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Potential Toxic Elements In The Soil Of a Closed Metalliferous Ore Mine

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DECLARATION

I, **Tlotlang Moncho**, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology and the North-West University.

29th April 2019

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ABSTRACT

Potential Toxic Elements (PTEs) contamination is a serious environmental concern in soils and sediments. In many ways, mining activities contribute negatively to the environment and its ecosystems with PTE pollution extending far beyond the seizure of mining activity. Some of the negative impact of mining industry includes formation of sinkholes, contamination of groundwater, surface water and as for the scope of this research study, PTE contamination of soils. Understanding PTE bioavailability and mobility in the contaminated soil near mining activity has become a public concern, and research towards the minimization of the PTEs ecological impact is required, thus the aim of this study, i.e. to evaluate the bioavailability and mobility of PTEs from a closed metalliferous ore mine, deemed to be a potential polluter.

The three-stage BCR sequential extraction procedure along with multivariate analysis techniques such as XRF and FTIR were employed to evaluate metal chemical fractions and total concentrations of selected PTEs, such as Aluminium (Al), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn) and Zinc (Zn) in the analysed soil samples. The total organic matter and distribution of particle size were investigated and the affinity of organic matter to grain size was highlighted. The results indicated that higher susceptibility and bioavailability of Cu, Zn and Mn with a strong affinity to the exchangeable fraction – carbonate bounded. Substantial amount of Fe was observed in the reducible fraction which may be due to the stable complexes formed and bound to the Fe-Mn oxides. In the oxidizable fractions, Al showed dominance with Fe and Cu also showing the strong affinity to be embedded in organic matter. Cr was generally the least mobile metal as indicated by the lowest concentration in all fractions. Generally, the mobility of PTEs in the sediments was as follows: exchangeable>reducible and oxidizable. The strong affinity of organic matter to attach to fine grain sized soil was observed with a high fine fraction being observed in samples obtained from the source of pollution. Furthermore, downstream from the source of pollution, there was an indication that the soil had lower organic matter content with coarser particle sized soil. The FITR and XRF results showed a strong association of silicates and quartz minerals, with the soil being constituted predominantly by SiO_2, Fe_2O_3, Al_2O_3 and traces of MgO, Cr_2O_3 and MnO. A Risk Assessment Code (RAC) was also used as a criterion to quantitatively evaluate the risks associated with the soil samples and PTEs risk to the environment decreased as follows Cu>Al>Fe>Mn>Zn> with the least risk posed by Cr.

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DEDICATION

To my mothers,

Kedibone G. Moncho

Mosetsanagape J. Matolo   **Sekgantsho M. Lechuti**

Thank you for the support on this journey

*With Love, **Your Son**.*

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TABLE OF CONTENTS

Cape Peninsula
University of Technology

Cape Peninsula
University of Technology

Cape Peninsula
University of Technology

LIST OF FIGURES

Cape Peninsula
University of Technology

LIST OF TABLES

Cape Peninsula
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GLOSSARY

Abbreviation/symbols	Definition (units)
AMD	Acid mine drainage
ARD	Acid rock drainage
BCR	Community Bureau of Reference
BioERG	Bioresource engineering research group
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EC	Electrical Conductivity
FTIR	Fourier transformed infrared
NRF	National Research Foundation
ORP	Oxidation – reduction potential
PTE	Potential toxic elements
SAMD	Synthetic acid mine drainage
SRB	Sulphate-reducing bacteria.
TOC	Total Organic Carbon
TOM	Total Organic Matter
XRD	X- ray diffraction spectroscopy
XRF	X-ray Fluorescence spectroscopy
HM	Heavy Metal

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OUTLINE OF THE THESIS

The research presented in this thesis was conducted at the Bioresource Engineering Research Group laboratories, Department of Biotechnology, Cape Peninsula University of Technology, Cape Town, South Africa, in collaboration with the School of Chemical and Minerals Engineering, North West University (NWU), Potchefstroom, South Africa.

CHAPTER 1: Introduction and motivation

This chapter provide a brief background of the origin of PTEs in conjunction with AMD generation in mining activity in South Africa and mining activity as a potential source of pollution in O'kiep, an area with a history of mining activity. Objectives and research questions of the study are also highlighted in this chapter.

CHAPTER 2: Literature review

This chapter review the literature about acid mine drainage generation and the environmental and ecological impact. The treatment methods of acid mine drainage were discussed with main focus on biological treatment options.

CHAPTER 3: Prediction of metals bioavailability in the soils of O'kiep, South Africa

This chapter investigates bioavailability of PTEs in the sediments near the mining zone in O'kiep, South Africa. This section primarily discusses the impact of mining activities on the surface water and a potential mobility of PTEs into rivers, which can culminate in their accumulation to toxic levels in the ecosystem downstream of the source.

CHAPTER 4: Effect of sediment grain size and total organic matter on metal bioavailability

This chapter investigate the total organic matter and sediment particle size distribution on the PTEs bioavailability and subsequently mobility to the pollutant free areas.

CHAPTER 5: General discussion, conclusions and recommendations

This chapter provides a general discussion, conclusion and recommendations for future studies.

CHAPTER 6: List bibliographical references

This section provides a list of bibliographical references consulted for the study.

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Chapter 1

Background and motivation

1. CHAPTER 1
INTRODUCTION

1.1 Background and motivation

Mining has been a major contributor to the South African (SA) economy for decades. SA's reputation as the leading minerals producer subsequently makes it the largest producer of mine waste with abandoned mines being the primary source of various environmental, human health and societal challenges (Mhlongo and Amponsah-Dacosta, 2016). Pollutants distribution from the source – i.e. abandoned mines, such as potential toxic elements (PTEs) in the form of heavy metals in mining waste, could also contribute to the pollution like other mine related environmental degradation processes such as acid mine drainage (AMD) and become the primary source of pollution, which can affect water resources in the vicinity of the mine (Amponsah-Dacosta and Reid, 2014). Environmental impact of AMD and SA's scarcity of quality drinking water, makes PTEs pollution a matter of high priority across various research institutions and the South African government.

Research and monitoring of water quality parameters in abandoned mines began in late-1990s, a programme initiated by purported of environmental harm caused by the mining industry. However, PTEs pollution and AMD was not reported until in 2002 in the Western Basin of the Witwatersrand (South Africa) whereby contaminated water was observed (Matsumoto et al., 2016). In SA, both PTEs and AMD is strongly associated with abandoned gold including coal mines for which their overburden and waste ore contain a high content of PTEs including pyrite (FeS_2), the primary contributor to AMD generation; however, numerous studies have shown that other sulphide copper minerals such as chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S) are susceptible to oxidation thus PTEs and AMD generation (Akcil and Koldas, 2006, Simate and Ndlovu, 2014); although minimal studies have been conducted to evaluate the distribution of PTEs bioavailability and mobility on surface runoff water from potential sources – i.e. abandoned mines, towards pollutant free areas thus PTEs mobility potential and ecological pollution threat downstream of the source.

The O'kiep Copper District (OCD) in the Namaqualand region, is a well-known copper mining region, and one of the oldest formal mining areas in South Africa with 2500 km^2 that yielded two million tons of copper between 1852 and 2002 as highlighted by

