# Geological related acid mine drainage of gold tailings and coal waste materials: A comparative study

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Signature .

Date: 10 September 2018

## Declaration

I declare that this research project is my own, unaided work. The outlined is being submitted for Master of Science carried out in the School of Geo- and Spatial Sciences (Geology and Soil Sciences) at the North-West University (Potchefstroom Campus) under the supervision of Mr. P.W van Deventer. It has not been submitted before for any degree or examination in any University.

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## Abstract

The study is aligned with the mining industry's transformation requirements using a range of combination of methods from quantitative to qualitative and action-based methods. Most sources of metal trace elements in the environment are from anthropogenic activities, in these cases, from mining sites. However, soil and/or mine pollution has had a number of lower profiles and is not so well visible and understood. Most importantly, previous research focused on Net Acid Potential; hence, in this comparative study case, the project will focus on the geochemical presence of Acid Mine Drainage (AMD) in gold mine tailings, coal waste materials, as well as associated metal trace elements that are leaching out of these tailings. The study utilises a wide range of methods from humidity cell testing (HCT), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), to Portable X-ray Fluorescence (P-XRF) and microwave digestion to identify and quantify the total soluble metal trace elements in the tailings.

Geochemical variation in gold tailings and coal waste material, top soil and sub-soil were measured in the laboratory by using ICP-MS to identify metal trace elements including: aluminium (Al), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), lead (Pb) and uranium (U), whereas XRF was used for analysis of gold tailings, coal waste materials and soils. Experiments were performed to determine the geochemical parameters in the AMD, which were pH, Electrical Conductivity (EC) and Oxidation Reduction Potential (ORP). It was discovered that when the pH decreases the ORP increases; this represents the oxidation state and formation of AMD. The results from the study uncovered the acidity potential that will lead to formation of AMD. The study concludes that gold tailings and coal waste materials do influence the geochemistry and geological presence of AMD and are contaminating the research sites. This study concentrated on the influence of metal trace elements concentrations in gold tailings, coal waste materials, topsoil and sub-soil.

Keywords: gold tailings, coal waste materials, metal trace elements, leaching, mine pollution, soil contamination.

## Opsomming

Die studie is in lyn met die mynbedryf se transformasievereistes deur van 'n verskeidenheid kombinasies van metodes gebruik te maak van kwantitatiewe tot kwalitatiewe en aktief gebaseerde metodes. Die meeste bronne van metaalspoorelemente in die omgewing kom van antropogeniese aktiwiteite, in hierdie geval in myngebiede. Grond en/of mynbesoedeling het egter 'n aantal laer profiele gehad en is nie so goed sigbaar en verstaanbaar nie. Die belangrikste is dat vorige navorsing gerig was op Netto Suurpotensiaal, dus in hierdie vergelykende studiegeval sal die projek fokus op die geochemiese teenwoordigheid van suur mynwater dreinering (SMWD) in goudmynuitskot, steenkoolafvalmateriale, asook geassosieerde metaal-spoorelemente wat uitvloei. Hierdie studie maak gebruik van 'n wye verskeidenheid metodes, naamlik humiditeit-seltoetse (HCT), induktief gekoppelde plasma massaspektrometrie (ICP-MS), draagbare X-straal Fluoressensie (P-XRF) en mikrogolf-vertering om die totale oplosbare metaal-spoorelemente in die uitskot te kwantifiseer.

Geochemiese variasie in goudmynuitskot en steenkoolafval van die bogrond en ondergrond is in die laboratorium gemeet deur ICP-MS te gebruik om metaal-spoorelemente te identifiseer, insluitend: aluminium (Al), chroom (Cr), mangaan (Mn), tster Fe), kobalt (Co), nikkel (Ni), koper (Cu), sink (Zn), arseen (As), kadmium (Cd), lood (Pb) en uraan (U), terwyl XRF gebruik is vir die analise van mynuitskot en grond. Eksperimente is uitgevoer om die geochemiese parameters in die SMA te bepaal, wat pH-meting, elektriese geleidingsvermoë (EC) en oksidasie-reduksiepotensiaal (ORP) ingesluit het. Daar is gevind dat wanneer die pH afneem, die ORP toeneem; beinvloed dit die oksidasietoestand en vorming van SMWD. Die resultate van die studie het die suurpotensiaal waargeneem wat tot die vorming van SMWD sal lei. Die studie het tot die gevolgtrekking gekom dat goudslikdamme en steenkoolafvalmateriale die geochemie en geologiese teenwoordigheid van SMWD wat ondersoek word, die navorsingsareas besoedel. Hierdie studie het gekonsentreer op die invloed van metaal spoorelemente konsentrasies in goudslikdamme, steenkoolafvalmateriale, asook in the onderliggende bogrond en ondergrond.

Sleutelwoorde: goudslikdamme, steenkoolafval, metaal-spoorelemente, uitloging, mynbesoedeling, grondbesoedeling.

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## List of Acronyms

| | |
|---|---|
| Al | Aluminium |
| AMD | Acid Mine Drainage |
| As | Arsenic |
| Cd | Cadmium |
| Ca | Calcium |
| Co | Cobalt |
| Cu | Copper |
| CM | Crown Mine |
| Cr | Chromium |
| DM | Dominion Reef |
| EC | Electrical Conductivity |
| Fe | Iron |
| FNB | First National Bank |
| Ga | Giga annum |
| GVC | Golf View Coal |
| HCT | Humidity Cell Testing |
| ICP | ICP Coal mine |
| ICP-MS | Inductively Coupled Plasma Mass Spectrometry |
| ICW | Imbabala Coal Waste |
| kg | Kilogram |
| KL | Klein Letaba |
| LM | Louise Moore |

| | |
|---|---|
| Ma | Mega-annum |
| mg/kg | Milligrams per Kilograms |
| ml | Millilitre |
| Mn | Manganese |
| MTE | Metal trace elements |
| Ni | Nickel |
| NM-BR | New Machavie Black Reef |
| NM-Hutton | New Machavie Hutton Form |
| NM-Seepage | New Machavie Seepage |
| NM-Shale | New Machavie Shale |
| ORP | Oxidation Reduction Potential |
| Pb | Lead |
| pH | Negative logarithm of the hydrogen ion concentration |
| ppm | Parts per Million |
| SA | South Africa |
| TM | Trademark |
| TSF | Tailings Storage Facility |
| U | Uranium |
| µm | Micrometre |
| XRF | X-ray Fluorescence |
| Zn | Zinc |
| VC | Vierfontein Colliery |

## Glossary

| | |
|---|---|
| Acid Mine Drainage | Flow and seepage of contaminated water from the mining sites. |
| EC | The capacity of a substance to conduct and /or transmit electrical current in soils and water measured in µm, also related to dissolved solids. |
| Geochemical weathering | The inorganic alteration of solid rock |
| Gold tailings | By-product of fine milled rocks treated with various physical processes and or chemical products to extract the specific valuable mineral or element from the ore. |
| Leaching | The removal of materials in a solution from the soil by percolating waters. |
| Metal trace elements | Include both essential and non-essential trace metals, which may be toxic to organisms depending on their own availability, properties, chemical speciation and concentration levels. |
| Mine pollution | Discharges of contaminated mine effluent and seepage from tailings and waste rock impoundments. |
| Mine water | Water contamination by mining activity, which would have been environmentally relevant if it had not formed part of the mining activity. |
| ORP | The amount of dissolved in water and other metal trace elements that function similarly to oxygen. |
| pH | The degree of acidity as determined by means of a suitable electrode at a specific moisture content and expressed in terms of the pH scale. |

| | |
|---|---|
| Soil contamination | The presence of anthropogenic substances which the composition of the soil is different from its natural composition. |
| Sub-soil | The layer of the soil below the topsoil. |
| Topsoil | The uppermost layer of the soil moved in cultivation. |
| TSF | A slurry embankment or impoundment that remains once the gold has been extracted from the crushed ore at the processing plant. |
| Waste rock materials | Materials that are non-mineralised or mineralised rocks that contain insufficient ore to process economically. |

# CHAPTER 1: Conceptualisation of the project

*"As the time passes, the damage mining has caused to the environment becomes more apparent".*

~Herman Cornelissen

## 1.1 Introduction

Mining operations produce different sorts of wastes, frequently in huge amounts. The vast majority of these wastes are discarded into surface facilities, making extensive structures that require reconnaissance and support to guarantee their long load solidness (Karlsson *et al.,* 2014:121). For many years, the gold mines of the Witwatersrand have been the cornerstone of the country's economy (Van Eeden, 2006). Any ore body or rock (such as coal and gold) which contains sulphide minerals, especially pyrite ($FeS_2$), has the potential to cause acid effluent as results of oxidation (Chelin, 2000:1).

Furthermore, mining disrupts geologic processes that took millions of years to form. This disruption character raises the essential issue of understanding the common foundation of contamination because of the mineral deposits versus contamination due to mining (Jordan, 2006:175). Likewise, related natural systems and processes are disrupted, e.g. water resources, soil structure, fauna and flora all represent significant risks to safety, human health and the environment (Obreque-Contreras *et al.,* 2015: 1). Once disruption has occurred an assortment of issues may emerge, from physical hazards to contamination of water and soil (Costello, 2003:2). However, the legacy of mining (specifically coal and gold in this context) has posed devastating challenges result in acid mine drainage (AMD). Considering the detrimental consequences of AMD, there is need for new initiatives for finding solutions for mine pollution and rehabilitation.

In most cases, sulphides are a prominent mineral in these ores and upon exposure to water and oxygen it easily form AMD, especially when milled or ground to smaller particles (Paulu & Babcock, 2016:6). The fine milled rocks are then treated with various physical processes and or chemical products to extract the specific valuable mineral or element from the ore. The by-products referred to as tailings or mine waste, are then pumped or washed away either in a dry state or semi-solid or paste condition to surface structures i.e. tailings dams, ponds, dumps or stacks (Dold, 2014:622). It is here where the AMD processes take place and where these processes then contaminate soil when it comes into contact with it and leaches acid out of tailings and waste dumps which subsequently contaminates groundwater. The metal trace elements present in the tailings material can invade the topsoil and subsoil; and remain at high risk for years (Smuda *et al.,* 2014:24). Soil, surface water, groundwater and dust pollution created by various mining operations are other threats to wildlife and human health.

AMD is a well-understood process with metal-rich water; the water may contain elevated levels of salts, sulphate, iron and aluminium, with potential metal trace elements such as cadmium and cobalt. Radioactive elements such as uranium and thorium can also pose environmental and human health risks for many years after mining has taken place (Blowes *et al.,* 2003; Oelofse *et al.,* 2007:3; McCarthy, 2011:2). In summary, the major cause is the quickened oxidation of pyrite and other sulphuric minerals associated with coal, gold, copper and base metals (Johnson & Hallberg, 2005:3). The actual problem caused by the AMD is the low pH conditions that are created in the tailings and waste material and at pH<4 many of the metal trace elements become soluble and more mobile and also ready for other geochemical weathering process reactions. It is these metal trace elements in a more soluble form that have potential toxic consequences and because of their high mobility in low pH conditions. It can leach much easier from TSF’s and dumps and into the soil and water systems. Dust associated with the TSF materials contains some of the metal trace elements and, therefore, the atmospheric dust is also a pathway and receptor for pollution (Dold & Fontbote, 2002; Van Deventer, 2016).

McCarthy (2011:6), however, concluded that the problem is of a far more extensive degree and to comprehend it completely it is important to take a considerably more extensive geographic view. In this instance the study has taken a stance on investigating a wider geographical variability of geologically related AMD on different sites for coal and gold. Eight sites across South Africa were fully investigated in accordance to their stratigraphic sequence from the Greenstone Belt, Dominion Group, Witwatersrand Supergroup, Transvaal Supergroup, and Karoo Supergroup. This means that only seven sites were studied comprehensively from the source, pathway and receptor i.e. gold tailings, coal waste material, topsoil and subsoil were studied. This is a comparative study on the presence of AMD in both coal and gold mines which involves the use of humidity cells (leaching columns) for discovering answers for mine contamination and rehabilitation approaches to deal with higher concentrations of trace elements. The investigation includes a survey of logically sound recovery methods that have mainly been centred on gold mines and coal mines. This is why the study relates to gold and coal mining giving careful consideration to land adjacent to mine waste sites. Concerns have been raised about areas, which have the potential of AMD formation and the subsequent release of such harmful substance to the environment. However, the transfer of metal trace elements from the gold tailings and coal waste materials to the topsoil and subsoil has not been fully investigated.

## 1.2 Problem statement

Due to the presence of sulphide minerals in gold tailings and coal waste materials, corrosive leaching can happen. If these materials generate acid it will increase the possibility of metal trace elements leaching and polluting the topsoil and subsoil (Labuschagne, 2008:8). High acidity causes toxic elements to leach from coal waste materials and gold tailings – Fe, Mn, Pb, As, Cd, Co, Cr, Zn, Cu, Ni, Al and U are the most common metal trace elements constituents (Chapman, 2011:1).

AMD is a standout amongst the most genuine ecological issues that the coal and gold mining industry is presently confronting (Saria *et al.,* 2006:134; Guedes, 2010:69; McCarthy, 2011:1; Naidoo, 2017:9), furthermore, the problem tends to wind up noticeably and progressively common in a several parts of South Africa; hence this project aims to address this challenge.

## 1.3 Justification

It is critical that the basic principles and implications of pollution pathways are properly comprehend before rehabilitation guidelines can be identified and ultimately implemented. The intention of this research is to provide a comprehensive analysis of AMD related environmental problems and be able to develop a multi-method approach to solving mine pollution in various environmental conditions. Kleinman

(1990:85) conducted a study of the occurrence and formation of acid mine drainage on coal and base metal mines.

## 1.4 Description of the study areas

The aim of this section is to describe the study area in terms of the difference in geographical distribution of mineral deposits. The research project is comprised of eight different sites:

1. Gold of Klein Letaba and Louise Moore mine from the Giyani Greenstone Belt in the Limpopo Province close to Gyani.
2. Gold of Dominion Reef gold mine from the Dominion Group west of Klerksdorp in North West Province
3. Gold of Crown mine from the Witwatersrand Supergroup west of Johannesburg in Gauteng Province
4. Gold of New Machavie from the Transvaal Supergroup west of Potchefstroom in North West Province.
5. Coal of Imbabala, Golf View mine and IPC in the Witbank-Middelburg area in Mpumalanga Province and Vierfontein Collieries in Free State Province, all from the Karoo Supergroup.

The sample reference is together with the Abridged schematic stratigraphic column in Table 1.1.

## 1.5 General geology of the selected study sites

Although Archaean crystalline basement rocks from Kaapvaal Craton characterise the study area, other lithologies, which outcrop locally and in adjacent areas will also be considered in this research (Petzer, 2009:18). Greenstone belt is an ancient volcanic crust that occurs as inclusions within Proterozoic granite craton. They include the oldest rocks on earth dated at 3.6Ga. The volcanic sequences and associated sedimentary rocks are variably metamorphosed to greenschist facies. The green colour is mainly due to chlorite (De Wit & Ashwal, 1995:506; De Wit *et al.*, 1992:112). The Kaapvaal Craton had stabilised to such a degree by 3.0 Ga that it could accommodate extensive deposition at that time and the rest of the planet (Hunter *et al*., 2006:1).

Table 1.1: Abridged schematic stratigraphic column of the study area and ages for the deposition of the strata (modified after Brink *et al*., 1997:109) and the sample reference.

| Age Ma | Supergroup | Group | Sub-group | Formation | Rock type/Lithologies | Sample reference |
|---|---|---|---|---|---|---|
| 180 | Karoo | Ecca | | Volkrust | Mudstone, iltstone, shale and coal | Coal waste material |
| 2200 | Transvaal | Chuniespoort | Malmani | Monte Christo | Chert-rich dolomite | |
| | | | | Oaktree | Chert-free dolomite | |
| | | | | Black Reef | Feldspathic quartzite, shale and conglomerate | New Machavie gold tailings |
| 2600 | Witwatersrand | West Rand | Jeppestown | Crown | Clastic sements such as quartzite, Ferruginous shale and andesitic volcanics | Gold tailings |
| 2800 | Dominion Group | | | Rhenosterspruit | Lava, quartzite and conglomerate | Gold tailings |
| 3200 | Giyani Greenstone Belt | | Khavagari Limb | | Ultramafic sediments such as iron formations and schists | Gold tailings |
| | | | Nsava Belt | | | |

## Giyani Greenstone Belt

The 3.2 Ma Limpopo Belt granulite terrane is situated between two lower-grade granite-greenstone cratons, the Kaapvaal Craton in the south and the Zimbabwe Craton in the north (Van Reenen *et al*., 1992:1). A limited passageway over the tectono-transformative progress between the greenstone landscapes, separately from the Giyani (otherwise called the Sutherland) Greenstone Belt into the hydrated granulites of the Southern Peripheral Zone of the Limpopo Belt, has been mapped in detail (De Wit *et al*., 1992:130). The formation is of a complex nature in the metamorphic environment of the northern extremity of the Giyani Greenstone Belt

(GGB) (Sutherland) succession, which impacted the structural metamorphic evolution of the GGB (Roering *et al*., 1992:2).

The Giyani Group is situated within the Murchison Sequence which is part of the Pietersburg Greenstone Belt (Brandl *et al*., 1996:229). The area is dominated by folding of mafic and ultramafic sequences of medium to course grained biotite gneiss (Potgieter & De Villiers, 1986:199) with economic viable mineralised zones confined to the garnet rich meta-quartzite chemical sediments with associated interbedding of banded iron formations (BIF) and its sulphide facies enrichment which also forms part of metamorphosed volcanic sedimentary sequence of mafic and ultramafic, known as the Giyani Group (Steenkamp & Clark-Mostert, 2012:2).

For the most part, the belt needs adequate introduction, which denies lithostratigraphic subdivisions. Be that as it may, agreeing with Brandl (1987:16), the progression can be partitioned into the accompanying rock types. Gold occurs preferentially in iron formation, in quartz and carbonate veins (Brandl *et al.,* 2006:10; Anhaeusser, 2014:686), yet additionally in quartzite, schist and amphibolites in contact with the granite-gneiss (Viljoen *et al*., 1978:56). Gold mineralisation was controlled partly by folding, which concentrated it in fold hinges and troughs. It is generally associated with sulphide minerals, mainly arsenopyrite (FeAsS), pyrite ($FeS_2$), chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and pyrrhotite (FeS) (Ogola, 2010:529).

## Dominion Group

The Dominion Group is a supracrustal sequence containing clastic sediments and volcanic rocks of late Archean age which unconformably overlies the granitoid basement and underlies the gold bearing sediments of the Witwatersrand Supergroup (Robb *et al.,* 1990:312; Manzi *et al*., 2013:96). The Dominion Group is the oldest member of the Witwatersrand Triad which also includes the Witwatersrand Supergroup and the Ventersdorp Supergroup (Altermann & Lenhardt, 2012:6; Jackson, 1994:63). The name Dominion Group derives from Dominion Mine, the presence of thick sequences of volcanic rocks lying conformably above the sedimentary rocks and these include the Dominion Reef Series (Jackson, 1992:170; Marsh, 2006:151; Nel *et al.,* 1939).

## Witwatersrand basin

The Witwatersrand gold producing area in South Africa is underlain by an underground geological formation also known as the Witwatersrand Basin (Goode, 1968). In spite of this being probably the most studied geological formation in Southern Africa, it is the greatest goldfield the world has ever seen into being (Allsopp & Welke, 1986:67, Handley, 2004:9). Furthermore, SACS (1980) placed the Witwatersrand Supergroup between the ages of *ca.* 2 800 and *ca* 2 300 Ma respectively. The Witwatersrand Basin is underlain by Archean crust referred to as Kaapvaal Craton in which ages of >3.1 Ga are recorded. However, owing to its great antiquity this Craton has been subject to many subsequent geological events (Robb & Meyer, 1995:68; Robb & Robb, 1998:295). Vorster (2000) suggest the various geological events of the Basin; Handley (2004:51) concurred with this view, as it is essential to have several major events in the geological history to drive the complications and developments which have been observed and which need to be explained in the sedimentary pile.

## Transvaal Supergroup

The Transvaal Supergroup overlies the Archean basement, the Witwatersrand Supergroup and the Ventersdorp Supergroup. It encompasses one of the earliest carbonate platform successions with very well preserved and extensive stromatolites. The basin contains auriferous-uraniferous conglomerates in the Black Reef Quartzite which is part of the Malmanie-subgroup which is the basal formation of the Transvaal Supergroup over much of its extent (Beukes, 1987:2; Catuneanu & Eriksson, 1999:230; Cheney, 1996:8). The focus in this study is on the Black reef gold mine of New Machavie mine (also called Eleaser) approximately 24 km west of Potchefstroom

## Karoo Supergroup

The dominant part of South Africa’s coal reserves are hosted in rocks of the Karoo Supergroup (Cairncross, 2001:531). The Karoo Supergroup is a thick succession of sedimentary rocks deposited in the vicinity of 300 and 180 million years back. The coal creases happen in a division of Groups in this study case being known as Ecca Group, consisting of mudstone and sandstone.

The residue of the Ecca Group of the Karoo Supergroup was deposited on an undulating Karoo floor, which influenced the dispersion and thickness of the sedimentary arrangements and also the coal seams (Smith & Whittaker, 1986:1971). The regional geology of the study area is characterized by numerous post-Karoo age dolerite sills and dykes which outcrop on the surface, while rocks of the Vryheid Formation of the Ecca Group covers most of the surface area (Cairncross, 2001:530; Cairncross *et al.,* 2005:547).

## 1.6 Research aims and objectives

### 1.6.1 General aims

The aims of this study were to draw attention on mine pollution and soil contamination underneath the TSF's and waste dumps. Then establish the leaching transfer of metal trace elements from gold tailings and coal waste materials to the topsoil and subsoil as well as to quantify the leach material underneath the tailings and correlate it with redox-influenced Humidity Cell Test assessments. The study also aimed to unpack the influences and presence of mine pollution on the topsoil to the subsoil by the means of investigating the intensity of oxidation of pyrite from the tailings, transfer factor and the composition of coal and gold AMD in severe conditions as presented in the humidity leaching columns.

It must be acknowledged that the challenges of AMD, given its magnitude and dynamics, need serious attention outside the government and mining sector. As such, this research aims to deepen the understanding of mine pollution on the soil environment and rehabilitation framework responses to contemporary risk and vulnerability in South Africa.

### 1.6.2 Objectives

To accomplish the above aims, the following project objectives were set:

(4) Identify the geological related presence and/or occurrence of AMD

(ii) Explore the nature and composition of gold and coal potential for acid mine drainage across the Giyani Greenstone Belt, Dominion Group, Transvaal Supergroup, Witwatersrand Supergroup, and Karoo Supergroup.

(iii) Find the transfer of metal trace elements from the gold tailings and coal waste materials to the original topsoil and subsoil.

### 1.7 Hypothesis

Due to a variation in sulphide mineralisation in different lithological units, the potentially toxic elements, which result from the AMD formation process, will vary from site to site.

Other factors including host rock composition, metallurgical treatment, rehabilitation amelioration, rainwater quality, process water quality, etc. which will have an impact on the metal trace elements will be available for environmental contamination.

### 1.8 Dissertation layout

This dissertation comprised of six chapters, each clarifying the investigations performed in detail. The synopsis of the chapters are given below:

*Chapter 1: Conceptualisation of the project:* Background, Site description, General geology, aims and objectives and Hypothesis feature in this chapter.

*Chapter 2: Literature review*

This chapter reviews the literature pertaining to the metal trace element contaminants within the environment, potential toxic influences of metals on the sub-soil and AMD potential. This chapter also introduces the reader to the various studies that have attempted geochemical characterisation of AMD and the chemistry involved in the process. It focuses on an understanding of the event and source of AMD and the impacts of conceivably potentially toxic components. Furthermore, the influence of low pH on the biological framework and the adjustment in context, focuses on dynamic potentially AMD redox conditions.

*Chapter 3: Materials and methods*

This chapter presents the experimental set-up and procedure used in the preparation of this study. As it is the norm in scientific studies, different approaches and sets of experiments were performed in order adhere to the aims and objectives of the research.

*Chapter 4: Results and discussions*

This chapter entails the analytical results and data processing obtained from the experiments performed to unpack the influences of mine pollution. This is followed by assessments of data and processing, diagrams, tables, graphs, photos and short conclusion after each discussion.

*Chapter 5: Conclusions*

This chapter complies with the aims and objectives and make table and/or graph conclusion as mentioned in chapter four.

*Chapter 6: Recommendations*

The recommendations for future work to be done in this study are outlined in this chapter.

*Annexures*

This section provides supportive analysis with length data in the dissertation.

# CHAPTER 2: Literature review

*“Our review of literature says this appears to be bigger than in the past”*

~ Bob Dietz

## 2.1 Background

The purpose of this literature review is to summarise the recent geological related environmental problems (mine pollution) and AMD with gold tailings and coal waste material. Taking into account, largely the AMD risk has not been drawn to completely and was halfway misjudged from the time it turned into a concern (Bobbins, 2015:1; Masondo *et al.,* 2011; Naidoo, 2014:1046; Slack, 2013). Only few studies have been performed on the underlying soil pollution with metal trace elements as a result of AMD (Weissentein & Sinkala, 2011:53).

Metal trace elements leaching from the sulphide ores occurs at a faster rate when exposed to the acidic waters generated by AMD (Aphane & Vermeulen, 2015:58). The dissolved metal trace elements are transported in solution to the waterways surrounding the mine where they are absorbed and concentrated by soils, animals and plants (Pollmann *et al.,* 2009:197). Once these elements have been absorbed into organic tissues, it enters the food chain and metal poisoning may result in humans and animals (Abegunde, 2015:28; Lishman, 2009:1; Suteerapataranon *et al.,* 2006:2045).

## 2.2 AMD in South Africa

According to NEMA Section 24G Guidelines, South Africa is one of the countries in which the greatest impact of mining on the environment is seen. From an environmental perspective, Funke *et al,* (2009:15) stressed that South Africa faces many difficulties that influence both its environmental biodiversity and socio-economy. As a product of mining (Gray, 1997:62) advocated that one of the most prominent challenges is acid mine drainage (AMD).

While this study is focused on gold and coal, Akcil & Koldas (2006:1140) stressed that AMD from these two types of mining is a serious environmental hazard. Given the current predicament, and the fact that South African society is ignorant, impartial and unfocused on this issue additionally muddles the issue. Unfortunately, Manders *et al.,* (2009) stated that precise effects of AMD require further research. Table 2.1 below depicts the two main sources of AMD from both gold tailings and coal waste materials. The majority of these sources emanate from unlined mine tailings that can cause extensive soil and water pollution (Turton, 2009:14).

