After 5 minutes' the sand had settled at the bottom of the beaker and a bold line was drawn using a black marker, after an hour the silt had settled on top of the sand and a marker was drawn and after 24 hours the clay had settled on top of the silt and a marker line was drawn. The lines were used to measure in cm the amounts of the textural components of the soil (Fig. 3.5) indicates the different soil textures percentages that the soil is made up of. Calculations for percentages were done and plotted on the textural triangle to determine the texture of the soil samples.

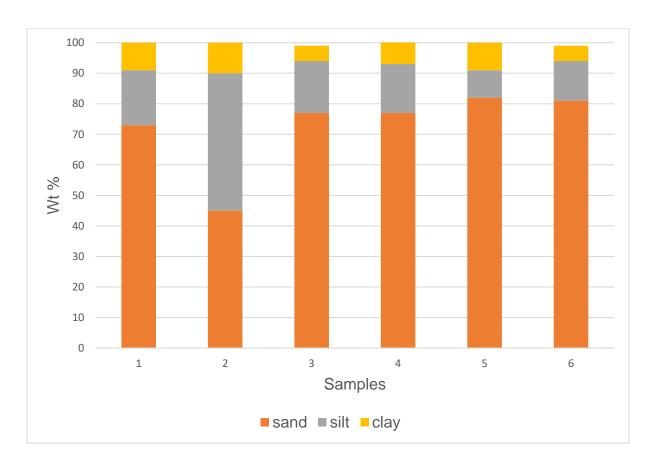


Figure 3.5: Soil Texture

3. 5.1. 2 Water Holding Capacity

To establish the Water Holding Capacity a filter paper, was placed at the bottom of a holed tin and weighed on the balance. Then soil was added in to the tin and weighed again to get the mass of the tin, filter paper and soil. The tin was placed inside a Petri Dish filled with water. The water was absorbed by the soil until the water reached to the surface of the soil. The tin was then weighed to obtain the mass of the wet soil. Table 3.1 shows the readings of the procedure. The percentages were calculated.

Determination of WHC



Figure 3.6: Image showing WHC procedure

Table 3.1. WHC readings

Soil Sample	Weight of tin + filter paper (g) (A)	Weight of tin + filter paper +soil (g) (B)	Weight of tin + filter paper + wet soil (g) (C)	Weight of dry soil (g) D=B-A	Weight of wet soil (g) E=C-A	Mass of water absorbed by soil (g) N=E-D	% of WHC= (N/D)*100
008T	41.80	195.50	239.80	149.70	198.00	48.30	32.20
008S	46.00	191.50	231.00	145.50	185.00	39.50	27.20
009T	46.00	191.50	220.60	145.50	174.60	29.10	26.20
009S	46.00	191.50	231.40	145.50	180.40	39.90	27.40
004T	46.00	191.50	226.30	145.50	180.30	34.80	24.00
004S	46.00	191.50	215.80	145.50	169.80	24.30	17.00
005T	41.80	191.50	228.30	149.70	186.50	36.80	25.00
005S	46.00	191.50	246.90	145.50	200.90	55.40	38.10
007T	41.80	191.50	230.00	149.70	188.20	38.50	26.00
007S	46.00	191.50	231.00	145.50	185.00	39.50	27.10

3. 5. 1. 3 Moisture Content

To establish the Moisture Content, the weighing tin + lid was cleaned and dried. Approximately 30g of moist soil was put in the weighing tin and closed with the lid and weighed. The lid was removed and the tin with the soil sample and lid was placed in the oven and heated to 110 °C overnight. The tin and lid were removed from the oven and placed in a desiccator to cool. The tin + lid was then weighed to establish the moisture loss.

3. 5. 1. 4 Bulk Density

To measure the Bulk Density a steel dolly of known volume in (M³) was placed on top of the cutter and hammer into the soil layer until the top edge of the cutter is a few millimetres below the soil surface. The core sample was dug out, taking care not to damage it. The ends of the core were trimmed by means of a garden spade. The core was packed in to Ziploc bags and transferred back to the laboratory. The sampled was weighed in the Ziploc bag (Mg), and an empty Ziploc bag was weighed. A crucible dish

was weighed and 30 g of the soil sample was poured in the crucible and weighed. The sample in the crucible was put into an oven at 105 °C for 30 minutes and weighed, again for 1 hour and weighed and lastly for 2 hours and weighed (Hutchison 1974). Calculations for bulk density were done using,

Bulk Density = Mass of dry soil/Volume of core (Mg/M³)

3. 5. 1. 5 pH and Electrical Conductivity

10 g of air dried soil was weighed in a beaker and 50 ml distilled water was added, and the. Solution mechanically stirred for 1 hour. A portable multi parameter meter was used. The meter was calibrated according to the manufacturer's instruction using pH 6.86 and 4.0 buffers. The pH electrode was immersed into the soil suspension and the pH values obtained was recorded. The EC electrode was immersed in to the soil suspension and values were recorded.

3. 5. 1. 6 Organic Carbon and Organic Matter

30g of soil was added into a 250 ml conical flask. 10 ml 1 N K₂Cr₂O₇ was accurately added and swirled the flask gently to disperse the soil in the solution. 20 ml concentrated H₂SO₄ was added directing the stream into the suspension. Immediately the flask was swirled until the soil and the reagent were mixed. A 200 °C thermometer was inserted and the mixture heated while swirling the flask and the contents on a hot plate until the temperature reaches 135 °C (approximately ½ minute). The sample was set aside to cool slowly on an asbestos sheet in a fume cupboard. When cooled, the mixture was diluted to 200 ml with deionised water and titrated using Ferroin.

Four (4) drops of Ferroin indicator was added and titrated with 0.4 N FeSO₄. As the end point is approached, the solution took on a greenish colour and then changed to a dark green. At this point, ferrous sulphate was added drop-by-drop until the colour changed sharply from blue-green to reddish-grey. Calculations were done and organic matter by using conversion factor of 1.724.

3. 6 X-ray fluorescence analysis

Major and trace element analysis was done using the Malvern Panalytical Epsilon 3, XRF machine (Fig. 3.7). The Epsilon 3 is capable of analysing data from samples of various physical states such as liquid, solid material in the form of pressed pellets or loose powder. The XRF was used to determine the chemical composition of the sample. For this analysis the major rock forming elements are presented as oxides in wt.%, and the minor elements as element in ppm.



Figure 3.7: The XRF Machine

CHAPTER 4: RESULTS AND DISCUSSIONS

4. 1 Introduction

This chapter presents the results of the study. Data was collected through procedures elaborated in the previous chapter. In addition to data presentation, a discussion of the results is also carried out in line with set themes that speak directly to the objective of the study.

4. 2 Discussions of physical-chemical parameters

4. 2. 1 Soil texture classes

The soil texture was determined using the settling method (Stolt et al., 2005) (<1 mm soil size) is given in Table 4.2, and Fig 4.2. Soil texture classes were based on varying proportions of sand, silt and clay, expressed as percentages.

In the soil samples of study area, the percentage of sand, silt and clay ranges from (45% to 81%), (9% to 45%) and (5% to 10%) with the average percentage of 72%, 20% and 8% respectively. Therefore, the main texture of soil in study area from the textural triangle (Fig.4.1) is sandy soil which is not best for agriculture as it is porous and has loose particles. The intermediate loam textures are generally best as agricultural soils. (Dhar and Rolterdem. 1993) reported the maximum sand content of 66% and clay only 8.6% in mined soil. The sandy soil texture might be due to the wind erosion from the tailing dam to the surrounding villages and the dust from the mine over the years.

Table 4.1: Soil texture determination

Sample	Sand %	Silt %	Clay %	Texture
005 S	73	18	9	Sandy loam
005 T	74	17	9	Sandy loam
009T	50	40	10	Sandy loam
009 S	45	45	10	Sandy loam
004 T	76	17	6	Sandy loam
004 S	77	17	5	Sandy loam
007 T	76	17	8	Sandy loam
007 S	77	16	8	Sandy loam
008T	82	9	9	Sand
008 S	82	9	9	Sand
Tailings	81	13	5	Sand

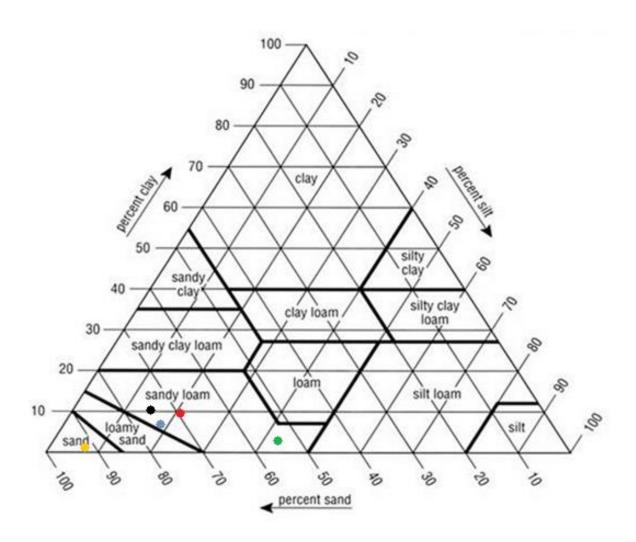


Figure 4.1: Textural Triangle showing different textures of soil. The coloured dots show the soil textures derived from the samples.

Table 4.2 shows the results of the physio-chemical parameters which are: pH, EC, WHC, Moisture content, bulk composition, organic carbon, organic matter and available P and K.

Table 4.2: Physio-chemical parameters results

Parameters	004T	004S1	005T	005S	007T	007S	008T	008S	009T	009S	Tailings	Min	max	Avg
рН	7.90	9.20	8.00	9.80	8.20	9.20	7.80	9.00	8.20	9.80	6.90	7.80	9.80	8.50
EC (dS/m)	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
WHC %	24.00	17.00	25.00	38.00	26.00	27.00	32.20	27.20	26.20	27.40	0.00	17.00	38.00	27.00
Available Phosphorus %	0.34	<0.05	0.37	0.37	0.30	0.33	<0.05	<0.05	<0.05	<0.00	0.31	<0.05	0.37	0.18
Available Potassium %	0.40	0.30	0.49	0.47	0.24	0.26	0.48	0.36	0.24	0.20	0.19	0.20	0.49	0.33
Organic Carbon %	0.07	0.07	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	<0.01	<0.01	0.07	<0.01
Organic Matter %	0.12	0.12	0.04	0.04	0.23	0.23	0.01	0.01	0.09	0.09	<0.01	<0.01	0.12	0.10
Moisture Content %	1.42	1.42	1.00	1.00	1.50	1.50	1.00	1.00	1.35	1.35	0.80	0.80	1.42	1.20
Bulk Density g/ml	1.90	1.90	1.82	1.82	1.90	1.90	1.80	1.80	1.90	1.90	1.90	1.80	1.90	1.87

4. 2. 2 Water Holding Capacity

The Water Holding Capacity (WHC) of the soil samples ranged from 17.00 to 38.00 % with an average value of 27.00%. The minimum 17.00 was found at site 004 and maximum 38.00 % at site 005, these site are 2 km apart. The WHC is related to particle size and texture because smaller particles have a large surface area and hold maximum water content (Ghosh et al., 1983). The soil texture in the area is sandy and this type of texture has small surface area causing the soil unable to store water hence the WHC is at lower percentages in all samples.