Cairncross (2004), Clarke et al. (2014) and Clifford and Barton (2012). This area is geographically situated in the Northern Cape Province, South Africa, 600 km North-west of Cape Town. O'kiep is a small town with a reported population of approximately 6,304 people in 2011 (Stats South Africa, 2011) and an averaged elevation and annual rainfall of approximately 900 meters and 1,75cm, respectively (Cairncross, 2004). High copper exploitations (Fig. 1) resulted in a large quantity of waste being generated. Thus, the abandoned mines which serve as a source of PTE pollutant to the nearby zones, including the O'kiep town.
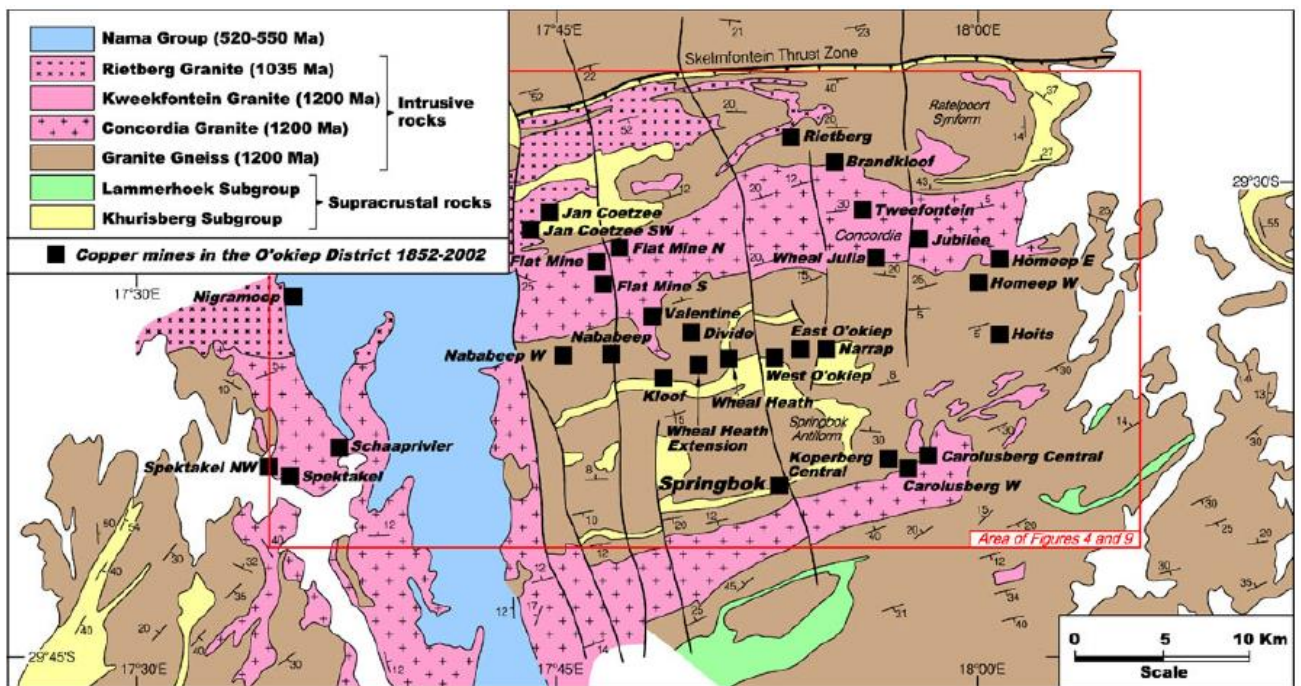
Figure 1: Copper mine activities in Okiep Mine District in 1852-2002. Exported from Clifford and Barton (2012)

Considering the environmental health challenges associated with the mining industry, the need for rehabilitation of abandoned mines including waste bodies is important in prevention of PTE pollution and mobility. Thus, the aim of this research study was to identify and evaluate PTE distributions from the source – a closed metalliferous ore mine (copper mine), and their potential to pollute the ecosystem downstream of the source - previously unpolluted areas.

2

1.2 Research questions

In light of the above, the following research questions were addressed:

- What is the potential metals mobility in the soil nearby the mine site?

- What is the mineralogical composition and major components of the metals in the soil?

- What is the relationship between organic matter, sediment grain size and metal bioavailability and mobility?

1.3 General objectives

The following objectives were fulfilled to accomplish the aim of the study. The project was divided into two (2) phases, namely;

Phase 1: Aim: To predict PTEs mobility and bioavailability by characterization of the soils near the mining areas in O'kiep, South Africa. To achieve this aim, the study focused on the following objectives:

Objective 1: to determine the total PTE content, i.e. Al, Cu, Fe, Mg and Mn, and compare their binding forms in representative soil samples,

Objective 2: to evaluate metal distribution in the sediment samples using sequential chemical extraction, and

Objective 3: to characterize PTEs constituents in the soil using XRF and FTIR.

Phase 2: Aim: To investigate the association of total organic matter in the soil as a function of sediment grain size and PTE bondage. To achieve this aim, the study focused on the following objectives:

Objective 1: to evaluate total organic matter using loss-of-ignition method.

Objective 2: to determine the particle size distribution of the sediments using a laser particle analyser.

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Chapter 2

Literature review

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2. CHAPTER 2
LITERATURE REVIEW

2.1 Acid mine drainage as a contributor to potential toxic elements (PTEs) mobility: An overview

Acid mine drainage (AMD), sometimes referred to as acid rock drainage (ARD) is generally characterised by a high concentration of potential toxic elements (PTEs) and sulphate contaminants. The process of AMD formation is commonly associated with mining operations producing sulphide ores, for both operational and abandoned mines (Simate and Ndlovu, 2014). AMD is as a result of the oxidation of sulphide-bearing minerals in a presence of water and bacterial activity, i.e. organisms such as *Acidithiobacillus ferroxidans*, that accelerates the sulphide breakdown to an acidic and high PTE concentration containing water. Mining activity expose a significantly amount of minerals to the surface, particularly pyrite containing gangue with high abundance PTEs, which is then oxidised in the presence of moisture, air and microbial activity (Simate and Ndlovu, 2014).

In an abandoned mine, surface water and ground water may enter mines via mine faults and adits and moisture exposure to sulphide minerals deep in the mine may lead to formation of AMD thus mobility of PTEs liquefied matrices. Akcil and Koldas (2006) stated that the rate of acid generation and the degree of PTEs leaching varies from site to site, due to the dependence on ore mineralogy, and combination of other factors affecting AMD formulation. These factors are temperature, dissolved oxygen content in the water phase, pollutant saturation in the water phase, chemical activity of PTEs such as ferric iron (Fe^{3+}), exposure of sulphide constitutes in the ore body and the bacterial activity.

2.2 Formation and constituents of acid mine drainage

As discussed above, pyrite is the primary contributor to most reported cases of AMD formation due to its sulphidic constituents as reported extensively by numerous authors (Akcil and Koldas, 2006, Kefeni et al., 2017, Simate and Ndlovu, 2014). However, acid generation is not limited to pyrite minerals only; other sulphide minerals have been reported

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as potential contributors to AMD generation. Table 2.1 present sulphide minerals and their PTE species.

Table 2.1: Predominant minerals that produce AMD and their associated PTE species (Abrosimova et al., 2015, Anawar, 2015, Lattanzi et al., 2008, Simate and Ndlovu, 2014)

Metal sulphide	Chemical formula	PTE species
Pyrite	FeS_2	Fe^{2+}; Fe^{3+}; SO_4^{2-}
Marcasite	FeS_2	Fe^{2+}; Fe^{3+}; SO_4^{2-}
Chalcocite	Cu_2S	Cu^{2+}; SO_4^{2-}
Covelite	CuS	Cu^{2+}; SO_4^{2-}
Chalcopyrite	$CuFeS_2$	Cu^{2+}; Fe^{2+}; SO_4^{2-}
Enargite	Cu_3AsS_4	Cu^{2+}; $HAsO_4^{2-}$; AsO_4^{3-}; SO_4^{2-}
Tennantite	$Cu_9Fe_2ZnAs_4S_{13}$	Cu^{2+}; Zn^{2+}; $H_2AsO_4^{-}$; SO_4^{2-}
Millerite	NiS	Ni^{2+}; SO_4^{2-}
Galena	PbS	Pb^{2+}; SO_4^{2-}
Sphalerite	ZnS	Zn^{2+}; SO_4^{2-}
Arsenopyrite	$FeAsS$	Fe^{2+}; Fe^{3+}; $H_2AsO_4^{-}$; SO_4^{2-}

2.2.1 Oxidation of pyrite

AMD generation and PTE availability by oxidation of pyrite initiated by exposure of the pyrite to water (H_2O) and oxygen (O_2) abiotically, culminates in the formation of dissolved ferrous iron (Fe^{2+}), hydrogen and sulphates. Undisturbed, the reaction happens slowly. It is described as the first and most important reaction of AMD generation PTE release in to water sources (Akcil and Koldas, 2006) – Eq. 2.1:

Pyrite oxidation:

$$FeS_2 + \frac{7}{2}O_2 + H_2O \xrightarrow{Bacteria} Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (2.1)$$
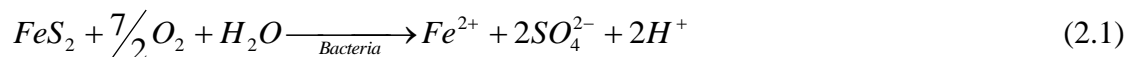
Ferrous iron may be oxidised to ferric iron (Fe^{3+}) under suitable environmental conditions (Eq. 2.2). This reaction is dependent on the concentration of dissolved O_2, and a pH greater than 3.5 including bacterial metabolic activity (Simate and Ndlovu, 2014):

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$$\text{Ferrous oxidation:} \quad Fe^{2+} + \frac{1}{4}O_2 + H^+ \leftrightarrow Fe^{3+} + \frac{1}{2}H_2O \tag{2.2}$$
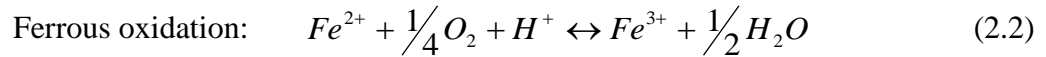
Subsequently the hydrolysis of ferrous iron, is the final stoichiometric step that result in the precipitation of ferric iron, as $Fe(OH)_3$, with minute residual Fe^{3+} in the solution while simultaneously producing an acidic solution at a pH range of 2.3 to 3.5 - Eq. 2.3 (Akcil and Koldas, 2006).