Table 2.1: Potential sources of AMD presented by Akcil & Koldas (2006:1141).

| **Sources** |
|---|
| Sulphide bearing rocks |
| Exposure mainly caused by mining activity, infrastructure development, agricultural practice and natural disasters |
| Abandoned mines |
| Pumped/nature discharged underground water |
| Diffuse seeps from replaced overburden in rehabilitated areas |
| Tailings deposits, ore stock piles and waste rock dumps |

### 2.2.1 AMD as result of gold and coal mining

Every aspect of gold mining in South Africa has been covered by vast literature (Janisch, 1986:274), hand in hand with South Africa's rich mining history and is a legacy of AMD and its negative effects (Viljoen, 2009:131). The Witwatersrand region has been celebrated globally for its rich gold deposits which have been mined for over a century. The host rocks to the gold mineralization are conglomerate layers (approximately 1-2 m thick) consisting of quartz pebbles in a quartz sand matrix (Handley, 2004:9).

Recent research has shown that soils in the mining districts of the Witwatersrand region are contaminated with metal trace elements and that the ground water within this mining area is severely polluted and acidic because as a result of AMD (Naicker *et al.,* 2003:29). Pulles *et al.,* (1995:5) emphasised that not only is AMD being generated from tailings and tailings material at the surface in gold mining areas but also at mined out areas.

Unlike the gold mine, the coal is disposed from the site and there is vast surface dumping of coal discard which is not good quality coal inter alia due to high sulphides. These discard dumps are very often just covered with thin layers of top soil which are by far not enough to isolate the AMD forming inside coal discard dumps. Both the coal and the host rock contain pyrite, however, it is mostly inexhaustible in the coal layers (McCarthy, 2011:3).

### 2.2.2 AMD control mechanism

The ability of gold tailings and coal waste materials to generate and release various contaminants into the environment is influenced through accelerated pyrite oxidation, pH, oxygen concentration and surface area to, mention just a few (Akcil & Koldas, 2006:1140; Rose & Cravotta III, 1998:9). The interactions of the abovementioned factors are complex with respect to locality of the ore body and / or except for occurrences where fundamental geology comprises of carbonate rocks (Van Deventer, 2016).

Typically, particle size, porosity, surface area of sulphide minerals and the homogeneous distribution of sulphide and alkaline mineral content differ for tailings and waste rock (Kuyucak, 2012:600); hence the latter being the case of this particular study. Balistrieri *et al.,* (2012:3349-3350) described ferrous and ferric iron as the major contributors to AMD. The presence of metal trace elements such as Cd, Co, Al, Mn, As, Cu and Zn on the environment depends on their concentration solubility (Aphane & Vermeulen, 2015:59).

The potential for a mine to produce corrosives and discharge contaminants is subject to many variables such as local conditions, geomorphology, extent and distribution of AMD generating deposits and it is site and mineralogy specific (USEPA, 1994:5). The AMD control mechanisms and factors can be comprehended as essential; which include generation of the corrosive, for example, oxidation responses. Optional variables act to control the results of the oxidation response, for example, responses with different minerals that expend acid and may neutralise acid.

Rock dumps with high porosity and large pore space have higher oxygen concentration and circulation and in this way encounter higher chemical response (Mane, 2013:12). The supply of atmospheric oxygen is required to drive the reaction (USEPA, 1994:6). Research done by Kempton & Atkins (2009:1) indicated that waste rocks and tailings would attract atmospheric oxygen and keep on driving the oxidation response. This is because oxygen plays a crucial role in maintaining the rapid bacterial catalytic oxidation at pH values below 3.5 (USEPA, 1994:6). Some TFS's have no oxygen in it due to crust formation on surface i.e. goethite and hematite crusts which prevent oxygen aeration.

Water fills in as both reactant and a medium for microbes in the oxidation process, since water likewise transports the oxidation reactants as a solvent (USEPA, 1994:7). From a theoretical point of view, if there is a crust with no water or oxygen then there are no bacteria. Bacteria play a crucial role in catalysing ferrous ion during AMD formation and if there is no water, no oxygen and bacteria then limited or no more AMD (Mane, 2013:12-13; Ferguson & Erickson, 1988:28).

## 2.3 Chemistry of AMD

Mining operations create many types of mine wastes, i.e. mine tailings, waste rock and slag; in particular, these wastes go about as a fundamental source of ecological tainting Lim *et al.,* 2009:2865; Roussel *et al.,* 2000:182). Metal trace elements are discharged from the mine wastes, which in this case is the source, to the soil that serves as the pathway and receptor. The geological condition also plays a role because of their solubility and mobility (Jang *et al.,* 2005:345). In an undisturbed natural environment, oxidation processes happen at moderate rates over a geologic era (Jennings *et al.,* 2008).

For dissertation purposes, the oxidation of pyrite ($FeS_2$) will be analysed. From Coetzee et *al.* (2007:81) and McCauley (2011:11) pyrite oxidizes to shape corrosive arrangement of ferrous iron ($Fe^{2+}$). Sulphates and the main essential response is the oxidation of the sulphide mineral into broken down iron (Fe), sulphate ($SO_4^{2-}$) and hydrogen ($H^+$) (Akcil & Koldas, 2006:1140):

(1) $FeS_2 + 7/2\ O_2 + H_2O = Fe^{2+} +2SO_4^{2-} + 2H^+$

(2) $Fe^{2+} + ¼O_2 + H^+ = Fe^{3+}\ ½\ H_2O$

(3) $Fe^{3+}\ 3H_2O = Fe\ (OH)_3 +3H^+$

(4) $FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-}\ 16H^+$

Pyrite + Oxygen + Water = 'Yellow boy' + Sulphuric acid (Sangita & Prasad, 2010:955).

(5) $4FeS_2+ 15O_2 + 14H_2O = 4Fe(OH)_3 + 8H_2SO_4$

The oxidation of pyrite (1) to sulphate discharges broken down ferrous iron ($Fe^{2+}$) into the water. In the event that the encompassing condition is adequately oxidising. After disintegration the ferrous iron experiences oxidation to ferric iron ($Fe^{3+}$) (2), which at that point hydrolyses to form 'insoluble' ferric hydroxide (3), increasing the acidity. Ferric iron can be lessened by pyrite itself, as seen in equation 4, where pyrite is again oxidized and corrosion discharged alongside extra ferrous iron which may re-enter the response cycle by means of (2). In light of this rearranged essential equation (4) corrosive age that mobilises iron which later precipitates as $Fe(OH)_3$ might be represented by a blend of equations 1 to 3. The overall sequence of reaction is acid producing (5) (Akcil & Koldas, 2006:1140; Banks *et al.,* 1997:158; Gaikwad & Gupta, 2007:286; Gray, 1997:62; Neculita *et al.,* 2007:1439; Singer & Stumm, 1970:1122).

From Coetzee *et al.,* (2007:81) $Fe\ (OH)_3$ can be identified as the deposit of undefined, yellow, orange on streambeds (Jarosite) as shown in Figure 2.1. Crown Mine, Johannesburg, the water in Figure 2.1 has a high total dissolved solids (TDS) concentration and a low pH value. If this water is not controlled it could acidify and re-enter the ecological system (Akcil & Koldas, 2006:1142; Koldas, 2000:125).

Figure 2.1: AMD in a solution trench at Crown Mine west of Johannesburg. Photograph taken by P.W van Deventer (2016, June) with permission.

Coetzee *et al.* (2006:12) and Wade *et al.* (2002) pointed out that once the acidity of the water liberates elements, including metal trace elements such Al, Ni, and radio nuclides from the rocks in which it cooperates and sometimes precipitates. It creates a toxicity exposure to both human user and the environment rendering this water unfit for utilisation. Wuana & Okieimen (2011:2) reviewed metal trace elements contamination on soils as it is released into the environment by aforementioned mining activities tend to be mobile, which pose risks and hazards to human and ecosystem.

## 2.4 Impacts of AMD

Repinga (2011:12) stressed that full implications of AMD effects have just been broadly recognized in the feasibility study recently. AMD has shown to be a multi-factor pollutant that affects the ecosystem in numerous and interactive ways either through direct or indirect pathways (Gray, 1997:63). The acidity of AMD and the elevated amount of dissolved metal trace elements, including As, Cu, Zn, Cd, Pb and Cr generally make AMD extremely toxic and is more promptly consumed by plants, animals and even human beings. These elements can also be *bioaccumulated* and *biomagnified* in the food chain (Penreath, 1994:124)

The effects of AMD can loosely be classified as chemical, physical, biological and ecological pollution. AMD has an interdisciplinary character involving natural and technical sciences (Gray, 1997:63; Luptakova *et al.,* 2012:31; Wolkersdorfer, 2008:9; Younger *et al.,* 2002:128).

With South Africa confronting various basic ecological difficulties going from landscape degradation to the pulverisation of limited assets, South Africa Department of Environmental affairs (2007) stressed that AMD poses a perilous hazard in terms of its ramifications AMD. Right now AMD debilitates the world heritage site that is situated in Krugersdorp, known as the Cradle of Humankind (Oelofse *et al.,* 2007:619). According to Feris & Kotze (2014:2106) threshold values of all forms of pollution, AMD pollution, concentration and contaminants are equipped for causing unsafe consequences for water uses.

An investigation by Naicker *et al.*(2003:33) uncovered that the groundwater in the mining region of Johannesburg, South Africa, is intensely contaminated and acidified by pyrite containing in the mine tailings, and has elevated concentration of metal trace elements.

The effect of AMD on the economy ought not to be thought little of (Name, 2013:15). AMD has destructive impacts on infrastructure and equipment (Davies, 2012:17). As previously mentioned the movement of untreated AMD can contaminate surface water and groundwater, bargaining nature of water assets and influencing the strength and quality of aquatic life negatively.

## 2.5 Mine pollution and metal trace elements contamination in soil

Soils are vital to life on earth and the world's biological communities are affected in extensive courses by forms completed in the soil (Brady & Well, 2008:1). Poor administration of a large portion of the mine tailings has brought about the discovery of AMD that much of the time caused soil degradation and pollution around the selected study locales (Ferguson & Erickson, 1988:25; Rösner, 1999). Soil chemistry recognizes substantial metal trace elements as an extraordinary accumulation of components due to the fixation and bio reactivity of non-poisonous elements (Vodyanitskii, 2016:257). Extraction of metals from sulphide minerals normally produces lot of waste materials, mine tailings and AMD, which frequently contain higher concentrations of metal trace elements (e.g., Cu, Zn, Cd, Pb, As, Mn, Al, Ni, V, Cr Co,). These potentially toxic elements stand out amongst the most dangerous components in the encompassing conditions which prompt oxidation of sulphide-bearing minerals, resulting in AMD. Metal trace elements are described by high acidity and salts content and an abnormal state of differentially oxidised elements (Boulet & Larocque, 1998:131; Chen *et al*., 2005:613; Moore & Luoma, 1990:1279; Naicker *et al*., 2003:31; Zhou *et al*., 2004:238; Zhou, 2007:295, 296).

Metallic components are natural parts of the environment and their quality is viewed as rare and it is impossible to remove them totally from the environment once they enter it (Mahurpawar, 2015:1). Potentially toxic elements have a density of 6.0 g/cm$^3$ (this also depends on the source) or more; it depends on the source which has a density higher than the average particle size density of naturally occurring soils which is 2.65 g/cm$^3$ (Koldabadi *et al.,* 2012:128). The total concentration of metal trace elements in gold tailings, coal waste material and soils was used to quantify the leaching transfer.

## 2.6 Rehabilitation of AMD

For more than 150 years of mining in South Africa, nature has been the recipient of accumulating polluted substances (Pollmann *et al.,* 2008:196). The main problem with this current environmental legacy of gold tailings and coal waste materials is that mine closures before 1956 were not subjected to legislation and often mines were just abandoned; hence mine sites from that era have now become the responsibility of the government of South Africa (Limpitlaw *et al.,* 2005:2). AMD impact is becoming extremely prevalent (Ferris & Kotze, 2014:2110). South Africa’s socio-institutional response dilemma is heightened by the fact that past mining activities, legislation and regulatory practice set-up, have not managed the recovery of ecological outcomes of operational mines (Ferris, 2012:3,4; Lwabukuna, 2016:123). Limpitlaw *et al.,* (2005:5) again presented that careful management of soil resources, promotion of diversity and latent post closure are now the norm for rehabilitation of mined lands.

The South African legislature has created instruments to advance sound administration of mine closure and rehabilitation by mining houses (Krause & Synman, 2014:1). The new South African legislation governing mine closure, the Mineral and Petroleum Resources Development Act (MPRDA) (Act 28 of 2002), presents a comprehensive cradle–to–grave way to deal with prospecting and mining by balancing financial benefits from mining against social and environmental concerns to achieve sustainable development (Van Tonder *et al.,* 2009:80)

Land rehabilitation is understood as the process of returning the land in a given area to some degree of its former state or functionality, after some process has resulted in its damage (Lamb, 2016). Mine rehabilitation of soil contaminated by AMD from abandoned mine sites requires the integrated implementation of a range of measures (Davies, 2012:17).

### 2.6.1 Rehabilitation guideline methodology

The selection of the appropriate sites was critical, criteria were developed in the context of contaminated land, and risk to the environment can be viewed as being involved the accompanying segments (Hattingh*et al.,* 2003:72; Van Deventer, 2012):

- **Source:** contaminated substance with the potential to cause harm.
- **Pathway:** a route by which a receptor could be exposed to, or affected by the contaminated substance.
- **Receptor:** a particular entity that is being adversely affected by the contaminated substance.

In this case Van Deventer (2012) unpacked (Figure 2.2) the three components outlined above based on the source and origin of low pH condition in rehabilitation methodology.

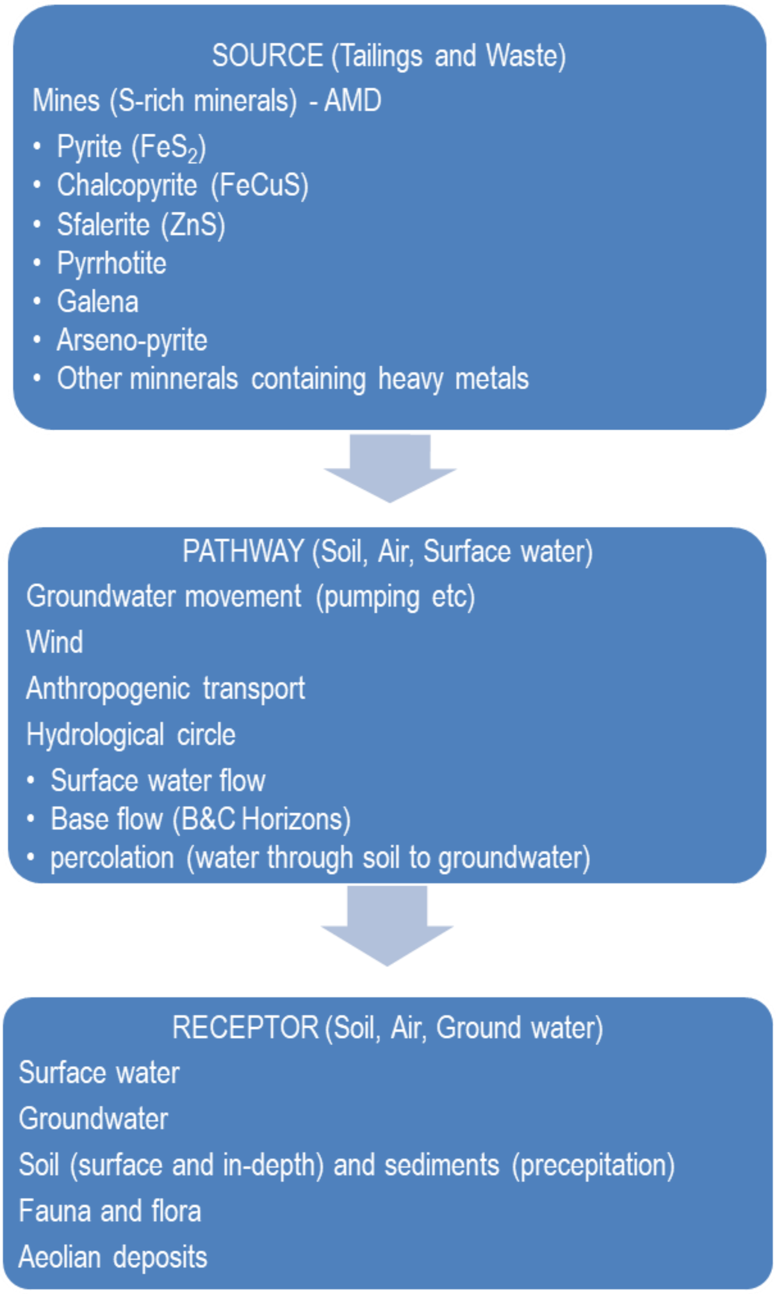

Figure 2.2: Transformation (oxidation and dissociation), transportation (movement) and precipitation/solution) (modified from Van Deventer, 2012).

Successful mine rehabilitation is reliant on many variables, two of the real issues being the short and long-term stability of the rehabilitated landform (Hancock *et al.,* 2006:104). While in the transient disintegration can prompt expanded residue loads and transport of contaminants in the long-term landform soundness is likewise imperative for coal and gold mines given the levels of containment required for the tailings (Schumm *et al.,* 1984:112). It is imperative that rehabilitation guidelines should be clearly defined and scientifically sound specifications been developed for gold tailings and coal waste materials are reviewed and assessed for post-mining landscapes. Steenekamp (2012) provided a quantified Rehabilitation methodology in the following format:

- Detailed site visit
- Assess erosion and landform stability
- Slime/soil/sub-soil sampling and analysis
- Development of rehabilitation plan
- Maximising the removal of slime material
- Final surface soil/sub-soil sampling and analysis
- Amelioration
- Vegetation with indigenous endemic species
- Monitoring and management

The subject of element mobility is essential with respect to the contamination capability of a metal trace elements loaded solution, for example, AMD (Smuts, 2015:9). Some rehabilitation strategies endeavour to immobilize metal trace elements by the addition of amendments to the soil, for example $CaMgCO_3$ and fly ash (Concas *et al.,* 2007:5187). Rehabilitation of gold tailings and coal waste materials will not be explored in this dissertation, yet the significance of leaching behaviour ought to be considered to comprehend the degree of contamination of metal trace elements and to assess future solutions to the problem as explained in their impacts of AMD and results will be discussed in Chapter 4.

# CHAPTER3: Materials, methods and sites description

*An experiment is a question which science poses to nature, and a measurement is the recording of nature's answer*

~ Max Planck

## 3.1 Introduction

Where literature might be prohibitive either in the openness to information or because of time imperatives, one can bypass such confinement by organizing a sensible exhaustive view on a particular point (Ewart, 2011:36). Therefore, sampling soil, tailings and waste rocks for AMD is one of the most important task that professional geoscientist perform in the field (Downing, 2014:124). This Chapter describes in detail the sites where the samples were taken, methods and procedures and materials used to fill the overview of previous research and current research studies concerning metal trace elements which before focused on Net Acid Potential (NAP). In this case, different methods were utilised to try establishing overall rates of oxidation and mining pollution of coal waste material and gold tailings, respectively.

This study handled the issue of AMD by inspecting the mineralogy of the tailings, and geochemical transmission of metal trace elements in the gold tailings and coal waste materials. As mentioned in the previous chapters, this research study was aimed to comprehend the processes that have led to the current conditions and AMD generation, and conceivable constriction mechanisms on how different tailings and waste material affect the soil geochemistry.

### 3.1.1 Site selection

For the purpose of this study, approximately 41 sites characterized by low pH values and potential elevated concentration of metal trace elements were visited to do proper site selection and to focus on those with distinct signs of pollution to the environment.

The study is comprised of the following selected sites as summarised in Table 3.1 with respect to their stratigraphy and lithologies: Louise Moore, Klein Letaba New

Machavie, Dominion Reef, Crown mine, Imbabala, Golf view, IPC and Vierfontein. Large mine sites were selected whose activities have the potential to generate AMD, including uranium, like the New Machavie mine. The geochemical testing programme was performed on samples of the gold tailings and coal waste materials to determine the present and potential long-term geochemical attributes of the waste materials. To collect data, accessible sampling sites were selected and identified at the eight study sites of the mining areas.

Table: 3.1 Summary of the main geological units and associated mineral deposits of Southern Africa where samples have been taken for this study (modified from Van Biljon, 1982).

| **Sample sites names** | **Main Geological Units** | **Main economic deposits** |
|---|---|---|
| Imbabala, Golf View and ICP and Vierfontein | Karoo Supergroup | Coal |
| New Machavie and Black Reef | Transvaal Supergroup | Gold |
| Crown mine | Witwatersrand Supergroup | Gold |
| Dominion Reef | Dominion Group | Gold |
| Klein Letaba and Louise Moore | Giyani Greenstone Belt | Gold |

The study sites were strategically chosen based on the problems which arise wherever gold and coal mining are undertaken. The project was acutely aligned with the mine rehabilitation industry’s transformation requirements using a range combination of different methods from quantitative, qualitative and action-based methods. According to McCarthy (2011:1) AMD notably vary widely in South Africa with dependent to specific local conditions which may be limited to location, geomorphology, climatic conditions, infrastructure concentration and the extent and distribution of AMD generating deposits. Hence the latter case in this study given the large concentration of gold and coal resources scattered around South Africa.

### 3.1.2 Sites locality and research areas

The research areas are located in the Limpopo Province, North-West Province, Gauteng Province and Mpumalanga Province where five gold tailings and three coal waste materials were drilled and sampled as shown in Figure 3.1.

#### *3.1.2.1 Louise Moore and Klein Letaba*

The two gold mine sites in the Giyani Greenstone Belt situated in the Limpopo Province of South Africa, the nearest town being Giyani with the Kruger National Park situated in the east. The region is extremely dry and warm, with a low yearly precipitation. Streams are regular and the range is overwhelmed by Mopani Veld. The two gold mines are found on the following locations: S $23^{0}$ $17^{I}$ $34^{II}$ and E $30^{0}$ $33^{I}$ $35^{II}$; S $23^{0}$ $13^{I}$ $06^{II}$ and E $30^{0}$ $41^{I}$ $45^{II}$

#### *3.1.2.2 Dominion Reef*

The Dominion Reef mine is situated approximately 20 km southwest of Klerksdorp and near the town Hartbeesfontein, between the latitude of S $26^{0}$ $54^{I}$ $51^{II}$ and longitude of E $26^{0}$ $22^{I}$ $60^{II}$.

#### *3.1.2.3 New Machavie*

The New Machavie is an old abandoned mine that falls under the responsibility of the Tlokwe Local Municipality. New Machavie is found roughly 22 km west of Potchefstroom and 24 km north of Stilfontein between the latitudes of E 26.665, E 26.68 and longitude of S 26.865, S 26.88 (Koch, 2014:24).

#### *3.1.2.4 Crown Mine*

Crown Mine is situated beside the First National Bank soccer stadium in Soweto on the following coordinates S $26^{0}$ $14^{I}$ $43^{II}$ and E $27^{0}$ $58^{I}$ $16^{II}$. It was for many years the largest producer of gold, due to earlier oxidation of contaminated pyrite and other sulphides in the tailings. Extensive pollution has taken place with widespread AMD and heavy metals contamination throughout the area (Viljoen, 2009:134).

### *3.1.2.5 Imbabala coal mine and Golf View coal mine*

The study sites lie within the Ermelo magisterial district and access to the mines is gained via the N17 and N11 routes (Tshivhandekano, 2005:26). The Imbabala coal mine is abandoned and adjacent to the township with reference to the following locations S $26^{0}$ $30^{I}$ $03^{II}$ and E $29^{0}$ $57^{I}$ $22^{II}$. Mine passages stretch out to the community and illicit mineworkers cut away at the underground columns supporting the mine (Olalde, 2017). Golf View mine (Colliery) is situated along the Ermelo/Hendrina road and can be found on the following coordinate S $26^{0}$ $28^{I}$ $8^{II}$ and E $29^{0}$ $58^{I}$ $33^{II}$.

### *3.1.2.6 IPC coal mine*

The site is located on the farm Elandspruit S $25^{0}$ $49^{I}$ $26^{II}$ and E $29^{0}$ $23^{I}$ $08^{II}$, 291JS, R555 Middelburg, Mpumalanga with an underground mining officially in progress, initiated in 2015.

### *3.1.2.7 Vierfontein colliery*

Vierfontein is an abandoned coal mine situated in the Viljoenskroon district in the Free State Province and 12 km south of Orkney. The study area is located by pin-pointing the following coordinates S 27 05’53.0” E 026 47’19.9”.

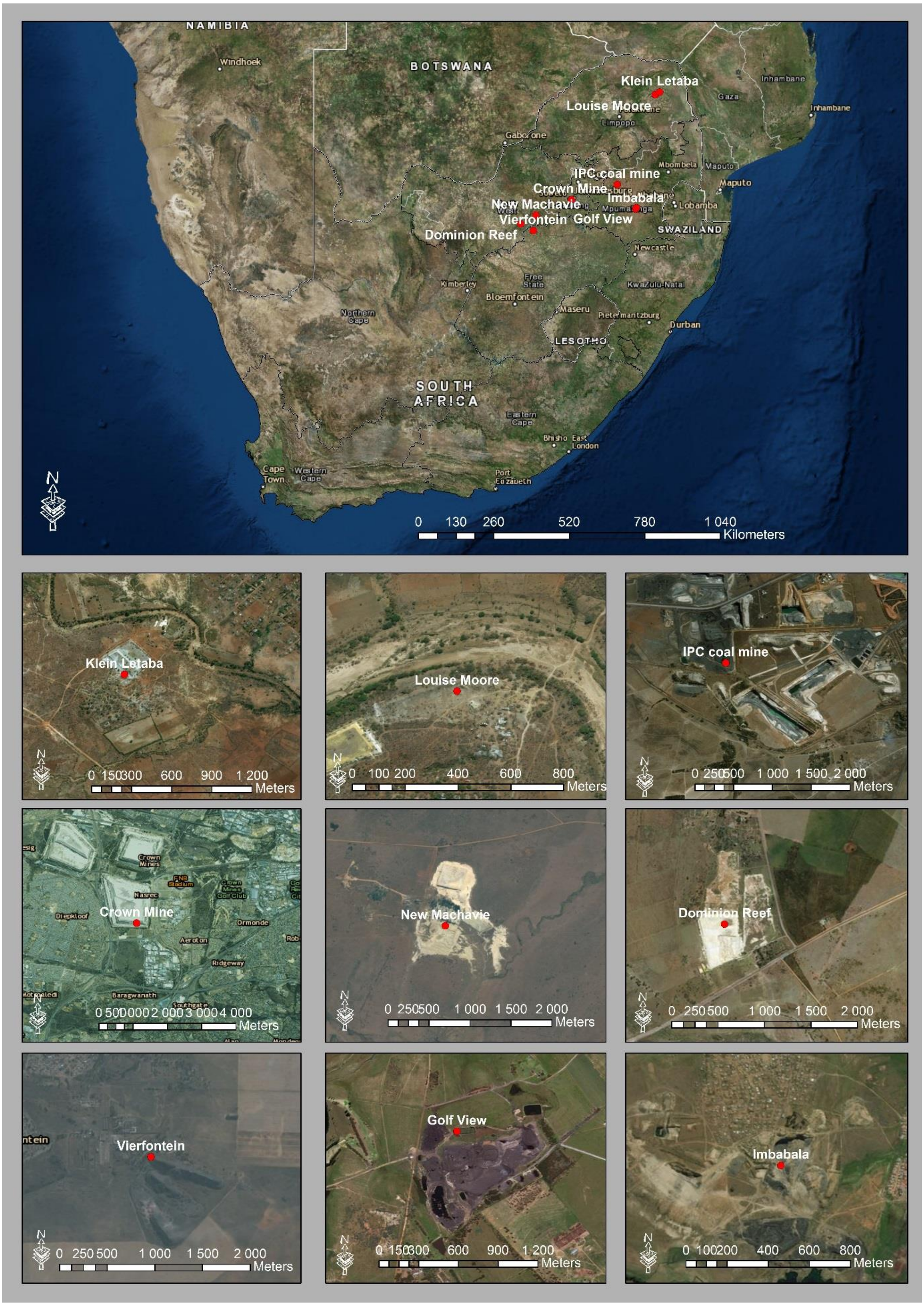

Figure 3.1: Location map of the study areas. Red dots indicate the study sites (Google Earth, 2017).

