AN INVESTIGATION INTO SOIL POLLUTION AND REMEDIATION OF SELECTED POLLUTED SITES AROUND THE GLOBE

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ABSTRACT

In this study, simulated soil (SS), as well as its constituents (quartz sand [QS], bentonite clay [BC] and peat moss [PM]) were used as a model to study the leaching behaviour of potential toxic elements (PTEs) in a batch process using EDTA as an extractant and comparing it with the extraction capacities of the other extractants EDDS, 2, 4-pentanedione [Hacac], citric acid [CA] and tartaric acid [TA]). Prior to leaching, SS and its constituents QS, BC, and PM were contaminated with single metals (SM) and multi-metals (MM) at different concentrations.

EDTA was the most efficient and TA the least efficient extractant. Hacac showed preferential recovery for Cu and Ni. Metal recovery by EDDS in SS was significantly diminished compared to EDTA. Once the leaching behaviour in the batch process had been established, other process configurations (column and heap) were investigated.

The effect of three different leaching processes and 4 different leaching agents on the extraction of five metals showed that total metal extraction of up to 50% efficiency could be achieved. EDTA proved to be the best overall extractant when used in a batch leaching process. Different metals showed preferential recoveries with specific processes and extractants.

The results obtained from the multi-metal leaching profile of the SS was used to predict the leaching capacities of the three environmental soils sourced from Nigeria (Nig-S) and Romania (Ro-SB and Ro-PH), using column and heap leaching processes. The behaviour of SS compared in practice with the leaching behaviour exhibited by the Ro-SB. The leaching profiles of the base metals from the different soils (both natural and simulated) was studied by using first-order, power function and Elovich equations. The Elovich equation provided the best fit of the experimental data. The rate of metal release was higher for the SS and Ro-SB soils than the Nig-S and Ro-PH soils.

Subsequently, the data were analysed to determine the B/C Ratio, NPV, and payback period of the study. The analysis gave a B/C Ratio of 0.2, negative NPV of £ 1797.70 and £ 351.77 (for 50% and 90% recovery of EDTA-Heap process respectively) and payback period of 4 years. These indicators are suggestively below the decision criteria. Thus, the process is not economically viable. However, a sensitivity analysis performed based on 25% and 50% changes in the prices of the various metals and extractants shows that when 90% of the

extractants could be recycled, a significant change in the process economics could be achieved.

Overall the results suggest that the design of a contaminant-specific leaching process performed in a sequential manner could practically leach all the metals, and offer a potential separation of the metals from the leach liqour.

ACKNOWLEDGEMENTS

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LIST OF ABREVIATIONS

EPA	Environmental Protection Agency
E-Waste	Electronic Waste
FAO	Food and Agricultural Organization
Hacac	Acetylacetone (2,4-Pentanedione)
HS	Heap Study
ICMM	International Council on Mining and Metals
ICP-OES	Inductively Couple Plasma Optical Emission Spectrometry
IMC	Intermediate Concentration
ISO	International Standard Organization
IVC	Intervention Concentration
JOGMEC	Japan Oil, Gas and Metal National Corporation
KC	Kaolinite Clay
LMWOA	Low Molecular Weight Organic Acid
LoD	Limit of Detection
LoQ	Limit of Quantification
MM	Multi-Metals
MMSD	Mining, Minerals and Sustainable Development
OECD	Organisation for Economic Corporation and Development
PM	Peat Moss
PTEs	Potential Toxic Elements
QS	Quartz Sand
SEI	Secondary Electron Images
SEM-EDS	Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy
SM	Single Metals
SOP	Standard Operating Procedures
SS	Simulated Soil
SSE	Sum of Squares due to error
TA	Tartaric Acid
UNEP	United Nations Environmental Protection

USGS   United States Geological Survey

WEEE   Waste Electrical and Electronic Equipment

WHO   World Health Organisation

Contributions from this investigation

Conferences:

The 31st International Conference on Solid Waste Technology and Management held in Philadelphia, PA USA on the 3rd through 6th April 2016. The conference focused on waste technology and management with *specific topics on innovative strategies for waste separation, recycling and recoveries, mining and mineral wastes & economics*. These topics hinges around my overall research objectives. Oral presentation at the conference enabled the demonstration of new knowledge on studies of adsorption-desorption dynamics of metals on simulated soil and their individual components for metal recovery, *an area that has limited published literature*. In the course of the presentation, new techniques in surface mining, waste management and sustainable recovery presented at the conference were explored. In addition, the conference provided opportunity to network with conference committee members, especially those from Nigeria and the UK, as well as congress attendees. Finally, paper preparation and submission for review in the special edition of the journal of solid waste technology and management.

Papers:

- *A comparison of batch, column and heap leaching efficiencies for the recovery of heavy metals from artificially contaminated simulated soil:* Authors: L. Mgbeahuruike, J. Barrett, J.H. Potgieter, L. van Dyk and S.S. Potgieter-Vermaak. Journal: Clean Technologies and Environmental Policy (CTEP). Status: Under revision

- *The predictive potential of individual soil components on leaching behaviour of metal contaminants from a simulated soil:* Authors: S.S. Potgieter-Vermaak, L. Mgbeahuruike, L. van Dyk, J. Barrett and J.H. Potgieter. Journal: Environmental Earth Science. Status: Submitted

- *Assessment, recovery, remediation and economics of contaminated sites influenced by sustained anthropogenic inputs:* Authors: L. Mgbeahuruike, J. Barrett, L. van Dyk, S.S. Potgieter-Vermaak and J.H. Potgieter. Status: in preparation

Chapter 1

Introduction

Metal depletion in the world has grown rapidly in recent decades. This has, in part, been driven by global population growth and increased consumption, especially in the high-tech industrial sectors (Wouters and Bol, 2009). Projections by the UK Environmental Protection Agency (EPA) (2009) confirmed that the consumption of metal resources over the last 50 years has been unprecedented. This is further aggravated by a trend in which ore grades continue to decline, with a major shift from high grade low-bulk to low grade but high bulk ores (ICMM, 2012). Numerous scholars (Gordon et al., 2006; Kesler, 2010) have voiced concern over the limit in the future availability of critical metals and their economic and technological importance (EC, 2010). According to predictions (2050 long-term forecast) reported by Japan Oil, Gas and Metals National Corporation (JOGMEC, 2005), Cu consumption will increase up to between 19 million tons and 37 million tons, Pb consumption will increase up to between 8.4 million and 9.55 million tons, Zn up to between 11.6 million and 14 million tons, and Ni up to between 1.8 million to 2.7 million tons. There are divergent views from environmental experts and economists on how material scarcity can be interpreted (Skinner, 2001; Bardi, 2013; Bleischwitz, 2010). That notwithstanding, the concentration of primary raw materials is continuously decreasing in a form that impairs the quality of the targeted/or critical metals in the ore (Bleischwitz, 2010; ICMM, 2006). Therefore, the current primary mining will require more energy consumption and cause higher environmental impacts per unit of raw material (Giurco et al., 2010) processed, a development that may become prohibitively expensive with narrowed profit margin (Mason et al., 2011). Most of the technologies associated with primary production processes are energy intensive and could cause large greenhouse gas-emission per mass unit of metal produced (Notgate and Haque, 2010). More so, effluent processes from the mining production are informally discharged and dispersed in the surrounding environment at elevated concentrations, which in turn, pose a significant threat to flora, fauna (Langmuir et al., 2005) and incidentally to humans via the food chain.

Because the easily accessible mineral deposits are being rapidly depleted, there is an urgent need to source these critical and scarce elements from alternative sources using existing but sustainable technologies to compensate for growing shortage of metal resources. Contaminated land beneficiation is considered as a potential alternative source for the recovery of such metals.

This research has focused on the recovery of heavy metals from various types of soils, ranging from contaminated simulated soil and its constituents (bentonite clay, peat moss and quartz sand) to industrially impacted soils (Nigerian soil and Romanian [Campina & Copsa-mica] soils) of natural origin using different chelating agents. The objective of this research is to compare the leaching potentials of the selected extractants and the chemistry and economies associated with their recoveries.

1.1   Background and motivation

Increased mining and ore processing activities has led to significant global environmental challenges because of depletion of virgin metal resources. This is of concern for several elements such as copper (Cu), zinc (Zn), etc. (Kesler, 2010; Gordon et al. 2006). Currently, the rate of extraction of many geologically scarce metals from the lithosphere has increased in excess of 3% per year through the last half century or longer and continues to do so (Gordon et al., 2006). Cu for instance, is considered as a scarce mineral with only 60 years of expected availability at current production levels (USGS, 2011). Soil is a natural body composed of minerals, organic compounds, living organisms, air and water in interactive combinations produced by physical, chemical and biological processes (EEA, 2007). In addition, soils can act as a natural buffer for transportation and distribution of chemical materials and elements in the atmosphere, hydrosphere and biosphere. However, in the recent past, the chemistry of urban soils associated with potentially toxic elements (PTEs) has become a significant environmental problem worldwide (Alloway, 1995). The main sources of metallic and non-metallic contaminations are atmospheric deposition, disposal of industrial waste, mining and smelting operations, use of fertilizers, auto mechanic waste, and fly ash from incineration and combustion processes (Mireles et al., 2012; Wei and Yang, 2010; Yaylali-Ababus, 2011). Although many of these metals occur naturally in the soil, and are intrinsic elements of the earth crust, excessive amounts introduced into the soils can affect soil matrices, particularly involving metal-soil interactions (Shi et al., 2008; Wei and Yang, 2010). At the interfaces of soils and soil solution phases, various competitive reactions occur. Many studies have demonstrated that as

metal concentrations in soils increase, the soils will become toxic to flora and fauna. However, the metal toxicity level will depend on the chemical form of the metal which controls both its mobility and reactivity in the environment (McBride et al., 2000).

The migration and accumulation of these PTEs is a function of the chemical, and mineral compositions of the soil, soil solution pH, cation exchange capacity, soil organic matter, land use patterns, the nature of the contaminants in terms of its origin and the characteristics of the deposition/composition and environmental conditions that may lead to weathering (Rogan et al., 2010). Many studies have demonstrated that adsorption-desorption and precipitation-dissolution are the most important processes affecting the behaviour of heavy metals in soils, and hence their bioavailability and potential toxicity (Backes et al., 1995; Sposito et al., 1999; Sparks, 2003). This may be the reason why a large proportion of many metals are adsorbed or occluded by carbonates, organic matter, Fe-Mn oxides, and primary or secondary minerals (Xian, 1987). Metal desorption from these forms vary, depending on their fractions and relative bonding strength to various phases. Water-soluble, exchangeable, and carbonate fractions are considered readily mobile and bioavailable, whereas other metal fractions, are considered immobile and tightly bound and are not easily released under natural conditions.

According to numerous studies, the contamination sources of PTEs in the environment are mainly derived from anthropogenic sources such as urban soil contamination (Sindern et al., 2007), urban road dust (Ahmed and Ishiga, 2006; Sezgin et al., 2003) and agricultural practices (Alloway, 1995). In particular, soils in such regions have been polluted from wide range of sources with lead (Pb), copper (Cu), cadmium (Cd) and other PTEs (Alloway, 1995; Xiangdong et al., 2004; Krishina and Govil, 2005). The situation is worrisome in developing countries where research efforts towards monitoring the environment has not been given the desired attention by all stakeholders.

Nigeria has a wide pipeline network and depots for the distribution of refined petroleum products (Renner et al., 2003). The unprecedented growth in the petroleum industry and the marketing of petroleum products have resulted in the pollution of the environment by oil spills involving blowouts, leakages from tanks or tanker trucks, and dumping of waste petroleum products (Alloway and Ayres, 1994; Osibanjo et al., 1983). The most commonly marketed hydrocarbon products, kerosene, gasoline, diesel oil and lubricating oil, contaminate the environment through spillage from auto-mechanic workshops, accidents

involving transporting trucks, overflow leaks from motor vehicles, poor handling at petrol retailing stations and other domestic activities. Remarkable accumulation of petroleum hydrocarbons and heavy metals found in contaminated soils can influence the ecosystem substantially, thereby resulting in significant losses in soil quality (Kelly and Tate, 1998; Amadi et al., 1996). This contamination is more pronounced in the Niger delta region where a large number of the oil wells are located, and most of the lands have been heavily contaminated by these activities.

In response to the growing need to address environmental contamination and sustainably reuse the land, recover and reuse of scarce metals (Cui and Forssberg, 2003), many remediation technologies have been developed to treat contaminated soil (Hursthouse, 2001; Scullion, 2006).

It is estimated that about 6.4 x10^9 metric tons of ore is extracted annually from the Earth, of which >90% is discarded as mill wastes and mine overburden (Worrel, 2004). This worrying scenario is further complicated by a decrease in some of the minable deposits. For instance, the average Cu grade mined in the United States decreased from approximately 2% to 0.4% at the end of the 20th century (Kesler, 2010; Rankin, 2011). The same scenario is seen for Zn, as the current usage increased rapidly. Over the last century and a half the rate was 13.5 million tonne per year (ILZSG, 2015). This unprecedented rise triggered speculations if reliable and sustainable alternative measures can be found to replace these scarce metals, and reduce the need to mine virgin ore to replace discarded ones. The exhaustion of these minable deposits may become evident in the near future (Kesler, 2010; Gordon et al., 2006). In accordance with this line of thought, the majority of studies (Li et al., 2001; Manta et al., 2002; Lee et al., 2006; Romic et al., 2007; Miao et al., 2008) are in agreement that in order to save virgin resources from depletion, cut down on fossil resources used to supply energy in primary mining processes, enhance resource efficiency, mitigate environmental and health impacts, consideration has to be given to resource recovery from secondary sources (contaminated soil) and adequately harnessed.

1.2   Problem statement

There is growing concern globally that the volume of heavy metal contents of soils is increasing as a result of the ever-increasing volume of waste generated by anthropogenic activities such as for example, sewage dumps, application of fertilizers and pesticides, industrial discharge, automobile repairs, mining/smelting processes (Liu et al., 2005; Wong et al., 2002). This causes a serious challenge for rehabilitation (Bian et al., 2012), to

decrease the negative ecological footprint as well as leaving negative ecological footprint on the natural environment. Heavy metals find their way into the soil environment through different land uses. Each land use has its own peculiarity, which could contribute a significant amount of metals into the soil (Zarcinas et al., 2004). Most importantly, leaching of mine tailing and drainage from mined areas can substantially expose the soil to metal residues. Unlike organic pollutants, PTEs are recalcitrant and difficult to remove from the environment, as they are often chemically and biologically inert (Anjum et al., 2009). They can sometimes be transformed to different redox stages or complexed by organic metabolites (Ren et al., 2009). This has made soil contaminated with PTEs an area of increasing scientific concern (Labanowski et al., 2008).

Several studies (Alloway, 1995; Xiangdong et al., 2004; Krishina and Govil, 2005) have revealed that the amount of PTEs contained in contaminated soil globally is significant. Besides their biological importance in living organisms, which occur at trace quantities, their unprecedented presence can present a potential environmental and health impact and as such must be removed from the soil or be physically and/or chemically contained therein (Lovely and Coates, 1997). While adequate remediation processes for contaminated soil exist and sometimes meet environmental requirements, it results in the loss of valuable metals, energy and economic resources. However, the predicted shortages in geological reserves for many metals, (Harmsen et al., 2013), could offer opportunities to innovatively harness value from the generated waste (secondary source) to deal with potential shortfalls virgin ore.

In order to investigate this prospect, ex situ soil washing processes with chelating substances, for the removal of metals from soils (Dermont et al., 2008), was undertaken. Their wide applicability and economic feasibility (Gidarakos and Giannis, 2006) was also considered. Previous studies of soil washing applications have only been limited to cleaning. The leachate generated during soil washing can potentially contain significant amounts of pollutants (Karin et al., 2013) and can serve as a source for metal recovery.

It was against this backdrop that it was decided to evaluate the feasibility of using industrially impacted soils, more especially Nigerian contaminated soil, as a case study for potential metal recovery and perform techno-economic analysis of the study using various chelating agents and existing refining techniques used. If the process is viable and adequately optimized, it may present potential economic and environmental benefits. In

addition to the diversification of the nation's hydrocarbons-dominated economy, it could open greener production routes for metals and reduce their carbon footprint.

1.3 Hypothesis

Contaminated soil can serve as a source for metal beneficiation and can be recovered using extractants that are efficient, environmentally sustainable and economically viable.