$$\text{Ferric iron hydrolysis:} \quad Fe^{3+} + 3H_2O \underset{2.3-3.5}{\overset{pH}{\leftrightarrow}} Fe(OH)_3(s) + 3H^+ \tag{2.3}$$
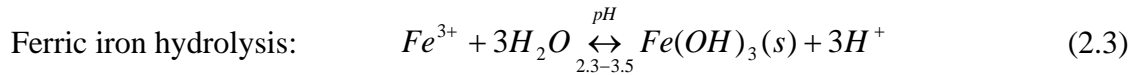
The stability of the ferric iron hydrolysis products is highly depended on the pH. Simate and Ndlovu (2014) highlighted that at a pH lower than 2, Fe^{3+} (Eq. 2.3) remains in the solution and it used to facilitate oxidation of pyrite along with any remaining Fe^{2+} (Eq. 2.2) according to Eq. 2.4:

$$\text{Pyrite oxidation:} \quad FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{2.4}$$
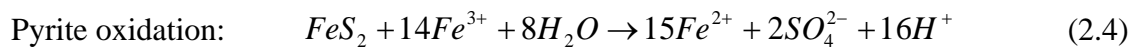
Oxidation of pyrite by Fe^{3+} (Eq. 2.4) is rapid, making Fe^{3+} the dominant oxidant of pyrite than dissolved oxygen at pH below 3. This reaction continues until Fe^{3+} or pyrite is depleted.

2.2.2 Oxidation of chalcopyrite

Chalcopyrite is a copper-bearing sulphide mineral that is associated with pyrite ore and may release PTEs such as copper metal ions into solutions. The reaction of the oxidation of chalcopyrite to produce ferrous iron (Fe^{3+}) and copper (Cu^{2+}) ions in non-acidic conditions can be written as Eq. 2.5 (Anawar, 2015):

$$\text{Chalcopyrite oxidation:} \quad CuFeS_2 + 4O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-} \tag{2.5}$$
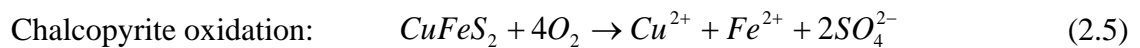
Furthermore, under acidic conditions the presence of ferric iron may oxidise chalcopyrite as follows (Eq. 2.6):

$$\text{Chalcopyrite oxidation:} \quad CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \tag{2.6}$$
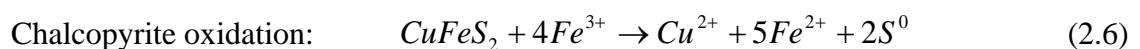
It is evident that the formation of AMD is a complex multistage process that involves biological, chemical and electrochemical reactions that vary site to site due to various factors

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that influence the rate of its production. These factors influence the oxidation of sulphide minerals (reported in Table 2.1) to produce AMD and PTEs.

2.3 Factors contributing to formation of AMD and release of PTEs

There are several reported factors that contributing towards weathering of mine sulphide minerals waste to form AMD and PTEs. These include water and air availability, sulphur and iron oxidation, microbial activity, mineralogical composition and characteristic of mine waste.

2.3.1 Water and air availability

Water and dissolved oxygen are the most important factor in oxidations of mineral ore waste. As indicated in Eq. 2.1, water and oxygen reacts with sulphide mineral (i.e. pyrite) under suitable conditions facilitated by micro-organisms to produce AMD which subsequently generates PTEs. Oxygen and carbon dioxide are required by micro-organisms, i.e. chemolithoautotrophs, for survival and water availability further facilitates the generation of AMD, which serves as both a reactant and transportation medium for metal leachates species, facilitating hydrolysis of other metal species further reducing the pH resulting in subsequent mobility of PTEs to pristine, pollutant free areas.

2.3.2 Microbial activity

Microbial activity plays an important role in the generation of AMD. *Acidithiobacillus ferrooxidans* is commonly studied due to high proliferation to ore-bodies containing a large quantity of pyrite. This organism lives under mesophilic conditions. A thermophilic *Leptospirilium* sp. is also more active at pH of less than 1.5 and in geothermal waters of temperature between 25 to 70°C (Nordstrom et al., 2015). Microbial communities significantly change from site to site at moderate conditions (temperature and pH), and there is a possibility for variation in the distribution of microbial communities from the source of pollution. González-Toril et al. (2011) reported that sulphate-reducing bacteria (*Desulfosporosinus* sp. and *Syntrophobacter* sp.) were predominantly detected and

congregated at the pollution source, with iron-reducing bacteria (*Acidiphilium* sp., *Acidobacterium* sp., and *Acidosphaera* sp) being found midstream of an AMD contaminated river while iron-oxidizing microorganisms (*Leptospirillum* sp., *Acidithiobacillus ferrooxidans*, and *Thermoplasmata*) were increasingly detected downstream of the pollution source. Generally, the micro-organisms proliferation of different communities highly depends on their optimum temperature and pH including AMD formation and PTE distribution, which is largely influenced by the mineralogical characteristics of the mine waste.

2.3.3 Effect of temperature and weather conditions

Generally, three microbial communities are commonly associated with AMD water sites i.e. mesophilic bacteria, thermophiles and thermophilic archaea. Mesophilic bacteria proliferate at temperatures of 10 to 45°C, thermophiles at temperatures of 5 to 60°C and extremophiles with a high temperature tolerance of 60 to 90°C. Moreover, there are microorganisms associated with proliferation at lower temperatures of between -20 to +10°C. These psychrophilic bacteria are rarely found in AMD as a result of warm water temperature due to exothermic reaction of oxidation of sulphide minerals (Rawlings & Johnson, 2007). Lower temperature increases the solubility of carbon dioxide (CO_2) thus decrease in pH and rapid dissolution and solubility of surrounding hydroxide and carbonate substrates (such as calcite, limestone and dolomite) including PTEs which provide alkalinity to neutralize AMD. Contrary to the low temperatures, an increased temperature as a result of oxidation of sulphide minerals facilitates a rapid proliferation of thermophiles and mesophilic bacteria. Temperature of the water-bodied highly influences the proliferation microorganisms and potential neutralization and impact of AMD water. *A. ferrooxidans* and *L. ferrooxidans* are Fe-oxidizing mesophilic bacterial species with optimum temperatures 30°C and 40°C, respectively.

2.3.4 Mineralogical and physical characterization of mine waste

The potential of AMD thus PTE availability and their impact, is highly dependent on mineralogical composition of the surrounding rocks, the abundance of oxidizable species in the waste rock, permeability of the waste rock and its particle size. Comminution to liberate of valuable minerals species through crushing and grinding (or/milling) of mineral ore to

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achieve different particle sizes and an increased surface area thus extractability of valuable species, also ensures the release of PTEs. Consequently, an increase in surface area exposes sulphide species to water and oxygen thus promote formation of AMD. Metallic sulphide species and PTEs in AMD water varies from site to site and is associated with the mineralogical composition of the geological rock, and the balance of different mineral ratios which can contribute towards the acidification of the immediate environment.

Oxidation of sulphides species produce acidity by liberation of protons (H^+) into the solutions and release metal elements (PTEs) via hydrolysis and thus deprotonation of water and liberation of protons into the solution further increasing acidity. The low pH increases solubility and mobility of PTEs (e.g. Zn^{2+}, Cu^{2+} and Al^{3+} among others). In contrary to acidification of the solution, gangue minerals in the parent rock might contain acid neutralizing minerals which buffer the pH and stabilize the solution by producing oxyanions (Dold, 2016).

2.3.5 Acid neutralization

Valuable minerals are often interlocked and/or form stable bonds with non-economical constituents referred to as gangue which may contain alkaline minerals such as hydroxides and carbonates. Metal hydroxides can receive protons releasing hydroxide ions in to the solution or metals further neutralising or increasing the pH depending on the pH of the solution. Hydroxides such as goethite, ferrihydrite and gibbsite are commonly found in gangue.

Carbonates are present in the waste rocks as Ca-Mg carbonates which play a crucial role in pH buffering of the AMD solution due to their high reactivity. Highly soluble calcite ($CaCO_3$) and magnesite ($MgCO_3$) dissolve and liberate bicarbonate (HCO_3^-) to the solution which neutralize protons (H^+) available in the acidic solution (Parbhakar-Fox and Lottermoser, 2015).

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2.4 Environmental and ecological impact of acid mine drainage and PTEs

2.4.1 Effect of PTEs in the soil and sediments

PTE-containing sediments and soils pose serious threat to agricultural land. PTE-enriched spoil heaps (i.e. mine tailings) can undergo water/or wind erosion increasing mobility of PTE to the nearby zones, and thus easily be absorbed by the plant roots and subsequently gain entry into the food chain (Sungur et al., 2014a, Sungur et al., 2014b). PTE have a significant impact on the plant nutritional cycle as a result of accumulation of toxic quantities of PTE by plants from soil, water or air, causing cellular damage to plants which then disrupts the physiology and morphology of the plants (Simate and Ndlovu, 2014).

