



**AN EVALUATION OF THE EFFECTS OF TEMPERATURE INTENSITY AND
DURATION ON THE SORPTION PROPERTIES OF MINE TAILINGS
CONTAMINATED SOILS AND THE IMPLICATIONS ON FIRE-AFFECTED SOILS**

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requirements of the degree of Master of Science in Environmental Science**

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DECLARATION

I Khathutshelo Constance Sebola declare that this dissertation is my own work. This work has not been submitted by me or any other individual in part or in full for any degree or examination in any other university. All the consulted sources have been acknowledged and duly referenced in the document.

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ABSTRACT

Soil heavy metal contamination that is caused by anthropogenic activities such as mining is a global concern and so it is necessary for a sustainable remediation strategy to be employed for the contaminated soil to be suitable for various purposes again. Sorption is a chemical process that is employed in most remediation strategies. The soil's sorption capacity is influenced by several soil properties which are in turn affected by soil management including fire events. Wildfires could occur naturally, accidentally or deliberately and may last for a few hours to several days depending on the availability of combustible material, with consequences on soil temperature. As soils experience fire, their temperature could increase, causing changes in soil properties like pH, cation exchange capacity (CEC), electrical conductivity (EC) and organic matter (OM) are observed. These soil properties also influence soil heavy metal absorption capacity and consequently their mobility in the soil environment which is important in the design of most remediation strategies aimed at eliminating or reducing heavy metals mobility in contaminated soils. Some heavy metal remediation strategies make use of organic amendments such as sewage sludge which is also used to improve soil fertility. The use of sewage sludge to remediate heavy metals in soils exploits its ability to immobilize these contaminants in the soil. This study aimed to evaluate the efficiency of sewage sludge as a heavy metal immobiliser in heat affected mine tailings contaminated soils with a view of understanding how fire events may affect the efficiency of sewage sludge as a heavy metal remediation material for soils that have experienced temperature changes. It also aimed to determine how soil properties are affected by different temperatures and the duration of the heating, and the implication of these temperature changes on the bioavailability of heavy metals in contaminated soil.

The mine tailings contaminated soils were collected around a gold mining environment and characterised for their basic physicochemical properties including texture, pH, OM, CEC, exchangeable bases, and heavy metal content. The soils were then heated at different temperatures (100, 200, 300, and 400°C) and for different periods of time (two, four, and six hours). A portion of the heated soil was kept aside as a control sample while the second portion was mixed with sewage sludge at ratios of 80:20 and 60:40 soil: sludge. The soil/sludge mixtures were kept in the open (under natural

conditions) for six months to allow equilibration between the soil and the sludge. The pH, electrical conductivity, cation exchange capacity and organic matter content of the soil/sludge mixtures were again measured. A three step BCR sequential extraction procedure was applied to assess and study the changes in segregation of As, Cd, Co, Cr, Cu, Ni, Pb and Zn in the different soil geochemical fractions. The BCR extraction procedure was applied on the heated, unheated, and sludge amended soils, as well as on the heated soils to which sludge had not been added.

The soil pH increased with increasing temperature and the duration of heating and at high temperatures, the soil organic matter was destroyed. At lower soil temperatures of below 200°C, there was a decrease in soil cation exchange capacity while at a temperature of 400°C, an increase was observed. An increase in soil electrical conductivity was observed when the soil temperature was raised above 200°C and when it was held at this temperature for long periods while the opposite pattern was observed at 100°C. Arsenic, Zn and Co had the highest concentrations in the tailings contaminated soil among the studied metals whereas Cd had the lowest. There was a decrease in the total concentration of the heavy metals after the soil experienced increased temperatures except for Cd and Cu where there were no significant impacts. Sludge addition was shown to be a good immobiliser for As, Cu and Pb in the heat affected tailings contaminated soils. For the success of any soil heavy metal remediation strategy that makes use of the sorption ability of the soil, information on whether the soil has experienced fire events is needed because the fire events affect soil OM and the mineralogical properties which play a pivotal role in the sorption capacity of soils.

Key words: Heavy metal mobility, tailings contaminated soil, sewage sludge, temperature intensity and duration, mobility factor

LIST OF ACRONYMS AND UNITS

AMD	Acid Mine Drainage
ANOVA	Analysis of Variance
AR	Analytical Reagent
BCR	Community Bureau of Reference
CEC	Cation Exchange Capacity
CF	Contamination Factor
Co	Average concentration of heavy metal
°C	degree Celsius
EC	Electrical Conductivity
ERWAT	Ekurhuleni Water Care company
F1	Exchangeable and Carbonate Fraction
F2	Reducible Fraction
F3	Organically Bound Fraction
F4	Residual Fraction
g	gram
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
kV	kilo volt
kW	kilo watt
L/min	Litres per Minute
mA	milli ampere
mg/kg	milligram per kilogram
ml	milli liter
MF	Mobility Factor
M	Molarity
N	Normality
OM	Organic Matter
ppm	parts per million
PSD	Particle size Distribution
rpm	revolution per minute
UNISA	University of South Africa
µm	micrometer
XRF	X-ray Fluorescence

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CHAPTER ONE

INTRODUCTION

1.1. Background

Soil is one of the environmental resources which humans need for survival and development. However, the quality of soil can be negatively affected by several anthropogenic activities such as mining, industrialisation and agriculture (Yao *et al.*, 2012), and management techniques such as the application of fertilisers and soil amendments as well as the prescribed fire incidents that are used for various land use practices. A common contaminant that is introduced to the soils from these various land uses is heavy metals. According to Fashola *et al.*, (2020), heavy metals describe the elements that have molecular weights, density and atomic numbers greater than 53g/mol and 20, 6g/cm³ respectively. They naturally occur in soils in trace amounts but due to human activities, their concentrations have been elevated. The human activities which have contributed to heavy metals in the environment include but are not limited to the mining of metals such as gold, platinum, nickel, and copper. The Acid Mine Drainage (AMD) that is produced during the mining of gold (Au), copper (Cu) and nickel (Ni) is associated with significant concentrations of heavy metals (Akcil & Koldas, 2006). Several studies have reported high concentration of arsenic (As), Iron (Fe), chromium (Cr), Ni, cobalt (Co), manganese (Mn), Cu, lead (Pb), Ni and zinc (Zn) in soils around gold (Antwi-Agyei *et al.*, 2009) Cobbina *et al.*, 2013; Naicker *et al.*, 2003) and platinum mines (Gzik *et al.*, 2003). Due to its acidity, AMD causes heavy metals to be more mobile in the environment with several consequences on plants (Naicker *et al.*, 2003).

Su *et al.*, (2014) stated that the high Cu concentration and its availability in soil could affect citrus seedlings whereas high Cd concentration was found to inhibit the growth of cabbage and bean seedlings. More information on the impacts that heavy metals have on plants can be found in Wang *et al.*, (2006), Seregin & Kozhevnikova, (2006) and Alaoui-Sossé *et al.*, (2004). The exposure of humans to high concentrations of heavy metals affects human health. Mercury for example damages the kidneys and it causes brain damage in the early stages of exposure while chronic exposure causes damage to the cerebellum (Fashola *et al.*, 2016). According to Su *et al.* (2014), Cd

disrupts calcium (Ca) metabolism which can damage bone structure. Arsenic is reported to cause lung, kidney, and bladder cancers, whereas Mn can affect the nervous system and causes malfunctioning in child development (Fashola *et al.*, 2016). The details regarding the dangers of heavy metal exposure to humans are also documented in studies conducted by Singh and Kalamdhad (2011) and Yang *et al.* (2018).

Soil is a major channel through which plants, humans and other animals become exposed to the heavy metals that are introduced into the environment through mining. The behaviour of these heavy metals in the soil environment is controlled by several soil properties which include soil texture, organic matter, pH, clay mineralogy and the Cation Exchange Capacity (CEC). These properties are affected by various management techniques including burning to improve soil productivity. Burning could occur naturally or through deliberate fire events.

Certini (2005) describes the two categories of fires that could occur in any environment; and these are prescribed fires (controlled) and wildfires. Prescribed or human induced or man-made fires are normally used as a management tool to clear land for agriculture, or to eliminate crop residue on cropped fields after harvest, and also to rid fields off plants (Bento-Goncalves *et al.*, 2012). They also promote habitat diversity, stop bush encroachment, and control and/or eliminate pathogens (Ngole-Jeme, 2019). Naturally occurring or wildfires are described as non-structured fires which occur due to natural processes or phenomena such volcanic eruptions, lightning, and sparks from rock falls (Certini, 2005; Bento-Gonçalves *et al.*, 2012). Whether prescribed or wild, fires can result in changes in soil temperatures which could result in unintended consequences including but are not limited to changes in the ecosystem structure and damage to the chemical, physical, and the biological properties of soil.

Depending on the intensity and duration of a fire, the soil could experience variable changes in its properties due to the changes in the temperature. According to Ngole-Jeme (2019), Certini (2005), and González-Pérez *et al.*, (2004), during fire events, soil organic matter (OM) could vaporise when the soil temperature gets to 100°C as moisture is lost. Lignin and hemicellulose decompose at soil temperatures of between

130°C and 200°C, whereas cellulose dehydrates at soil temperatures of 280°C. At soil temperatures of between 500 and 600°C, soldering takes place, and when soil temperatures are raised to between 800 and 1500°C flaming/igniting occurs. The mineralogical changes that take place in soil as a result of the temperature changes that are caused by fire are influenced by the soil moisture content and they differ according to the type of soil. According to Tan *et al.*, (1986), a fire which results in soil temperatures that are below 500°C does not affect soil mineralogical assemblage but Zihms *et al.*, (2013) as well as Yusiharni and Gilkes (2010) have also reported that at soil temperatures of between 200°C - 600°C, there are changes in soil mineralogical structure. Shaheen *et al.*, (2013b) states that soil organic matter and mineralogical composition affect soil CEC and consequently soil sorption capacity. The variation in organic matter and the minerals composition could therefore impact the soil's CEC. According to Zavala *et al.* (2014), the soil CEC decreases after a soil experiences fire while Ulery *et al.*, (1996) reported a 50 to 70 % decrease in CEC of burnt soil compared to unburnt soil. Ulery *et al.*, (1996) further indicates that at a soil temperature of 250°C where soil experience charring of humified organic matter, a greater percentage of CEC gets lost.

Due to their high CEC and influence on heavy metal sorption, organic materials including biosolids are frequently used to address issues of heavy metal contamination in soil (Khalid *et al.*, 2016). The use of organic amendment is environmentally friendly because organic materials do not only adsorb heavy metals, but they also improve the physical properties of the soil, enhance plant growth, and reduce bio-accessibility and plant absorption of heavy metals (Khan *et al.*, 2017). The effectiveness of the organic materials is, however determined by the soil's mineralogical composition, CEC, pH, and organic matter content, which interacts with the organic material to increase the adsorption of heavy metals. When the soil experiences changes in temperature because of fire events, these properties are affected which in turn directly influences the interactions between the soil and the organic amendment as well as the ability of the organic amendment to adsorb heavy metal in the contaminated soil.

Research has been conducted to evaluate the utilisation of organic amendments in the remediation of mine-derived-heavy-metal contaminated soils (Borkowski &

Kwiatkowska-Malina, 2017; Khan *et al.*, 2017). These studies have focused on the soils which have not been affected by fire events. There is paucity of knowledge regarding the effect of soil temperature changes on soil sorption properties. This study was designed to assess how soil properties are affected by changes in soil temperature and the implication of these changes on the mobility of metals in contaminated soils. It also aimed to evaluate the effectiveness of biosolids as a remediation material for heavy metal contaminated soils that have undergone temperature induced changes and the implication of the use of biosolids to remediate fire-affected heavy metal contaminated soils.

It is of paramount importance that mining companies and corporations in any area have full knowledge of the impacts that their operations are having on the environment and neighbouring communities. Mining operations introduce heavy metals into the soil and cause air pollution which has detrimental effects on soils, plants, water resources, and human health. It has been reported that people in mining villages suffer from various types of sickness including tuberculosis (Hota & Behera, 2015). Hota and Behera (2015) further report that crop yield and the nutritional value of crops can be diminished due to soil heavy metal contamination. If the water and soil in the surrounding areas of mines are contaminated, the farmers will be affected as their crop yields will decrease. This may contribute to food insecurity and the poor nutritional status of residents that are reliant on food supplies from such areas. The information from this study will, therefore, be beneficial to farmers in the surrounding areas of mines in understanding the level of soil heavy metal contamination in their area.

The study's results will also assist gold mining areas with the provision of data that will inform them of the types of, and the levels of heavy metals which are being introduced into the surrounding soils so that appropriate remediation strategies may be employed. This study will bring to light the potential changes that may be brought about by fire events on the physical properties of soils, and the effect that fire would have on the ability of the soil to attenuate heavy metals. The results will also be beneficial to environmentalists as it will give them an idea on whether sewage sludge can be used as a remediation material for contaminated soils that have been affected by fire events. The results from this study would also be beneficial to other mining regions with similar soil type and climatic conditions.

1.2. Problem statement

Heavy metals affect soil productivity, crop yields, and water resources. The contamination of arable soils with heavy metals may affect crop productivity with dire consequences on food security. Mining has been going on in south Africa for decades. Few studies have, however, explored the effect of mining activities on soils in some mining areas. There is a need to know how mining activities are contributing to the heavy metal content in soils in their vicinity.

In many agricultural communities around the world, fire is utilised as a soil nutrient management tool. In some instances, burning takes place underneath the soil and fires could sometimes persist for more than a week (Certini, 2005). Under these circumstances, the soil temperatures could be considerably increased resulting in changes in soil organic matter, and mineralogical composition which affects the soil sorption capacity (Certini, 2005). Fires have also been shown to increase soil pH which is associated with the oxidation of some elements in soils. It is, therefore, necessary to determine how soil temperature changes affect the properties of soils contaminated with heavy metals in an endeavour to understand the implication on the mobility of heavy metals in such soils.

Diverse remediation techniques have been employed to remediate heavy metals in soils. These methods vary in their conditions of use and the cost involved. Su *et al.* (2014) indicated that the physical methods of soil remediation are very costly in that they need manpower and material resources and can only be utilised in a small area of the contaminated soil. Khalid *et al.*, (2016) stated that metalloids and heavy metals contamination in soil can be completely alleviated by physical remediation techniques but these are destructive and can have a huge financial implication. It is further indicated that phytoextraction is a time consuming technique and is applicable for soils where the level of contamination is low to moderate. Sarwar *et al.*, (2017) state that the phytoremediation method can be applied as a soil remediation procedure but for the process to be effective it will need to be modified or complemented by either physical or chemical techniques which can then make the process to be costly. Khalid *et al.*, (2016) further indicated that chemical methods are not good for the environment because additional contaminants could be released during the process with

detrimental effects to the environment. These limitations can be dealt with by applying organic amendments such as sewage sludge which decrease metal bioavailability.

Recent advances have been to convert sewage sludge into a resource by using it to stabilise heavy metals in soils among other uses. This however depends on the properties of the soil which may be altered during fire events. The changes in the soil properties that are caused by the soil temperature changes during a fire event could have an implication on the efficiency of sewage sludge as an organic heavy metal immobilisation material. The effectiveness of organic amendments on soils which have been subjected to fire events of different temperature and duration has not been studied.

1.3. Research Objectives

1.3.1. Main objective

The main objective of this study is to evaluate the effects that changes in soil temperature and the duration of heating have on the mobility heavy metals in mine tailings contaminated soil and the efficiency of sewage sludge as a heavy metal immobilizer in heat affected soils.

1.3.2. Specific objectives

The specific objectives for this study are:

- To determine the level of heavy metal contamination in soils around a gold mine.
- To determine the effects of temperature changes and duration of heating on the properties of contaminated soil.
- To determine how temperature changes affect the heavy metal mobility in soils contaminated with gold mine tailings.
- To determine whether the ability of sewage sludge to bind heavy metals differs in soils that have been experienced temperature fluctuations
- To understand the implications of fire events on contaminated soils.

1.4. Research Questions

- What are the effects of temperature increases and the duration of heating on the properties of contaminated soils?
- How does changes in soil temperature and the duration of heating affect heavy metal mobility in the soil environment?
- Does a change in the temperature of contaminated soils affect the effectiveness of sewage sludge as a heavy metal immobiliser?
- What are the implications of using sewage sludge to remediate mine tailings contaminated soils that have been affected by fire events?

1.5 Layout of the study

Chapter 1: Introduction

This chapter introduces the content of the study, explains why the topic was chosen and further discuss the objectives of the study as well as presenting the research questions which the study aimed to answer.

Chapter 2: Literature review

This chapter discusses the theoretical basis of the study and what other researchers found out on the topic.

Chapter 3: Research methodology

This chapter explains how the research was done. It explains how the samples were collected and prepared for analyses and further explains the methods followed for the determination of all soil parameters. How the data that was generated during this study was analysed and interpreted is also included in this chapter.

Chapter 4: Discussion of results

This chapter presents the results of all the analyses that were done on the samples. The chapter discusses the effect of temperature intensity and duration of heating on soil properties and the concentration of heavy metals in the soils.

Chapter 5: Discussion of results

The chapter discusses the effects of temperature changes and sludge addition on the fractionation of heavy metals in soils

Chapter 6: Concluding remarks

This chapter provides overall concluding remarks of the study, explains the recommendations based on the study as well as explains possible future studies.

1.6 Concluding remarks

Fire events may occur naturally, or they could be accidentally or deliberately started. Whatever the reason of any fire event, it results in changes in soil temperature with unintended consequences on soil properties which could render the soil unusable or some remediation technologies ineffective. Methods such as phytoextraction, phytoremediation, and chemical methods can be used to remediate heavy metal contaminated soil, but these methods can be expensive and require a lot of resources which then necessitates the use of more affordable methods and resources including organic amendments. Studies such as these are necessary in South Africa where there is a high density and history of mining activities and a high probability of fire events.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Heavy metals are present naturally in the soil as a result of chemical and physical processes of weathering and pedogenesis, but they could also be introduced into the soil by human activities. Soil management techniques such as the addition of compost and manure, the application of fertilisers, the use of mulch and the use of fire to burn shrubs or vegetation improve soil fertility (Bronick & Lal, 2005) but some of these techniques introduces heavy metals into the environment. Hundreds of thousands of hectares of both forest and bush land are annually burnt by both man-made and natural fires which could result in an increase in soil temperature. In some instances, these fires take place underneath the soil and the fires could sometimes persist for more than a week (Certini, 2005). Under these circumstances, the soil temperatures could be considerably increased resulting in fluctuations in soil properties (Certini, 2005). This could have an implication on the remediation technologies that are used to treat soils that are contaminated with heavy metals. This chapter reviews literature on the sources of heavy metals in soils and looks at the effects that these heavy metals may have on the different environmental sectors. It also looks at the various heavy metal remediation strategies used in managing heavy metals in soils with emphasis on sewage sludge. The factors affecting the efficiency of sewage sludge as a heavy metal immobilizer in soils are examined and the role that changes in soil temperature may have on the factors and the consequences on the choice of remediation strategies for heavy metals in contaminated soils are presented.

2.2 Sources of heavy metals in soils

2.2.1 Natural sources

Heavy metals occur naturally as they originate from parent materials through physical and chemical processes of weathering, and pedogenesis. The types of rocks that constitute the parent material and the prevailing environmental conditions determine the concentrations and the types of the heavy metals that are present in any soil. Table 2.1 indicates typical ranges of heavy metals in igneous and sedimentary rocks (Nagajyoti *et al.*, 2010). Elements such as Cr, Zn, Ni and Cu have the highest

concentration among those metals that occur naturally or those that are found in rocks while As and Cd have the lowest concentration according to the data summarised in Table 2.1 below.

Table 2.1: Typical concentrations of heavy metals in different rock types

Metals	Metal concentration (mg/kg)				
	Basaltic igneous	Granite igneous	Shales and Clays	Black shales	Sand stone
As	0.2 – 10.0	0.2 – 13.8	-	-	0.6 – 9.7
Cd	0.006 – 0.6	0.003 – 0.2	0.0 - 11	0.3 – 8.4	-
Cr	40.0 – 600.0	2.0 – 90.0	30.0 - 590	26.0 –	-
Co	24.0 – 90.0	1.0 – 15.0	5.0 - 25	7.0 – 100.0	-
Cu	30.0 -160.0	4.0 – 30.0	18.0 - 120	20.0 – 200.0	-
Pb	2.0 - 18.0	6.0 -30.0	16.0 - 50	7.0 -150.0	1.0 – 31.0
Mo	0.9 – 7.0	1.0 – 6.0	-	1.0 – 300.0	-----
Ni	45.0 – 410.0	2.0 – 20.0	20.0 - 250	10.0 – 500.0	-----
Zn	48.0 -240.0	5.0 -140.0	18.0 – 180	34 – 1500.0	2.0 – 41.0

(Nagajyoti *et al.*, 2010)

2.2.2 Anthropogenic sources

Anthropogenic activities including agriculture, vehicular emissions, waste disposal and industrial activities have contributed to an increase in the heavy metal content that is found in soils which are harmful to plants, humans and animals (Khalid *et al.*, 2016). Heavy metals in soils tend to build-up as a results of the constant application of fertilisers to the soil (Nagajyoti *et al.*, 2010). Cadmium, As and Pb have been detected in soils where pesticides such as potassium nitrate, zinc sulphate, ammonium sulphate and potassium sulphate are used for disease control in wheat growing fields, thereby implying that their constant use could also result in soil pollution with heavy metals (Atafar *et al.*, 2010). The utilisation of organic manure to enhance soil productivity has also been reported to increase heavy metal concentrations in soil. A study conducted by Ramadan and Al-Ashkar (2007) shows that chicken manure contains Zn and Pb which can be distributed to the soil when this type of manure is utilised. Hseu (2004) also reports that pig manure contains high levels of Cu and Zn with Nicholson *et al.*, (1999) reporting the same for cattle manure. Cadmium, Pb and Zn concentration have been shown to increase in vegetables grown in soils where farmyard manure was

utilised as fertilizers (Malan *et al.*, 2015). Ngole and Ekosse (2012) also report an increased level of heavy metals including Co, Cu, Ni, Zn, and Pb in sludge-amended soils. These studies also indicate the influence of agricultural activities on heavy metals concentrations in soils.

Various industries including mining, tannery, paint, photography, chemical and refineries release different heavy metals during various processing activities. Metals such as Cd, Pb, As, Cr, Cu, Ni, Hg, Zn and Mn are associated with mining and smelting and they have been reported in soils around coal, and gold mining environments (Wuana & Okieimen, 2011; Rösner & Van Schalkwyk, 2000). It is also reported by Abdul-Wahab & Marikar (2011) that heavy metals such as Co, Cu, Cd, Pb and Zn were found to be in high concentration in soil around the gold mining area in Oman. In another study conducted by Ako *et al.*, (2014) and Nuhu *et al.*, (2014) in the gold mine tailings in Nigeria and Kenya As, Pb, Hg, Cu, Ni, Cd, Co, Zn were among the heavy metals which were found in high concentrations. At times, this contamination is as a result of poor management of the tailings dams during mining operations and long after mining has ceased, which can result in the escape of seepage that may adversely affect the environment (Rösner & Van Schalkwyk, 2000). Strezov and Chaudhary (2017) report that steelmaking industries were linked to a higher concentration of As, Fe, Cr, Cu, Ni and Mn in soils. The refining of crude oil generates large quantities of hazardous waste and so does the burning of fossil fuel. The improper disposal of these wastes can lead to soil contamination by metals such as Cd, Cr, Ni, Pb, Sr, Ti, V and Zn (Schroder *et al.*, 2000). Other industries such as dye and pigment industries, pharmaceuticals, glass, nuclear technology and chloro-alkali production industries introduce metals such as, Cu, Pb, Hg and Fe into the environment which results in soil and environment pollution (Nagajyoti *et al.*, 2010).

Vehicular emissions contribute greatly to heavy metal pollution as they continually burn fossil fuels and release metals such as Pb, As, Zn, Ni and Cd along the roadside (Ozaki *et al.*, 2004). Though Pb is no longer added to fuel due to various regulations, a study conducted by Ozaki *et al.*, (2004) reported that the yellow and red markings as well as the grey guardrail on the roads were the sources of Pb in the soils that are found on road sides. The metals such as, Zn, Ni, Cd and Zn in the soil along the roadsides originate from tyre rubber and its abrasions. As the traffic volume increases

during the holiday season and at peak hours, these metal concentrations increase as well (Ozaki et al., 2004). Chen et al. (2010) opines that in Beijing, traffic volume has affected the concentrations of As, Pb, Ni, Cd, Cr and Cu that are present in roadside soils. Similar studies conducted in Iran (Solgi et al., 2016), and in Cameroon (Ngole-Jeme, 2016) produced similar outcomes.

The heavy metals which are found in wastewater streams and in municipal waste include Zn, Pb, As, Ni, Cd, Hg Cr and Cu (Su *et al.*, 2014). Although the heavy metal concentrations in wastewater are low, the continuous watering of land with waste water can ultimately lead to a heavy metal build-up in the soils (Wuana & Okieimen, 2011). The municipal garbage which is discarded in landfills comprises of dangerous substances in the form of paints, pharmaceuticals, batteries and metal products (Slack *et al.*, 2005) which all contain various heavy metals. Hence the leachate from the municipal waste could contain high level of heavy metals which could be eventually introduced into the surrounding soils. In the studies that were conducted by Abu-Daabes *et al.* (2013) and Xie *et al.* (2015), heavy metals such as Pb, Al, Zn and Co were present in landfill leachate but at a very low concentration, whereas As, Cr, Mn, Ni, and Cd were present in high concentrations.

The mining and processing of metal ores have a dualistic outcome for the society; enhancing the economy of the country through its production but also ushering serious detrimental environmental contamination especially in the form of soil contamination (Liao *et al.*, 2016). During mining, Acid Mine Drainage (AMD) which contains high amounts of heavy metals and radionuclides is produced (Rosner & van Schalkwyk, 2000). Mine tailings and AMD are considered the principal sources of soil and ground water contamination in mining areas (Rosner & van Schalkwyk, 2000). Antwi-Agyei *et al.*, (2009) have shown that As is the main contaminant in soils around gold mine tailings in Ghana. Vogel and Kasper (2002) indicate that soils in different areas around abandoned gold mining tailings in Francistown Botswana contain elevated levels of heavy metals. Another study by Gzik *et al.* (2003) at a platinum mine indicated that Cu, Cd, Pb, Cr, Ni and Zn were the main soil contaminants. These studies show that mining contributes heavily to environmental pollution.

2.3 The effects of heavy metal on the environment

2.3.1 Effect on soils

Heavy metals present in the soil negatively influence soil properties, processes, plant productivity, and other ecological functions (Friedlova, 2010). At elevated levels, they reduce soil fertility by disrupting microbial activities (Khalid *et al.*, 2016). As the metal concentrations increase, there is a decrease in the number of beneficial microorganisms which in turn affects the organic matter turn-over negatively thereby resulting in less nutrients in the soil (Chibuike & Obiora, 2014). Friedlova (2010) reports that the microbial enzyme activities of dehydrogenase and arylsulphatase decrease with heavy metal contamination because of the bonding between heavy metals and their substrate. The build-up of Cu and Ni in the soil may result in extreme shortage of nutrients such as Ca, Mg and K in the organic layer as a result of the strong inhibition on mineralisation of these nutrients from litter fall (Derome & Lindroos, 1998).

2.3.2 Effects on plants

Plants can take up essential elements such as Ca, Mg, Co, K, Cu, Mn, Fe, K, Mo, Se, Na, Zn, Ni, and V from the soil. They also possess the ability to store non-essential elements such as Al, Cd, As, Cr, Au, Hg, Sb, Pb, Te, Pd, and U, which are of no biological significance (Jadia *et al.*, 2009). Elevated levels of heavy metals in soil can damage plant cell structure and replace essential cations (Boonyapookana *et al.*, 2005). Boonyapookana *et al.* (2005) showed that Pb causes chlorosis and stunted growth in sunflower and tobacco plants. Wang *et al.* (2007) showed that rice height decreases with an increase in soil arsenic concentrations. The study further reported that in the presence of Cd and Pb, there is a decline in photosynthetic rate and CO₂ deficiency occurs in plants as a result of the meta- induced distorted chloroplast ultrastructure and stomatal closure. Vassilev and Yordanov (1997) show that water content and transpiration rate decrease in a plant that has been continuously treated with a solution of Cd. According to Alaoui-Sossé *et al.* (2004), the high concentrations of Cu in the soil lead to an unbalanced nutrient uptake by the plants. A high heavy metal content in soils could therefore have an implication on agricultural productivity and vegetation cover generally. This may explain the existence of barren land around mines where soil heavy metal concentrations are high.