1.4 Aims and Objectives

1.4.1 Specific Aim

The overall aim of this study was to compare the extraction capability of various chelating agents for the removal/recovery of base metals from different environmental soil types and constituents with the ultimate intention of providing an economically sustainable solution to recover metals from contaminated soil. To achieve this, the following overall objectives were pursued:

1.4.2 Objectives

- Development of a leaching profile for an artificial contaminated simulated soil (SS) of known composition and character using various extractants (EDTA, EDDS, ACAC, CA, and TA)
- Contaminate individual substrates with single and multi-metals at various concentrations of interest and determine loading and recovery efficiencies using a batch process approach
- Compare recovery efficiencies of the multi-metal contaminated SS using batch, column, and heap leaching methods of extraction
- Compare and contrast leaching potentials of some real natural contaminated soils with the SS
- Determine the economies of the study using a real contaminated soil of Nigerian origin as a case study

1.5 Potential contribution and value

Research methodologies adopted for this study will reveal the capacity and suitability of exploring contaminated soils for metal beneficiation. It is expected that environmental soil clay content will affect the mineral extraction efficiency of the process. Extraction of metals with the various chelating agents from specific soils is anticipated to take less time and be

cheaper when compared to conventional mining (geological metals). This study will investigate the efficiencies of different leaching agents as well as the economies of their recoveries from different soil matrices.

1.6   Thesis structure

In the literature review section of Chapter 2, is a discussion of metals in the environment, their sources and associated impacts, soil constituents, soil chemistry (adsorption/desorption mechanism), kinetics, treatment and remediation types.

Chapter 3 will give details of the experimental section. This will include study sites, and descriptions, reagents sourced substrates analysis, artificial soil preparation and contamination, washing experiments and analytical procedure applied.

Chapter 4 discusses the influence of soil constituents on the potential recovery of metals in terms of implications of single metal and multi-metal systems.

Chapter 5 explores the possibilities of enhanced contaminated land beneficiation for metal recovery and compare various process options of batch, column and heap leach processes with one other in terms of operational efficiencies.

Chapter 6 compares the capacities of the various natural soils for metal recovery using extracting agents on both heap leach and column techniques to compare global suitability of methodology. A technical and economic study to ascertain the potentials of contaminated land beneficiation for metal recovery, using one of the selected soils, as a case study will be explored in Chapter 7. Lastly, Chapter contains the overall conclusions of this work, and recommendations for further investigations in future. The impact and value of the work will also be assessed.

Chapter 2

Literature review

The Environmental Protection Agency highlighted in 2009 that the consumption of metal resources over the last 50 years has been unprecedented. As a result, concerns have been raised over the future supply of critical metals such as Cd, Cu, Ni, Pb and Zn (Kesler, 2010; Gordon et al., 2006). Furthermore, availability of productive agricultural land is contracting; in part due to soil contamination by potentially toxic elements (PTEs), for example, Cd, Cu, Ni, Pb and Zn. Such contamination is an increasing occurrence and constitutes a threat to the sustainability of development and food security (Eswaran et al., 2002). This is a particular concern in developing countries where environmental laws do not exist or enforcement is lax (Ongondo et al., 2011). Thus, to resolve the widespread depletion of metal resources and increased metal contamination of agricultural soil resources solutions need to be investigated. It could well be feasible to consider a simultaneous process whereby remediation of the contaminated soil also facilitates metal recovery as a sustainable resource of these critical metals.

This chapter focuses on the general behaviour of metals in the soil and parameters associated with their distribution/mobility. This will further review the sources, causes and degrees of contaminated soils as well as the type of treatment and extraction methods previously employed to minimize or ameliorate their toxicity.

2.1   Soils overview

For the purpose of this study, a soil is defined from the context of Nikitin (2001), who considered soil as "A system with numerous biosphere functions and emphasized that soil acts as a habitat, accumulator, and source of substances for all terrestrial organisms, as a sink between the biological and geological cycles of matter, and as a planetary membrane (protective barrier and buffer system) that maintains suitable conditions for normal development of the biosphere. It is a dynamic system that is subject to short-term fluctuations because of physico-chemical changes in its properties". Soil properties vary from place to place with differences in parent rock composition, climate, and other factors.

Soil is composed of three major components, minerals (e.g. quartz, feldspar, etc.), clays and organic matter, which are discussed in more detail below (Kesler, 2010).

2.1.1 Soil components

Soil minerals are natural inorganic compounds that exhibit specific physical, chemical and crystalline properties. They are generally classified as primary or secondary minerals, which could be either a silicate (such as quartz) or non-silicate (such as calcite) (Conley et al., 2006). The primary minerals are the inherited minerals of the parent rock, which has not been substantially modified chemically or structurally. However, when these primary minerals are subjected to significant structural and chemical modifications (weathering), driven by physical, chemical and biological processes, it results in the formation of secondary minerals. Most soils contain silica as their predominant structural constituent. The silicate minerals are mainly quartz, feldspar, mica etc. Silicate minerals are composed of atoms arranged in a three dimensional periodic pattern, resulting in the formation of a Si-tetrahedron (one Si^{4+} is coordinated with four O^{2-}).

Clay minerals are an important group of minerals because they are among the most common products of chemical weathering. They are dominated by secondary minerals (product of primary minerals that has been chemically and structurally modified under ambient condition, e.g. alumina-silicates (kaolinite, montmorillonite), amorphous, carbonates, sulfates, oxides and hydroxides), either formed *in-situ* or transported from another environment. Based on the clay structures and chemical compositions, the clay minerals can be divided into three main classes; Kandites (most common is kaolinite, a one to one (1:1) layered silicate) smectites (most common are bentonite and montmorillonite, with a two to one (2:1) layered silicate structure) and lastly illite (Tucker, 1991). The layers of these minerals differ from each other depending on their cation make-up. For instance, fairly weak bonds hold the layers in kaolinite together, whereas there is strong bonding in montmorillonite and illite due to the presence of positively charged metal ions. However, for the purpose of this study, our discussion would be limited to the kaolinite and bentonite groups.

Most clay minerals are layer silicates composed of sheets of alumina octahedral (an atom of aluminium bonded to six atoms of oxygen) and silica tetrahedral (an atom of silica bonded to four atoms of oxygen). Both tetrahedral (T) and octahedral (O) layers are organized around central Al, Fe, or Mg cations. These sheets generally are bonded together either in a 1:1 structure (TO) in which each layer of alumina octahedra is paired with a layer

of silica tetrahedra, or in a 2:1 structure (TOT) in which each octahedral layer is sandwiched between two tetrahedral layers. These building blocks are themselves interlayered and bound together by shared ions between the sheets (Schultz, 1989). They exhibit isomorphous substitution, a situation that describe how elements share edges or faces and subsequently compensate for the charges in the minerals- for example, in the tetrahedral layer, the Si is replaced by Al, leaving a charge deficit that is balanced by a monovalent or divalent cation or in the octahedral layer where Al is replaced by Mg or other divalent cation with a charge deficit similarly balanced by cations that are not integral part of the octahedral of tetrahedral network (Onal et al., 2001). This phenomenon is responsible for cation exchange capacity (CEC) which a clay mineral possess, and describes the extent to which metal cations can be adsorbed and absorbed.

Kaolinite, with 1:1 structure (Figure 1) is the most important mineral in the kandites group of clay minerals and it is a product of advanced weathering processes (Miranda-Trevino and Coles, 2003). Adjacent layers of the kaolinites are held together by ionic bonds that are strong enough to prevent cations or water from entering the spaces between the sheets. Because it has few exchangeable cations held between its layers, resulting from negligible isomorphous substitution, kaolinite does not swell much when wetted, and has low plasticity (and thus little capacity to be moulded). The octahedrons consist of two planes of hydroxyl ions between which lies in a plane of magnesium or aluminium ions, which is typically coordinated by hydroxyl sheets octahedrally (Uddin, 2016). These octahedrons are also arranged in a hexagonal pattern often called octahedral sheets (Uddin, 2016). Because of this structure, the silica/oxygen and alumina/hydroxyl sheets are exposed and interact with different components in the soil (Miranda-Trevino and Coles, 2003). The outer hydroxyl groups of the alumina hydroxyl sheet are situated along the unshared plane of the alumina hydroxyl sheet, while the inner groups are located along the plane that is shared with and borders on the silica oxide sheet. The movement of the inner hydroxyl plane is restricted because of chemical bonding between the silica and alumina sheets (Frost, 1998; Miranda-Trevino and Coles, 2003). This well-packed structure and high molecular stability exhibited by kaolinite layers makes it difficult to be separated and its sorption activity occurs along the edges and surfaces of the structure. Kaolinite has a relatively low surface area, low absorption capacity and low cation exchange capacity (CEC) in comparison to smectite (Uddin, 2016; Farrokhpay et al., 2016).

Montmorillonite, a common mineral in the smectite group (Figure1), has a 2:1 layer structure consisting of an octahedral alumina sheet sandwiched between two opposing tetrahedral silica sheets (Brigatti et al., 2013). The physical state of montmorillonite and corresponding smectite can be changed with increasing water content, from anhydrous solid to a hydrated material, semi-rigid plastic gel, a phenomenon known as swelling (Murray, 2001). Montmorillonite clay, however, exhibit much more variability in the chemical composition of their octahedral sheets of Fe^{2+} and Mg^{2+} for Al^{3+} and of Al^{3+} for Si^{4+}, typically due to isomophous substitution in their sheets, which is balanced by exchangeable cations such as Na^+, and Ca^{2+} located between the layers and around the edges. As such, it develops weak bonds between the silicate layers, which allows water and ions to readily penetrate the crystal structure. This, however, influences their physicochemical properties (such as swelling, plasticity, cohesion, thixotropic, etc.). Montmorillonite is capable of adsorbing heavy metals via two different mechanisms that include cation exchange in the interlayer resulting from the interactions between ions and negative permanent charge and secondly, the formation of inner-sphere complexes through Si–O and Al–O groups at the clay particle edges (Mercier and Detellier, 1995; Akpomie et al., 2015). The expandable nature of montmorillonite, its negative charge, and a large total surface area greatly influences their metal retention, transport, and persistence in the soil-subsurface systems. Commercial bentonites predominately contain either Na-montmorillonite (NaM) or Ca-montmorillonite (CaM) and too a much lesser extent other smectites.

T-O-sheet for Kaolinite   T-O-T sheet for montmorillonite
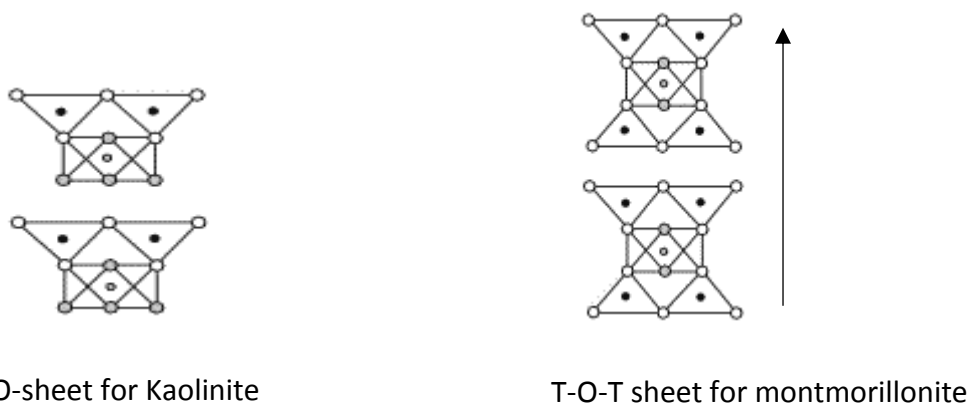
Figure 2 1 Tetrahedral (T) and octahedral (O) sheets for alumina octahedral T-O (1:1) and T-O-T (2:1) for kaolinite and montmorillonite structure (redrawn based on Murray 2007)

Organic matter, one of the constituents that make up soil, is a product of decomposed biomass containing carboxylic, amino, nitroso, hydroxyl, and phenolic groups. It is

characterised by a complex mixture of partially decomposed and otherwise transformed organic materials known as humic substances. Humic substances vary in forms (humic acid, fulvic acid and humin)-depending on the pH of the soil (Stevenson, 1994). In an alkaline medium, humic acid is soluble. At all pH conditions (acidic, neutral, and alkaline) fulvic acid becomes soluble while humins are not soluble in either acid or alkaline condition.

Organic matter contains carboxylic, amino, nitroso, sulfhydryl, hydroxyl, and phenolic groups substantial fraction of the mass of the humic acid contains carboxylic acid functional groups. These functional moieties enable the molecules to exhibit chelating properties with positively charged multivalent ions. They form metal-humate complexes (chelates) with toxic metals with different degrees of stability (Datta et al., 2001). These complexation properties and the nature of organic compounds, the stability of the dissolved organo-metal complex and the interaction of the newly formed complex with other soil constituents invariably determine the mobility of metal ions in the environment (Connell and Miller, 1984; Karaca, 2004; Ghosh and Singh, 2005).

Generally, organic matter in soils serves as a reactive adsorbent pool for trace metals due to their reactivity associated with various S-, O- and N- functional groups. They can reduce or increase the bioavailability of heavy metal in soil through immobilization or mobilization by forming various insoluble or soluble heavy metal –organic complexes. The effect of soil organic matter on metals in soils largely depends on its amount, composition and dynamics. Specifically, humic acid (HA) and fulvic acid (FA) in the soil are involved in three specific chemical reactions that can interact with metal ions, clays and several organics because of their high specific surface area and chelating properties. Though they differ in molecular weight, elemental and functional groups, they have similar structures (Yong and Wandruszka, 2001; Evangelou and Marsi, 2001). Humic acids (HA) are higher in molecular weight and contain less oxygen-containing functional groups when compared to fulvic acids (FA) (Stevenson, 1994). Thus, FA becomes more chemically reactive because of the high exchange capacity, which is due to the total number of COOH groups present. The mechanism involved in metal retention by organic matter could be described by both complexation and adsorption, i.e. inner sphere reactions may take place as well as ion exchange (Evans, 1989). The chemical active components (phenol, carboxyl (-ate), amino groups) are influenced by increased pH. They ionize increasingly as pH rises and the organo-metal complexes thus become stable at higher pH (Jones and Jarvis, 1981). Several studies

revealed that the reactions between organic acid and heavy metal are related to the amount and place of carboxyl and hydroxyl groups (Gao et al., 2003; Schwab et al., 2008).

2.1.2 Sources of metals in soil

Naturally, certain chemical elements occur in soils as components of minerals. The low levels of their content in soils and plants as well as their biological roles make them microelements (Lacatusu, 1998) with some of these metals being vital for the proper growth of plants and the human metabolism in trace amounts. By contrast, when metals occur in excess, their uptake may exceed plant requirements, thus resulting in toxic effects (Nagajyoti et al., 2010). These effects could be directly or indirectly affect plant development. For instance, direct toxic effect of these heavy metals (especially Cd and Pb) on plants include inhibition of cytoplasmic enzyme damage to cell structure due to oxidative stress (Jadia and Fulekar, 2009; Assche and Clijsters, 1990). While the indirect toxic effect could be seen as the replacement of essential nutrients at cation exchange sites of plants(Taiz and Zeiger, 2002). However, it is worthy of note to mention that of the five metals (Cd, Cu, Ni, Pb and Zn) of interest being investigated, cadmium (Cd) and lead (Pb) serve no biological function and are classed as cumulative poisons, and are toxic even at low concentrations (Nriagu, 1989).

However, anthropogenic activities resulting from the use of fertilizers (Chirinda et al., 2010) and pesticides (Linn et al., 1993), accidental spills and leaks of chemicals used for commercial and industrial purposes (Alloway and Ayres, 1994; Osibanjo et al., 1983), the leaching of mine tailings and its subsequent drainage from mined areas (Garbarino et al., 1995) can introduce substantial amounts of metal residues into the soil. Some of these are further transported via air and water processes, resulting in transference of metal contamination from the original source sites to pristine soils (Hudson-Edward et al., 1999).

PTEs contaminations find their way into the soil environment through different land uses. Each land use has its own peculiarity , which could contribute significant amounts of metals into the soil (Zarcinas et al., 2004). However, their migration and accumulation is a function of the chemical and mineral compositions of the soil, soil solution pH, cation exchange capacity, soil organic matter, land use patterns, the nature of the contaminants in terms of its origin and the characteristics of the deposition/composition and environmental conditions that may lead to weathering (Rogan et al., 2010). Unlike water and air pollution, for which the contamination can be reversed by dilution and self-purification, soil contamination is persistent and very difficult and expensive to reverse (Gombert, 1994).

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The contaminants, mostly find specific absorption sites in the soil where they are retained very strongly either on the inorganic or organic colloids, making it very demanding for remediation.