Among the other components of the ecosystem, soils are exposed to PTE pollution most since they constitute the largest receiving bodies of the toxic PTEs (Sparks, 2005). Soil is a highly dynamic system formed by weathering of parent rocks and heavy contamination can be derived from both natural (geogenic) and anthropogenic sources. Anthropogenic deposition includes via soil augmentation in agriculture, metallurgical operations, energy production, microelectronics manufacturing and sewage sludge disposal, which are the primary contributors of PTEs which are up taken by plants, particularly in an ecosystem whereby arid or semi-arid conditions are sustained, as in South Africa (Sparks, 2005). On the other hand, the total metal concentration of arable lands usually dependants on parent rock composition and metal mobility (Sungur et al., 2014a).

Sediments can operate as PTE carriers to the nearby water systems which may result in increased plant uptake. Many studies focus on the analysis of the total PTE concentration in the soil, this however, does not provide a necessary information about the bioavailability of metals in the soils (Sungur et al., 2014a). A speciation method is required to understand the bioavailability and toxicity of PTEs in a groundwater system (Thanh et al., 2016). PTE mobility in the environment, among other factors such as the parent rock composition, primarily depends on the PTE binding forms in the soil. In order to quantify PTE bioavailability a sequential extraction method is used to access the binding forms of PTE in the soil. Understanding the PTE mobility and bioavailability is the starting point of controlling and remediation of AMD constituents (Zhang et al., 2014b).

2.4.2 Effects of PTEs on human health

Exposure to AMD including PTEs might have a direct impact on humans and aquatic animal health. Humans need not be exposed to the PTE pollutants found in the AMD; however, the toxicity of a high quantity of PTEs, such as copper ions, is known to be toxic to humans with negative health outcomes (Simate and Ndlovu, 2014). Biochemical and physiological functions of copper in humans and animals, makes copper an essential element in minute quantities for the maintenance of some cellular functions. PTEs have the ability to exist in the ecosystems for elongated periods, with the persistent loading of PTEs culminating in unacceptable toxicity levels to both humans and animals, generating reactive oxygen species, thus increasing cellular deactivation in the body (Brewer, 2009, Cherfi et al., 2014). Simate and Ndlovu (2014) highlighted that copper may have negative effects on human health as follows; anaemia, liver and kidney damage, stomach and intestinal irritation.

Chapter 3

Prediction of Potential Toxic Elements Bioavailability in the soils of O'kiep, South Africa

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3. CHAPTER 3

PREDICTION OF POTENTIAL TOXIC ELEMENTS BIOAVAILABILITY IN THE SOILS OF O'KIEP, SOUTH AFRICA

General overview of the article

This papers aim was to predict the PTE bioavailability and mobility in the soils of O'kiep, South Africa.

To archive this, the following objectives were addressed; (I) to determine the total PTE content, such as Al, Cu, Fe, Mg and Mn, and compare their binding forms in representative soil samples, and, (II) to evaluate metal distribution in the sediment samples using sequential chemical extraction, and (III) to characterize PTEs constituents in the soil using XRF and FTIR.

The results indicated that PTEs that adsorbed weakly onto solid surface of sediments bound by weak electrostatic forces such as Copper (Cu) and aluminium (Al), are readily remobilized and thus an increase in bioavailability downstream from the source of pollution. PTEs bound to Fe-Mn oxides are mobilized under reductive conditions and this was evident by a de-bound and redistribution of Fe in the fractions 2 of BCR. Overall, mobility and bioavailability of PTEs in the OCD sediment samples decreased in order of exchangeable> reducible> oxidizable with a high inorganic material, such as clay and quartz, being observed in the sample studied.

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Prediction of Potential Toxic Elements Bioavailability in the soils of O'kiep, South Africa

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Abstract— Mining activities cause environmental pollution problems by contaminating nearby areas with PTEs such as Cu, Fe, Zn and Al from overburden and leachates. PTEs can leach into groundwater, be transferred into rivers, and streams by surface run-off, in a form of dissolved species or as a part of suspended solids, culminating in their accumulation to toxic levels in the ecosystem downstream of the source. In view of such mobility attributed to bioavailability, the objective of this study was to assess the bioavailability and mobility of PTE species in the sediments around a closed copper mine and subsequent to analysis with XRF, FTIR and a three-step sequential extraction process. Cu, Zn and Mn were predominantly bound to carbonates and could thus be easily desorbed during moisture laden periods, which will increase their bioavailability thus mobility, away from the source. The BCR fractions also showed that under oxidative reductive conditions, Fe species bound to Fe-Mn oxides, thus can be de-bonded in the presence of an acidified environment; therefore, be mobile for redistribute further downstream from the point of source and further contaminating pollutant free areas.

Index Terms— Bioavailability, Sequential chemical extraction, Potential Toxic Elements, O'kiep

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3.1   Introduction

PTE-containing sediment from mining activities is a common environmental problem that poses threat to arable land and groundwater sources [1], [2]. Metal bioavailability, including transfer via numerous transportation mechanism, have led to an increase in toxic heavy metal mobility [3], thus are easily absorbed and accumulate and subsequently bioaccumulate in the food chain [2]. The presence of PTE in an environment have a significant impact on plant functionality in an ecosystem as a result of their accumulation potential including toxicity with some having shown to cause cellular damage in plants and animal cells [4]. The environmental risks of metal(loid)s is primarily associated with their chemical forms or the type of their binding forms and reactivity [5], [6], with metal speciation being vital to the assessment of environmental risks, particular in various matrices such as water, dust, air, soil and sediments [3], [7]. The understanding of these risks is a prerequisite for the development of suitable remediation strategies [8]. To understand such risks, numerous extraction procedures can be used as an assessment guideline to determine mobility and availability.

Sequential extraction procedures are widely used for assessing PTE fractionation, bioavailability including reactivity in soils and sediments [9], with the modified three-stage sequential extraction method being used by The European Community Bureau of Reference (BCR) as a reliable, indicative and widely accepted method, to quantify such concentration of PTE interaction in the environment. In the BCR extraction, PTE fractions are evaluated in three steps: exchangeable and bound to carbonates; reducible (bound to Fe–Mn oxides) and oxidisable (bound to organic matter and sulfides) [10]. Limited studies have been reported on the mobility and bioavailability of PTE in O'kiep.

The objective of this study was (I) to determine the total PTE content, i.e. Al, Cu, Fe, Mg and Mn, and compare their binding forms in representative soil samples, and, (II) to evaluate metal distribution in the sediment samples using sequential chemical extraction (BCR), including (III) to characterize PTEs constituents in the soil using XRF and FTIR.

3.2   Materials and Methods

O'kiep is a small town in the Northern Cape, South Africa and it is a well-known copper mining yielded approximately two million tons of copper [11]– [13].   Okiep located approximately 600 km from North-West of Cape Town as shown in Fig. 3.1.

Figure 2: Map of study area and sampling points

3.2.1   Sediment samples and reagents

Sediment samples (n = 12) were collected from upstream, midstream and downstream along the dried stream bed where there was evidence of effluent flow from a closed mining area, downstream to a surrounding community. For each sampling site, the sediment samples were collected 5 cm below surface, sieved through a 2mm mesh and stored in sterile plastic bags and transported to the laboratory. The sediment samples were milled (<100 µm), dried (25 ℃) for 24

17

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h [2] and homogenized to make composite samples C1 – C6 (Table 3.1) prior to analyses. All the chemical reagents used in this study were of analytical grade. Working solutions were prepared from stock standard solutions by dilution with sterile Milli-Q water (Millipore, USA). The stock standard solutions used in this study were prepared using; Acetic acid (Merck, Germany), Hydroxylamine hydrochloride (HIMEDIA, India), Hydrogen peroxide (Sigma-Aldrich, USA) and Nitric acid (Merck, Germany).

Table 3.1: Description of samples

Sample Name	Sample description	Latitude	Longitude
C1	Upstream	-29.5956707	17.888709
C2	Upstream	-29.597764	17.883976
C3	Slime dams*	-29.5818611	17.876694
C4	Midstream	-29.5961502	17.879916
C5	Tailings*	-29.5964278	17.879167
C6	Downstream	-29.582329	17.87114194

*Potential sources of heavy metals

3.2.2 Experimental procedure

A modified BCR sequential extraction procedure was used to analyze the binding forms of PTE in the sediment samples. The analyses were conducted according to the following standard methods namely; 1) fraction 1: acid soluble PTE bound to carbonates which are susceptible to cation exchange, 2) fractions 2: reducible PTE bound to Fe–Mn oxides and 3) fraction 3: oxidizable PTE bound to organic matter and sulphide [6], [10]. Each stage, the extractant were analyzed using a Thermo iCAP 6000 series (Thermo Scientific, USA) ICP-AES, with NIST traceable standards being used for calibration and quality control. The calibration curve

18

acceptance criteria of $R^2 > 0.9995$ was used, with the instrument conditions set at: RF Power of 1350 W, Carrier gas (Argon) at 0,65 L/min, Aux gas (Argon) at 1.0, Micromist Nebuliser at 2 mL/min and 1 mg/L of Yttrium internal standard.