4. 2. 3 Moisture content

The Moisture Content indicates the amount of water present in the soil. The moisture content of soil is expressed in percentage of the total mass. The amount of water stored in the soil is not constant, but may varies with time. Moisture content of the soil samples was found to range from 0.80% to 1.42% with an average of 1.20%. According to the January issue of landscape Architecture Magazine, soil with moisture Content of 5% is dry soil and 25% is wet soil. Therefore, the Moisture Content of soil in Atok was found to be lower than 5.00% reason being: the soil is very low in clay and organic matter content.

4. 2. 4 pH

Acidity (pH) is an important index of the ecological condition of terrestrial environments (Rai et al.,2010). At greater depths pH is usually found to be lower i.e. more acidic (Tripathy et al., 1998). The maximum availability of the primary nutrients such as nitrogen, phosphorus and potassium as well as secondary nutrients such as sulphur, calcium and magnesium are found in the pH range between 6.5 to 7.5 (Ghosh et al., 1983; Saxena, 1987). The optimum pH for plant growth ranges between 5.5 to 6.8. pH exercises a significant influence on the availability of nutrients for plants, as plants cannot absorb macro-elements and micro-elements in all their forms. pH measures the acidity and alkalinity of soil water suspension and pH provides a clear identification of soil chemical nature. pH values ranging between 6.5 - 7.5 are acceptable for plant growth but in the present study the pH of the soil was found to be moderately alkaline

ranging from 7.80 - 9.20. The major reason for the alkalinity is the fact that the rocks in the area are rich in Fe and Mg bearing minerals. Since the soils pH in the area is moderately alkaline with (pH >8.0), the solubility of nutrients such as potassium, phosphorus and nitrogen decreases.

4. 2. 5 Electrical Conductivity

The Electrical Conductivity (EC) is the most common measure of soil salinity and is indicative of the ability of an aqueous solution to carry an electric current. It is well established that conductivity at 0.2 dS/m - 0.8 dS/m is the optimal range for plant growth (Saxena, 1987). Plants are affected, both physically and chemically, by excess salts in some soils and by high levels of exchangeable sodium in others (Saxena, 1987). During the study period, EC were found to be below detection limit <0.50 dS/m in different sites of Atok. These low values are considered to be due to the minimal quantities of moisture and soluble salts in the soils (Saxena, 1987).

4. 2. 6 Soil Organic Carbon

Soil Organic Carbon (SOC) is important parameters of soil because it improves both the physical and chemical properties of soil and has several beneficial effects on soil quality. It also improves soil structure, enhances aeration, water penetration, and increases water-holding capacity and supplies nutrients for growth of plants. Soils with an organic carbon levels greater than 0.80% are considered as good quality of soil (Saxena 1987). A level of organic carbon greater than 0.75% indicates good fertility (Ghosh et al., 1983). The amount of Soil Organic Carbon (SOC) depends on soil texture, climate, vegetation and historical and current land use/management. In the present study, the organic carbon content in soil samples varied from 0.00% to 0.07% in sampling sites of Atok Region. The organic carbon in the soils were found to be at low quantity due to low water content. Soil texture affects SOC because of the stabilizing properties that clay has on organic matter.

4. 2. 7 Soil Organic Matter

Soil Organic Matter (SOM) is a complex mixture of organic components, ranging from recent plant residues to complex products of transformation processes and including the microbial biomass. Soil Organic Matter can be trapped in the very small spaces between clay particles making SOM inaccessible to micro-organisms and therefore slowing decomposition. Soil Organic Matter is the major source of nutrients such as nitrogen, and available phosphorus and potassium in unfertilized soils (Donahue et al., 1990). The Soil Organic Matter in the studied areas varied between 0.01% to 0.12% with an average value of 0.10%. The organic matter was found to be of low content in the soil due to low organic carbon and low clay content in the soil.

4. 2. 8 Available Phosphorus

Phosphorus (P) is an essential element and classified as a macronutrient because of the relatively large amounts required by plants. Phosphorus is one of the three nutrients generally added to soils in fertilizers. Brabr and et al., 1990 found that the main roles of phosphorus in plants is in the transfer of energy. A sufficient quantity of phosphorus availability for plants, stimulates early plant growth and hastens maturity. In the present study, available phosphorus was found in the range between <0.05% to 0.37%. The phosphate content of the soil in Atok recorded to insufficient amounts of 0.37%, this might be due to high Mg content which causes the soil to be depleted in P. The depletion of phosphorus was evident by the yellowish colour on the vegetation found in the area. The reasons for low concentration of phosphorus was caused by the low P content in the parent rock and lack of organic matter in the soil.

4. 2. 9 Available Potassium

Potassium (K) is a major plant growth limiting nutrient element and influences plant productivity. The K used by plants comes from organic matter, fertilizer application and legumes plants (Maiti et al., 2000). In the present study, the available K content range between 0.20% to 0.49%. with an average of 0.33%, this implies that the K content in the soil is low and this causes the plants to suffer potassium deficiencies such as Chlorosis and slow growth. The low K content was caused by low content of K in the parent rock.

4. 2. 10 Bulk Density

It is an indicator of soil compaction and soil health. Bulk density affects infiltration, rooting depth, WHC, soil porosity plants nutrient availability and microorganism activity which influences soil processes and productivity (Janakiram et al., 2010). Soil bulk density is correlated with soil organic matter levels. Soils with a high bulk density normally have low organic matter levels and are more prone to nutrient leaching. Bulk density values that ranges from 1.00 - 1.50 g/cc are for fertile soils. Therefore, the BD of the soil in Atok is prone to nutrients leaching because the BD ranges from 1.80 - 1.90 g/cc this is considered to be due to the texture of the soil.

4. 3 The X-Ray Fluorescence Results and discussion

The concentration of metals in soil can be evaluated by several analytical techniques such as inductively coupled plasma-mass spectroscopy (ICP-MS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), atomic absorption spectroscopy and atomic fluorescence spectroscopy. However, these approaches are severely limited by high costs of analysis, laboratory consumable and time used in the laboratory processing (McLaren et al., 2012; Weindorf et al., 2012). Consequently, there is a need for fast and accurate analytical method. Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an X-Ray technique used to identify the elemental composition of materials. Applications include materials and product research, troubleshooting, deformulation (Fujimori et al., 2014; Hu et al., 2014). EDXRF is an alternative analytical technique widely used for quantitative determination of the chemical composition in several type of geological or industrial samples: rocks, soils, sediments, cement (Dirken, 2003).

The results in Table 4.3 are obtained from the XRF analysis. The results are expressed as metal oxides and were used to draw the graphs below.

Table 4.3: XRF analysis results of the major metals as oxides

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na₂O	K ₂ O	P ₂ O ₅	Total
top-004	34.99	0,23	11.19	8.28	0.14	8.03	6.51	0.25	0.40	0.34	70.36
sub1-004	33.22	0.91	10.85	7.73	0.12	7.33	9.45	0.24	0.30	<0.05	70.15
Sub2-004	31.25	0.23	9.55	7.11	0.11	5.14	8.30	0.20	0.39	0.37	62.65
top-005	35.33	0.24	13.49	6.95	0.13	5.07	6.59	0.85	0.49	0.37	69.51
sub1-005	35.33	0.24	12.55	6.90	0.13	4.68	6.67	<0.05	0.47	0.37	64.38
sub2-005	32.37	0.24	12.55	6.92	0.13	4.68	6.67	<0.05	0.47	0.37	64.40
top-007	35.37	0.27	12.09	9.95	0.17	6.26	5.12	0.17	0.17	0.30	69.94
sub1-007	32.35	0.19	11.16	7.63	0.14	4.47	5.88	0.06	0.26	0.33	62.47
sub2-007	34.38	0.20	11.76	7.19	0.14	4.54	6.19	0.14	0.29	0.35	65.18
top-008	31.52	0.22	10.24	6.11	0.12	6.15	12.52	0.19	0.48	<0.05	67.55
sub1-008	28.64	0.23	9.79	5.97	0.12	6.14	13.55	0.08	0.23	<0.05	64.88
sub2-008	28.84	0.23	5.38	6.79	0.13	20.2	13.67	<0.05	0.23	0.25	47.63
top-009	29.82	0.16	11.30	5.09	0.09	4.95	7.60	0.19	0.16	<0.05	59.44
sub1-009	32.64	0.16	12.80	6.18	0.10	5.79	8.00	<0.05	0.16	<0.05	65.90
sub2-009	34.82	0.18	12.49	14.82	0.11	8.65	4.02	0.28	0.18	0.35	75.93
tailings	34.81	0.41	12.449	14.82	0.25	8.65	4.02	0.28	0.41	0.31	76.23

Fig. 4.2 shows the concentrations of four major oxides in the soil samples. The concentrations of these metals are very high compared P, K, Ni, Zn, Cu, V, and As; this is due to the fact that the parent rocks found in the area are bearing these minerals. Magnesium ranges between 2.02 and 8.64%, calcium between 4.02 and 13.65%, iron between 5.97 and 14.82% and aluminium between 5.80 and 12.80%. High concentration of these metals in soil limits soil fertility and plant growth. Mg acts as blocking agent it coats the roots of the plant and prevents water and nutrients absorption resulting in plant death. The Al bearing mineral causes the soil to be acidic; as the level of dissolved aluminium increases, a chemical reaction occurs with phosphorus compounds, making them insoluble and unavailable to plants. Aluminium is present in soils in a variety of forms and bound to the soil constituents, particularly clay particles and organic matter. When soil pH drops, aluminium becomes soluble and the amount of aluminium in the soil solution increases. Soil aluminium concentration of 2 - 5 parts per million (ppm) is toxic to the roots of sensitive plant species and above 5ppm is toxic to tolerant species. Therefore, the soil in the Atok

has aluminium toxicity causing plants death. Iron is a catalyst required for chlorophyll formation and iron is called a micronutrient not because it isn't important, but because only a small amount is required by plants. According to Weeks (2000), plants need only a small amount of iron, and toxicity problems are encountered when iron is in oversupply. The Atok the soils are over concentrated with iron because it is 14.82%, this causes metabolism problems such as chlorosis in the plants and crops in the area.