There are two main sources of metals in the environment: natural and anthropogenic. While the natural source may be limited to environmental variables, including parent material and soil properties, the anthropogenic inputs of metals to soils result from agricultural emissions (fertilizers, pesticides, insecticides), industrial activities (battery breaking and automobile wastes, oil refining, paint manufacturing, mining and smelting) or as a consequence of historic environmental disposal practices (Abumaizar, 1999; Peters, 1999)

Natural sources: The dispersion of PTEs, such as Cu, Pb and Zn, in the environment occur through several processes including geogenesis and paedogenesis. These processes are the major natural sources of PTEs in the soil. Some mineral ores like arsenopyrite, galena, cassiterite, can undergo dissolution via chemical weathering thereby releasing PTEs contained in their structure (Lara et al., 2016). Other natural sources include enrichment of soils by precipitation (Nriagu, 1989), marine aerosols and forest fires (Nagajyoti et al., 2010). Naturally, influenced PTEs in the soil have limited mobility and remain more strongly occluded in soil fractions than those from anthropogenic origin (Passos et al., 2010; Wuana and Okieimen, 2011). However, the movement and availability of these natural PTEs are largely influenced by the presence of sesquioxides such as oxides of Fe, Al and Mn. PTEs occluded in the oxides of these metals are often referred to as active fractions (Shauman, 1985). The effect of pedogenic PTEs may override that of anthropogenic sources especially when the parent material contains high level of PTEs (Brown et al., 1999).

Anthropogenic source: Increased inputs of metals and metalloids in the terrestrial environment has been principally attributed to anthropogenic activities arising from rapid industrialization and urbanisation. As reported by Nriagu (Nriagu, 1989), direct activities, processing for industrial and consumer use contributes substantially to the global mobilization of PTEs in the environment. Thus, the rapid increase in industrial mining, atmospheric decomposition of dust and aerosols, vehicular emission, automobile waste and other activities has continuously added to the pool of contaminants, thereby potentially exposing the soil to metal-bearing concentrates (UNEP, 2000).

Mining has been recognized as a primary source of abundant heavy metal contamination in the surrounding environment. Its primary activities may affect a relatively small area, but the impact it creates could be significant over a localized area (Webber, 1981; Freedman and Hutchinson, 1981). Mineral exploration, extraction and processing in mining vicinity generates acid pollutants which could be modified to acid mine drainage (AMD) when in contact with precipitation water. Recent studies have shown that most widespread contaminated sites are characteristics of AMD, which is due to the oxidation of metal sulphides (e.g., pyrites (FeS_2)), leading to the acidification of the drainage water (Salomons, 1995; Bell et al., 2001; Mian and Yanful, 2003).Deleterious effects of mining, metal processing, and informal recycling on the environment are widespread. According to (Lichti and Mulcahy, 2012) report, the United States alone had over 250,000 acid mine drainage sites, which contaminated over 20,000 km of rivers and streams, as well as 180,000 lakes and reservoirs. Uncontrolled and poorly managed metalliferous mine spoils, especially those generated following mine closure or decommissioning, are occasionally disposed onto surrounding soils where they become ecological risk to plants and other organisms growing in such media (Khan et al., 2008) and consequently a risk to humans throughout the food chain (Nagajyoti et al., 2010). Heavy metals taken into the human body at doses higher than limit values proposed by the World Health Organization (WHO) are known to cause carcinogenic, teratogenic and cardiovascular related problems. Therefore, such an area presents a great concern for the public.

Automobile repairs and its associated activities has in no small measure generated and released heavy metals, mainly including Pb, Zn, Fe, Cu, Cd, Cr, Ni, Al, into residential and community soils (Shi et al., 2009). Many possible contaminants could be associated with these activities, including abrasions and wear from tyres and engine parts, spent batteries, spent petrol, organic and inorganic chemicals used in oil additives and metals. For example, soils from the south-eastern part of Nigeria were found to be contaminated with several heavy metals (Nwachukwu et al., 2010). Investigation on road traffic emission revealed that Cu was mainly due to break wear; Ni and Pb were principally from exhaust fumes while Zn was mainly from tire wear and brake lining wear (Johansson et al., 2009). The source of contamination was attributed to increased automobile repairs/workshop activities due to ever-increasing demand for personal vehicles. Most of these are used as '' Tokunbo'' vehicles. Most heavy metals are contained as additives in some lubricants also known as organic solvents. These solvents are non-degradable in the soil. According to Charlesworth

et al. (2003), high concentrations of heavy metals in roadside dust were identified in association with junctions controlled by traffic lights, where vehicles were likely to stop regularly in Birmingham, UK.

Agricultural practices have significantly contributed to the metal pool of soils, via fertilizer application intended for increased grain production. The application of some phosphate fertilizers enhances the fertility of the soil by releasing major elements, including magnesium, potassium, calcium, phosphorus, and nitrogen, used for plant nutrition. Some of these chemical fertilizers, however, contain potentially toxic elements, including As, Cd, Cr, Pb, Hg, Ni, and V (Mortvedt, 1996). These metals can be accumulated in the soil, taken up by plants, and eventually, passed on in the food chain to animals and humans (Langdon et al., 2003). A study conducted by Parkpian et al. (2003), revealed that long term simultaneous application of chemical fertilizers and organic manure on commercial farms showed higher metal accumulation in the soil and plants than those of a cooperative farm. Some pesticides like the organochlorine used for pest prevention and control contain arsenic (As) and copper (Cu) as part of their formulation. They exert harmful effects on microorganisms due to their persistence in the soil and potential movement into water streams may lead to their entry into the food chain and cause health hazards. At present, a good number of the organochlorine pesticides has been out rightly banned in the USA and England (Provoost et al., 2006; Apitz, 2008), due to their degree of toxicity and persistence in the soil for a considerable time without losing their potency.

Industrial discharge of untreated effluents into the environment is often observed in areas of intense industrial activity. The particular chemicals that may be present due to the industrial activities will be solely dependent on the type of industry and specific procedures used on site. In addition, the degree of contamination will also depend on many factors, such as closeness to the site where the contamination occurred, duration of occurrence, etc. For instance, coal-burning plants can produce hundreds of tons of fly ashes per year, depending on the plant size. The fly ash residues, in turn, are deposited directly on the soil, depending on the local climate conditions and prevailing wind direction (Veneva et al., 2004). Studies have also linked contaminated soils to the vicinity of a cement producing plant (Mandal and Voutchkov, 2011).

Several heavy metal cations can be available at the same time in the soils and, therefore their selective retention and competitive adsorption by the soil and its constituents becomes of major importance in determining their availability to flora, fauna and their

movement throughout the soil. Adsorption of cations on different constituents of soil has been studied (Mclaren, 1991) and described in terms of two molecular mechanisms: (i) non-specific adsorption where the metallic cations behave as counter-ions in the diffuse layer; and (ii) specific adsorption resulting from surface complexation (Msaky and Calvet, 1990). Sequential extraction studies (Gomes et al., 1997) on the retention of different metals in soils of different fractions demonstrated that Cd, Ni, Pb and Cu were adsorbed both specifically and as exchangeable cations. However, of all physico-chemical variables such as pH, concentration, ionic strength and complexing ions that affect the extent of adsorption, pH is arguably the main force governing the adsorption of metal cations, metal-solution and soil-surface chemistry onto oxide minerals. pH solution can influence heavy metal adsorption on soil constituents. The number of negatively charged surface sites increases with pH. In general, heavy metal adsorption is small at low pH values. Adsorption then generally increases at intermediate pH from near zero to near complete adsorption over a relatively small pH range; this pH is referred to as the pH-adsorption edge. At high pH values, the metal ions are completely complexed. Among the common metals found in contaminated soils, Pb is reportedly the least mobile. Cu has been shown to remain bound up as insoluble complexes in soil and sediment, whereas Zn and Cd are considerably mobile. This implies that Cd and Zn have a greater tendency to dissociate from insoluble inorganic and organic complexes to form soluble ionic species that remains stable at neutral or slightly alkaline pH (Kabata-Pendias and Pendias, 1984).

2.1.3 Factors that Influence the Retention of Metals in the Soil Matrix

Metal mobility and bioavailability in the environmental media depend on their on their sorption and desorption by soil constituents, which in turn, is predominately expressed in terms of the relative proportion and compositions of soil fractions such as organic matter, clay minerals and metallic oxides or hydroxides, notably, Fe and Mn oxides (Elliott et al., 1986). However, the inherent capacity of the soil to bind metal strongly or loosely onto the surface will depend on the soil texture and total cation exchange capacity (CEC) which itself depends on soil organic matter and clay content. Accordingly, it can be hypothesized that the substantial differences in metal retention or solubility can be likely attributed to sites where metals are complexed or surfaced bound to clay (Foth, 1978), while its mobility is greatly controlled by its chemical speciation (Peakall and Burger, 2003), generally evaluated by selective sequential extraction (Tessier and Campbell, 1979). By this technique, trace

elements were classified into five fractions: exchangeable, bound to carbonate, bound to Fe-Mn oxides, bound to organic matter and residual.

The tendency of metals to bind with organic compounds (such as fulvic acid) and with ligands which have varying affinities for adsorption onto the soil surface is described by the general equation 1.1 below. In terms of Fe & Mn, studies by several researchers (Kinniburgh and Jackson, 1981; Elliot et al., 1986; Chuan et al., 1996) have demonstrated that hydrous Fe and Mn may potentially reduce concentrations of metals in soil solution by both precipitation and specific adsorption reactions:

$$xM^{2+} + yH_{n-m}L^{m-} = M_x(H_{n-m}L)_y^{2x-my} \qquad (1.1)$$
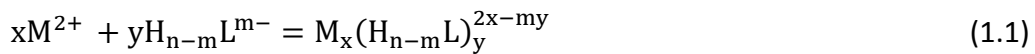
$$ML_{Tot} = \sum M_x (H_{n-m}L)_y^{2x-my} \qquad (1.2)$$

$$M_{Tot} = M_{aq} + ML_{Tot} \qquad (1.3)$$

In general terms, equation 1.1 can be re-written as;

$$M^{m+} + L^{n-} \leftrightarrow ML^{(m-n)} \qquad (1.4)$$

According to the principle of mass action, the activities of M, L and ML are as follows;

$$K_{ML} = \frac{[ML^{(m-n)}]}{[M^{m+}][L^{n-}]} \qquad (1.5)$$

Where M, metal; L, Ligand, ML Metal-Ligand complex, x and y are stoichiometric values; m and n represent number valence electrons

2.1.4   Soil pH

Soil pH is considered a very important aspect of soil chemistry. It is described as a measure of the number of free hydrogen ions (H^+) present in a soil. The various chemical constituents in the soil components are greatly influenced by the pH of the soil. Cation nutrients (Ca, Mg, K, etc.) of a particular soil vary markedly as a result of pH variations. For example, cation nutrients are naturally adsorbed onto soil particles, especially soils high in clay and organic matter (high cation exchange capacity (CECs)). Cations adsorbed to these soil particles are not permanently adsorbed and can be replaced by other compounds that are more strongly attracted to the cation exchange sites as pH changes (Evans, 1989).

Soil pH can change over time owing to natural and human processes. Rainfall percolates through the soil leaching basic ions such as calcium and potassium from the matrix and replacing them with acidic ions such as hydrogen and aluminium. This process naturally

lowers the pH of the soil. Conversely, pH can be elevated by root growth and decay of organic matter via microorganisms. Other human activities that increases soil acidity include fertilization with ammonium-containing fertilizer and production of industrial by-products such as SO_2 and nitric acid, which ultimately enter the soil via rainfall.

Soil have several mechanisms that can buffer pH to varying extents. For instance, an investigation by Hellios-Rybicka et al. (Helios-Rybicka et al., 1994) revealed that a high carbonate content of smelter-impacted soils enhanced the soils' buffering capacity and that, because of the constant and elevated pH, the high concentrations of metals in the soils would not be rapidly leached. More so, Yong and Wandruszka (2001) found that the ability of clay soils to retain metals as pH decreases was directly dependent on the initial soil pH and on the soils' buffering capacities. pH effects in metal solubility were also described in an investigation conducted by Xiong and Lu (Xiong and Lu, 1993). They reported that the solubility of Zn in soil decreased 100-fold for each unit increase in pH.

In sequential extraction studies, a decrease in soil pH generally results in increases in the water-soluble or exchangeable metal forms. In general, heavy metal cations are most mobile under acidic conditions and increasing the pH by liming usually reduces their bioavailability. Higher pH also enhances the electrostatic attraction between soil surfaces and cations.

Urban soils and contaminated land legislation

Legislative and regulatory framework are elemental tools/instrument used for proper management and remediation of contaminated land that in its current state is causing or has the potential to significantly cause harm. Most countries of the world have national legislation (or in some cases regional legislation) to deal with local soil contamination. However, in this study, the Nigerian and UK guideline values for soil contamination are discussed.

In Nigeria, legislation on contaminated land are enshrined under environmental policy, standards, regulation and administration and adopted to control activities with potential damaging effects on the country's environment. These laws are formulated to deal with numerous environmental issues such as harmful chemicals and control activities like mining, smelting automobile wastes etc. and subsequently provide general guidelines for protecting basic natural resources such as soil, water and air (Eneh, 2010; Anukam, 2011). The environmental policy and management falls under the responsibility of different governmental departments and agencies at federal, state and local levels. However, only

two agencies (Department of Petroleum Resources [DPR] and National Oil Spill Detection and Response Agency [NOSDRA]). The responsibilities of these agencies are clearly defined. The DPR is responsible for managing legacy sites (i.e. spill sites that existed over time and no polluter has taken responsibility) and NOSDRA is saddled with the responsibility to detect and manage emergency of oil spill (Oyefusi, 2007; Rim-rukeh, 2015). These regulatory process although in use, their functionality is still lax or weak due to fragmented responsibility across government (e.g. federal, state and local) and between agencies (e.g. DPR and NOSDRA).

In the UK, legislation on contaminated land was stimulated by the need to redevelop land previously impacted by activities such as mining, smelting, landfilling and a variety of industrial activities significant to cause risk or harm to human health from long-term exposure to chemicals in soils (DEFRA, 2012). In the UK, land can be perceived as contaminated when there is a risk of significant harm to humans, ecosystems and other associated media based on the existence of a pathway by which pollutants may influence these receptors. The source-pathway-receptor is a critical component for determining a potential pollutant linkage that indicates the potential presence of possible risk (EA, 2004). The identification of a pollutant linkage is normally supported by soil guideline values (SGVs) and serve as screening tools to determine whether or not a site requires further assessment, based on the effects to human health. SGVs are scientifically derived contaminant thresholds designed to protect human health from exposure to long-term contamination in soil (EA, 2009b). SGVs are normally dependent on specific land use, assumptions about contaminant behaviour and the sources, pathway and receptors (Cheng and Nathanail, 2009) and derived using the Contaminated Land Exposure Assessment (CLEA) model (DEFRA and Environment Agency 2002a). This model estimates exposures to soil contaminants for those living, working and/or exposed on contaminated sites. However, if guideline values are unavailable, professional bodies (e.g. Land Quality Management) might provide generic assessment criteria (GACs) to simplify the risk assessment process and provide a benchmark for decision making (DEFRA and ES, 2004).

2.2   Rationale for metal recovery

With the numerous sources of anthropogenic activities discussed, it is not surprising that many areas near urban complexes, metalliferous mines or major road systems contain enormously high concentrations of these heavy metal elements with Pb, Cd and other PTEs prominently incorporated in the soil (Alloway, 1995; Xiangdong et al., 2004; Krishina and

Govil, 2005). As corroborated by numerous researchers, the presence in urban environments world-wide is well documented for a number of cities, such as Minneapolis, USA (Mielke et al., 1984); (Paterson et al., 1996);Wang et al., 1997; (Birke and Rauch, 2000); (Bityukova et al., 2000); Burt et al., 2003; Mesilio et al., 2003; Takeda et al., 2003; (Madrid et al., 2004); (Hooker and Nathanail, 2006); (Odewande and Abimbola, 2008). In Europe, polluted agricultural lands likely encompass several million hectares (Flathman and Lanza, 1998). For example, in Sweden alone, more than 80,000 sites are polluted due to earlier industrial activities (Dermont et al., 2008). On a global scale, in China, the degraded land associated with mining activities reached about 3.2 Mha by the end of 2004, and it is estimated that that degradation of land is increasing at an alarming rate of 46,700 ha per year (Li, 2006).

Metal contaminants from anthropogenic sources are generally perceived as hazardous due to their mobility, toxicity and persistence in the environment (Passos et al., 2010). Moreover, their concentration in the soil can be 100-1000 times greater than their background levels (Elliot et al., 1986; Siegel, 2002; Jiang et al., 2004). In such situations, this suggests that (i) the soil may be ecologically impaired and (ii) could potentially serve as an alternative source of metals. In view of this, it becomes possible to recover metals from such secondary sources to minimize ecological impact (Nagajyoti et al., 2010; Hu et al., 2014; Kesler, 2010; Gordon et al., 2006), increase resource utilization (Wright et al., 2002; Kesler, 2010), and safe virgin resource from undue exploitation (Kesler, 2010).