2.3.3 Effects on water

According to Naicker *et al.* (2003), surface water quality is directly influenced by mining. Not only does it lower the pH of the water, it also contributes to the high levels of various metallic elements in the water. The low pH and high sulphate of surface water resources around mines caused by the oxidation of pyrite renders it unsuitable for drinking purposes. Naicker *et al.* (2003) further indicated that mining affects not only the pH of surround surface water bodies but its quality generally. A study done by Ravengai *et al.* (2005) in the gold mining belt in Zimbabwe showed surface water pollution with Zn, Pb and Ni. Mining activities do not only affect surface water bodies but the aquifer could also become contaminated due to seepage of contaminated water which could result in the contamination of groundwater. Studies by Naicker *et al.* (2003) indicated that in Au mining areas in Johannesburg South Africa, the surface and ground water were rich in Zn, Pb, Ni, Cr, and Co. Cobbina *et al.* (2013) also reported similar results in the gold mining areas in Ghana. Cobbina *et al.* (2013) further report that due to mining activities, the water which is used for consumption is found to contain high levels of heavy metals such as, Mn and Cd. Nitrate which originates in leachate from spent ore was also found to be high in the water presenting a health threat to infants. Due to the presence of Fe, Cd, Cr, Zn, Pb and Mn in soils, the ground water was found not to be suitable for consumption purposes while it was suitable for irrigation purposes (Zakir *et al.*, 2020).

2.3.4 Effects on man

The increased heavy metal concentrations in agronomic soil results in an increase in heavy metal absorption by crops with dire consequences for people ingesting these crops (Khalid *et al.*, 2016). Ingestion, inhalation and dermal contact are routes through which heavy metals can find their way into the human body (Khan *et al.*, 2017). Of the three ways, food consumption or ingestion is the most common pathway (Ferré-Huguet *et al.*, 2008). Heavy metals have long biological half-lives and can be stored in the human body for extended periods (Arora *et al.*, 2008). Depending on the frequency and the period of exposure, the repercussion of heavy metals on humans can be acute or chronic. Health issues such as kidney problems, bone diseases and cardiovascular problems are triggered by the continuous consumption of foodstuff which contain high heavy metal content and can result in the build-up of these metals in different human tissues (Järup, 2003). Zhuang *et al.* (2009) showed that children

who grew up around mining areas had higher Pb levels in their blood than those living in non-contaminated sites because of the consumption of drinking water and vegetables that were planted in the area. Table 2.2 presents a summary of the heavy metals that are associated with human health threats.

Table 2.2 Health effects of metals on humans and sources of heavy metals

Metal	Target organs	Primary sources
Arsenic	Lungs, skin, and nervous system,	Dusts from industrial sources, use of polluted water
Cadmium	The pulmonary system, the kidneys, and the skeletal, system	Dusts from industrial sources, fumes from various factories and ingestion of polluted water and food
Chromium	Lungs	Industrial dust, fumes and polluted water and food
Manganese	Nervous system	Dusts from industrial sources and fumes from various sources
Lead	Nervous system, kidneys	Dusts from industrial sources, fumes and polluted water and food
	Hematopoietic system	
Nickel	Lungs, skin	Dusts from industrial sources, aerosols
Tin	Nervous, lungs system	Medicinal uses, dusts from industrial sources
Mercury	Nervous system	Dusts from industrial sources fumes and polluted water and food
	Kidneys	

(Adopted from Mahurpawar, 2015)

2.4 Methods used in remediating heavy metal contaminated soil

Soil remediation is the process of restoring soil to its original condition before disturbance (Jadia & Fulekar, 2009). Wuana and Okieimen (2011) indicated that there are three technologies that are capable of remediating soil heavy metal contamination namely: physical, biological, and chemical methods.

2.4.1 Physical remediation methods

These techniques are mainly suitable for small contaminated sites (Yao *et al.*, 2012b) and include methods such as vitrification, soil isolation, soil replacement, and electrokinetic remediation. **Soil replacement** is a physical remediation method where the contaminated soil is replaced with uncontaminated soil. **Soil isolation** is divided into three types namely: isolation, capping and surface barriers. Soil isolation involves separating the heavy metal contaminated soil from the uncontaminated soil (Khalid *et al.*, 2016). Soil capping is used to provide an un-penetrable obstacle to avoid the additional release of contaminants from the soil into surrounding environments. Subsurface barriers are commonly utilised as isolation barriers to prevent the coming together of contaminated water and the soil while ensuring that ground water at a contaminated site does not flow. **The vitrification** technology involves heating soil at temperatures of about 1 400 to 2 000°C to volatilise and liberate the pollutants from the soil (Yao *et al.*, 2012). Liu *et al.*, (2018) states that vitrification process is very destructive and soil which has undergone this process cannot be used for agricultural purposes because the soil becomes glass-like. In the **electrokinetic remediation** technology, a current is transported between a cathode and an anode that is implanted in soils that are contaminated with heavy metals. It is suitable for soils with low permeability and low ground water flow rates (Martin & Ruby, 2004).

2.4.2 Biological methods

These methods employ plants or microorganisms to eliminate, degrade or stabilise the contaminants in the soil (Song *et al.*, 2017). **Phytoremediation** uses metal hyper-accumulating plants to remove and clean up contaminated soil (Mendez & Maier, 2008). The plant type, the physico-chemical properties of the soil and the bioavailability of the heavy metal in the soil environment are the factors upon which the success of this process relies (Khalid *et al.*, 2016). Phytoremediation is categorized into three different types namely phytovolatilisation, phytoextraction and phytostabilisation based on the different uptake mechanisms. **Phytovolatilisation** is used to remedy contaminants such as Hg because of the high volatility (Xu *et al.*, 2014). Plants with this ability are, however, scarce thus a genetically modified plant is commonly used in phytovolatilisation (Khalid *et al.*, 2016). **Phytoextraction** involves the utilisation of plants that are able to hyper-accumulate the metals from the soil in their above ground biomass followed by the recycling of the plant to remove the

collected metals (Mendez & Maier, 2008). The examples of the plants that are used as phyto extractants include the Chinese break fern (Zhang *et al.*, 2002) and Sunflower, *H. annuus* (Jadia & Fulekar, 2009). The **phytostabilisation** technique makes use of metal-tolerant plants to eliminate heavy metals from the soil by up taking the metals and precipitating them in the rhizosphere (Mendez & Maier, 2008).

2.4.3 Chemical methods

The chemical methods of heavy metal remediation render the heavy metal to be inert, non-toxic or non-bioavailable (Martin & Ruby, 2004). A chemical agent is usually involved. The role of the chemical reagent can be oxidation, reduction, adsorption or elimination of the heavy metal from the soil matrix (Song *et al.*, 2017). **Soil washing** as a chemical method of heavy metal remediation in soils includes the use of reagents such as inorganic or organic acids, or chelating agents to get rid of heavy metals from the soil (Mulligan *et al.*, 2001). The effectiveness of this process hinges on the capability of the extractants to dissolve the heavy metals and the metalloids in soils (Khalid *et al.*, 2016). **Soil flushing** makes use of solutions such as water or any other appropriate reagents to remove pollutants from the soil matrix (Martin & Ruby, 2004). This process is mostly suitable for sites which are highly contaminated with a single metal and soils which are homogeneous as well as permeable (Mulligan *et al.*, 2001). **Metal immobilisation** refers to the reduction in metal mobility, bioavailability and bio-accessibility in soil by applying immobilising agents (Khalid *et al.*, 2016). Wuana and Okieimen (2011) indicated that the principal role of immobilising agents is to transform heavy metals to a more stable state through sorption, precipitation, and complexation processes. The common materials used for soil heavy metal immobilisation include animal manure, compost and biosolids or sewage sludge. A study conducted by Alvarenga *et al.* (2009) showed that the addition of sewage sludge reduced Cu, Zn and Pb in pyrite mine contaminated soil. Bolan *et al.* (2003) also showed a decrease of Cd after applying biosolids to a contaminated soil. The treatment of heavy metal contaminated soils with sewage sludge results in high organic matter and pH which lead to a decrease in metal availability (Cerezo *et al.*, 1999). The immobilisation of heavy metals in soils exploits the capacity of soils to sorp heavy metals which is determined by several soil properties.

2.5 The use of sewage sludge as a heavy metal immobiliser in contaminated soil

Sewage sludge usage as a remediation tool for soils which are contaminated is increasingly being employed, more especially on soils that have arable potential. Regulating bodies highly endorse the practice of using sludge due to its agronomic value as well as its ability to rehabilitate degraded soils in a mining environment (Kidd *et al.*, 2007; Poggere *et al.*, 2019). The use of sludge to remediate contaminated soil is to ensure that the heavy metals contained in the soil are not transported to the plants should the soil be used for agricultural purpose as it will have a detrimental effect to the growth of the plant and on human and animal health should the plant be consumed by man or other animals. Singh and Agrawal (2007) as well as Mattana *et al.*, (2014) further indicated that using sludge as a soil amendment is also an effective disposal technique of waste as compared to the disposal of sewage sludge in a landfill or by incineration.

Kidd *et al.*, (2007) and Agrawal (2007) reported that sewage sludge is a good source of macronutrients such as N,P,K and organic matter which are required by plants and it is also known for improving soil quality. Sewage sludge can also be used in place of, or as a supplement for commercial fertilisers. However, the use of sewage sludge for agricultural purposes has been labelled as the origin of heavy metal in some agricultural soils (Ngole & Ekosse, 2009). Using sewage sludge for the amendment of mine tailings has resulted in high organic matter; N and P, Cu, Cd, as well as Zn contents whereas the total extractable contents of Pb were reduced (Wang *et al.*, 2010).

2.5.1 Factors influencing the efficiency of sewage sludge in heavy metals remediation in soils

2.5.1.1 Concentration of heavy metals

Elevated levels of the heavy metals in sludge would render it inappropriate for use as a heavy metal immobilisation material especially for agricultural soils as they would instead be introducing metals in the soils which can be absorbed by plants or vegetables. The sewage sludge that is used for heavy metal immobilisation should have an acceptable level of heavy metal concentration. According to research done by Wang *et al.* (2008), the application of sewage sludge to soil increases the

concentrations of Pb, Cu and Zn in the soils. Kidd *et al.* (2007) indicated that in a soil where sewage sludge was used as a remediation material, the acid-extractable, reducible components of Mn and Zn, and the oxidizable components of Cu and Zn greatly increased, however, the plant uptake remained at an acceptable level.

2.5.1.2 *Soil properties*

The physico-chemical properties of a soil and the nature of a metal influence the behaviour of any heavy metal in the soil environment (Kidd *et al.*, (2007). The changes in the soil CEC, pH, and OM are known to decrease the available concentration of metals in the soil (Zheng *et al.*, 2012). Khan *et al.* (2014) observed that in a paddy soil, sewage sludge application decreased the bioavailability of Cd. The bioavailability of Cu was high in an alkaline soil and lower in an acidic soil and this is directly influenced by the OM content in the soil which complexes the Cu and impairs its uptake by plants whereas an acidic soil medium favours the bioavailability of Zn (Morera *et al.*, 2002). Bolan *et al.* (2002) also indicated that Cd, Cu and Ni bioavailability in soils was reduced by the presence of high OM which forms stable complexes with the heavy metals. In another study done by Vaca-Paulín *et al.* (2006), it was shown that adding either sewage sludge or compost to the soil increased the sorption of Cu and Cd due to an increase in the OM caused by the addition of the sludge. According to Udomu *et al.* (2004), there is a relationship between the high soil OM status and the low soil pH which results in metal complexation with OM to reduce metal mobility. The application of some organic amendment to the soil may, however, improve the OM content of the soil and increase its pH which could lead to an increase in the binding sites on the soil, an increase in metal sorption, and a decrease in the metal uptake by the plants (Khan *et al.*, 2017). Poggere *et al.* (2019) showed that in soils where gibbsite and hematite (Fe – Al oxides) are dominant, using sewage sludge to reduce the exchangeable and soluble Pb is more effective, while in kaolinite rich soils, only the reduction of soluble fractions of Pb is effective. It is further stated that the organic matter influences Pb's behaviour as it tends to alter the pH and CEC thus diminishing its availability and the likelihood of contamination.

2.5.1.3 *Sludge management*

Thermal drying and composting are the two commonly used processes to treat sewage sludge. Sludge composting involves the blending of sewage sludge with a

fibrous plant residue which is rich in carbon and other woody material at a certain ratio, thereby allowing the mixture to stabilise for a certain period thereafter. The end result is a bio-based product with a profile of favourable nutrient and less pathogens and pollutants (Owusu-Twum & Sharara, 2020 ; Alvarenga *et al.*, 2015). The disadvantage with compositing is that during the initial stage of the process, there is a release of ammonia and nitrous oxide, and this technique takes up a lot of space (Owusu-Twum & Sharara, 2020). Despite this, Alvarenga *et al.* (2015) and Poggere *et al.* (2019) proved that composting is a recommended technique to turn sewage sludge into a material that is no longer regarded as waste, but which can be used as a remediation material that cannot endanger the plants and human health. Khan *et al.* (2014) report that the addition of composted sewage sludge to soils reduces the concentration and availability of heavy metal such as Cd, Co and Cu in the soil. Gondek *et al.* (2018) also reported that the adding of sewage sludge compost to soil immobilised the mobile forms of Pb, Cu, Cd and Zn.

Thermally, drying sewage sludge involves subjecting the sludge to temperatures of up to 150°C until the moisture content is less than 14% to non-existence (Poggere *et al.*, 2019; Mattana *et al.*, 2014). Sewage sludge that has been thermally dried below 95°C has showed a higher sorption capacity for Cd and Pb as compared to those dried at higher temperature due to the decrease in floc size which provided an extended surface area for better availability of binding sites (Laurent *et al.*, 2011; Hammamini *et al.*, 2002). Poggere *et al.* (2019) also reported that thermally dried sludge is more effective in Pb sorption in clayey soil which has predominance of Fe and Mn oxides. The advantage of thermally treating sewage sludge is that the volume of the sludge is decreased but there is a disadvantage of altering the physico-chemical properties of the sludge (Owusu-Twum & Sharara, 2020). Gibson *et al.* (2007) indicated that there was a decrease in organic matter during the drying process; and Collard *et al.*, (2017) show that there was a decrease in pH. These two properties play a significant role in the immobilisation of the heavy metals by the sludge and so the efficiency of the thermally treated sewage sludge as a heavy metal immobilisation material may be compromised.

The pyrolytic transformation of sewage sludge into biochar is shown to be a promising process for treating the sludge that is designed for use as a heavy metal immobilisation

material for contaminated soil. The production of sewage sludge biochar involves pyrolysing sewage sludge in a muffle furnace at a temperature ranging from 350 to 750°C for a duration of 15 minutes to two hours as detailed by several authors (Mendez *et al.*, (2012); Liu *et al.*, (2021). It has been reported by Wang *et al.*, (2021) and Mendez *et al.* (2012) that sewage sludge- biochar showed a high pH compared to sewage sludge, but it had low CEC, EC and OM. Mendez *et al.* (2012) and Penido *et al.*, (2019) reported that when sewage sludge biochar is applied on contaminated soil, there is a reduction in bioavailability and the mobility of heavy metals. Mendez *et al.*, (2012) also reported that there was a reduction of heavy metals in the soil leachate when sewage sludge biochar was applied as compared to an un-pyrolyzed sewage sludge while Penido *et al.* (2019) report an increase in heavy metals in the leachate. When the sewage sludge derived biochar was applied on the sandy loam soil, the bioavailable forms of heavy metals diminish when compared to the application of un-pyrolysed sewage sludge (Wang *et al.*, 2021). Chagas *et al.*, (2021) reported that irrespective of the temperature to which the sewage sludge biochar was pyrolysed, the immobilisation of the heavy metal was effective compared to when the sewage sludge was un-pyrolysed.

2.5.1.4 *Soil management techniques*

Soil management techniques are aimed at improving soil quality for various purposes. These management techniques affect various soil processes through their effect on soil properties. The addition of compost and manure, the application of fertilisers, and the use of mulch and the burning of vegetation to improve soil fertility are some of the techniques that are used for soil management (Bronick & Lal, 2005). Walker *et al.*, (2004) state that the most imperative benefit of manure and compost addition to the soil is linked to the elevated levels of organic matter and biological activity. The study further indicated that the organic matter increases the CEC of the soil, and it reduces the bioavailability of the metals in the soil to plant and their uptake by plants growing on the soil. The desired outcome of fertiliser application on soil properties according to Haynes and Naidu (1998) is to improve crop yield and increase plant nutrient levels in the soils. Jordán *et al.* (2010) reported that adding wheat straw mulch to the soil resulted in a remarkable rise in soil organic matter after three years of treatment. Another soil management technique that is commonly used is the burning of vegetation referred to as prescribed burning to improve soil fertility. Prescribed burning

is defined as applying fire in a knowledgeable and controlled manner as a soil management tool (Wade & Lundsford, 1990). It is further indicated that using fire as a soil management tool has benefits such as site preparation for planting season, controlling diseases, removal of unwanted logs and wildlife habitat improvement. Hundreds of thousands of hectares of both forest and bush land are annually burnt by either prescribed or man-made fires. In some areas, the burning of stubbles is encouraged because the farmers believe that the burning of stubbles increases crop yields and reduces phytotoxicity (Giovannini, 1994). Certini (2005) and Zavala *et al.* (2014) report that such fires increases soil temperature which may alter the soil properties.

2.6 Factors affecting the mobility of heavy metals in soil

Bioavailability and mobility of heavy metals is mainly controlled by the sorption process (Jing *et al.*, 2018). According to Jing *et al.*, (2018); Sherene (2010) and (Fija *et al.*, 2012) it is indicated that soil **pH**, **soil texture**, **organic matter (OM)**, **soil temperature**, **residual time** and **CEC** are among factors which affect the mobility of heavy metals in soil. The most important factor which determines the mobility is pH. It is indicated that when the **pH** is neutral (around 7) mobility of heavy metal is low and for the mobility to increase the pH should be lowered (Sherene, 2010). Among different soil textures, **Clay fraction** has a high binding capacity because is mainly comprised of clay minerals while a **loamy sand** is known to have low sorption capacity which leads to weak absorption of metals (Fija *et al.*, 2012). Jing *et al.*, (2018) further indicated that fine textured soil exhibits a high adsorption capacity compared to a coarse soil. It is further reported that increasing **OM** lead to reduced absorption of heavy metals and this is because there can be a strong formation of metallic complexes with organic matter (Fija *et al.*, 2012). According to Ma and Liu (1997), it is reported that at high **temperatures** adsorption of metals such as Zn is low while at low temperatures it is high. At high temperatures OM is degraded thereby releasing organic acids which are known to increase mobility of heavy metals (Sherene, 2010). It is further indicated that after the application of organic amendments OM present may decompose after some **time** which results in loss of sorption sites followed by the decrease in pH which in turn affect mobility of heavy metals in soil. De Matos *et al.*,

(2001) has also reported that there is a strong association between **CEC** and metal retention.

2.7 The effects of soil temperature increases on soil properties

The soil's temperatures could increase because of fire events. Fire events therefore affect soil properties differently based on how high the temperature of the soil is raised during a fire event, and how long the fire event lasts. This may affect the interaction between the soils and the added materials such as sewage sludge and consequently, the efficiency of sewage sludge as a heavy metal immobilising agent in contaminated soils. The effects of soil temperature increase on selected soil properties with a significant role in soil sorption properties are presented below.

2.7.1 Soil pH

Lombao *et al.* (2015) reported that soil which has experienced a fire has a higher pH compared to soil that has not, and this is due to the increase in base forming elements that are contained in the ash of burnt soils. Certini (2005) also indicated that increased pH in burnt soil is due to organic matter denaturation, the release of base forming elements, the oxidation of certain elements, the removal of hydroxides (OH) groups from the clay, formation of the oxides of several elements. An increase in the pH of soil after the soil has been heated occurs as a result of the cation release as OM undergoes combustion and decomposition of ashes but the sharp increase in the soil's pH at high temperatures is a result of the elimination of the hydroxyl groups not from the formation of oxides according to Badía and Martí (2003). Merino *et al.* (2018) further indicate that the relationship between the temperature of the soil and the pH is directly proportional. When the temperature of the soil during a fire event is around 80°C, the soil pH is around 3.8, whereas during hotter fires when the soil temperature is raised to about 450°C, the soil pH is around nine (9). Terefe *et al.* (2008), however, indicated that heating soils at 250°C and 500°C results in a decrease in the soil's pH and this has been observed mostly for the experiments that are carried out in the laboratory because there is no effect from the alkaline nature of the ashes that are resulting from burning plant residue which can affect the pH. Ngole-Jeme (2019)

reported an increase in pH when soil was heated up to 150°C but thereafter, no significant changes were observed in soil pH.

2.7.2 Soil organic matter

The three factors which determine the consequences of fire induced temperature increases on soil organic Matter (OM) are fire intensity, vegetation type and fuel load. Depending on the fire severity, the impact of fire on OM is in three steps, firstly, the minor constituent will volatilise, followed by charring, and lastly complete oxidation (Certini, 2005). A study done by Fernández *et al.*, (1997) at different soil temperatures of 150°C, 220°C, 350°C and 490°C showed that lower temperatures do not result in a reduction or removal of OM in soil, but high temperatures completely eliminate soil organic matter. When soil is heated at a temperature of up to 170°C, there is no detectable change in the soil organic matter (Kennard & Gholz, 2001; Giovannini, 1994). The substantial decrease in OM is observed between 200 to 250°C while at a temperature of up to 460°C, there is complete elimination (Giovannini *et al.*, 2001). Mehdi *et al.*, (2012) also reported that soil which experienced a high severity of fire had a lower organic matter content compared to soil which experienced a low severity fire. The loss of soil OM leads to a decrease in water retention and this is attributed to the loss of carbon. However, the decrease is mostly observed at a temperature of 300°C while at higher temperature of about 500°C water retention increases because at high temperature there is an increase of silt and clay fraction (Stoof *et al.*, 2010) and Ebel, 2012). It has been further reported that at high temperatures, organic carbon and water retention increases (Rawls *et al.*, 2003)

2.7.3 Soil Cation Exchange Capacity

Giovannini (1994) reports that soil CEC decreases progressively with increasing soil temperature. Zavala *et al.* (2014) also reported that soil CEC decreases after a fire event especially in the first few centimetres of the soil. Soil which has experienced a high severity fire had a higher CEC compared to the soil that was subjected to a lower severity fire according to studies carried out by Mehdi *et al.* (2012). Badía and Martí (2003) opine that the relationship between soil CEC and soil temperature is indirectly proportional. When soil temperature increases, the soil experiences a decrease in CEC. The study showed that at 25°C, the CEC of the soil studied was 27meq/100g and at 500°C the CEC was 21,7 meq/100g. Shaheen *et al.* (2013b) stated that the soil

organic matter elevates the CEC of the soil and since the soil OM is affected by higher temperatures, the fraction of the soil CEC that is contributed by the soil's OM is expected to decrease. This is supported by the findings published in Certini (2005) where it was reported that in a soil that experiences fire, the soil CEC and OM decreases in the same manner.

2.7.4 Soil mineralogy

An increase in the soil temperature could affect various soil components including soil mineralogy. According to Reynard-Callanan *et al.* (2010), an unburned soil which contained illite, mixed layer of illite/smectite, illite/vermiculite, kaolin, mixed layer chlorite, quartz and feldspar showed the evaporation of mixed layer illite/smectite and illite/vermiculite with an increase in temperature whereas, the soil which was sampled on the surface (less than 7,7cm) showed a decrease of the mixed layer of illite/smectite. The study further indicated that the kaolinite layer remained unchanged in both soil layers as the soil temperature increases because kaolin can only be destroyed at a temperature of above 550°C and that as the fire penetrates the soil profile, there is a decrease in temperature. Arocena and Opio (2003) also report that kaolinite was not affected by a soil temperature of below 500°C as kaolinite will only decompose at higher temperatures. According to Iglesias *et al.* (1997), soil samples containing minerals such as mica-illite, vermiculite, kaolinite, quartz, feldspars and goethite, before temperature increases showed an alteration of vermiculite and an existence of calcite as a new mineral after the temperature of the soil was increased (Iglesias *et al.*, 1997). Ketterings *et al.* (2000) state that temperatures beyond 600°C reduce gibbsite content and further convert goethite into ultra-fine maghemite. The study further reports that more changes in mineralogy can be experienced with a lower soil temperature. Ulery *et al.* (1996) observe that at the upper 1 to 8 cm of a soil, chlorite, chlorite/vermiculite, vermiculite, and hydroxyl- interlayered vermiculite were converted to illite after a fire event that did not cause excessive temperature changes. These various studies do show that increases in soil temperature may affect the mineralogical composition of the soil and consequently all the properties that depend on soil mineralogy. Water retention is directly related to clay content of the soil and this is because clay content favours the occurrence of micropores and menisci that generates capillary forces (Reichert *et al.*, 2009).It is further reported that clay

mineralogy which is mainly composed of kaolinite, smectite and montmorillonite-beidellite has higher water retention.

2.8 The effects of temperature-induced changes in soil properties on soil sorption capacity

According to Deliyanni and Matis (2005), sorption is a phenomenon where a charged species like a heavy metal ion in a solution attaches itself to a coexisting solid phase. Hooda (2010) further indicated that the sorption process includes both adsorption, when a solute adheres to a solid phase; and absorption, a diffusion of a solute into porous solid thereby adhering to the inner surfaces. Zhang *et al.*, (2018) stated that sorption is the primary reason for the retention of contaminants on the solid surface. Vidal *et al.*, (2009) also stated that sorption determines the fate of heavy metals in soil, and this is because the mobility of heavy metals has a direct relationship with the partitioning of metals between soil solid phase and soil solution. Organic matter, CEC, clay mineralogy, and pH are the soil properties which drive the sorption and desorption processes of metal ions (Shaheen *et al.*, 2013b). Gao *et al.*, (1997) opine that organic matter plays a pivotal role in the sorption of Pb while the mineralogical structure of the soil has an influence in the sorption of Cr. It is further stated that the soil sorption capacity of Pb, Cr, Ni, Cd and Zn were high at a pH of 6.5 as compared to a pH of 4.5. These properties are affected by fire events to different extents due to the temperature changes and will therefore affect soil sorption capacity differently. Hooda (2010) further indicates that the availability of the pH-dependent sorption sites, the development of metal-hydroxyl complexes, and the affinity of metals to the organo-mineral complex and their stability are some of the factors which have an impact on the selective sorption of trace elements.

The sorption of the trace elements is directly related to soil pH, as soil pH increases the heavy metal retention on soil surface increases (Shaheen *et al.*, 2013). In a study conducted by Jović *et al.*, (2017) on Co sorption, it was reported that soil pH governs the sorption capacity of soils and thus a direct relationship exists between soil pH and the amount of cation which a soil can sorb. Sahraoui *et al.*, (2015) indicated that cations such as Co Ni, Cu, Pb and Zn have showed a high sorption capacity because of their alkaline pH. An increased soil pH due to increase in soil temperature may

therefore affect the sorption capacity of the soils. Shaheen *et al.* (2013) stated that organic matter plays an imperative role in the sorption of trace elements. Garrido *et al.*, (2012) further reported that an increase in organic matter leads to an increase in the sorption sites for metals such as Cu. Asensio *et al.*, (2016) also reported that soil organic carbon and dissolved organic carbon showed a strong positive relationship on the sorption of Ni, Pb and Zn. The soil which contains a high concentration of imogolite and vermiculite has a high sorption capacity for heavy metals (Shaheen *et al.*, 2013b). Sahraoui *et al.* (2015) also indicated that the sorption of Pb, Zn, Ni, Cu and Co cations were strongly related to the clay fraction that was present in the soil. Sheikhhosseini *et al.*, (2013) show that on palygorskite silicate clay, the sorption of metals such as Cu, Zn, Cd and Ni increase with increasing metal concentration while on sepiolite silicate clay, only Zn, Ni and Cd show sorption capability. Sipos *et al.*, (2008) also indicate that the Pb, Zn and Cu showed a higher sorption capacity in swelling clay minerals. Ngole-Jeme (2019) indicated that the alteration of secondary to primary minerals as a result of fire events in the soil leads to a decline in soil sorption capacity and its ability to sorp both inorganic and organic compounds. The fires that raise soil temperatures to levels below 600°C have little or no impact on the oxides of iron and aluminium and this would result in no impact on the soil sorption capacity. Heating soils above 600°C can, however, lead to an increase or decrease in the oxides (SiO_2 , Al_2O_3 and Fe_2O_3) and these would lead to an increase in the contribution to the soil sorption complex (Ngole-Jeme, 2019).