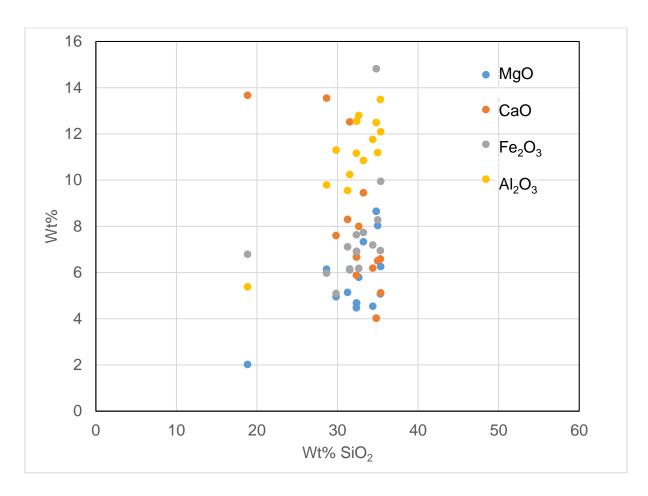


Figure 4.2: A graphical illustration of concentration of MgO, CaO, Fe₂O₃ and Al₂O₃

The graph in Fig 4.3 shows the concentrations of important nutrients that the soil needs to be fertile; however, in the soils from Atok, these are all present only in very low concentrations. Phosphorus ranges between <0.05 and 0.37%, potassium ranges from 0.19 to 0.49% and sodium ranges between <0.00 and 0.85%. Phosphorus (P) is very important for photosynthesis and healthy roots. Phosphorus (P) is very low in the soil because of low levels of P bearing minerals in the parent rock which the soil was derived. Furthermore, the high concentrations of Ca and Fe capture phosphorus and render it unavailable to plants. The deficiency of these nutrient (P) affects leaves of

the plants and limits movement of water. Sodium is a good source of salts in the soil, however, the Atok soils have very low salinity levels, these causes the soil to have very little soil nutrients.

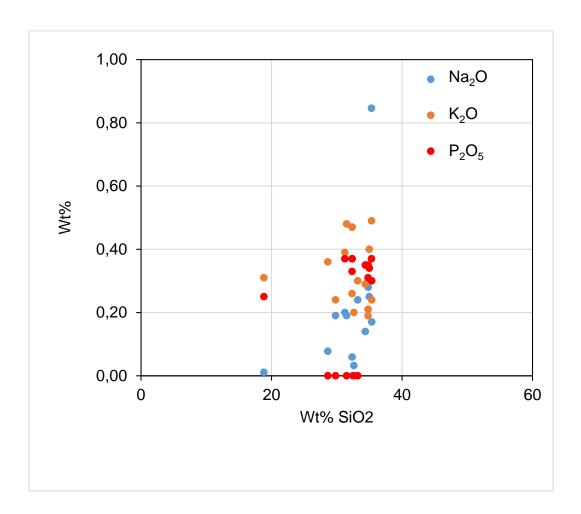


Figure 4.3: A graphical illustration of concentrations of P₂O₅, K₂O and Na₂O

Fig. 4.4 shows that the heavy metals in the soil and are in very low concentrations except for Ni. Vanadium ranges between <0.50 and 0.05%, copper always <0.50% and zinc from 0.00 to 0.02% and nickel concentration is high ranging between 0.02 - 0.09%, this is expected because the rocks are mafic from the Bushveld Igneous Complex. Therefore, these concentrations are not harmful for plants nor human beings.

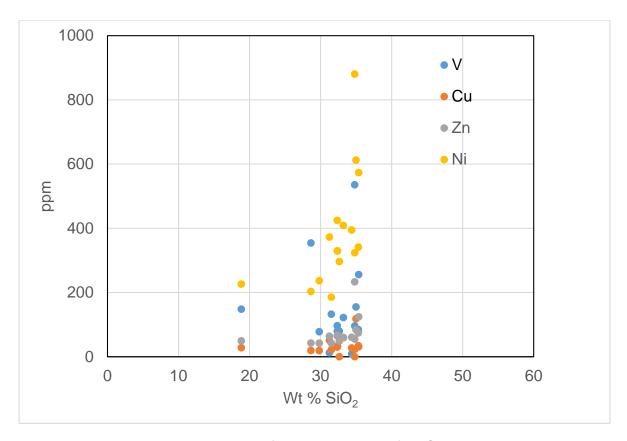


Figure 4.4: A graphical illustration of concentrations of V, Cu, Zn and Ni.

The graph in Fig 4.5 shows high concentrations of chromium in the soil. These concentrations are expected because chrome is mined in the area. The concentrations ranges between 0.11 and 9.76% which are very harmful to plants and living things. High levels of chromium in the soil can affect pregnant women by attacking the foetus and it is a lung cancer hazard, this results from digestion or inhalation of the soil (McDermott et al, 2014).

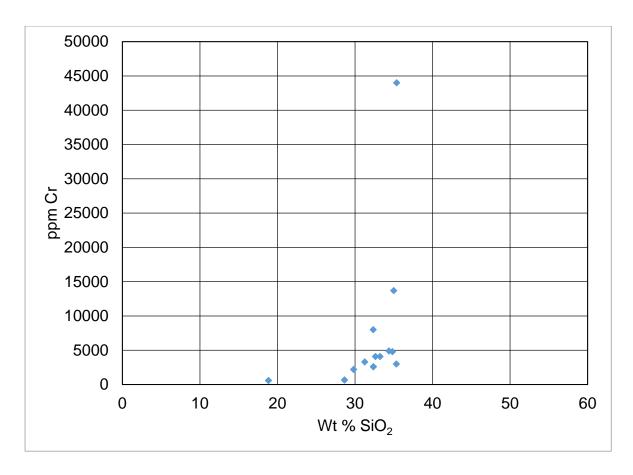


Figure 4.5: A graphical illustration of concentration of Cr

The following are the results obtained from the XRF analysis of the samples collected at the Potlake Nature Reserve.

Table 4.4: XRF analysis results of the control samples of Potlake Nature Reserve (H Du Plessis pers. Comm. 2019) (note values for Cr, Ni and V are in ppm, all others are in wt.%)

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Cr	Ni	V
HDP1	40.88	0.25	16.91	5.41	0.09	2.58	8.39	0.67	0.68	0.52	411	114	91
HDP2	37.18	0.25	14.32	4.99	0.09	2.76	11.19	0.59	0.45	<0.02	274	102	104
HDP3	41.21	0.24	17.55	5.49	0.09	2.78	9.16	1.16	0.46	0.45	350	119	103
HDP4	43.70	0.17	20.44	4.56	0.08	2.84	10.23	1.43	0.39	<0.02	251	9	79
HDP5	38.13	0.28	14.64	6.24	0.13	2.53	7.45	0.46	0.61	0.57	511	129	99
HDP6	39.10	0.26	14.04	5.58	0.10	3.39	10.91	0.31	0.46	0.02	279	111	114
HDP15	45.07	0.12	2.45	9.47	0.14	25.77	3.81	<0.02	0.16	0.41	3850	910	41
HDP16	40.97	0.22	17.66	5.29	0.09	2.89	9.32	1.03	0.44	0.44	403	119	97
HDP17	39.10	0.26	14.04	5.58	0.10	3.39	10.91	0.31	0.46	<0.02	279	111	114
HDP18	46.44	0.18	3.67	11.76	0.15	18.91	1.72	<0.02	0.26	0.43	4010	938	45
HDP19	44.58	0.20	4.07	12.76	0.16	17.39	1.44	<0.02	0.33	0.43	5850	1160	56
HDP20	44.23	0.29	3.39	11.40	0.14	18.71	2.28	<0.02	0.43	0.65	5510	1230	52

HDP21	44.23	0.19	3.39	11.40	0.14	18.71	2.28	<0.02	0.43	0.65	5340	1100	45
HDP22	42.32	0.15	2.87	10.29	0.14	24.48	3.06	<0.02	0.25	0.66	12090	961	86
HDP23	46.35	0.25	3.87	11.87	0.19	15.91	1.55	<0.02	0.36	0.45	7170	874	67
HDP24	43.64	0.15	2.10	10.04	0.17	18.99	1.24	<0.02	0.21	0.35	6090	1230	59
HDP25	41.86	0.19	3.53	12.24	0.19	15.66	1.70	<0.02	0.27	0.49	7590	977	61
HDP26	46.93	0.18	3.49	10.87	0.18	20.81	1.71	<0.02	0.27	0.49	4010	938	45
HDP27	46.44	0.18	3.67	11.76	0.15	18.91	1.72	<0.02	0.26	0.43	4070	1270	50
HDP28	36.34	0.25	3.32	9.97	0.14	12.22	4.01	<0.02	0.34	0.55	6370	929	63
HDP29	46.49	0.18	3.67	<0.02	<0.02	19.75	1.56	<0.02	0.29	0.47	7340	1300	70
HDP30	45.46	0.21	4.12	10.21	0.13	16.10	2.29	<0.02	0.39	0.75	7660	1010	48

The following graphs below Fig. 4.6 to 4.7 are from the data of the control samples collected from Potlake Nature Reserve which is situated in the vicinity of Atok in the Lower Zone of the Bushveld Igneous Complex. The samples were collected in order to explain why the vegetation in the nature reverse is healthy and growing compared to the ones in the other surrounding areas in Atok. The reason being that this area is from the same geological setting where the rocks have similar geochemistry. The results indicated that in deed the soils are very similar with high concentrations of MgO, Fe₂O₃, CaO and Al₂O₃ and low concentrations of P₂O₅, K₂O and Na₂O. Furthermore, there are related low concentrations of the heavy metal Zn, Cu, As, Pb Sr and Ga; but, the Cr concentrations are considered to be very high. The great similarity of these soils in the two areas is considered to be because of similarity of the underlying parent rock, as but are mafic and ultramafic and dominated by minerals rich in Fe, Mg and Ca. Furthermore, not only was the parent rock material that weathered to produce the soils was very similar, but the climatic conditions are essentially the same. Thus, the natural processes involved in soil formation were equivalent although the human impacts on the two areas differ significantly. Therefore, it can be concluded that the vegetation found in Potlake Nature Reserve is that of indigenous and alien species not crops that require nutrients from the soil and proper irrigation to survive.

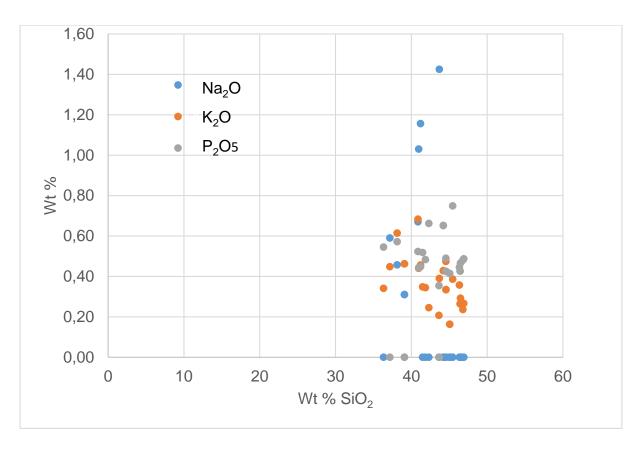


Figure 4.6: A graphical illustration of concentrations of Na₂O, K_2 O and P₂O₅ from Potlake

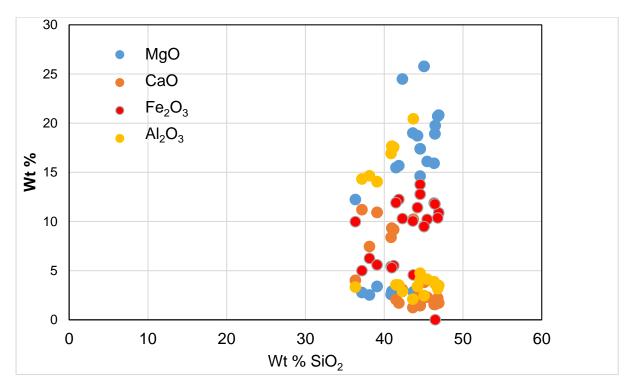


Figure 4.7: A graphical illustration of concentrations of MgO, CaO, Fe_2O_3 and Al_2O_3 of Potlake.