Mineralogical analyses were performed according to Stellenbosch University's internal standard method, to determine major component analyses with X-Ray Fluorescence (XRF) spectrometer, PANalytical Axios Wavelength Dispersive spectrometer fitted with a 2.4kW Rhodium tube with five analysing crystals (LIF200, LIF220, PE 002, Ge 111 and PX1). To determine the binding groups in the sediment samples, Bruker ALPHA Platinum spectrometer, Germany. Fourier Transform Infrared Spectroscopy (FTIR) was used at wavelength range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

3.3   Results and Discussion

Bioavailability and PTE mobility

Bioavailability of PTEs in the sediments was examined by a BCR sequential method to quantify the redistribution or partitioning of the metals including their various chemical binding forms, i.e. adsorbed (with exchangeable sites), reducible and oxidisable (Table 3.2). It was evident that PTEs in the sediments of the O'kiep are entrapped within the sediment in different binding forms of varying strength, which is indicative of metal reactivity in the sediments. This can be utilized to assess the risk of PTE dispersion and subsequently uptake including mobility within an ecosystem.

19

Table 3.2: BCR Sequential Extraction Results

	Al	Cr	Mn	Fe	Cu	Zn	∑
Sample name	Fraction 1: exchangeable fraction (mg/kg)						
C1-F1	185.9	0.6	154.6	2.5	5103.5	139.0	5586.1
C2-F1	687.6	1.0	62.7	325.1	1685.3	33.4	2795.1
C3-F1	1265.5	4.4	127.5	137.5	956.7	85.0	2576.6
C4-F1	664.5	4.5	27.0	427.8	6013.0	25.8	7162.7
C5-F1	3763.2	10.2	69.0	2677.6	13628.3	1105.8	21254.1
C6-F1	427.4	10.1	29.3	502.9	258.2	16.6	1244.5
	Fraction 2: reducible fraction (mg/kg)						
C1-F2	186.5	4.8	39.0	263.2	21.9	7.8	523.2
C2-F2	196.4	5.2	6.3	213.3	9.4	2.3	432.9
C3-F2	126.4	7.5	0.8	49.5	7.8	1.6	193.5
C4-F2	840.7	8.7	7.1	5904.3	666.0	4.7	7431.4
C5-F2	92.6	4.2	1.6	11552.2	210.0	14.5	11875.3
C6-F2	205.7	7.9	12.4	494.4	63.5	3.4	787.3
	Fraction 3: oxidisable fraction (mg/kg)						
C1-F3	3001	5	3	147	726	36	3919
C2-F3	704	4	21	2345	194	8	3276
C3-F3	304	4	2	87	13	3	412
C4-F3	165	12	2	187	64	4	435
C5-F3	221	4	2	144	40	4	414
C6-F3	504	8	2	157	133	5	809

Slime dams (sample C3) and mine tailings (sample C5) were considered to be potential sources of PTEs as indicated by the high presences of heavy metals, with sample C5 being a greater threat due to the proximity to a densely populated residential area. Sample C5 also had a stronger smell (sulphurous smell) which was observed during sampling, with dark, fine grains, as a result of the mined ore being processed by froth flotation in the past [15]. PTEs in samples C4 and C5 could be as a result of PTE physical mobility, i.e. erosion, owing to finer particle size (200 - 63µm) and other mineralogical characteristics of the sediments collected at these sites [16].

Fraction 1: BCR sequential method indicated that, PTE that were weakly adsorbed onto the solid surface of the sediment, i.e. bounded to carbonates with weak electrostatic bonds, could be easily influenced by the change in the ionic composition of the matrices, and are thus prone to be exchangeable and remobilized downstream of the source point. [17]. The results showed that samples C5 (mine tailings) had the highest total exchangeable PTEs with sample C3 having the lowest exchangeable heavy metals in the sediments. Sample C5, also showed a higher Cu concentration (13628.3 mg.kg^{-1}) which was indicative of the high mobility of metal, in comparison to other metals. The total PTEs extracted in all the sediment samples collectively using the BCR method decreased in the order of Cu> Al> Fe> Zn> Mn> Cr.

Fraction 2: Furthermore, for fraction 2 of the BCR, which involved the mobilization of PTEs bound to an amorphous Fe-Mn oxides constituent including hydroxides, which simulate reductive mobility conditions, indicated that a large quantity (11875.3 mg.kg^{-1}) of PTEs downstream (sample C5) of the source with the largest contribution being attributed to Fe. The concentration of metals bound to the Fe-Mn oxides in all the sediment samples collectively, decreased in the order of Fe> Cu> Al> Mn> Zn> Cr.

Fraction 3: PTEs assessed which are bound to natural organic matter which bioaccumulate in living organisms [18], and which are largely bound to sulphides thus prone to redistribution under oxidation conditions, were largely immobile, with the dominant species being Al (3001 mg.kg^{-1}), which is prone to oxidation. Accordingly, the concentration of metals prone to oxidation decreased in the order of Al> Fe> Cu> Zn> Cr> Mn.

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Generally, the concentration of Al, Cu and Fe indicated a higher extractability in the sediment and thus higher mobility and risk (Table 3.3) in the O'kiep environment. In all the sediment samples, Cu, Zn and Al were predominantly bound to carbonates and were hypothesized to be readily mobilized as previously reported [3]. Cr was determined to be the least bioavailable PTEs as shown by its low acid solubility and oxidisability [17], [19]. Sample C1, C4, C5, and C6 indicated that under reductive conditions, i.e. condition associated with acid mine drainage (AMD), immobile Fe bounded to Fe-Mn oxides including hydroxides, could easily degrade and thus become bioavailable.

Table 3.3: Risk and Mobility Of Potential Toxic Elements

Heavy Metals	Less Risk (Low mobility)		High Risk (High mobility)
Al			■
Cr	■		
Cu			■
Fe		■	
Mn		■	
Zn	■		

Risk Assessment Code (RAC), previously reported by Jain [20], can therefore be used as a criterion to quantitatively determine the risk of PTEs contamination in an environment, by evaluating the percentage of the total metal content present in individual sediment fractions, as determined by the BCR. Organic matter bound PTEs were therefore determined to pose the highest risk to the OCD population [21] due to the weak electrostatic binding mechanism of the PTEs, with PTE contaminants source points (slime dams and tailing stream) being considered to constitute a high risk thus environmental health problem. Generally, the mobility and bioavailability of total PTEs in the sediments decreased in order of exchangeable> reducible> oxidisable, PTEs."