2.9 The effect of fire on the efficiency of organic materials as heavy metal immobilising agents

The soil organic matter content has been reported to increase with the addition of sewage sludge (Hussein, 2009; Liu *et al.*, 2018). The addition of the OM through sewage sludge in the soil results in the formation of stable organometallic complexes which lower the mobility of heavy metals and enhances soil binding capacity (Kahapanagiotis *et al.*, 1991). It is also reported that the presence of humic acid decreases the mobility of heavy metals due to the formation of stable chelates which increase the binding capacity (Alvarenga *et al.*, 2009). Alvarenga *et al.*, (2009) has attributed a decrease in the mobile fraction of heavy metals to the organic amendments. The addition of organic amendment such as sewage sludge increases

the soil acidity and this is attributed to the formation of organic acids that accompany mineralisation or the decomposition of sludge (Penido *et al.*, 2019; Liu *et al.*, 2018). This increase in soil pH causes a decrease in the mobility of heavy metals in the soil environment. Hussein (2009) also reports that soil EC and CEC increase as a result of the sewage sludge addition on soil which is attributed to the high content of salt in the sludge. The role of soil CEC in metal binding is widely documented. According to Kumar and Chopra (2015), both the pH and EC of soil increases with sludge addition. However, Wang *et al.*, (2003) indicated that the sorption capacity of heavy metals increases in acidic and neutral environments where organic amendment has been applied as compared to the alkaline environment. Planquart *et al.*, (1999) reports an increase in the mobility of Zn and Cu with a decreasing pH as a result of sludge addition, while Kumpiene *et al.*, (2008) also report that Zn mobility is affected by the presence of oxide and OM. Most of the soil properties affected by an increase in soil temperature affect the interaction between organic amendment and soil components to reduce the mobility of heavy metals in the soil environment. Changes in soil properties due to fire events may therefore influence the efficiency of organic materials to bind metals in the soils. Not much information on this is available. This study provides baseline information that would give an idea of what happens to the heavy metals in fire affected contaminated soils when sewage sludge is applied.

2.10 Concluding remarks

Heavy metals' contamination in soil resulting from industrial sources, mining, vehicular emission, and agricultural sources is a global environmental concern as it is a threat to human health. The literature reviewed in this study has shown that soils that are in these areas commonly contain high levels of heavy metals which could end up in various environmental sectors. There are methods of remediation which can be employed to restore these soils so that they can be used again for agricultural purposes. One of those methods is the immobilisation of the heavy metals which involves the use of sewage sludge or other organic amendment. The changes in soil temperatures that may be caused by fire events could affect soil properties such as pH, organic matter, cation exchange capacity and soil mineralogy which in turn might affect the ability of the soil to sorp the present heavy metals. The changes could also affect the efficiency of soil organic amendments as heavy metal remediation materials.

The efficiency of sewage sludge as a heavy metal remediation technique of burnt soil needs to be investigated.

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Introduction

In this chapter, the details of the area from where the soil samples were collected, the experimental setup, the analytical methods which were employed in the analysis of the soil and the sludge samples, as well as the details of how the data that was generated from the laboratory analysis was analysed are presented.

3.2 Description of the study area

The soil samples were collected from Carletonville, which is in Merafong City Local Municipality within the West Rand District Municipality of Gauteng. The area is about 79km from Johannesburg, and it is also a part of Gauteng province (Figure 3.1).

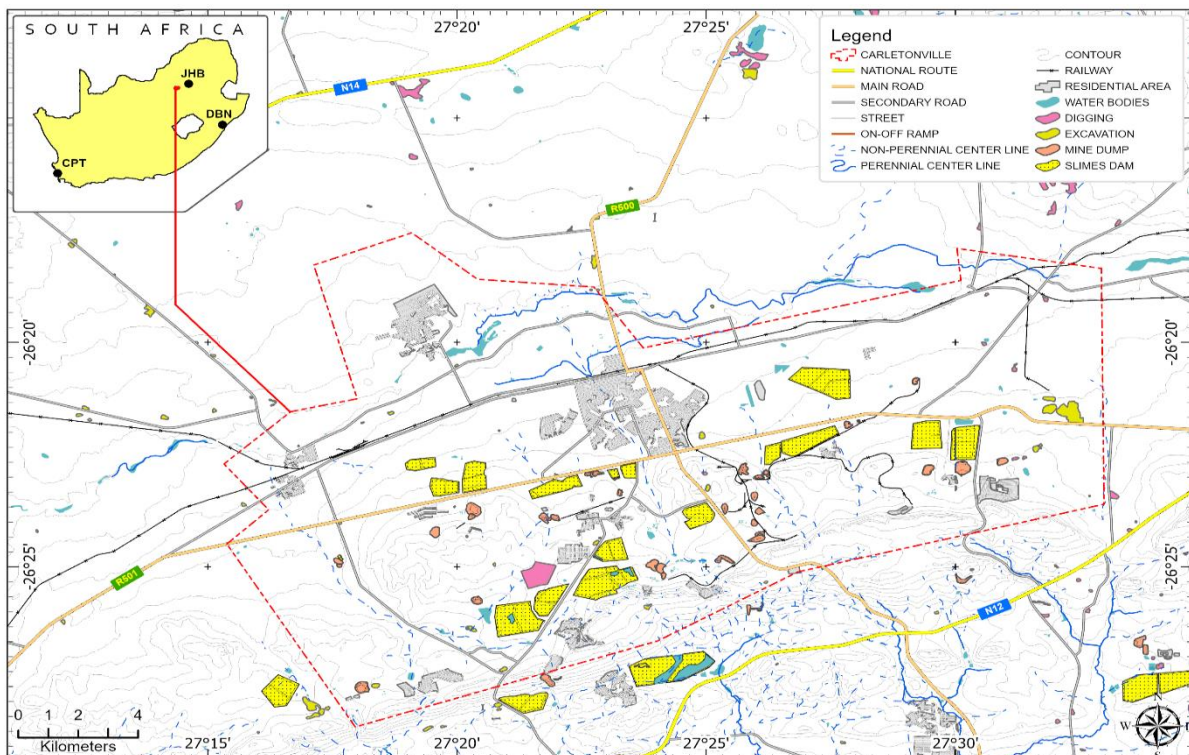


Figure 3.1 Carletonville: Sampling area

Carletonville falls within the summer rainfall region where rainfall normally occurs from October to March yearly. The average rainfall annually in the area is 668mm (Morotoba, 2014). Summer months which occur from November to February are warm to hot whereas the winter months have a more moderate temperature especially from June to August. The maximum temperature experienced in the area during the summer months is around 30°C, while the minimum temperature during winter months is below 5°C (Robinson, 2017). The topography of the area is characterised by undulating plains, consisting of grassland with livestock farming practiced around the area (Royal Bafokeng Platinum, 2020). Dolomite and chert of the Malmani subgroup make up the geology of the area while deep red and yellow apedal soils occur sporadically (Morotoba, 2014). Pharoe and Liu (2018) further indicate that quartzite of black reef formation, manganese bearing carbonate, ferruginous rocks, and stromatolitic dolostones from the Malmani subgroup and malachite, a copper carbonate can be found in the area.

The agricultural activities in the area are dominated by maize farming though vegetables and flower production take place as well (Merafong Growth and development Strategy, 2016). The mines in this area are the dominant contributors to the economic sector of the country with a contribution of 50.7 % to the GDP. The mines also contribute 61% of employment in the area as compared to agriculture, trade, finance, and insurance (West Rand District Municipality, 2013). Mining in Merafong City is dominated by gold mining (Lieverink, 2019). The mining of gold can either be open-pit or deep shaft and the location of the mine is also a driving factor on the type of the mining process to be used. The separation of gold from mineral rock is done by either mercury amalgamation or cyanide leaching (Fashola *et al.*, 2016). However, the most common process that is used in the mines around the study area is cyanide leaching because during mercury amalgamation, there is a reaction between mercury and sulphur thereby making it less selective towards gold (Stafford, 2016). Pollution and waste in South Africa are mainly associated with gold mining.

With the mining of gold, there is a resultant legacy of tailings dumps around the mining area. These tailing dumps are not covered, and no vegetation is planted, thus they are a significant source of contaminants to the soil and water resources in the surrounding areas (Lieverink, 2019). The communities living in these areas are also exposed to

dust from these dumps through inhalation. Periodic fire events occur in the area though it is not certain whether these fires are accidental, or they are deliberately set. The soils around the tailing dumps in the area are therefore subjected to periodic temperature changes.

3.3 Research Design

A quantitative research design was employed in this research. Welman *et al.* (2012) describe a quantitative research design as a measurement and analysis of the causal relationship between variables. Under the category of quantitative research design, there is experimental research, which is the type of research where there is some form of intervention on the intended sample of the study. In this study, the collected samples were subjected to different temperature conditions and mixed with sludge at different rates while some which served as controls were not. Thus, a quantitative experimental research approach was deemed the most appropriate design for this study.

3.4 Data collection

3.4.1 Soil and sewage sludge samples collection

Soil samples were collected from three different tailings dumps around Carletonville. The map presented in Figure 3.1 does not show the exact sampling points due to the terms of the non-disclosure agreement. Using a grid sampling approach, six samples each weighing about 6kg were collected from each tailings dump using a steel spade and hand trowel. The samples were collected at depths of between 0 – 30cm which is the layer of soil explored by most plants and from where particles are eroded by the different agents of erosion. The soils at this depth therefore present a greatest threat to the environment. The samples were then transported to the UNISA College of Agriculture and Environmental Sciences laboratory at the UNISA Science Campus in Florida, Roodepoort, where samples from each of the three sites were passed through a 2mm sieve. The particles measuring above 2mm in diameter were discarded. The < 2 mm fraction of the samples from each site were then mixed to make a representative sample of the site. Three samples were also collected from an area that was 10km away from the tailings site but had similar lithology as the soils around the tailing dumps. These samples were also homogenised together to obtain a representative sample from the site. The samples from this site represented the control sample in the

study. A total of four composite samples representing soil samples from the vicinity of the three tailings dumps, and a control site were therefore used for the study.

Stabilised sewage sludge was collected from the ERWAT wastewater treatment plant in Heidelberg, Johannesburg. This wastewater treatment plant treats wastewater from domestic and municipal institutions in the area and does not receive any industrial wastewater. The plant uses the activated sludge method of wastewater treatment with no chemicals used at any stage of the wastewater treatment process. The sewage sludge generated from the wastewater treatment process is stabilised in digesters to reduce the pathogen load after which it is spread on sludge drying beds from where it is piled for disposal. Sewage sludge was collected randomly from the sludge drying beds at the plant into plastic sampling bags, after which they were taken to the laboratory at UNISA, Florida campus, and air-dried. The sludge samples were then crushed and used for further experiments and analysis.

3.4.2 Experimental setup

The composite soil samples from each of the four sites were subjected to various temperatures for different lengths of time to mimic the soil temperature and the duration of heating in natural bush fires. Each composite sample was split into two and one portion was kept aside to serve as the control for the heating experiment. This portion was not subjected to heat. According to Neary *et al.* (1999), bush fires could increase soil temperature anywhere between 50°C to less than 1 500°C. In a pilot study in this research, it was determined that no changes take place in the mineralogy and geochemistry of the soil samples beyond 750°C. The other portion of each composite sample from the different sites was therefore heated at temperatures of 100 ± 1°C, 200 ± 3°C, 300 ± 3°C, and 400 ± 3°C for two hours, four hours, and six hours in a muffle furnace to explore the consequences of temperature increases and the duration of heating on soil properties. Thereafter, the portion of each composite sample from the tailings dumps which was treated at the same temperature and duration were mixed to make composite samples of soils treated at the same temperature. For example, all samples which were heated at 100°C for two hours were mixed to form a composite of soils heated at 100°C for two hours resulting in 13 samples including the sample which was not treated. The heated composite samples were each divided into two to make replicates resulting in 26 samples in total.

3.4.3 Mixing of soils with sewage sludge

From each soil sample that had been heated, about 500g was also kept aside as the control for the sludge experiment. This portion was not mixed with the sludge. The ground sewage sludge was then mixed with the remaining heated tailings contaminated soil samples at three different soils: sludge volume ratios of 100:0, 80:20, and 60:40. Table 3.1 presents the details of the experimental set up and the total number of analysed samples. A total of 117 samples were analysed in this study. All soil samples and their respective controls were kept under natural weather conditions in a protected environment for six months to mimic natural conditions. During this period, the samples were thoroughly moistened and mixed every two weeks to allow for equilibration between the sewage sludge and the tailings contaminated heated soil samples (Akhtar *et al.*, 2002).

3.5 Sample analyses

3.5.1 Determination of soil texture

Laser diffraction technology was used in the determination of the Particle Size Distribution (PSD) of the samples. The equipment used was a Malvern Mastersizer 2000 fitted with Hydro 2000G dispersion unit. The samples were first treated with 30% hydrogen peroxide (H_2O_2) and 10% hydrochloric acid HCl for the removal of OM and carbonates as well as iron oxides respectively, then they were mixed to make a representative sample (Malvern Instrument Ltd, Worcester, UK). A suspension of the samples was then prepared by mixing sodium pyrophosphate ($Na_4(PO_4)_6$) and then loaded onto the instrument. As the sample suspension was scattering light from particles that are passing through the analyser beam, snapshots were recorded. A refractive index of 1.533 with an adsorption of 0.1 and a polydisperse mode of analysis were selected for the instrument setup. The collection of data was done in the range of 10-20% at a constant obscuration. To determine the size distribution of these particles, the relationship between the angles of scattered light resulting from particles in a laser beam was utilised. The texture of each sample was then determined using a texture Auto Lookup Software Package (TAL Version 4.2).

Table 3.1 Experimental set up

Temperature at which samples were heated	Soil: sludge ratio (v/v)	Duration of heating and number of samples					
		Tailings contaminated soil samples			Control soil samples		
		2 hours	4 hours	6 hours	2 hours	4 hours	6 hours
100°C	100:0	2	2	2	1	1	1
	80:20	2	2	2	1	1	1
	60:40	2	2	2	1	1	1
200°C	100:0	2	2	2	1	1	1
	80:20	2	2	2	1	1	1
	60:40	2	2	2	1	1	1
300°C	100:0	2	2	2	1	1	1
	80:20	2	2	2	1	1	1
	60:40	2	2	2	1	1	1
400°C	100:0	2	2	2	1	1	1
	80:20	2	2	2	1	1	1
	60:40	2	2	2	1	1	1
Samples not heated (0°C)		6 samples; 2 for each of the different sludge: Soil ratios			3 samples; One sample for each of the different sludge: Soil ratios		
Total number of samples		78			39		

3.5.2 Determination of soil pH and electrical conductivity

Approximately 20g of each soil sample was separately weighed into 100ml plastic bottles after which, 50ml ultrapure water was added. The bottles were closed using a screw cap after which they were shaken for one hour on a reciprocating shaker and allowed to settle for 30 minutes thereafter. The pH of the soil-water suspension was then measured with a calibrated pH meter. The solution was allowed to stand for a further 30 minutes after which the Electrical Conductivity (EC) of each soil: water suspension was measured with a calibrated conductivity meter (van Reeuwjik, 2002). This was repeated thrice for each sample and the mean of the three respective readings was taken as the pH and EC of the sample respectively.

3.5.3 Determination of soil organic matter content

The modified Walkley Black method of determining soil organic carbon was used to determine the OM content of the soil samples. Approximately 0.2g of each soil sample was weighed into a 500ml Erlenmeyer flask, after which 10ml of 1N potassium dichromate ($K_2Cr_2O_7$) solution was added, followed by 20ml of concentrated sulphuric acid (H_2SO_4). The solution was swilled gently and allowed to stand for 30 minutes in the fume hood. 200ml of ultrapure water was then added followed by 10ml of concentrated phosphoric acid (H_3PO_3). The mixture was then titrated with 0.5N ferrous sulphate ($FeSO_4 \cdot 7H_2O$) using barium diphenylamine sulphonate as an indicator. The endpoint was reached when the solution changed from dark purple to turquoise green. The volume of the titre used to arrive at the endpoint was noted and used to calculate the organic carbon content in the sample as shown in Equation 1 below. The organic carbon content in each soil sample was then converted to its OM content by multiplying by a factor of 2 (van Reeuwjik, 2002).

$$\% Carbon = \frac{M \times (V1 - V2)}{m} \times 0.39 \times mcf \quad (1)$$

where %C = Carbon content, M = molarity of ferrous sulphate (N), V1 = volume of the ferrous sulphate used for the blank (ml), V2 = volume of the ferrous sulphate used for the sample (ml), m = mass of the sample (g), 0.39 = equivalent weight of carbon incorporating incomplete combustion, mcf = moisture correlation factor, Percent organic matter (% OM) = 2 x %C

3.5.4 Determination of soil Cation Exchange Capacity (CEC)

In the determination of CEC, 5g of each soil sample was weighed into a 50ml centrifuge tube and 30ml of 1M ammonium acetate ($\text{NH}_4\text{COOCH}_3$) added. The mixture was shaken overnight at room temperature at 60rpm after which the suspension was centrifuged for five minutes at 3 500 rpm. The supernatant liquid was poured out into a clean 50ml centrifuge tube. An additional 20ml of $\text{NH}_4\text{COOCH}_3$ was added to the sample and shaken for several minutes, centrifuged at 3 500rpm for 5 minutes and the supernatant liquid decanted into the same 50ml centrifuge tube with the first decanted solution. The concentration of the exchangeable cations Ca, Mg, Na, and K in the supernatant of each decanted sample was determined using Shimadzu ICP-OES. The calibration standards used for metal analysis ranged from 0 to 25ppm, with the torch on axial view. The plasma gas flow was set at 10 L/min, the auxiliary gas flow at 0.6 L/min, and the carrier gas flow at 0.7 L/min . A radio frequency power of 1.2 kW was used. The sum of the exchangeable bases present in the sample was taken as the CEC of that sample (Buurman *et al.*, 1996).

3.5.5 Determination of heavy metal content of the soils

The heavy metals analysed in this study included As, Co, Cd, Cr, Cu, Pb, Ni and Zn. The Community Bureau of Reference (BCR)'s three-step sequential extraction method was utilized for the determination of heavy metals in the soil samples. In this protocol, the different extractants are used in each step to extract different pools of heavy metals in the soils. This method enables an assessment of the potential bioavailability and mobility of metals in the soils (Ptistišek *et al.*, 2001).

The first step of the BCR sequential extraction protocol involved the extraction of the exchangeable and weak acid-soluble fraction otherwise called the carbonate-bound fraction. In this step, 40ml of 0.11M acetic acid (CH_3COOH) was added to 1g of the soil sample and weighed into a 50ml polyethylene sample bottle. The mixtures were then shaken for 16 hours at room temperature at a speed of 135rpm, after which each was centrifuged for five minutes at 3 000 rpm and the supernatant liquid decanted into clean tubes. The heavy metals concentrations in this supernatant represent those in the exchangeable and carbonate bound fractions. The sample residue was then rinsed by adding 20ml of ultrapure water followed by shaking and centrifugation for five minutes at 3 000 rpm. The supernatant liquid was discarded.

For the reducible fraction in the second step, 40ml of 0.5M of hydroxylamine hydrochloride ($\text{HONH}_2\cdot\text{HCl}$) solution which had been adjusted to a pH of 2 with concentrated nitric acid (HNO_3) was added to the residue from step 1 and the mixture shaken for 16 hours at room temperature at a speed of 135rpm. The mixture was then centrifuged for five minutes at 3000rpm, and the supernatant liquid decanted into another set of clean tubes. The residue was again rinsed by the addition of 20ml ultrapure water followed by shaking and centrifugation for five minutes at 3 000rpm and the supernatant liquid discarded.

In the third step (Oxidizable fraction- organic matter and sulphide bound), 10ml of the 8.8M H_2O_2 which had been adjusted to a pH of 2 using concentrated HNO_3 was added to the residue from step 2 and the mixture was allowed to stand for one hour at room temperature, followed by an addition of another 10ml of 8.8M H_2O_2 . The mixture was shaken at 45rpm for 16 hours at 55°C and then placed in a steam bath at 85°C to evaporate until the sample was reduced to almost 3ml. Approximately 40 mL of 1.0M $\text{NH}_4\text{COOCH}_3$ was then added to the sample which was again shaken for 16 hours at 135rpm. The sample was then centrifuged for five minutes at 3 000rpm, the supernatant liquid was then decanted into a clean tube. The sample residue was rinsed by the addition of 20ml ultrapure water followed by shaking and centrifugation for five minutes at 3 000rpm and the supernatant liquid was then discarded.

In the fourth step, 12ml of aqua regia (3:1 HCl/HNO_3) was added to the sample and the solution was then transferred to a clean 100ml beaker followed by digestion on the hotplate at 130°C until the solution was almost dry. The residue was then washed with 2% HNO_3 and diluted to 50ml in a volumetric flask (Li *et al.*, 2016). The concentrations of the heavy metals in the extract from each of the four steps were then determined using a Shimadzu ICP-OES. The calibration standards used for metal analysis was ranging from 0 to 50ppm. The instrument set up was as indicated in the determination of exchangeable bases and CEC.

3.5.6 The geochemical characterisation of soil samples

For trace and major element oxide analysis, the methods used were those described in Fitton (1997). The soil samples were crushed, and each crushed sample was placed in a muffle furnace at 1 000°C for three hours to allow for the oxidation of Fe^{2+} and S

as well as for the determination of Loss On Ignition (LOI). A total of nine grams of flux (consisting of 34% LiBO_2 and 66% $\text{Li}_2\text{B}_4\text{O}_7$) and one gram of heated sample were fused at 1050°C to form a stable glass bead which was then analysed for the major oxide including water (H_2O). The geochemical characterisation of the soil sample was done using a PANALYTICAL Axios sequential WD XRF spectrometer. The instrumental set-up was done according to the manufacturing instruction.

3.5.7 The mineralogical characterisation of soils

The mineralogical composition of the samples was determined using the X-Ray Powder diffractometry. In this analytical technique, each sample was pulverised to a fine powder (10 μm to 15 μm sizes) with a mill. A sub-sample of the fine powder was pressed onto the sample holder on which a rough filter paper had been placed to ensure random orientation. Samples were analysed using an X-Ray Diffractometer (XRD) with a LYNXEYE detector (40Kv and 40 mA) equipped with Cu-K radiation and scanned at 0.02° 2θ and a step size of 0.5 seconds. Semi-quantitative estimates of the concentrations of the different mineral phases were determined using peak relative height/area proportions (Brime, 1985) and Reference-Intensity-Ratio (RIR). The Mineral Powder Diffraction File Data Book (MPDFDB 2001) was used to identify each scanned mineral phase. This was then compared with the data presented in the International Center for Diffraction Data (ICDD) 2001.

3.6 Data analysis

Data analysis was done for each of the objectives of the research study as detailed below. **To determine how soil temperature increase and the duration of heating could affect soil properties and heavy metal mobility** - A comparison of how soil organic matter, electrical conductivity, cation exchange capacity, pH and soil mineralogy and geochemistry changed with varying temperatures and duration of heating was compared between the tailings contaminated soil sample and the control sample. ANOVA was used to determine differences in soil properties whereas Tukey test was used to separate the means of the different parameters.

To determine the level of heavy metal contamination in the soils around gold mine tailing dumps, the heavy metal concentrations in soil samples from the control

site were compared with those collected around the tailing dumps. The Contamination Factor (CF) of each heavy metal in each of the samples was determined using equation (2) (Ngole-Jeme & Fantke, 2017).

$$CF = \frac{C_o}{C_n} \quad (2)$$

Where C_o is the average concentration of heavy metal in the soils from around the mine, and C_n is the concentration of metal in soils from the control site.

To determine how soil temperature changes affect the heavy metal binding capacity of soils contaminated with mine tailings from a gold mine, the Mobility Factor (MF) was used. The mobility factor is the capacity of the soil to pass through a compartment where it is energetically retained (Achiba *et al.*, 2009). The mobility factor of the heavy metals in each sample was calculated using metal concentration from the different fractions of metals extracted using the BCR extraction procedure as indicated in Equation 3.

$$MF = \frac{F_1}{F_1+F_2+F_3+F_4} \times 100 \quad (3)$$

Where F_1 = exchangeable and carbonate bound metal fraction; F_2 = Iron and manganese oxyhydroxide bound metal fraction, F_3 = Organic matter and sulphide bound metal fraction, and F_4 = residual fraction bound to components such as silicates in the soils. The MF of heavy metals in the soils heated at different temperatures and for different duration was compared to evaluate how MF changed as properties of soil changes due to heating at different temperatures and duration.

To determine the ability of sewage sludge to bind heavy metals in burnt and un-burnt soil, the MF of the heavy metals in all samples both heated and unheated and amended with sewage sludge at different sludge/soil ratios was determined. A comparison of the MF of the various heavy metals in the different samples was done to determine how MF changes with different temperatures, the duration of heating and sludge application rate. The implications of the changes in soil properties and the mobility factor caused by changes in soil temperature and the duration of heating the soil on fire affected contaminated soils was then inferred. The efficiency of using sewage sludge as a heavy metal immobiliser in heat affected contaminated soils was also evaluated using the changes in the mobility factor as a result of sludge addition.

3.7 Quality control/quality assurance steps taken

Quality assurance is described by Taverniers *et al.*, (2004) as a measure that a laboratory undertakes to ensure that it always achieves high-quality data that is precise and accurate. Quality assurance measures were undertaken in this study. All plastic ware and glassware that was utilised during the study were cleaned with dilute HCl and rinsed with distilled water followed by ultrapure water to reduce contamination. Samples were thoroughly mixed to ensure homogeneity. All reagents and the chemicals that were used were the Analytical Reagent (AR) grade to guarantee precision and accuracy of the data generated, but also because these reagents contain minimum levels of impurities. While samples were being treated under natural conditions, each sample was individually placed in its own sample pots and stirring was done with clean spatula to avoid any cross contamination. The instruments used for analysis were calibrated and verified. The samples were done in duplicate to ensure the repeatability of results.

3.8 Ethical implications

Permission to collect the soil samples from the mining area was obtained from the gold mine. Permission was also granted by the wastewater treatment plant for sewage sludge to be collected and used for the study. Sewage sludge contains pathogens which pose risks to human health, and it was also assumed that the soil samples were contaminated with heavy metals which are hazardous. Therefore, the appropriate personal protective equipment for laboratory use were utilised during the handling of the sewage sludge and the soil samples. All analytical protocols that were used followed respective laboratory rules and procedures. The disposal of used reagents and samples followed the laboratory guidelines. Care was taken to ensure that there was adherence to the respective safety data sheets.

3.9 Conclusion

In this chapter, a detailed explanation of the data was that was generated from the experimental research was discussed. The area where the samples and the sewage sludge were taken was discussed together with the sample preparation. A detailed

explanation of the methods followed to measure pH, CEC, EC, OM, texture, geochemical and mineralogical characteristics including heavy metals preparation and analyses were explained, followed by how the data generated was analysed and interpreted. The following chapter provides the results as well as a discussion of the generated results.

CHAPTER FOUR

RESULTS AND DISCUSSION: EFFECT OF TEMPERATURE INTENSITY AND DURATION OF HEATING ON SOIL PROPERTIES

4.1 Introduction

This chapter presents the results, and a discussion of the data that was obtained from the laboratory analysis that was conducted on the soil samples. The chapter first presents the characteristics of the soils and then explains how the soil properties varied with different temperatures and duration of heating. The presentation and discussion of the results of each soil property is then followed by an inference of how soil properties are likely to be affected by fire events.

4.2 Physicochemical properties of the soils

4.2.1 Soil Textural properties

The soil samples used in this study varied in their particle size distribution, but all had high amounts of sand (Figure 4.1). The tailings contaminated soil sample had 61.31% sand, followed by silt with 35.78 % with the clay fraction having the least weight percent (2.91%). The dominant particle fraction in the control soil sample was also sand with 70.18%, followed by the silt fraction with 27.7%, then the clay fraction with 2.12%. Both the control and contaminated soil samples had a loam sandy texture. Among the soil physical properties, the soil texture is most stable and requires prolonged periods to change from one textural class to the other. It is therefore not easily affected or changed even by changes in soil temperature. Studies have, however, shown that soil texture could be affected by heat. Kettering *et al.* (2000) for example showed that clay soil may experience changes when exposed to higher temperatures. Neary *et al.* (2005) reports that because sand and silt have higher threshold temperatures, they are not affected by temperature increases attained during wildfires, but clay is more susceptible as it undergoes changes at 400°C. Therefore, the textural properties of the soils in this study are highly unlikely to be affected by temperature increases as they are mainly dominated by sand particles, which comprise of quartz with a melting point of 2 577°C.