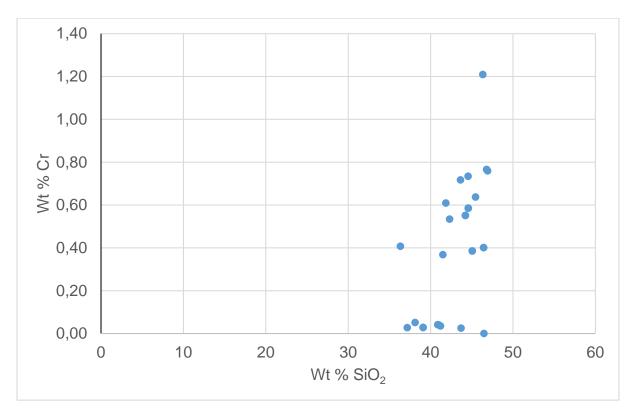


Figure 4.8: A graphical illustration of concentration of Cr in Potlake.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5. 1 Introduction

The findings from the analysis and discussions in this chapter conclude that the mining activities in the Atok Area are not the major source of soil infertility of the soil. The major source is the geology of the area which is rich in mafic/basic rocks. The rocks are rich in minerals bearing Mg, Fe and Al and are depleted in P, K and N bearing minerals that help in plant production. The soil has very low amounts of As, Pd, Zn, Cu, Cs which are associated with heavy metal contamination in mining areas but has high amounts of chromium which is can be harmful to living things. The physicochemical parameters outlined the type of soil in the area was sand texture. The soil has very low amounts of clay which is very important in plant growth as the clay minerals acts as a sponge and store water for a long period of time and clay does not have big pours. Sand has low WHC and moisture content because of the coarse grains size, it is permeable and very porous and cannot store water. The nutrient minerals are easily leached out and depleted. The soil has very low levels of organic matter which is very important in providing nutrients to the soil. There are no minerals salts in the soil that are needed for plant growth hence the very low electrical conductivity.

5. 2 Recommendations

Upon a detailed analysis of the current situation in Atok area, the study came up with the following recommendations to minimize soil infertility associated with mining activities happened in the area.

- i. The most important recommendation is to create environmental awareness campaigns and education in Atok, the community need knowledge about the geological setting the area it's in and how does the geology of the areas affect the soil.
- ii. Irrigation of crops will help increase the food yield and productivity.
- iii. The use of K-N-P (potassium, nitrogen, phosphorous) fertilizers will help enhance soil fertility.

REFERENCES

- Aanooraq Resource Cooperation, (2010). PGE mineral resources Eastern Bushveld Complex, South Africa, Economic Geology, 85, 556-84.
- Abdul-Kareem, A.W. and McRae, S.G. (1984). The effects on topsoil of long-term storage in stockpiles. Plant and Soil, 76(1-3), 357-363.
- Akala, V.A. and Lal, R. (2001). Soil organic carbon pools and sequestration rates in reclaimed mine soils in Ohio. Journal of Environmental Quality, 30(6), 2098-2104.
- Akça, M.O. and Namlı, A. (2015). Effects of poultry litter biochar on soil enzyme activities and tomato, pepper and lettuce plants growth. Eurasian Journal of Soil Science, 4(3), 161-168.
- Albiach, R., Canet, R., Pomares, F. and Ingelmo, F. (2000). Microbial biomass content and enzymatic activities after the application of organic amendments to a horticultural soil. Bioresource Technology, 75(1), 43-48.
- Alloway, B.J. (1995). Heavy metals in soils. Editor BJ. Alloway. Second edition. Blackie, Glasgow. 368 pp.
- Anhaeusser, C.R., and Maske, S. (1986). Mineral Deposits of Southern Africa, 2, Johannesburg: Geol. Soc. S. Afr., 1041-1060.
- Aslibekian, O. and Moles, R. (2000). Environmental Contamination Related to Mine Drainage Distribution from Old Mine Sites by Waterways, in: Mine Water and the Environment. Proceedings of the 7th IMWA Congress, Poland, 2000, 49–58.
- Aslibekian, O., Childs, P. and Moles, R. (1999). Metal contamination of surface water in the vicinity of the Silvermines Abandoned Mine Sites (AMS), Environmental Geochemistry and Health, 21, 339–345.
- Bandick, A.K. and Dick, R.P. (1999). Field management effects on soil enzyme activities. Soil Biology and Biochemistry, 31(11), 1471-1479.
- Barnes, S.J. (1986a). The distribution of chromium among orthopyroxene, spinel and silicate liquid at atmospheric pressure. Geochim. Cosmochim. Acta, 50, 1889-1909.
- Barnes, S.J. (1986b). The effect of trapped liquid crystallization on cumulus mineral compositions in layered intrusions. Contr. Miner. Petrol., 93, 524-531.

- Barnes, S.J. (1989). Are Bushveld U-type parent magmas boninites or contaminated komatiites? Contr. Miner. Petrol., 101, 447-457.
- Batista, M. J., Abreu, M. M., and Serrano Pinto, M. (2007). Biogeochemistry in Neves Corvo mining region, Iberian Pyrite Belt, Portugal. Journal of Geochemical Exploration, 92, 159–176.
- Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L. and Wolf, M. (1996). Schwertmannite and the chemical modelling of iron in acid sulfate waters. Geochimica et Cosmochimica Acta, 60(12), 2111-2121.
- Bohn, H.L., McneaL, RL. and O'connor, G.A. (1985). Soil Chemistry (2nd Ed.). Wiley, New York, 339 pp.
- Boudreau, A.E. (1994). Crystal aging in two-crystal, two-component systems and the formation of fine- scale layering. S. Afr. J. Geol., 97, 473-485.
- Boudreau, A.E., and McCallum, I.S. (1992). Concentration of platinum-group elements by magmatic fluids in layered intrusions. Econ. Geol., 87, 1830-1848.
- Bourg, AC. (1995). Speciation of heavy metals and implications for their mobility, Springer-Verlag, New York. 19-31.
- Brink, A.B.A (1979). Engineering geology of Southern Africa. Volume 1. Building Publications, Pretoria, 319 pp.
- Bristow, D.M. (1989). The petrology and geochemistry of the Lower Critical Zone, Winterveld Chrome Mine. Ph.D. thesis (Unpubl.), Univ. Natal, 356 pp.
- Brooks, R.R. (1987). Serpentine and its vegetation: a multidisciplinary approach. Dioscorides Press. Kent, England. 454 pp.
- Buchanan, D.L. (1975). The petrography of the Bushveld Complex intersected by boreholes in the Bethal area. Trans. geol. Soc. S. Afr., 78, 335-348.
- Buchanan, D.L. (1977). Cryptic variation in minerals from the Bushveld Complex of the Bethal area. Trans. geol. Soc. S. Afr., 80, 49-52.
- Button, A. (1976). Stratigraphy and relations of the Bushveld floor in the Eastern Transvaal. Trans. geol. Soc. S. Afr., 79, 3-12.
- Cameron, E.N. (1978). The Lower Zone of the Eastern Bushveld Complex in the Olifants River trough. J. Petrology, 19, 437-462.
- Cameron, E.N. (1980). Evolution of the lower Critical Zone, central sector, eastern Bushveld Complex. Econ. Geol., 75, 845-871.
- Cameron, E.N. (1982). The upper Critical Zone of the eastern Bushveld Complex. Econ. Geol., 77, 1307-1327.

- Campbell, I.H., Naldrett, A.J., and Barnes, S.J. (1983). A model for the origin of the platinum-rich sulfide horizons in the Bushveld and Stillwater complexes. J. Petrology, 24, 133-165.
- Candeias, C., Melo, R., Ávila, P.F., da Silva, E.F., Salgueiro, A.R. and Teixeira, J.P. (2014). Heavy metal pollution in mine–soil–plant system in S. Francisco de Assis–Panasqueira mine (Portugal). Applied Geochemistry, 44, 12-26.
- Castillo, S., Jesús, D., de la Campa, A.M.S., González-Castanedo, Y. and Fernández-Camacho, R. (2013). Heavy metal deposition fluxes affecting an Atlantic coastal area in the southwest of Spain. Atmospheric Environment, 77, 509-517.
- Cawthorn, R.G., (1996). Re-evaluation of magma compositions and processes in the uppermost Critical Zone of the Bushveld Complex. Miner. Mag., 60, 131-48.
- Cawthorn, R.G., and Barry, S.D. (1992). The role of intercumulus residua in the formation of pegmatoid associated with the UG2 chromitite, Bushveld Complex. Austral. J. Earth Sci., 39, 263-276.
- Cawthorn, R.G., and Biggar, G.M. (1993). Crystallization of titaniferous chromite, magnesian ilmenite and armalcolite in tholeiltic suites in the Karoo Igneous Province. Contr. Miner. Petrol., 114, 221- 235.
- Cawthorn, R.G., and Davies, G. (1983). Experimental data at 3 Kbars pressure on parental magma to the Bushveld Complex. Contr. Miner. Petrol., 83, 128-35.
- Cawthorn, R.G., and Davies, G. (1985). Possible komatiitic affinity of the Bushveld Complex, South Africa. In: Arndt, N.T. and Nisbet, E.G. (eds.) Komatiites. London: George Allen and Unwin, 91-96.
- Cawthorn, R.G., and McCarthy, T.S. (1980). Variations in Cr content of magnetite from the Upper Zone of the Bushveld Complex evidence for heterogeneity and convection currents in magma chambers. Earth Planet. Sci. Lett., 46, 335-343.
- Cawthorn, R.G., and Molyneux, T.G. (1986). The vanadiferous magnetite deposits of the Bushveld Complex. In Anhaeusser, C.R. and Maske, S. (eds.) Mineral Deposits of Southern Africa. Johannesburg: Geol. Soc. S. Afr., 1251-1266.
- Cawthorn, R.G., and Walsh, K.L. (1988). The use of phosphorus contents in yielding estimates of the proportion of trapped liquid in cumulates of the Upper Zone of the Bushveld Complex. Miner. Mag., 52, 81-89.