## 3.2 Sampling, sample preparation, assays and data processing

### 3.2.1 Sampling design

Sampling and geochemical testing programs were developed to integrate a comparative study of both coal and gold. A key requirement of the sampling strategy was to ensure that auger samples were selected to represent the various mining waste materials and tailings likely to be associated with potential toxic elements and associated metal trace elements.

Eight samples of approximately one kilogram each per study site were selected for assessment, which was based on a number of factors from geological variability, complexity of mineralogy and the size of the operation. Due to high analytical cost, duplication of analyses were not done because composite samples were made up from the eight taken. The tailings and waste material samples were from the bottom slope approximately 1.5 meters above the ground level and the top and sub-soil from the original natural soil present immediately below the tailings and waste sample.

Key issues that the study aimed to address through this methodology are as follows:

- Tailings and waste materials that often contain metal sulphides.
- Leachate generation over a long period of time, sulphide oxidation creating acid metal-laden.
- Sulphide oxides to oxygen and water.

On all the selected sites of gold tailings, samples were collected using a manual auger drilling. Soil samples were collected at the bottom slope of the tailings down to the top soil as shown in Figure 3.2, Figure 3.3 and Figure 3.4.

Figure 3.2: Manual augering of a gold TSF at New Machavie, Potchefstroom, South Africa. Photograph taken by Mphinyane (2016).

The manual auger as shown in Figure 3.3 allowed for detailed sampling up to 2.4 metres depth. Boreholes were drilled to the underlying top soil and sub-soil as far as possible, though some areas like Vierfontein had very little soil between the waste and the old natural soil.

Illustrated in Figure 3.4 is the soil sampling procedure of soils with the extracted materials from the boreholes using an auger. Samples were then sealed in plastic bags for transportation and prepared for analysis.

Figure 3.3: Auger drilled samples, New Machavie, Black Reef tailings, Potchefstroom, South Africa. Photograph taken by Mphinyane (2016).

Figure 3.4: Sampling at the bench of a slope of the tailings dam, Crown mine, South Africa. Photograph taken by Kruger (2016), with permission.

### 3.2.2 Sample preparation

For this study, three experimental designs were incorporated; (a) Humidity cells (b) Microwave Digestion (c) Redox-potential. In line with the research objectives, these experiments will unlock substantial opportunity to restore mine-out lands. Although the passive acid generation potential of these tailings is known, the real time leaching potential determine by humidity cell leaching columns is limited. For control purposes, NM- Hutton is the top soil under the NM-Seepage. The rest of the samples are gold tailings and coal waste materials.

#### *3.2.2.1 Humidity cell testing*

Figure 3.6 is essentially an encased chamber through which air is passed and after indicated timeframes, the chamber is opened and the samples are rinsed with water of known chemical qualities (Lapakko & Antonson, 2006; Sobek *et al.,* 1978:182). The motivation behind the occasional rinse is to remove all the reactants that accumulated since the previous rinse (Morin & Hutt, 1999:180). Columns in the Spoor laboratory at the North-West University Potchefstroom Campus with sample size of approximately one kilogram. A standardised leaching column testing procedure, allow some flexibility in size and material for fabrication of columns (Broughton & Robertson, 1992:10).

The test as indicated by the schematic diagram in Figure 3.5 consists of the simulation of mine drainage generation from samples of mine tailings. It is then followed by geochemical analyses of effluent quality from these simulated conditions as also discussed in the leaching study methodology under Section 3.2.2.1.1 (De Wet, 2015a:1; EPA Method 1627, 2011:8; Banerjee, 2013:1329; Lapakko & Trujillo, 2015:4; Price & Errington, 1998:17)

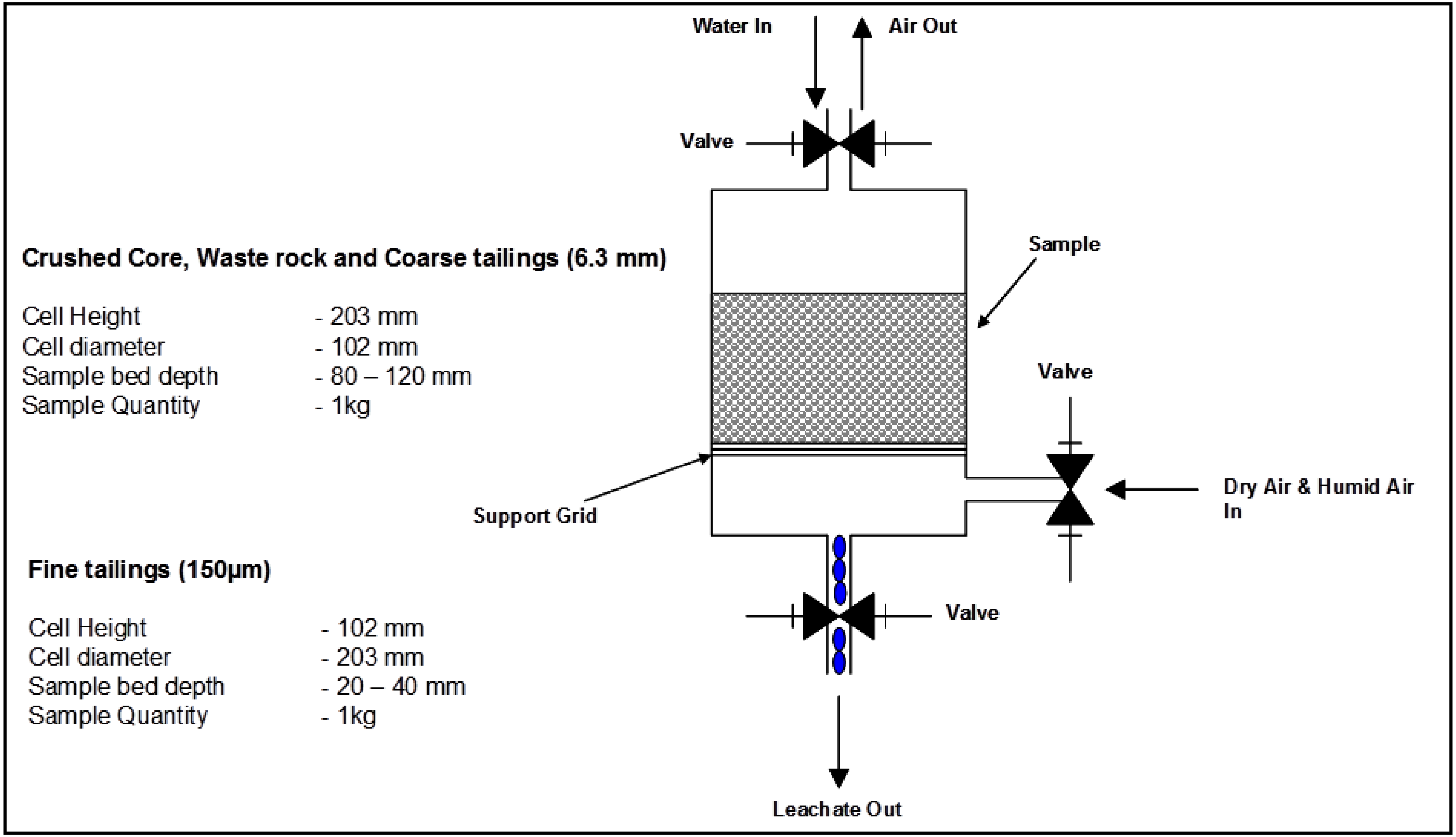

Figure 3.5: Schematic diagram of a humidity cell (Morin & Hutt; 1999:109; 2000:662).

The procedure of this experiment as explained by Price & Errington (1998:18), showed that leaching column tests have some disadvantages over leaching methods such as humidity cells. These include the retention of primary weathering products. Consequently, leachate chemistry cannot be utilised as a measure of the relative rates of acid generation to mineral depletion.  Humidity cells are intended to quicken the natural weathering rate of a solid material. They are expected to give leachates that are equivalent to the actual leachate produced from a strong material in the field (Bradham & Caruccio, 1995:410; Gitari, 2006:46; Robertson & Broughton, 1992:7; Shaw, 1996:20). From this research and the literature study, it emerges that humidity cell tests can be used to quantify the leach materials and correlate them with the redox-influence humidity cell assessment and be able to establish the leaching transfer of metal trace elements from the tailings to the sub-soil in different redox conditions.

Shaw *et al.,* (1998:211) described the humidity cell testing procedure as it is used to study the weathering of coal waste rock and gold tailings to determine the kinetic behaviour of such material. In either case, the object is to screen water (leachate) quality with time by periodic sampling (Gitari, 2006:47). The experiment consisted of the following aspects:

Humidity cell tests were carried out in a chamber consisting of a Perspex cylinder with suggested dimensions of 12 cm and 135 cm length capped at both end. The procedure followed the description of De Wet (2015a:5). Gold tailings and coal waste samples of one kg were placed at the bottom of the humidity cell. Then 750 ml deionized water was added and the tailings were allowed to soak for approximately 2 hours. Figure 3.6 shows an example of a humidity cell testing experiment. The humidity cell testing was run for 10 weeks, with each weekly cycle consisting of the following procedure (De Wet, 2015b:2):

- Leach cycle (one day) – Leach humidity cells with distilled water
- Dry cycle (three days) – Flush dry air through the system
- Humid/moist air cycle (three days) – Flush moist air through the system

After the week cycle, the filtrate was collected in a jar. The volume was recorded then filtered into a 350 ml polyethylene bottle. A 55% nitric acid ($HNO_3$) was prepared and two ml placed in a 100 ml polyethylene bottle. The pH, Electrical Conductivity (EC) and oxidation-reduction potential (ORP) were measured immediately after an overnight leaching and the samples were then analysed for acidity, salinity, sulphate and metal trace element concentrations.

After week ten of the geochemical experiment, the leachate water samples were divided into acid treated and non-treated for Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) analyses. The following aspects were considered for further geochemical investigation (De Wet, 2015b:8):

- Calculation of acid generation and neutralization capability depletion
- Calculation of metal release
- Prediction of water quality (AMD at this stage)

The procedure helps in monitoring the weathering of a tailings material sample so that the weathering products can be collected and quantified. Soluble products are mobilized by a fixed-volume of an aqueous leachate (750 ml of deionized water). Prior to the commencement of the procedure, the materials to be tested are weighed, characterised chemically and mineralogical. Some materials are known to undergo complex mineralogical changes during the extended period of leaching.

The final dry sample is submitted to the following analyses for comparative purposes, since this is a comparative study for coal and gold:

- Portable X-Ray Fluorescence (major & trace elements) using the soil mode of detection (Section 3.2.3 explained the use of XRF in detail).
- ICP-MS (30 element scan on leachate). Leachate water samples from HCT collected were analysed for metal trace elements using ICP-MS at Eco-Analytica Laboratory, North-West University in Potchefstroom. The samples were poured in pre-cleaned polyethylene bottles, instantly acidified (i.e. diluted $HNO_3$) to prevent precipitation.

Figure 3.6: Humidity cell leaching experiment set up, showing moist air outlets, water heater and air supply. Photograph taken by Mphinyane (2017), Spoor Lab, North-West University.

### *3.2.2.1.1 Leaching study's methodology*

Outlines of a considerable number of the more frequently utilised leaching methods have been given by (Aranda, 2008:32; ASTM D4874-95, 2014; Barman*et al.,* 2012:680; Chezom *et al.,* 2013:4; Hasset, 1994:446; Kim, 2005:91).

Since the industrial revolution, anthropogenic activities introduced various hazardous metal trace elements into soils (Alghanmi *et al.,* 2015:196). Humidity cell is broadly perceived for geochemical analysis by acquiring bulk mineral reaction rates under controlled laboratory conditions (Morin & Hutt, 1997:36; Price & Errington, 1998:15). Humidity cell testing is one of the key tools for predicting the long-term weathering of mine waste materials and their potential environmental impacts (Barnes *et al.,* 2015:2; Kwong, 2000: 676; Van der Sloot & Van Zomeren, 2012:93).

The standard methodology commonly undertaken for kinetic testing of mine waste related to this study is the ASTM D 5744-96 humidity cell test procedure (ASTM.D5744-96, 2000:2). Kinetic tests are not optional, but are critical in predicting drainage chemistry even in the absence of acid generation (Hutt & Morin, 1999:363). The humidity test cells are intended to imitate weathering at research facility scale in a controlled environment. The test decides the rate of acid generation and the difference after some time in leachate water quality (Jambor *et al.,* 2003:821; Perkins *et al.,* 1995:325; Sibbick & Murphy, 1999:7).

The objective of this section is to present data from the study of humidity cell tests using this experiment to analyse controls on weathering rates and discharge rates. The comparison of weathering environments involves two common methods of data interpretation i.e. identify and portray geological material; and predict their AMD potential (Johnson & Day, 1999; Paktunc, 1998:104).

Figure 3.7 explains field and laboratory work consisting of piles of non-ore overburden material which in the long run have become the cause of an environmental hazard. As illustrated in Figure 3.7 (a) gold tailings pose AMD problems, leaching of potentially toxic elements, erosion and undesirable aesthetic views (Johnson & Hallberg, 2005:5; Kosson *et al.,* 2014:163; Sunkavalli, 2014:1). AMD is a noteworthy source of water contamination emerging from the weathering of sulphide bearing minerals and weathering of this nature is complicated, hence under specific suppositions it can be re-enacted in chemical, physical and geochemical terms to help foresee geochemical changes as shown in Figure 3.7 (b) (Lapakko *et al.,* 2006:1027; Naicker *et al.,* 2003:30; Sunkavalli *et al.,* 2013:170).

However, there is an insignificant amount of literature available on coupling Humidity Cell Tests (HCT) data. Sapsford & Williams (2005:57) mentioned that HCT represent to an alternate draining condition than that in the field thus coordinate scaling up of results by weight adjustment will give erroneous outcomes. Hence there is a critical need of ground-breaking research on methodology for incorporating HCT information in expectation of recorded field geochemical models (Ochieng et *al.,* 2010:3353; Sunkavalli, 2014:1).

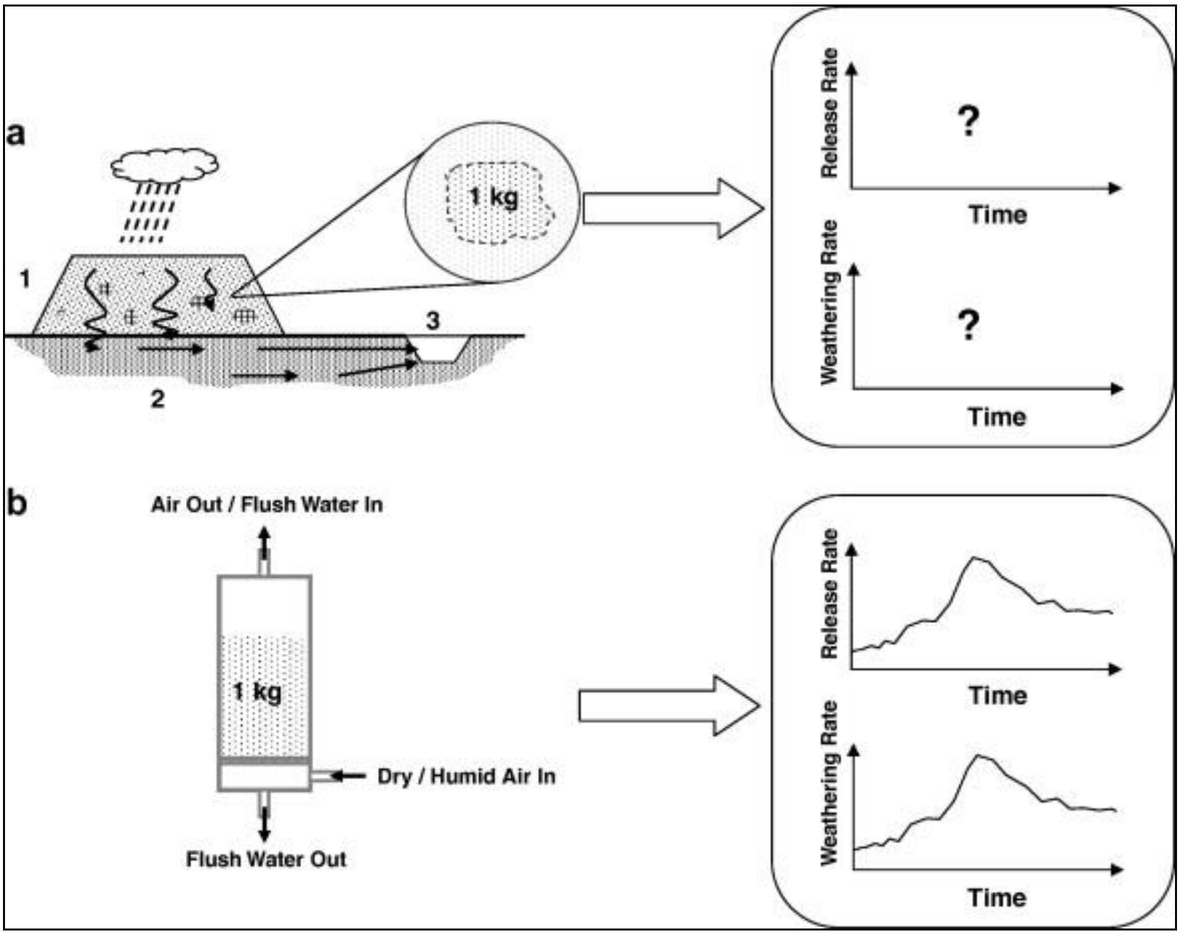

Figure 3.7: Comparison of weathering environments in the field (a) and laboratory (b) showing moist air outlets, water heater and air supply (Sapsford *et al.,* 2009:26).

The Humidity cell is based on the technique which was adapted by Sobek *et al.* (1978:182) and has been utilised for more than 30 years ever since (Morin & Hutt, 1997:34; Sapsford & Williams, 2005:58). HCT and comparative leaching tests are regularly run to decide the geochemical conduct of different mine wastes, particularly to determine weathering rates and additionally discharge rates relying upon the particular interpretation that exists (Frostad *et al.,* 2002:185; Richardson, 1993:40; Sapsford *et al.,* 2009:27).

### *3.2.2.2 Microwave digestion*

Based on the methods described by Bervoets *et al.* (2004:445); Blust *et al.* (1988:389) and Degger (2010:12) for the digestion experiments, the ETHOS EASY MAXI-44 Microwave digestion-system was used. It has a very high throughput rotor holding up to 44 TFM vessels with a volume of 100 ml and can perform easy digestion of leaching-type materials in a variety of samples, in this case soils, in a laboratory environment. In this investigation microwave digestion was utilised for the examining the draining exchanges of possibly metal trace elements from tailings to the top soil and sub-soil as shown in Figure: 3.8 (Baez *et al.,* 2013:2; Bettinelli *et al.,* 2000:290; Kingston & Walter, 1997:33).

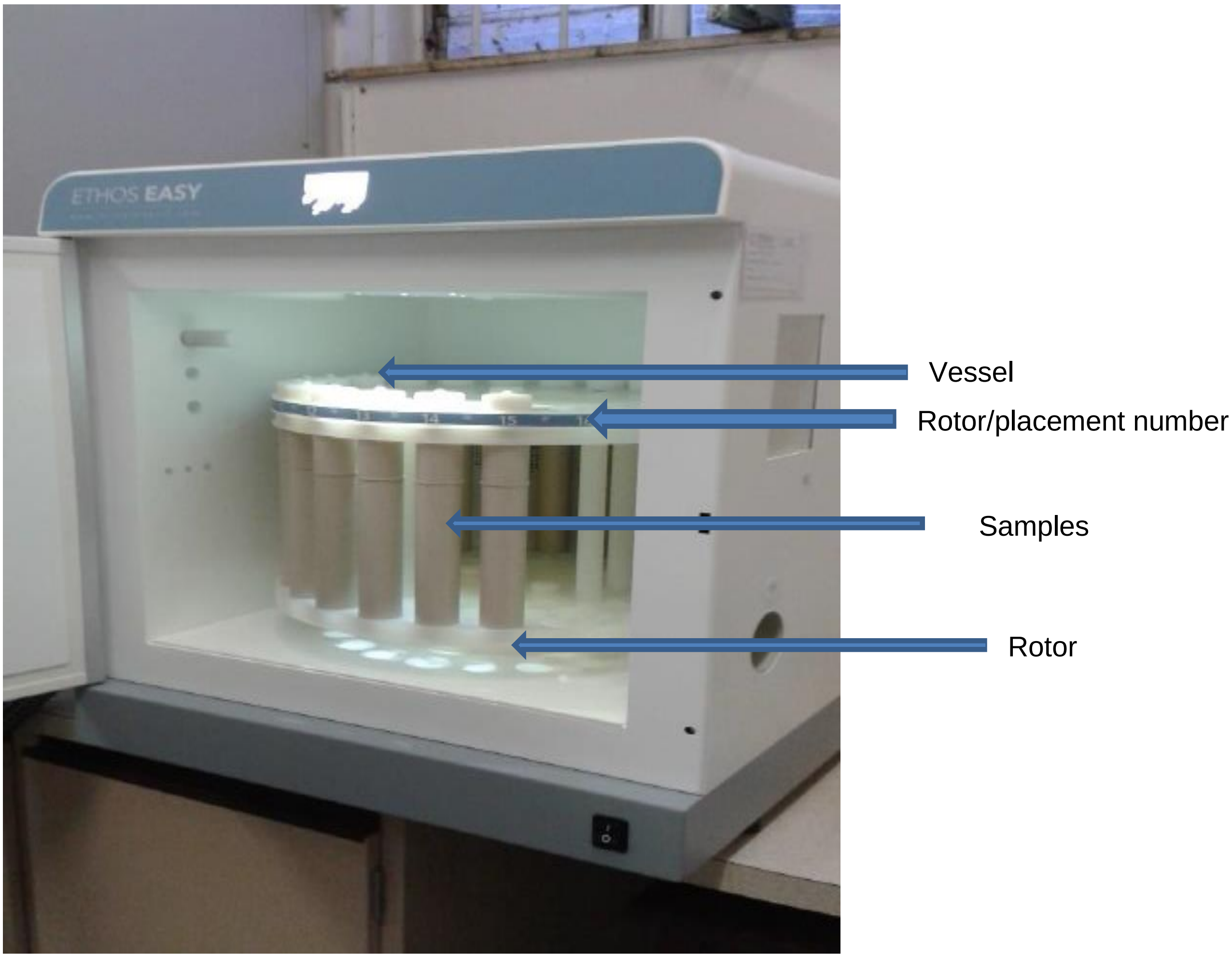

Figure 3.8: The microwave oven interior. Photograph taken by Greying (2017), with permission.

The digestion process is controlled by temperature. The system consists of the following:

1. Pre-digestion

Soil samples were oven dried at 60°C for 48 hours. Samples were weighed and noted according to the method description (up to 200 mg sample and 10 ml $HNO_3$), together with the Certified Reference Material (CRM) weighed with same mass for every microwave digestion batch.

2. Digestion – Ethos Easy MAXI-44 Microwave Digestion System

Weighed samples were added to vessels using plastic weighing boats, and then 10 ml of $HNO_3$ was added to the vessels. All sample residues were thoroughly washed from the inside of the vessels in order not to create hotspots during digestion. Ventilation lids were secured, and vessels were distributed evenly in the rotor and order of placement was noted and rotor started.

3. Post-digestion

After the digestion and cool-down, the door unlocked automatically. The samples were left to cool down for a further 20-30 minutes until it reached a temperature of 50 degree Celsius. The rotor was removed from the chamber and each sample decanted into a 50 ml volumetric flask using a glass funnel. The vessels (x three) and the funnel were rinsed with one % $HNO_3$ and the samples further diluted with one % $HNO_3$ up to a volume of exactly 50 ml.

4. Clean-up

All glassware were put through acid and soap baths (i.e. 24 hours in acid and 24 hours in soap). The vessels were rinsed with one % $HNO_3$ and together with glassware left to air dry after cleaning.

5. Pre ICP-MS

Diluted samples were filtered through a 0.45 micrometre (µm) cellulose nitrate filter using a vacuum pump. Ten ml was decanted into ICP-MS tubes. The remaining 40 ml of each sample was stored in labelled Falcon$^{TM}$ tubes. The vacuum jar was emptied and rinsed after each filtration and discarded filters placed in the allocated biological waste box.

6. ICP-MS

The operation of the apparatus was performed by the responsible certified technician.

A stock solution of a 50/50 volume of Ultra-pure $HNO_3$ and deionized water is prepared. A solution mix is then prepared by taking three ml stock solution and bringing it to volume in a litre of deionized water. Every sample is then diluted 10 times with the Solution Mix. The ICP-MS does the calculation of the dilution before results are logged. Samples are analysed using an Agilent ICP-MS.

Figure: 3.9 shows the sample preparation of topsoil and sub-soil for microwave digestion for elemental analyses of top soil and sub-soil. Samples were prepared in a similar manner described in Section 3.2.2.2.

Figure 3.9: Microwave digestive set-up. Photograph taken by Greyling (2017), with permission.

Figure: 3.10 shows tests being set up for ICP-MS after assimilation for Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb and U using nitric acid after microwave digestion. This is sufficient for ascertaining metal trace elements composition of soils.

Figure 3.10: Preparation of soil samples. Photograph taken by Greyling (2017), with permission.

### 3.2.3 Assays and geochemical analysis

The measurements of pH, ORP and EC were made for each of the leaching tests samples using standard operating procedures (Radojevic̀ & Bashkin, 1999:281). This included the analyses by a semi-quantitative 30-element ICP-MS scan performed on the leachate. Results for samples other than liquid samples are given in mg/kg (later converted into ppm) dry matter and all dilutions are taken into account. Microwave digestions of solid samples are done with an Ethos UP, Milestone Magna Analytical microwave digester using the EPA 3051A method.