Ecological Impact: Soil is a complex multi-media system characterized by many different functional dynamics, such as being a sink and a source for metals, nutrients as well as being an essential component of the water filtration that make up the ecosystems service. The soil functions as a link between the air, water, rocks, and animals, and hence regulates the biogeochemistry of the system. For instance, the hydrologic cycle of the terrestrial and freshwater aquatic life is governed and sustained by the ability of the soil to percolate, filter and store up precipitation water for plant utilization, and may redistribute stored water across flow paths to recharge ground water and surface water. In this manner, sustainability of water resources is maintained (O'Geen and al., 2010).

Contaminant percolation via the soil is filtered by the soil's capacity to refrain the contaminants through multiple reactive mineral and organic components, which via forming inner and outer-sphere complexes are involved in metal retention (Evans, 1989). However, ecosystems can become altered when their ability to process pollution (waste) is

compromised due to human influences. Deleterious effects of mining, metal processing, and informal recycling on the environment are widespread. In the United States over 250,000 acid mine drainage sites, which contaminated over 20,000 km of rivers and streams, 180,000 lakes and reservoirs have been reported (Lichti and Mulcahy, 2012). Uncontrolled and poorly managed metalliferous mine spoils, both current and historic, can find their way into different ecological environments, where they a pose ecological risk to fauna and flora alike, growing in such ecosystems (Khan et al., 2008) and, consequently pose a risk to humans through the food chain (Nagajyoti et al., 2010).

Protection of Virgin Resource: Ore deposits are the primary source of the vast bulk of our material endowment including metals, industrial minerals and materials (Guilbert et al., 1986). They represent parent rocks that has been subject to diagenetic changes resulting in the concentration of elements of interest at economically viable abundances (Guilbert et al., 1986). However, in light of resource shortages caused by unprecedented demand for metals and overexploitation of the virgin ore, the need for an aggressive sustainable approach that is aimed at recovering resources from secondary sources becomes a case for consideration (Sapsford et al., 2016). It is generally believed that resource recovery from waste may present some significant benefits to both overall economics in the industry and the environment, in terms of resource extraction and avoidance of the associated environmental burdens from the extraction process if a proper application of the waste hierarchy is implemented (Psomopoulos et al., 2009). the waste hierarchy is a preferential order of waste treatment options that aims to reduce environmental impacts by prioritizing prevention, reuse, recycling and recovery over contaminated sources (Hultman and Corvellec, 2012). However, the key to the success of this concept lies on the implementation of strict environmental rules on the industries to recover, reuse and recycle the waste generated thereby reducing pressures to mine virgin ore to replace discarded metals (Kesler, 2010).

Sustainable Resource Utilization: The exponential increase in the use of base metals has been fuelled by the need to provide materials required for socio-economic development. Their global demand in the past half century ignited a huge demand in the mining of metals from the virgin ores to meet fast expanding market demands (Binnemans et al., 2013; Williams et al., 2008a). Although historically, industries processing metals and minerals were essential to economic development. Metals such as Cd, Cu, Ni, Pb and Zn still remain essential in the functioning of a modern society and are apparently becoming increasingly

indispensable worldwide as affluence and population number increase (Wouters and Bol, 2009). The importance of these metals differ, with each having distinct chemical and physical characteristics that is dependent on its nuclear and/or electronic structure. With Cd being used in certain types of electrical accumulators (solar panels with Cd-Se/Cd-Te), whilst Cu is used in infrastructures, Ni is used in the manufacture of stainless steel, Pb is integral to renewable photo-voltaic electricity and Zn is used in the galvanisation of iron and steel to prevent corrosion. Similarly, Fe and other light metals are used in the bodies and engines of cars, trains, aeroplanes and shipping for the mobility of people and goods (Berkel, 2007). All these are mostly products of primary sources.

Products of primary sources are mostly mined, and subsequently, the base ore is subject to extraction and separation processes. Conventionally these include hydrometallurgy, where aqueous chemistry is employed or pyrometallurgy, whereby the ore is extracted using thermal processes (Cox et al., 1985) in order to obtain the metal. However, both mining and refinement of the base ore produce by-products that are hazardous to the environment, for example, the production of large volumes of $SO_{2(g)}$ from pyrometallurgy, and similarly, the production of acid fumes and large volumes of effluent from hydrometallurgy (Reck and Graedel, 2012; Hageluken and Meskers, 2010). Moreover, both processes are associated with the generation large volumes of solid waste as by-products that are usually discarded as slag dumps (Williamson et al., 2004; Piatak et al., 2004). Such mine tailings themselves present an environmental concern; since even the low concentration of metals found in the slag material can potentially impair ground water via leaching (Groot and Pistorius, 2008). Life Cycle Assessment studies reveals that various gaseous emissions occasioned by pyro- and hydro-metallurgy are precursors to the environmental influences of global warming and acid rain respectively (Norgate and Rankin, 2000).

According to United Nations, it is estimated that by 2050; the world's average population will grow to 9.6 billion, with the greater part of the growth occurring in Africa and Asia, where the demand for an improved quality of life will drive the need to access goods and services. This is illustrated in the consumption per capita of copper compared from an industrialising country such as China and an industrialized country e.g. USA (MMSD, 2002). However, other researchers (Gordon et al., 2006);(Kesler, 2010) have expressed concern on the rate,3% per annum, at which many of the geologically scarce metals are extracted and their likelihood of exhaustion in the near future. With recent estimates, as depicted in

Table 1, that Zn is at a current usage rate of 12 -13.9 million tonne per year, depletion is likely by the end of the 21st Century (WBMS, 2015) whilst for Cu it is estimated that a depletion time will occur between 60 - 150 years following the current production levels (USGS, 2011), This raises the question of how long these extraction rates can be sustained.

Therefore, in order to sustain the usage of these metals in the face of predicted eminent scarcity it is necessary to explore valuable metals from secondary sources as a sustainable alternative to conventional mining and resource utilization (Sapsford et al., 2016; Sadhukhan et al., 2016b).

Table 2 1 Remaining lifetime after 2050 for exploitation of metals until depletion (USGS, 2012

Metal	A 1000 Ton	B 1000 Ton	C 1000 Ton	D 10^6 Ton	E 10^6 Ton	F
Cd	21.1	69	1700	39	37	540
Cu	15,900	51,866	1,300,000	1,000	6,200	120
Ni	1590	5187	130,000	1800	1700	320
Pb	4140	13,505	330,000	680	3400	250
Zn	12,000	39,144	940,000	2,800	1,900	47

A: Extraction in 2010; B: Yearly extraction in 2050. Yearly growth 3%, C: Approximate total extraction between 2010 and 2050; D: Extractable global resources according to UNEP; E: remaining available resources in 2050; F: remaining years after 2050 until depletion

2.3 Secondary Sources of Metals

A paradigm shift in the last decades has progressively culminated in the recovery of metals from secondary sources. The scale of recovery of such metals has been phenomenal (Sadhukhan et al., 2016). There are potentially numerous sources of metals from waste materials, e.g. E-wastes, construction and demolition wastes, steelmaking dust, wastewater (effluents), municipal waste and metalliferous soil (Sadhukhan et al., 2016). For the scope of this study, sources of metal from wastes will be limited to metalliferous soils, because of its status as a major biogeochemical sink for contaminants (Cheng et al., 2011). Some of the sources and their scale of recovery are briefly discussed.

Spent batteries: The last decades have seen a tremendous growth in the use of portable devices such as cellular phones, batteries, remote controls, calculators, laptop computers, and video cameras, arising from technological advances and societal affluence. Metals are used as electrodes in batteries and their composition varies depending on the use of the metals. For example, for a typical 1.5 V single use portable battery, the composition of zinc

in an alkaline manganese battery is 16%, in a carbon battery it is 11%, in a silver oxide battery it is 9% and for a zinc-air battery it is 35% (EPBA, 2007). The waste generation resulting from their short life span of about 1.5 to 2 years has been significant (Belardi et al., 2012). It is estimated that in 2013 alone, nearly 211,000 tonnes of portable batteries entered the European Union's consumer market, out of which, only 38% (80,000 tonnes) of the battery waste generated were collected (Sadhukhan et al., 2016). In the treatment of spent batteries to recovery of valuable metals, several methods have been proposed. However, the existing approach typically involves physical processes, for example, magnetization to separate magnetic metals from non-magnetic metal components, followed by either pyrometallurgy (Paulino et al., 2008), hydrometallurgy (Rao, 2006), or biometallurgy, using micro-organisms to extract specific metals (Mishra et al., 2008). Depending on the separation technique applied, the recovery rate from these processes is usually greater than 50% for the metals Fe, Ni, Co, Cu, and Zn, and in the case of Pb recoveries of 80% are possible(Reck and Graedel, 2012). Variations in recycling rates are mostly attributed to differences in the actual recycling protocol applied. However, the relatively efficiency in the recovery of the target metals has to be counterbalanced with the environmental costs of using hydrometallurgical and pyrometallurgical processes.

E-Waste: An exponential increase in population, urbanization, and changes in lifestyle behaviour, has in the rapid consumption and generation of substantial amounts of waste electrical and electronic equipment (WEEE) or E-waste. On a global scale, China produces 64% of the world's generated e-waste, with India and Brazil producing 13% and 11% of the World's E-waste, respectively (Schluep, 2009). E-waste is heterogeneous in nature, and contains considerable amounts of precious metals, such as Au, Ag and other base metals (Cu, Ni, and Zn). The metallic component of the E-waste varies from < 100g up to >80kg (Huisman et al., 2008). For example, laptop mother-boards (printed panel) may contain approximately 40% of value of base metals and precious metals (Khaliq et al., 2014). This makes recovery from such E-waste economically appealing. In addition to economic incentives, environmental benefits include the reduction in the waste being landfilled, high-energy savings, as well as minimization of gaseous emissions and toxic compounds generated. Formal recovery of valuable metals from E-waste can be achieved via pyrometallurgy, hydrometallurgy, or biometallurgy, similar to those utilized for recovering metals from spent batteries as previously mentioned. However, formal e-waste recycling has not fully realized its potential in countries such as China and India, although crude,

informal practises of recovery are in place. However, substantial amounts of valuable metals of recoverable potential end up being lost to the surrounding environs (Chi et al., 2011).

Wastewater: Potential toxic elements in wastewater generation is commonly associated with partially treated or untreated discharge from industries such as mining operations, pulp and paper industry, fertilizer and pesticides manufacturing and metal plating. The resultant wastewater may contain significant amounts of PTEs including Cd, Cu, Ni, Pb, and Zn However; the specific type of metal contamination found in the wastewater will be dependent on the operation that occurred at a particular site. The scale and impact of this source of contamination is increasingly common in developing countries where either (i) environmental law do not exist or (ii) enforcement is lax. Recently in Harare Zimbabwe, a study was carried out on wastewater used for irrigation at Pension, Crowborough and Mukuvisi vegetable production sites. The study has shown that the metals were found to be between 3 and 13 fold greater than the maximum allowable limit set in Zimbabwe (Manpanda et al., 2005). The removal of heavy metals from wastewater can be achieved via conventional physicochemical methods such ion-exchange (Alyuz and Veli, 2009), chemical precipitation (Ku and Jung, 2001), reverse osmosis (Shahalam et al., 2002), coagulation and flocculation (Samrani et al., 2008), electrochemistry and solvent extraction (Kurniawan et al., 2006; Gupta et al., 2008). Given the economic value of metals such as Cu and Zn, and in the case of Cd and Pb, the toxicity status, recovery of such metals is considered a priority.

Metalliferous soil: Metalliferous soils, defined for the purpose of this study as soils that are enriched in metals due to inputs from anthropogenic activities, are acknowledged as a major biogeochemical sink and conversely, a source of PTEs (Li et al., 2013). A review undertaken by Chao et al. (Chao et al., 2014), highlighted the existence of elevated loadings of PTEs in soils. The study reveals that the average content in urban soils for Cd, Cu, Ni, Pb and Zn are 1.52, 49.60, 29.14, 1733.94 and 289.78 mg kg^{-1}, respectively. In agricultural soils, concentrations of these five metals are typically found to be lower than those in urban soils (Cd: 0.28; Cu: 38.03; Ni: 26.12; Pb: 51.19 and Zn: 117.35 mg kg^{-1}). In both soils the concentration of Cu, Pb and Zn are observed to be enriched compared to the World median values (30; 35 and 90 mg kg^{-1}, respectively) reported by Bowen (Bowen, 1979).

Within the soil matrix PTEs find specific adsorption sites where they are retained very strongly, either on organic or inorganic colloids by natural attenuation (Sauve et al., 2000).

The introduction of PTEs can be via a number of routes. For example, dry deposition of metals was a key mechanism in the contamination of Pb and Zn in agricultural soils near the non-ferrous smelter site at Copşa Mica, Romania. Hydrological processes of heavy metals have played and continue to play a major role in the contamination of floodplain soils, as reported for the Ouse basin, U.K. (Hudson-Edward et al., 1999). A more recent development in contamination, in particular, in agricultural soils is through the increased use of wastewater and by-products from domestic sewage treatment as a soil conditioner. Although offering an alternative and potentially more cost effective, source of crop nutrients than inorganic chemical fertilizers (Candela et al., 2007; Angelakis et al., 1999), the extensive and sustained application of such waste sludges/water has the potential to result in the accumulation of PTEs in soils at concentrations that are dangerous to human health and pose long-term environmental damage and health risks (Manpanda et al., 2005; Chang et al., 1992). Globally, it is estimated that 20 million hectares of arable land are irrigated with wastewater (Ensink et al.2004; Cockram, 2002).

The need to maintain and secure land globally that is suitable for agricultural production means that a number of techniques have been developed with the aim to remove PTEs from contaminated soil or minimize the leaching potential of the soil/residue. These techniques include solidification/stabilization; in-situ biochemical stabilization (soil amendments with inorganic and organic compounds) and soil washing technologies, including physical separation methods (such as flotation) and chemical extraction processes (such as acid and chalet extraction). In situ soil flushing; and bioleaching, electrokinetic remediation, and phytoremediation are other techniques of interest (Lestan et al., 2008). These techniques are discussed in Section 2.5.

2.4   Soil Remediation Techniques`

The sole aim of remediating any contaminated soil will be to create a final solution that is protective of human health and the environment (Martin and Ruby, 2004). This approach is usually in line with the regulatory requirements of an individual country where such regulations exist, or can also be based on evaluation of human health and ecological risk where the regulation is non-existent. In the recent past, many remediation technologies have been developed to treat contaminated soil with the purpose of minimizing the risk of pollution (Hursthouse, 2001; Scullion, 2006). However, the clean-up of soils contaminated with PTEs is one of the most difficult tasks facing environmental engineering (Gombert, 1994) today.

A number of techniques have been developed with the aim to remove PTEs from contaminated soil or minimize the leaching potential of the soil or residue and are discussed below:

Solidification/stabilization (S/S): The approach involves a number of techniques that use physical and chemical means to reduce the mobility of contaminants in the environment and involves the addition of inorganic or organic amendments such as coal fly ash, iron and manganese oxides, phosphates, aluminosilicates, clays (bentonite and kaolinite) and zeolites (Fawzy, 2008) to encapsulate contaminants within their host medium. Thus, the contaminants become immobile and less available for plants and hence their bio-concentration through the food chain is reduced (Guo et al., 2006). However, they are not destroyed. Many of the amendments used in soil stabilization are by-products of industrial activities, and are therefore inexpensive and readily available in large amounts (Soltan et al., 2012). This group of remediation techniques also includes the process of in-situ vitrification (ISV), whereby most organic and inorganic contaminants are destroyed or immobilized through the application of an electric current to the soil. Due to its low electrical conductivity, the soil begins to heat up to temperatures between 1450 - 2000°C; as a result, a melt is produced that hardens into a block of glass-like material that is chemically stable and leach resistant. Since a large amount of electricity is necessary, the technique is costly but applicable to soils with mixed organic and metallic contamination, for which few technologies are available (Buelt and Farnsworth, 1991)**.** S/S techniques do have limitations. In particular, the chemical composition of the contaminated matrix, the amount of water present, and the ambient temperature and the matrix of the binder may compromise the immobilization and therefore, the efficiency of this technique (Goodarzi and Mvahedrad, 2017). Furthermore, the process is likely to restrict the future use of the soil for agricultural production.