FTIR spectroscopy

The FTIR spectra (Fig. 3.2 and 3.3) are indicative of functional groups within the range of $4000 – 1500$ cm^{-1} whereas spectra between 1500 to 400 cm^{-1} presents the fingerprint region. Spectra bands between 3000 and 3730 cm^{-1} attributed to the hydroxyl group (-OH) were more prominent in samples C1 and C4, with symmetric and asymmetric vibrations being observed at 997 cm^{-1} for samples C1, C2 and C4 and at 1016 cm^{-1} for samples C3 and C5. Sample C5 was associated with a high concentration of silicates and quartz functional groups [22]. The peaks observed in all samples at 517 cm^{-1} and between 766 and 790 cm^{-1} can be assigned to the Si-O-Si functional group [23].
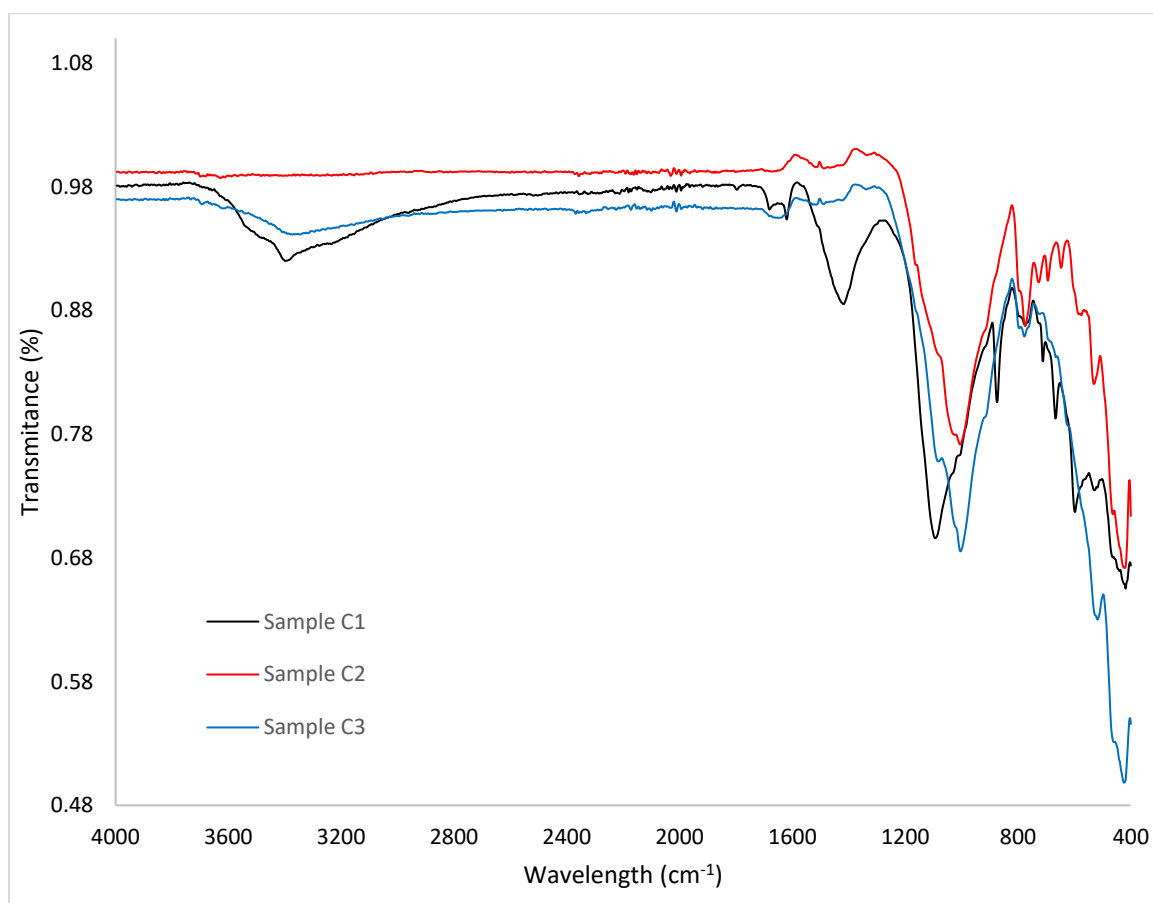
Figure 3: FTIR spectra of sample C1, C2 and C3

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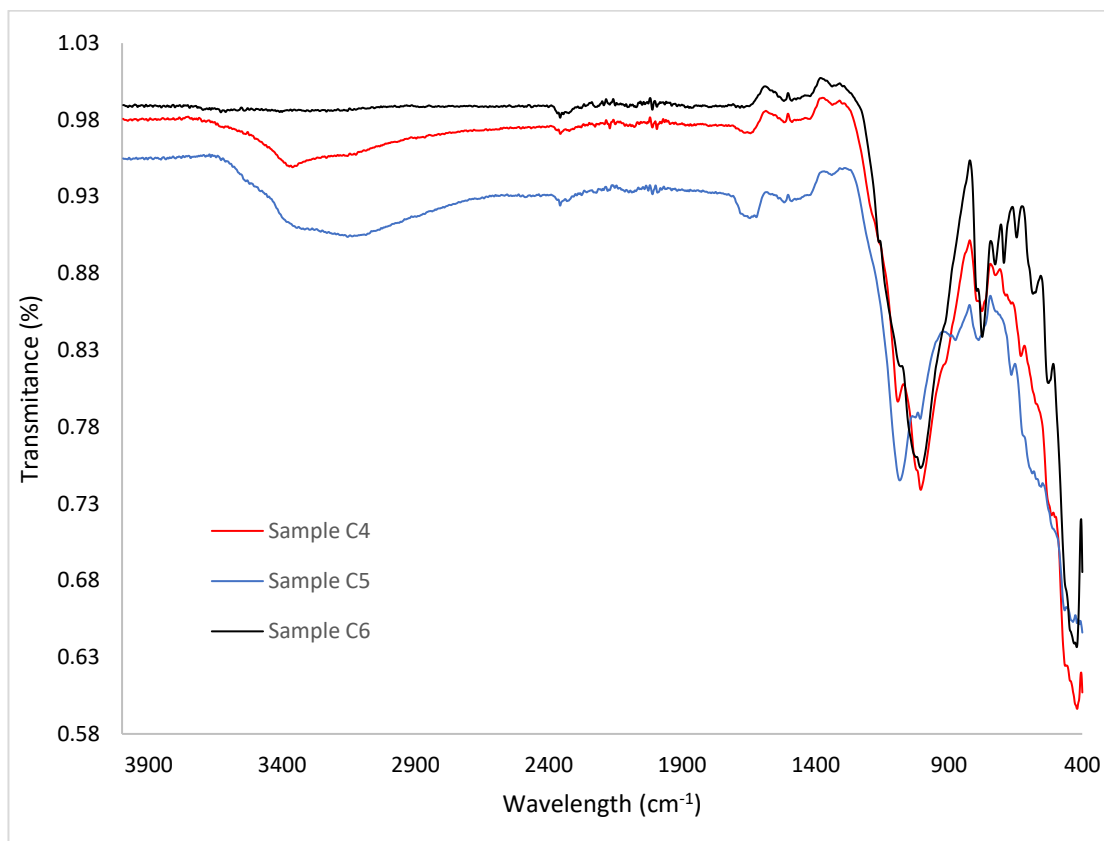
Figure 4: FTIR Spectra of sample C4, C5 and C6

The XRF chemical compositions (Table 3.4) of all the samples indicated the presence of inorganic silicate minerals, such as clay and quartz, with predominant SiO_2, Fe_2O_3, Al_2O_3 and traces of MgO, $Cr2O_3$ and MnO. The dominant minerals represent in the samples (70.2% - 83.4%) for C2-C6 were only accounted for being 52% in sample C1. Sample C4 showed a higher Fe_2O_3 composition (3.84%), compared to downstream, i.e. sample C6, which further supports the hypothesis that the appreciable concentration of PTEs in sample C4 is primarily due physical mobility from sample C4. Although the toxic compounds (heavy metals) were not recorded in the investigated samples, ICP-AES analyses indicated a high copper concentration in sample C1 and thus the lower silicate mineral composition observed.

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Table 3.4: Chemical Composition by XRF Analysis

Chemical composition (wt.%)	Sample name					
	C1	C2	C3	C4	C5	C6
SiO_2	26.06	79.50	44.05	50.82	11.25	78.35
Al_2O_3	7.16	9.91	10.87	11.91	2.12	9.13
Fe_2O_3	3.91	1.66	23.29	16.18	58.11	3.84
MgO	1.30	0.15	1.51	0.93	1.38	0.31
Cr_2O_3	0.11	0.12	0.13	0.13	0.03	0.19
MnO	0.06	0.03	0.08	0.05	0.05	0.05

3.4   Conclusion

Slime dams and mine tailings were considered to be potential sources of PTEs, with mine tailings being identified a greater threat to the community of the OCD due its proximity to a residential. Primarily, Cu, Zn and Al bound to carbonates by a weak electrostatic interaction, were determined to be readily mobilizable and bioaccumulative in the sediments studied. Under reductive conditions, immobile Fe bounded to Fe-Mn oxides including hydroxides, could degrade and thus become bioavailable. Overall, mobility and bioavailability of PTEs in the OCD sediments samples decreased in order of exchangeable> reducible> oxidisable with a high inorganic material, such as clay and quartz, being observed in the sample studies.

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this study are the opinion of the authors.

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Chapter 4

Effect of sediment grain size and total organic matter on potential toxic element bioavailability

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4. CHAPTER 4

THE EFFECT OF SEDIMENT GRAIN SIZE AND TOTAL ORGANIC MATTER ON METAL BIOAVAILABILITY

General overview of article

This research paper serves as a supplementary material to article 01 (Chapter 03). The research paper aims to determine the total organic carbon and particle size distribution in the sediments previously mentioned in article 01.

To archive this aim, the following objectives were addressed; (I) to evaluate total organic matter using loss-of-ignition method and (II) to determine the particle size distribution of the sediments using a laser particle analyser in relation to the effect of solubility and subsequently mobility and bioavailability of PTEs from the sources which further contaminates pollutant free areas.

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The effect of sediment grain size and total organic matter on metal bioavailability

Abstract — Heavy metals in the form of PTEs associated with sediments have been recognized as largest sources of contamination. Among other factors influencing PTE bioavailability and mobility in the sediments, is organic matter (OM) which has a significant role as geo-biosorbent of pollutants including PTEs. In the present study, total organic matter (TOM) and sediments grain size were determined to predict potential PTEs sorption and subsequently mobility in the sediments. The results indicated a high correlation between TOM and fine grain size of the sediment samples with the highest fine fraction (200 – 63 µm) being observed for mine tailings thus highest TOM. Downstream from the source of pollution, TOM was significantly lower with sediments having a coarser particle size (63 – 2 µm).