- Cawthorn, R.G., Barton, J.M., and Viljoen, M.J. (1985). Interaction of floor rocks with the Platreef on Overysel, Potgietersrus, northern Transvaal. Econ. Geol., 80, 988-1006.
- Cawthorn, R.G., Davies, G., Clubley-Armstrong, A., and McCarthy, T.S. (1981). Sills associated with the Bushveld Complex, South Africa: an estimate of the parental magma composition. Lithos, 14, 1-15.
- Cawthorn, R.G., Meyer, S.P., and Kruger, F.J. (1991). Major addition of magma at the Pyroxenite Marker in the western Bushveld Complex, South Africa. J. Petrology 32, 739-63. Cheney, E.S., and Twist, D., 1991. The conformable emplacement of the Bushveld mafic rocks along a regional unconformity in the Transvaal succession of South Africa. Precamb. Res., 52, 115-132.
- Chibuike, G. and Obiora, S.C. (2014). Heavy Metal Polluted Soils: Effect on Plants and Bioremediation Methods. Applied and Environmental Soil Science Volume 2014, Article ID 752708, 12 p.
- Chopin, E.I.B., and Alloway, B.J. (2007). Distribution and Mobility of Trace Elements in Soils and Vegetation Around the Mining and Smelting Areas of Tharsis, Río Tinto and Huelva, Iberian Pyrite Belt, SW Spain. Received: 17 May 2006 / Accepted: 2 January 2007 / Published online: 30 January 2007 Springer Science and Business Media B.V. 2007.
- Cobârzan, B., 2008. Environmental Rehabilitation of Closed Mines. A Chase Study on Romania. Transylvanian Review of Administrative Sciences, 4(22), pp.34-43.
- Coetzee, H. (1995). Airborne radiometric mapping of the environmental impact of gold and uranium mining in Gauteng Province, South Africa. In Symposium on the Application of Geophysics to Engineering and Environmental Problems 1995 (pp. 859-863). Society of Exploration Geophysicists.
- Coetzee, M.J., Bennie, A.T.P., and Hoffman, J.E. (1995). Sustainable crop production on aeolian sandy semi-arid soils in South Africa. African Crop Science Journal, 3(1) 90-94.
- Cogho, V.E. (2012). Optimum Coal Mine: striving towards a zero effluent mine. Journal of the Southern African Institute of Mining and Metallurgy, 112(2), 119-126.
- Crounse, R.G. Pories, W.J. Bray, T. and Mauger, R.L. (1983). Geochemistry and Man: Health and Disease. (2) Elements possibly essential, those toxic and others. (In: Thornton, I. ed. Applied Environmental Geochemistry, 309-330, Academic Press Geology Series, Academic Press, London.

- Daldoul, G., Souissi, R., Souissi, F., Jemmali, N. and Chakroun, H.K. (2015). Assessment and mobility of heavy metals in carbonated soils contaminated by old mine tailings in North Tunisia. Journal of African Earth Sciences, 110, 150-159.
- Davies, G., and Cawthorn, R.G. (1984). Mineralogical data on a multiple intrusion in the Rustenburg Layered Suite of the Bushveld Complex. Miner. Mag., 48, 469-480.
- Davies, G., Cawthorn, R.G., Barton, J.M., and Morton, M. (1980). Parental magma to the Bushveld Complex. Nature, 287, 33-35.
- de Klerk, W.J. (1982). Geology, geochemistry and silicate mineralogy of the Upper Critical Zone of the North-Western Bushveld complex. Unpubl. M.Sc. thesis, Rhodes Univ., Grahamstown, 200 pp.
- de Klerk, W.J. (1991). Petrogenesis of the Upper Critical Zone in the western Bushveld Complex. Ph.D. thesis (Unpubl.), Rhodes Univ. 294 pp.
- de Waal, S.A. (1975). The mineralogy, chemistry and certain aspects of reactivity of chromite from the Bushveld Igneous Complex. National Institute for Metallurgy, Johannesburg, S. Africa. Report No. 1709, 80 pp.
- Degens, B.P. (1998). Decreases in microbial functional diversity do not result in corresponding changes in decomposition under different moisture conditions. Soil Biology and Biochemistry, 30(14), 1989-2000.
- Deng, S.P. and Tabatabai, M.A. (1994). Cellulase activity of soils. Soil Biology and Biochemistry, 26(10), 1347-1354.
- Dick, H.J.B., and Bullen, T. (1984). Chromian spinel as a petrogenetic indicator in abyssal and alpine- type peridotites and spatially associated lavas. Contr. Miner. Petrol., 86, 54-76.
- Dick, R.P., Breakwell, D.P. and Turco, R.F. (1996). Soil enzyme activities and biodiversity measurements as integrative microbiological indicators. Methods for Assessing Soil Quality, (methods for asses), 247-271.
- Dirken, M.W. (2003). Determining trace concentrations. World Cement, 34(4), 64-69.
- Eales, H.V., and Reynolds, I.M. (1986). Cryptic variations within chromites of the Upper Critical Zone, Northwestern Bushveld Complex. Econ. Geol., 81, 1056-1066.

- Eales, H.V., Botha, W.J., Hattingh, P.J., De Klerk, W.J., Maier, W.D., and Odgers, A.T.R., (1993a). The mafic rocks of the Bushveld Complex: a review. J. Afr. Earth. Sci., 16, 121-142.
- Eales, H.V., De Klerk, W.J., and Teigler, B. (1990b). Evidence for magma mixing processes within the Critical and Lower Zones of the Northwestern Bushveld Complex. Chem. Geol., 88, 261-278.
- Eales, H.V., De Klerk, W.J., Butcher, A.R., and Kruger, F.J. (1990a). The cyclic unit beneath the UG1 chromitite (UG1FW unit) at RPM Union Section Platinum Mine. Miner. Mag., 54, 23-43.
- Eales, H.V., De Klerk, W.J., Teigler, B., and Maier, W.D. (1994). Nature and origin of orthopyroxenites in the Western Bushveld Complex, in the light of compositional data. S. Afr. J. Geol., 97, 399-407.
- Eales, H.V., Field, M., De Klerk, W.J., and Scoon, R.N. (1988). Regional trends of chemical variation and thermal erosion in the Upper Critical Zone, Western Bushveld Complex. Miner. Mag., 52, 63-79.
- Eales, H.V., Maier, W.D., and Teigler, B. (1991). Corroded plagioclase feldspar inclusions in orthopyroxene and olivine of the Lower and Critical Zones, Western Bushveld Complex. Miner. Mag., 55, 479-486.
- Eales, H.V., Marsh, J.S., Mitchell, A.A., De Klerk, W.J., Kruger, F.J., and Field, M. (1986). Some geochemical constraints upon models for the crystallization of the upper Critical Zone Main Zone interval, Northwestern Bushveld Complex. Miner. Mag., 50, 567-582.
- Eales, H.V., Teigler, B., and Maier, W.D. (1993b). Cryptic variations of minor elements AI, Cr, Ti and Mn in Lower and Critical Zone orthopyroxenes of the Western Bushveld Complex. Miner. Mag., 57, 257-264.
- Economopoulos, A.P. and World Health Organization, (1993). Assessment of sources of air, water, and land pollution: a guide to rapid source inventory techniques and their use in formulating environmental control strategies (No. WHO/PEP/GETNET/93.1-AB. Unpublished). Geneva: World Health Organization.
- Engelbrecht, J.P. (1985). The chromites of the Bushveld Complex in the Nietverdiend area. Econ. Geol., 80, 896-910.
- Engelbrecht, J.P. (1990). The Marico hypabyssal suite, and the marginal zone of the Bushveld Complex in the Marico district. S. Afr. J. Geol. 93, 318-328.

- Evans, R., (1990). Fluids adsorbed in narrow pores: phase equilibria and structure.

 Journal of Physics: Condensed Matter, 2(46), p.8989.
- Ferguson, K.D. and Erickson, P.M, (1988). Pre-mine prediction of acid mine drainage. In Environmental Management of Solid Waste (pp. 24-43). Springer, Berlin, Heidelberg.
- Field, M., (1987). The petrology and geochemistry of the Upper Critical Zone of the Bushveld Complex, at the Amandelbult Section of Rustenburg Platinum Mines, Ltd. Unpubl. M. Sc. thesis, Rhodes Univ., Grahamstown, 129pp.
- Fisheries, F.A.O. (2011). Aquaculture Department. 2013. Global Aquaculture Production Statistics for the year.
- Forstner, U. and Kersten, M. (1988). Assessment of metal mobility in dredged material and mine waste by pore water chemistry and solid speciation. (In: Salomons W. and Forstner U. (eds.) Chemistry and Biology of Solid Waste, Dredged Materials and Mine Tailings. 214-237, Springer Verlag, New York).
- Freeman, K.R., Pescador, M.Y., Reed, S.C., Costello, E.K., Robeson, M.S. and Schmidt, S.K., (2009). Soil CO2 flux and photoautotrophic community composition in high-elevation, 'barren' soil. Environmental Microbiology, 11(3), pp.674-686.
- Fresquez, P.R., Aldon, E.F. and Sorensen, D.L. (1985). Microbial and soil enzyme activities in stockpiled topsoil and coal mine spoil materials. In Proceedings of the National Meeting of the American Society for Surface Mining and Reclamation, (pp. 340-345).
- Fujimori, T. and Takigami, H. (2014). Pollution distribution of heavy metals in surface soil at an informal electronic-waste recycling site. Environmental Geochemistry and Health, 36(1), 159-168.
- Gain, S.B. (1985). The geologic setting of the platiniferous UG2 chromitite layer on the farm Maandagshoek, Eastern Transvaal. Econ. Geol., 80, 925-943.
- Gauert, C.D.K., de Waal, S.A., and Wallmach, T. (1995). The geology of the Uitkomst Complex, eastern Transvaal evidence for a magma conduit. J. Afr. Earth Sci., 21,553-570.
- Gee, J.P. (1999). Critical issues: Reading and the new literacy studies: Reframing the national academy of sciences report on reading. Journal of Literacy Research, 31(3), 355-374.