Electrokinetic Extraction or Remediation: The technique involves the electrokinetic movement of charged particles suspended in a soil solution, initiated by an electric gradient. The target metals can be separated by precipitation at the electrodes (Hicks and Tondorf, 1994). The significance of this technique is its low operation cost and potential applicability to a wide range of contaminant types (Pamukcu and Wittle, 1994). Low contaminant removal efficiencies have been reported for Electrokinetic Extraction (Reddy et al., 2001). Soil type, the speciation of the contaminants and the reduced species, such

as sulphides being found, strongly influence the removal efficiencies further(Reddy and Chinthamreddy, 1999)

Bioleaching: The process of bioleaching involves the use of microorganisms for example *Acidithiobacillus* species, to transform the metals of interest from solid phase into soluble and extractable form (Mulligan et al., 2001). This technique is considered technologically and economically feasible to reduce PTEs from a waste stream (Anand et al., 2006). Moreover, the technique is perceived as a much more environmentally benign (green) approach, involving much lower temperatures (and hence energy costs) and smaller carbon footprints (Hsu and Harrison, 1995). During a bio-leaching process, elemental or reduced sulphur compounds are oxidized to sulfuric acid by a variety of *acidithiobacillus* species to obtain energy via the oxidation process, leading to metal solubilisation by acidification (Babel and Dacera, 2006; Pathak et al., 2009). Some of the dominant mesophilic species applied in bioleaching process are known as the chemolithrophic bacteria such as *acidithiobacillus* thioxidans and ferrooxidans (Chen and Lin, 2004). However, the practical application of bioleaching is still limited due to the substantial time required to obtain economic levels of metal extraction, as well as the robustness and reliabilities of the biological systems involved, most especially for mineralized ores (Watling, 2006).

*Phytoremediation***:** This technique is also known as agro-remediation or green remediation, and uses plants to detoxify, restore or purify the soil, water, and/or sediments. It has the advantage that it can be applied in-situ without moving or excavating large amounts of contaminated soil and leaves the top soil in an undisturbed and usable condition. This technique is applicable to a broad range of organic pollutants and heavy metals (Chen et al., 2004; Zhang et al., 2010). There are numerous of plant species including *Brassica.*sp, *Helianthus*.sp and *Sorghastrum* sp that have been identified as accumulators of metal contaminants. Of particular note is the group of plants know as hyper-accumulators, which have the ability to grow in metalliferous soils as well as possessing a natural tendency to extract unusually high amounts of metals from such soils and efficiently translocate them to shoots. Such ability has given rise in the last 20 years to the concept of using these plants to decontaminate metal polluted soils (Brooks, 1998; Rascio and Navari-Izzo, 2011). Phytoremediation is still mostly in its testing phases and as such not been used in many places as a full-scale application. However, there are several factors to take into account in terms of its efficiency, for example, it may take several years or longer to clean up and /or recover a soil (USEPA, 2000). Furthermore, slow desorption of heavy metals in the soils can

potentially impair on the remediation efficiency (Ebbs et al., 1997) of the process. In addition, some plant species may have low-biomass and are unable to accumulate a combination of metals combined (Kramer, 2005; McGrath and Zhao, 2001; Clemens et al., 2002). For instance, Pb, one of the major soil contaminants, is unfortunately not available in soil for plant uptake (Lestan et al., 2008). Such traits disqualify the certain plant species from commercial phytoremediation of metal polluted soils, especially at multi-metal contaminated sites.

Soil Washing: This is an ex-situ treatment method for separating contaminants from contaminated media via chemical, physical, or physicochemical procedures (Dermont et al., 2008). Physical separation of soil washing differ fundamentally from chemical separation. The physical treatment concentrates metal contaminants into smaller volume of soil by taking into account the differences in certain physical characteristics between the metal bound particles and soil particles (hydrophobic surface properties, size, density and magnetism). Mechanical screening, hydrodynamic classification, gravity concentration, froth flotation, magnetic separation, and attrition are characteristic operational units of physical separation technology. Although the physical separation processes are effective, relatively simple and often inexpensive (Wills and Napier-Munn, 1992), their application is limited and only commercialized for sandy soils in which the clay, silt and organic matter content (particles less than <63 μm) is less than 30-35% of the soil (Pearl et al., 2006). Chemical extraction, on the other hand, tries to desorb and solubilize the metal contaminants from soil with an extracting aqueous fluid containing chemical reagents such as acids or chelating agents (Labanowski et al., 2008; Voglar and Lestan, 2013). The application of chemical extraction is not constrained by soil texture. It is one of the few treatments available for the permanent removal of metals from soils, especially highly contaminated soils (Dermont et al., 2008). The selection of chemical extractant or leaching agent depends on number of factors, for example, the properties of the contaminants at each specific site and on the remediation goal, i.e. the acceptable levels of the pollutants in the soil after remediation (Dermont et al., 2008). Acid and chelating extractions are the two main processes involved in the recovery of metals from contaminated soil. Extraction with acids changes the physicochemical properties of soils, thereby leading to irreversible damage to the soil matrix. By contrast, chelating agents largely preserve soil properties (Pichtel and Pichtel, 1997; Peters, 1999). The advantages of using chelating agents in soil washing are high efficiency of metal extraction, high thermodynamic stabilities of metal

complexes formed, and good solubility of metal complexes, and normally low adsorption of the chelating agents and their metal complexation compound on soils (Fischer et al. 1998).

However, a limitation of chemical washing, especially in the case of large contaminated sites, is the prohibitive cost because of the use of the large quantities of reagents and the need to treat considerable quantities of wastewater produced. Nevertheless, this is made economically efficient with the application of recovery and recycling techniques in chelating agents-enhanced soil washing. The chemical agents are recycled and reused at least several times using simple and cost-effective treatments (Peters, 1999).

Among the various applied techniques for removal and recovery of metal laden contaminated soils, chelate-enhanced soil washing offers an important opportunity for potential recovery of the released metals. The leachate generated from the enhanced soil washing is rich in pollutants and can act as a source for metal recovery (Karin et al., 2013). This concept is not much studied and the washing procedures conventionally applied focused extensively on metal contaminated soil assessment and remediation, while it's economic and recovery potentials has not been fully optimized or addressed (Peters, 1999; Lestan et al., 2008; Hasegawa et al., 2010). Therefore, for the purposes of this proposed study the soil-washing technique is applied with the aim of achieving concomitantly both soil remediation and metal recovery. The chelating agents ethylenediaminetetraacetic acid (EDTA) and ethylenediaminedisuccinic acid (EDDS), the organic solvent, acetylacetone (Hacac) and the two low molecular weight organic acids (LMWOA) citric acid (CA) and tartaric acid (TA) were selected for metal solubilisation/mobilization from the soil on the basis of cost, environmental sustainability, potential leaching efficiency, and capacity to be used in a different phase or modified for selective recovery. The extractants are discussed in further detail below.

Aminopolycarboxylic acids (EDTA and EDDS): The ability of aminopolycarboxylates such as EDTA and EDDS to form stable metal complexes for the treatment of soil laden with heavy metals has been widely researched in analytical chemistry and industrial application (Peters, 1999; Lestan et al., 2008; Sun et al., 2001b; Nowack, 2002). Due to their chelating ability, they have industrial applications, in particular in the paper and pulp industry, as well as the nuclear industry (Knepper, 2003; Wuorimaa et al., 2006). In comparison with other chelating agents, EDTA which forms stable and water-soluble complexes with metals, presents certain advantages, mainly the treatment of a broad range of soil types and in

addition, a high level of complexing capacity with respect to heavy metals (Sun et al., 2001). Conversely, EDTA is less efficient in extracting metals bound to the reducible/Fe-Mn oxide fraction (Abumaizer, 1999; Wasay et al., 2001; Papassiopi et al., 1999) and practically unavailable for metals occluded to the residual fraction of the soil **(**Dermont et al., 2008**).** A study undertaken by Peters and Shem (1992) to compare the potential extractive capabilities of EDTA with those of nitrilotriacetic acid (NTA) and water for Pb in soils, showed that the overall removal percent of Pb were 68.7%, 19.1%, and 7.3% when using, EDTA, NTA, and water, respectively. However, several studies in recent times have shown the suitability of EDDS as a substitute for EDTA for many industrial applications, such as laundry detergents, cosmetics, pulp and paper and photographic industries as well as in the purification of contaminated soils and phytoremediation (Kolodyńska, 2013). Moreover, EDDS has been found to be superior to EDTA around neutral pH in extracting metals from soils during soil washing, because the competition with major cations like calcium is much less important (Tandy et al., 2004). However, the dissociation and subsequent re-adsorption of the newly formed metal-chelant due to metal exchange with sorbed metals and soil minerals could compromise the metal recovery efficiency of EDDS (Tsang et al., 2009).

EDTA and its metal complexes are biologically inert (Hong et al., 1999) and as such exhibit refractory behaviour towards biodegradation in the environment. In addition, their mobility in the subsurface environment and possible contamination of groundwater via leaching has become a cause for concern (Nowack, 2002; Sun et al., 2001). After soil washing, some of the metal-EDTA complexes are retained in the soil by the formation of bonds with soil iron oxides, especially the hydroxide goethite(Nowack and Sigg, 1996) and may increase eutrophication through release of phosphates (Kolodyńska, 2013). With the environmental defects posed by the use of EDTA and with stiffer regulatory mandate on the use of environmentally friendly chemical agents (OSPAR, 2000), it has become desirable to replace EDTA by a more environmentally friendly chelating agent that would not only be biodegradable, but at the same time has a high metal binding capacity (Kolodyńska, 2013).

The emergence of S,S-ethylenediaminedissunic acid (referred to as EDDS hereafter), a structural isomer of EDTA (Schowanek et al., 1997; Kolodyńska, 2011), has recently received much attention as a potential replacement for EDTA (Jaworska et al., 1999). EDDS has two chiral carbons and of the three stereoisomers (S,R- (50 %), R,R- (25 %) and S,S- (25 %)), only one (S,S) is readily biodegradable according to the OECD guidelines (Takashashi

et al., 1997; Schowanek et al., 1997); the others (S,R and R,R) biodegrade to more persistent metabolites (Boethling et al., 2007). It was commercialized by Innospec Inc., UK as Enviomet[TM]. Their biodegradability largely depends on the isomeric form of the compound: the S,S-isomer of EDDS is synthesised by some bacteria and fungi and is rapidly and completely biodegradable (Nishikiori et al., 1984), the S,R-isomers degrade partially, whilst the R,R-isomer is resistant to biodegradation (Luo et al., 2011). Although the metal complexes with S,S-EDDS are somewhat lower in stability than the corresponding complexes with EDTA, the stabilities of M-S,S-EDDS complexes are powerful enough for most conventional applications (Orama et al., 2002).

Acetylacetone (Hacac): An important class of chelating acidic ligands, are the β-diketones, which have been widely used in analytical separation of metal ions (Ozel et al., 1997; Bereket et al., 1997)(Ozel et al., 1997; Bereket et al., 1997)(Ozel et al., 1997; Bereket et al., 1997)(Ozel et al., 1997; Bereket et al., 1997). The simplest β-diketones is Hacac, were the substituents on both carbonyl groups are the methyl group. All other β-diketones can be considered as derived from Hacac (Lis et al., 2011). Acetylacetone is known as excellent extractant for metals and it forms chelate complexes of different structures with metals (Ando et al., 2009). Most of them exhibit low solubility in the aqueous phase, but dissolve readily in organic solvents (Otway and Rees, 2000). Hacac tends to exhibit distinct chemical properties, which is mostly due to its keto-enol tautomerism. Primarily, under appropriate conditions, the enolic hydrogen atom of the β-diketone ligand as shown in Figure 2.2 can be replaced by a metal ion to produce a chelate ring, thereby shifting the keto-enol equilibrium in favour of the enol form, and ultimately resulting in the synthesis of metal acetylacetonates as described in Equations 1.7 and 1.8.

However, because of the presence of the two carbonyl groups, the proton on the α-carbon is quite acidic, and as such show high selectivity towards Cu and/or Ni ions by changing their hydrogen-bonding ability.
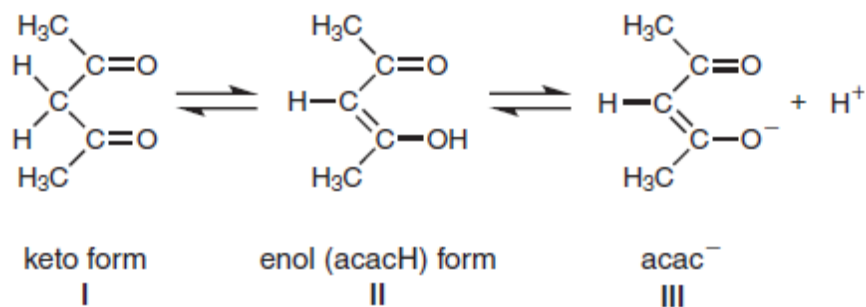
Figure 2.2 Structures of β-diketone with the molecules in keto-enol equilibrium in acetylacetone

$$Hacac \rightarrow acac^- + H^+ \qquad \text{Eq. 1.7}$$

$$2acac^- + M^{2+} \rightarrow M(acac)_2 \qquad \text{Eq. 1.8}$$
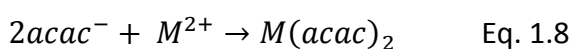
Organic Acids (LMWOA – CA and TA): The low molecular weight organic acids CA and TA are natural products of roots, microbial metabolites, plant and animal residue, and the decomposition of soil organic matter located in the upper soil horizons (Naidu and Harter, 1998; Jones, 1998; Strobel, 2001).

Recently, there has been an increase in the attention of the role that natural organic acid can play in the solubilisation and mobilization of heavy metals in the soil (Coles and Yong, 2006; Eick et al., 1999; Wang and Mulligan, 2009a) due to the potential reactivity, mobility, and toxicity of synthetic chelators such as EDTA. By comparison with most synthetic chelators, LMWOA are completely biodegradable (Di Palma and Mecozzi, 2007), present the lowest eco-footprint characteristics, are more cost effective and cause the least disruption in the remediation of contaminated soils (Kantar and Honeyman, 2006; Wen et al., 2009; Liu et al., 2008). As such, LMWOA are considered more promising with the potentials to dislodge the exchangeable, carbonate and reducible fractions of heavy metals by washing (Peters, 1999). Several investigations have demonstrated the successful use of CA and TA (Peters, 1999; Evangelou et al. 2007; Naidu and Harter, 1998; Ke et al., 2006) for soil washing. However, most of the studies have reported lower effectiveness of LMWOA compared to the conventional extractants such EDTA in mobilizing metals such as Cu, Zn, Ni (Kos and Lestan, 2004; Lombi et al., 2001). The low effectiveness of LMWOA has been potentially attributed to their fast degradation and mineralization influenced by soil microorganisms (Krishnamurti et al., 1997; Cieslinski et al., 1998; Meers et al., 2004; Romkens et al., 2002).

The metal ligand complex (also referred to as wastewater or effluent hereafter) leached from the solid phase using remedial techniques (discussed in section 2.5) can undergo further treatment for the potential separation and recovery of the metal ions from their wastewater using some of the existing applications in the industry. However, some of these conventional applications are saddled with some limitations such as operational cost, sensitive operating conditions and less output efficiency that impact on their usage. This is discussed in section 2.6

2.5   Industrial Removal and Recovery Processes

The diminishing supplies of ores as earlier mention in the introductory section of this study has increased interest in the development of hydrometallurgical alternatives for the concentration and separation of metals of interest. Although, various leaching processes are used, solvent extraction (SX) is one of the most commonly applied techniques for the separation of metal ions (Binnemans et al., 2013; Tasker et al., 2012). SX has been commercially operated in the extractive metallurgy as a unit process in the last century or more (Douglas, 1992). It involves a procedure for processing material by using a solvent to separate a variety of components within a material sample, due to its versatile applicability in metal separation, purification and analysis. In this process, the aqueous phase, containing a metal solute, reacts with a water-immiscible organic phase (often consisting of a volatile and flammable solvent such as toluene, kerosene) containing an extracting agent (Rydberg et al., 2004; Rao, 2006; Kislik, 2011), to form a hydrophobic complex, which may be further treated to recover pure metals using processes such as chemical precipitation,   ion-exchange,   electrolysis,   membrane   processes   and flocculation/coagulation (Kolodyńska, 2013; Rudnicki et al., 2014; Keranen et al., 2015; Beltran H and Sanchez, 2009). This is schematically described by the sequence of operation shown in Figure 2.3 (Habashi, 2005). adaptability of SX to a wide range of potential extractants has made it a preferred technique for the separation of most metals. For instance, reagents such as β-diketones are usually employed for copper extraction and have undergone constant improvement to suit different leaching solutions (Koppiker, 2002; Kordosky, 1992). However, reagent costs and other characteristics such as use of volatile, combustible, and toxic solvents carried into effluent streams sometimes impose stringent limitations on the use of the technique commercially (Anastas and Eghbali 2010**)**
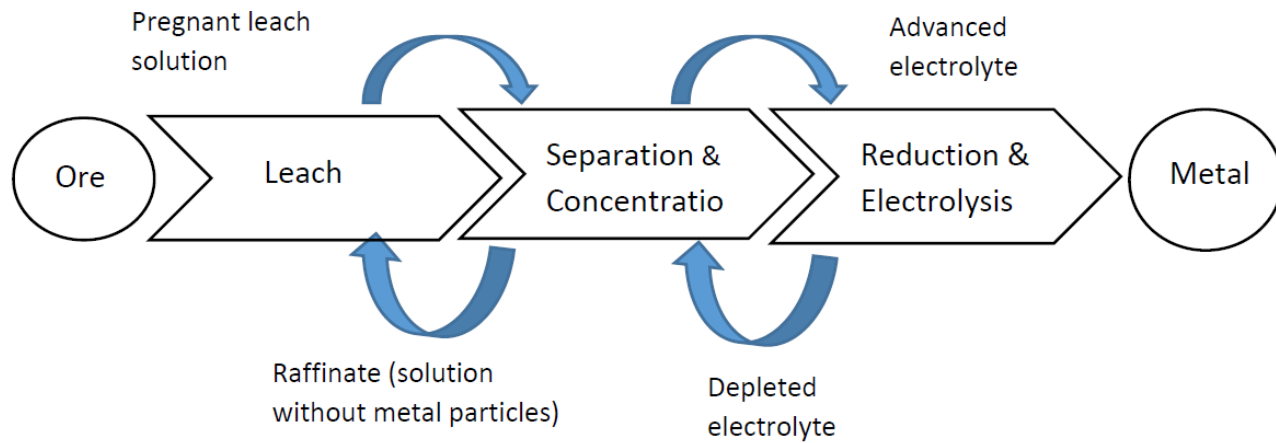
Figure 2 3 Major steps in a hydrometallurgical process flow sheet operated in a closed loop with leaching and electrolysis to produce metal while recycling the reagents in the system (redrawn based on Kordosky, 1992).