X-ray Fluorescence is one of the tools of choice for geologists (Ferguson, 2012). This technique was used to determine major and trace components in a single speedy analysis with a minimum of specimen preparation required (Anzelmo & Lindsay, 1987a: 181& 1987b:200).

This investigation involves the determination of geological related AMD of gold tailings and coal waste materials. Ene *et al.,* (2009:816) prescribed the X-ray Fluorescence procedure to assess soil contamination with more toxic elements (As, Cd, Fe, Mn, Co, Cr, Cu, Ni, Pb, U and Zn) in the vicinity of mining waste transfer sites. The soil samples were collected in open spots at various profundities and distinctive separations from all eight selected study sites. Since the presence of metal trace elements in soil affects its quality (Cojocaru *et al.,* 2006:71), the study also assessed the metal trace elements distribution and compare soil metal trace element concentrations from gold and coal mining.

The samples were prepared at the North-West University (Potchefstroom Campus) using PANalytical Axios X-ray Fluorescence (XRF) instrument in order to give accurate quantitative multi elemental results. Soil, gold tailings and coal waste materials were examined utilizing WROXI (Wide range Oxides) (fused bead) investigation and trace elemental analysis (Pro trace) that gave fast and solid quantitative outcomes, outfitted with a Helium framework for quick screening and programming for examinations; adjusted utilizing various universal and national certified reference materials (CRMs).

#### 3.2.3.1 pH, Electrical Conductivity (EC) and Oxidation-Reduction Potential (ORP)

All readings were done using PC5 Tester ECO PACK–XS Instrument for all samples of leachate water. The instrument was calibrated with buffer solutions at pH = 4, 7 and 10 prior taking measurements at Spoor Laboratory. Calibration for EC was done using EC buffer solution at 1413 µs and1880 µs. The instrument also tested the ORP by utilising a switch mode. After use the electrode was washed with distilled water and then dried to prevent contamination of subsequent tests. The pH meter was then stored in KCl solution to prevent desiccation.

# CHAPTER 4: Results and Discussions

*All truths are easy to understand once they are discovered; the point is to discover them*

~ Galileo Galilei

## 4.1 Introduction

Experimental results are presented and discussed in this Chapter. The geochemical analyses involved the use of XRF, humidity cell testing, microwave digestion and ICP-MS for characterization of gold tailings, coal waste materials and soils. The detailed experimental procedures are discussed in Chapter 3. Summarised below in Table 4.1 is the sites reference names.

Table 4.1: Reference of different gold tailings and coal waste materials.

| **Samples** | **Full samples name** | | **Samples** | **Full samples name** |
|---|---|---|---|---|
| NM-Hutton | New Machavie- Hutton Series | | NM-BR | New Machavie- Black Reef |
| NM-Seepage | New Machavie-Seepage | | NM-Shale | New Machavie- Shale |
| VC | Vierfontein Coal | | DM | Dominion Reef |
| GVC | Golf View Coal | | KL | Klein Letaba |
| ICP | ICP Coal mine | | LM | Louise Moore |
| ICW | Imbabala Coal Waste | | | |
| CM | Crown Mine | | | |

Soil contamination with metal trace elements is a serious concern to the environment. Table 4.2 shows the Soil Screening values for contaminated sites which can also be referred as the Threshold values or standard values.

Table 4.2: Descriptive statistics of metal trace elements concentrations in soils expressed in ppm.

| **Parameter ppm** | **Ref.[a] Value** | **Ref.[b] Value** |
|---|---|---|
| As | 5.8 | 12 |
| Al | NA | NA |
| Cr | 80 | 64 |
| Cd | 7.5 | 14 |
| Co | 300 | 40 |
| Cu | 16 | 63 |
| Fe | NA | NA |
| Mn | 740 | NA |
| Ni | 91 | 50 |
| Pb | 20 | 70 |
| Zn | 240 | 200 |
| U | NA | 300 |

[a] National Norms and Standards for Remediation of contaminated Land and Soil Quality in South Africa (2014).

[b] Based on Canadian Soil Quality guidelines for the protection of Human and Environmental Health (Canadian Council of Ministers of the Environment, 2007).

NA: Not available

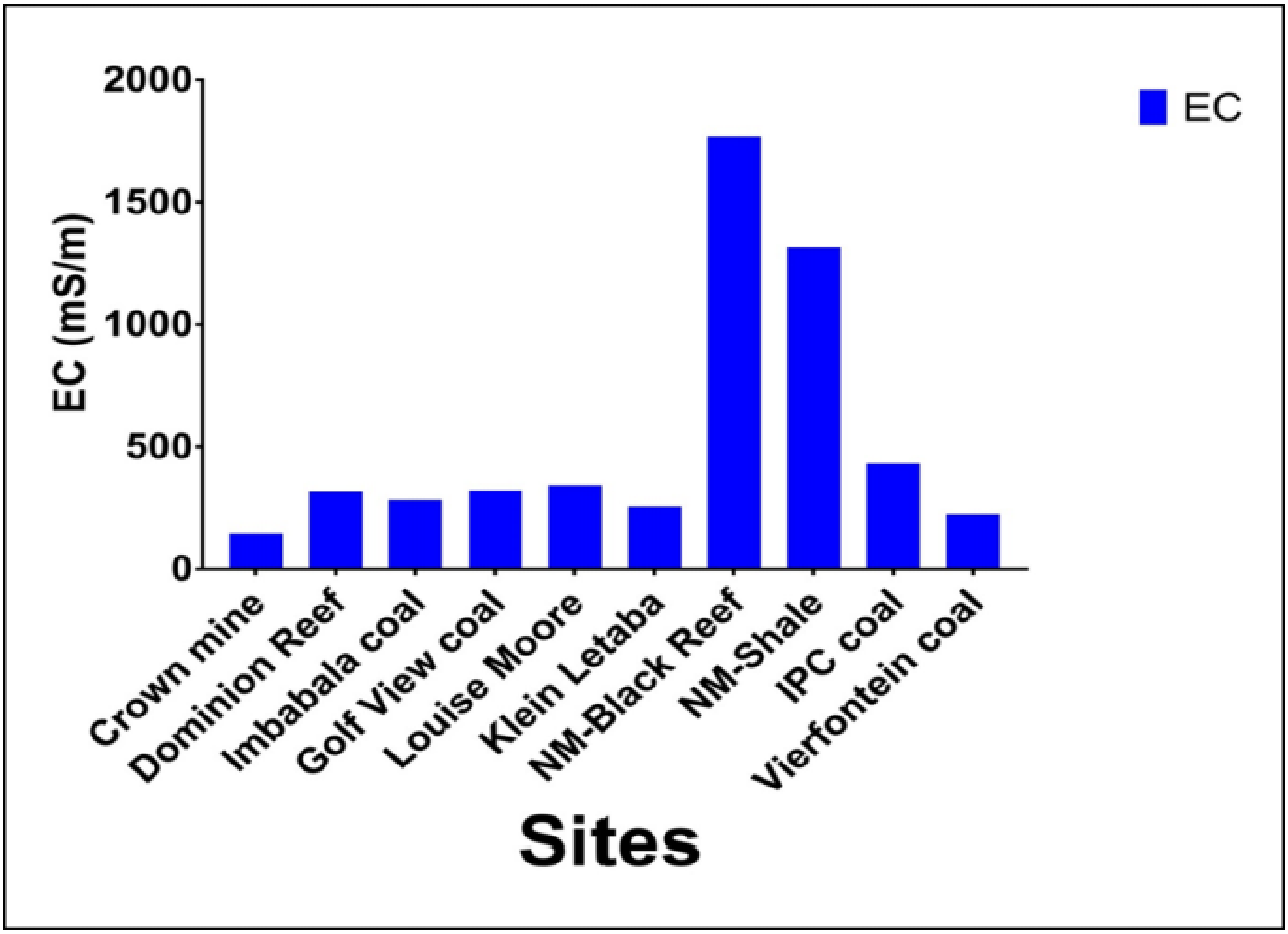

Figure 4.1: EC values of original samples before leaching gold tailings and coal waste materials.

### 4.1.1 pH water versus pH Potassium Chloride and Electrical Conductivity

Table 4.3 shows pH values in different solutions and EC values of gold tailings and coal waste materials. Discussions of the leachate and metal trace elements in solution are based on pH and should also include discussions of interactions with EC as well as clay content i.e. LM. It is anticipated that LM have a higher CEC and could therefore influence leaching process. The LM exhibit a pH of slightly alkaline, above 8; which could be caused by high carbonate content (Annicaert, 2013:28).

### 4.1.2 Electrical Conductivity (EC)

The EC analyses results conducted on the gold tailings and coal waste materials are presented in Figure 4.1. The EC values in this study are utilised to categorise the salt hazard related to geological presence of AMD. The original samples with high EC values, indicated in Table 4.3 and Figure 4.1, respectively, show high values of 1317 mS/m and 1769 mS/m. AMD from gold and coal mining causing serious environmental catastrophe in this case, EC is a function of the dissociated ions mobility determined by solution viscosity (Daniell, 2015:89; Makgae, 2012:332; Hubert & Wolkersdorfer, 2015:490).

### 4.1.3 pH in water ($H_2O$) vs pH in potassium chloride (KCl)

This section presents the gold tailings and coal waste materials pH in different solutions and compares them. The graph was plotted with standard error bars as referred in Figure 4.2. The pH value is probably the most important chemical characteristics of soil and plays a critical part in determining the solubility of metal trace elements detected in this study. Consequently, pH measured in KCl solution is always lower than in water, this is due to higher concentration of hydrogen ions been released from the soil by means of the potassium in the KCl. (Bloom *et al.,* 2005:411; Gavriloaei, 2012:396; Moore & Loeppert, 1987:908).

The distinction between pH in water and pH in KCl is essential. Given the low clay fraction, exchangeable acidity is lower as appeared in Table 4.3. The pH measure in water show signs of AMD should be with pH values from 2.8 to 4.5. The reason for the low pH observed in most sites is attributed to the presence of pyrite in the gold tailings and gold waste material (Fan *et al.,* 2016:5).

Table 4.3: The pH (in deionized water and in KCl and EC values together with soil particle size characteristics of the mine wastes.

| Samples | > 2 mm | Sand | Silt | Clay | | | EC |
|---|---|---|---|---|---|---|---|
| | | (%< as 2 mm) | | | pH($H_2O$) | pH(KCl) | (mS/m) |
| CM | 0.0 | 72.1 | 24.8 | 3.1 | 4.09 | 3.85 | 145 |
| DR TTS | 0.0 | 51.4 | 45.3 | 3.3 | 6.42 | 6.2 | 318 |
| ICW | 17.6 | 89.7 | 6.9 | 3.5 | 3.82 | 3.35 | 284 |
| GVC | 20.8 | 92.5 | 4.0 | 3.5 | 3.68 | 3.65 | 323 |
| LM | 0.0 | 6.0 | 68.6 | 25.5 | 8.08 | 7.85 | 342 |
| KL | 0.4 | 65.0 | 31.7 | 3.3 | 7.35 | 7.18 | 257 |
| NM-BR | 5.4 | 61.9 | 28.4 | 9.7 | 3.58 | 3.51 | 1769 |
| NM-Shale | 0.1 | 65.1 | 26.1 | 8.9 | 2.8 | 2.7 | 1317 |
| IPC | 32.0 | 91.8 | 4.4 | 3.9 | 3.81 | 3.65 | 432 |
| VC | 21.2 | 86.8 | 12.6 | 0.5 | 4.9 | 4.44 | 225 |

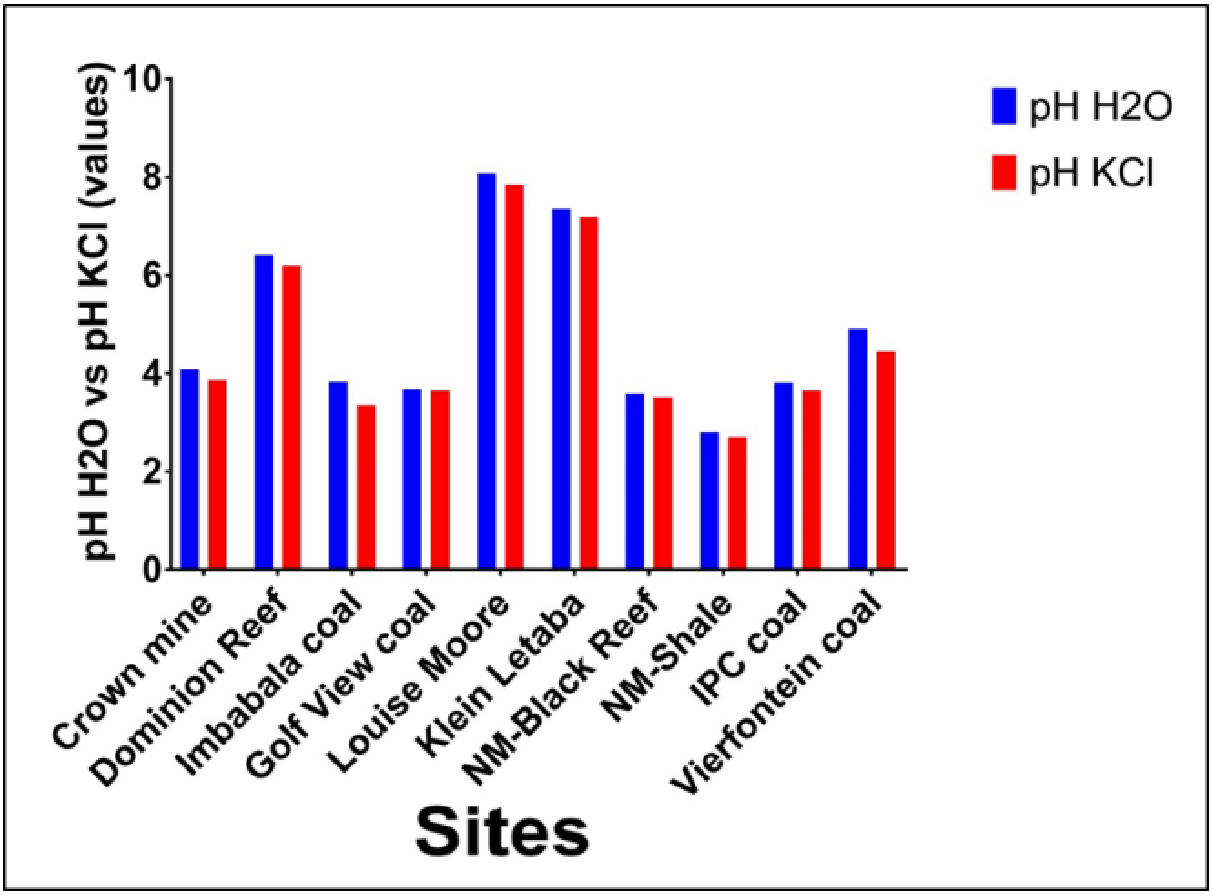

Figure 4.2: pH values of gold tailings and coal waste materials.

### 4.2 Weathering rates of gold tailings and coal waste materials

The following Section (4.2.1) presents data from numerous leaching tests. HCT experiments were run for 10 weeks. Recently it has been recommended that this duration be increased to allow the leachate concentrations to geochemically stabilise (Lapakko, 2003:158; Nicholson, 2016:12). The HCT was carried out on the gold tailings and coal waste materials collected from the coal and gold storage facilities. The specific end goal was to calculate the phases that are controlling the solubility of dissolved constituents of AMD generation rates and release of metal trace elements (De Wet, 2015b:8; Fosso-Kankeu, 2016:92). A customary test term time of 10 weeks was considered with reference to the aim of this project as outlined in Section 1.5.

#### 4.2.1 pH ($H_2O$) of the HCT leachates

Humidity cell test leachates are elevated in a similar suite of elements as EPA leachates (Barnes *et al.,* 2009:1986). These include: Al, Mn, Cr, Fe, Co, Ni, Cu, Zn, As, Cd, Pb and U. The presence of these metal trace elements in the acid solutions, results from the leaching of minerals especially silicates, oxides and sulphides associated with the gold and coal (Campaner *et al.,* 2014:539). The results pointed out that the gold tailings and coal waste materials are potential sources of leachate metal trace elements to the environment. The acidity production in the HCT is of major significance as it expresses the oxidation of sulphide minerals. Figure 4.3 shows the leachate pH of 12 sites over a 10-week period. According to the results, it is observed that acidity was immediately produced from the first three weeks for samples KL, NM-Shale, ICP, GVC, DM, CM, DM, CM and NM-Seepage samples with the pH ranging from below 3 to 4, respectively. Low pH values in the leachate samples indicate pyrite oxidation in samples (Campaner *et al.,* 2014:539).

This indicates that the bacterial activity did not play any role in the oxidation process (Lottermoser, 2007:114).The acidity level remained relatively constant throughout the test for all the samples tested with slight variation on NM-Hutton (Topsoil), which rapidly increased the pH after second week. In this case, pyrite presence which result in slow reaction rates and minimum acid release (Barnes *et al.,* 2009; Fosso-Kankeu, 2016:92; Stoch & Winde, 2010:84).

In this regard, results of acid production at week ten in samples LM, NM-Hutton, NM-Seepage and VC of higher pH values show that acidity production results from the fact that neutralization capacities of the carbonate and silicate minerals contained in the solid rock cannot counterbalance the acidity produced by oxidation of sulphide minerals (Plante *et al.,* 2012:61; Sraek *et al.,* 2010:26). Therefore, the oxidation of pyrite is likely to be of low intensity but it is possible that the samples that initially produce alkaline pH conditions will become acidic over a longer timeframe.

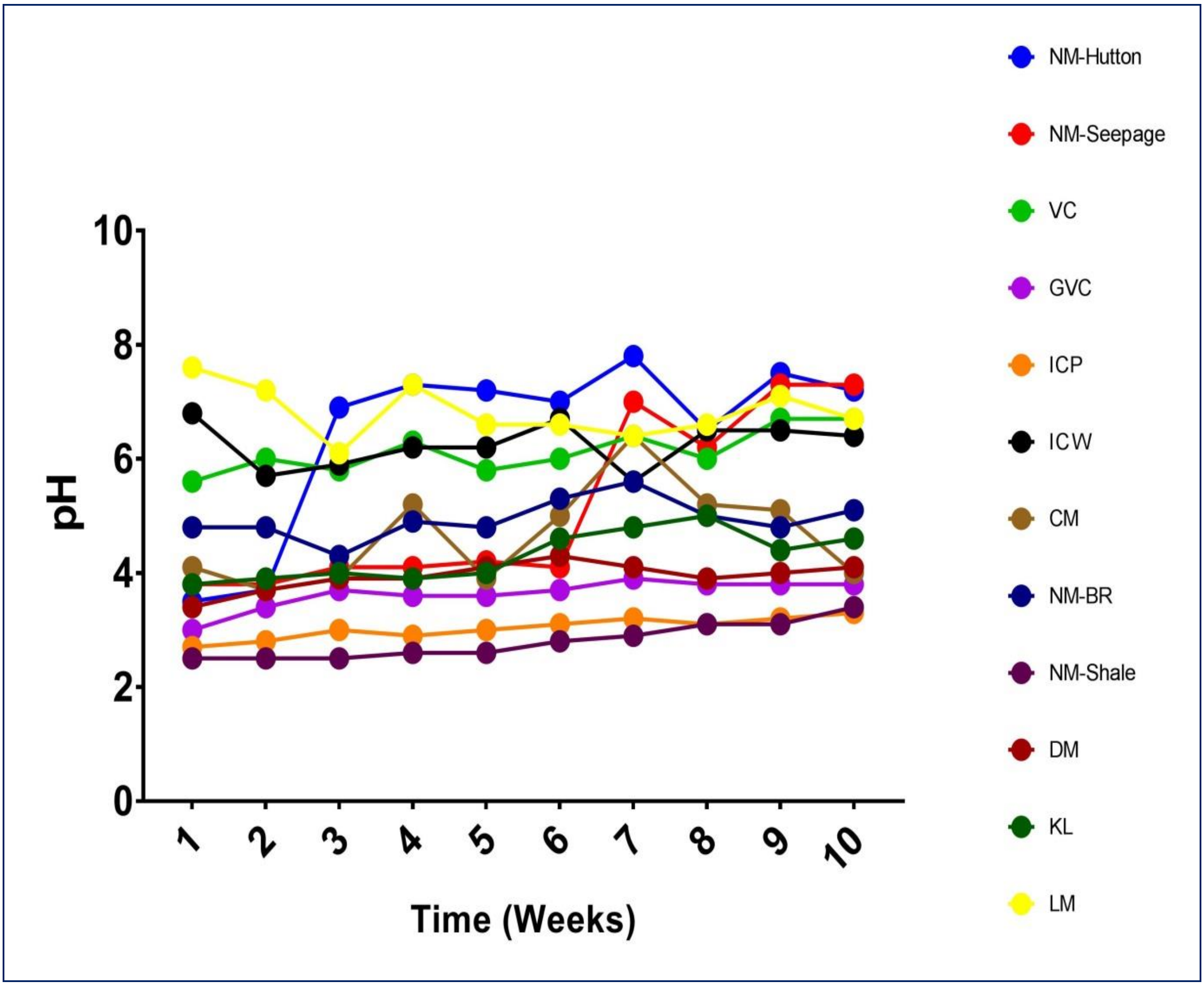

Figure 4.3: Variation of leachate pH water of different tailings, waste and topsoil over a period of ten weeks.

### 4.2.2 Electrical Conductivity (EC) of the HCT leachates

The variation of the conductivity as a function of time (weeks) in the leachates of the HCT is shown in Figure 4.4. Leachate results show EC values ranging from 2 to 11 mS/m for the first five weeks. It can be seen that at week 2, the EC value decreased from all the sites. LM commenced at 11 mS/m vividly showing as the salts were leached to the top soil and sub-soil, which could be attributed to the decrement of pH from these other sites. It is precisely in these sites where the lowest conductivities were achieved reaching 0.054 mS/m in NM-Hutton topsoil.

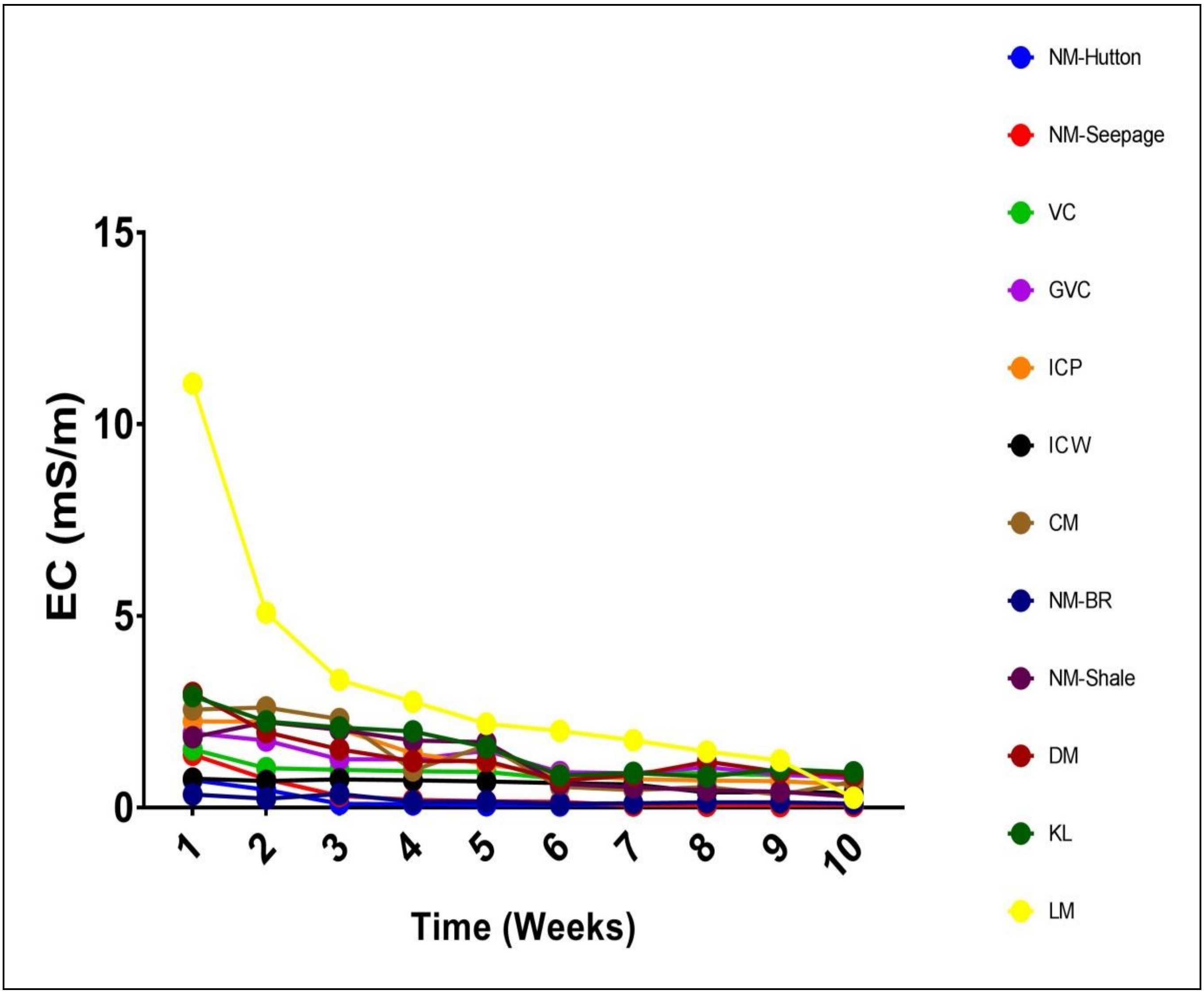

Figure 4.4: Variation of leachate EC of different tailings, waste and topsoil over a period of ten weeks.

### 4.2.3 Oxidation Reduction Potential (ORP) of the HCT leachates

The increase of the ORP is analogous to the increase of metal trace elements concentration (Bourg & Loch, 1995:90; Koch, 2014:47; Sarai *et al.,* 2006:137); these outcomes showed that ionic interactions of constituents occurred in the solution. A high ORP value indicates increasing oxidation (from 200 mV and above) of pyrite by utilisation of oxygen and synergist bacterial action. Samples from Sites DM, ICP, NM-Shale and GVC attest to the presence of oxidant media favourable to sulphides oxidation process. However, in LM, NM-Hutton, VC, CM, NM-seepage NM-BR and ICW the leachates presented lower redox potential values of below 200 mV (Rösner & Van Schalkwyk, 1999:138; Smedley & Kinniburgh, 2005:269; Tutu, 2012:355). (Refer to Figure 4.5).