Index Terms — Bioavailability, Potential Toxic Elements, Total organic matter, Particle size distribution

4.1   Introduction

Metals and metalloids pollutants, herein referred to as Potential Toxic Elements (PTEs), are released to the environment by human activities and are known to accumulate in sediments. Organic matter (OM) in the sediment is a complex heterogeneous component predominantly derived from plants, animal detritus and faecal matter. Plant matter forms a large portion of OM as leaves are deposited as residues within the soil matrix (Baldock et al., 2014, Zhang et al., 2014a), serving as a geo-biosorbent for high affinity contaminants including PTEs in the sediments. To quantify the OM in the sediments, organic carbon is estimated, and in an arid ecosystem organic carbon is presented as total organic carbon (TOC) and inorganic carbon. In addition to metal binding forms, sediment texture, mineralogical composition and physical-chemical transportation, TOC has been previously observed to affect the eco-toxicity and geochemical behaviour of PTEs in the sediments (Armid et al., 2014).

Pollutants such as PTEs interact with OM in sediments forming complex compounds which influence PTEs solubility and bioavailability. PTEs interaction significantly depends on the sediments particle size, and OM have high affinity to fine sediment particle size, and adversative compared to coarse particles size in the sediment (Zhang et al., 2014a, Guven and Akinci, 2013). In the fine sediments, OM phases are considered for their binding of PTEs and reduce their solubility thus reducing bioavailability and mobility due to high TOC (Strom et al., 2011).

Accumulation of PTEs in fine particle sediment enriched with OM will be partitioned in the organic solid phase. Although, this binding form is deemed stable, oxidation of OM by bacterial and animal activities and electron acceptors which influence microbial metabolic processes may alter the OM properties (Hong et al., 2010, Fernandes et al., 2011), thus decomposition of OM and increase in PTEs release, and subsequently high mobility and bioavailability. Degrading of OM may lead to lower sediment pH which is consistent with an increase in oxidative-reduction potential (ORP) which measures the electron availability and facilitate the oxidization rate in the sediment thus an accelerated solubilization of adsorbed PTEs (Zhang et al., 2014a).

The objectives of this part of the study to evaluate total organic matter using loss-of-ignition method and to determine the particle size distribution of the sediments using a laser particle analyser in relation to the effect of solubility and subsequently mobility and bioavailability of PTEs from the sources which further contaminates pollutant free areas.

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4.2 Materials and Methods

4.2.1 Sediment sample collection and analytical method

Sediments samples collected and presented in the study of bioavailability and mobility (Moncho et al., 2017) were also used for this part of the study. Twelve (12) sediment samples were collected and transported to the laboratory in sterile plastic bags and were homogenized to make composite samples C1-C6 (Table 4.1) prior to total organic matter analyses by the loss-of-ignition method. Briefly, the composite samples were dried at 70 °C for 24 h and combusted in the oven at 550 °C for 4 h. Total organic matter, as described by , was calculated using Eq. 4.1:

$$TOM\ (\%) = \left[(B - C)/B\right]x100 \tag{4.1}$$

where B and C: are the weights (g) of dried sediment before and after combusting in the oven, respectively. Particle grain size analysis was performed using laser particle size analyser. Micromeritics Saturn DigiSizer 5200 V1.12 (Germany) laser analyser was used to measure sediment size grain in water aqueous medium.

Table 4.1: Description of Samples

Sample ID	Latitude	Longitude	Sample description of potential source
C1	-29.5956707	17.888709	Upstream of closed copper mine
C2	-29.597764	17.883976	Close proximity to C1 – on route of surface running water towards downstream
C3	-29.5818611	17.876694	Slime dams
C4	-29.5961502	17.879916	Midstream – proximity to tailings, on route to surface running water from tailings
C5	-29.5964278	17.879167	Tailings of the closed copper mine
C6	-29.5823290	17.871141	Downstream on route of surface running water

4.3   Results and discussion

4.3.1   Influence of soil organic matter (SOM)

Soil organic matter (SOM) plays an important role in the environmental ecosystem as a source of nutrients for crops as well as a means of carbon sequestration (Rasmussen, 2006). Thus, evaluating SOM and/or total organic carbon (TOC) is as important in assessment of possible soil contamination and the soils ability to retain pollutants. The SOM values in investigated samples (See Table 4.2) were 15.27% (C1), 0.93 (C2), 9.59% (C3), 9.51% (C4), 20.82% (C5) and 0.88% for C6, respectively. The results showed a higher value of SOM at C5 – sample from copper mine tailings while a minimum value associated with downstream samples from the possible source of PTEs. It is well established that industrial activities are able to impel accumulation of organic matter into the sediments. A study conducted by Seddaiu et al. (2013) concluded that lower total organic carbon is associated with undisturbed soils, this correlates to the results that higher values of SOM values shows a high anthropogenic disturbances near the PTE source, i.e. samples C1, C3 and C5 while undisturbed sediments, i.e. samples C2 and C6 showed minimum SOM values, respectively.

Table 4.2: Soil Organic Matter and Grain Size

Sample ID	SOM (%)	Grain Size (%)		
		Fine	Silt	Clay
C1	15.27	40.49	36.47	6.67
C2	0.93	28.99	9.10	2.67
C3	9.59	11.41	75.65	12.82
C4	9.51	30.77	47.87	11.20
C5	20.82	51.53	27.95	2.05
C6	0.88	7.47	3.16	1.88

The XRF results previously report by Moncho et al (2017) showed that sample C4 showed a higher $FeSO_3$ composition compared to the downstream Sample C6 which suggested the physical mobility of sediment particles from sample C5 (Tailings). Although sample C4 was

considered undisturbed sediments, results showed an appreciable value of SOM which further support the mobility between sample C4 and C5. Furthermore, SOM could enhance the soil and thus increased water holding capacity (Wu et al., 2013) and subsequently PTEs dissolution and mobility through surface runoff water.

4.3.2   Influence of grain size

Total organic carbon values are often associated with finer sediment, with lower TOC values being observed in coarser sediment (Armid et al., 2014). Fig. 4.1 represents the grain size distribution curve for all sediment samples. The results illustrated that coarser grain size were predominantly associated with sample C6, downstream as illustrated by lower overall volume percentage passing through a 200 – 63 µm sieves.

Table 4.2 represent the sediment grains size categorized into fine (200 – 63 µm), silt (63 – 2 µm) and clay (< 2 µm) fractions. Generally, the sediments samples contain appreciable fine and silt fraction with a range of 7.47 - 51.53 % and 3.16 - 75.65%, respectively. The highest fine fraction was observed at sample C5 – mine tailings, while sample C6 – downstream showed a lowest percentage across all fractions and subsequently courser grain size observed. A positive correlation between SOM and clay has been reported in several studies; this correlation is indicated by a lower SOM observed in sample C2 (0.93%) and sample C6 (0.88%) which is consistent with low clay fraction content observed, 2.67% and 1.88%, respectively. Contrarily, appreciable content of SOM (9.59% and 9.51%) was observed in samples with a high percentage fraction of clay, sample C3 and C4, respectively. A negative correlation between clay fractions and SOM was observed in sample C5 – mine tailings, with the results showing the highest SOM (20.8%) of all the samples with low clay content (2.05%) being observed. This suggested that mobility and migration of lower grain size (clay) sediment from sample C5 to close proximity of sample C3; moreover, the physical water channels from mine tailings (sample C5) towards sample C3 further support this hypothesis.
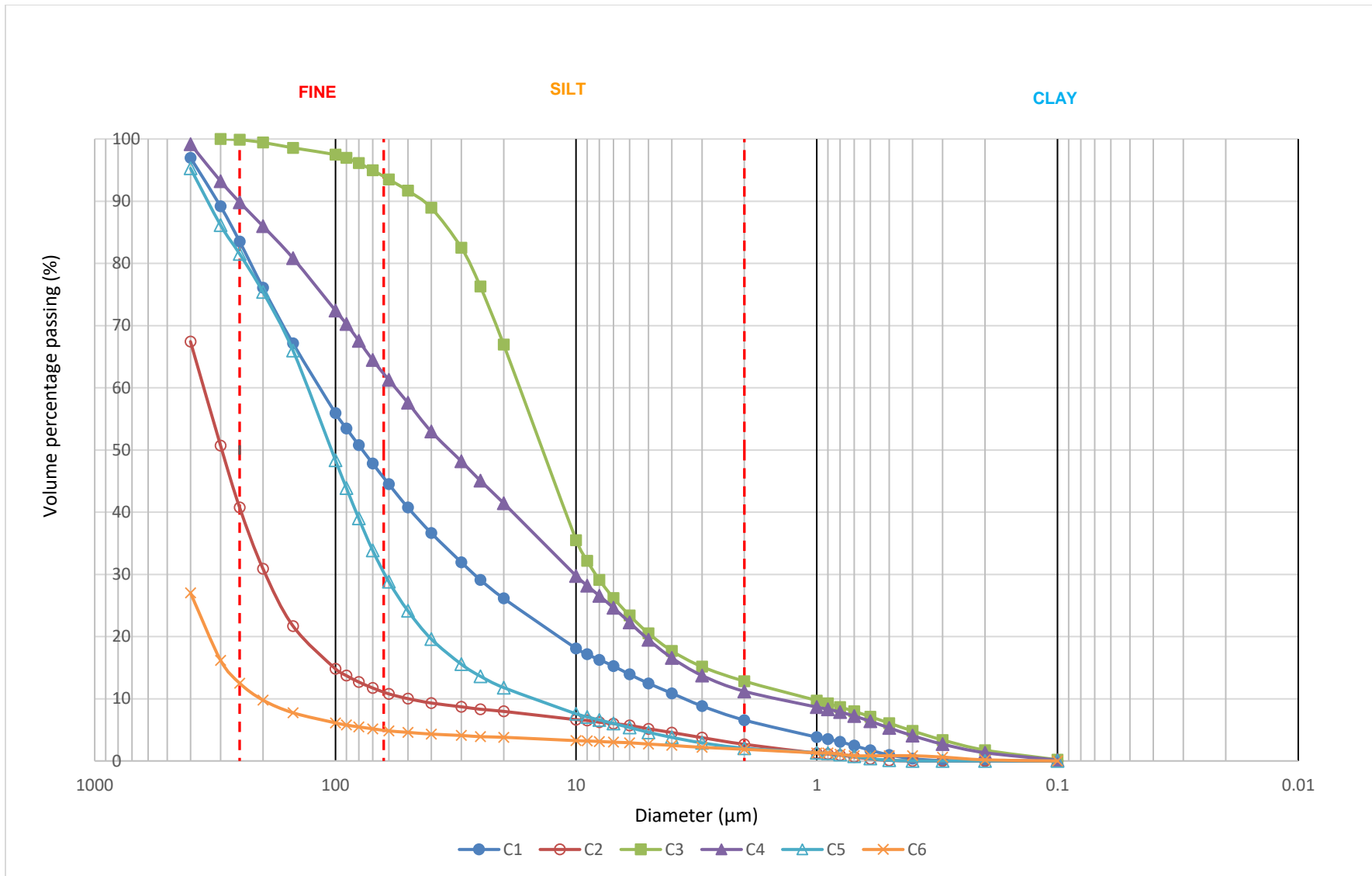
Figure 5: Grain Size Distribution Curve