2.5.1 Recycling of process water – EDTA as a case study

In a bid to comply with the regulated guidelines for effluent discharge under the Environmental Protection Act (EPA, 1981), the need for recycling of process water is critical. In view of the foregoing, EDTA conventionally used as extractant for soil washing has been chosen as a case study, given its potential reactivity, non-degradability, high mobility, and related toxicity. Besides, EDTA is placed on the EU priority list of substances for risk assessment (Conrad, 2000). However, considering the extractive potency of EDTA for cationic heavy metals, it becomes crucial to evaluate different strategies aimed at recovering metals from leaching solutions and subsequently recycling EDTA. To this end a number of studies (Zeng et al., 2005; Juang and Wang, 2000; Finzgar and Lestan, 2006) have investigated the regeneration (or degradation) of EDTA leachate in order avoid the release of EDTA into the environment. These studies are briefly discussed below

Zeng et al. (2005) proposed the separation of metals (Cd, Cu and Pb) from EDTA complex using Na_2S and Ca $(OH)_2$ under alkaline conditions. This resulted in the significant recovery of metals through precipitation in the form of insoluble metal sulphides. However, this method has found limited application due to the hazardous nature of the produced reagents and the sludge.

In the case of Di Palma et al. (2003), reverse osmosis and chemical precipitation were used as techniques for the treatment of solutions extracted from the artificial soil laden with metals, using 0.05 molar concentration of EDTA in the following sequence: soil flushing, membrane treatment, acidification and metal precipitation. The findings showed

significant variations in the percentage of metals recovered from and remaining in the treated soil as 98.2% and 37.96 mgkg^{-1} for Pb and 95.4% and 59.20 mgkg^{-1} for Cu respectively, with 75% reduction in the water content. Although, the protocol was not influenced by harmful by-products, the cost of the membrane and the potential fouling of the membrane may pose a significant limitation for further development and application of this approach.

Juang and Wang (Juang and Wang, 2000), employed an electrochemical process that used a two-chamber electrolytic cell separated with a cation exchange membrane to prevent EDTA anodic oxidation, as well as to separate the target metals and EDTA. The efficiency of this study was later validated by the integration of advanced oxidative process (AOP) proposed by Finzgar and Lestan (Finzgar and Lestan, 2006). The effectiveness of this process depended on the chemical destruction of the chelant as a viable option, because EDTA is considered a relatively inexpensive chemical (approximately €1.5 kg^{-1}). An AOP combination of ozone and UV light was used to generate hydroxyl radicals for the oxidative decomposition of EDTA-metal complexes. The metals released were afterwards removed from the washing solution by absorption (such as with clay, zeolite, activated carbon). However, the potential limitation of this process is the fact that the washing solution contains colour and particles that absorb and scatter UV light (Shu and Chang, 2005). Typically, soil washings contain an intensive yellow brown colour due to the formation of Fe-EDTA complexes. It is likely that this will limit the application of AOP to only fairly colourless and non-turbid solutions resulting from the washing process. (Finzgar and Lestan, 2006a). Besides, the released metals may consumed a significant quantity of absorbent. In addition, caution is to exercise in the handling of ozone, as the gas is poisonous and poorly water-soluble. However, the palpable limitations envisaged in AOP (H_2O_2-UV) can be overcome with the development of a boron-doped diamond anode (BDDA) (Troster et al., 2002). The BDDA is efficient, more robust, technically simple and more cost effective than most AOPs (Kraft et al., 2003). The unique feature which AOP-BDDA has over AOP-(H_2O_2-UV) is in the production of hydroxyl radicals at the anode directly from the electrolyzed water (Kraft et al., 2003; Oliveira et al., 2007)

2.6 Kinetics

Fate and transport of contaminants in the soils are potentially influenced by three main processes, such as the removal of metals from the soil solution by sorption onto soil matrix, the reverse process where mobilized metals from the soil matrix migrate to the soil solution

phase and thirdly, the process that involves the precipitation-dissolution of the metals as an independent phase in the soil matrix (Sparks, 2003; Elkhatib et al., 2007). Conventionally, the first process has been widely documented (Elkhatib et al., 2007) with little interest devoted to the other two processes. However, the recent depletion in the primary ores around the globe, has stimulated research interest in the desorption of targeted metals of interest from secondary sources such as contaminated soil to complement critical supply. Desorption is an important process that controls the amount and rate of release of metals of interest into solution for recovery. Hence, studies on the kinetics of metal release from soil and/or soil constituents are of importance in evaluating the mobility/lability of soil metals for leaching and recovery purposes. Studies by Garcia-Rodeja and Gil-Sotres (Garcia-Rodeja and Gil-Sotres, 1997) showed that the release of metals are strongly influenced by the amount and type of soil constituents such as metallic (iron and aluminium) oxides, carbonates, clay content and organic content. For instance, soluble Cu in surface soil preferentially and organically form complexes with organic matter more strongly than any other micronutrients (Havlin et al., 1999). In addition, metal solubility or dissociation kinetics of a contaminated soil can be significantly altered because of the presence of organic materials in the soil (Del Casthilo et al. 1993). Bermond and Ghestan (Bermond and Ghestem, 2001) conducted a kinetic study on the feasibility of metal fractionation in a soil using EDTA as the complexing ligand. It was observed from their findings that lability of the metals were differentiated into two phases, the first being rapidly released and second being slowly released under same equilibrium conditions. For the purpose of this study, the essence of the kinetic study was to study the influence of the different soil constituents for metal leaching (recovery) behaviour of the simulated soil as well as the environmental soils for the basis of comparison, and to determine the suitability of different models for the description of the kinetics of the targeted metals under investigation.

2.7   Economic and environmental consideration

The economic recovery of base metals from non-conventional resource (low grade) via sustainable hydrometallurgical technologies (leaching, precipitation, electrochemistry and liquid-liquid extraction) is a vital component that could have viable potential economically. Although the recovery of resources from waste repositories is not a new concept in the circular economy, this concept has not been widely harnessed, especially beyond the limited extraction of landfill gas for energy separation (Sapsford et al., 2016). It is arguable

that waste usually contain sub-economic concentrations of valuable resources, which varies with time and in turn is influenced by the economics of ore processing (Sapsford et al., 2016). Besides, the economic potential of any waste stream depends on the value of the metals recovered, which in turn is a function of associated metal market prices (Yang et al., 2008). Therefore, there is need to assess the cost-benefit analysis of a given waste stream such as contaminated soil to ascertain the lowest capacity in which the proposed plant process will be economically feasible for recovery of metals out of a secondary source. For this purpose, the economic study of potentially recoverable metals from different environmental soils sourced from Romania and Nigeria using soil-washing techniques that is evaluated for both resource efficiency and environmental sustainability using laboratory-scale generated data will be explored.

2.8   Conclusion

Generally, this chapter enabled the background understanding of some of the recent research that has been carried out in recent times, as well as findings reported in similar circumstances. Most of the studies reported here were conventionally focussed extensively on metal contaminated media (e.g. soil, e-waste etc.) assessment and remediation performed under different environmental and operational conditions. However, the concept of contaminated land beneficiation via leachate generated from the enhanced soil washing and its recovery and economic potentials has not been given attention. It is on this premise that the investigation of some contaminated soils around the globe are evaluated for metal recovery purpose as well as quantify their economic prospect.

It is believed that this section will be used as a resource to justify, compare, contrast and inform the authors' discussion on observation made in the subsequent chapters of the present study.

Chapter 3

Materials and Methods

3.1   Methodology and analytical protocols

This section reports the investigation carried out with the aim of determining the influence of that individual components might have on the leaching efficiencies of the single and multi-metal components to enable predict a real soil scenario. An outline of the methodology followed during this investigation is illustrated in the schematic diagram below, figure 3.1. Detailed procedures will be discussed hereafter
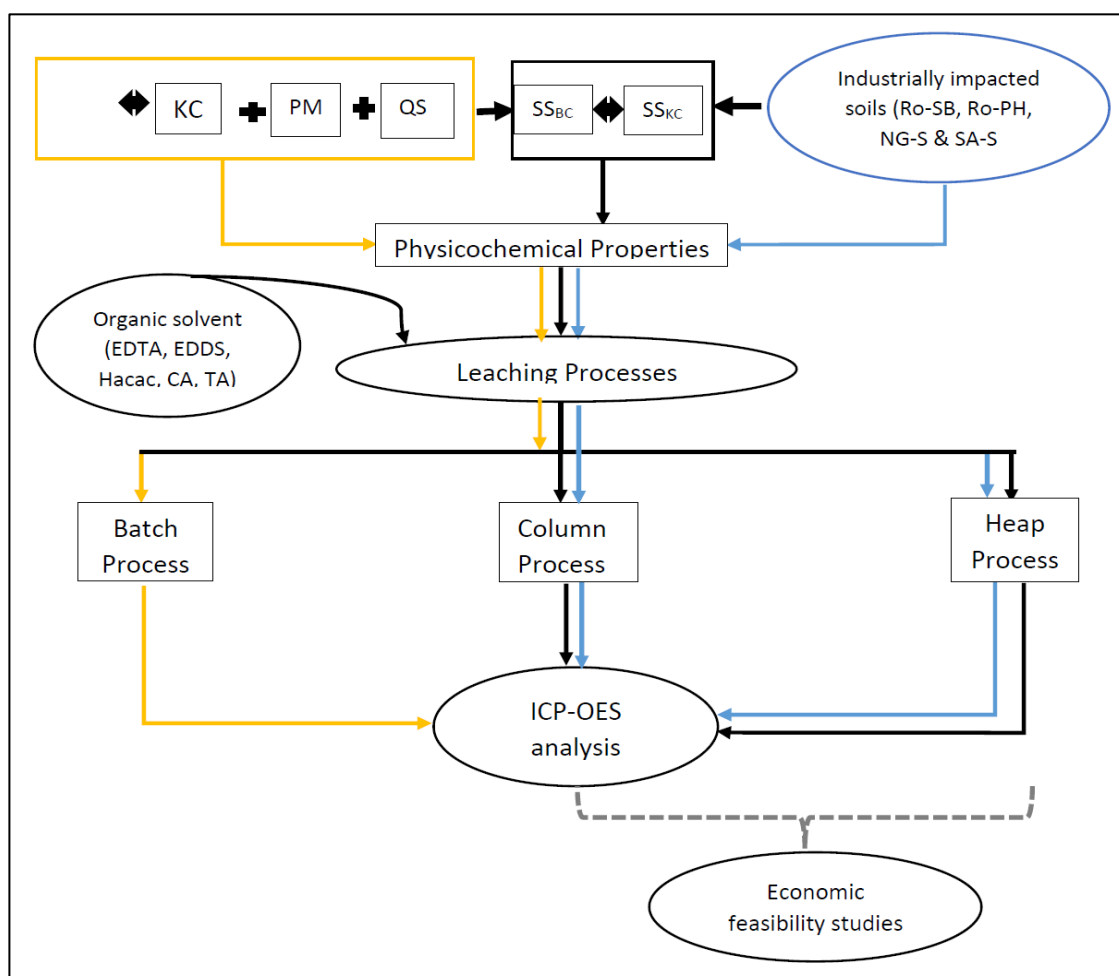
Figure 3 1 Schematic diagram showing the methodology followed during this investigation. Key: the yellow stream indicate constituent materials; black stream indicate simulated soil; blue stream indicate industrially impacted real soil samples. KC, BC, QS, and SS represent kaolinite clay, bentonite clay, quartz sand and simulated soil of the artificial constituents respectively. Ro-SB, Ro-PH, NG-S and SA-S represent Copsa-mica, Campina, Nigerian and South African soils of the natural origin respectively

3.2   Materials

3.2.1   Chemicals

Most reagents used for this study were of analytical grade. To contaminate the substrate used in the investigation, metal nitrate atomic absorption standard solutions of 1000 mgdm^{-3} each were used. The reagent grade nitric acid, reagent grade hydrochloric acid, and EDTA ($C_{10}H_{14}N_2O_8Na_2.H_2O$) were purchased from Sigma Aldrich. EDDS ($C_{10}H_{16}N_2O_8$) was obtained from Innospec and. acetylacetone ($C_5H_8O_2$) and industrial methylated spirit (IMS) from Alfa Aeser. Throughout the investigation, high purity deionized water (18.2 mΩcm) as used. All glassware and PTFE containers were previously soaked in 10% (v/v) nitric acid for 12 h and then rinsed with high purity deionized water

3.2.2   Substrates and soil samples

In this section, the four soil samples, namely simulated soil (SS), the Nigerian soil (referred to as Ng-S hereafter), and the two Romanian soils (Câmpina & Copşa Micã) are discussed individually with respect to their specific sites of collection.

Simulated soil (SS)

This investigation aimed to determine some of the forces that drive and control the leaching of pollutants from natural soils. To enable us to understand the influence of the different components found in soil on its leaching behaviour, a simulated soil (SS) was prepared containing three components. These were bentonite clay (BC) or Kaolinite clay (KC), peat moss (PM) and quartz sand (QS), all sourced from local shops in the Manchester (UK) area. The SS also known as the artificial soil was prepared according to the ''recipe'' described in the guidelines of the organisation for Economic Cooperation and Development (OECD, 1984) and also corresponds to ISO guidelines, (1998b) and had a ratio of 70:20:10 for QS: BC/KC: PM respectively. The PM was air dried to a constant weight, ground in a porcelain mortar and pestle, and sieved before use (< 1 mm). The QS was washed with nitric acid to remove extraneous contamination, then washed with deionized water and allowed to air dry to constant mass and sieved to < 2 mm. The BC/KC were used as received. The substrates were contaminated using atomic absorption standard solutions (1000 mgdm^{-3}), as explained in section 3.2.1.

Romanian soil 1(Câmpina site)

Campina (referred to as Ro-PH hereafter) in Prahova County, Romania, is indicated in Figure 3.2 and is an industrial town that houses both the Romanian star oil refinery and the Central

Orion Foundry. Campina is located on the national route DN1 that links the capital with the city of Brasov in the north of Romania. Campina is approximately 110km northwest of Bucharest, 77km south of Brasov and 35km north of the country town of Ploiesti, between the latitudes 45° 07^l 48^{ll}N and 25° 44^l 24^{ll} E. The area delineated for the site lies within the city of Campina with an approximated total surface area of 0.82 ha and is north of the Central Orion Foundry. The physiographic characteristics will no doubt influence the soil, as it is known to have been used historically as a dumping site for industrial waste (e.g. wastes from sulphur dioxide and steel manufacturing). To the east of the site, there is a lagoon that served as a receptor for oil refinery waste. Due to the significant historical anthropogenic influences, the soil can rather be described as anthrosol or technosol.