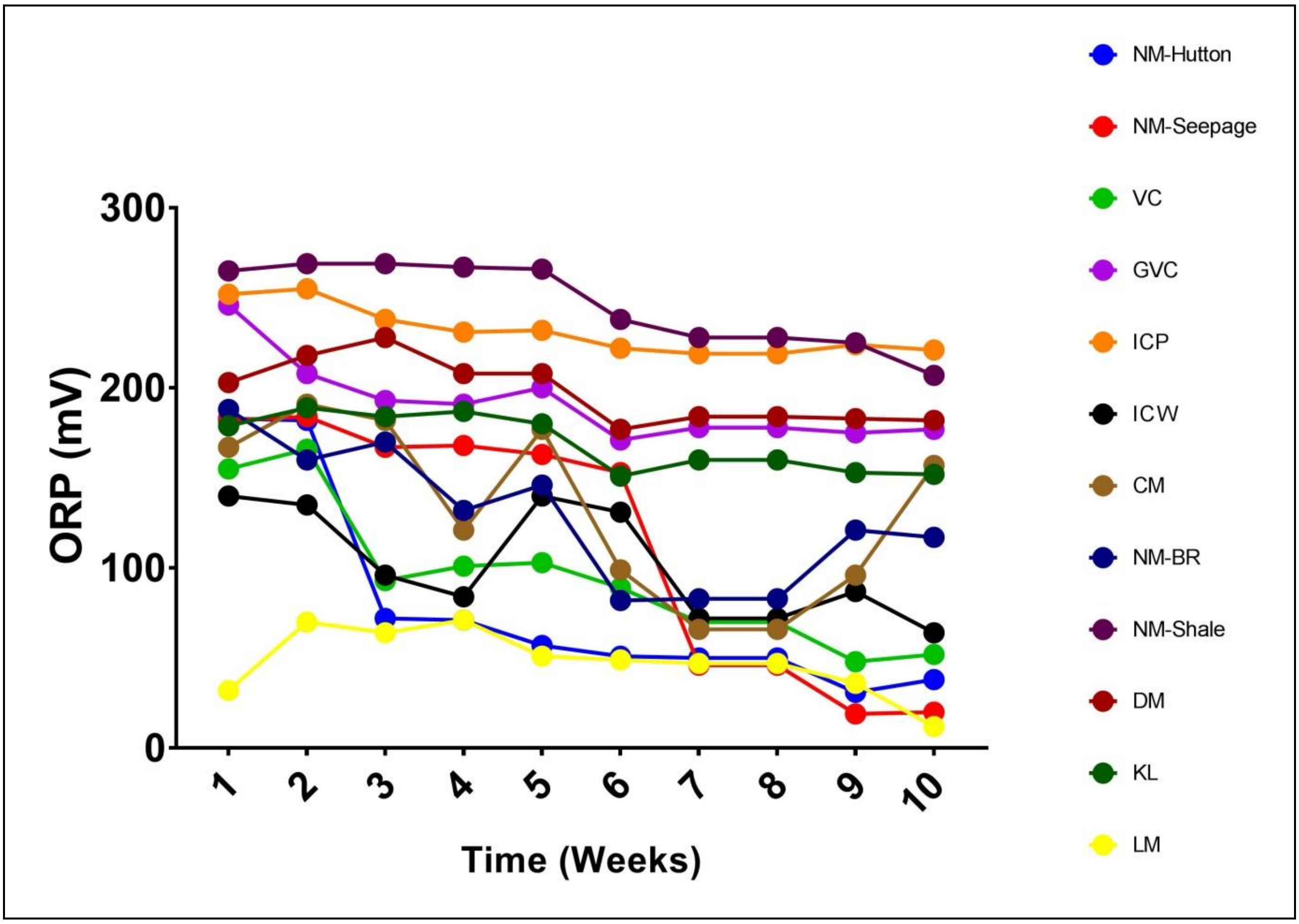

Figure 4.5: The variation in redox potential (ORP) measured over a period of ten weeks of gold tailings and coal waste materials with an anomalous values at week 6 to 7.

## 4.3 Metal trace elemental composition of gold tailings, coal waste materials, topsoil and sub-soil using portable XRF

The concentration of metal trace elements in the gold tailings, coal waste materials and soil (top and sub) confirm the differing mineralogical results of sulphide elements. XRF results for the samples proved the occurrence of the following elements: Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb and U. Soil represents the ultimate sink for metal trace elements in mining areas (Purakayastha & Chhonkar, 2010:390). Metal trace elements are immobile in soils due to their high affinity for the soil matrix and the cation exchange capacity (CEC) and the elements get adsorbed onto the clay particles of soils and tend to accumulate there(Cunningham *et al.,* 1995:394; Purakayastha *et al.,* 2008:374).

Graphical results illustrated in Figure 4.6 show the variations of the measured metal trace element concentrations of gold tailings, coal waste materials, topsoil and sub-soil. Metal trace element concentrations in the gold tailings show different values per sampling site. For Mn, Fe and Ni sampling site KL gold tailings had high metal trace elements concentrations, respectively. A relinquishing trend continues on the top soil with the decrease in concentration and subsequently on the sub-soil. These high concentrations of metal trace elements were also reported near mining sites (Sebei, 2007). Moreover, the concentration of Fe showed higher values in LM; these escalated levels can be attributed to high concentration of Fe and Mn in South African soils.

The low detectible concentrations of Cu at KL illustrate that the Cu concentration was leached to the groundwater and initially low.

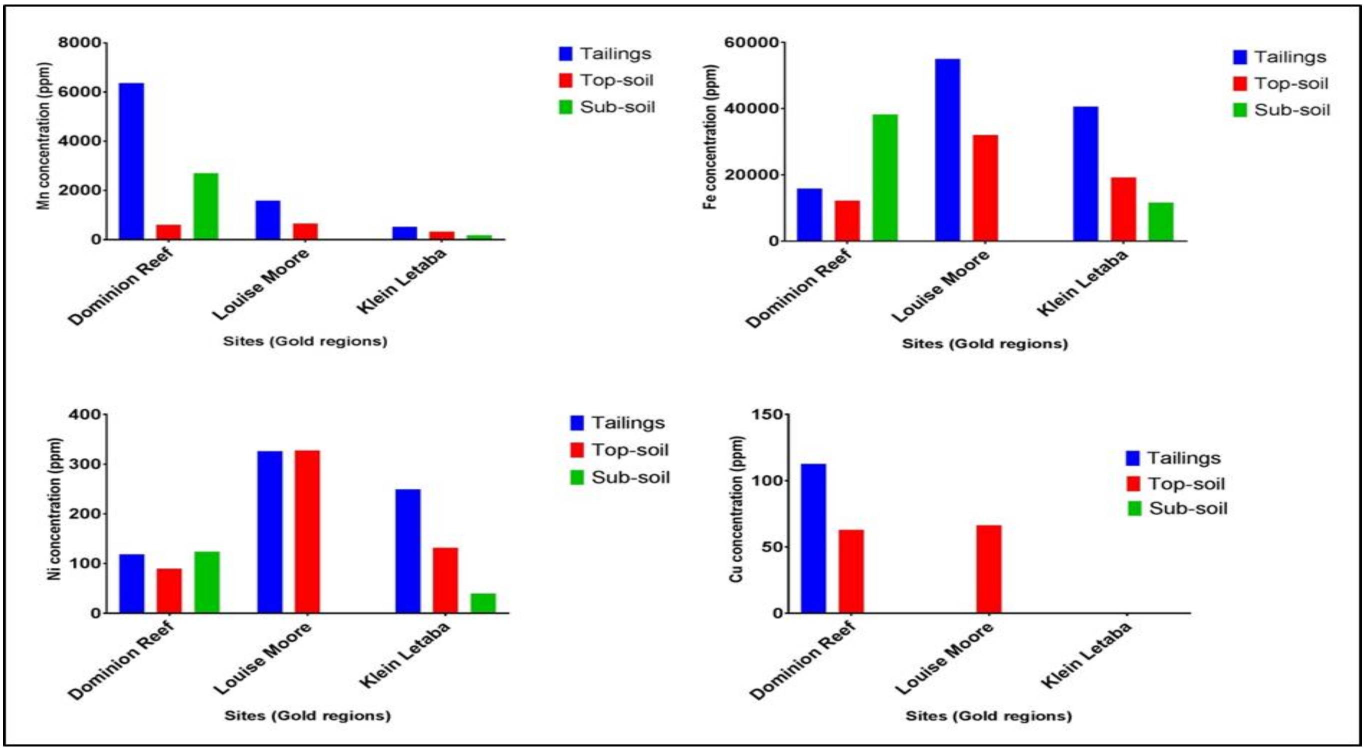

Figure 4.6: The variation of Mn, Fe, Ni and Cu concentrations in gold tailings, topsoil and sub-soil using Portable XRF.

High concentrations of Pb, Zn and U at Dominion Reef illustrate the impact of metal trace elements through mining activity on the topsoil and sub-soil. This is based on the observation that the concentrations of the metal trace elements at different sites as shown in Figures 4.6, Figure 4.7 and Figure 4.8, which display very similar trends when contrasted with different sites. Its available fraction is more influenced by soil texture and pH. The low detection limit of Pb concentration in tailings and availability in topsoil at LM and KL sub-soil as Jung 2001 (cited by Jung, 2008:212) suggested that Pb may increase in soil depth due to leaching from the surface under acidic conditions. Downward leaching if it occurs can result in contamination of underground aquifers. The absence of U in LM is attributed to the extensive erosion of the tailings dam.

It is obvious from the XRF results shows that there is a variety in wealth of different metal trace elements in all coal waste material, topsoil and sub-soil samples investigated. It is imperative to take note of that fundamentally higher values were measured for all metal trace elements when contrasted with some past investigations (Adedosu *et al.,* 2007:3103). Golf View coal in Figure 4.7 and Figure 4.8 exhibited high concentrations of Zn and Ni. The high concentration of Zn could be an indication of the presence of sphalerite mineral in these localities. The Zn concentration is rising unnaturally, due to anthropogenic additions, in this case coal mining (Antwi-Agyei *et al.,* 2009:357; Van Niekerk & Begley, 1991:233; Wuana & Okieimen, 2011:6).

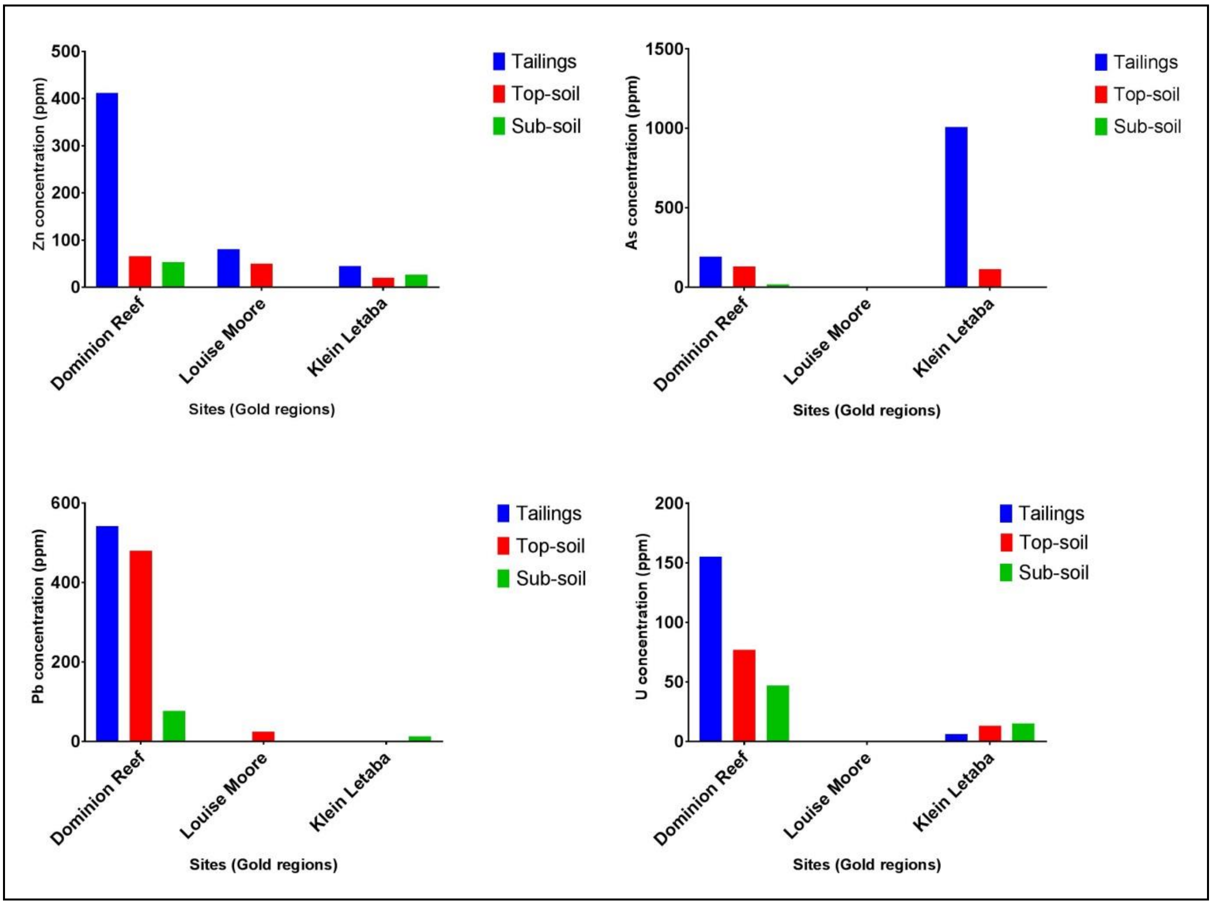

Figure 4.7: The variation of Zn, As, Pb and U concentrations in gold tailings, topsoil and sub-soil using Portable XRF.

The absence of Mn at ICW is a results of mobility and biological availability. Mn depend not only on the total concentration but also on the physicochemical forms in which they occur (Wuana & Okieimen, 2011:6). Whereas in other sites Mn is showing a steady decrease in concentration except for IPC where coal waste and topsoil have similar levels of 180 ppm concentration. Fe occurs in two states: the soluble reduced Fe (II) and oxidised Fe (III) insoluble at pH >4. This explains the variations in Fe concentrations and gives a reflection of the chemistry of water leaching from the coal waste material through to the topsoil and sub-soil (Norrström, 1995:6). Ni is a natural constituent of soils. Ni concentration levels vary widely depending on the local geology and anthropogenic input as can be depicted from Figure 4.8 from 39 ppm to 60 ppm. It evident that soil play a crucial role in Ni mobility and it is site specific depending mainly on soil type and pH. Hence Ni mobility is increased at low pH levels. The concentration of Cu is <40 ppm in GVC coal waste site. The presents of Cu at GVC represents a form of insoluble sulphides or silicates or fixation of the Cu.

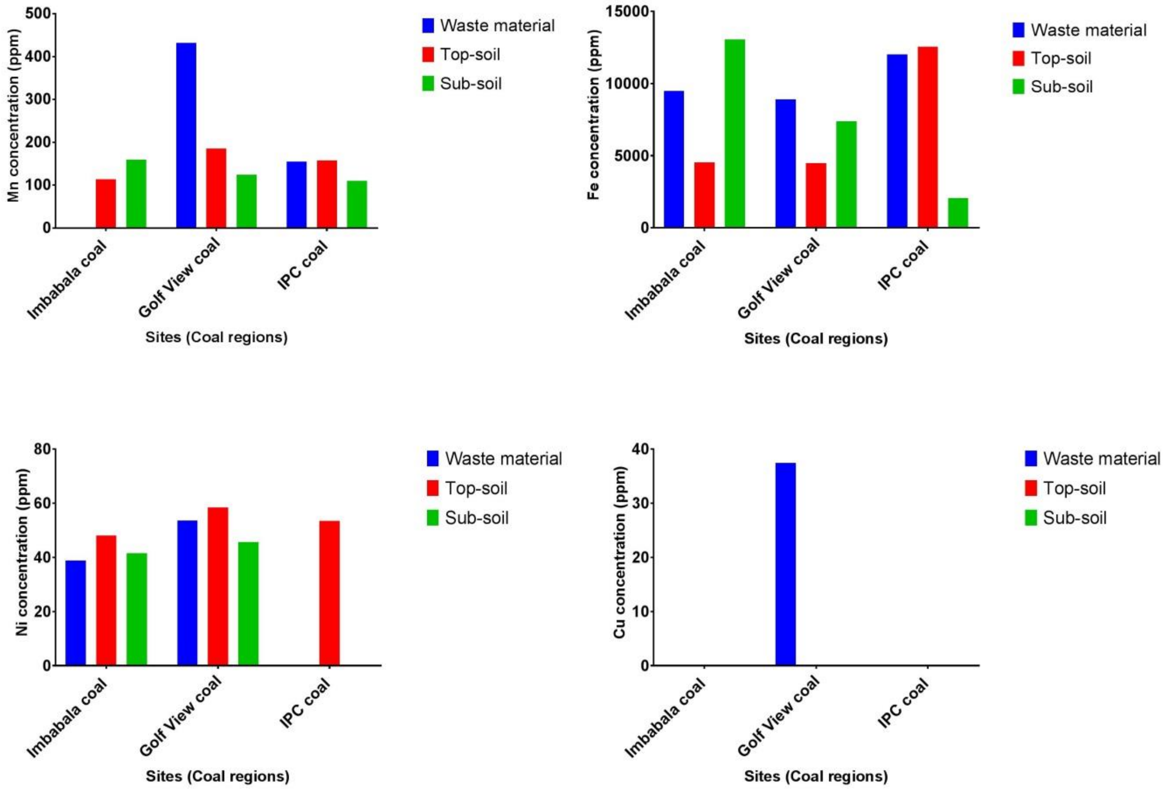

Figure 4.8: The variation of Mn, Fe, Ni and Cu concentrations in coal waste materials, topsoil and sub-soil using Portable XRF.

As can be seen in results illustrated in Figure 4.9, Zn is present in all the investigated sites. Zn is subject to the chemical composition of the parent material. Once formed, advance physicochemical reactions due to weathering, leaching and mining industry affect the background concentration. Zn concentrations differ broadly between soils and this causes complications for the general threshold for different soils (Mertens & Smolders, 2013:468; Smolders *et al.,* 2009:1637).

As was only detected at the Golf View coal. Knowing the geology of the coal deposit and given the information exhibited in this work, As mineralogy is uncommon and is generally bound in coal, in the structure of pyrite. When As is oxidised, it can only be released when coal is burnt (Kolker *et al.,* 2000:173). Pollution from Pb in Golf View coal topsoil was detected. High Pb concentrations found in such a site increase Pb mobility relative to what it found in uncontaminated soils (Steinnes, 2013:3). The proportion of Pb present in coal waste increased significantly at pH values below 5, the latter being the case in this study where Golf View coal has reported low pH values. In a similar study conducted by Kabala & Sigh (2001:489) it was found that Pb in the coal waste materials from a Cu mine increased with increasing metal load and that Pb in contaminated areas was present in exchangeable forms (Jensen *et al.,* 2006:359). The presence of Cd in the topsoil with a concentration of 40 ppm can be referenced to pH, soil conductivity, organic carbon content and calcium carbonate content, because they all exerted a direct influence on the availability of Cd (Murti, 1987:322). Thus, soil retains Cd more tightly than other elements.

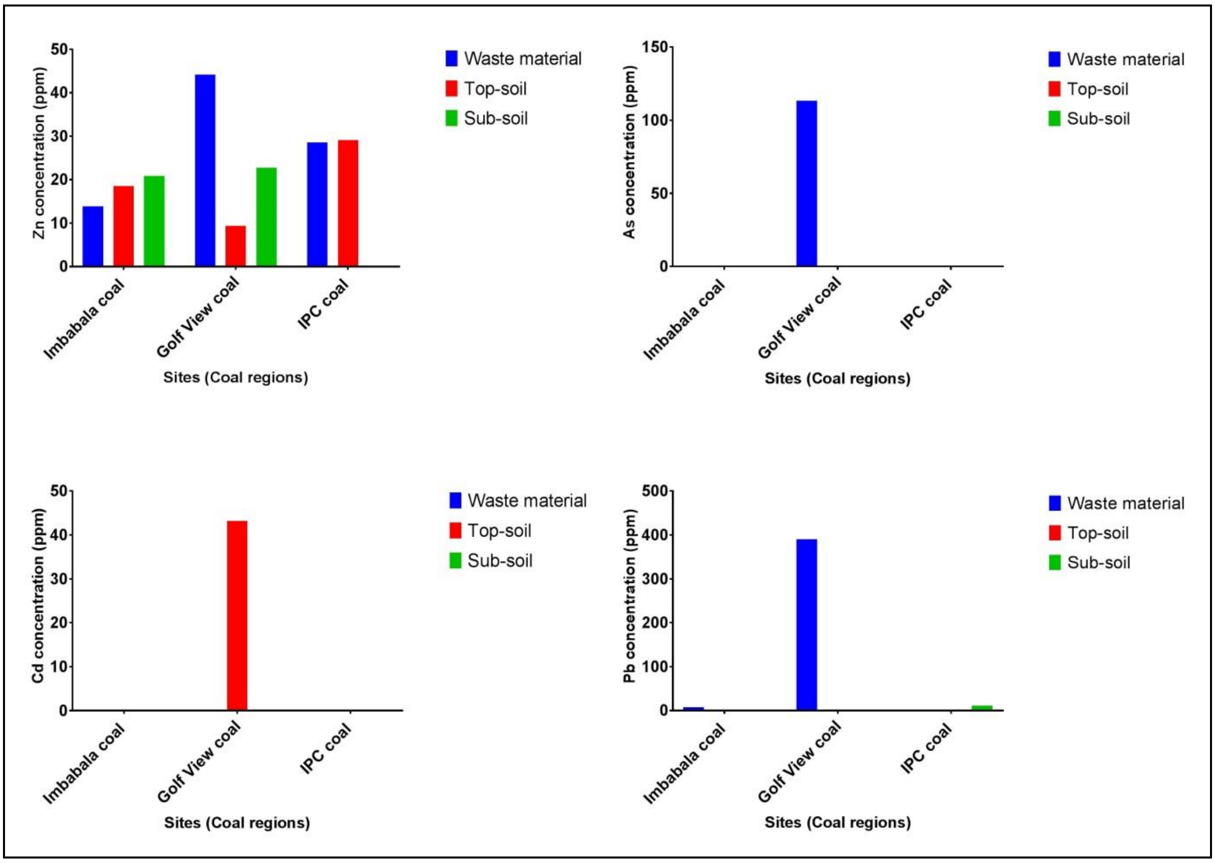

Figure 4.9: Variation of Zn, As, Cd and Pb concentrations in coal waste materials, topsoil and sub-soil using Portable XRF.

U is frequently found in zones underlain with coal waste material containing noteworthy concentrations (Alloway, 2010:12) and this is proved in Figure 4.10. In Figure 4.10 it is shown that the U concentration for Imbabala is 9 ppm and 60 ppm for Golf View coal. The speciation of U in topsoil and sub-soil is highly dependent on the pH and redox status, since U dominates in oxidising environments (Smedley *et al.,* 2006:12).

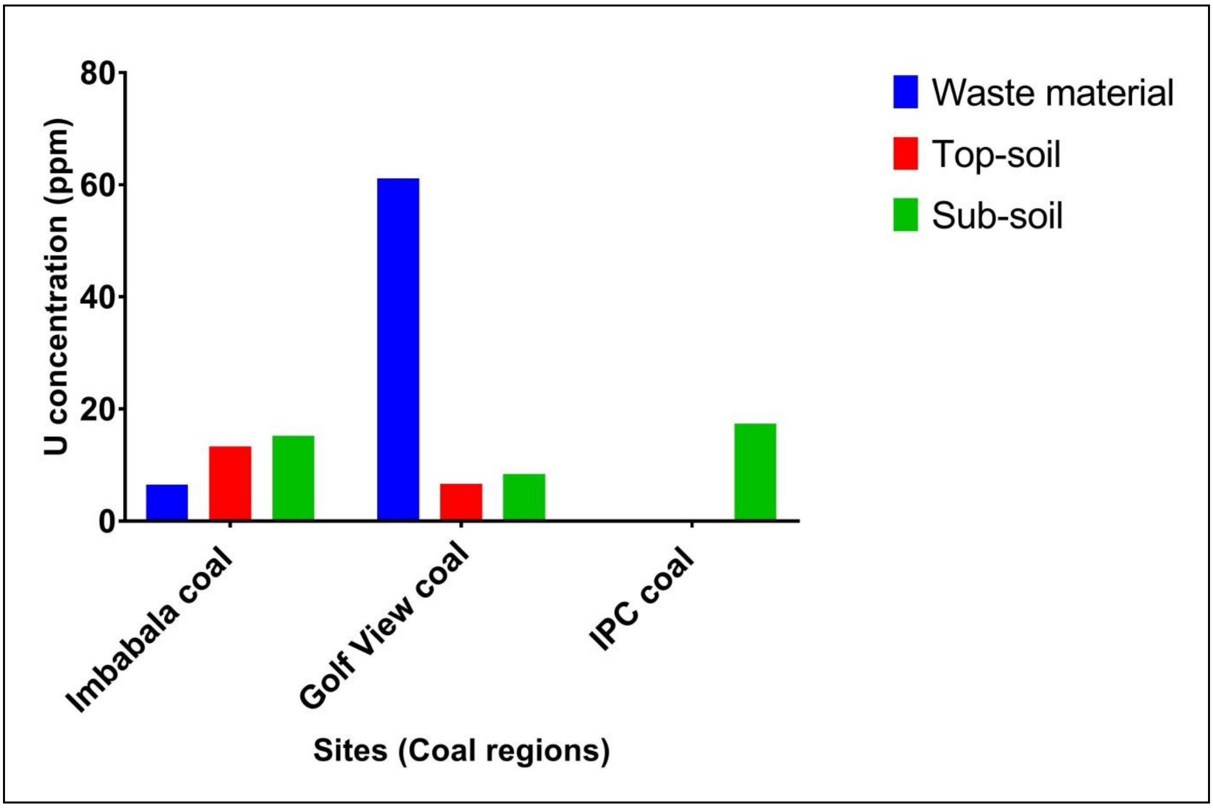

Figure 4.10: Variations of U concentrations using Portable XRF.

### 4.4 Metal trace element release rates

This section presents data from numerous HCT leachates to determine primary elemental release rates that influence metal trace element concentrations in AMD. Measured parameters are documented in ppm. The given values provided consistent representations of the number of metal trace elements released and facilitated the 10-week cycle comparison.

The complete HCT metal trace element release data set is provided in Appendix A. Selected metal trace elements (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and U) from the different gold tailings and coal waste materials HCT leachates are discussed in depth below. In order to determine efficiency of leaching rates for longer term leaching predictions, this Section compares results from week one to week ten in which metal trace elements measured provides a more conclusive indication of long term metal trace elements leaching rates from gold tailings and coal waste materials.

The results shown in Figure 4.11 for Al and Cr with non-treated acid and treated acid. There is no distinctive difference between the two with Al in most of the sites was leached up to the last week except in Louise Moore (LM) where after the third week no further leaching occurred. The time trends of Cr also showed a steady decline up to week nine, and on the 10th week Cr was below the detection limit.