- Ghosh, S.P., Kumar, B.M., Kabeerathumma, S. and Nair, G.M., (1989). Productivity, soil fertility and soil erosion under cassava based agroforestry systems. Agroforestry Systems, 8(1), pp.67-82.
- Giusquiani, P.L., Gigliotti, G., Businelli, D. and Macchioni, A. (1994). Spectroscopic comparison between humic and fulvic acids from urban waste compost and soil. Humic substances in the global environment and implications on human health, Elsevier, Amsterdam, 1303-1310.
- González-Pérez, J.A., Rumpel, C., Bardoux, G., Largeau, C., Gonzalez-Vila, F.J. and Valentin, C. (2007). Composition and reactivity of morphologically distinct charred materials left after slash-and-burn practices in agricultural tropical soils. Organic Geochemistry, 38(6), 911-920.
- Govil, P., Reddy, G. and Krishna, A. (2001). Contamination of soil due to heavy metals in the Patancheru industrial development area, Andhra Pradesh, India. Environmental Geology, 41(3-4), 461-469.
- Green, T.H., and Watson, E.B. (1982). Crystallization of natural magmas under high pressure, hydrous conditions with particular reference to 'orogenic' rock series. Contr. Miner. Petrol., 79, 96-105.
- Grobler, N.J., and Whitfield, G.G. (1970). The olivine-apatite magnetitites and related rocks in the Villa Nora occurrence of the Bushveld Igneous Complex. Geol. Soc. S. Afr. Spec. Publn. 1,208-227.
- Groeneveld, D, (1970). The structural features and the petrography of the Bushveld Complex in the vicinity of Stoffberg, Eastern Transvaal. Geol. Soc. S. Afr., Spec. Publ., 1, 36-45.
- Grove, T.L., and Bence, A.E. (1977). Experimental study of pyroxene-liquid interaction in quartz- normative basalts. Proc. Eighth Lunar Sci. Conf. 1549-79. Hamilton, P.J., 1977. Sr isotope and trace element studies of the Great Dyke and Bushveld mafic phase and their relation to early Proterozoic magma genesis in Southern Africa. J. Petrology, 18, 24-52.
- Harmer, R.E., and Sharpe, M.R. (1985). Field relations and strontium isotope systematics of the marginal rocks of the Eastern Bushveld Complex. Econ. Geol., 80, 813-837.
- Harney, D.M.W., Merkle, R.K.W., and von Gruenewaldt, G, (1990). Plagioclase composition in the Upper zone, eastern Bushveld Complex support for

- magma mixing at the Main Magnetite Layer. Inst. Geol. Res. Bushveld Complex, Univ. Pretoria, 87, 19 pp.
- Harris, J.A., Birch, P. and Short, K.C., (1989). Changes in the microbial community and physico-chemical characteristics of topsoils stockpiled during opencast mining. Soil Use and Management, 5(4), pp.161-168.
- Hatton, C.J. (1986). Regional variations in the Middle Group of chromitite layers, Bushveld Complex. Extended Abstracts Geo-congress '86, Geol. Soc. S.A., Johannesburg, 595-598.
- Hatton, C.J., and Sharpe, M.R. (1989). Significance and origin of boninite-like rocks associated with the Bushveld Complex. In: Crawford, A.J. (ed.) Boninites. London: Unwin Hyman, 174-203.
- Hatton, C.J., and von Gruenewaldt, G, (1987). The geological setting and petrogenesis of the Bushveld chromitite layers. In: Stowe, C.W. (ed.) Evolution of chromium ore fields. New York: Van Nostrand Reinhold Co., 109-143.
- Holmgren, G.G.S., Meyer, M.W., Chaney, R.L., Daniels, R.B. (1977). Cadmium, Lead, Zinc, Copper, and Nickel in Agricultural Soils of the United States of America. Journal of Environmental Quality, 22(2), 335-348.
- Hoyle, P. (1993). Chemical and modal variations at the top of the Upper Zone in the Northwestern Bushveld Complex. Symposium on Layering in Igneous Complexes, Abstracts Vol., Univ. Witwatersrand, Johannesburg. 359 pp.
- Hu, W., Huang, B., Weindorf, D.C. and Chen, Y. (2012). Metals analysis of agricultural soils via portable X-Ray Fluorescence Spectrometry. Bulletin of Environmental Contamination and Toxicology, 92(4), 420-426.
- Hu, W., Huang, B., Weindorf, D.C. and Chen, Y. (2014). Metals analysis of agricultural soils via portable X-ray fluorescence spectrometry. Bulletin of Environmental Contamination and Toxicology, 92(4), 420-426.
- Hulbert, L.J., and von Gruenewaldt, G. (1982). Nickel, copper and platinum mineralization in the Lower Zone of the Bushveld Complex, south of Potgietersrus. Econ Geol., 77, 1296-1306.
- Hulbert, L.J., and von Gruenewaldt, G. (1985). Textural and compositional features of chromite in the Lower and Critical Zones of the Bushveld Complex south of Potgietersrus. Econ. Geol., 80, 872-895.

- Huppert, H.E., and Sparks, R.S.J. (1980). The fluid dynamics of a basaltic magma chamber replenished by influxes of hot, dense ultrabasic magma. Contr. Miner. Petrol., 75, 279-289.
- Hutchison C.S. (1974). Laboratory Handbook of Petrographic Techniques. John Wiley and Sons Inc. Hoboken, New Jersey, 527 pp.
- Irvine, T.N. (1977). Origin of chromitite layers in the Muskox intrusion and other stratiform intrusions. Geology, 5, 273-277.
- Irvine, T.N. (1980). Magmatic density currents and cumulus processes. Amer. J. Sci., 280-A, 1-58.
- Irvine, T.N., Keith, D.W., and Todd, S.G. (1983). The J-M platinum-palladium reef of the Stillwater Complex, Montana. II. Origin by double diffusive convective magma mixing and implications for the Bushveld Complex. Econ. Geol., 78, 1287-1334.
- Irving, A.J. (1978). A review of experimental studies of crystal/liquid trace element partitioning. Geochim. Cosmochim. Acta, 42, 743-770.
- Janakiram, T. and Sridevi, K. (2010). Conversion of waste into wealth: A study in solid waste management. Journal of Chemistry, 7(4), 1340-1345.
- Jang, M. (2010). Application of portable X-ray fluorescence (pXRF) for heavy metal analysis of soils in crop fields near abandoned mine sites. Environmental Geochemistry and Health, 32(3), 207-216.
- Johnson, D.B. and Williamson, J.C. (1994). Conservation of mineral nitrogen in restored soils at opencast coal mine sites: I. Results from field studies of nitrogen transformations following restoration. European Journal of Soil Science, 45(3), 311-317.
- Kabata-pendias, A. (1992). Behavioural properties of trace metals in soils. Applied Geochemistry, Suppl. Issue No.2: 3-9.
- Kabata-pendias, A. and Pendias, H. (1986). Trace elements in soils and plants. C.R.C. Press, Florida, 315 pp.
- Karathanasis, S.K., Sastry, K.N., and Seedorf. (1988). Different cis-acting DNA elements control expression of the human apolipoprotein AI gene in different cell types. Molecular and Cellular Biology, 8(2), 605-614.
- Kenyon, A.K., Attridge, R.L., and Coetzee, G.L. (1986). The Uitkomst nickel-copper deposit, Eastern Transvaal. In: Anhaeusser, C.R., and Maske, S. (eds.)

- Mineral Deposits of Southern Africa, 1, Johannesburg: Geol. Soc. S. Afr., 1009-1017.
- Kiss, S., Drăgan-Bularda, M. and Rădulescu, D. (1975). Biological significance of enzymes accumulated in soil. In Advances in Agronomy (Vol. 27, 25-87). Academic Press.
- Klemm, D.D., Ketterer, S., Reichhardt, F., Steindl, J. and Weber-Diefenbach, K, (1985a). Implications of vertical and lateral compositional variations across the Pyroxenite Marker and its associated rocks in the upper part of the Main Zone in the eastern Bushveld Complex. Econ. Geol., 80, 1007-1015.
- Klemm, D.D., von Gruenewaldt, G., Henckel, J., and Dehm, R. (1985b). The geochemistry of titanomagnetite in magnetite layers and their host rocks. Econ. Geol., 80, 1075-1088.
- Kolker, A. (1982). Mineralogy and geochemistry of Fe-Ti oxide and apatite (nelsonite) deposits and evaluation of the liquid immiscibility hypothesis. Econ. Geol., 77, 46-58.
- Kruger, F.J, (1990). The stratigraphy of the Bushveld Complex: a reappraisal of the Main Zone boundaries. S. Afr. J. Geol. 93, 376-381.
- Kruger, F.J, (1994). The Sr-isotopic stratigraphy of the western Bushveld Complex. S. Afr. J. Geol., 97, 393-398.
- Kruger, F.J. (1992). The origin of the Merensky Cyclic Unit: Sr-isotopic and mineralogical evidence for an alternative orthomagmatic model. Austral. J. Earth Sci., 39, 255-261.
- Kruger, F.J., and Marsh, J.S. (1982). Significance of ⁸⁷Sr/⁸⁷Sr ratios in the Merensky Cyclic Unit of the Bushveld Complex. Nature, 298, 53-55.
- Kruger, F.J., and Marsh, J.S. (1985). The mineralogy, petrology and origin of the Merensky Cyclic Unit in the western Bushveld Complex. Econ. Geol., 80, 958-974.
- Kruger, F.J., and Smart, R. (1987). Diffusion of trace elements during bottom crystallization of double-diffusive convection systems: the magnetitite layers of the Bushveld Complex. J. Volcanol. Geotherm. Res., 34, 133-142.
- Kruger, F.J., Cawthorn, R.G., and Walsh, K.L. (1987). Strontium isotope evidence against magma addition in the Upper Zone of the Bushveld Complex. Earth. Planet. Sci. Lett. 84, 51-8. Lee, C.A., 1981. Post-deposition structures in the Bushveld Complex mafic sequence.

- Kujur, M. and Patel, A.K. (2012). Quantifying the contribution of different soil properties on microbial biomass carbon, nitrogen and phosphorous in dry tropical ecosystem. International Journal of Environmental Sciences, 3, 2272-2284.
- Labovitz, M.L., Masuoka, E.J., Bell, R., Siegrist, A.W. and Nelson, R.F. (1983). The application of remote sensing to geobotanical exploration for metal sulfides; results from the 1980 field season at Mineral, Virginia. Economic Geology, 78(4), 750-760.
- Lad, R.J. and Samant, J.S. (2015). Impact of bauxite mining on soil: a case study of bauxite mines at Udgiri, Dist-Kolhapur, Maharashtra State, India. International Research Journal of Environment Sciences, 4(2), 77-83.
- Lee, C.A., and Butcher, A.R. (1990). Cyclicity in the Sr-isotopic stratigraphy through the Merensky and Bastard Reef Units, Atok Section, Eastern Bushveld Complex. Econ. Geol., 85, 877-883.
- Leeb-du Toit, A. (1986). The Impala Platinum Mines. In: Anhaeusser, C.R., and Maske, S. (eds.) Mineral Deposits of Southern Africa, 2, Johannesburg: Geol. Soc. S.A., 101-106.
- Lipin, B.R. (1993). Pressure increases, the formation of chromite seams, and the development of the Ultramafic Series in the Stillwater Complex, Montana. J. Petrology, 34, 955-976.
- Lopez, M.V., Álvaro-Fuentes, J., Cantero-Martinez, C., Arrúe, J.L. (2008). Tillage Effects on Soil Organic Carbon Fractions in Mediterranean Dryland Agroecosystems. Soil Science Society of America Journal, 72(2), 541-547.
- Maaloe, S. (1978). The origin of rhythmic layering. Miner. Mag. 42, 337-345.
- Maier, W.D. (1991). Geochemical and petrological trends in the UG2-Merensky Unit interval of the Upper Critical Zone. Ph.D. thesis (Unpubl.), Rhodes Univ., Grahamstown, 241 pp.
- Maier, W.D., and Eales, H.V, (1994a). A facies model for the interval between the UG2 and Merensky Reef, Western Bushveld Complex, South Africa. Trans. Inst. Min. Metall., (Sect. B: Appl. Earth Sci.), 103, B22-30.
- Maier, W.D., and Eales, H.V. (1994b). Plagioclase inclusions in orthopyroxene and olivine of the UG2- Merensky Reef interval: regional trends in the western Bushveld Complex. S. Afr. J. Geol., 97, 408- 414.