Random sampling resulted in a grid of about 400m^2 (20x20 m) to yield 25 samples per hectare according to BS ISO 10381-1: 2002 and BSDD (1988) specifications. Within individual grids, a single 200-700g soil sample (0-20 cm depth) was collected using a soil augur, which was cleaned with deionized water between each sampling as originally sampled in the ITAKA project. Soil samples were bagged in polyethylene bags and labelled with both sample ID and sample point GPS coordinates. Collected samples were transported to the laboratory for storage, processing and analysis.

Romanian soil 2 (Copşa micã)

Copşa Micã (referred to as Ro-SB hereafter) indicated in Figure 3.2, is an industrial town in Sibiu County, Transylvania, Romania and lies between latitude 46° 06^L 56.6^{LL} N and 24° 13^L 56.7^{LL} E. Copşa Micã is a town within the river Tarnava Mare watershed and surrounded by hills. It is located approximately 320km northwest of Bucharest, 43 km northeast of Sibiu and 12 km southwest of Medias. The study site is located between the national routes DN 14 B and the river Tarnava Mare and approximately 1000m west of the Sometra smelter plant. The physiographic characteristics at the northern boundary of the site is influenced by the daily hauling of sand /aggregates conveyed in trucks from the quarry to the east of the study site. Copşa Micã is considered one of the most polluted towns in Europe, because of industrial activities in the 1960s. The Carbosin factory and Sometra metallurgical smelter, although no longer operational, are the two major pollutant sources located in the area and are responsible for the emission of black carbon and non-ferrous substances The site is approximately 0.92 ha and characterized by a 20 m wide strip of dark brown silty loam. The soil depth is between 30 – 40 cm deep underlain with yellow sand and widely used for agricultural activities. Soil sampling techniques adopted to this site was similar to

the technique previously discussed for Campina site and originally sampled in the frame of the ITAKA project and combined into a composite sample.

Used for agricultural activities. Soil sampling techniques adopted to this site was similar to the technique previously discussed for Campina site.

Nigerian soil

Imo state of Nigeria, indicated in Figure 3.3, houses three major ''mechanic'' villages, situated at Nekede, Orji, and Okigwe towns. At these villages, mechanical repairs are performed on various types of vehicles on open and bare ground. Therefore these sources are believed to be amongst the major sources of heavy metal pollution in Imo state, as inferred by studies previously carried out by Nwachukwu et al. (Nwachukwu et al., 2010). However, the study site focuses on Nekede mechanic village (MV) because of the heterogeneous activities (agricultural, informal industrial activities-mechanical repair shops, commercial shops & residential houses) common within the geographical location. Nekede is a town within Otamiri watershed in south-eastern Nigeria and lies between latitude 5º 27$^{\text{I}}$ 888$^{\text{II}}$ N and 7º 02$^{\text{I}}$ 02 250$^{\text{II}}$E. The topography of the area is generally flat but towards the Otamiri riverside, bordering on the western side, it is eroded. The Nekede communities are mainly agrarians and farm within the vicinity of the mechanic village, a development that can increase the anthropogenic levels of these metals across the food chain and result in bioaccumulation of the metals by living organisms.

The soil character can be described as reddish brown (5YR ¼) ferrasols, with grain size of 0.05 – 2.00 mm and an average clay-silt content of ≈ 20%, showing great potential for high infiltration rates. Average erodibility index (K) of the study area is put at 0.034 with a predicted soil loss in the range of 9.23 – 9.93 tons/ha/yr, based on the analysis of satellite imagery (Nwachukwu et al , 2011) These properties are probably partly the reason for the metalliferous soil found at these mechanical workshops, due to vehicle oil spillages, discarded batteries, residues due to panel beating activities, and other waste spillages associated with mechanical and vehicle repairs.

Soil samples were randomly collected at drainage points along the flow direction, within the mechanic village environment At each location, samples were collected at selected depths of 0-15 cm, 15-30 cm, and 30-45 cm within 10 m radius of each other using a soil auger. The three samples from each depth were homogenized to make a composite sample of each depth, resulting in four homogenised samples from the area. Sampled soils were

placed in white polythene bags properly tagged with yellow cards containing sample information and conveyed directly to the containment facilities authorized under the licensed soil. All activities relating to the use and storage, processing and analysing of the licensed Nigerian soil was confined to the approved containment facility as described in the provisions of standard operating procedures (SOP) of the Department for Food, and Rural Affairs (DEFRA), United Kingdom.
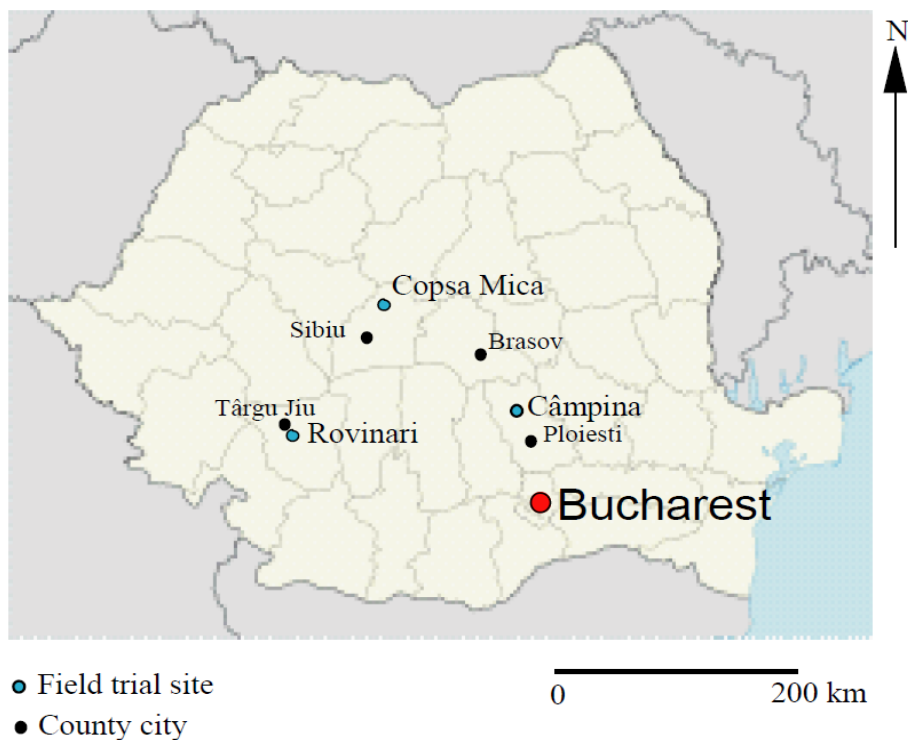
Figure 3 2 Location of the two Romanian contaminated study sites providing samples for this investigation
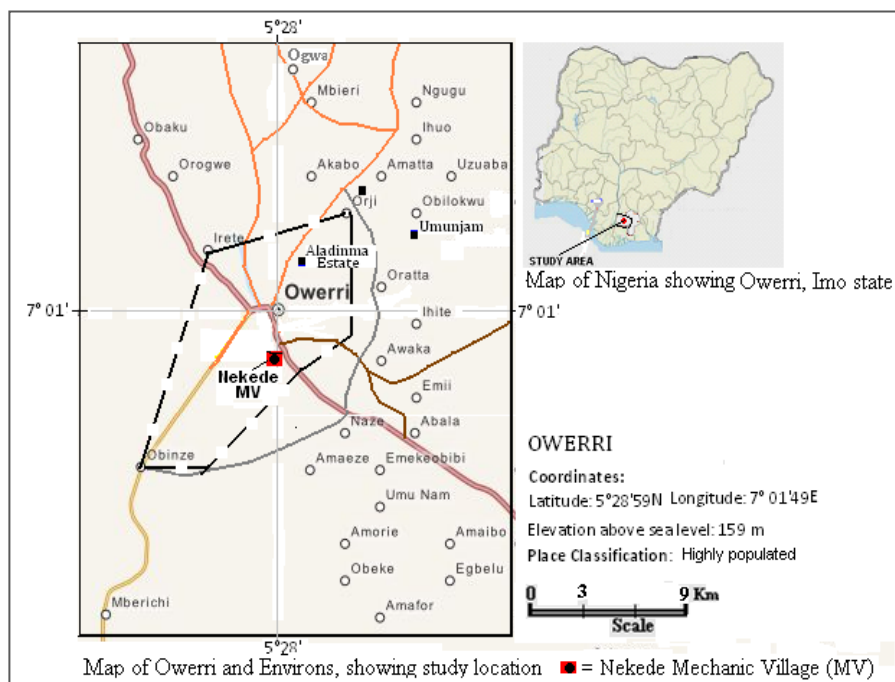
Figure 3 3 Map of Owerri and surrounding environment, showing the study location

3.3   Sample preparation

3.3.1   Contaminated substrates

The individual substrates and the Simulated soil (SS) prepared as described in section 3.1.2.1, were contaminated with the standard solutions at various concentrations as illustrated in Table 3.1. The purpose of deliberately contaminating the soil and individual substrate samples is that a rather homogenous test sample with known metal concentrations, soil / substrate composition contamination process, and contamination period can be obtained. This will minimize ambiguity in the extraction results arising from sample heterogeneity. It is however expected that the laboratory contaminated soil Substrate would give a better extraction efficiency compared to natural soils, as the potentially toxic element PTEs in the laboratory sample tend to be present in the more mobile fractions. To minimize this discrepancy between the natural contaminated soil and the laboratory contaminated soil / substrate, the latter had to be aged before extraction. The use of varying concentrations was aim at conducting a comprehensive study that includes 1) arbitrary constant concentrations, to compare the leaching potentials of ethylene diamine tetra acetic acid (EDTA) ethylene disuccinic acid, (EDDS), 2,4-Pentanedione (Hacac), Citric acid (CA) and Tataric acid (TA). 2) An intermediate concentration, to mimic a realistic contaminated level in Nigeria. 3) Intervention concentration, to mimic the Department of Petroleum Resources (DPR regulatory values.

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4) A selected concentration higher than the intervention values, to mimic highly enriched metalliferous soils.

The air-dried individual substrates, as well as the SS, were accurately weighed to constant weight (20.000 ± 0.0005 g for QS and BC and 5.000 ± 0.0002 g for PM), transferred to a beaker and rewetted to a moisture content of 15% (by dry weight). The substrates were artificially contaminated using 200ml of solutions (for QS, BC, and SS but 50 ml for PM) of the target metal (Cd, Cu, Ni, Pb and Zn) at varying concentrations (substrate were contaminated with single metals as well as a multi-metal solutions) to reach a final concentration that is in line with the Department of Petroleum Resources **DPR, 2002)** of Nigeria as indicated in Table 2. The metals were chosen based on their potential to generate revenue when recovered, their toxicity, their toxicity and resource shortage. A solid/liquid ratio of 1:10 were maintained throughout. The solution suspensions were mechanically stirred for homogeneity and later placed on a mini orbital shaker (Stevart) for a given period to reach equilibrium. The agitation speed was kept constant (300 rpm for 1 hour) for each run to ensure equal mixing. After completion of a pre-selected shaking time, the beakers containing the samples were taken from the shaker and then allowed to equilibrate for a minimum of 10 days to enhance surface stability. Thereafter, 1-cm^3 aliquots of the supernatant (leachate) was collected and the concentrations of metal not retained by the SS, determined by ICP OES, using procedures describe elsewhere. Afterwards, the remaining solution was carefully decanted and the metal spiked samples were put in the oven at 40°C to dry and finally stored in the dark (avoiding degradation by light) for leaching studies later. The metal retention efficiency was determined by subtracting the supernatant concentration from the initial spiked concentration. This is expressed in Eq. (1), where, C_o and C_t are the initial and supernatant concentration of metal ion in mgdm^{-3}, respectively.

$$\text{Retention efficiency} = \frac{C_0 - C_t}{C_o} \times 100 \qquad (1)$$

Table 3 1 Theoretical values for Initial concentrations of metals of interest calculated as a function of the Department of Petroleum Resources (DPR, 2002) Nigeria guidelines

		Concentration in mgkg^{-1} soil dry weight					DPR (2002) in mgkg^{-1}	
Metal	Metal species	Control	ACC	IMC	IVC	3*IVC	Target value	Intervention value
Cd	Cd(NO$_3$)$_2$	0	200.0	20.0	17.0	51.0	0.8	17.0
Cu	Cu(NO$_3$)$_2$	0	200.0	385.0	190.0	570.0	36.0	190.0
Ni	Ni(NO$_3$)$_2$	0	200.0	40.0	210.0	630.0	35.0	210.0
Pb	Pb(NO$_3$)$_2$	0	200.0	1160.0	530.0	1590.0	85.0	530.0
Zn	Zn(NO$_3$)$_2$	0	200.0	824.0	720.0	2160.0	140.0	720.0

3.3.2   Sample preparation for analysis

Samples for micro-Raman analysis and SEM-EDX were prepared by dusting a small quantity of the sample on double-sided tape mounted on a glass slid or a SEM stub. The samples for ICP-OES analysis was digested as described in section 3.3.1.7

3.4   Experimental analysis

The individual substrates, SS and their contaminated samples underwent various analytical procedures, all of which are discussed below.

3.4.1   Physicochemical analysis of the substrates

The substrates were analysed for their physical and chemical properties, using standard techniques and approaches.

Determination of Loss on Ignition (LoI)

Total organic content of the various baselines and soil samples were estimated by loss on ignition (LoI). A 3.000 ± 0.0002g sample was weighed in each crucible and heated at 550°C for 4 hours using an electrical muffle furnace (Omegalux-LMF 3550) and weighed after cooling down in a dessicator. Subsequently the mass difference is taken as the organic content as described by Goldin (1987).

pH measurement

The pH values of the selected slurries of solid: liquid (w : v). (1:10) ratio were determined after they were mechanically agitated at 120 revolutions min^{-1} using the reciprocating shaker for a minimum of 60 min at room temperature (Mettler Toledo, Gawlik et al., 2001). Between each sample, the probe was rinsed thoroughly with DI water to minimize undue

error. The pH meter was calibrated prior to pH measurement of the samples, and periodically with pH7 and pH4 buffers for acid measurements.

Cation exchange capacity

CEC estimation was determined by the methylene blue (MB) method. In the spot test experiment, the MB is exposed to the substrates, where adsorption takes place. The optimum flocculation point is attained when the unabsorbed MB forms a permanent light blue halo around the sample aggregate spot on the filter paper. This is described as a point of saturation for the estimation of CEC as determined by Cokca and Birand (1993)**.**

Specific surface area determination

The specific surface area (SSA) of the substrates and SS was determined by the methylene blue spot test procedure. 1 g dried powder of MB was weighed into a 200mL of DI water. This was followed by 10 g of oven-dried soil measured into 30 mL DI water. Subsequently, the MB solution was added to the solution suspension incrementally in 0.5 mL aliquots and the content stirred periodically for homogeneity. Then a small drop was withdrawn from the solution and placed onto a filter paper (Fisher brand). When this is followed by the appearance of a permanent blue halo around the unabsorbed MB around the soil aggregates, it was an indication that the MB has potentially replaced all the cations in the double layer with coated surfaces. Subsequently, the filtrate was transferred into a micro-vials and centrifuged at 3000 rpm for 30 min. This process reduces the precipitation of MB dye and evaporation of the solution. Later, this solution was appropriately diluted and analysed to determine the concentration of MB with UV-spectrophotometer (Shimadzu, Japan, Santamarina et al. 2002).

Particle size determination

Particle sizes of the various substrates and the SS samples were determined with a Malvern Mastersizer 2000 with a measurement range of 0.02 μm to 2.00 mm. The soil samples were dispersed by ultra-sonication of 35 W and 4 min for the power of the probe and the probe interval respectively. The light intensity were measured according to the Mie theory (ISO 13320: 2009). For each of the substrates, the particle size distribution curve was determined based on three-repeated measurements averaged by the laser diffractometer software.

Surface morphology, mineralogy, and semi-quantitative elemental profile

The mineral characterization of the baselines used in this study was analysed using X-ray diffraction technique. This technique is a unique method to determine the crystallinity of a compound. Comparative assessment of the various baselines before and after metal concentration enhancement is interpreted using the 2θ intensity and d spacing and subsequently referenced with a Ruff data base crystal sleuth software for validation of spectra phases.

The Bragg angular zone was measured by X-ray diffraction (X'Pert) with Kα Cu radiation (ϒ = 1.54 Å), monitoring the diffraction 2θ angles, at 46.6 seconds signal accumulation time, 40kV voltage and 30 mA current. The total 0.02-degree step sizes ranged from 3-100° and used for BC and PM, while the range 10-100° was used for QS and SS.