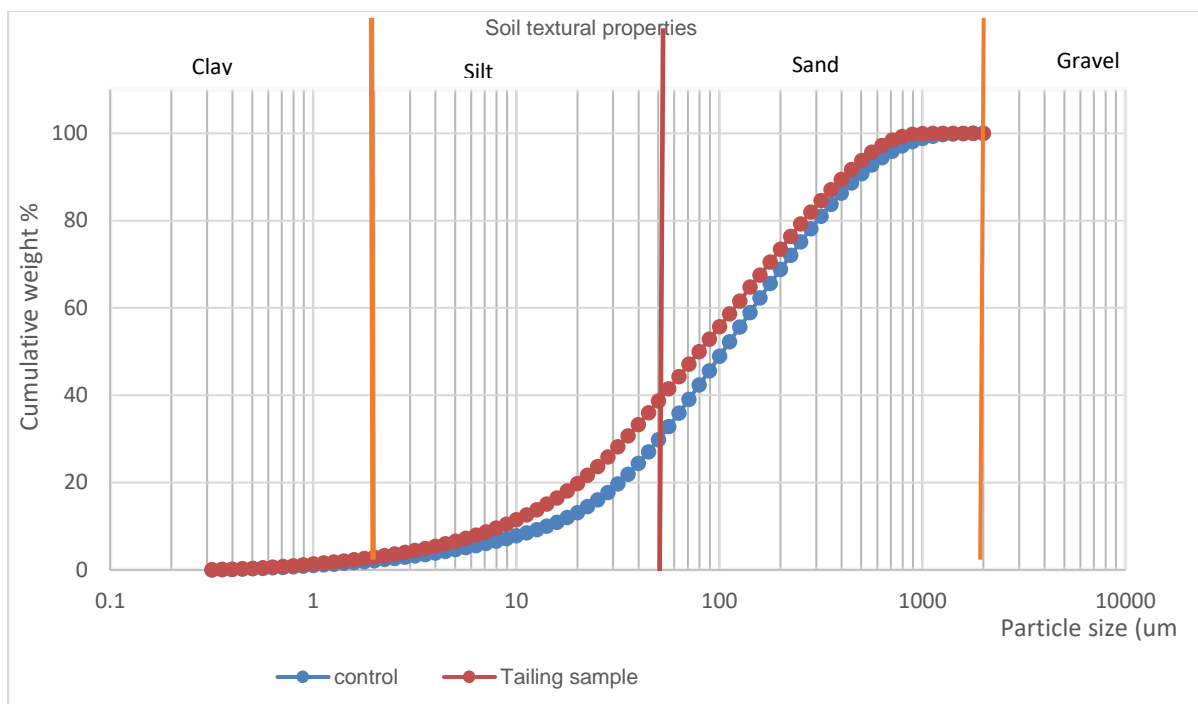


Figure 4.1 Cumulative frequencies of sand, silt, and clay particles in the different samples

4.2.2 Soil electrical conductivity

The control soil sample recorded a mean EC value of $131.3\ \mu\text{s}/\text{cm}$ with values ranging from 65.6 to $186\ \mu\text{s}/\text{cm}$ whereas the mean EC value of the tailings' contaminated soil was $205.9\ \mu\text{s}/\text{cm}$ with a range of 128 to $311\ \mu\text{s}/\text{cm}$. Thus, the EC value for the tailings contaminated soil was higher than that of the control sample (Table 4.1). The results obtained are similar to that obtained by Ngole-Jeme and Fantke (2017) in gold mine tailings contaminated soils. The values of EC obtained in this study indicate that both the control and the tailings contaminated soils were low in salinity. The higher conductivity of the tailings contaminated soil can be attributed to the presence of exchangeable bases such as K, Na, Ca, Mg, and SO_4^{2-} in mine tailings which may have contributed to the high amounts of dissolved salts and consequently higher EC values observed. These observations are similar to that of Tycholiz *et al.*, (2016).

Heating the control soil sample at 100°C for two hours resulted in an increase in EC but when the duration of heating at this temperature was increased to four hours and then six hours, a decrease in EC values was observed (Figure 4.2a). Increase in soil EC with increase in soil temperature has also been reported by Badía and Martí (2003)

and they have attributed this to the increase in soluble inorganic compound that are produced as a result of burning as well as the ash.

Table 4.1 Properties of soil samples used in the study

Parameter	Sample	Mean	Minimum	Maximum	Standard deviation
pH	Control	6.5	5.5	7.3	0.53
	Contaminated	6.1	5.6	6.7	0.36
EC (μcm)	Control	131.3	65.6	186.4	27.6
	Contaminated	205.9	128.6	311.5	59.7
CEC (meq/100g)	Control	4.97	2.64	6.9	1.36
	Contaminated	3.61	0.84	8.29	3.00
OM (mass %)	Control	0.71	0.17	0.98	0.30
	Contaminated	0.52	0.22	0.86	0.29
Exch -Ca (mg/kg)	Control	413.4	142.1	533.1	101
	Contaminated	249.6	110.3	511.8	141.4
Exch -Mg (mg/kg)	Control	214.7	118.5	340.4	75.8
	Contaminated	162.7	9.8	442	167.5
Exch-Na (mg/kg)	Control	8.5	4.2	15.3	3.6
	Contaminated	62.2	13.3	135.4	53.7
Exch -K (mg/kg)	Control	29.7	16.6	56.8	12.5
	Contaminated	285.2	33.2	637.1	274.4

Exch = Exchangeable

Increasing the soil temperature further to 200 °C resulted in a slight decrease in EC for the control soil sample but the same pattern of soil EC observed with increase in duration of heating the soil at temperatures of 100°C was also observed at soil temperatures of 200°C (Figure 4.2a). However, at soil temperatures of 300 and 400°C, the control soil EC values increased with increase in duration of heating (Figure 4.2a). On heating tailings contaminated samples at temperature of 100°C for two hours, an increase in EC was observed but increasing the duration of heating at this temperature resulted in a decrease in EC (Figure 4.2b). Increasing the soil temperature to 200, 300 and then 400°C reduced the overall EC relative to the unheated soil sample but an

increase in EC with the duration of heating at these temperatures was observed (Figure 4.2b). These results indicate that the EC values of the tailings contaminated soil are likely to decrease with increase in soil temperature whereas an extended fire event especially if the soil temperature is significantly increased may cause soil EC values to increase.

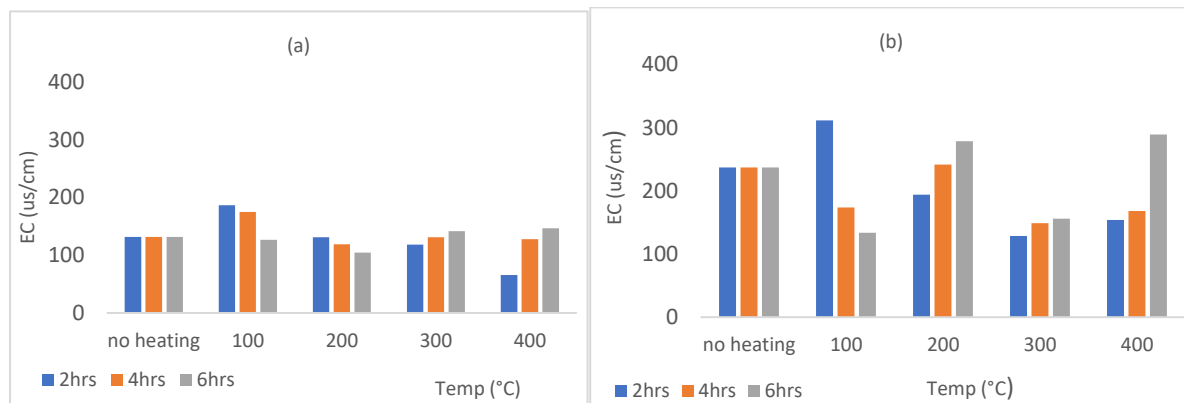


Figure 4.2: Changes in soil electrical conductivity with increase in temperature, and duration of heating. (a) Control (b) Tailings contaminated soil

Hernández *et al.* (1997) opine that soil EC increases with an increase in soil temperature caused by fire events is due to the release of ions from OM that is broken down during its combustion. It is reported that soil EC could also decrease with temperature due to precipitation, salt fixation and leaching. A study conducted by Yusiharni and Gilkes (2012) also showed that at soil temperatures above 350°C, the soil EC decreases due to the soluble salts which are present. The results obtained in this study are therefore not unusual.

4.2.3 Soil pH

The mean pH of the control soil sample was 6.5 with values ranging from 5.5 to 7.3 whereas the tailings contaminated soil samples recorded a mean pH value of 6.1 and a range of 5.6 to 6.7 (Table 4.1). The results show that the mine tailings contaminated soil samples were slightly more acidic compared to the control sample, but the differences were insignificant ($p = 0.09$). It is expected that the pH of the tailings contaminated soil would be more acidic than the control due to the acidic nature of the pyrite which is the main constituents present in the gold mine tailings as described in other studies (Ngole-Jeme & Fantke, 2017; Nengovhela *et al.*, 2006). This was,

however, not the case and could imply that the natural buffering reactions that occur in soils might have contributed to neutralising the acidity of the soils around the tailings dumps. It has also been reported that at a depth of 0 to 35m, the tailings samples show a near neutral pH with increasing depth while the surface soil showed an acidic pH due to the oxidation of the exposed surfaces (Rao & Reddy, 2006). For the current study the samples were collected within surface horizon where neutrality is expected (See section 3.4.1).

Heating the control soil sample at 100°C caused a slight decrease in pH whereas at a temperature of 200°C, there was a slight increase (Figure 4.3a). The soils that were subjected to temperatures of up to 300°C showed a decrease in pH values but those heated at higher temperatures showed no further changes in pH. The pattern observed in the pH of the heated tailings contaminated soil sample was, however, different where pH values increased with an increase in temperature of heating (Figure 4.3b). For both the control and the contaminated soil samples, an increase in the duration of heating caused a slight decrease in the pH of the soils (Figure 4.3a and 4.3b).

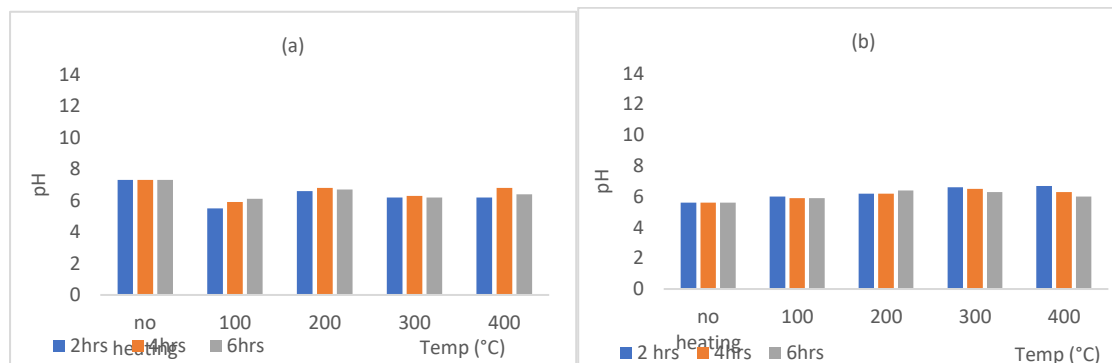


Figure 4.3: Changes in soil pH with increase in temperature and duration of heating (a) Control (b) Tailings contaminated soil

The increase in pH observed as the soil samples were heated could be caused by organic acids denaturation which leads to an increase in basicity as base forming elements are released (Stankov Jovanovic *et al.*, 2011). It is further reported that a significant increase in soil pH is also observed at a soil temperature of 450 and 500°C which according to Certini (2005) is caused by the release of ash which is alkaline and comprises of cations such as Mg, Ca, K and Na that were bound to OM in the soils. The ash is formed as a result of the oxidation of certain elements, dehydration of

colloids and exposure of new surfaces (Parlak, 2011). The increase in soil pH observed in this study as the samples were heated is comparable to the ones Merino *et al.* (2018) and Lombao *et al.* (2015) have described.

4.2.4 Soil Organic matter content

The mean OM content in the control soil sample was 0.71% with the values ranging between 0.17 and 0.98% \pm 0.15%. The tailings contaminated soil samples showed a lower mean value for OM content with a value of 0.52% and a range of 0.22% to 0.86% \pm 0.09% (Table 4.1). Though the control soil sample showed a higher mean OM content, the differences in OM content between the control and tailings contaminated soil were insignificant ($p = 0,16$). It is expected for the tailings contaminated soil to have a low OM content because the mining environment lacks plant nutrients and microbial activities (Chibuike & Obiora, 2014) which promote plant growth and are thus not conducive for vegetation growth, which contributes to soil OM content. From Figure 4.4(a) and (b) both for the control and tailings contaminated sample, the OM content decreased with an increase in the temperature to which the soil was subjected up to about 200°C after which, soil OM was no longer detectable.

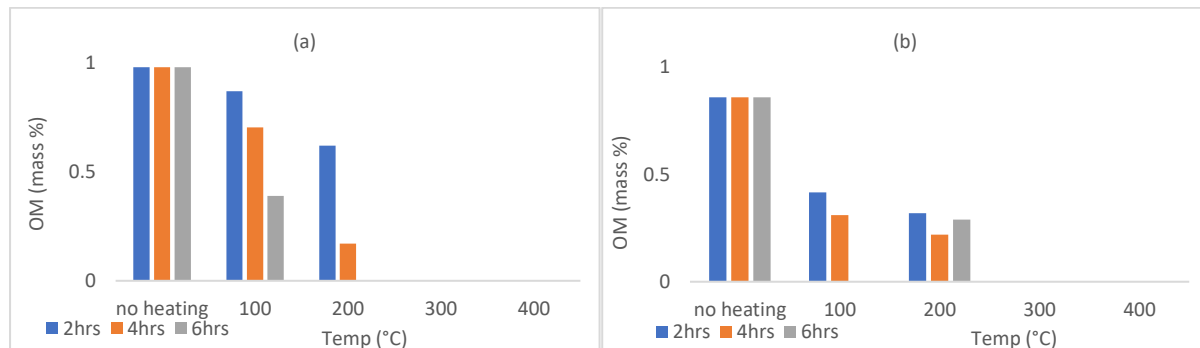


Figure 4.4: Changes in soil organic matter content with temperature, and duration of heating. (a) Control (b) Tailings contaminated soil

The OM content also decreased with an increase in duration of heating at all temperatures (Figure 4.4a and 4.4b). These observations are in line with studies conducted by Fernández *et al.*, (1997) and Certini (2005) who all reported that as the soil is heated, OM in the soil undergoes volatilisation of minor constituents and at temperature of between 250 and 460°C, there is a complete oxidation of the soil OM. Kennard and Gholz (2001) also report that at low soil temperatures, there is a slight decrease in OM as the sample is heated, but as the temperature increases there is

complete elimination of OM. During fire events, the soil OM undergoes several changes such as free vaporisation of moisture, degradation of lignin and hemicellulose, chemical dehydration of cellulose, smouldering and flaming at different temperatures ranging from 100 to 1 500°C (Rabenhorst, 1988) which all contribute to its disappearance from the soil as temperature increases.

4.2.5 Soil Cation exchange capacity

The mean CEC value for the control samples was 4.97 meq/100g soil whereas the tailings contaminated soil samples showed a mean CEC value of 3.61 meq/100g soil (Table 4.1). These values are both within the range of CEC in soils with low clay and OM contents which characterised these samples. When the control soil samples were exposed to a temperature of 100°C, there was a decrease in CEC but an increase in the duration of heating at the same temperature caused an increase in CEC values (Figure 4.4a). However, as the temperature to which the soil was subjected was increased to 200°C, and then to 400°C, there was an overall decrease in soil CEC even though the CEC values were higher than those of the unheated soil sample as shown Figure 4.4a. The CEC of the tailings contaminated soil sample decreased significantly after heating (Figure 4.5b). The decrease is observed mainly at a temperature of 100°C through to 300°C. When the samples were heated at 400°C, a significant increase which later decreased as duration of heating increase was observed (Figure 4.5b).

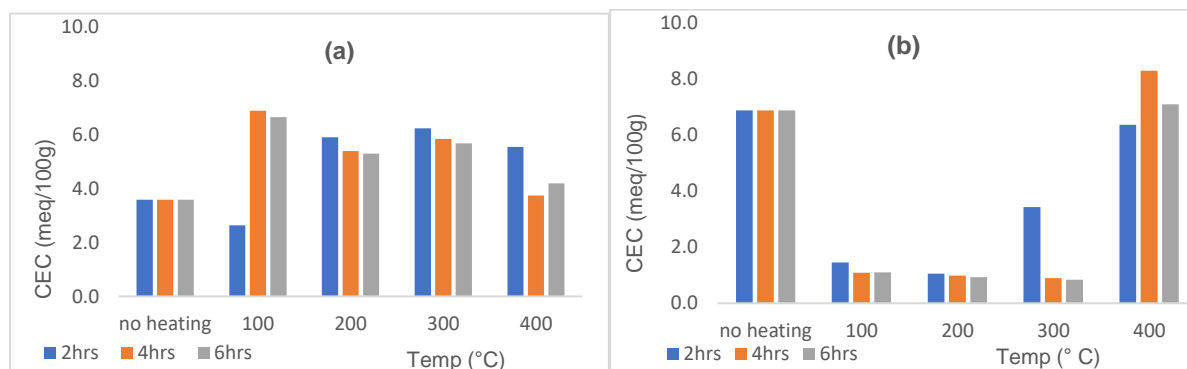


Figure 4.5: Changes in soil cation exchange capacity with increase in soil temperature and duration of heating. (a) Control (b) Tailings contaminated soil

This observation compares with what Zavala *et al.* (2014) reported where soil CEC decreased after a fire event in the first few centimetres of soil. Mehdi *et al.*, (2012) also reported that the soil which experienced a high severity fire had a higher CEC as

compared to the soil that was subjected to low severity fire. However, Certini (2005) reported that as soil experiences high temperature, the decrease in OM and reduction in clay mineralogy leads to a decrease in CEC and this might be the reason for the pattern observed in CEC with increase in soil temperature in this study. Ulery *et al.* (1996) and Olorunfemi *et al.* (2016) indicate that there is a linear relationship between CEC and OM and in this experiment, OM decreased with increase in temperature which might have contributed to the same pattern observed in soil CEC.

The results of the exchangeable bases show that in the tailings contaminated sample Ca and Mg were low compared to the control whereas Na and K were higher compared to the control sample (Table 4.1). Higher exchangeable bases contribute to higher CEC which might affect the ability of the soil to retain metals. A study conducted by De Matos *et al.*, (2001) showed that CEC has an impact on the retention of heavy metals. ANOVA analysis indicated the differences observed among different soil properties as a result of the duration of heating were not significant, while the differences among different soil properties observed as result of increase in temperature were significant (see p-values in Table 4.2 below)

Table 4.2 P-values of the different soil properties

Soil properties (p-values)	Time	Temperature
pH	0.938	0.00
EC	0.931	0.008
OM	0.677	0.00
CEC	0.992	0.00

4.3 Heavy metal concentration in the soil

4.3.1 Heavy metal concentration in soil samples

The results from the heavy metal analysis showed that the tailings contaminated soil sample had higher metal concentrations compared to the control sample (Fig 4.6). In the tailings contaminated sample As, Co, and Ni (578, 467 and 479 mg/kg respectively) were found to have the highest concentration whereas Cd (73 mg/kg) had the lowest concentration. The control sample contained high levels of As, Co, and

Zn (533, 431 and 309 mg/kg respectively) with Cd also having the lowest concentration (68 mg/kg).

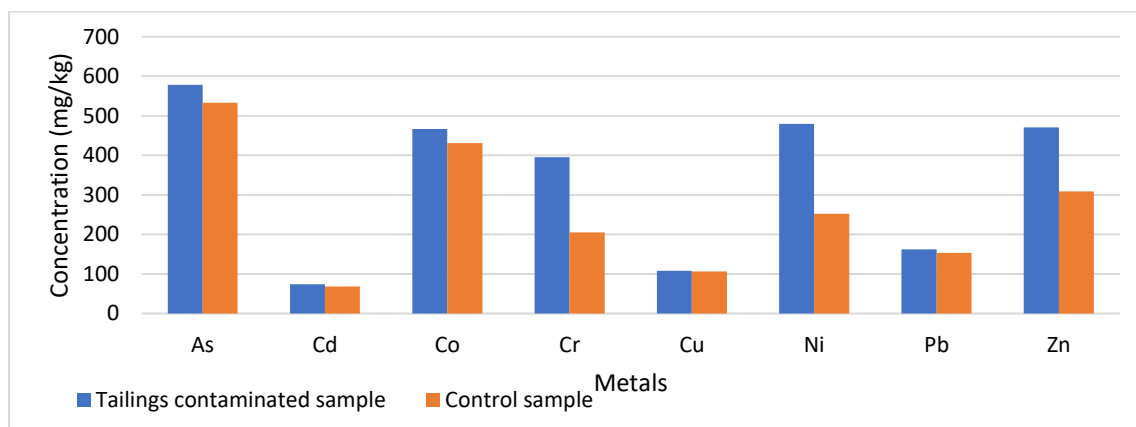


Figure 4.6 Concentration of heavy metal in the control and tailings contaminated soil samples

These results are similar to a study conducted by Antigwei-Agyei (2009) in a gold mine in Ghana, where high concentrations of As, Zn, Cu and Pb were reported in a mining environment. Rosner and Schalkwyk (2000) also reported high concentrations of Ni, Co, and Zn among the metals present in a gold mining area in Johannesburg, South Africa whereas Da Silva (2004) reported high concentrations of As and Pb in a gold mining area in Portugal, with Ngole-Jeme and Fantke (2017) reporting high concentration of Cr and As in another study around other gold mines in South Africa. The heavy metal contamination of the soils might have occurred as a result of leaching from the tailings or dispersal of tailings particles by wind into the surrounding areas.

4.3.2 Effect of temperature and duration of heating on soil heavy metal concentration

Heating the control sample at 100 and 200°C for two hours caused a decrease in the As, Co, Ni and Zn concentration but as the temperature was increased to 300 and 400°C and the duration of heating at this respective temperature also increased, so did the metal concentration (Fig 4.7 a, g, k, o). As the tailings contaminated sample was exposed to a temperature of 100 and 200°C for a two-hour duration, a different pattern in the concentration for these metals was observed (Figure 4.7 b, h, l, p). After the soil was exposed to high temperatures, the metals which had high content remained high even though there was a general decrease as compared to the samples not heated for both tailings contaminated, and the control soil samples.

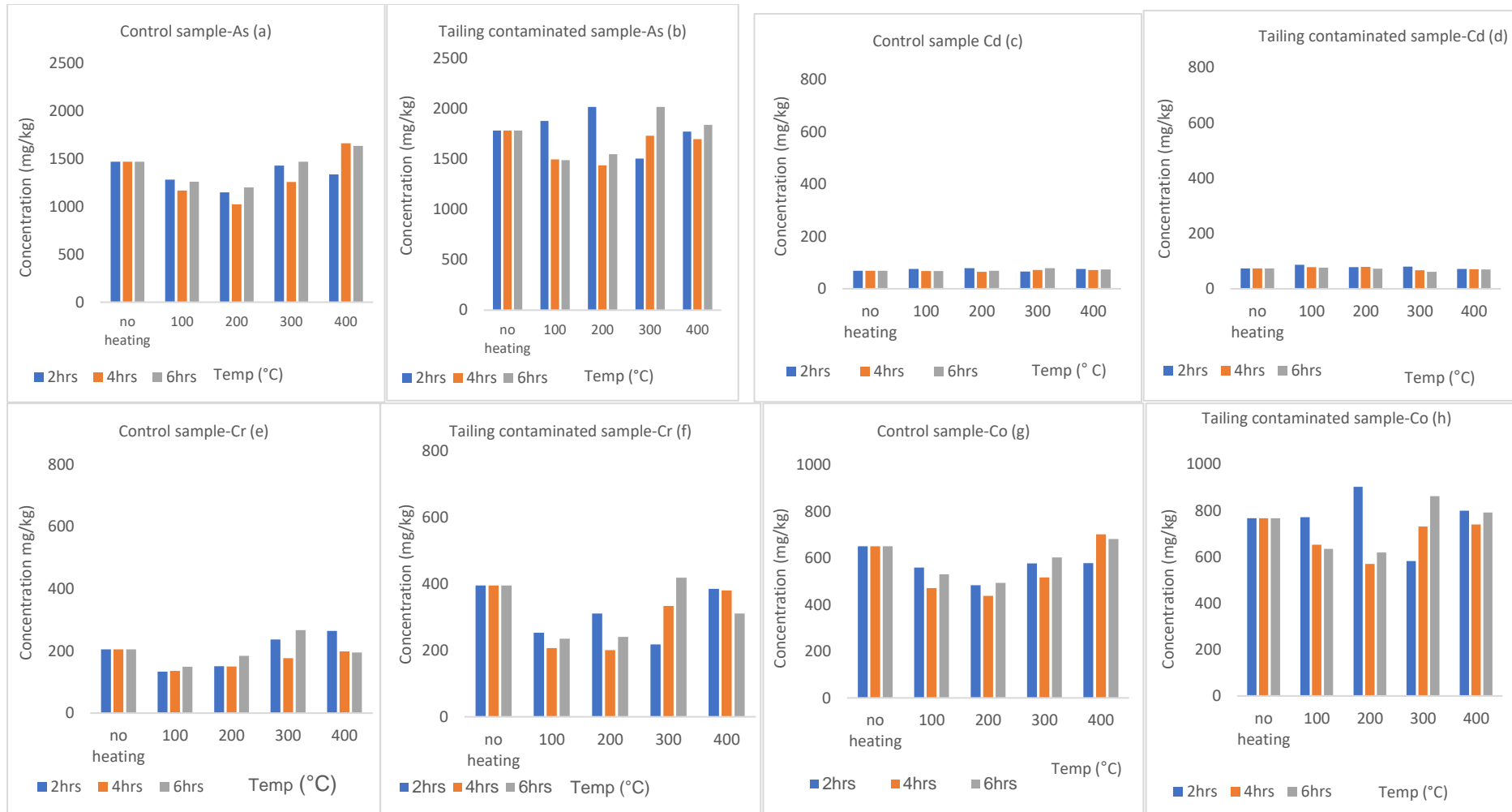


Figure 4.7 Changes in soil metal content with increasing temperature and duration of heating

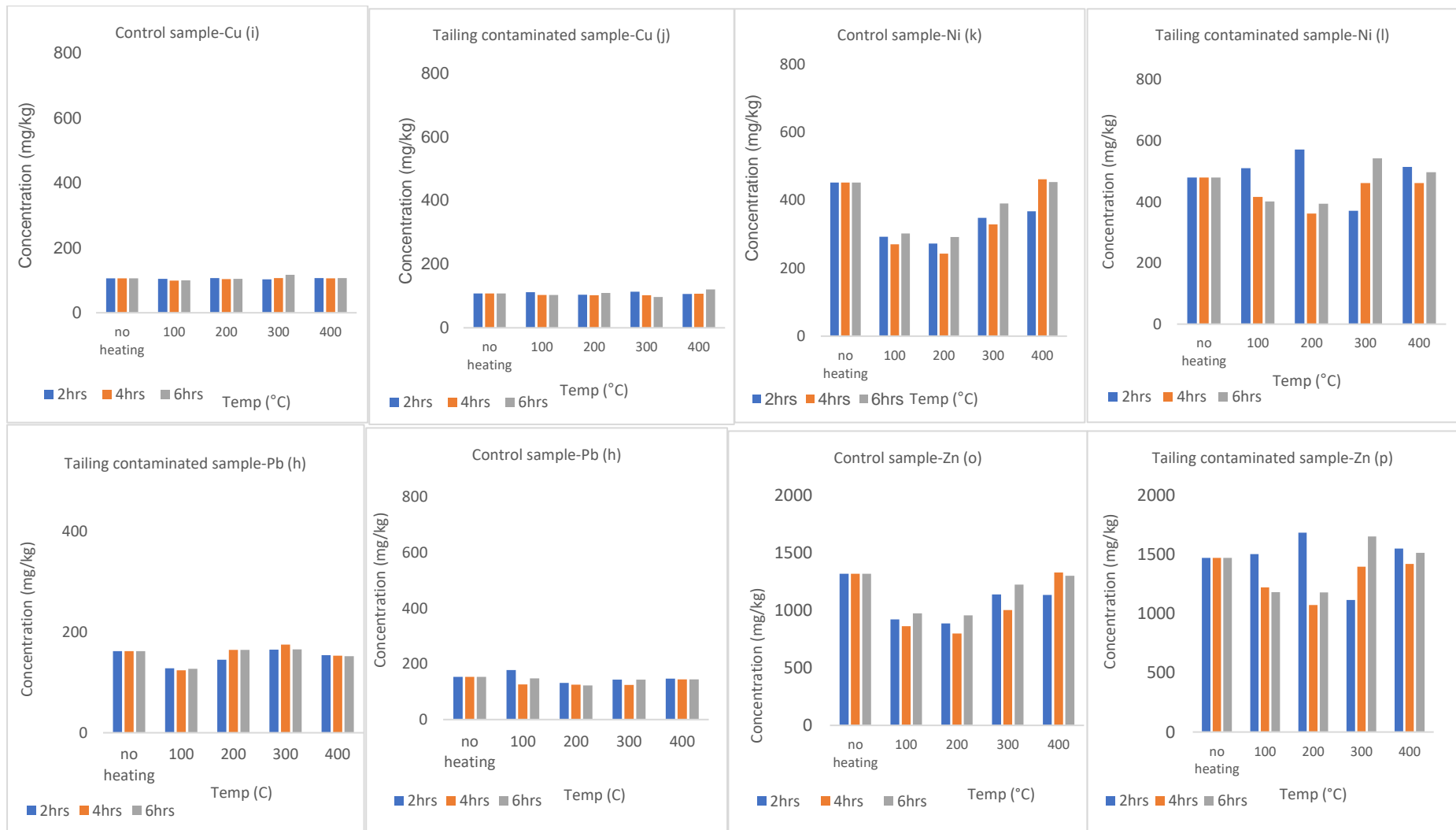


Figure 4.8 Changes in soil metal content with increasing temperature and duration of heating

A slight increase in the concentration of As, Ni, Co, and Zn (as compared to the concentration of the sample not heated) was observed with an increase in temperature to 200°C in the tailings contaminated sample whereas increasing the duration of heating at the same temperatures caused a slight decrease. However, increasing the soil temperature of the soils from 200°C to 400°C and holding it at these temperatures for two hours resulted in a decrease in the concentration of these metals (Figure 4.7). Increasing the duration of heating at these temperature levels also increased the metal concentration to values that are close to the samples not treated (Figure 4.7 b, l, n, p). The observation in this study is comparable to that which was seen by Johnston *et al.*, (2019b) where an increase in As concentration after a fire in an OM-rich soil was observed. Memoli *et al.* (2020) also indicated an increase in Cd, Pb, and Ni concentration in soil after experiencing a fire event while Co and Cu concentration post-fire did not differ significantly. Abraham *et al.* (2018b) together with Stankov Jovanovic *et al.* (2011) also recorded an increase in Zn concentration after fire.