The concentrations of Mn and Fe as indicated in Figure 4.12 are known to be high in South African soils, chemically associated and are usually found in the same geologic environments (Ekosse & Fouche, 2006:31). It was only in five sites where Mn was detected. The release rate for DM during week 1 was the maximum at 200 ppm, while NM-Hutton showed the minimum rate of 30 ppm during week 2. The release of Mn at LM and KL appear to be stabilising after an initial decrease while rates at ICP were below detection limit after week five as shown in Figure 4.12.

No values for sites KL, DM, NM-Hutton, NM-Seepage VC, ICW, and GVC for Fe were detected from week one to week 10 in Figure 4.12. The results of these sites were well below the detection limit. The maximum concentration of 120 ppm appeared for NM-Shale in week two, and the minimum concentration of 0,001 ppm appeared for CM and NM-BR during week one. LM shows the lowest concentration of 0.001 ppm throughout the leaching period, with ICP leaching all the Fe after week four.

Co concentrations in all sites are below 0.5 ppm by week six. A trend can most clearly be seen in ICP, where concentrations increased steadily from week one and then a steep decline from week three to week 10. In general, Co and Ni are released in high concentrations initially, which declined to a more constant rate after week six, except DM that increased at week eight and then returned to a constant concentration.

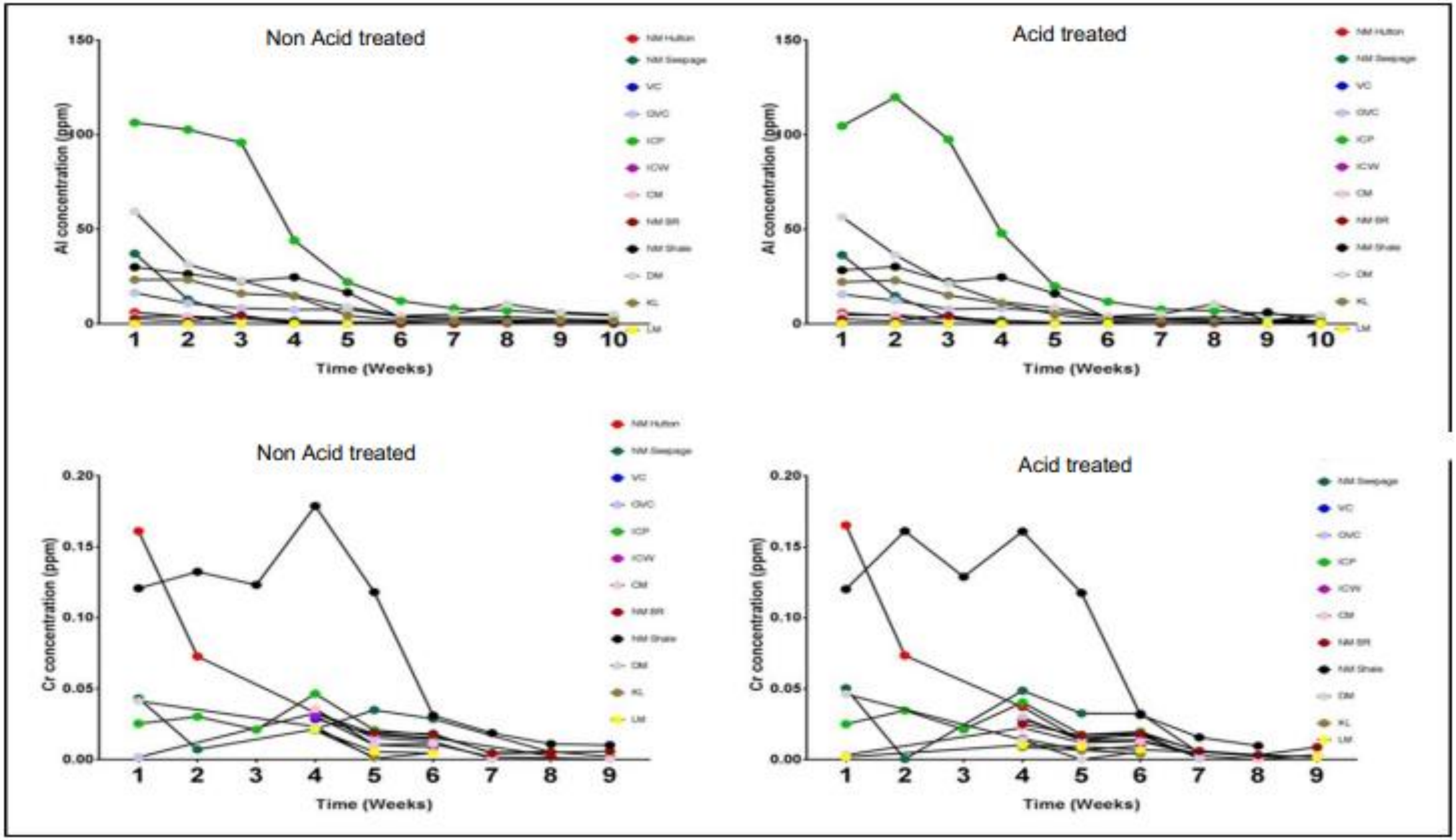

Figure 4.11: Time trends of HCT leachate for Al and Cr (non-acid and acid treated) using ICP-MS.

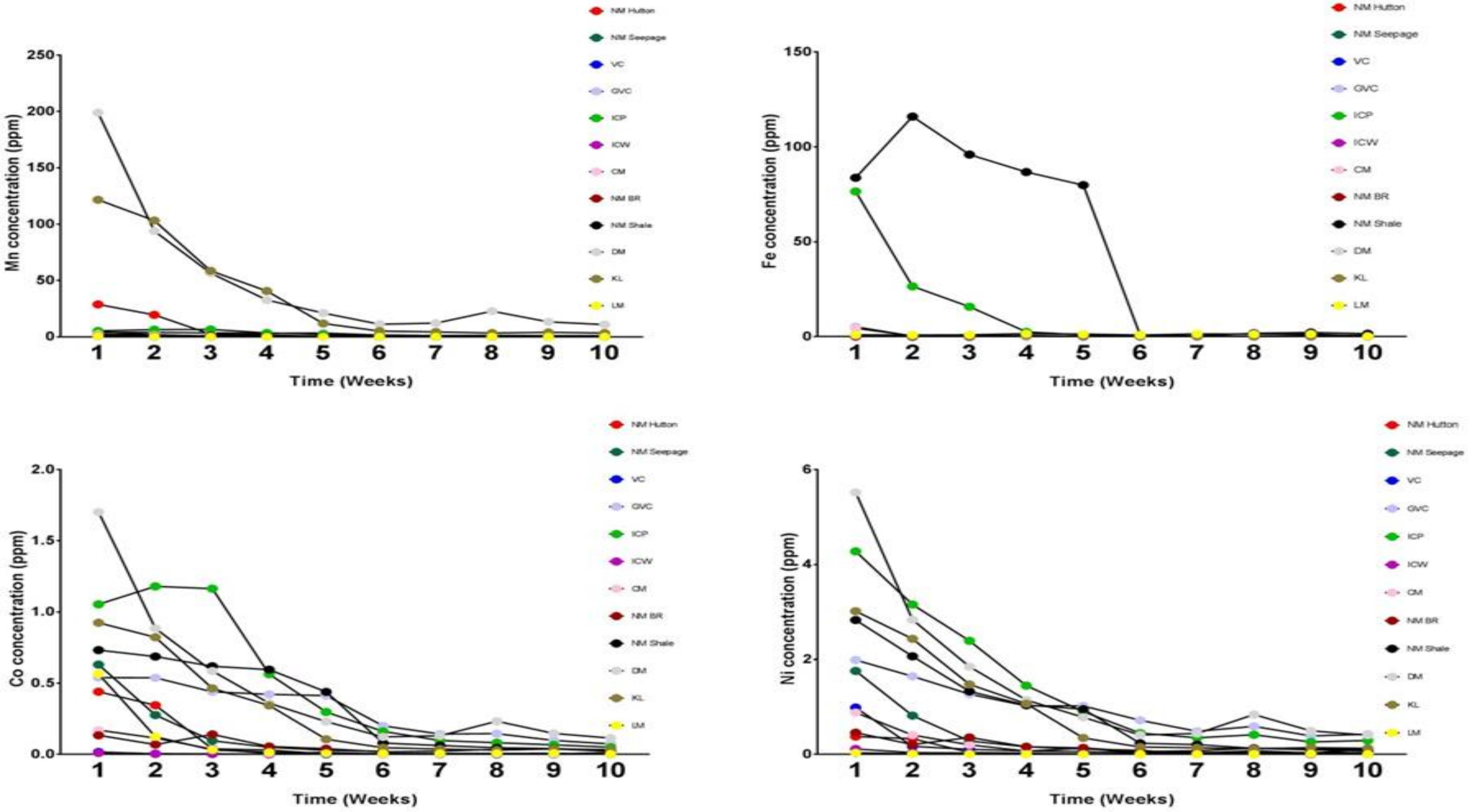

Figure 4.12: Time trends of HCT leachate for Mn, Fe, Co and Ni using ICP-MS.

It can be seen in Figure 4.13 that very high concentrations of Cu are present initially in all the samples. The highest concentration detected was in NM-Shale during week 2 with a concentration of 9 ppm. The minimum concentrations were observed from most of the sites; however, LM consistently showed the lowest leaching rates throughout the experiment.

Zn has showed highest concentrations. It can be seen in Figure 4.13 in almost all sites, except for LM, ICW and NM-BR, which are below 4 ppm. The highest concentration of 36 ppm was found in NM shale during week one and it leached out until week 10. ICP-MS analyses showed a steady drop during week two until all Zn was leached out after week four.

As concentrations are below 0.1 ppm. As concentrations range from a maximum of 0.8 ppm, seen in KL in week one, to a minimum of 0.001 ppm, for ICP-MS analyses during week three. For all the sites represented in the graph represented in Figure 4.13, concentrations appear to be decreasing over time, as detected concentrations are only in few selected sites.

Detected concentrations of Cd ranged from 0.0011 ppm in LM and CM in week 1 to 0.13 ppm in DM of week one. From week nine to week 10, only Cd concentrations from DM, KL and NM-BR could be detected. Furthermore, values detected in week one just below 0.05 ppm concentrations returned to lower or no value after week seven. Detected values appear to be sporadic and no clear trend could be identified.

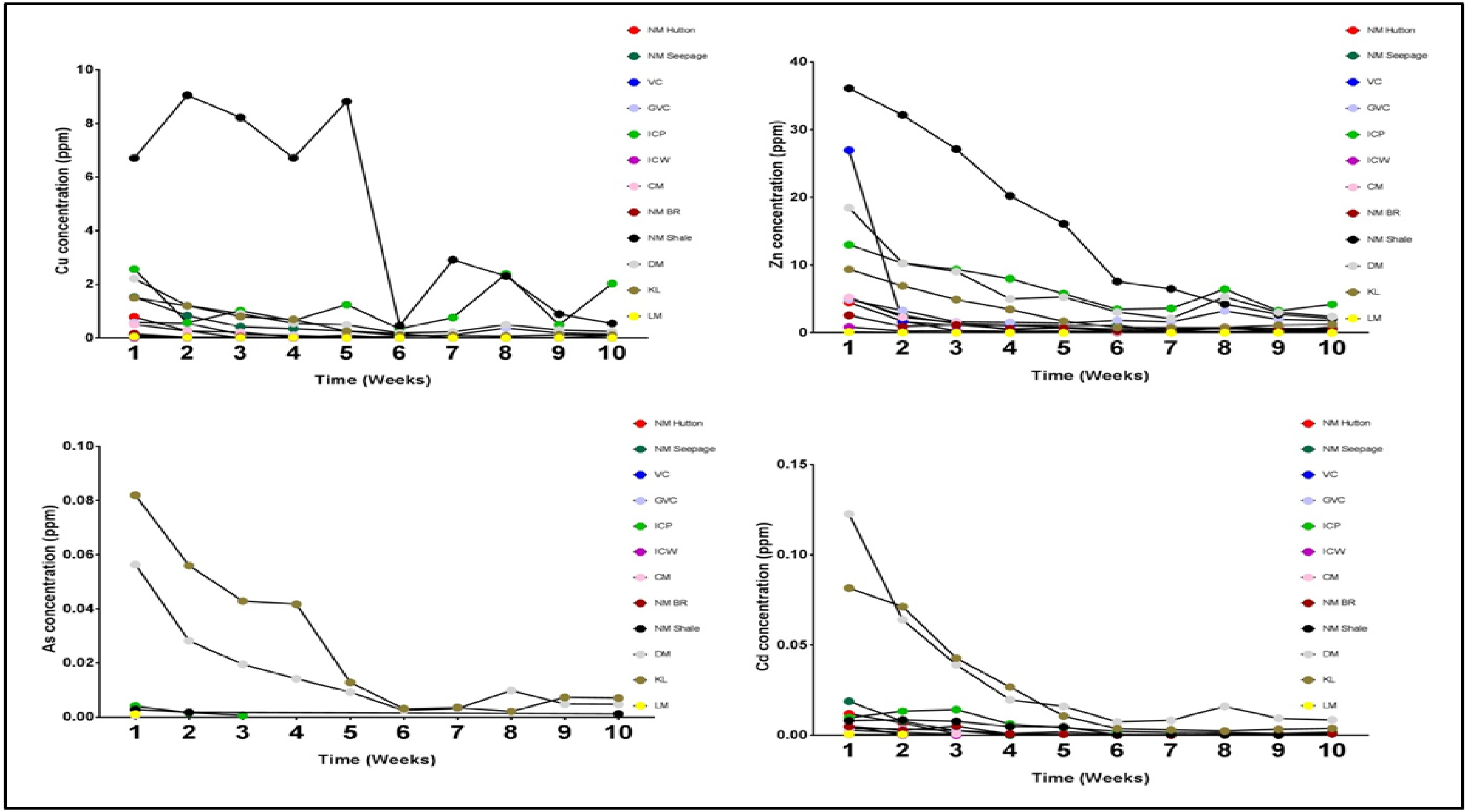

Figure 4.13: Time trends of HCT leachate for Cu, Zn, As and Cd using ICP-MS.

Figure 4.14 shows Pb concentrations increase in ICP, GVC, KL, CM, NM-Shale and DM. The increase can be clarified by oxidation of sulphides that generates acid as well as metal trace elements (Holmström *et al.,* 1999:267). The concentration of Pb increased with time in the leachates in most sites, but the concentration of U decreases with time also for most sites.

This can be clarified by the way that these metal trace elements occurs in an effortlessly mobilised form (Kooner, 1993:243). U was detected in only six sites as shown in Figure 4.14, with DM having the highest concentration in the week one with 5 ppm followed by KL. This shows that gold tailings and coal waste materials still liberated significant quantities of U despite the deactivation Dominion Reef mine. Campos *et al.* (2010:858) observed high concentrations of U in waters drained from gold tailings, from a pit mine and in the interface between the mine and the surrounding environment.

In general, the concentrations appeared to be decreasing; however, U was only detected in a different time variation, at sites NM-Hutton and NM-Seepage appeared in week one and in NM-Shale during week five. U Concentration in LM during week five was below the detection limit. No trend is apparent in these samples; however, ICW maintained a constant concentration from week six to week 10.

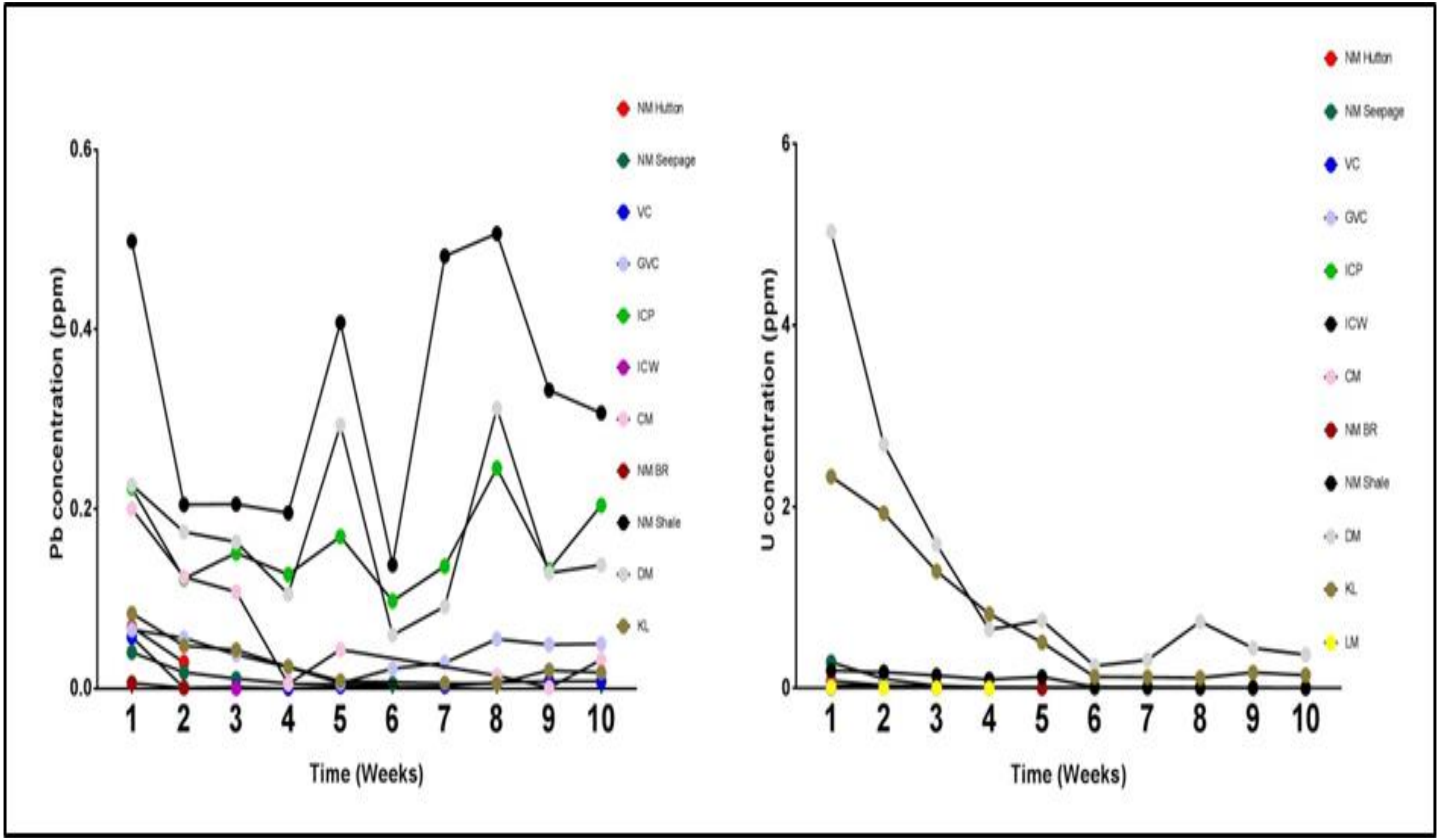

Figure 4.14: Time trends of HCT leachate for Pb and U using ICP-MS.

## 4.5 Total metal trace elements in the top soil and sub-soil.

The total metal trace elements pollution has been reported from areas surrounding mines across many countries with elevated levels of toxicity discharged from gold tailings and coal waste materials to cause adverse environmental effects; they are leached into the nearby topsoil and sub-soil (Kabala & Singh, 2001:488; McMartin *et al.,* 2002:59; Rawlins *et al.,* 2006:417; Sichorova *et al.,* 2004:525; Susaya *et al.,* 2010:427). Metal trace elements (Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb and U) stood out as the most common analyses throughout this project. The main concern is the threat that AMD postures to the environment which is closely identified to the unnaturally low pH of the leachate as explained in Section 4.2.1 and the metal trace elements released into the topsoil and sub-soil as discussed below in this Section.

The concentrations of metal trace elements in soil samples from different sites are presented by graphs in Figure 4.15. Al exhibited the highest concentration for all the sites in both in topsoil and sub-soil. The concentration for Al ranged between 18 ppm – 79 ppm. The highest concentration for Al was recorded at LM from the topsoil with the lowest concentration in the sub-soil for IPC. The mobilisation of Al ions, resulting from changes in pH of the gold tailings and coal waste materials has adverse effect on the soil quality. Whenever the Al stayed in the solution or was leached in the aquatic system, it would be hazardous to the ecosystem (Zhang *et al.,* 2013:2938). All the sites have an increase in Al concentration in the topsoil rather than in the sub-soil except for GVC and KL. The leaching of Al in sub-soil may be attributed to the decomposition of alumina silicate under low pH conditions (Kauppi *et al.,* 1986:239).

Elevated levels of Cr were recorded from all the sites having reported values of lower than 0.3 ppm. In the NM and CM the Cr concentrations in topsoil were greater than in sub-soil; however the Cr concentration in the abovementioned sites were not significantly different from those of sub-soil of 0.3 ppm. There is a difference in Cr concentrations in topsoil at 0.4 ppm and sub-soil at 2.4 ppm for KL. These suggest that anthropogenic activities might be the major factor in areas of higher Cr concentrations (Wu *et al.,* 2010:1244).

Mn concentrations in the sub-soil of NM were higher than the topsoil 30 ppm and 15 ppm respectively. This is as a result of Mn being leached and carried downwards as water washed through the tailings. Although the metal trace elements can become mobile in neutral pH conditions, in this case leaching is particularly accelerated in low pH conditions, which created a high concentration of Mn in sub-soil (Abdul-Wahab & Marikar, 2012:309). It is generally known that Fe is the major component of most soils (Oti *et al.,* 2012:184); this is also evident from Figure 4.15. The variation in the trends for Fe concentration in topsoil and sub-soil can be explained in terms of the gold tailings and coal waste material pH taken from the HCT leachates, given the fact that South African soils are known to have elevated concentrations of Fe (Onianwa, 2001:578). NM and LM reported higher values at 150 ppm in topsoil. Nganje *et al*. (2014:125) explained the variations in levels of concentration in topsoil and sub-soil around coal and sites as partly due to climatic conditions.

Figure 4.16 shows the contamination of topsoil and sub-soil by metal trace elements leached from gold tailings. Co shows the highest values at NM of 0.19 ppm for topsoil. For the sub-soil the highest value was recorded at KL at 0.17 ppm. The concentrations of Ni were less than 1 ppm, except for LM and KL where values were 1.5 ppm for topsoil and 1.1.ppm for sub-soil. Cu recorded lowest concentrations in all coal sites for topsoil and sub-soil with about 0.03 ppm being the lowest and 0.08 ppm being the highest value at GVC, ICW and IPC. The gold sites were just below 0.3 ppm in NM and 0.22 ppm in KL both for sub-soil. Cu is easily adsorbed and precipitated in sediments at alkaline pH levels (Dallas & Day, 1993).

The sudden decrease of pH levels in the gold tailings and coal waste material plays a direct role in soil acidity, which then influences the availability of Zn more than any other factor (Davies, 1997:79). The lowest concentration of Zn recorded was 0.04 ppm at CM for topsoil which is slightly the same to GVC value. The highest recorded concentration was at NM for sub-soil at just below 0.4 ppm, which is not surprising as Zn is the 23rd most abundant element on Earth and an essential micro nutrient (Butu & Iguisi, 2012:886).

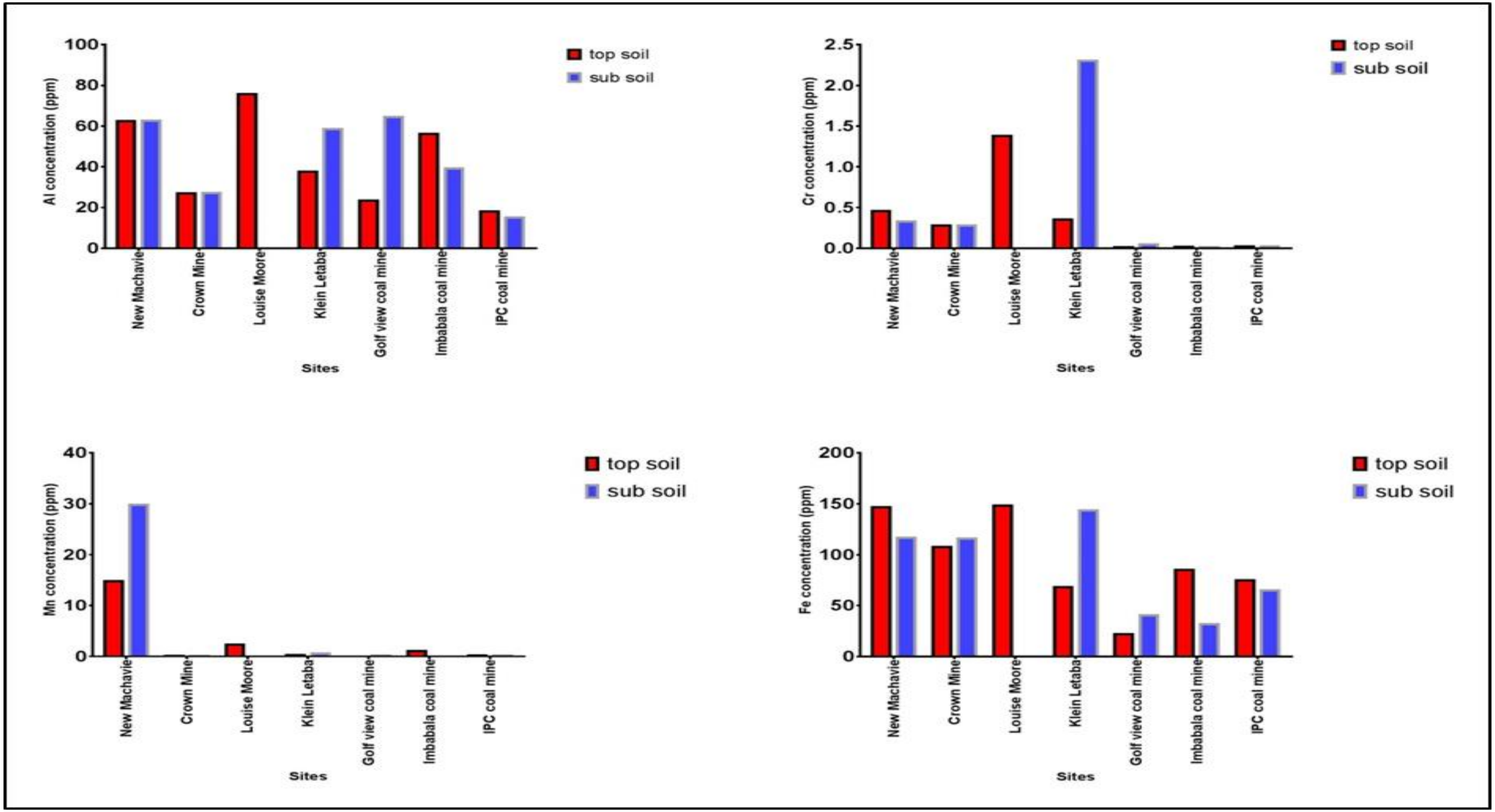

Figure 4.15: Concentrations of Al, Cr, Mn and Fe in topsoil and sub-soil using ICP-MS.