37

4.4 Conclusion

Some conclusion could be draw from this part of the research: High TOC observed on sample C5 – mine tailings was due to a anthropogenic source. The distribution of sediment grain size suggested the potential mobility of finer particles of sediment from the pollutant, PTEs) source (Sample C5) further polluting downstream areas by surface running water. A positive correction between sediment grain size and TOM with high content of TOM was observed as evidenced in samples with finer sediments grain size.

Acknowledgment

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Chapter 5

General discussion, conclusions and recommendations

5. CHAPTER 5
GENERAL CONCLUSIONS &
RECOMMENDATIONS

5.1 General conclusions

PTEs and other pollutants are bound to the sediment in various binding strengths which influence PTEs bioavailability and mobility in addition to geo-biosorbent in the form of OM, including mineralogical composition, sediment texture and physical-chemical transportation can influence PTEs mobility to prestine areas – with human exposure being a challenge of great concern. The 3-step (fractions) BCR sequential method was used as an indicative method of the reactivity of the PTEs in the sediments to evaluate various binding forms. Generally, the results showed a high concentration of metalloids extracted in fraction 1 where PTEs are bound to carbonates with weak electrostatic bonds that are susceptible to dissolution and redistribution with change of ionic compositions. Slime dams (sample C5) and mine tailings (sample C5) had the highest PTEs with sample C5 considered a high risk to the community surroundings and in close proximity to a closed metalliferous mine.

Soil organic matter (SOM) is geo-biosorbent of PTEs in the sediment which was determined as a function of sediment grain size. Sediments with finer grain size were enriched with organic matter which is susceptible to decomposition by bacterial oxidation and subsequently PTEs dissolution and mobility. Generally, the results showed a high SOM content (20.8%) in sample C5 – mine tailings with majority (51.53%) grain size percentile partitioned in the fine fraction (250 – 63 µm). Sample C3 (Slime dams) and sample C4 (close proximity to mine tailings) showed a clay (>2 µm) content of 12. 82% and 11.20% which appreciable SOM content of 9.59% and 9.51% respectively which is aligned with the literature reviewed with a high content of SOM observed in samples with high clay content. Sample C6 had the lowest content of SOM and clay content which affirms sample C5 as the source of anthropologic pollution by industrial activities – mining.

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Table 5.1: Summary of Results

Sample ID	BCR sequential extraction results			XRF Analysis chemical composition						Soil Organic Matter	Grain size analysis		
	Fractions	Total per fraction	Total per sample	Al$_2$O$_3$	Cr$_2$O$_3$	Fe$_2$O$_3$	MgO	MnO	SiO$_2$		Fine	Silt	Clay
		mg/kg	mg/kg	(%)	(%)	(%)	(%)	(%)	(%)	(%)	<250	250 - 63	>2
C1	F1	5586.12	10027.96	7.16	0.11	3.91	1.30	0.06	26.06	15.27	40.49	36.47	6.67
	F2	523.22											
	F3	3918.61											
C2	F1	2795.11	6503.76	9.91	0.12	1.66	0.15	0.03	79.50	0.93	28.99	9.1	2.67
	F2	432.91											
	F3	3275.75											
C3	F1	2576.63	3182.47	10.87	0.13	23.29	1.51	0.08	44.05	9.59	11.41	75.65	12.82
	F2	193.53											
	F3	412.32											
C4	F1	7162.72	15028.86	11.91	0.13	16.18	0.93	0.05	50.82	9.51	30.77	47.87	11.2
	F2	7431.39											
	F3	434.76											
C5	F1	21254.07	33543.19	2.12	0.03	58.11	1.38	0.05	11.25	20.82	51.53	27.95	2.05
	F2	11875.29											
	F3	413.84											
C6	F1	1244.49	13928.39	9.13	0.19	3.84	0.31	0.05	78.35	0.88	7.47	3.16	1.88
	F2	11875.29											
	F3	808.62											

Furthermore, XRF chemical composition (Table 5.1) indicated the presence of inorganic silicate minerals such as clay and quartz. Sample C6 (downstream) is predominately SiO_2 (78.35%) content while sample C5 (mine tailings) showed a lowest SiO_2 (11.25%) content. The results showed a significant Fe_2O_3 content (16.18%) in sample C4 which suggested physical mobility of sediments from Fe_2O_3 enriched sample C5 (58.11%) towards sample C4. Moreover, high content of Fe_2O_3 is primarily associated with the potential pollution source, i.e. sample C3 (23.29%) and sample C5 (58.11%).

Risk Assessment Code (RAC) criterion is required to evaluate the risks associated with sediments in the Okiep District. Generally, the results showed that the PTEs were weakly bound to sediments and thus susceptible to mobility with copper (Cu) found to pose the highest risk due to the weak bound to carbonates (Table 3.3 – chapter 3). The risk of mobility of the PTEs in the sediments decreased as follows Cu> Al> Fe> Mn> Zn> Cr.

5.2 Recommendation

This research report was a preliminary study of distribution of metalloids thus PTEs pollution in the Okiep Copper District and the following research question/point of interest arose:

- The literature suggests that high soil organic matter (SOM) content correlates to higher clay content, however, the results showed a negative correlation between clay content and SOM of sample C5 (mine tailings) which could be as a results of process ore, this phenomenon requires further investigation.
- In our limited studies, the results showed that an increased sample size would be beneficial to graphically represent the PTEs pollution gradient towards pollutant free areas.

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Appendices

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Majors and Trace analysis by Inductively coupled plasma Optical Emission Spectroscopy (ICPOES/AES)

Instrument used: Thermo iCAP 6000series supplied by Thermo Scientific
Instrument Conditions:

RF Power (W)	1350
Carrier gas (L/min) (Argon)	0,65
Aux gas (L/min) (Argon)	1.0
Nebuliser	2ml/min Micro mist
Internal Standard used	1ppm Yttrium

Element	Wavelength nm	Element	Wavelength nm
Al	396,1	Mn	257,6
As	189	Mo	202
B	249,6	Mo	281,6
Ba	493,4	Na	330,2
Be	234,8	Na	589,5
Be	313	Ni	221,6
Ca	315,8	P	177,4
Ca	396,8	Pb	220,3
Cd	228,8	S	180,7
Co	228,6	Sb	206,8
Cr	283,5	Se	196
Cu	224,7	Si	251,6
Cu	324,7	Sr	421,5
Fe	239,5	Ti	334,9
K	769,8	V	309,3
Li	670,7	Zn	206,2
Mg	285,2	Au	242.7

Figure 6: Google Map Showing Study Area