With Pb content in the control sample, an increase was observed after heating the soil at 100°C for two hours followed by a decrease after increasing the temperature to 200°C and holding it at this level for two hours. Further increasing the soil temperature to 300 and 400°C and holding the soil temperature at this level for two hours resulted in an increase in Pb concentration in the samples. (Figure 4.7 k). When the tailings contaminated sample was heated at 100°C, the Pb content decreased (as compared to the sample that was not heated) irrespective of the duration during which the soil was held at this temperature. Increasing the temperature to 200°C and 300°C and the duration of heating resulted in an increase in metal concentrations but at a temperature of 400°C, a slight decrease was observed (Figure 4.7 l). The Cd and Cu content in both the tailings contaminated soil and the control soil sample did not change significantly with heating at different temperatures and duration of heating (Figure 4.7 c, d, i, j). The results are comparable with what Stankov Jovanovic *et al.* (2011) reported, where Cd concentration was not affected by fire. Chromium content in both the tailings contaminated sample and the control sample decreased when the samples were heated at 100°C, but increased duration and intensity of heating resulted in an increase in Cr concentration (Figure 4.7 e, f). Burton *et al.*, (2019b) and Panichev *et al.*, (2008b) reported that in burnt soil, there was an oxidation of Cr (III) to Cr (VI) which lead to an increase in Cr concentration. The oxidation of Cr could, therefore, have

accounted for the increase observed in Cr content in the soils with increase in temperature.

Increasing the temperature of the soil has a profound impact on the concentration of the present heavy metal. It has been reported by Abraham *et al.*, (2018), Memoli *et al.* (2020) and Johnston *et al.*, (2019) that heavy metals such as Cd, Co, Cu, Cr, Zn, Pb, Ni and As can either decrease, increase, or remain unchanged as the soil experiences high temperature. Arsenic has been reported to change from As(V) oxidation state to As(III) which is more soluble as soil temperature increases (Burton *et al.*, 2019). The formation of ash, combustion of vegetation and OM reduction during heating has been attributed to the increase or decrease in some of these metals (da Costa *et al.*, 2020 ; (Stankov Jovanovic *et al.*, 2011). The metals of interest in this study have high volatilisation temperature, with Cr having the lowest volatilisation value of 550°C and Ni the highest at 2 730°C. The maximum temperature to which the soil samples were exposed to in this study was 400°C which is below the minimum volatilisation temperature hence metals could not have been lost through vaporisation.

According to ANOVA analysis, difference observed in the metal concentration of the tailings contaminated soil sample as results of the increase in temperature were significant only for As, Ni, Co, Cr, Pb and Zn while for Cd and Cu the differences were insignificant. ANOVA analysis also indicated the differences observed as a result of the duration of heating had no significant effect on all the metals (see Table 4.3 below).

Table 4.3 P-values of different metals

Metals (p-values)	Time	Temperature
As	0.660	0.001
Ni	0.760	0.00
Cd	0.147	0.151
Co	0.688	0.002
Cr	0.853	0.00
Cu	0.386	0.505
Pb	0.753	0.00
Zn	0.676	0.001

4.3.3 Contamination factor of heavy metals in the soils

The high concentrations of heavy metals in the tailings contaminated soil sample indicate the contribution by mining to heavy metal dispersal in the environment. The extent of heavy metal contamination is highlighted by the values for heavy metal Contamination Factors (CF) obtained for the different metals. The values for heavy metal CF indicated that Cu contamination was the lowest with a CF value of 1.02 whereas Cr had the highest CF value (1.92) as shown in Figure 4.9. The CF for the heavy metals followed the order Cu > As > Se > Zn > Cd > Co > Ni > Pb > Cr (Figure 4.9).

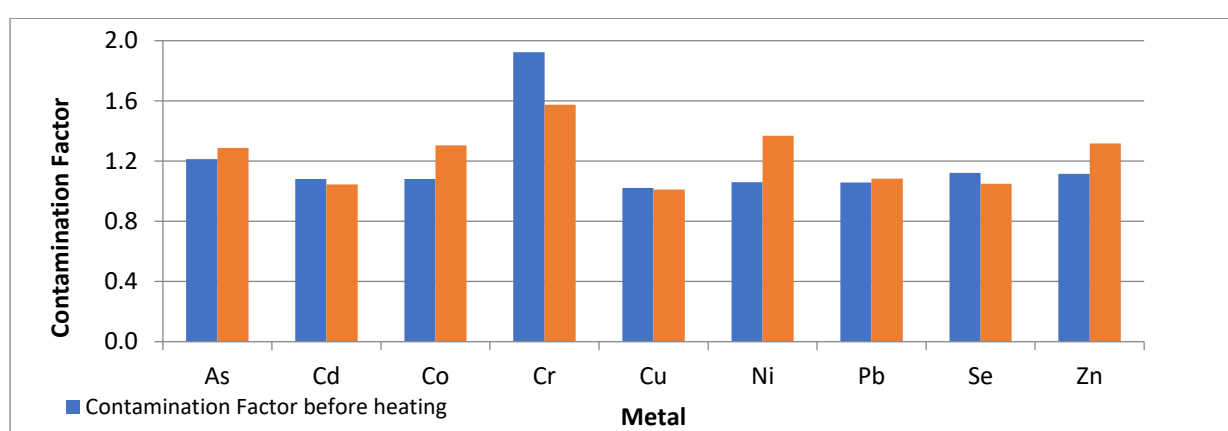


Figure 4.9 Heavy metal contamination factors in tailings contaminated soil samples before and after heating

After the soil samples were heated, the CF decreased to 1,01 for Cu and 1,57 for Cr. The order of CF values for the different metals observed in the unheated soils changed to Cu > Cd > Se > Pb > As > Co > Zn > Ni > Cr. The CF of Co, Ni, and Zn increased significantly with increase in temperature whereas that of Cr decreased with Cu remaining constant (Figure 4.9). The changes in CF can be associated with the fact that with heating the contaminated tailings sample, pH of the soil moved to a neutral state and in a neutral state metals are mostly present in less available forms (Anguissola *et al.*, 1999); and Lee *et al.*, 2019).

4.4 Soil geochemical properties

In both the control and the tailings contaminated sample, quartz (SiO_2) was the dominant oxide followed by Al_2O_3 and Fe_2O_3 . Other oxides such as CaO, MgO and

MnO were in trace amounts while water constituted less than 1% by weight of the samples (Table 4.2). The control soil sample which was not heated contained 82.89% SiO₂, 6.05% Al₂O₃ followed by 5.9% of Fe₂O₃. The tailings contaminated soil samples which were not heated contained 85.48% SiO₂, 5.6% Al₂O₃ followed by 4.4% of Fe₂O₃. This pattern is typical of soils where quartz usually constitutes the greatest percentage of trace and major element oxides.

When the control sample was heated at 300°C and 750°C for two hours the amount of SiO₂, Al₂O₃ and MnO increased as compared to the sample that was not heated while a decrease was observed in Fe₂O₃ at 300°C followed by an increase thereafter. However, when the same sample was heated at 300°C for four hours instead of two hours, there was a decrease in SiO₂ content followed by an increase in Al₂O₃ and Fe₂O₃ while the content of MnO remained unchanged. Increasing the duration of heating to six hours at 300°C increased the SiO₂ and MnO but decreased the Al₂O₃ and Fe₂O₃ contents. A further increase in temperature and duration of heating to six hours resulted in further increase in the concentration of SiO₂ content followed by an increase in Fe₂O₃, Al₂O₃ and Mn.

With the tailings contaminated sample, heating the sample at 300°C for two hours resulted in an increase in SiO₂ content while Al₂O₃ content decreased slightly. The concentration of Fe₂O₃ increased when the soil temperature was raised to 300°C and held at this level for two hours. Further increasing the duration of heating of the soil at this temperature caused a further increase in Fe₂O₃ while MnO content remained unchanged throughout the heating experiment. Heating the sample for two hours at 300°C did not impact the content of Al₂O₃, however, increasing the duration of heating caused a decrease in the content of MnO in the tailings contaminated soil sample. A further increase in the duration of heating to six hours at 300°C caused a decrease in SiO₂ and Fe₂O₃ content, an increase in Al₂O₃ while MnO content remained unchanged. The tailings contaminated soil sample showed an increase in SiO₂ content two hours after heating at 750°C and increasing the duration of heating to six hours at the same temperature caused a slight increase in SiO₂, and a decrease in Al₂O₃ whereas MnO and Fe₂O₃ contents remained unchanged (Table 4.4). Yusiharni and Gilkes (2012) indicated that heating soil above 500°C increases silica and aluminium oxide content as a result of the formation of meta-kaolinite and amorphous alumina.

Table 4.4 Geochemical properties of soil samples used in the study

Sample	Units	No heating		Heated 300 degrees for 2hours		Heated 750 degrees for 2hours		Heated at 300 degrees for 4hours		Heated at 300 degrees for 6hours		Heated at 750 degrees for 6hours	
		Control sample	Tailing sample	Control sample	Tailing sample	Control sample	Tailing sample	Control sample	Tailing sample	Control sample	Tailing sample	Control sample	Tailing sample
SiO ₂	%	82.89 ^a	85.48 ^g	84.24 ^b	86.3 ^h	85.52 ^c	87.58 ⁱ	83.74 ^e	87.43 ⁱ	84.23 ^b	86.43 ^h	85.44 ^f	87.77 ⁱ
TiO ₂	%	0.51 ^a	0.4 ^c	0.51 ^a	0.4 ^c	0.55 ^b	0.43 ^d	0.52 ^a	0.39 ^c	0.52 ^a	0.41 ^c	0.55 ^b	0.42 ^c
Al ₂ O ₃	%	6.05 ^a	5.6 ^d	6.27 ^b	5.5 ^d	6.7 ^c	5.9 ^e	6.4 ^d	4.89 ^f	6.26 ^b	5.57 ^d	6.73 ^c	5.88 ^e
Fe ₂ O ₃ (t)	%	5.9 ^a	4.4 ^a	5.65 ^b	4.53 ^a	6.22 ^c	4.8 ^b	5.9 ^a	4.68 ^c	5.87 ^a	4.42 ^a	6.25 ^c	4.83 ^b
MnO	%	0.173	0.18	0.175	0.19	0.203	0.2	0.189	0.18	0.207	0.19	0.219	0.19
MgO	%	<0.01	0.14	<0.01	0.15	<0.01	0.14	<0.01	0.04	<0.01	0.15	<0.01	0.15
CaO	%	0.05	0.07	0.05	0.07	0.05	0.07	0.05	0.06	0.04	0.07	0.05	0.08
Na ₂ O	%	0.03	0.05	0.02	0.08	0.41	0.2	<0.01	<0.01	0.04	0.05	0.07	0.08
K ₂ O	%	0.24	0.34	0.24	0.35	0.29	0.37	0.25	0.23	0.25	0.34	0.26	0.36
P ₂ O ₅	%	0.069	0.06	0.071	0.07	0.074	0.07	0.071	0.07	0.074	0.07	0.075	0.07
Cr ₂ O ₃	%	0.055	0.04	0.05	0.04	0.053	0.04	0.054	0.05	0.05	0.04	0.056	0.04
L.O.I.	%	4.15	3.31	2.82	2.15	0.2	0.3	2.72	2.03	2.59	2.04	0.21	0.23
Total	%	100.08	100	100.06	99.81	100.25	99.97	99.84	100.01	100.11	99.69	99.88	100.01
H ₂ O-	%	0.95	0.78	0.63	0.6	0.31	0.32	0.71	0.58	0.72	0.61	0.36	0.34

*Note that comparison of the means has been made between control and tailing contaminated soil samples

Koshovskii et al., (2014) also described an increase in Fe₂O₃, Al₂O₃, CaO, and MnO after a soil experiences fire. Calcium oxide showed an increase while SiO₂ decreased in concentration after soil experiences fire and the increase is attributed to burned litter and plant residue (Maksimova & Abakumov, 2014).

4.5 Soil mineralogy

Quartz dominated the mineralogical composition of the soil samples (Table 4.5). The control sample which was not heated contained 97% quartz, 2% kaolinite and 1% goethite. Subjecting the control sample to temperatures of 100°C and 300°C, caused an increase in kaolinite content to 3% but decreased to 2% with longer heating duration (six hours). Increasing the temperature further to 500°C resulted in complete disappearance of kaolinite and an increase in both quartz and goethite contents (Table 4.5). Further increase in temperature resulted in the appearance of feldspar mineral in the control sample and this is because feldspars is the main constituent in sand and silt fractions (Radoslovich, 1975) which is the main composition of the soil (see section 4.2.1), but as the duration of heating increased to six hours, this mineral disappeared whereas the quartz content increased to 99 % with a decrease in goethite content observed.

The tailings contaminated soil sample was also dominated by quartz with a relative abundance of 94% whereas other minerals such as chlorite, kaolinite, mica, and goethite were present in trace quantities. When the sample was subjected to temperatures of 150°C, minerals such as feldspar and pyrophyllite appeared in trace quantities with a slight decrease in quartz content observed. As the duration of heating at this temperature increased, those minerals also disappeared (Table 4.5). With an increase in temperature to 300°C and 500°C, other minerals appeared but as the duration of heating increased, these minerals also disappeared. At higher temperatures, whether the sample was heated for a shorter or longer duration, only quartz (99%) and goethite were present (1%) in the sample. Ngole-Jeme (2019) states that quartz has a melting temperature of 2 577°C and so it can only be affected at very high temperatures which the soil is not likely to attain during fire events.

Table 4.5 Mineralogical composition of the soil (effect of temperature and duration)

Sample	Temperature (degree Celsius)	Duration	Gypsum	Hematite/ Goethite	K-feldspar	Plagioclase	Quartz	Mica	Kaolinite	Chlorite	Amphibole	Pyrophyllite
Control soil samples	0	0	-	1	-	-	97	-	2	-	-	-
	150	2 hours	-	1	1	-	96	-	3	-	-	-
	150	4 hours	-	1	-	-	96	-	3	-	-	-
	150	6 hours	-	1	-	-	97	-	2	-	-	-
	300	2 hours	-	1	-	-	96	-	3	-	-	-
	300	4 hours	-	2	-	-	95	-	3	-	-	-
	300	6 hours	-	1	-	-	97	-	2	-	-	-
	500	2 hours	-	2	-	-	98	-	-	-	-	-
	500	4 hours	-	2	-	-	98	-	-	-	-	-
	500	6 hours	-	1	-	-	99	-	-	-	-	-
	750	2 hours	-	2	1	-	97	-	-	-	-	-
	750	4 hours	-	2	-	-	98	-	-	-	-	-
750	6 hours	-	1	-	-	99	-	-	-	-	-	

Tailings contaminated soil sample	0	0	-	1	-	1	94	2	2	4	-	1
	150	2 hours	-	1	1	-	93	3	2	5	-	2
	150	4 hours	-	1	-	1	94	2	2	5	-	5
	150	6 hours	-	1	-	-	96	1	2	-	-	-
	300	2 hours	-	1	-	1	94	2	2	5	-	2
	300	4 hours	-	1	-	-	95	2	2	-	-	1
	300	6 hours	-	1	-	-	98	-	2	-	-	-
	500	2 hours	-	1	-	-	97	2	-	2	-	2
	500	4 hours	-	1	-	-	97	2	2	-	-	-
	500	6 hours	-	1	-	-	98	1	2	-	-	1
	750	2 hours	-	2	-	-	98	-	-	-	-	-
	750	4 hours	-	1	-	-	99	-	-	-	-	-
750	6 hours	-	1	-	-	99	-	-	-	-	-	

Reynard-Callanan et al., (2010) showed that in an unburnt soil, mineral such as smectite, kaolin and chlorite were present but, these minerals disappeared as soil temperature increased whereas mineral such as illite decreased in concentration. Arocena and Opio (2003)) as well as Ulery et al. (1996) also report that the mineralogical composition of the soil varies between burned and unburnt portions of soil. Yusiharni and Gilkes (2012) have also shown that kaolinite dehydroxylate transforms into meta-kaolinite while goethite transforms into hematite, while quartz remains unchanged.

4.6 Implications of temperature induced changes in soil properties

Increased temperature and duration of heating affected the physicochemical properties of soils. In this study, the increase in temperature was used to simulate fire intensity whereas an increase in the duration of heating simulated fire duration. The results obtained indicate varying effects of temperature increases and duration of heating on soil properties. For example, soil OM is eliminated as both intensity and duration of heating increases with soil OM disappearing at temperatures of 200°C. Soil CEC showed an initial decrease with increase in soil temperature but increased thereafter. Temperature increases also affected soil geochemistry.

These results indicate that fire events are likely to affect various soil properties in different ways. An increase in fire intensity is expected to result in an increase in major metal oxides such as SiO_2 , Al_2O_3 and Fe_2O_3 but an increase in the duration of the fire could decrease the content of these oxides in the soil. There is likely to be no significant impact of fire duration or fire intensity on the amounts of other oxides such as MnO, CaO and MgO. The effect of fire intensity and duration on soil metal concentrations is also likely to vary but the changes are relatively insignificant. Though the overall concentration of the metals in the soil were not affected, it is not clear whether the speciation/segregation of the heavy metals into the different geochemical fractions are changed as a result of changes in temperature. The soil mineralogy was also affected by changes in soil temperature. When samples were heated at higher temperatures and for different durations, minerals such as feldspar and plagioclase appeared but in trace quantities. As the temperature and the duration of heating

increased, quartz and goethite remained unchanged. The changes in soil mineralogy that may occur as a result of fire events may vary depending on the mineral assemblage of the soil.

Soil physicochemical properties influence the mobility of metals in the soil. The mobility of metals such as Zn and Cu has been shown to increase with decreasing pH (Planquart *et al.*, 1999), while Zn mobility and bioavailability can be altered by OM content and oxides which are present (Kumpiene *et al.*, 2008). Soil texture has also been reported to increase the mobility of metals (Kabala & Singh, 2001). It has also been reported that soil CEC influences the sorption and mobility of heavy metals.

4.7 Concluding remarks

The results of this study showed that the sample had a loamy sand texture which was characterized by high EC, and with increasing temperature EC increased whereas a decrease in CEC was observed. The sample was slightly acidic which might have been a result of a natural buffering process. With increasing temperature there was a decrease in OM and at high temperature there was a complete elimination. The mineralogical results showed that the sample was dominated by quartz (SiO_2) and oxides such as Al_2O_3 and Fe_2O_3 , and with increasing temperature quartz remained dominant followed by a decrease in these oxides. All the heavy metals which were analysed were present in the soil but As, Co and Zn had the highest concentration whereas Cd had the lowest. The following chapter discusses the changes in the fractionation of the different heavy metals that are caused by temperature changes. It also looks at how the mobility of the metals in soils are affected by changes in soil temperature and the implication of using sludge as a remediated material for fire affected contaminated soils.

CHAPTER 5

RESULTS AND DISCUSSION: EFFECT OF SOIL TEMPERATURE CHANGES AND SLUDGE ADDITION ON THE FRACTIONATION OF HEAVY METALS

5.1 Introduction

The chapter firstly explains the impact of sludge addition on heavy metal content in the soils, then explains how the partitioning of the heavy metals into the different geochemical fractions was affected by sludge application, temperature increases and the duration of heating. The variation in sorption capacity of the soils under different temperature conditions and different sludge application rates is then inferred from the changes in the mobility factor of the metals in the soils. The chapter concludes by inferring how soil metal mobility and sorption is likely to be affected by fire intensity and duration.

5.2 Concentration of heavy metals in the soils after sludge addition

The heavy metal which had the highest concentration both in the tailings contaminated soil and in the control soil sample after sludge addition was As whereas Cd had the lowest (Table 5.1). At a soil: sludge application ratio of 80:20, As and Cd concentrations increased compared to the same samples with no sludge whereas at a soil: sludge ratio of 60:40, the concentration of As increased and Cd decreased in the tailings contaminated soil sample. Sludge addition seemed to cause a slight increase in concentration for all metals in the control sample whereas for the tailings contaminated soils, the addition of sludge had varied effects (Table 5.1). Whereas the concentration of Cu and Pb increased with an increase in sludge application rate, the pattern was not so clear with the other metals as they increased with the application of sludge at a rate of 80:20 but decreased as the amount of sludge increased. These results may indicate that the content of the metals was higher in the sludge than in the control sample but lower than what was obtained in the tailings contaminated soils. This is not uncommon as sludge addition to soil has been documented as one of the ways through which heavy metals are introduced into the environment.

Table 5.1 Total concentrations of Heavy metals in sludge amended soils

Metal	Metal concentration (mg/kg)					
	No sludge applied		80:20 soil: sludge		60:40 soil: sludge ratio	
	contaminated	control	contaminated	control	contaminated	Control
As	586.1 ^b	471.7 ^a	653.7 ^c	473.4 ^a	711.0 ^d	409 ^a
Cd	74.1 ^b	68.5 ^a	80.3 ^b	65.5 ^a	77.3 ^b	67.3 ^a
Co	567.0 ^b	450.2 ^a	771.0 ^c	490.2 ^a	728.2 ^c	480.0 ^a
Cr	395.0 ^c	205.3 ^b	332.6 ^c	185.5 ^a	485.2	190.7 ^a
Cu	108.3 ^a	112.4 ^a	116.9 ^a	112.4 ^a	129.0 ^b	125.7 ^b
Ni	479.9 ^a	452.8 ^a	621.1 ^c	390.9 ^b	578.9 ^d	379.5 ^b
Pb	162.3 ^a	153.5 ^a	188.4 ^a	172.7 ^a	216.5 ^b	200.3 ^b
Zn	471.4 ^c	318.9 ^a	688.8 ^d	325.0 ^a	473.9 ^c	387.89 ^a

*Note: mean separators represent comparison of the metal concentration at different sludge application rate not across different metals

5.3 Partitioning of heavy metals in the soils after sludge addition

The partitioning of the different heavy metals into the different geochemical fractions of the tailings contaminated soils varied. In the tailings contaminated and control soil samples where no sludge was applied, the dominant fraction of **Arsenic** was the residual fraction (S4) followed by the organically bound fraction (S3) (Figure 5.1). The addition of sludge at ratios of 80:20 and 60:40 soil: sludge in both the tailings contaminated and control samples caused a proportionate increase in As concentration in the S4 fraction followed by the exchangeable and carbonate fraction (S1).

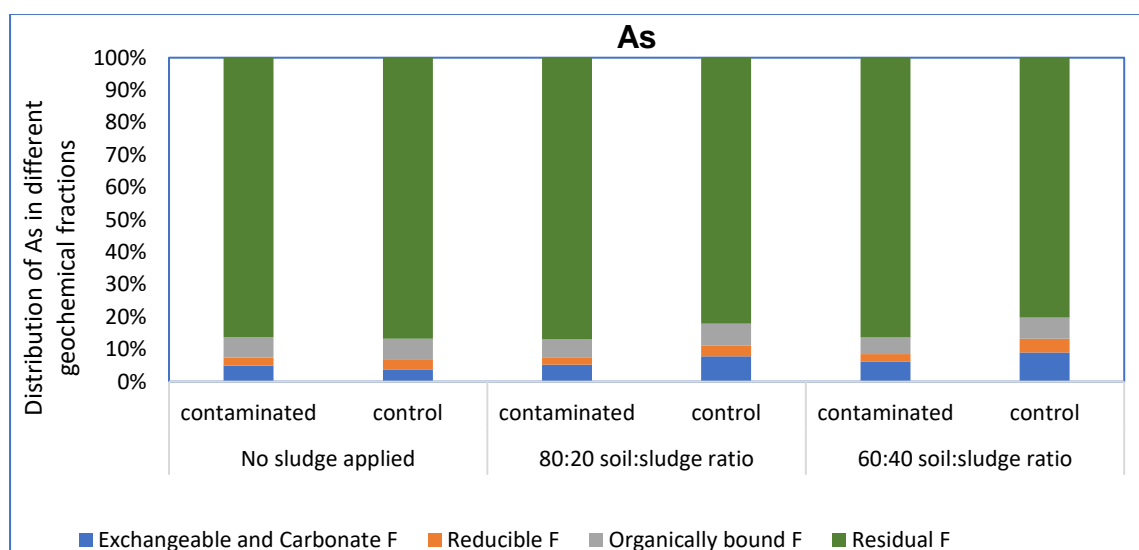


Figure 5.1 Partitioning of As in the tailings contaminated and control soil samples with and without sludge

Cao and Ma (2004) also showed that As segregated preferentially into the S3 and S4 fractions but after treatment with biosolids, the S3 fraction became the dominant fraction. Their results differed from the pattern obtained in this study where the As concentration in the S1 fraction increased with sludge application. The increase in the As concentration in the S1 fraction of these samples could be associated with the decreases in the As concentration in the S4 fraction after sludge addition (Figure 5.1).

Cadmium in both the tailings contaminated and the control soil samples segregated mainly into the S1 and reducible (S2) fractions (Figure 5.2). An increase in the Cd content in the S4 fraction was observed in the tailings contaminated soil sample with the addition of sludge while the opposite was observed in the control sample as indicated in Figure 5.2. In both the tailings contaminated and the control soil samples, there was no effect of sludge addition on the partitioning of Cd thus the S1 and S2 fractions remained the dominant Cd fractions after sludge addition (Figure 5.2).