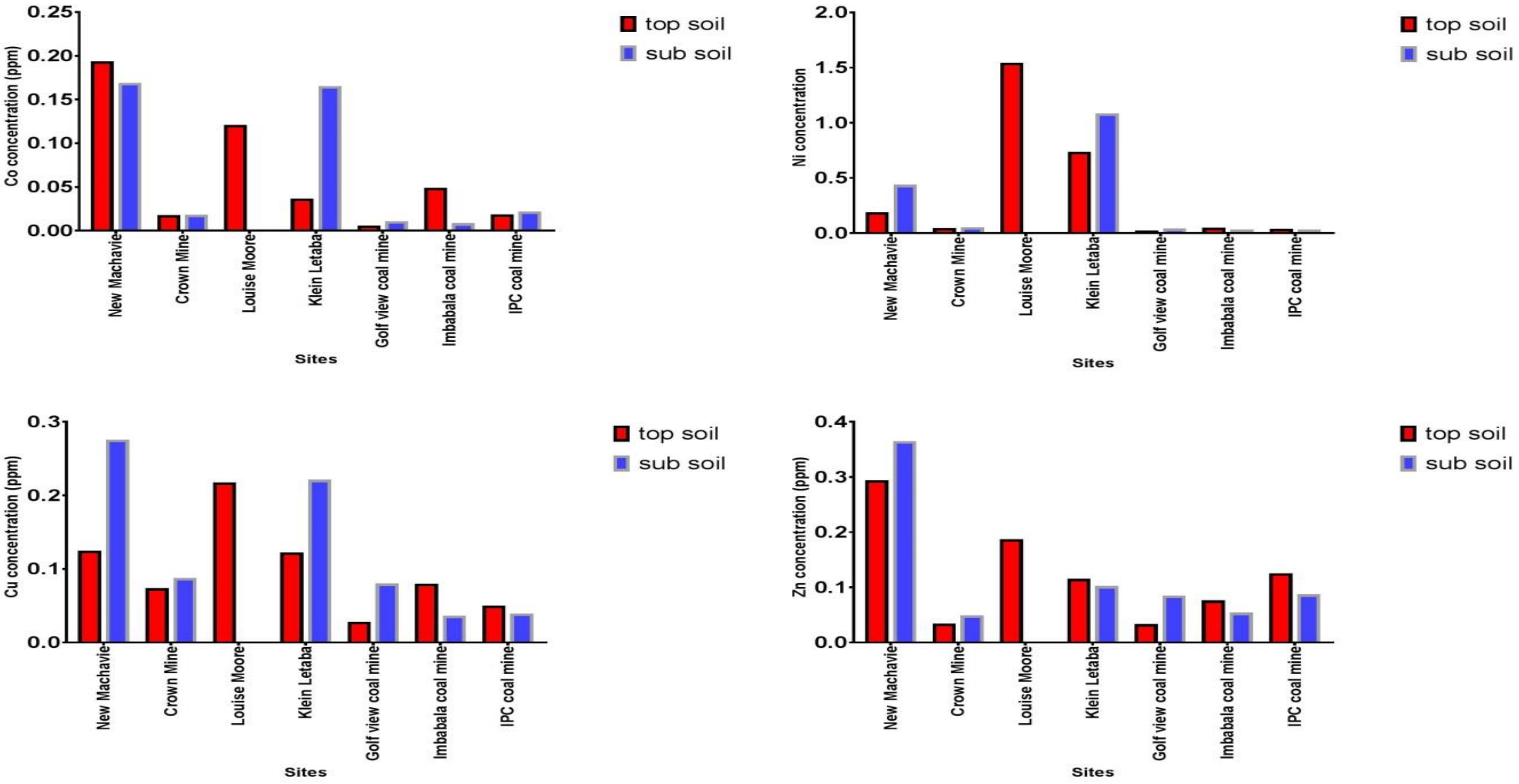

Figure 4.16: Concentrations of Co, Ni, Cu and Zn in topsoil and sub-soil using ICP-MS.

Arsenic concentration in KL reported values of 1 ppm for topsoil and 6ppm for sub-soil. The higher As value in sub-soil supports the idea reported by Ko *et al.* (2003:72) of high amounts of reduced compounds and progressive oxidation. In the rest of the sites As was below the detection limit; significant amounts could have been released to the groundwater through leaching and mobility.

Apart from the soil samples collected from other sites discussed in previous Sections, Cd was only detected in four sites, which are listed on the graph below, Figure 4.17. Cd had the lowest concentration values recorded for both topsoil and sub-soil below 0.0015 ppm. The concentration of Cd in soils decreased with distance from the gold tailings and variation in geological structure (Sanchez *et al.,* 1999:1385).

Pb studied in the topsoil and sub-soil indicated a broad range of concentrations with the highest recorded at ICW at 0.07 ppm in top soil and NM at 0.07 in sub-soil. Pb's relative abundance in topsoil and sub-soil with respect to contamination from the gold tailings and coal waste materials may be somewhat reliant on potential intrusions of the metal trace elements into the soils and their rate of mobility in the topsoil and sub-soil from the gold tailings and coal waste materials (Agyei *et al.,* 2009:357).

The results obtained of U in topsoil and sub-soil revealed astonishing concentrations with sub-soil values higher at 0.25 ppm and topsoil at 0.04 ppm, with CM having a very low concentration together with GVC, ICW and IPC. The two Limpopo sites (LM and KL) were below the detection limit. The mobility of U in soils depends largely on many properties of the soils, which in this case is the oxidation-reduction potential and the amount of water available (Allard *et al.,* 1983:2; Bibler & Marson, 1992:34).

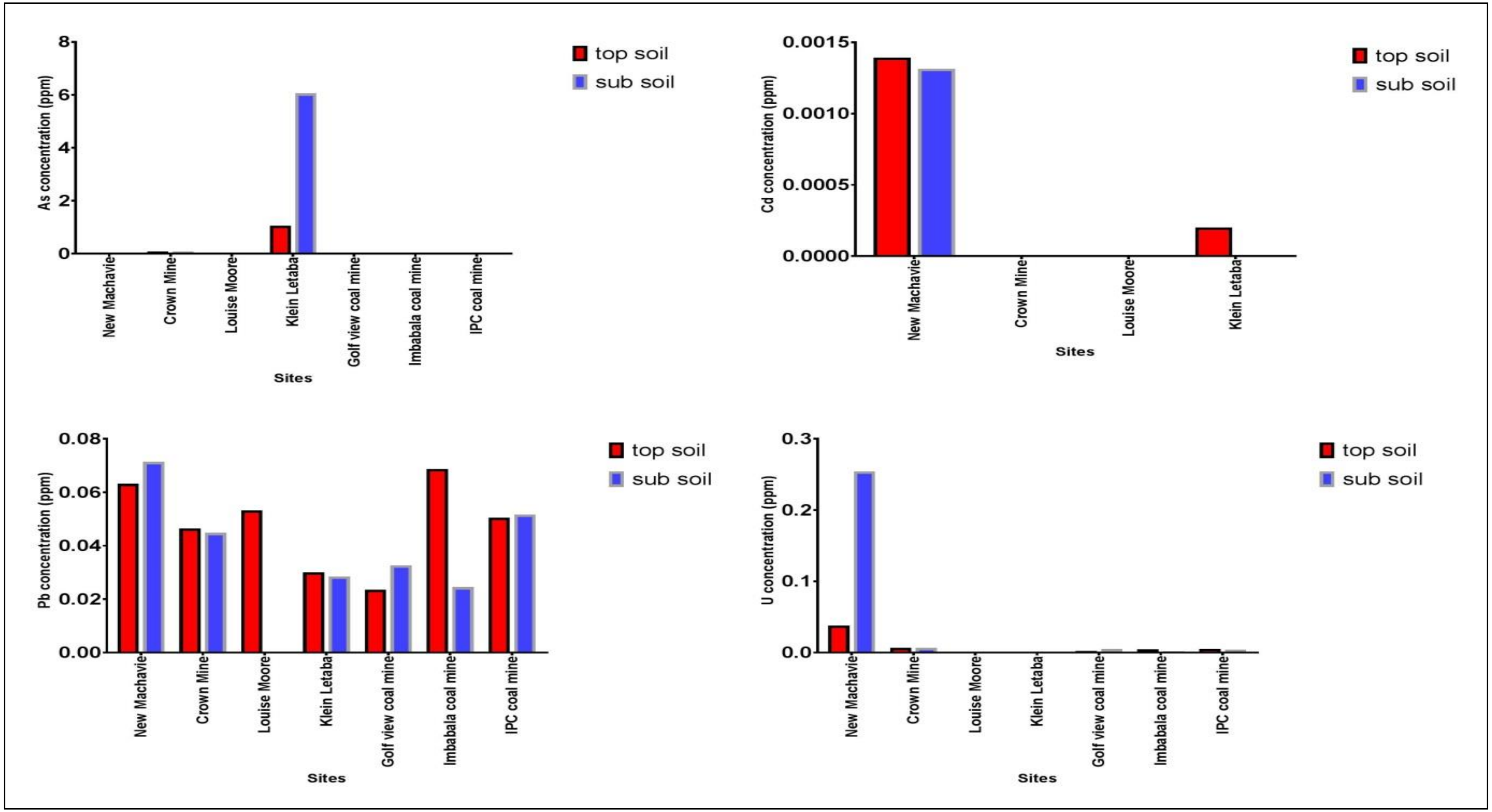

Figure 4.17: Concentrations of As, Cd, Pb and U in topsoil and sub-soil using ICP-MS.

## 4.6 Geological presence and occurrence of metal trace elements

Total metal trace elements concentration was determined and the analysis of geochemical characteristics of different gold tailings and coal waste materials are represented graphically below (Figures 4.18 – 4.20). These samples are the same as those from the HCT, however, this Section is not discussing water analysis but rather results of the solid samples prior leaching.

Figure 4.18 shows the concentrations of metal trace elements of samples with the exception of NM-Seepage and NM-Hutton. The results of gold tailings and coal waste materials concentration are shown in Figures 4.18 – 4.20. The values differed relying upon the geology of each mine. The degree and level of metal trace elements contamination got from the mining activities may differ contingent on the sort of mineralisation, composition of ore minerals, and geology technique of mining and so forth (Lee *et al*., 2001:1377; Jung & Thornton, 1996:53). Jung (2001:1369) revealed that gold tailings from less sulphide mineralisation contained moderately low levels of Cd, Cu, Pb and Zn while gold tailings with high extents of sulphide contained elevated levels of those metal trace elements. This is because of the weathering processes of metal-rich gold tailings and coal waste materials (Jung, 2008:211).

The bioavailability of Cd depends on the concentration, environmental factors, time and speciation (Vig *et al.,* 2003:1). It occurs in gold bearing ore bodies as isometric trace element (Fashola *et al.,* 2016:1051). This is evident as shown in Figure 4.20 where Cd is present mostly gold tailings such as DM, NM-BR and NM-Shale.

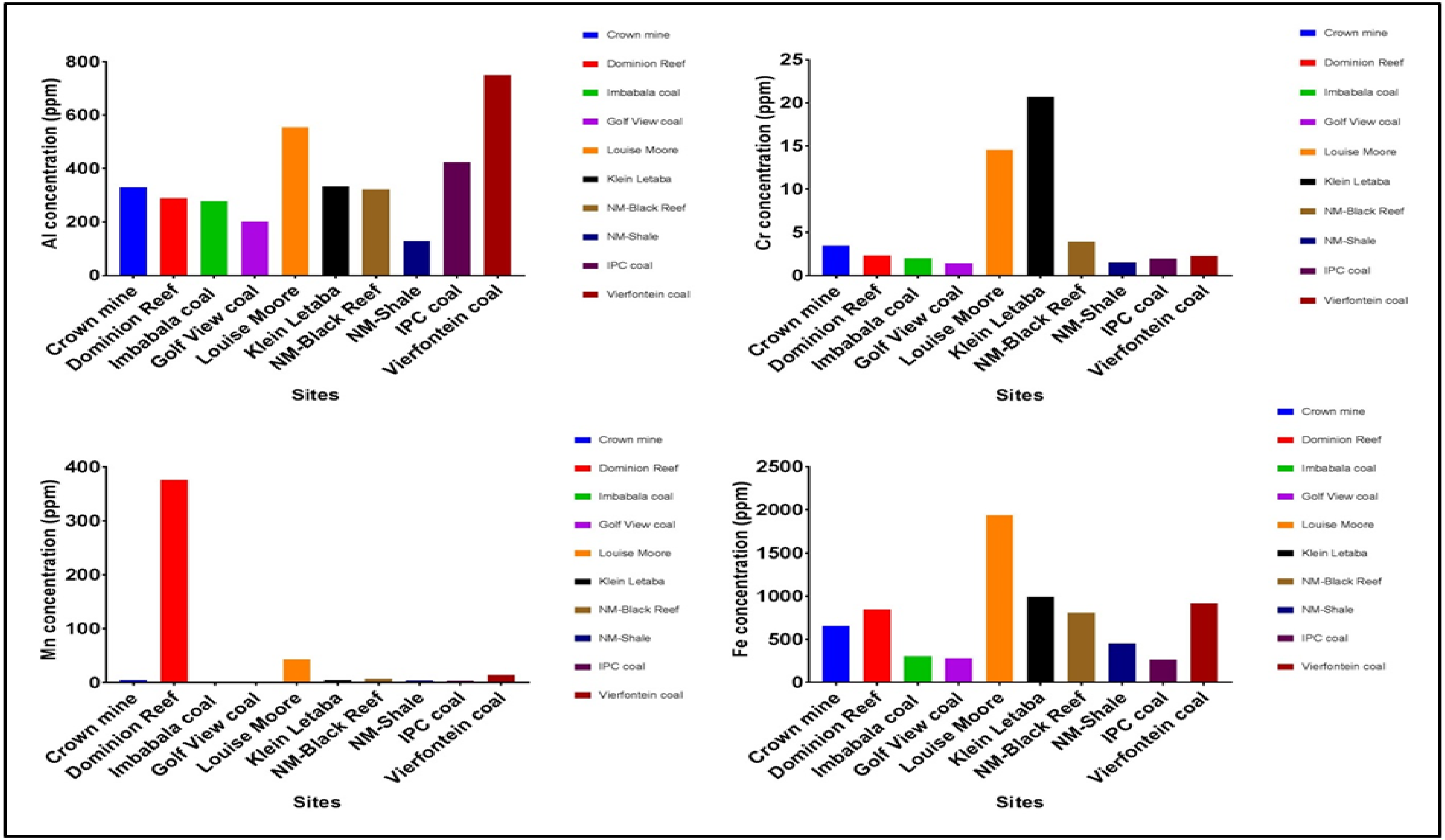

Figure 4.18: Geochemical analysis of EPA method used before leaching for total acid digestion and chemical wet analyses on solid samples for Al, Cr Mn and Fe.

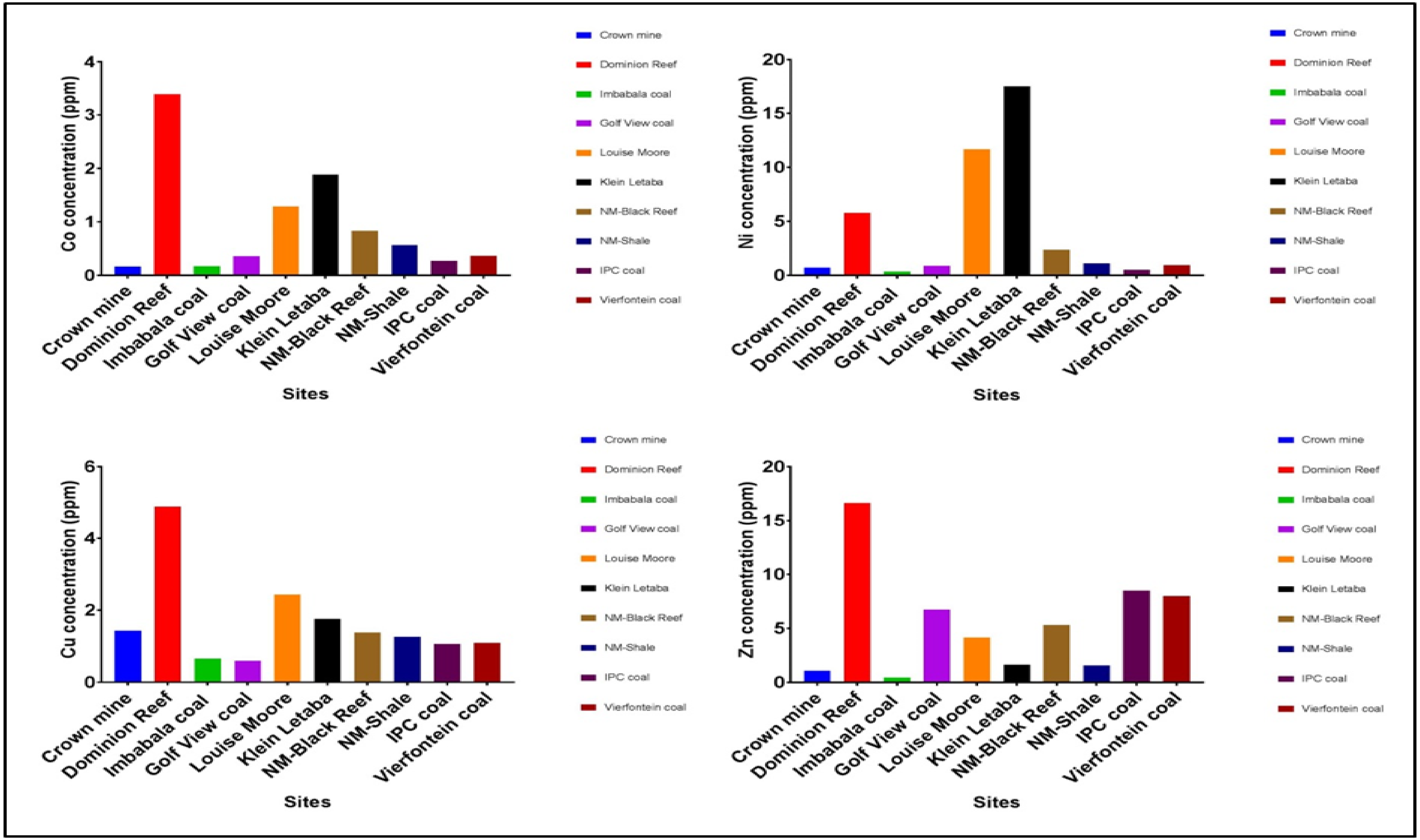

Figure 4.19: Geochemical analysis of EPA method used before leaching for total acid digestion and chemical wet analyses on solid samples for Co, Ni, Cu and Zn.

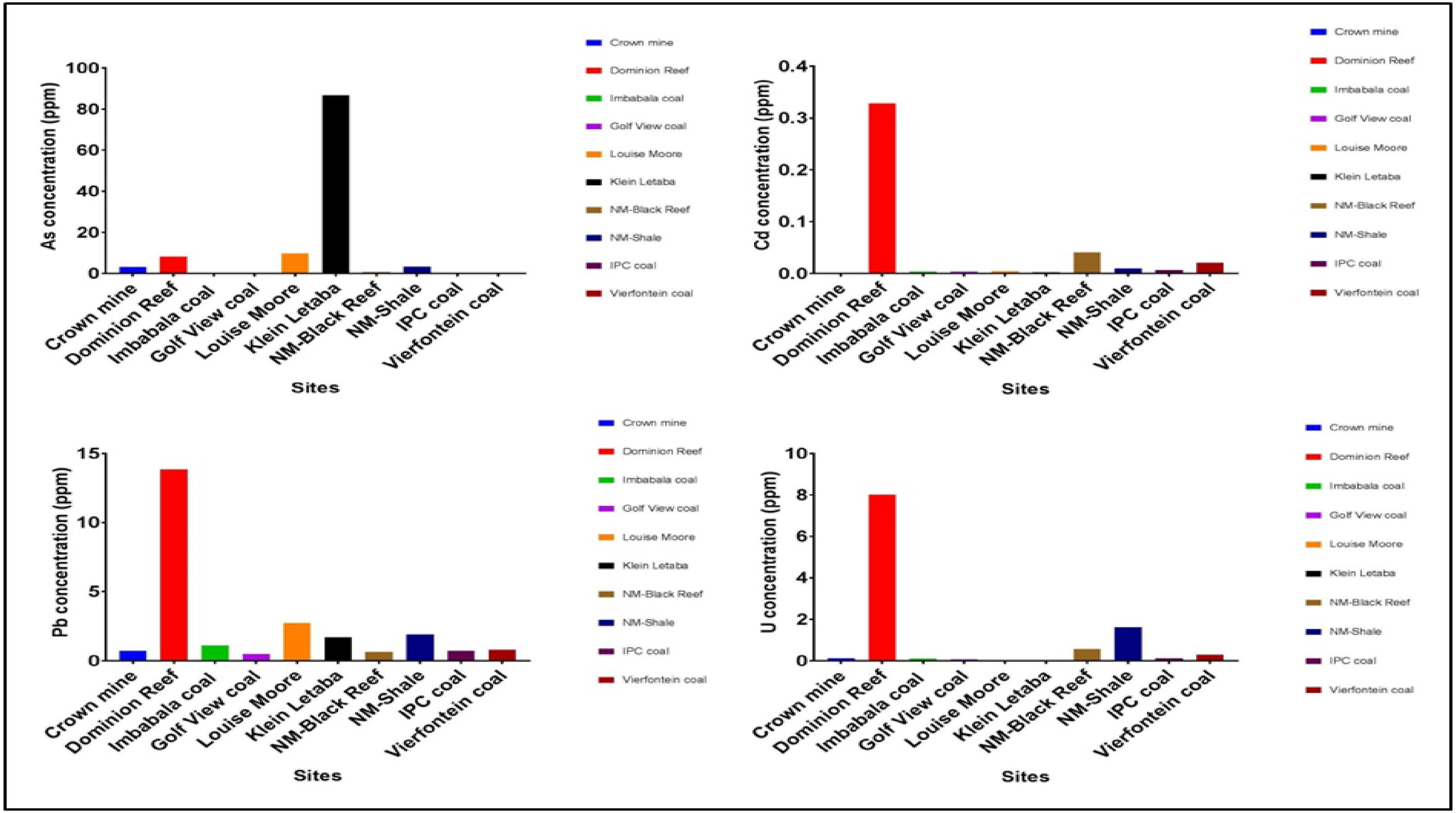

Figure 4.20: Geochemical analysis of EPA method used before leaching for total acid digestion and chemical wet analyses on solid samples for As, Cd Pb and U.

### 4.7 Conclusions pertaining to the metal trace elements

Although the test samples and conditions, under which they were subjected, do not truly represent the conditions found at the gold tailings and coal waste material sites. The results from these experiments help to increase the understanding of environmental contamination from metal trace elements. The examination completed in this investigation has uncovered that the gold tailings and coal waste materials through AMD can possibly create acidity and discharge pollutants, for example, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb and U into the solution. The toxicity development from AMD will happen ceaselessly and the contamination leaches to the topsoil and sub-soil. It can be seen that metal trace elements of concern are leached from gold tailings and coal waste materials at significant concentrations.

# CHAPTER 5: Conclusions

A field study to understand the effectiveness of geological related AMD of gold tailings and coal waste materials was conducted. For this purpose, approximately 41 sites characterized by low pH values and potential elevated concentration of metal trace elements (MTE) were visited to do proper site selection and to focus on those with distinct signs of pollution to the environment. Sampling and subsequent geochemical and physical analyses were done on 10 selected sites. Data was collected by sampling gold tailings, coal waste materials, topsoil and sub-soil from gold and coal mines. To assess the extent of the increase in MTE and to indicate the relation of geological presence of AMD several experiments were performed in the laboratory

The MTE in gold tailings and coal waste materials were measured and the results of the selected sites were compared. In this research, it is demonstrated that mining activities influence the geological presence of AMD in tailings, waste materials and soils. This influence can be of more substantial or minor depending on the type of mine, the mining methods employed and the way mine contains its tailings and waste materials. Findings show that mining activities do influence geochemistry of AMD in gold and coal. These research findings show that investigated research areas are contaminated. However, this study only concentrated on the input of MTE concentration of gold tailings, coal waste materials, topsoil and sub-soil.

This chapter presents the conclusions that can be drawn from this study.

The objectives set at the beginning of the study were met, i.e.

(i) ) Identify the geological related presence and/or occurrence of AMD.

(ii) Explore the nature and composition of gold tailings and coal waste materials potential for AMD across the Giyani Greenstone Belt, Dominion Group. Transvaal Supergroup, Witwatersrand Supergroup, and Karoo Supergroup.

(iii) Establish the leaching of MTE from gold tailings and coal waste materials to the topsoil and sub-soil.

## 5.1 Conclusions

The study found that the geochemical characteristics and metal trace elements concentrations correspond to AMD characterization. Metal trace elements found in HCT samples were high in the investigated zones. The transfer of metal trace elements from gold tailings and coal waste materials to the topsoil and sub-soil are strongly influenced by low pH levels of less than 4.5. However, soils adsorb these metal trace elements at different rate in different sites, most probably due to the clay content and cation exchange capacity of the specific soil. Gold tailings and coal waste material of these abandoned mines still contains sulphide minerals but also sulphate salts, in both cases it has the potential to form AMD. The results of this study proved that AMD is concentrated with different types of metal trace elements including Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb and U. These resulted in pollution to the environment through radioactive and metal trace element contamination.

The differences in the trends observed by the patterns depicted in the pH, EC and ORP results (Figures 4.3 – 4.5) and for the XRF, HCT and EPA method for sample results (Figures 4.6 – 4.20). The different pattern and trends observed support the hypotheses of variation in sulphide mineralisation in different lithological units; metal trace elements vary from site to site. The concentration of U, Zn, Pb and As in the studied gold tailings and coal waste materials were in the ranges of 150 ppm, 400 ppm, 580 ppm and 200 ppm.

The geological presence of AMD and mine pollution was identified in Crown Mine, Golf View Coal, New Machavie Black Reef, New-Machavie Shale, Imbabala Coal and IPC Coal. The pH of the oxidised AMD showed a distinctive pH values of 2.5 to 4.0 from week one until week 10 of the HCT experiment. AMD by its very nature and composition revealed that both gold tailings and coal waste materials has the potential to generate acidity and discharges metal trace elements into the topsoil and sub-soil, for examples, Ni 40 ppm concentration for coal waste material in Imbabala Coal and the top soil and sub-soil have 50 ppm and 45 ppm whereas in Gold tailings at Dominion Reef showed 110 ppm, 95 ppm and 120 ppm, respectively. This proved that AMD formation will vary from site to site alongside its nature and composition across the study sites. It also reveals that leaching of MTE to the top soil and subsoil is present because in both cases the concentration is lower in the source than in the pathway and receptor.