- Maiti, S.K. Mukhopadhyay, S., and Masto, R.E. (2000). Development of mine soil quality index (MSQI) for evaluation of reclamation success: A chronosequence study. Ecological Engineering, 71, 10-20.
- Marais, C.L. (1977). An investigation of the Pyroxenite Marker and the associated rocks in the Main Zone of the eastern Bushveld Complex. Unpubl. M.Sc. thesis, Univ. Pretoria, 87 pp.
- Maria.L, and Azevedo, S. (2003). Biosolids and heavy metals in soils. Sci. agric. (Piracicaba, Braz.) 60 no.4 Piracicaba Oct./Dec. 2003.
- Mathez, E.A. (1989). Interactions involving fluids in the Stillwater and Bushveld Complexes: observations from the rocks. Rev. Econ. Geol. 4, 167-79.
- Mbendi, P. (2004). Metal pollution of soils and vegetation in an area with petrochemical industry. Science of the Total Environment 321, 59–69.
- Mcbride, M.B. (1994). Metal mobility at and old heavily loaded sludge application site. Environmental Pollution 99, 365–377.
- McCarthy, T.S., Cawthorn, R.G., Wright, C.J., and McIver, J.R. (1985). Mineral layering in the Bushveld Complex: implications of Cr abundances in magnetite from closely-spaced magnetitite and intervening silicate-rich layers. Econ. Geol., 80, 1062-1074.
- McClure, R. and Schneider, A. (2001). The General Mining Act of 1872 has left a legacy of riches and ruin. Seattle Post-Intelligencer, 11, 1-7.
- McDermott, S., Bao, W., Aelion, C.M., Cai, B. and Lawson, A.B. (2014). Does the metal content in soil around a pregnant woman's home increase the risk of low birth weight for her infant? Environmental geochemistry and health, 36(6), pp.1191-1197.
- McLaren, R.G., Shiowatana, J., Chanmekha, N. and Samphao, A. (2001). Fractionation of arsenic in soil by a continuous-flow sequential extraction method. Journal of Environmental Quality, 30(6), 1940-1949.
- Mentis, M.T. (2006). Restoring native grassland on land disturbed by coal mining on the Eastern Highveld of South Africa: news and views. SA J. Science, 102(5), 193-197.
- Merkle, R.K.W., and von Gruenewaldt, G. (1986). Compositional variation of Copentlandite: relation to the evolution of the Upper Zone of the western Bushveld Complex. Can. Miner., 24, 529-546.

- Michálková, Z., Komárek, M., Šillerová, H., Della Puppa, L., Joussein, E., Bordas, F., Vaněk, A., Vaněk, O. and Ettler, V. (2014). Evaluating the potential of three Fe-and Mn-(nano) oxides for the stabilization of Cd, Cu and Pb in contaminated soils. Journal of Environmental Management, 146, 226-234.
- Michelsen, A., Graglia, E., Schmidt, I.K., Jonasson, S., Sleep, D. and Quarmby, C, (1999). Differential responses of grass and a dwarf shrub to long-term changes in soil microbial biomass C, N and P following factorial addition of NPK fertilizer, fungicide and labile carbon to a heath. The New Phytologist, 143(3), 523-538.
- Mitchell, A.A. (1990). The stratigraphy, petrography and mineralogy of the Main Zone of the Northwestern Bushveld. S. Afr. J. Geol., 93, 818-831.
- Molyneux, T.G. (1970). The geology of the area in the vicinity of Magnet Heights, Eastern Transvaal, with special reference to magnetic iron ore. Geol. Soc. S. Afr., Spec. Publ., 1, 228-141.
- Molyneux, T.G. (1974). A geological investigation of the Bushveld Complex in Sekhukhuneland and part of the Steelpoort valley. Trans. geol. Soc. S. Afr., 77, 329-338.
- Municipality, D. (2012). Integrated development plan (IDP) 2012-2017. IDP, 2012(2017).
- Murck, B.W., and Campbell, I.H, (1986). The effects of temperature, oxygen fugacity and melt composition on the behaviour of chromium in basic and ultrabasic melts. Geochim. Cosmochim. Acta, 50, 1871-1887.
- Naldrett, A.J., Cameron, G., von Gruenewaldt, G., and Sharpe, M.R. (1987). The formation of stratiform PGE deposits in layered intrusions. In: Parsons, I. (ed.) Origins of igneous layering. Dordrecht: Reidel Publ. Co., 313-98.
- Naldrett, A.J., Gasparrini, E.C., Barnes, S.J., von Gruenewaldt, G., and Sharpe, M.R. (1986). The Upper Critical Zone of the Bushveld Complex and the origin of Merensky-type ores. Econ. Geol, 81, 1105- 1017.
- Nannipieri, P., Ascher, J., Ceccherini, M., Landi, L., Pietramellara, G. and Renella, G. (2003). Microbial diversity and soil functions. European Journal of Soil Science, 54(4), 655-670.
- O'Connor, G.A., Elliott, H.A., Basta, N.T., Bastian, R.K., Pierzynski, G.M., Sims, R.C. and Smith, J.E. (2005). Sustainable land application. Journal of Environmental Quality, 34(1), 7-17.

- Pérez-de-Mora, A., Burgos, P., Madejón, E., Cabrera, F., Jaeckel, P. and Schloter, M. (2006). Microbial community structure and function in a soil contaminated by heavy metals: effects of plant growth and different amendments. Soil Biology and Biochemistry, 38(2), 327-341.
- Pevzner, P.A., Jones, N.C., and Pevzner, P. (2004). An introduction to bioinformatics algorithms. MIT press, 256 pp.
- Philpotts, A.R., and Doyle, C.D. (1983). Effect of magma oxidation state on the extent of silicate liquid immiscibility in a tholeitic basalt. Amer. J. Sci., 283, 967-986.
- Pierzynski, G.M. Sims, TJ. and Vance, G.F. (1994). Soils and environmental quality. Lewis, London, 313 pp.
- Quadling, K., and Cawthorn, R.G. (1994). The layered melagabbronorite-leucogabbronorite succession from the Main Zone of the Bushveld Complex. S. Afr. J. Geol., 97, 442-454.
- Ramakadi, K.A. and Dunlevey, J.N. (2020). Mineralogy and geochemisty of soils around Atok, Limpopo Province, South Africa. S.A. J. Sci. (in press).
- Reichhardt, F.J. (1994). The Molopo Farms Complex, Botswana: history, stratigraphy, petrography, petrochemistry and Ni-Cu-PGE mineralization. Explor. Mining Geol., 3, 263-284.
- Renella, G., Nannipieri, P., Ascher, J., Ceccherini, M., Landi, L., and Pietramellara, I. (2003). Microbial diversity and soil functions. European Journal of Soil Science, 54(4), 655-670.
- Reynolds, I.M. (1985). Contrasted mineralogy and textural relations in the uppermost Ti-magnetite layers of the Bushveld Complex in the Bierkraal area north of Rustenburg. Econ. Geol., 80, 1027-1048.
- Rice, A.R., and Eales, H.V. (1995). The densities of Bushveld melts: textural and hydrodynamic criteria. Miner. Petrol., 54, 45-53.
- Robins, B. (1982). Finger structures in the Lille Kufjord layered intrusion, Finmark, northern Norway. Contr. Miner. Petrol., 81, 290-5.
- Rosner, M., Toiber-Yasur, I., Hadas, A., Russo, D. and Yaron, B. (1999). Leaching of terbuthylazine and bromacil through field soils. Water, Air, and Soil Pollution, 113(1-4), 319-335.
- SACS: South African Committee for Stratigraphy (1980) Stratigraphy of South Africa.

 Part I (Comp. L.E. Kent). Lithostratigraphy of the Republic of South Africa, South

- West Africa/Namibia and the Republics of Bophuthatswana, Transkei and Venda. Handb. Geol. Surv. S. Afr, 8, 690 pp.
- Saviozzi, A., Levi-Minzi, R., Cardelli, R. and Riffaldi, R. (2001). A comparison of soil quality in adjacent cultivated, forest and native grassland soils. Plant and Soil, 233(2), 251-259.
- Saxena, M.C., Linke, K.H., Sauerborn, J. and Masri, H. (1991). Effect of soil solarization on the yield of food legumes and on pest control. In Proceedings of the First International Conference on Soil Solarization. (Eds.) De Vay, J.E., Stapleton, J.J. and Elmore C.L (pp. 139-154).
- Schellekens, M., Hoppeler, R., Perrin, A., Gomes, J.V., Boiron, D., Aspect, A. and Westbrook, C.I. (2005). Hanbury Brown Twiss effect for ultracold quantum gases. Science, 310(5748), 648-651.
- Schiffries, C.M. (1982). The petrogenesis of a platiniferous dunite pipe in the Bushveld Complex: infiltration metasomatism by a chloride solution. Econ. Geol., 77, 1439-1453.
- Schimel, J.P. and Weintraub, M.N. (2003). The implications of exoenzyme activity on microbial carbon and nitrogen limitation in soil: a theoretical model. Soil Biology and Biochemistry, 35(4), 549-563.
- Schlüter, K. (2000). evaporation of mercury from soils. An integration and synthesis of current knowledge. Environmental Geology, 39(3-4), 249-271.
- Schurmann, L.W. (1993). The geochemistry and petrology of the Upper Critical Zone of the Boshoek section of the Western Bushveld Complex. Geol. Surv. S. Afr. Bull.,113, 88 pp.
- Scoon, R.N., and de Klerk, W.J, (1987). The relationship of olivine cumulates and mineralization to cyclic units in part of the Upper Critical Zone of the Western Bushveld Complex. Can. Miner., 25, 51-77.
- Scoon, R.N., and Mitchell, A.A. (1994). Discordant iron-rich pegmatites in the Bushveld Complex and their relationship to iron-rich intercumulus and residual liquids. J. Petrology, 35, 881-917.
- Scoon, R.N., and Teigler, B. (1994). Platinum-group element mineralization in the Critical Zone of the western Bushveld Complex. Econ. Geol. 89, 109-121.
- Scoon, R.N., and Teigler, B. (1995). A new LG6 chromite reserve at Eerste Geluk in the boundary zone between the central and southern sectors of the Eastern Bushveld Complex. Econ. Geol., 90, 969-982.