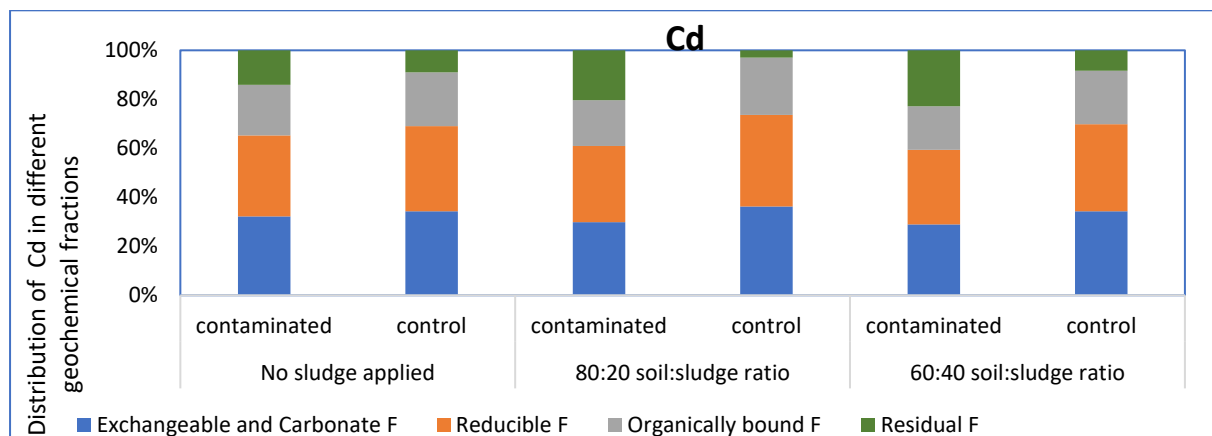


Figure 5.2: Partitioning of Cd in tailings contaminated and control soil samples with and without sludge

These results are slightly different from those obtained by Shrivastava and Banerjee, (2004) who reported that in sludge-amended soils, a high Cd concentration is present in the S4 followed by S2 fractions. Chaudhuri *et al.* (2003) also found that Cd segregated into the S4 fraction followed by S1 fraction. The dominance of Cd in S1 and S2 fractions which are the most mobile fractions can be attributed to the fact that Cd is less likely to form organic ligands (Shrivastava & Banerjee, 2004) and so it is not likely to be found in the S3 fraction which represents the metals bound to organic

matter. According to Sánchez-Martín *et al.*, (2007), Cd mainly segregates into the S2 and S3 fractions at lower sludge application rates but with increased rate of sludge addition, the segregation is mainly into the S4 and S1 fractions with a decrease in the S3 fraction. A similar pattern was observed in these samples.

Chromium in the tailings contaminated soil sample where no sludge was applied preferentially segregated into the S3 and S4 fractions with the S4 fraction being the dominant fraction (Figure 5.3). A different pattern was observed in the control sample where Cr preferentially segregated into the S4 and S2 fractions (Figure 5.3). After sludge addition, Cr concentration in the S3 and S4 fractions of the tailings contaminated soil increased further. In the control soil sample, sludge addition did not change the partitioning of Cr as the S4 and S2 fractions remained the dominant fractions though the overall concentration decreased compared to the samples with no sludge.

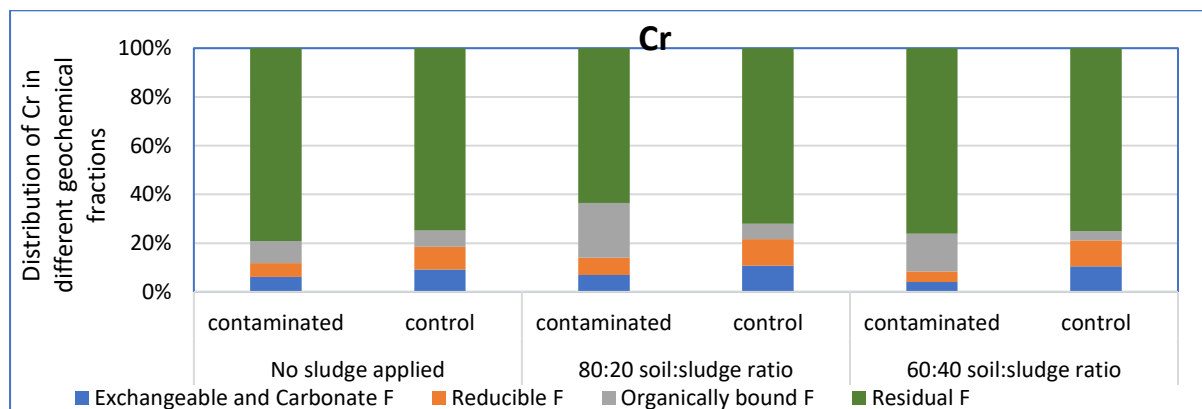


Figure 5.3 Partitioning of Cr in tailings contaminated and control soil samples with and without sludge

In sludge-amended soil, Cr has been shown to have low bioavailability (Walter & Cuevas, 1999) hence its dominance in the less available fractions is not unexpected. Chaudhuri *et al.* (2003) as well as Shrivastava and Banerjee (2004) also reported that Cr segregated preferentially into the S4 fractions before and after sludge addition. Similarly, Sánchez-Martín *et al.* (2007) and Malinowska (2017) showed that at high and low sludge application rates, the Cr segregated preferentially into S3 and S4 fractions and this reduces the bioavailability of Cr in soil since these fractions are not labile. The segregation of Cr into the S3 and S4 fractions may highlight the ability of

Cr to form complexes with OM and silicates which dominate the S3 and S4 fractions respectively.

Cobalt in the tailings contaminated and control soil samples without sludge preferentially segregated into the S4 fraction. After the application of sludge at different rates in both samples, Co concentration remained dominant in the S4 fraction (Figure 5.4). These results are comparable to that of Malinowska and Jankowski (2020) who also reported that in a sludge-amended soil, Co segregates preferentially into the S4 fraction and an increase in the dosage of sludge leads to a further increase of Co concentration in the S4 fraction. Cobalt normally segregates preferentially into the S1 and S2 fractions but in soil which has low concentration of Fe and Mn oxide, Co is said to prefer other fractions (Jovic *et al.*, 2017). These oxides had relatively low concentrations in these samples (Table 4.2) which may explain why Co segregated preferentially into the S4 instead of the S2 fraction.

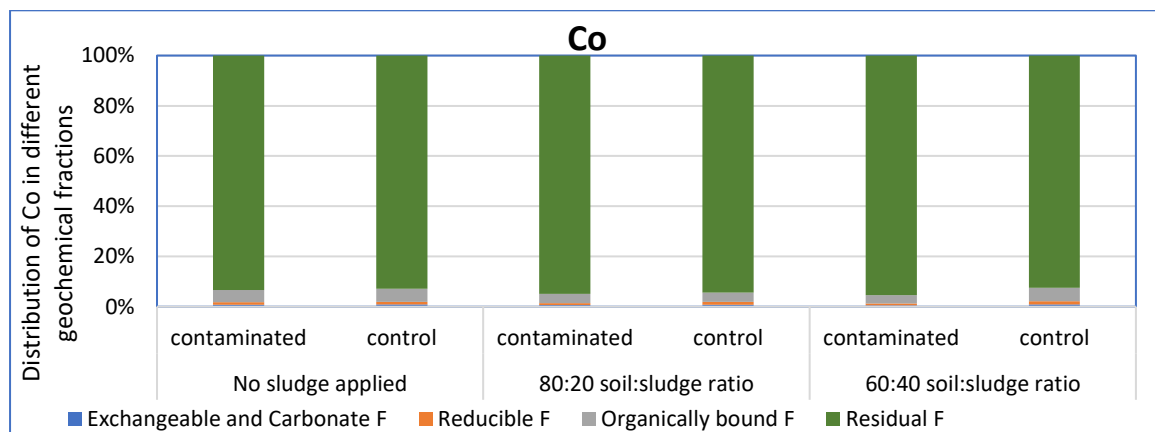


Figure 5.4 Partitioning of Co in tailings contaminated and control soil samples with and without sludge

The dominant fraction of **Copper** in the tailings contaminated and control soil samples was the S4 fraction whereas the other three fractions (S1, S2 and S3) had similar amounts of Cu (Figure 5.5). This pattern of Cu segregation in the tailings contaminated samples was not affected by sludge addition. However, as the rate of sludge application increased, the Cu concentration in the S3 fraction increased in both soil samples. The results are similar to what was observed by Ngole (2011) and Chaudhuri *et al.*, (2003) who all stated that in a sludge-amended soils, Cu segregated into the

organic matter bound fraction (S3) with an increase in sludge application rate. Mendoza *et al.*, (2006) also reported that in a loamy sand soil amended with sludge, Cu segregated mostly into the residual fraction (S4). Rosen and Chen (2014) also reported an increase in S3 fractions with an increase in compost addition. These results all show that Cu will preferentially segregate into the S3 or S4 fractions. The increase of Cu concentration in the S3 fraction with sludge addition is explained by the fact that Cu has a strong affinity for organic complexation and will therefore mostly sorp unto the organic matter fraction (Ashworth & Alloway, 2008).

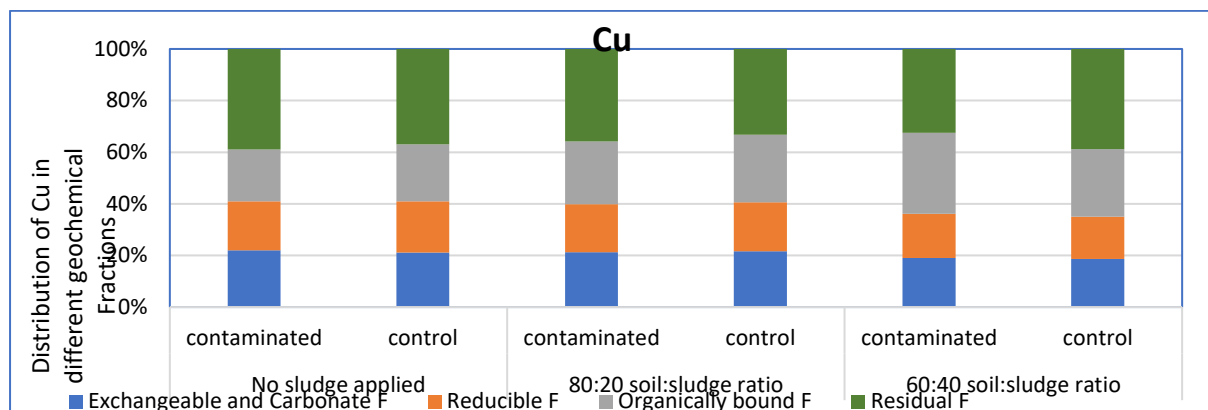


Figure 5.5 Partitioning of Copper in tailings contaminated and control soil samples with and without sludge

Nickel in the control and tailings contaminated soil samples where no sludge was applied also preferentially segregates into the S3 and S4 fractions (Figure 5.6). After the application of sludge, the Ni concentration in both fractions of the tailings contaminated soil increased further but in the control sample, though after sludge addition the Ni concentration in the S3 and S4 fractions remained high, the concentration decreased as compared to the samples with no sludge. The pattern of Ni segregation observed in this study are similar to what Chaudhuri *et al.* (2003) reported where they found that Ni segregated preferentially into S4 fraction but with the application of sludge at different rates, the concentration of Ni in the S4 fraction decreased but remained dominant. Shrivastava and Banerjee (2004) and Sánchez-Martín *et al.*, (2007b) have also reported that Ni segregates preferentially into the residual (S4) followed by reducible (S2) fractions. The preferential segregation of Ni into the S3 and S4 fractions has also been reported by Alloway (1995). Nickel forms covalent bonds with organic ligands (Parkpian *et al.*, 2002; Ashworth & Alloway, 2008),

which may explain the high Ni concentration found in the S3 fraction and the increase in this fraction of Ni with increase in sludge application rate.

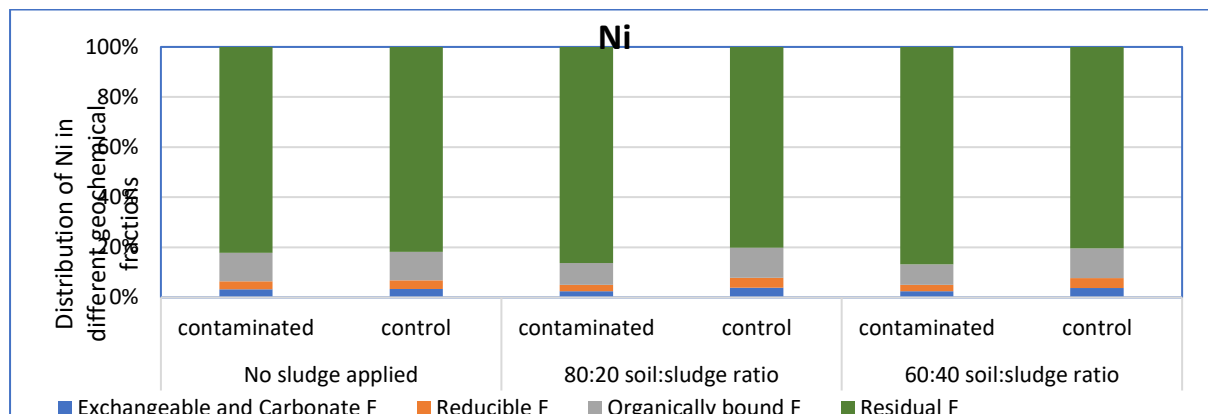


Figure 5.6: Partitioning of Ni in tailings contaminated and control soil samples with and without sludge

The exchangeable and carbonate (S1), and the reducible (S2) fractions contained the highest amount of **Lead** in both the tailings contaminated and control soil samples (Figure 5.7). With the addition of sludge at rates of 80:20 and 60:40, Pb content in the two fractions increased further. Ngole (2011) also reported a high amount of Pb in the residual (S4) and exchangeable (S1) fractions after sludge application at different rates. Illera *et al.*, (2000) similarly observed an increase in the S1 fraction of Pb after sewage sludge amendment. The segregation of Pb into the S1 fraction is attributed to the fact that Fe and Mn oxides play an important role in the retention of Pb and carbonates are a strong adsorbent for this metal which results in co-precipitation as lead carbonate (Illera *et al.*, 2000)

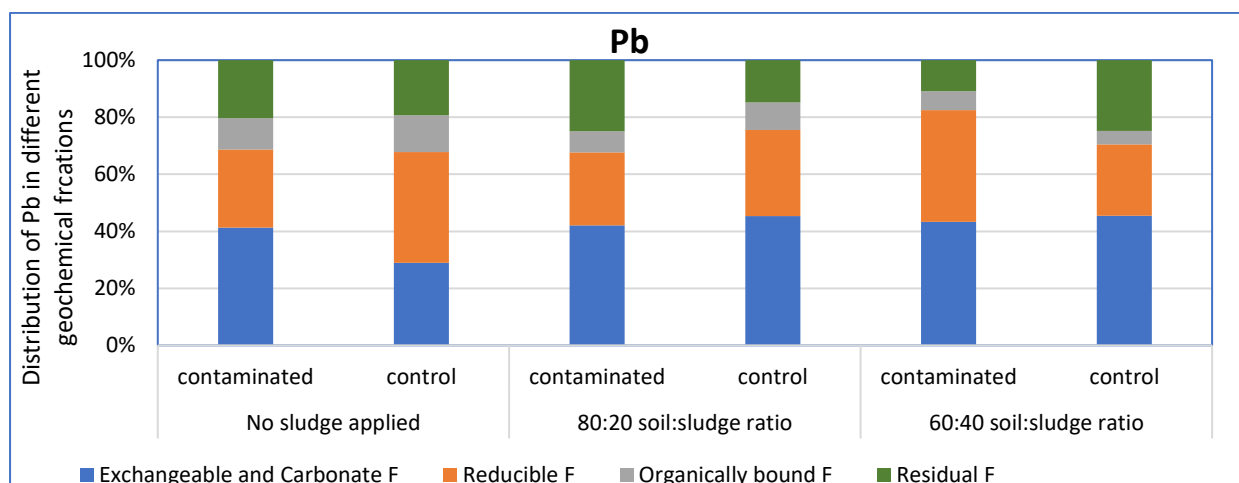


Figure 5.7: Partitioning of Pb in tailings contaminated and control soil samples with and without sludge

The adsorption is easily facilitated in an environment where the pH is high which was the case in the current study as reported in Chapter 4. The outcome of this study is related to the findings by Planquart *et al.*, (1999) who report that the highest amount of Pb were contained in the S1 and S4 fractions while sludge amendment at different rates especially at 30 ton per hectare resulted in the S4 and S2 fractions of Pb being the highest.

In the tailings contaminated and control soil samples, the highest amount of **Zinc** was found in the S4 fraction with this fraction of Zn increasing further with the addition of sludge (Figure 5.8). Sánchez-Martín *et al.* (2007a) and Mendoza *et al.*, (2006) have also all reported the segregation of Zn into the S4 fraction even after sludge addition. According to Parkpian *et al.*, (2002) and Vulkan *et al.*, (2002), about 60% of Zn in contaminated and natural soils is mainly bound to silicate lattice which may explain the elevated concentrations of Zn in the S4 fraction of these samples. This pattern of segregation is also favoured by soil pH since Zn inclines to become sorbed and unavailable in soils with high pH values.

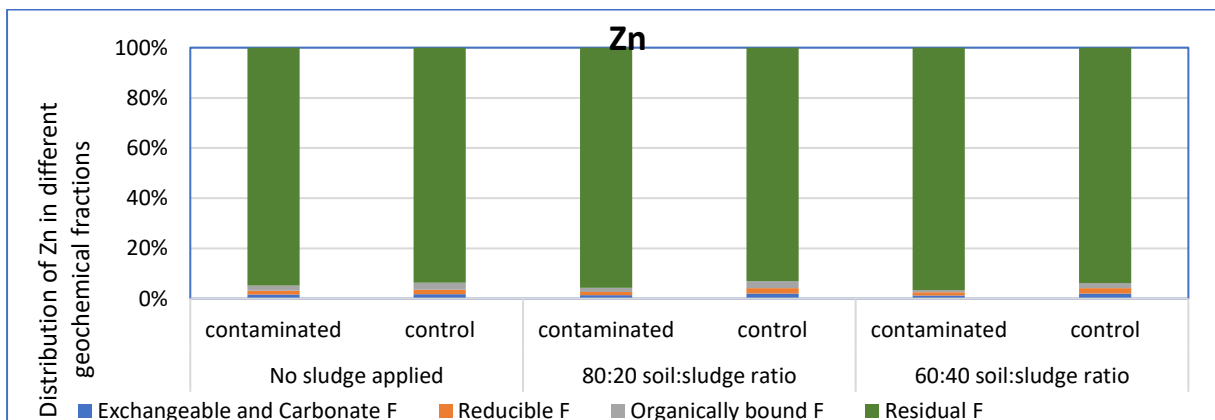


Figure 5.8 Partitioning of Zn in tailings contaminated and control soil samples with and without sludge

5.4 Mobility of Heavy metals in sludge-amended heat affected soils

5.4.1 Arsenic

On average, the Mobility Factor (MF) of As in the unheated tailings contaminated soil sample with no sludge was 5.0% while the MF of the control sample was 3.7% (Appendix 1) indicating a higher mobility of As in the tailings contaminated soil. An increase in soil temperature to 300°C resulted in an increase in the mobility of As but further increase in temperature and duration of heating resulted in a decrease in its

mobility (Figure 5.9a). The changes in mobility of As might have been driven by the fact that in the sample which had been subjected to temperatures of up to 300°C there was an increase in As concentration in the S1 fraction from 89.3 to 115.9 mg/kg but further increase in the soil temperature resulted in a decrease in As concentration in this fraction from 115.9 to 89.5 mg/kg whereas an increase in S4 fraction from 1250 to 1543 mg/kg was noted (Appendix 2 for details). The addition of sludge at a ratio of 80:20 to the tailings contaminated soil sample that had been heated to 300°C caused in an increase in the MF of As (Figure 5.9b), but in samples that had been subjected to higher temperatures of up to 400°C and a duration of heating of up to six hours, a decrease in the MF of As was observed. The increase in As MF in the samples might be explained by the increase in As concentration in the S1 fraction from 113.9 to 144.4mg/kg in soils that had been heated to 300°C (Appendix 1).

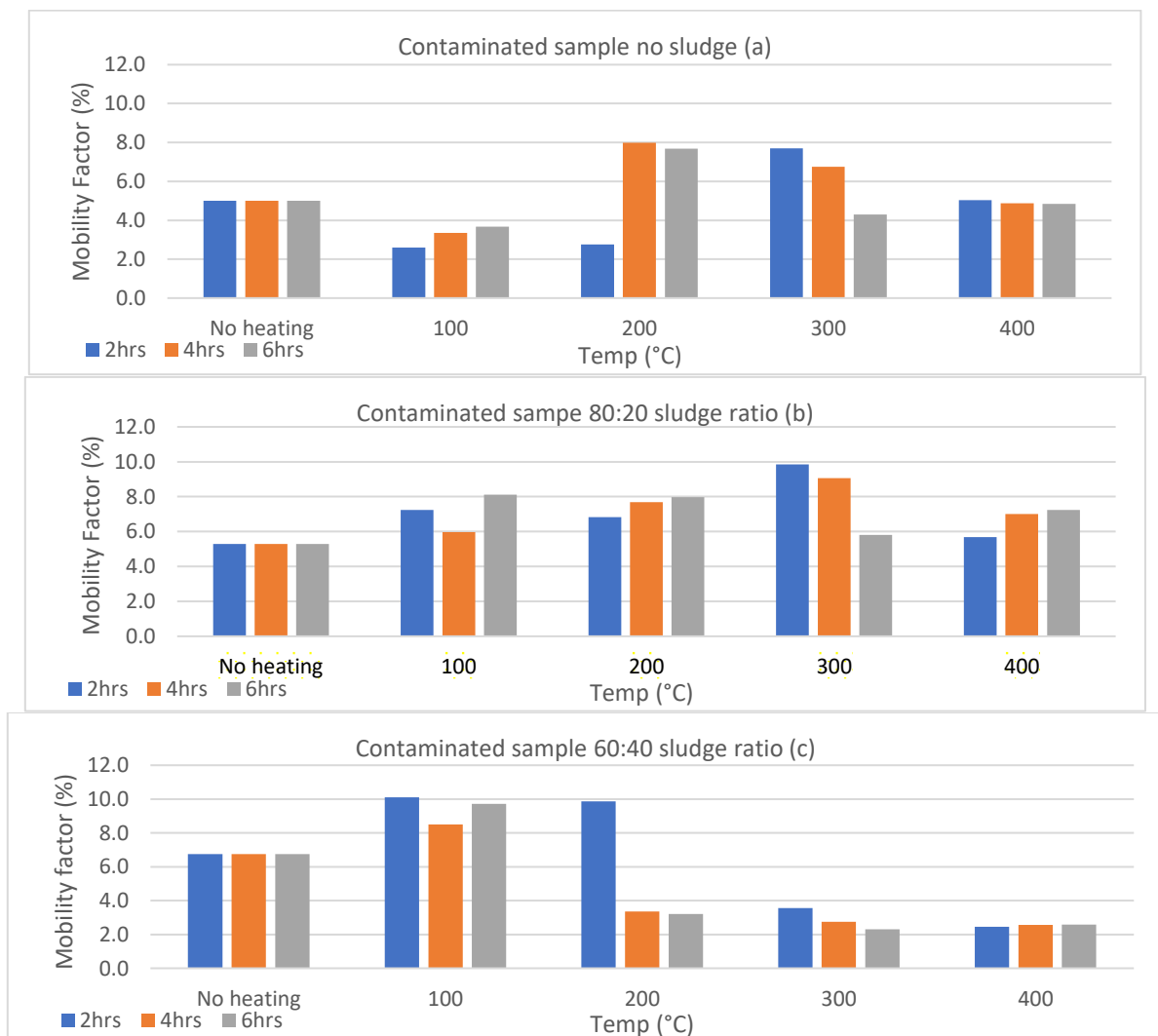


Figure 5.9: Mobility factors of Arsenic in tailings contaminated soils subjected to different temperatures and amended with sewage sludge at different rates

The S1 fraction comprises of the concentrations of heavy metals in the soil solution and those that are bound to soil carbonate. These metal fractions are highly mobile and so an increase in the concentration of metals in these fractions would translate to a higher mobility. Sludge addition at ratios of 60:40 to the tailings contaminated soil that had been heated to 200°C caused an increase in MF of the As but increasing the temperature and duration of heating resulted in a decrease in MF of As (Figure 5.9c). In samples that had been subjected to temperatures above 200°C, As segregated preferentially into the S2 fraction which is the reducible fraction comprising of Fe and Mn oxides. This fraction is less available and might have resulted in the decrease in MF observed. A further increase in temperature to 400°C resulted in a decrease in the As concentration in the S1 fraction to 40 mg/kg (See appendix 2).

5.4.2 Cadmium

The average mobility of Cd in the unheated tailings contaminated and control soil samples were 32.2% and 34.3% respectively. Heating the tailings contaminated soil sample up to 400°C at different durations slightly increased the mobility of Cd (Figure 5.10a). This might have been caused by the fact that at temperatures of up to 400°C, the concentration of Cd in S1 fraction increased from 23.9 to 25.2 mg/kg. With the addition of sludge at ratios of 80:20 to the samples that had been heated, the MF of Cd did not change except in soils that had been subjected to temperatures of up to 400°C where a slight increase in Cd MF was observed (Figure 5.10b). At a higher sludge application rate of 60:40, there was an increase in Cd mobility in the sample heated at 100°C but further increase in the temperature and duration of heating did not have any significant impact on Cd mobility (Figure 5.10c) and this was also reflected in the pattern of Cd concentration in the S1 fraction at 100°C.

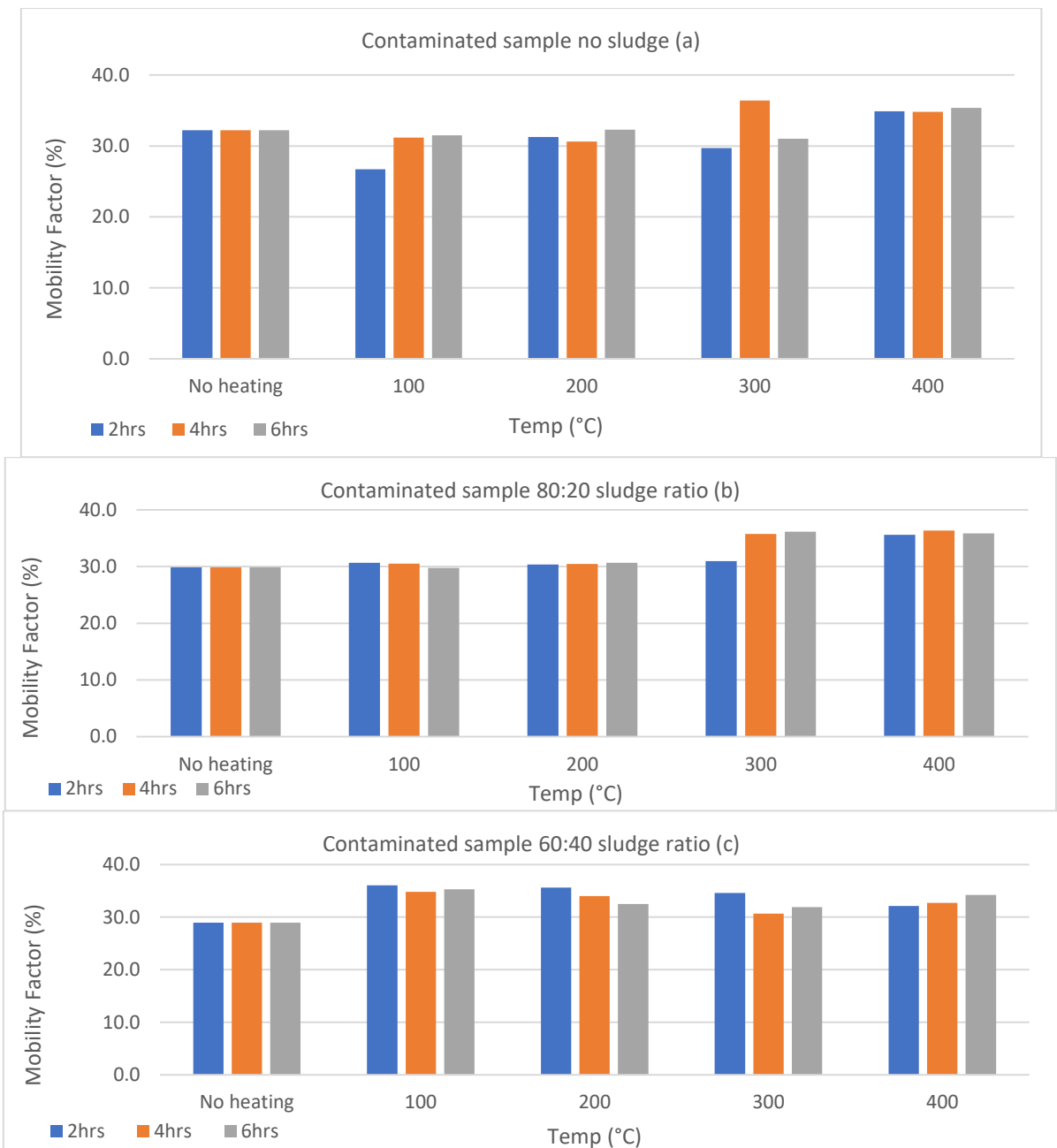


Figure 5.10: Mobility factors of Cd in tailings contaminated soils subjected to different temperatures and amended with sewage sludge at different rates

5.4.3 Cobalt

The average MF of Co in the tailings contaminated soil sample which was not heated was 0.8% compared to 0.97% MF of the control sample reflecting low mobility of Co in these soils. An increase in Co MF was observed in the sample that had been subjected to a temperature of 100°C but increasing the temperature up to 400°C and duration of heating resulted in a slight decrease in the MF of Co (Figure 5.11a). The changes observed in Co MF in the heated soils are due to an increase in Co

concentration in the S1 fraction at 100°C from 6.2 to 7.0 mg/kg and at 400°C the S1 fraction of Co decreased in concentration to 5.7 mg/kg (See appendix 1 for details). At a sludge application ratio of 80:20, the MF of Co decreased slightly but in soils that had been heated to temperatures of up to 400°C for a longer duration, the Co mobility increased (Figure 5.11b). With sludge addition at ratios of 60:40, the MF of Co showed a general increase as the temperature and duration to which the soil had been heated increased to 400°C and 6 hours respectively (Figure 5.11c). The pattern in Co MF mirrors the pattern observed in the segregation of Co where an increase in Co concentration was also observed in the S1 fraction from 5.3 mg/kg in soils that had been heated at 100°C to 6.9 mg/kg in soils that had been heated at 400°C. See appendix 1 for details.