Results reveal that MTE migrate from gold tailings and coal waste materials to the topsoil and sub-soil as a function of solubility of MTE, pH and ORP. Leaching of the MTE has occurred as the experiments revealed, for example Figure 4.11, concentration of 110 ppm for Al at week one until all vanished in week nine, it was below detection limit on both acid treated and non-acid treated. These attest to the fact that the transfer of metal trace elements from tailings to the sub-soil occurred. The ORP of the leach material underneath the tailings as discussed in Figure 4.5 from the HCT assessment revealed DM, CM, NM-Shale, ICP and GVC tailings with values of above 200 mV from week one to week 10 will influence AMD formation and chemistry for the years to come.

# CHAPTER 6: Recommendations

Recommendations for future studies on the study sites are listed. Future studies should endeavor to guarantee a superior examination on the oxidation rate of pyrite on the gold tailings and coal waste materials influencing the soil quality, rehabilitation standards and mine closure; changes and alterations of the inspecting procedure, experimental configuration, modeling and statistical analyses are required of top soil and sub-soil after microwave digestion.

## 6.1 Key lessons from this study and recommendations for future studies are:

- From the learning assembled amid the successful completion of this study, future work should concentrate on setting up oxidation rates of pyrite in the gold tailings and coal waste materials affecting the soil quality
- Further research should be carried out to ascertain the transfer factor of metal trace elements from the tailings, soils and then groundwater.
- The period of Humidity Cell Testing should also be increased to a maximum of 20 weeks; this will enable exploration of metal trace elements which start to break down after 10 weeks. This should be done to determine the solubility of MTE over a long period of time.
- Set out rehabilitation experiments where species can tolerate such soil contamination from all the different lithological units.
- Some materials need to experience complex mineralogical changes amid the broadened period of leaching.

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# Appendix A: EPA method of analyses used

**PIET VAN DEVENTER - ANDANI**

**EPA METHOD USED - RESULTS ARE *mg/kg***

**14/6/2017**

| Sample: | CROWN MINE | Dr TTS 1 A32 | ERMELO (1CW) | ERMELO (GVC) | LOUISE MOORE | KLEIN LETABA | NM-Br | NM-Shale | IPZ (IPC) | VIERFONTEIN FS |
|---|---|---|---|---|---|---|---|---|---|---|
| | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* |
| **Be 9** | 0.1732 | 0.8873 | 0.9989 | 2.29 | 0.4949 | 0.06387 | 0.3098 | 0.1214 | 0.9764 | 2.513 |
| **B 11** | ND | 1.4 | 13.52 | 219.2 | 7.558 | ND | 3.12 | 2.314 | 219.2 | 218.3 |
| **Na 23** | 114 | 92.11 | 156.6 | 1976 | 722.2 | 292.5 | 50.74 | 180.1 | 2266 | 2250 |
| **Mg 24** | 2562 | 1358 | 300.6 | 920.8 | >15500 | 15350 | 4502 | 410 | 704.6 | 732.8 |
| **Al 27** | 8240 | 7229 | 6966 | 5048 | 13880 | 8338 | 8071 | 3231 | 10560 | 18740 |
| **P 31** | 84.66 | 283 | 84.22 | 45.19 | 140.6 | 144.2 | 143.4 | 72.37 | 496.3 | 115.3 |
| **K 39** | 484.1 | 1650 | 785.9 | 1055 | 5725 | 2774 | 1746 | 1387 | 1831 | 710 |
| **Ca 43** | 432.6 | 33600 | 3717 | 4563 | 41580 | 7109 | 340.2 | 2485 | 2836 | 20080 |
| **Ti 47** | 58.24 | 431 | 296.8 | 266.1 | 879.6 | 468.4 | 41.32 | 41.9 | 268 | 1375 |
| **V 51** | 11.28 | 11.37 | 23.26 | 15.31 | 77.3 | 35.1 | 16.67 | 7.218 | 33.22 | 30.64 |
| **Cr 53** | 87.06 | 58.58 | 48.46 | 35.26 | 364.3 | 517.3 | 97.95 | 38.79 | 47.34 | 57.09 |
| **Mn 55** | 126.4 | 9385 | 10.54 | 35.21 | 1082 | 120.9 | 190.5 | 96.06 | 78.14 | 359.1 |
| **Fe 57** | 16380 | 21260 | 7549 | 7014 | 48470 | 24870 | 20170 | 11380 | 6600 | 23020 |
| **Co 59** | 4.156 | 84.82 | 4.313 | 9.008 | 32.14 | 47.04 | 20.87 | 14.23 | 6.802 | 9.168 |
| **Ni 60** | 18.29 | 144.6 | 8.796 | 21.77 | 292.4 | 438.9 | 59.61 | 28.02 | 12.87 | 23.53 |
| **Cu 63** | 35.71 | 122.3 | 16.56 | 15.03 | 60.97 | 43.98 | 34.59 | 31.68 | 26.74 | 27.36 |
| **Zn 66** | 27.06 | 415.9 | 11.58 | 168.5 | 104.1 | 41.19 | 132.9 | 39.58 | 212.6 | 200.4 |
| **As 75** | 77.95 | 205.5 | 3.564 | 5.2 | 243.4 | 2171 | 14.23 | 84.22 | 5.085 | 6.355 |
| **Se 82** | 0.8969 | 10.65 | 1.549 | 1.491 | 0.5924 | 0.3672 | 0.6034 | 0.8845 | 1.465 | 1.392 |
| **Rb 85** | 2.488 | 15.33 | 10.74 | 10.04 | 37.83 | 22.62 | 10.71 | 8.029 | 21.63 | 1.799 |
| **Sr 88** | 6.42 | 38 | 120.1 | 167.1 | 220.7 | 20.83 | 2.939 | 14.77 | 302.8 | 147.4 |
| **Mo 95** | 0.7114 | 8.534 | 1.207 | 0.9239 | 0.9741 | 0.5326 | 0.8115 | 2.894 | 1.392 | 4.302 |
| **Pd 105** | 0.1152 | 6.54 | 0.386 | 0.5535 | 0.5149 | 0.0805 | 0.1507 | 0.2008 | 0.7295 | 0.9105 |
| **Ag 107** | 2.486 | 20.13 | 1.855 | 1.192 | 5.148 | 0.6655 | 1.935 | 3.342 | 1.949 | 13.61 |
| **Cd 111** | 0.02825 | 8.206 | 0.08148 | 0.08041 | 0.09751 | 0.04985 | 1.01 | 0.2458 | 0.1651 | 0.5104 |
| **Sb 121** | 0.9217 | 1.251 | 0.1505 | 0.1418 | 0.6466 | 85.36 | 0.8245 | 1.725 | 0.2131 | 0.285 |
| **Ba 137** | 23.38 | 293.4 | 205.5 | 814.2 | 346.7 | 113.5 | 18.19 | 36.64 | 988.3 | 1381 |
| **Pt 195** | 0.002494 | 0.02339 | 0.01256 | 0.007303 | ND | ND | 0.0038 | 0.002197 | 0.02114 | 0.04999 |
| **Au 197** | 0.4318 | 0.5005 | ND | ND | 0.2379 | 0.3785 | 0.09629 | 0.3115 | ND | 0.5439 |
| **Hg 202** | 2.24 | 0.4922 | 0.2166 | 0.2873 | 1.333 | 0.6952 | 0.1419 | 0.6461 | 0.01731 | 0.3499 |
| **Tl 205** | 0.03231 | 0.5309 | 0.3553 | 0.5255 | 0.4743 | 0.2349 | 0.1233 | 0.1324 | 0.449 | 0.4548 |
| **Pb 208** | 17.98 | 346.2 | 27.97 | 12.75 | 68.21 | 42.01 | 16.05 | 47.65 | 18.23 | 19.84 |
| **Bi 209** | 0.983 | 14.73 | 1.136 | 0.8242 | 0.7085 | 0.2971 | 0.3077 | 1.945 | 0.9655 | 0.629 |
| **Th 232** | 4.723 | 313.7 | 13.15 | 12.14 | 0.7322 | 1.012 | 9.646 | 28.13 | 15.99 | 21.99 |
| **U 238** | 2.875 | 200.6 | 2.558 | 1.868 | 0.534 | 0.2336 | 14.41 | 40.76 | 2.899 | 7.562 |

**AMMONIUM NITRATE - RESULTS ARE *mg/kg***

| | CROWN MINE | Dr TTS 1 A32 | ERMELO (1CW) | ERMELO (GVC) | LOUISE MOORE | KLEIN LETABA | NM-Br | NM-Shale | IPZ (IPC) | VIERFONTEIN FS |
|---|---|---|---|---|---|---|---|---|---|---|
| | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* |
| **Be 9** | ND | 0.0003855 | 0.005003 | 0.0447 | ND | ND | 0.08422 | 0.03473 | 0.02197 | 0.006652 |
| **B 11** | 0.07635 | 0.03507 | ND | ND | 0.5046 | ND | 0.1232 | ND | ND | 0.3288 |
| **Na 23** | 2.86 | 9.135 | 3.545 | 3.196 | 31.98 | 9.49 | 2.504 | 0.9236 | 1.397 | 8.558 |
| **Mg 24** | 13.17 | 72.99 | 80.14 | 194.7 | 603.2 | 80.68 | 1558 | 318.4 | 62.68 | 18.45 |
| **Al 27** | 41.02 | 1.23 | 137.4 | 130.1 | 0.06834 | 0.05543 | 1174 | 830.9 | 124.2 | 10.11 |
| **P 31** | 0.0002233 | ND | ND | 0.008508 | 0.06684 | 0.03862 | 0.4034 | 0.2352 | 0.0502 | 0.03001 |
| **K 39** | 9.413 | 9.033 | 4.043 | 11.77 | 348.8 | 87.51 | 6.331 | 0.5274 | 7.461 | 52.28 |
| **Ca 43** | 273.5 | 5753 | 3085 | 4574 | 1683 | 4893 | 315.8 | 2966 | 739.9 | 5597 |
| **Ti 47** | 0.01258 | 0.005933 | 0.002276 | 0.005558 | 0.002225 | 0.002685 | 0.008197 | 0.01488 | 0.0007161 | 0.01769 |
| **V 51** | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| **Cr 53** | 0.01481 | -0.002881 | 0.006677 | ND | ND | ND | 0.1837 | 4.322 | ND | ND |
| **Mn 55** | 2.116 | 871.3 | 2.808 | 21.65 | 0.2163 | 0.2373 | 134.9 | 79.28 | 9.617 | 18.51 |
| **Fe 57** | 0.8443 | 5.251 | 9.042 | 152.6 | 2.294 | 4.736 | 1.077 | 230.7 | 103 | 5.259 |
| **Co 59** | 0.09674 | 1.062 | 0.2445 | 2.636 | 0.05891 | 0.0842 | 21.43 | 12.72 | 1.979 | 0.05534 |
| **Ni 60** | 0.3617 | 3.426 | 0.6113 | 5.669 | 0.05484 | 0.9442 | 43.91 | 26.08 | 3.256 | 0.1241 |
| **Cu 63** | 0.1251 | 0.1277 | 0.05529 | 0.06445 | 0.03838 | 0.02151 | 7.38 | 12.03 | 0.3449 | 0.03869 |
| **Zn 66** | 0.2701 | 5.701 | 0.3977 | 1.121 | 0.009084 | 0.00935 | 161.8 | 37.87 | 4.529 | 0.09016 |
| **As 75** | 0.0008441 | 0.01018 | 0.01904 | 0.01995 | 0.2866 | 0.4369 | 0.02364 | 0.09204 | 0.0037 | 0.0003232 |
| **Se 82** | ND | 0.006682 | 0.02859 | 0.05063 | ND | ND | 0.08845 | 0.1713 | 0.02005 | ND |
| **Rb 85** | 0.05221 | 0.2116 | 0.159 | 0.527 | 0.4267 | 0.1721 | 0.2496 | 0.03498 | 0.3099 | 0.1281 |
| **Sr 88** | 0.1483 | 4.273 | 29.45 | 36.28 | 6.277 | 5.527 | 0.03839 | 1.339 | 5.021 | 11.14 |
| **Mo 95** | ND | ND | ND | ND | 0.02602 | ND | ND | ND | ND | ND |
| **Pd 105** | ND | 0.01913 | 0.04127 | 0.06184 | 0.006069 | 0.005125 | 0.05172 | 0.07867 | 0.01536 | 0.01338 |
| **Ag 107** | 0.0004573 | 0.001728 | 0.001186 | 0.00105 | 0.00127 | 0.0004234 | 0.002643 | 0.002727 | 0.0009316 | 0.0005081 |
| **Cd 111** | 0.0001839 | 0.5592 | 0.004261 | 0.01404 | ND | ND | 1.248 | 0.2117 | 0.01169 | 0.0001067 |
| **Sb 121** | ND | 0.0005441 | ND | 0.0001398 | 0.001468 | 0.2209 | ND | ND | ND | ND |
| **Ba 137** | 0.3499 | 0.7235 | 2.693 | 2.269 | 1.713 | 2.712 | 0.06655 | 0.06813 | 2.247 | 1.919 |
| **Pt 195** | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| **Au 197** | ND | ND | ND | ND | 0.007949 | 0.006196 | ND | ND | ND | ND |
| **Hg 202** | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| **Tl 205** | 0.000846 | 0.04594 | 0.001899 | 0.02757 | 0.0104 | 0.001788 | 0.004196 | ND | 0.01177 | 0.02631 |
| **Pb 208** | 0.00771 | 0.02199 | 0.0643 | 0.117 | 0.001582 | 0.0008287 | 0.004516 | 0.08127 | 0.02358 | 0.00465 |
| **Bi 209** | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| **Th 232** | ND | ND | ND | 0.0001066 | ND | ND | 0.002066 | 10.22 | 0.001923 | 0.001095 |
| **U 238** | 0.003447 | 0.00199 | 0.01009 | 0.001289 | 0.001328 | ND | 4.391 | 31.2 | 0.006484 | 0.007479 |

| Sample: | CROWN MINE | Dr TTS 1 A32 | ERMELO (1CW) | ERMELO (GVC) | LOUISE MOORE | KLEIN LETABA | NM-Br | NM-Shale | IPZ (IPC) | VIERFONTEIN FS |
|---|---|---|---|---|---|---|---|---|---|---|
| | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* |
| **Be 9** | 0.006928 | 0.035492 | 0.039956 | 0.0916 | 0.019796 | 0.0025548 | 0.012392 | 0.004856 | 0.039056 | 0.10052 |
| **B 11** | <DL | 0.056 | 0.5408 | 8.768 | 0.30232 | <DL | 0.1248 | 0.09256 | 8.768 | 8.732 |
| **Na 23** | 4.56 | 3.6844 | 6.264 | 79.04 | 28.888 | 11.7 | 2.0296 | 7.204 | 90.64 | 90 |
| **Mg 24** | 102.48 | 54.32 | 12.024 | 36.832 | <DL | 614 | 180.08 | 16.4 | 28.184 | 29.312 |
| **Al 27** | 329.6 | 289.16 | 278.64 | 201.92 | 555.2 | 333.52 | 322.84 | 129.24 | 422.4 | 749.6 |
| **P 31** | 3.3864 | 11.32 | 3.3688 | 1.8076 | 5.624 | 5.768 | 5.736 | 2.8948 | 19.852 | 4.612 |
| **K 39** | 19.364 | 66 | 31.436 | 42.2 | 229 | 110.96 | 69.84 | 55.48 | 73.24 | 28.4 |
| **Ca 43** | 17.304 | 1344 | 148.68 | 182.52 | 1663.2 | 284.36 | 13.608 | 99.4 | 113.44 | 803.2 |
| **Ti 47** | 2.3296 | 17.24 | 11.872 | 10.644 | 35.184 | 18.736 | 1.6528 | 1.676 | 10.72 | 55 |
| **V 51** | 0.4512 | 0.4548 | 0.9304 | 0.6124 | 3.092 | 1.404 | 0.6668 | 0.28872 | 1.3288 | 1.2256 |
| **Cr 53** | 3.4824 | 2.3432 | 1.9384 | 1.4104 | 14.572 | 20.692 | 3.918 | 1.5516 | 1.8936 | 2.2836 |
| **Mn 55** | 5.056 | 375.4 | 0.4216 | 1.4084 | 43.28 | 4.836 | 7.62 | 3.8424 | 3.1256 | 14.364 |
| **Fe 57** | 655.2 | 850.4 | 301.96 | 280.56 | 1938.8 | 994.8 | 806.8 | 455.2 | 264 | 920.8 |
| **Co 59** | 0.16624 | 3.3928 | 0.17252 | 0.36032 | 1.2856 | 1.8816 | 0.8348 | 0.5692 | 0.27208 | 0.36672 |
| **Ni 60** | 0.7316 | 5.784 | 0.35184 | 0.8708 | 11.696 | 17.556 | 2.3844 | 1.1208 | 0.5148 | 0.9412 |
| **Cu 63** | 1.4284 | 4.892 | 0.6624 | 0.6012 | 2.4388 | 1.7592 | 1.3836 | 1.2672 | 1.0696 | 1.0944 |
| **Zn 66** | 1.0824 | 16.636 | 0.4632 | 6.74 | 4.164 | 1.6476 | 5.316 | 1.5832 | 8.504 | 8.016 |
| **As 75** | 3.118 | 8.22 | 0.14256 | 0.208 | 9.736 | 86.84 | 0.5692 | 3.3688 | 0.2034 | 0.2542 |
| **Se 82** | 0.035876 | 0.426 | 0.06196 | 0.05964 | 0.023696 | 0.014688 | 0.024136 | 0.03538 | 0.0586 | 0.05568 |
| **Rb 85** | 0.09952 | 0.6132 | 0.4296 | 0.4016 | 1.5132 | 0.9048 | 0.4284 | 0.32116 | 0.8652 | 0.07196 |
| **Sr 88** | 0.2568 | 1.52 | 4.804 | 6.684 | 8.828 | 0.8332 | 0.11756 | 0.5908 | 12.112 | 5.896 |
| **Mo 95** | 0.028456 | 0.34136 | 0.04828 | 0.036956 | 0.038964 | 0.021304 | 0.03246 | 0.11576 | 0.05568 | 0.17208 |
| **Pd 105** | 0.004608 | 0.2616 | 0.01544 | 0.02214 | 0.020596 | 0.00322 | 0.006028 | 0.008032 | 0.02918 | 0.03642 |
| **Ag 107** | 0.09944 | 0.8052 | 0.0742 | 0.04768 | 0.20592 | 0.02662 | 0.0774 | 0.13368 | 0.07796 | 0.5444 |
| **Cd 111** | 0.00113 | 0.32824 | 0.0032592 | 0.0032164 | 0.0039004 | 0.001994 | 0.0404 | 0.009832 | 0.006604 | 0.020416 |
| **Sb 121** | 0.036868 | 0.05004 | 0.00602 | 0.005672 | 0.025864 | 3.4144 | 0.03298 | 0.069 | 0.008524 | 0.0114 |
| **Ba 137** | 0.9352 | 11.736 | 8.22 | 32.568 | 13.868 | 4.54 | 0.7276 | 1.4656 | 39.532 | 55.24 |
| **Pt 195** | 0.00009976 | 0.0009356 | 0.0005024 | 0.00029212 | <DL | <DL | 0.000152 | 0.00008788 | 0.0008456 | 0.0019996 |
| **Au 197** | 0.017272 | 0.02002 | <DL | <DL | 0.009516 | 0.01514 | 0.0038516 | 0.01246 | <DL | 0.021756 |
| **Hg 202** | 0.0896 | 0.019688 | 0.008664 | 0.011492 | 0.05332 | 0.027808 | 0.005676 | 0.025844 | 0.0006924 | 0.013996 |
| **Tl 205** | 0.0012924 | 0.021236 | 0.014212 | 0.02102 | 0.018972 | 0.009396 | 0.004932 | 0.005296 | 0.01796 | 0.018192 |
| **Pb 208** | 0.7192 | 13.848 | 1.1188 | 0.51 | 2.7284 | 1.6804 | 0.642 | 1.906 | 0.7292 | 0.7936 |
| **Bi 209** | 0.03932 | 0.5892 | 0.04544 | 0.032968 | 0.02834 | 0.011884 | 0.012308 | 0.0778 | 0.03862 | 0.02516 |
| **Th 232** | 0.18892 | 12.548 | 0.526 | 0.4856 | 0.029288 | 0.04048 | 0.38584 | 1.1252 | 0.6396 | 0.8796 |
| **U 238** | 0.115 | 8.024 | 0.10232 | 0.07472 | 0.02136 | 0.009344 | 0.5764 | 1.6304 | 0.11596 | 0.30248 |

| | CROWN MINE | Dr TTS 1 A32 | ERMELO (1CW) | ERMELO (GVC) | LOUISE MOORE | KLEIN LETABA | NM-Br | NM-Shale | IPZ (IPC) | VIERFONTEIN FS |
|---|---|---|---|---|---|---|---|---|---|---|
| | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* | *mg/kg* |
| **Be 9** | <DL | 0.00001542 | 0.00020012 | 0.001788 | <DL | <DL | 0.0033688 | 0.0013892 | 0.0008788 | 0.00026608 |
| **B 11** | 0.003054 | 0.0014028 | <DL | <DL | 0.020184 | <DL | 0.004928 | <DL | <DL | 0.013152 |
| **Na 23** | 0.1144 | 0.3654 | 0.1418 | 0.12784 | 1.2792 | 0.3796 | 0.10016 | 0.036944 | 0.05588 | 0.34232 |
| **Mg 24** | 0.5268 | 2.9196 | 3.2056 | 7.788 | 24.128 | 3.2272 | 62.32 | 12.736 | 2.5072 | 0.738 |
| **Al 27** | 1.6408 | 0.0492 | 5.496 | 5.204 | 0.0027336 | 0.0022172 | 46.96 | 33.236 | 4.968 | 0.4044 |
| **P 31** | 0.000008932 | <DL | <DL | 0.00034032 | 0.0026736 | 0.0015448 | 0.016136 | 0.009408 | 0.002008 | 0.0012004 |
| **K 39** | 0.37652 | 0.36132 | 0.16172 | 0.4708 | 13.952 | 3.5004 | 0.25324 | 0.021096 | 0.29844 | 2.0912 |
| **Ca 43** | 10.94 | 230.12 | 123.4 | 182.96 | 67.32 | 195.72 | 12.632 | 118.64 | 29.596 | 223.88 |
| **Ti 47** | 0.0005032 | 0.00023732 | 0.00009104 | 0.00022232 | 0.000089 | 0.0001074 | 0.00032788 | 0.0005952 | 0.000028644 | 0.0007076 |
| **V 51** | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL |
| **Cr 53** | 0.0005924 | -0.00011524 | 0.00026708 | <DL | <DL | <DL | 0.007348 | 0.17288 | <DL | <DL |
| **Mn 55** | 0.08464 | 34.852 | 0.11232 | 0.866 | 0.008652 | 0.009492 | 5.396 | 3.1712 | 0.38468 | 0.7404 |
| **Fe 57** | 0.033772 | 0.21004 | 0.36168 | 6.104 | 0.09176 | 0.18944 | 0.04308 | 9.228 | 4.12 | 0.21036 |
| **Co 59** | 0.0038696 | 0.04248 | 0.00978 | 0.10544 | 0.0023564 | 0.003368 | 0.8572 | 0.5088 | 0.07916 | 0.0022136 |
| **Ni 60** | 0.014468 | 0.13704 | 0.024452 | 0.22676 | 0.0021936 | 0.037768 | 1.7564 | 1.0432 | 0.13024 | 0.004964 |
| **Cu 63** | 0.005004 | 0.005108 | 0.0022116 | 0.002578 | 0.0015352 | 0.0008604 | 0.2952 | 0.4812 | 0.013796 | 0.0015476 |
| **Zn 66** | 0.010804 | 0.22804 | 0.015908 | 0.04484 | 0.00036336 | 0.000374 | 6.472 | 1.5148 | 0.18116 | 0.0036064 |
| **As 75** | 0.000033764 | 0.0004072 | 0.0007616 | 0.000798 | 0.011464 | 0.017476 | 0.0009456 | 0.0036816 | 0.000148 | 0.000012928 |
| **Se 82** | <DL | 0.00026728 | 0.0011436 | 0.0020252 | <DL | <DL | 0.003538 | 0.006852 | 0.000802 | <DL |
| **Rb 85** | 0.0020884 | 0.008464 | 0.00636 | 0.02108 | 0.017068 | 0.006884 | 0.009984 | 0.0013992 | 0.012396 | 0.005124 |
| **Sr 88** | 0.005932 | 0.17092 | 1.178 | 1.4512 | 0.25108 | 0.22108 | 0.0015356 | 0.05356 | 0.20084 | 0.4456 |
| **Mo 95** | <DL | <DL | <DL | <DL | 0.0010408 | <DL | <DL | <DL | <DL | <DL |
| **Pd 105** | <DL | 0.0007652 | 0.0016508 | 0.0024736 | 0.00024276 | 0.000205 | 0.0020688 | 0.0031468 | 0.0006144 | 0.0005352 |
| **Ag 107** | 0.000018292 | 0.00006912 | 0.00004744 | 0.000042 | 0.0000508 | 0.000016936 | 0.00010572 | 0.00010908 | 0.000037264 | 0.000020324 |
| **Cd 111** | 0.000007356 | 0.022368 | 0.00017044 | 0.0005616 | <DL | <DL | 0.04992 | 0.008468 | 0.0004676 | 0.000004268 |
| **Sb 121** | <DL | 0.000021764 | <DL | 0.000005592 | 0.00005872 | 0.008836 | <DL | <DL | <DL | <DL |
| **Ba 137** | 0.013996 | 0.02894 | 0.10772 | 0.09076 | 0.06852 | 0.10848 | 0.002662 | 0.0027252 | 0.08988 | 0.07676 |
| **Pt 195** | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL |
| **Au 197** | <DL | <DL | <DL | <DL | 0.00031796 | 0.00024784 | <DL | <DL | <DL | <DL |
| **Hg 202** | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL |
| **Tl 205** | 0.00003384 | 0.0018376 | 0.00007596 | 0.0011028 | 0.000416 | 0.00007152 | 0.00016784 | <DL | 0.0004708 | 0.0010524 |
| **Pb 208** | 0.0003084 | 0.0008796 | 0.002572 | 0.00468 | 0.00006328 | 0.000033148 | 0.00018064 | 0.0032508 | 0.0009432 | 0.000186 |
| **Bi 209** | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL |
| **Th 232** | <DL | <DL | <DL | 0.000004264 | <DL | <DL | 0.00008264 | 0.4088 | 0.00007692 | 0.0000438 |
| **U 238** | 0.00013788 | 0.0000796 | 0.0004036 | 0.00005156 | 0.00005312 | <DL | 0.17564 | 1.248 | 0.00025936 | 0.00029916 |