- Shandro, J.A., Veiga, M.M., Shoveller, J., Scoble, M. and Koehoorn, M. (2011). Perspectives on community health issues and the mining boom–bust cycle. Resources Policy, 36(2), 178-186.
- Sharpe, M.R. (1981). The chronology of magma influxes to the eastern compartment of the Bushveld Complex as exemplified by its marginal border groups. J. Geol. Soc. Lond., 138, 307-326.
- Sharpe, M.R. (1985). Strontium isotope evidence for preserved density stratification in the Main Zone of the Bushveld Complex. Nature, 316, 119-126.
- Sharpe, M.R., and Hulbert, L.J. (1985). Ultramafic sills beneath the eastern Bushveld Complex. Econ. Geol., 80, 849-871.
- Shearer, C.K., Papike, J.J., Simon, S.B. and Shimizu, N. (1989). An ion microprobe study of the intra- crystalline behaviour of REE and selected trace elements in pyroxene. Geochim. Cosmochim. Acta, 83, 1041-1054.
- Singer, MJ. and Munns, D.N. (1992). Soils, introduction. Second edition. Macmillan, New York, 473pp.Silicate Minerals, Editors Mineralogical Society of America, Washington, D.C).
- Sinsabaugh, R.L. and Moorhead, D.L. (1994). Resource allocation to extracellular enzyme production: a model for nitrogen and phosphorus control of litter decomposition. Soil biology and biochemistry, 26(10), 1305-1311.
- Sparks, D.L. (1995). Environmental soil chemistry. Academic Press, New York, 267pp
- Sparks, R.S., Huppert, H.E., Koyaguchi, T., and Hallworth, M.A. (1993). Origin of modal and rhythmic igneous layering by sedimentation in a convecting magma chamber. Nature, 361, 246-249.
- Stolt, P., Asp, H. and Hultin, S., (2006). Genetic variation in wheat cadmium accumulation on soils with different cadmium concentrations. Journal of Agronomy and Crop Science, 192(3), 201-208.
- Strohmayer, P. (1999). Soil stockpiling for reclamation and restoration activities after mining and construction. Student On-Line Journal 4(7), pp 109-121.
- Tankard, A.J., Jackson, M.P.A., Eriksson, K.A., Hobday, D.K., Hunter, D.K. and Minter, W.E.L. (1982). Crustal Evolution of Southern Africa, 3.8 billion years of Earth History. Springer-Verlag, Berlin, 523 pp.
- Teigler, B. (1990). Mineralogy, petrology and geochemistry of the Lower and Lower Critical Zones, Northwestern Bushveld Complex. Ph.D. thesis (Unpubl.), Rhodes Univ., Grahamstown, 247 pp.

- Teigler, B., and Eales, H.V. (1993). Correlation between chromite composition and PGE mineralization in the Critical Zone of the Western Bushveld Complex. Mineral. Deposita, 28, 291-302.
- Teigler, B., and Eales, H.V. (1996) The Lower and Critical Zones of the western limb of the Bushveld Complex as intersected by the Nooitgedagt boreholes. Bull. Geol. Surv. S. Afr., 111, 126 pp.
- Teigler, B., Eales, H.V., and Scoon, R.N. (1992). The cumulate succession in the Critical Zone of the Rustenburg Layered Suite at Brits, western Bushveld Complex. S. Afr. J. Geol., 95, 17-28.
- The Institute of Statistical Social and Economic Research, (ISSER), (2001). The state of the Ghanaian economy in 2000. University of Ghana, Legon.
- Thomas, D. and Jansen, I. (1985). Soil development in coal mine spoils. Journal of Soil and Water Conservation, 40(5), pp.439-442.
- Thornton, I. (1996) Impacts of mining on the environment; some local, regional and global issues. Applied Geochemistry, 11, 355–361.
- Thornton, I. (1999). Bioavailability of trace elements in the food chain. (In: Wenzel, W.W. Adriano, D.C. Alloway, B. Doner, H.E. Keller, C. Lepp, N.W. Mench, M. Naidu, R. and Pierzynski, G.M. eds. Proceedings of the 5th International Conference on the Biogeochemistry of Trace Elements, Vienna, Austria), 109-121 pp.
- Tripathy, S. and Rao, K.S.S. (2009). Cyclic swell–shrink behaviour of a compacted expansive soil. Geotechnical and Geological Engineering, 27(1), pp.89-103.
- Tripathy, S. and Rao, K.S.S., (1998). Cyclic swell–shrink behaviour of a compacted expansive soil. Geotechnical and Geological Engineering, 27(1), pp.89-103.
- UNDESA, (2013): "World Population Prospects: The 2012 Revision DVD Edition.
- Van der Burgh, J., van Konijnenburg-van Cittert, J.H., Collinson, M.E., Pearce, M.A., Bujak, J., Heilmann-Clausen, C., Speelman, E.N., van Kempen, M.M., Reichart, G.J. and Lotter, A.F. (2012). Coeval Eocene blooms of the freshwater fern Azolla in and around Arctic and Nordic seas. Palaeogeography, Palaeoclimatology, Palaeoecology, 337, pp.108-119.
- Van der Merwe, M.J. (1976). The layered sequence of the Potgietersrus limb of the Bushveld Complex. Econ. Geol. 71, 1337-51.
- Vermaak, C.F., (1976). The Merensky Reef- thoughts on its environment and genesis. Econ. Geol., 71, 1270-98.

- Viljoen, M.J. (1994). A review of regional variations in facies and grade distribution of the Merensky Reef, Western Bushveld Complex, with some mining implications. In: Anhaeusser, C.R. (ed.) Proc. XVth CMMI Congress. S. Afr. Inst. Mining Metal., Johannesburg, 3, 183-94.
- Viljoen, M.J., and Hieber, R. (1986). The Rustenburg Section of Rustenburg Platinum Mines Limited. In: Anhaeusser, C.R., and Maske, S. (eds.) Mineral Deposits of Southern Africa, 2 Johannesburg: Geol. Soc. S. Afr., 1107-34.
- Viljoen, M.J., and Scoon, R.N. (1985). The distribution and main geologic features of discordant bodies of iron-rich ultramafic pegmatoid in the Bushveld Complex. Econ. Geol., 80, 1109-28.
- Viljoen, M.J., De Klerk, W.J., Coetzer, P.M., Hatch, N.P., Kinloch, E., and Peyerl, W. (1986a). The Union Section of Rustenburg Platinum Mines Limited. In: Anhaeusser, C.R., and Maske, S. (eds.) Mineral Deposits of Southern Africa, 2, Johannesburg: Geol. Soc. S. Afr., 1061-90.
- Viljoen, M.J., Theron, J., Underwood, B., Waiters, B.M., Weaver, J., and Peyerl, W. (1986b). The Amandelbult Section of Rustenburg Platinum Mines Limited. In:. von Gruenewaldt, G., 1973. The Main and Upper Zones of the Bushveld Complex in the Roossenekal area, eastern Transvaal. Trans. geol. Soc. S. Afr., 76, 207-27.
- Von Gruenewaldt, G. (1993). Ilmenite-apatite enrichments in the Upper Zone of the Bushveld Complex: a major titanium-rock phosphate resource. Internat. Geol. Rev. 38, 987-1000.
- Wager, L.R., and Brown, G.M, (1968). Layered Igneous Rocks. Edinburgh: Oliver and Boyd, 588 pp.
- Waldrop, M.P., Balser, T.C. and Firestone, M.K, (2000). Linking microbial community composition to function in a tropical soil. Soil biology and biochemistry, 32(13), 1837-1846.
- Waliser, D.E., Moncrieff, M.W., Burridge, D., Fink, A.H., Gochis, D., Goswami, B.N., Guan, B., Harr, P., Heming, J., Hsu, H.H. and Jakob, C. (2012). The "year" of tropical convection (May 2008–April 2010): Climate variability and weather highlights. Bulletin of the American Meteorological Society, 93(8), 1189-1218.
- Walraven, F. (1985). Genetic aspects of the granophyric rocks of the Bushveld Complex. Econ. Geol. 80, 1166-80.

- Walraven, F. (1987). Geochronological and isotopic studies of Bushveld Complex rocks from the Fairfield borehole at Moloto, northeast of Pretoria. S. Afr. J. Geol., 90, 352-60.
- Walraven, F., and Wolmarans, L.G. (1979). Stratigraphy of the upper part of the Rustenburg Layered Suite, Bushveld Complex, in western Transvaal. Geol. Surv. S. Afr. Annals, 13, 109-14.
- Walraven, F., Armstrong, R.A., and Kruger, F.J. (1990). A chronostratigraphic framework for the north- central Kaapvaal Craton, the Bushveld Complex and Vredefort structure. Tectonophysics, 171, 23-48.
- Walton, D., Verhagen, B. and Taussig-Duthé, D.M, (1993). September. The practical applications of environmental isotopes in pollution studies. In International Groundwater Convention: Africa needs Groundwater, Groundwater Division, GSSA, Johannesburg.
- Weeks, T. and Wan, R.Y. (2000). Behaviour of arsenic in refractory gold ore processing- a case study of PT Newmont Minahasa Raya. In Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi as held at the 2000 Annual Meeting of the Society for Mining, Metallurgy and Exploration, Salt Lake City, (pp. 125-133).
- White, A.F. (1995). Chemical weathering rates of silicate minerals in soils. (In: White, A.F. and Brantley, S.L. (eds.) Reviews in Mineralogy, 31, 407 458.
- White, J.A. (1994). The Potgietersrus prospect geology and exploration history. In: Anhaeusser, C.R. (ed.) Proc. XVth CMMI Congress. S. Afr. Inst. Mining Metal., Johannesburg, 3, 173-81.
- Whiteman, C.D. (1982). Breakup of temperature inversions in deep mountain valleys: Part I. Observations. Journal of Applied Meteorology, 21(3), 270-289.
- Willemse, J. (1969). The vanadiferous magnetic iron ore of the Bushveld Igneous Complex. Econ. Geol. Monogr., 4, 187-208.
- Wilson, J.R., Cawthorn, R.G., Kruger, F.J., and Grundvig, S. (1994). A major unconformity in the western Bushveld Complex: the northern "gap". S. Afr. J. Geol., 97, 462-72.
- Wilson, J.R., Menuge, J.F., Pedersen, S., and Engell-Sorensen, O. (1987). The southern part of the Fongen-HyUingen layered mafic complex, Norway. In: Parsons, I. (ed.) Origins of Igneous Layering. Dordrecht: Reidel Publ. Co., 145-84.

- Wyszkowska, J. and Kucharski, J. (2004). Biochemical and Physicochemical Properties of Soil Contaminated with Herbicide Triflurotox 250 EC. Polish Journal of Environmental Studies, 13(2), 223-231.
- Yaron, B. Calvert, R. and Prost, R. (1996). Soil Pollution, Processes and Dynamics. Springer- Verlag, Berlin, Heidelberg, 313p.
- Zaccardelli, M., Villecco, D., Celano, G. and Scotti, R., (2013). Soil amendment with seed meals: Short term effects on soil respiration and biochemical properties. Applied soil ecology, 72, 225-231.
- Zelikman, E. and Carmina, E. (2013). The spectral response characteristics of the soils and their possible estimation by using partial least square regression (PLSR) analysis. International Journal of Geomatics and Geosciences, 3(3), 438.