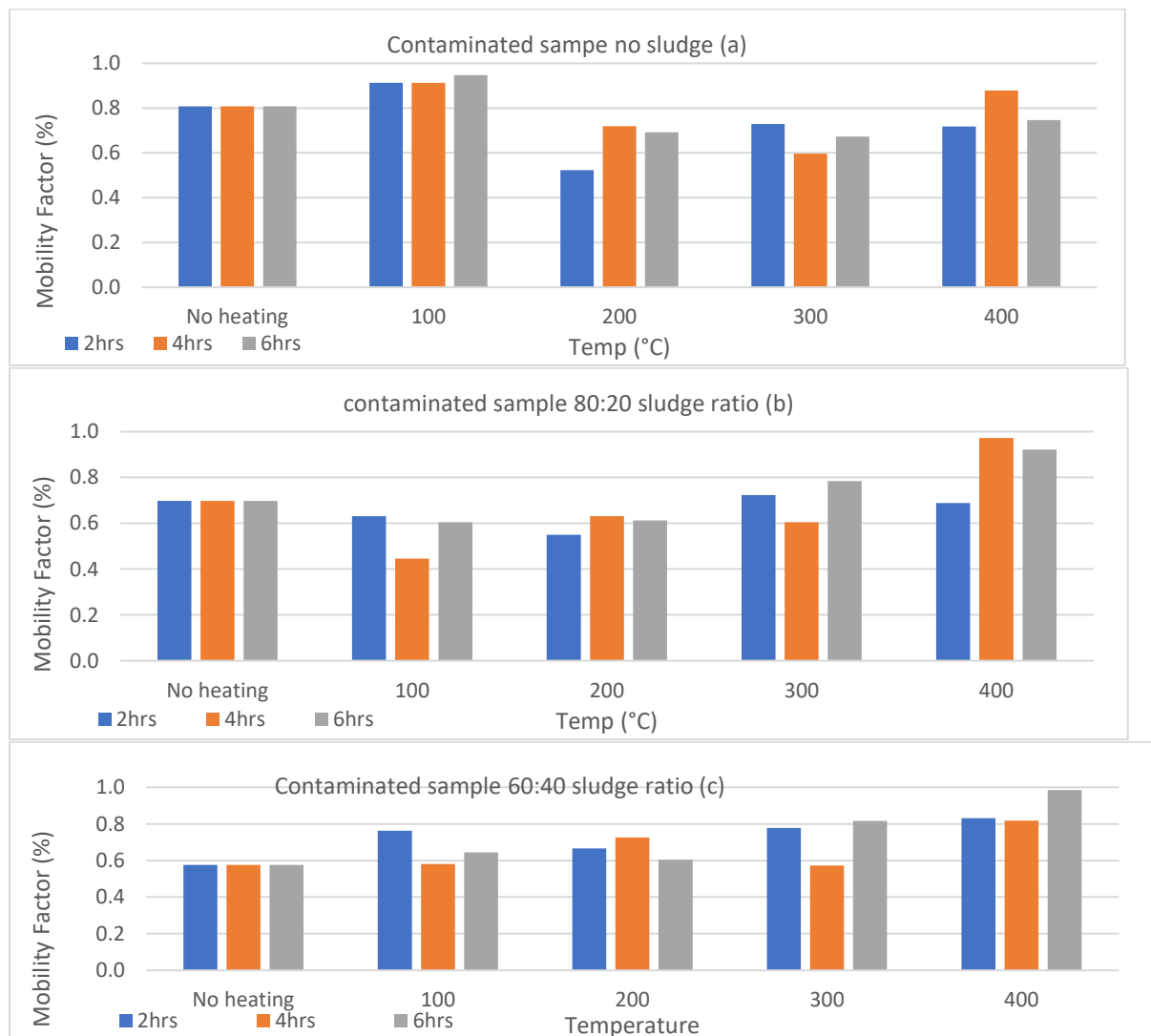


Figure 5.11: Mobility factors of Cobalt in tailings contaminated soils subjected to different temperatures and amended with sewage sludge at different rates

5.4.4 Chromium

The average MF of Cr in the tailings contaminated and control soil samples which had not been heated were 6.1% and 9.1% respectively indicating a high mobility of Cr in the control sample compared to the tailings contaminated soil. In the tailings contaminated soil sample that had been subjected to temperatures of 100 and 200°C for durations of more than two hours, an increase in Cr MF was observed (Figure 5.12a) whereas in soils that had been heated to temperatures of up to 400°C a decrease of the MF of Cr was observed.

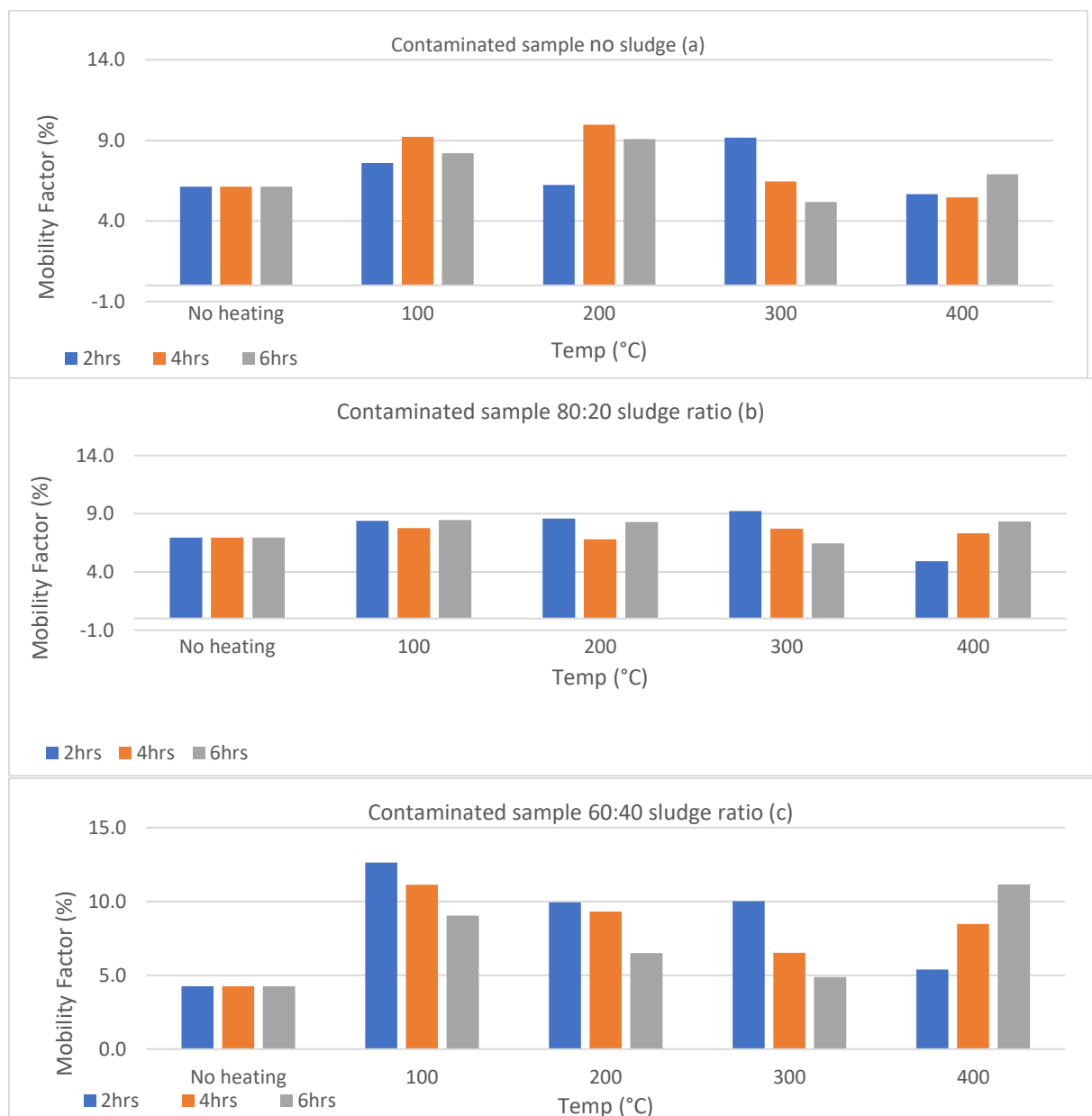


Figure 5.12 Mobility factors of Chromium in tailings contaminated soils subjected to different temperatures and amended with sewage sludge at different rates

A decrease in Cr concentration was observed in the S1 fraction from 24.2 to 21.4 mg/kg whereas there was an increase in Cr content in the S2 fraction from 22.4 to 24.1 mg/kg (Appendix 1 for details) which might explain the patterns in Cr mobility factors observed. Applying sludge at a ratio of 80:20 to the tailings contaminated soils that had been subjected to temperatures of 100 and 300°C for prolonged periods of time slightly increased the MF of Cr (Figure 5.12b). At a sludge application ratio of 60:40, there was an increase in the MF of Cr in the samples that had been heated up to 400°C (Figure 5.12c). An increase in the Cr concentration in the S1 fraction from 20.6 to 29.4 mg/kg was observed. These observations indicate an increase in Cr mobility in soils that had been heated even though sludge is expected to bind these metals.

5.4.5 Copper

On average, the MF of Cu in the tailings contaminated and control soil samples which had not been heated were 22.0% and 21.1% respectively. A decrease in MF of Cu was observed when the tailings contaminated soil sample was heated up to 300°C, but an increase in temperature and duration of heating caused an increase in Cu MF (Figure 5.13a). These changes in mobility are attributed to a decrease of Cu concentration in the S1 fraction from 23.8 to 15.7 mg/kg at a temperature of up to 300°C accompanied by an increase in S3 fraction from 21.7 to 23.5 mg/kg and an increase of Cu concentration in the same fraction from 15.7 to 27.4 mg/kg at 400°C (Appendix 1). Sludge application at a ratio of 80:20 did not have a substantial impact on the MF of Cu in the heated soils (Figure 5.13b), as the MF values for Cu in the sludge-amended soil samples remained similar irrespective of the temperature to which the soil had been subjected prior to sludge amendment. At a higher sludge application rate of 60:40 (Figure 5.13c) the MF of Cu was also not impacted as the temperature to which the soil had been heated increased to 400°C and the duration of heating at this temperature increased to six hours. These results indicate that remediation of heat affected contaminated soils with sewage sludge may have no effect on the mobility of Cu in the soils.

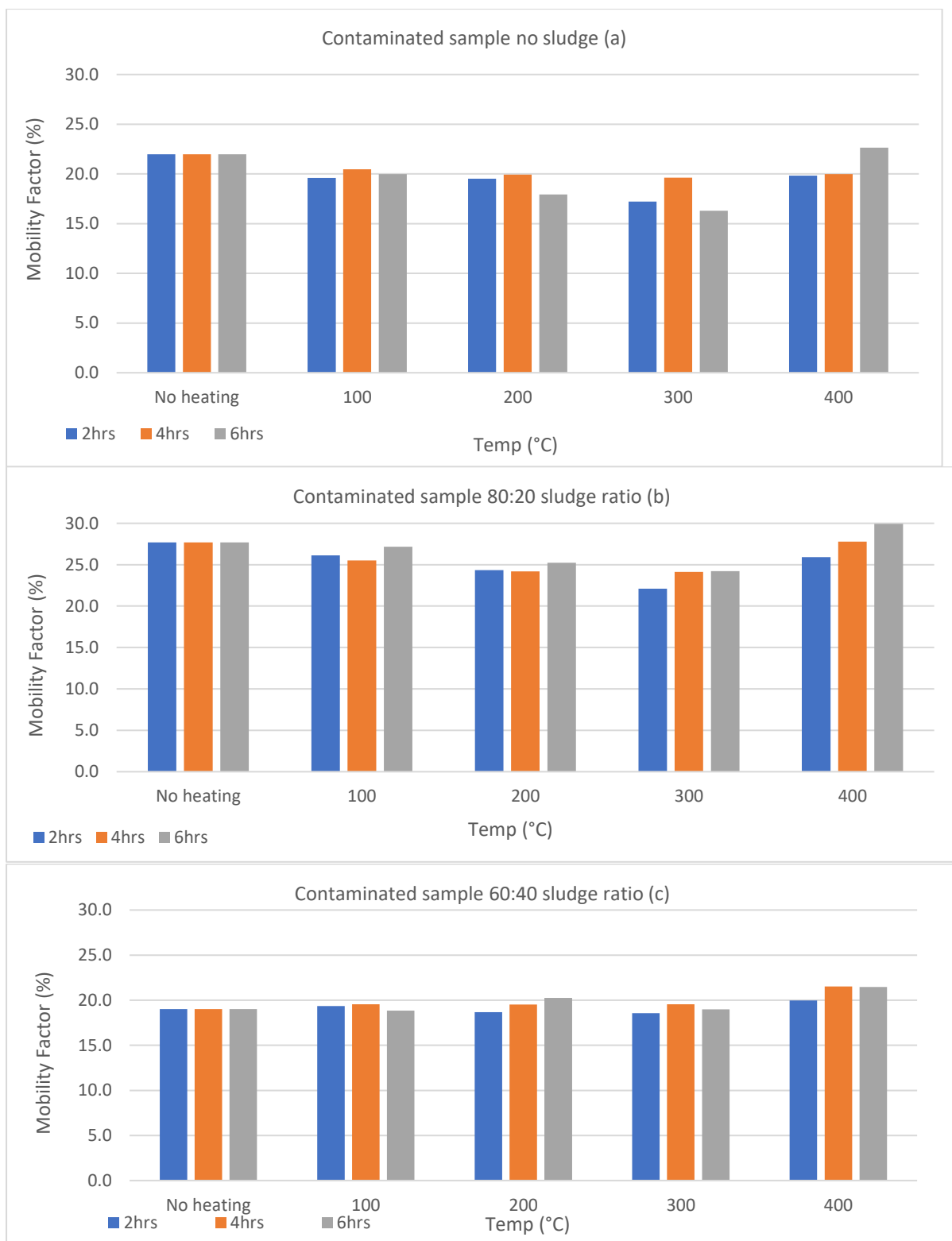


Figure 5.13 Mobility factors of copper in tailings contaminated soils subjected to different temperatures and amended with sewage sludge at different rates

5.4.6 Lead

The MF of Pb in the tailings contaminated soil samples which had not been heated was 41.3% indicating a very high mobility of the metal compared to the control sample

which had a mobility factor of 28.9%. Heating the tailings contaminated soil sample to a temperature of 100°C resulted in a decrease in Pb MF. This is attributed to a decrease of Pb concentration in the S1 fractions from 67.1 to 42.3 mg/kg whereas an increase in the concentration of Pb in the S3 fraction from 17.7 to 19.1 mg/kg was observed. Further increase in soil temperature to 300°C and a duration of heating to four hours resulted in an increase in MF whereas soil temperatures of 400°C decreased Pb mobility to values similar to the samples not heated (Figure 5.14a). At elevated temperatures and duration of heating, the concentration of Pb in the available fractions increased which resulted in an increase in MF of Pb.

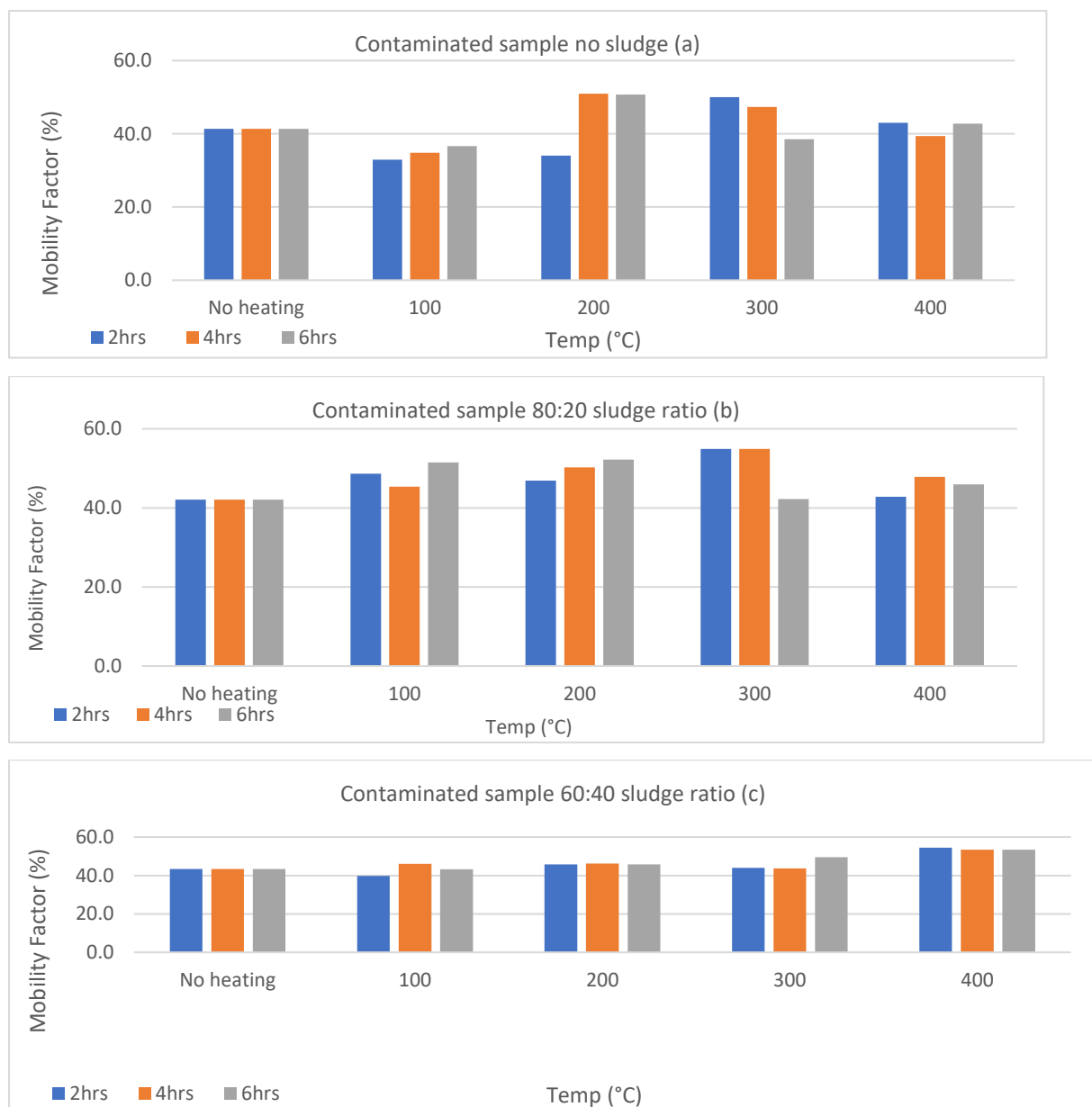


Figure 5.14: Mobility factors of lead in tailings contaminated soils subjected to different temperatures and amended with sewage sludge at different rates

The addition of sludge to the heated soil samples at a ratio of 80:20 resulted in an increase in the MF of Pb in samples that had been heated to temperatures of up to 200°C. The mobility of Pb was further increased in soils that had been heated at this temperature for six hours. A decrease in Pb mobility was observed in soil samples which had been heated up to a temperature of 400°C and amended with sludge at a ratio 0 80:20 but increasing the duration of heating the soil at the same temperature prior to sludge addition did not have any significant impact on Pb mobility (Figure 5.14b). In samples that were heated up to 300°C, an increase in Pb concentration was observed in the S1 fraction from 79.2 to 98.7 mg/kg after sludge addition but the concentration of Pb in this fraction decreased in soils which had been heated to 400°C prior to sludge addition (See details in Appendix 1). This change in S1 fraction resulted in the changes observed in MF of Pb. There was no impact of sludge addition at a ratio of 60:40 on Pb MF in the heat-treated soil samples except in samples that had been heated at a temperature of 400°C where a slight increase in the MF of Pb was observed (Figure 5.14c). Lead will normally bind to organic matter in soils (Brown *et al.*, 2003). The destruction of OM in the soil due to high temperatures would have liberated the Pb bound to this fraction, resulting in its higher mobility in the soils that were not amended with sludge. In the sludge amended soils, increase in Pb mobility as indicated by the increase in Pb MF (Figure 5.14) could be caused by the inability of the soil minerals to form stable organo-mineral complexes with the OM from sludge which would have assisted in the stabilization of metals. This might have been caused by the heat effect on the soil mineral composition.

5.4.7 Nickel

On average, the MF of Ni in the unheated tailings contaminated soil sample was 3.21% while the MF of the control sample was 3.4%. There was a general increase in MF of Ni with an increasing temperature of the soil up to a temperature of 300°C after which the Ni MF dropped (Figure 5.15a). An increase in MF is attributed to an increase of the Ni concentration in the S1 fraction from 15.4 to 15.7 mg/kg more especially at low temperature while a decrease is observed at higher temperatures (Appendix 1).

With the addition of sludge at a ratio of 80:20, there was an increase in Ni mobility in the samples that had been exposed to a temperature of up to 400°C and a duration of heating of six hours (Figure 5.15b). Increasing the amount of sludge added to a ratio

of 60:40 in the heat-treated soil samples caused an increase in the MF of Ni (Figure 5.15c). The increase in MF is due to an increase of Ni concentration in the S1 fraction from 14.1 to 16.0 mg/kg. The application of sludge to the tailings contaminated soil resulted in a slight increase in Ni mobility which may indicate that the use of sludge to stabilize Ni in contaminated soil that have been subjected to heat may be ineffective.

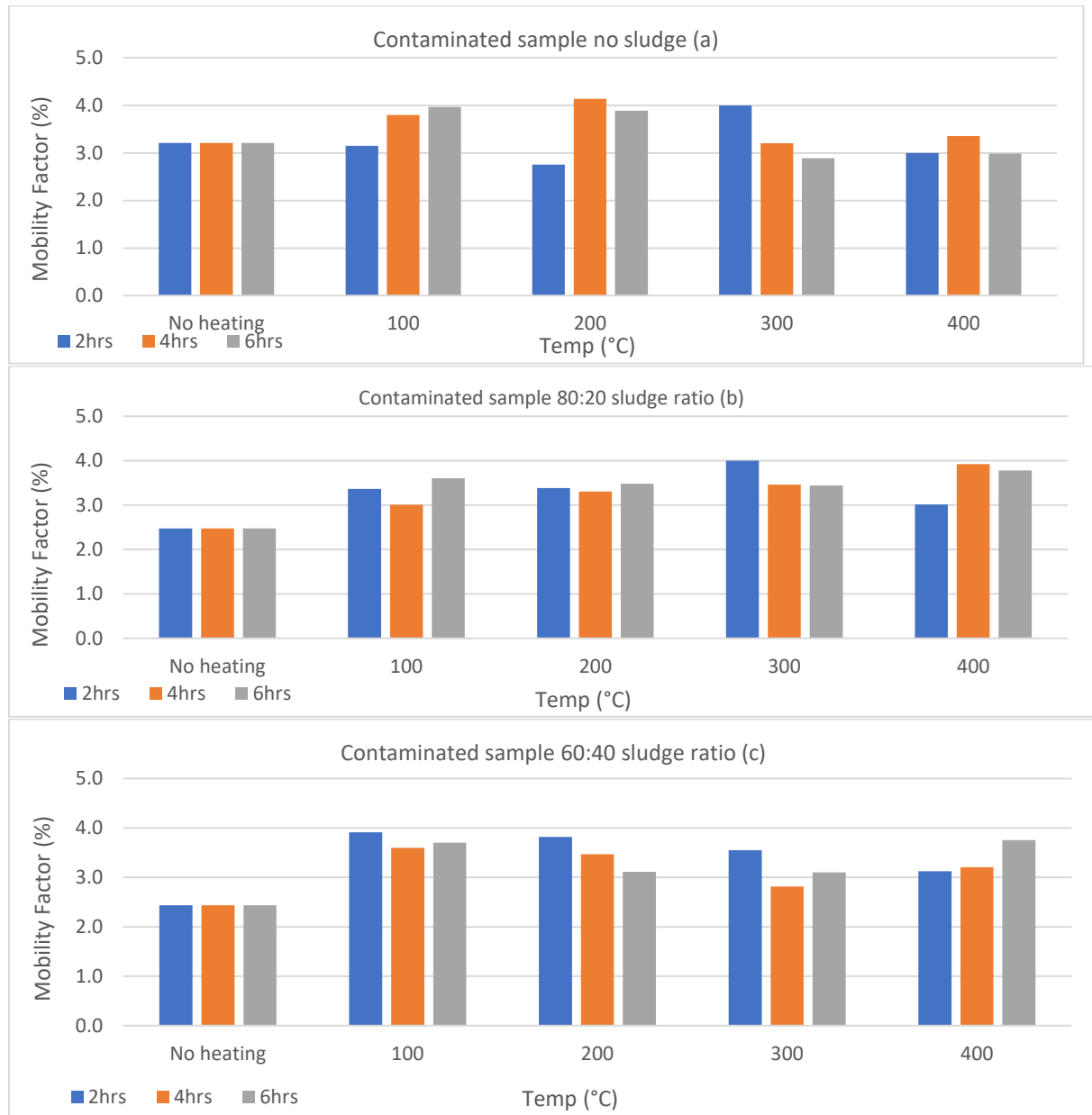


Figure 5.15: Mobility factors of Nickel in tailings contaminated soils subjected to different temperatures and amended with sewage sludge at different rates

5.4.8 Zinc

The average mobility factor of Zn in the tailings contaminated soil sample which was not heated was 1.60% with the control sample having a mobility factor of 1.79%

reflecting low mobility of Zn in these soil samples. Increasing the temperature of the soil to 300°C and the duration for which the soil was held at this temperature to four hours resulted in an increase in Zn MF while further increase in temperature of the soil lead to a decrease (Figure 5.16a). An increase in Zn concentration in the S1 fraction from 23.6 to 23.9 mg/kg at a temperature of 300°C and a further decrease led to the same kind of shift in MF.

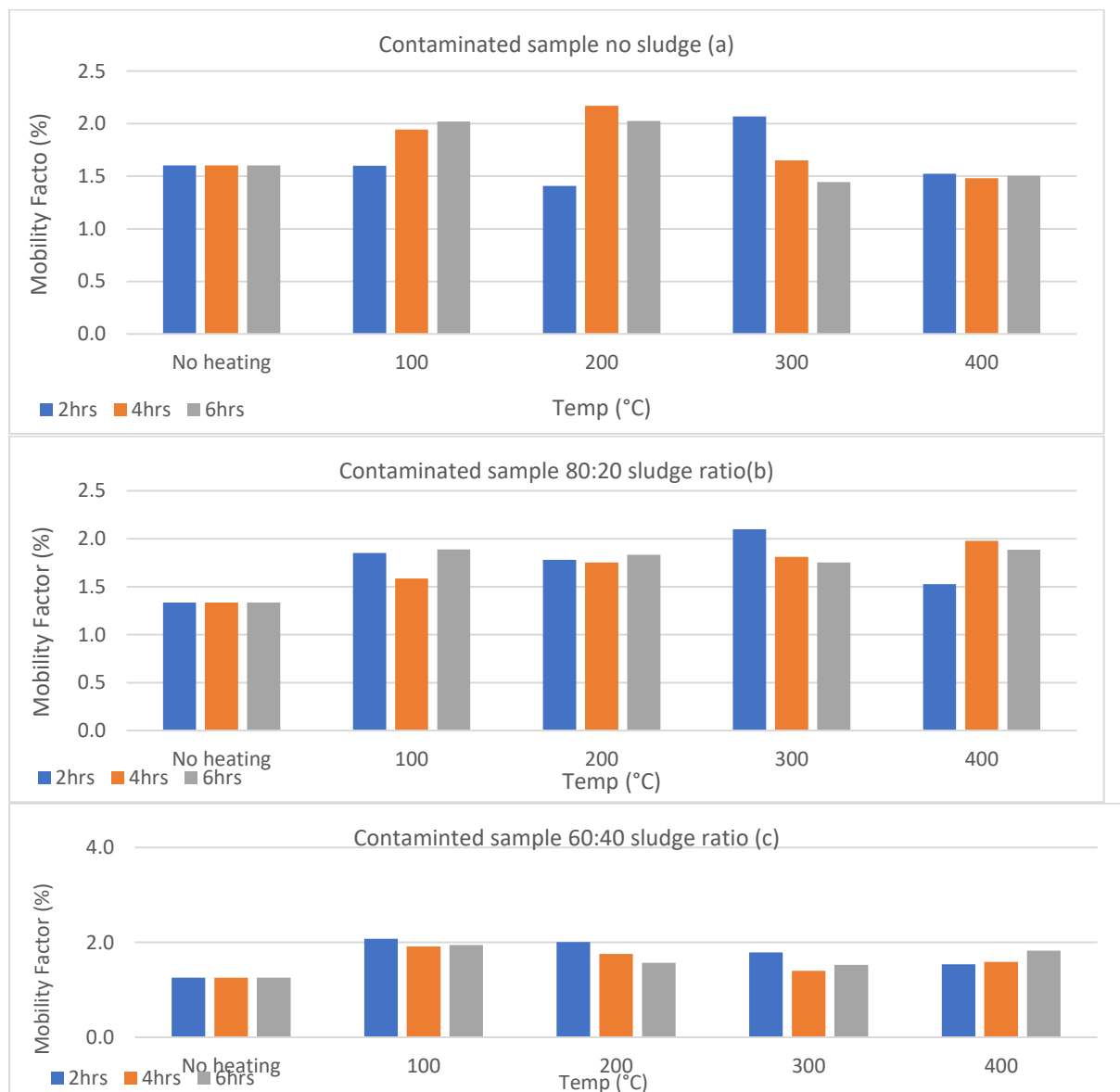


Figure 5.16 Mobility factors of Zinc in tailings contaminated soils subjected to different temperatures and amended with sewage sludge at different rates

Sludge application at a ratio of 80:20 on soil samples that had not been heated led to a decrease in MF compared to samples where no sludge was applied. In soils that had been heated, no significant difference was observed in Zn MF between the

sludge-amended soil and soils which had not been amended with sludge (Figure 5.16a & b). After the sludge application at 60:40, Zn MF decreased further in the samples that were heated compared to those that were not heated but had received sludge at the ratio of 80:20. In soils that had been subjected to higher temperatures of up to 200°C, there was an increase in Zn MF with sludge addition at a ratio of 60:40 but as the temperature and duration to which the soils had been subjected prior to sludge addition increased, there was no significant increase in Zn MF (Figure 5.16c).

The differences observed in mobility factor as a result of increased duration of heating were not significant for all metals according to ANOVA analysis, whereas the differences observed as a result of increase in temperature were significant except for Cu. ANOVA analysis further showed that the differences in mobility factor observed as a result of different sludge application rate were significant for As, Cu and Pb and not significant for Ni, Cd, Co, Cr and Zn (See p-values in Table 5.2 below).

Table 5.2 P-values on the mobility factor of different metals

Mobility Factor (p-values)	Duration	Temperature	Sludge application rate
As	0.899	0.00	0.001
Ni	0.972	0.00	0.690
Cd	0.765	0.003	0.766
Co	0.678	0.01	0.195
Cr	0.886	0.01	0.648
Cu	0.792	0.264	0.00
Pb	0.747	0.06	0.008
Zn	0.984	0.00	0.720

5.5 Implications of changes in the mobility of metals observed as a result of increased temperature and addition of sludge

The mobility factor of heavy metals in the soils were affected by both increases in temperature and the duration of heating as well as sludge application at different rates.

The MF of Cr, Ni, Pb and Zn increased when the tailings contaminated soil sample were heated up to 300°C but a further increase in temperature to 400°C resulted in a decrease in MF whereas Cu showed an opposite pattern. In the same samples, the MF of Co increased when the soil temperature was raised to 100°C followed by a gradual decrease as temperature intensity increased whereas As showed an opposite pattern. There was no impact on the mobility of Cd at low temperature but as the temperature increased so did the MF.

The impact of duration of heating on the MF of As, Pb, Cd, Zn and Ni in the tailings contaminated soil samples showed that up to a temperature of 200°C, there is an increase in MF while at 300°C there is a decrease and at 400°C, MF is not impacted. With increased duration of heating, the MF of Co increased at soil temperatures of 200°C but at higher temperatures of up to 400°C, there is a decrease whereas an opposite pattern was observed in the MF of Cr. At a soil temperature of 100°C and increased duration of heating, the MF of Cu is not affected but at higher temperatures there is a decrease in MF.

These findings are in line with what Jing *et al.*, (2018) reported that for metals such as Zn, Pb and Cd any temperature above 20°C will increase MF. Latosińska & Gawdzik (2012) also reported that with increasing temperature an increase in MF of heavy metals such as Zn was observed on sewage sludge. It is further indicated that increasing the time of heating resulted in a further increase on MF. Mobility factor of heavy metal such as Cr has a direct relationship with increasing temperature (Latosińska & Gawdzik, 2012).

Sludge application resulted in an increase in the MF of As and Pb in heat affected soils with the 60:40 ratio of sludge application having the biggest impact compared to 80:20 ratio. The MF of Cu, Cd, Ni, Co, and Zn in heat affected soils decreased with sludge application with the 60:40 ratio having a huge impact. Sludge application rate at a ratio of 80:20 caused an increase of Cr MF followed by a decrease with increase sludge application rate of 60:40. The MF of Cu was not impacted in heat treated contaminated soils amended with sludge. The scenario with Co was slightly different in heat treated samples where sludge was applied at lower rates. An increase in Co MF was observed when the sludge application rate was higher. An increase in As MF was observed in

the soil, which was heated, and sludge applied at a low rate compared to a decrease in MF at high sludge application ratio. This implies that to remediate As in tailings contaminated soil which has been heated, higher sludge application rate should be employed. The increased mobility of heavy metals even after sludge addition may indicate low sorption capacity and could indicate that sludge may not be effective in the remediation of these heavy metals in a heat affected contaminated soil.

The heat treatment in the study was carried out in a laboratory setting which is a controlled environment. In case of a fire event, soils could experience changes in temperature in a natural environment which could last for days and could even result in increased soil temperature to above 400°C (Santin *et al.*,2016; and Badia *et al.*,2017) which could have an impact on the mobility factor of different metals. The results of this study have indicated that the effectiveness of using sludge to remediate heavy metals in a heat affected soil can be impacted by fire events. For a successful remediation of As in contaminated soils using sewage sludge, a high sludge application rate should be employed while sludge cannot be effective in the remediation of Pb, Cd, Ni, Cr and Zn in heat affected soils due to an increased mobility.

5.6 Concluding remarks

Arsenic, Co, and Zn contained the highest metal concentration in tailing contaminated sample and with the application of sewage sludge, the concentration of these metals increased further. Metals such as, Cr, Cu, Ni and Zn segregated preferentially into the residual fraction, whereas Cd and Pb segregated into the exchangeable and carbonate and residual fractions. The mobility of these metals has been shown to be affected by both an increase in temperature intensity and duration. The sludge application rate has also been shown to have an impact on the mobility factor of these metals.

CHAPTER SIX

SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

6.1 Introduction

This chapter presents a summary of what is contained in this report. The chapter further presents conclusions based on the different objectives of the study and the recommendations based on what the study found out.

6.2 Summary findings from empirical investigation

6.2.1 Effect of temperature of the physical properties of soil

Varied effects of heat on soil properties were observed. There was an increase in pH of the soil as both temperature and duration of heating increased. An increase in the temperature and the duration of heating led to a decrease in organic matter and at higher temperatures and increased duration of heating, there was a complete elimination of OM in the soils. At low temperatures of 100°C, an increase in EC was observed. An increase in the duration of heating to six hours at the same temperature led to a decrease in EC, but as temperature and duration of heating increased to 400°C and six hours respectively, an increase in EC was observed. The CEC of the contaminated soil decreased as soil temperature was increased to 100°C and duration of heating also increased, but at a higher temperature of up to 400°C and increased duration of heating at this temperature, an increase in CEC was observed. The concentrations of trace and major element oxides in the soil samples were dominated by quartz (SiO₂) followed by Fe₂O₃ and Al₂O₃. An increase in soil temperature and duration of heating to six hours caused an increase in the concentration of these oxides while there was no significant impact on the content of MnO and MgO. The soil mineralogical composition further showed that quartz was the dominant mineral in the soil throughout the heating process with minerals such as kaolinite and hematite occurring in trace amounts in some samples. Heating the soils at different temperatures resulted in the disappearance of other minerals whereas the content of quartz increased.

6.2.2 Heavy metal concentration

Of the metals investigated in this study, As, Co and Zn contained the highest concentration while Cd contained the lowest. There was a slight decrease in the total metal concentration of heavy metals with increased the soil temperature and duration of heating, but these changes were insignificant as metals which contained the highest concentration remained high and those with low concentration remained low. The segregation of Co, Cr, Cu, Ni and Zn into different geochemical fractions was not affected by heat as the residual fraction (S4) remained the dominant fraction though there was a decrease in the concentration of the metals, Pb and Cd continued to segregate into the exchangeable and carbonate (S1) and reducible (S2) fractions with increase in soil temperature and duration of heating. The partitioning of heavy metals showed that As, Co, Cr, Cu, Ni and Zn segregated preferentially into the S4 fractions even after sludge application at different rates. Lead and Cd segregated into S1 fraction which is the more mobile and readily available fraction, and this is further supported by the fact that Pb had the highest mobility factor (41.3%) followed by Cd (32.2%) whilst Co and Zn had the lowest mobility factor of 0.8% and 1.6% respectively. Mobility factor of As and Pb increased as a result of sludge application while MF of Cu, Cd, Cr, Co, Ni and Zn decreased.

6.3 Conclusions from results of the study

This study aimed at evaluating the effects of an increase in soil temperature and duration of heating on the sorption properties of mine tailings contaminated soils and the implications on fire-affected soils. From the results, the following conclusions have been arrived at:

6.3.1 Determination of the level of heavy metal contamination in soils around gold mine.

- Among the heavy metals analysed in this study, As, Zn and Co were found to have the highest concentration while Cd was found to contain the lowest concentration;
- The heavy metal contamination factors show that Cu had lowest contamination factor while Cr had the highest.

6.3.2 Determination of the effect of increase in soil temperature on the heavy metal binding capacity of contaminated soil from gold mine tailings

- The exchangeable and carbonate (S1), reducible (S2), organically bound (S3) and residual (S4) fractions of As, Co and Cr decreased in concentration because of increase in soil temperature and the S4 fraction of all the metals remained the dominant fraction after heat treatment. A decrease in the concentration of metals in the S4 fraction because of increased soil temperature was observed followed by an increase in S3 fraction of Zn and Cu concentration while an opposite pattern was observed with Cd. The organic bound (S3) and S4 fractions of Ni and Pb decreased as a result of heat while S1 and S2 fractions was not affected.
- After heat treatment As, Co, Cr, Cu, Ni and Zn continued to segregate preferentially into the S4 fraction which is the less available fraction. Lead and Cd segregated preferentially into the S1 and S2 fractions which are the readily available fractions, and this segregation was not affected by increased soil temperatures. Therefore, heat did not cause a shift in the segregation of metals into the different fractions.
- The exchangeable and carbonate fraction (S1) of Cd, Ni and Zn was not affected by increased soil temperatures and as a result, the MF were not affected. There was thus no impact of increased soil temperature on the Cd, Ni and Zn binding capacity of the soils whereas in As, Co, Cr, Cu and Pb, the S1 fraction decreased because of increased soil temperature indicating that the MF decrease which thereof implies that metal binding capacity will increase.

6.3.3 Effect of increased soil temperature and duration of heating on soil properties and sorption capacity

- Soil EC increased with increasing soil temperature and duration of heating with soil temperatures of 100°C and duration of heating of two hours, as well as 200°C and 400°C and six hours duration having the most significant effect;
- Soil pH was generally found to increase with increasing soil temperature and duration of heating, but at temperatures of 300 and 400°C and a duration of heating of two hours, a significant impact was observed;

- Soil CEC decreased at low soil temperatures of 100°C but increased at high temperature of 400°C and increased duration of heating;
- Soil OM was destroyed at soil temperature above 200°C and higher duration of heating;
- Quartz and SiO₂ remained the dominant soil minerals in the soil samples with increasing temperature and duration of heating;
- The MF of As, Cr, Ni, Pb and Zn increased with heating duration and temperature whereas that of Cu decreased indicating that temperature changes may decrease the sorption capacity of soils as far as these metals are concerned while increasing that of Cu. The MF of Cd and Co were not impacted by soil temperature increases and duration of heating which could mean soil sorption capacity of these two metals was not affected by changes in soil temperature.

6.3.4 *To determine whether the ability of sewage sludge to bind heavy metals differs in heat affected contaminated soils*

- The addition of sludge at two different application rates did not affect the MF of Cu in the heat-treated soil and this implies that metal binding capacity was not impacted;
- Sludge application at a low rate increased the MF of As in a heat-treated soil but a decrease in MF of As was observed at a high sludge addition rate, which implies that at low rates of sludge application in a heat-treated soil, As binding may decrease whereas at higher sludge application rates, an increase may occur;
- The MF of Cd, Co, Cr, Pb, Ni and Zn increased as a result of sludge application in heat treated soil, thereby indicating a decrease in binding capacity of these metals in heat treated contaminated soils amended with sludge. The MF of Co was only increased at high sludge application rates in the heat-treated soil with no impact observed at lower sludge application rates. This means that at high sludge application rates the metal binding capacity decreased.

6.4 Limitations

The study was undertaken on a loam sandy textured soil using sewage sludge as a biosolid organic amendment and in a laboratory-controlled environment and not in a field. Therefore, the results obtained in this study might not be replicated on soil with a different texture and if the experiment is carried out in a field setting.

6.5 Recommendations

Based on the results obtained and the conclusions drawn from the results, the following recommendations are made:

- In a soil that is contaminated with As and has experienced significant changes in temperature because of fire or any other heat related incidents, a high application rate is recommended if sludge is to be used to immobilise the As. However, sludge contains high amounts of plant nutrients which should be taken into consideration when a high sludge application rate is considered for remediation purposes as the introduction of excess nutrients may result in surrounding surface water contamination.
- Any soil remediation strategy that is employed in a fire-affected soil where OM is a vital requirement will need to increase the organic matter content of the soil for the strategy to be successful because organic matter is significantly affected by an increase in soil temperature. It will also be of importance to consider the time when the fire occurred and when remediation is taking place, as natural vegetation can re-establish over time to restore soil OM.
- Soil pH plays a significant role in sorption. For enhanced soil sorption capacity, an increase in soil temperature may contribute towards the increased immobilisation of metals because of increased pH. This may be the relevant for soils with pH dependent charges where an increase in pH would result in an increase in available sorption sites and consequently an increase in soil CEC. The temperature of the fire and duration of the fire events should be considered as they play a big role in the pH and the EC of the soil.

- An increase in soil temperature affects the mineralogical composition of any soil. In a heavy metal contaminated soil which has been affected by fire, quartz is the dominant mineral. Any remediation strategy which is dependent on sorption or by the formation organo-metallic complexes would need to be reconsidered as this will not be effective on such soils.

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List of appendices

8.1 Appendix 1

Impact of increased soil temperature and duration of heating on metal concentrations in various Geochemical Fractions of a Tailings Contaminated soil

Arsenic (mg/kg)									
Exchangeable and Carbonate (S1)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	89.3	89.3	89.3	113.9	113.9	113.9	135.5	135.5	135.5
100	49.0	50.3	54.7	111.3	108.2	116.8	132.9	121.9	137.3
200	55.7	115.1	119.2	105.2	135.3	138.7	129.1	51.1	58.7
300	115.9	117.0	86.8	144.4	148.4	100.1	53.5	55.4	40.9
400	89.5	83.0	89.3	109.6	105.9	115.0	43.1	42.6	40.0
Reducible (S2)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	42.5	42.5	42.5	47.0	47.0	47.0	51.2	51.2	51.2
100	36.5	38.7	37.1	45.9	46.0	44.5	57.6	49.5	61.2
200	40.2	33.3	33.6	44.8	47.0	47.3	51.8	51.9	60.7
300	37.4	43.3	36.1	44.6	41.4	54.2	61.0	60.1	56.0
400	37.6	45.2	37.7	46.3	37.5	55.5	58.4	41.1	47.0
Organic Bound Fraction (S3)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	114.2	114.2	114.2	120.9	120.9	120.9	112.2	112.2	112.2
100	102.4	105.0	110.2	98.2	97.1	101.3	94.1	100.9	104.5
200	97.5	111.2	109.6	103.1	110.6	110.4	103.9	104.1	114.1
300	103.8	105.9	112.4	106.5	109.3	116.9	105.5	115.8	112.0
400	104.1	116.2	105.3	113.8	113.4	100.2	112.7	113.5	102.3
Residual Fraction (S4)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	1540.1	1540.1	1540.1	1871.9	1871.9	1871.9	1896.5	1896.5	1896.5
100	1693.8	1305.2	1289.1	1282.1	1560.0	1177.4	1220.0	1332.4	1309.7
200	1828.4	1180.5	1289.7	1286.6	1465.4	1443.7	1205.9	1419.2	1711.6
300	1250.5	1467.6	1785.4	1171.4	1336.4	1453.4	1397.6	1893.0	1659.9
400	1543.6	1455.8	1610.3	1657.4	1255.6	1317.5	1651.3	1544.9	1451.5

Cadmium (mg/kg)									
Exchangeable and Carbonate (S1)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	23.9	23.9	23.9	24.0	24.0	24.0	22.4	22.4	22.4
100	23.4	24.6	24.2	23.6	24.1	23.4	23.5	23.0	23.5

200	24.5	24.4	23.6	23.3	23.5	23.8	22.5	23.5	24.8
300	23.9	24.6	19.2	24.3	23.9	23.5	23.6	24.6	24.1
400	25.2	24.6	24.8	23.9	24.1	24.0	24.5	24.8	24.3
Reducible (S2)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	24.5	24.5	24.5	25.0	25.0	25.0	23.5	23.5	23.5
100	24.8	24.9	24.3	24.0	24.8	24.2	24.4	24.0	24.4
200	24.9	24.7	24.0	24.0	24.1	24.5	23.4	23.5	24.6
300	24.0	24.7	22.0	24.7	24.3	24.1	23.2	24.6	24.0
400	24.9	24.7	24.8	25.0	24.9	23.9	24.4	24.9	24.3
Organic Bound Fraction (S3)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	15.3	15.3	15.3	15.0	15.0	15.0	13.8	13.8	13.8
100	25.9	26.1	26.3	25.5	26.0	26.1	15.4	14.9	15.1
200	26.2	26.1	25.2	25.3	25.5	26.5	14.3	14.5	14.9
300	25.3	15.5	13.7	26.2	15.2	15.4	14.1	14.8	15.0
400	15.4	15.1	15.3	16.75	15.07	14.73	14.9	14.8	14.6
Residual Fraction (S4)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	10.4	10.4	10.4	16.37	16.37	16.37	17.6	17.6	17.6
100	13.4	3.2	2.0	3.81	4.11	4.93	1.9	4.2	3.6
200	2.8	4.5	0.3	4.02	4.08	3.00	2.9	7.5	12.0
300	7.2	2.8	7.1	3.35	3.41	2.03	7.2	16.3	12.4
400	6.8	6.4	5.3	1.39	2.13	2.20	12.4	11.3	7.7

Cobalt (mg/kg)									
Exchangeable and Carbonate (S1)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	6.2	6.2	6.2	6.8	6.8	6.8	5.3	5.3	5.3
100	7.0	6.0	6.0	4.3	3.4	3.9	4.6	3.7	4.0
200	4.7	4.1	4.3	3.8	4.3	4.0	3.9	5.0	5.0
300	4.2	4.4	5.8	4.0	4.0	5.6	5.3	5.3	6.5
400	5.7	6.5	5.9	5.6	6.1	5.9	6.9	6.7	6.7
Reducible (S2)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	7.3	7.3	7.3	7.3	7.3	7.3	6.9	6.9	6.9
100	6.5	6.5	6.7	7.0	6.6	6.7	6.8	6.9	6.9
200	6.9	7.3	7.6	6.7	7.1	6.9	6.8	6.8	7.1
300	7.1	6.7	7.5	7.0	7.3	6.8	6.7	7.2	6.9
400	7.4	7.0	7.0	7.2	7.5	7.3	7.0	7.6	7.4
Organic Bound Fraction (S3)									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		

Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	
0	37.1	37.1	37.1	35.1	35.1	35.1	30.0	30.0	30.0	
100	9.5	35.8	36.1	9.7	33.2	32.9	31.9	33.5	26.1	
200	34.7	36.2	37.1	32.5	9.7	33.7	25.0	9.4	32.6	
300	35.4	29.8	30.5	33.3	34.6	31.4	31.2	32.6	9.7	
400	9.9	35.7	35.2	36.0	33.2	35.1	33.0	32.3	32.0	
Residual Fraction (S4)										
no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio				
Temp °C	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	
0	716.4	716.4	716.4	921.8	921.8	921.8	886.0	886.0	886.0	
100	749.0	604.3	585.9	663.3	716.4	598.1	558.5	589.5	583.7	
200	856.1	522.0	569.9	655.1	656.7	600.7	544.3	667.3	783.9	
300	535.9	690.4	818.7	514.3	615.0	672.3	645.0	874.9	772.1	
400	776.7	691.4	743.9	761.9	576.5	588.9	784.0	770.0	635.9	

8.2 Appendix 2

Mobility Factor of metals in Control samples

Mobility Factor									
Arsenic									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp (°C)	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	3.7	3.7	3.7	7.8	7.8	7.8	9.0	9.0	9.0
100	4.5	4.8	4.2	9.0	7.6	8.7	10.7	9.6	10.1
200	5.2	5.5	4.6	8.9	9.0	8.5	10.5	11.3	11.1
300	3.8	4.3	3.2	6.1	6.9	7.3	9.9	9.6	10.6
400	2.2	3.4	3.3	8.4	7.3	8.2	11.8	10.9	10.0
Cadmium									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp (°C)	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	34.3	34.3	34.3	36.2	36.2	36.2	29.1	29.1	29.1
100	32.7	35.6	36.1	34.7	32.2	35.2	30.4	29.7	30.1
200	30.6	36.4	35.2	34.1	33.6	33.8	30.5	29.0	27.3
300	35.3	32.5	30.7	35.8	33.9	33.8	29.1	29.9	31.2
400	31.6	33.0	31.1	31.5	35.1	33.2	31.0	31.4	33.1
Cobalt									
	no sludge applied			80:20 soil sludge ratio			60:40 soil sludge ratio		
Temp (°C)	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs	2hrs	4hrs	6hrs
0	0.97	0.97	0.97	0.77	0.77	0.77	0.92	0.92	0.92
100	0.87	1.31	1.16	0.94	0.94	1.14	0.91	0.70	1.00
200	0.70	0.95	0.81	1.01	1.01	1.06	1.01	1.21	1.04
300	0.71	0.94	0.55	0.81	1.01	1.06	1.24	1.26	0.97
400	1.31	0.53	0.72	0.84	0.66	0.72	0.72	0.88	1.01

8.3 Appendix 3

Ethical clearance



UNISA GENERAL RESEARCH ETHICS REVIEW COMMITTEE

Date: 19/02/2018

Dear Ms Tshisikhawe

**Decision: Ethics Approval from
16/02/2018 to 31/01/2019**

NHREC Registration # : REC-170616-051
ERC Reference # : 2018/CAES/023
Name : Ms KC Tshisikhawe
Student # : 44406282

Researcher(s): Ms KC Tshisikhawe
44406282@mylife.unisa.ac.za

Supervisor (s): Prof VM Ngole-Jeme
ngolevm@unisa.ac.za; 011-471-3878

Working title of research:

An evaluation of the effects of fire on the sorption properties of contaminated soil

Qualification: MSc Environmental Science

Thank you for the application for research ethics clearance by the Unisa CAES General Research Ethics Review Committee for the above mentioned research. Ethics approval is granted for a one-year period, subject to submission of the signed nondisclosure agreement with ERWAT. After one year the researcher is required to submit a progress report, upon which the ethics clearance may be renewed for another year.

Due date for progress report: 31 January 2019

Please note the points below for further action:

1. The signed nondisclosure agreement with ERWAT is outstanding. This must be obtained and submitted to the Committee before data collection may commence.

*The **medium risk application** was reviewed by the CAES General Research Ethics Review Committee on 16 February 2018 in compliance with the Unisa Policy on Research Ethics and the Standard Operating Procedure on Research Ethics Risk Assessment.*




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The proposed research may now commence with the provisions that:

1. The researcher(s) will ensure that the research project adheres to the values and principles expressed in the UNISA Policy on Research Ethics.
2. Any adverse circumstance arising in the undertaking of the research project that is relevant to the ethicality of the study should be communicated in writing to the Committee.
3. The researcher(s) will conduct the study according to the methods and procedures set out in the approved application.
4. Any changes that can affect the study-related risks for the research participants, particularly in terms of assurances made with regards to the protection of participants' privacy and the confidentiality of the data, should be reported to the Committee in writing, accompanied by a progress report.
5. The researcher will ensure that the research project adheres to any applicable national legislation, professional codes of conduct, institutional guidelines and scientific standards relevant to the specific field of study. Adherence to the following South African legislation is important, if applicable: Protection of Personal Information Act, no 4 of 2013; Children's act no 38 of 2005 and the National Health Act, no 61 of 2003.
6. Only de-identified research data may be used for secondary research purposes in future on condition that the research objectives are similar to those of the original research. Secondary use of identifiable human research data require additional ethics clearance.
7. No field work activities may continue after the expiry date. Submission of a completed research ethics progress report will constitute an application for renewal of Ethics Research Committee approval.

Note:

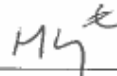
*The reference number **2018/CAES/023** should be clearly indicated on all forms of communication with the intended research participants, as well as with the Committee.*

Yours sincerely,



Prof EL Kempen
Chair of CAES General Research ERC

E-mail: kempeel@unisa.ac.za
Tel: (011) 471-2241



Prof MJ Linington
Executive Dean : CAES

E-mail: lininmj@unisa.ac.za
Tel: (011) 471-3806

URERC 25.04.17 - Decision template (V2) - Approve

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8.4 Appendix 4

Language Editor



You Write. We Edit. You Love it.

28 February 2022

TO WHOM IT MAY CONCERN



RE: CONFIRMATION OF LANGUAGE EDITING SERVICES

I confirm that I have done language editing for SEBOLA CONSTANCE's dissertation titled:

AN EVALUATION OF THE EFFECTS OF TEMPERATURE INTENSITY AND DURATION ON THE SORPTION PROPERTIES OF MINE TAILINGS CONTAMINATED SOILS AND THE IMPLICATIONS ON FIRE-AFFECTED SOILS

The dissertation now conforms to the University of South Africa's language editing standards.



Yours sincerely

A handwritten signature in black ink that reads "Lynn N Sibanda Moyo".

Lynn N Sibanda Moyo

Tel: 011 050 0376

Mobile: 071 989 0983

Email: lynn@lovetoedit.co.za



Member of the [Professional Editors Guild](#)



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Website: www.lovetoedit.co.za | Registration Number: 2016/ 425723/ 07