In order to evaluate the morphology of the samples SE (secondary electron)images were collected using scanning electron microscopy (SEM) (Smart instrument (Supra 40.VP). For better conduction and therefore reducing charging , samples were coated with a sputter coater (Emitech SC 7460) by Au which was operated at 20 mA, 0.06 bar for 2 min. In addition, semi-quantitative elemental concentrations were determined by EDS, using an acceleration voltage of 25kV, a working distance (WD) of 14.2mm and a magnification of 1000x. Each individual EDS spectrum was allowed to run for 1min. The X-ray spectra were collected with the EDX detector. The energy dispersive X-ray technique (Apollo 40SDD) enable qualitative evaluation of the chemical composition, as well as a semi-quantitative determination of the concentration profile.

Acid-soluble metal concentration of the substrates

Firstly, the samples were exposed to acid soluble digestion using aqua regia [HCl (aq) (36%) and HNO$_3$ (aq) (68%), in a ratio of 3:1 v/v)], after which the elemental concentrations of target elements (Cd, Cu, Ni, Pb and Zn) were determined using ICP-OES analysis.

Air-dried samples (0.5g ±0.0002g) were ground in a porcelain mortar and pestle, sieved through a 2mm mesh sieve and digested in a microwave oven (MarsXpress) in 10 cm^3 of aqua regia (60 min at 175^{0}C). For each sample three aliquots were taken to determine the repeatability of the analysis. Aqua regia was made in situ with HCl (aq) being added sequentially to HNO$_3$ (aq) in Teflon tubes, properly capped and fed into the microwave oven set-up to run. After each run, the digested contents were cooled, vacuum filtered through Whatman no. 4 filter paper (pore size 0.45 μm) and diluted volumetrically to 50 ml

using DI water. The pseudo-total concentration of Cd, Cu, Ni, Pb, and Zn were determined by utilizing the Varian Thermo Scientific iCAP 6300 duo ICP-OES, with the torch operated horizontally, to enable measurement of targeted metals in the axial view (end-on viewing allowing for maximum sensitivity). Argon (99.999%) was used as the carrier gas and 1% HNO_3 (aq) was used as the rinse agent. Some specifications of the ICP-OES system used are given in Table 3.2.

Table 3 2 Specifications of ICP-OES spectrometer for analysis of soil materials

Parameter	Settings
Radio frequency (RF) power	1250 w
Pump tubing	Tygon orange/white
Spray chamber	Glass concentric
Torch	2 mm centre tube
Coolant flow	12 Lmin^{-1}
Auxiliary gas flow	0.50 Lmin^{-1}
Nebulizer gas flow	0.55 Lmin^{-1}
Flush pump speed	50 rpm
Analysis pump speed	50 rpm
Nebulizer	Glass concentric
Rinse time	50 sec
Sample flush	50 sec
Repeat	3
Wavelength (nm)	
Cd	2144
Cu	3347
Ni	2316
Pb	2203
Zn	2062

All sample concentrations were corrected for matrix effects by procedural blanks, normalized to the sample mass and reported as mgkg^{-1} dry weight (Waldron 1980; Zodl and Wittmann, 2003). A 4-point calibration was undertaken using a multi-element standard solution (100 mgdm-^{3}) for each calibration curve and yielded a calibration coefficient of $\geq$ 0.9995 for each of the metal concentrations analysed and shown in Table 3.3. This analysis procedure was followed throughout the investigation to determine the target metal concentrations. The method of analysis was tested against 3 replicates of a standard reference material used in inter-laboratory comparisons (sedimentary clay-LGC 6139) which were digested and analysed according to the experimental procedures of partial

(*aqua regia*) digestion of sample substrates. The coefficient of variance and recoveries of the replicates analysed samples (CRM) ranged between 0.79 – 1.1% and 71 – 100%, respectively. The limit of detection and quantification for Cd, Cu, Ni, Pb, and Zn on the instrument used in this study was also measured by analysing 10 replicates of acid blanks and the standard deviation (σ) determined. The data obtained is summarized in Table 3.4, where the limit of detection and limit of quantification are respectively defined as 3 X σ and 10 X σ. Reagent blank and analytical duplicates were also used where appropriate, in order to ensure accuracy and precision in the analysis

Table 3 3 Concentration of standards used for the analysis of both artificially spiked soil and industrially impacted soils across the globe

Metal	Blank	Cal-1	Cal-2	Cal-3	Cal-4
Cd	0.0000	0.1005	1.0050	10.0500	N/A
Cu	0.0000	0.1003	1.0030	10.0300	20.0200
Ni	0.0000	0.1007	1.0070	10.0700	20.1400
Pb	0.0000	0.1003	1.0030	10.0300	20.0600
Zn	0.0000	0.1002	1.0020	10.0200	20.0400

3.5   Analysis of leachate samples

For all leachate experiments, aliquots of leachate was collected and diluted 1 in 10. At all times samples were collected in triplicate and 3 analyses per replicate were performed on the ICP-OES using the methodology described in 3.3.1.7

Table 3 4 Limit of Detection (LoD) and limit of Quantification (LoQ) of the metals of interest (ppm) using ICP-OES

Limit (ppm)	Cd (2144)	Cu (3347)	Ni (2316)	Pb (2203)	Zn (2062)
Limit of Detection (LoD)	0.0001	0.0022	0.0009	0.0008	0.0027
Limit of Quantification (LoQ)	0.001	0.022	0.009	0.008	0.027

3.6   Batch study

The single- and multi-metal contaminated single substrates and SS were subjected to batch experiments with the leaching agents EDTA, EDDS, CA, and TA (of which chemical structures are provided in Table 3.5) used to extract the metals. The influence of different contaminant concentrations, combination of metals of interest, time of extraction, substrate type and leaching agent type were investigated.
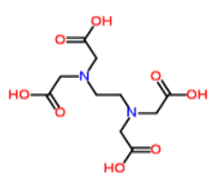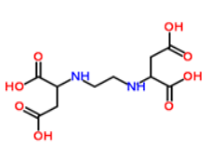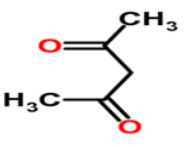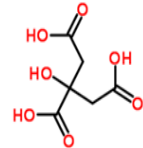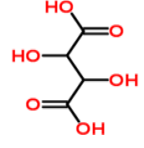
To obtain washing solutions and determine their metal extraction efficiencies on the various contaminated substrates used in this study, selected chelating agents viz; Ethylene diamine tetra acetic acid (EDTA), Ethylene diamine disuccinic acid (EDDS), Acetylacetone (Hacac), Citric acid (CA), and Tartaric acid (TA) were prepared at the following concentrations: 0.034 moldm^{-3}, 0.034 moldm^{-3}, 3.0 moldm^{-3}, 0.026 moldm^{-3}, 0.033 moldm^{-3} respectively. A solid/liquid ratio of 1:10 were maintained throughout the tests(Hendershot and Tejowulan, 1998). Factors influencing the choice of leaching agents were: 1) cost, 2) environmental sustainability 3) potential leaching efficiency, and 4) potential to be used in a different phase or modified for selective recovery. The single and multi-metal spiked substrates were subjected to batch extraction treatments using a biodegradable chelant (EDDS), Hacac (organic solvent) and low molecular weight(LMW) organic acids (CA and TA) with EDTA as a reference chelant, at a soil/solution ratio of 1:10(w/v). 20g of each soil sample was placed in polypropylene tubes of 500ml capacity containing 200ml of solution. All samples were strongly agitated using an orbital shaker (Stevart) at a speed of 300-revolution min^{-1} at room temperature for 3 h. The change in pH upon exposure to the leaching agent was monitored by measuring the pH of the solution. A procedural blank was performed by using deionized water as extractant on all substrates, to determine the contribution of the leaching agent. In the findings of Peters and Shem (Peters and Shem, 1992) and Evangelista and Zownir (1989), it was observed that extraction of Pb (relatively less mobile) with EDTA was rapid, with an equilibrium time of 1 h. Therefore, an extraction time of 30 min (varied at 5, 10, 20, and 30) and 3 h (varied at 30, 60, 90, 120, and 180) were chosen for the artificial soil and natural soils respectively, for the rest of this study. After mixing of the soil and solution at intervals specified above, the suspensions were centrifuged at 3000 rpm, to enable separation of the liquid from the solid. Following centrifugation, 1 mL aliquot (washing solution) from the supernatant in each of the tubes were filtrated with a syringe filter (0.45µm) into a plastic vial of 15 mL capacity and later made up to 10 mL with deionized water. Subsequently, the filtrates were analysed by ICP-OES and the selected metal concentrations retained in the adsorbent phase (mgkg^{-1}) were calculated.

The percentage metal leached from the soil were calculated using Equation (1).

$$\% \, metal \, leached = \frac{mass \, of \, metal \, in \, supernatant}{mass \, of \, metal \, originally \, loaded \, on \, substrate} \times 100 \tag{2}$$

To ensure repeatability, this procedure was carried out in triplicate for all substrates

Table 3 5 Molecular and Structural formula of selected extractants used in this study

EDTA	EDDS	ACAC	CA	TA
$C_{10}H_{16}N_2O_8$	$C_{10}H_{16}N_2O_8$	$C_5H_8O_2$	$C_6H_8O_7$	$C_4H_6O_6$

3.7 Column study

In this phase of the study, column tests were conducted to is considered to examine the in-situ leaching behaviour as well as extraction-recovery of Cd, Cu, Ni, Pb, and Zn from both the natural soils (Ng-MV, Ro-SB and Ro-PH) and SS (previously studied on a batch mode) (Cote, 1981). The application to the multiple soils was to evaluate and compare the robustness and variation of the selected leaching agents to leach metals from different global soils. For the simulated soil, kaolinite clay (KC) was used as substitute for the bentonite clay (BC), a constituents part of the SS and used in the same ratio (70:20:10 for QS: KC: PM) as before. The use of KC as a constituent substrate in the place of BC was due to systematic clogging encountered during the leaching of the SS in the column, which resulted in the loss of hydraulic conductivity. This phenomenon was largely attributed to the rheological behaviour (agglomeration, shrink and swell tendencies) of the bentonite clay as it tends to exhibit thixotropic properties when suspended in solution **(Malfoy et al. 2003)**. Loading and leaching processes of the simulated soil was achieved by spiking at 3*intervention (3*IV) concentration for the selected metal ions (Zn [2160], Cu [570], Ni [630], Cd [51], and Pb [1590] mgkg^{-1}). This limit was used to mimic a typical highly enriched contaminated soil.

Metal extractions from the natural soils and simulated soil were carried out in a glass column as shown in Figure 3.4.The packed soil was placed into the column (internal diameter 0.2cm and 30cm in height) between two layers of sand (0.5cm each). The slurry technique was adopted rather than a dry packing technique, as this practically seems to be the most suitable approach for the type of soil been studied. The soil seated at a height of 8cm by gently tapping the column with a rubber rod to achieve a uniform bulk density as

well as minimize band broadening. The sand layer placed at the bottom of the leaching column prevented loss of sample during the leaching process. Before exposure of the slurry to leaching solutions, DI water used in making the slurry was removed via the column outlet with small amount left to keep the column intact and hydrated. The volume and metal concentration of the water leachate was used as a control to assess the contribution of the solution extractants used. Each column was initially saturated with the leaching solution after which leaching experiment started immediately. The pH of the leaching solutions used in this experiment were 4.75 ± 0.1, 3.51 ± 0.1, 2.71 ± 0.2, and 4.2 ± 0.2 for EDTA, EDDS, CA, and ACAC respectively. TA however, was not considered in this phase because of its poor performance in the batch phase.

The solution level in the columns varied slightly according to outflow rate, and was maintained at approximately 10cm above the soil surface by the addition of the leaching solution, as it demands. A sand layer placed on the soil surface minimized sample disturbance from the addition of leaching solution. Leaching of Cd, Cu, Ni, Pb, and Zn from the soil samples was determined using different of chelating agents (EDTA, EDDS, CA and pure Hacac) over a leaching time intervals of 30, 60, 90, 120, and 150 min. Each extractant run was replicated in three columns each. Preliminary studies (not reported here) was conducted to optimize experimental conditions. The flow rate was initially set at 0.8 mL min^{-1} with a constant head of 10 cm. However, it was difficult to maintain this flow rate throughout the study as slight variations within the range of $\pm (0.046 - 0.154)$ was observed for the different soils investigated. The reason for this variation in flow rate could be attributed to some of the physical properties of the soils such as channelization, porosity, bulk density etc. The pH measurements of the leachate samples was taken before metal analysis on the ICP-OES instrument.
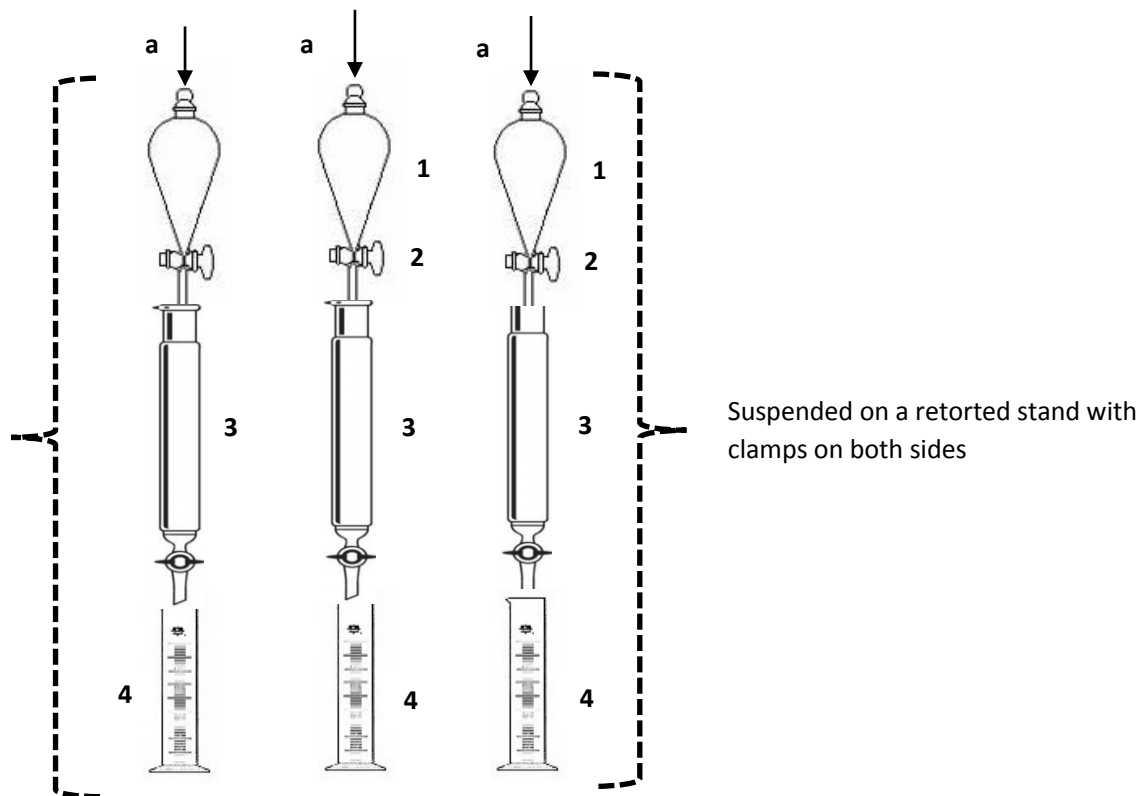
Figure 3 4 Schematic sketch of the experimental set up for in situ column leaching. Key: 1, glass separating funnel (reservoir); 2, stopper; 3, glass column with sintered disc frit; 4, measuring cylinder. Flow stream; a, recharge leaching substance

3.8   Heap study

Heap leaching, is a dynamic process and was also considered for comparison to the column leaching method. This involves stacking of metal-bearing soil into a heap on an impermeable pad, irrigating it with a chemical solution for an extended period to dissolve the preferred metals, and collecting the leachate as it percolates from the base of the heap. However, in order to mimic this approach for a laboratory study, the heap configuration was simulated as illustrated in Figure 3.5. In short, a perforated Buchner funnel (70 mm) with a filter paper (0.45 um) was used to contain the heap and facilitate collection of the leachate over time for subsequent metal analysis. The irrigation was effected using a watering can rose of which same perforations were blocked to control flow rate. The supply of extractants to the rose was ensured by a continuous flow from a reservoir, for which a 250 ml separating funnel was used. The Buchner funnel was charged with 20 ± 0.0004 g of soil and then irrigated with the different chelating agents described previously. An average flow rate under gravity of 11.22 cm^3min^{-1} was initially set and the leachate collected over time intervals of 30, 60, 90, 120, and 150 min. However, variation in the flow rate ranging from ± (0.244 – 0.651) was calculated for the different soils investigated. The reason for this could be attributed to the nature of the soils investigated. The leachate was analysed

for Cd, Cu, Ni, Pb, and Zn. Each extractant run was conducted in triplicates. The pH measurements of the leachate samples was taken before metal analysis on the ICP-OES instrument.
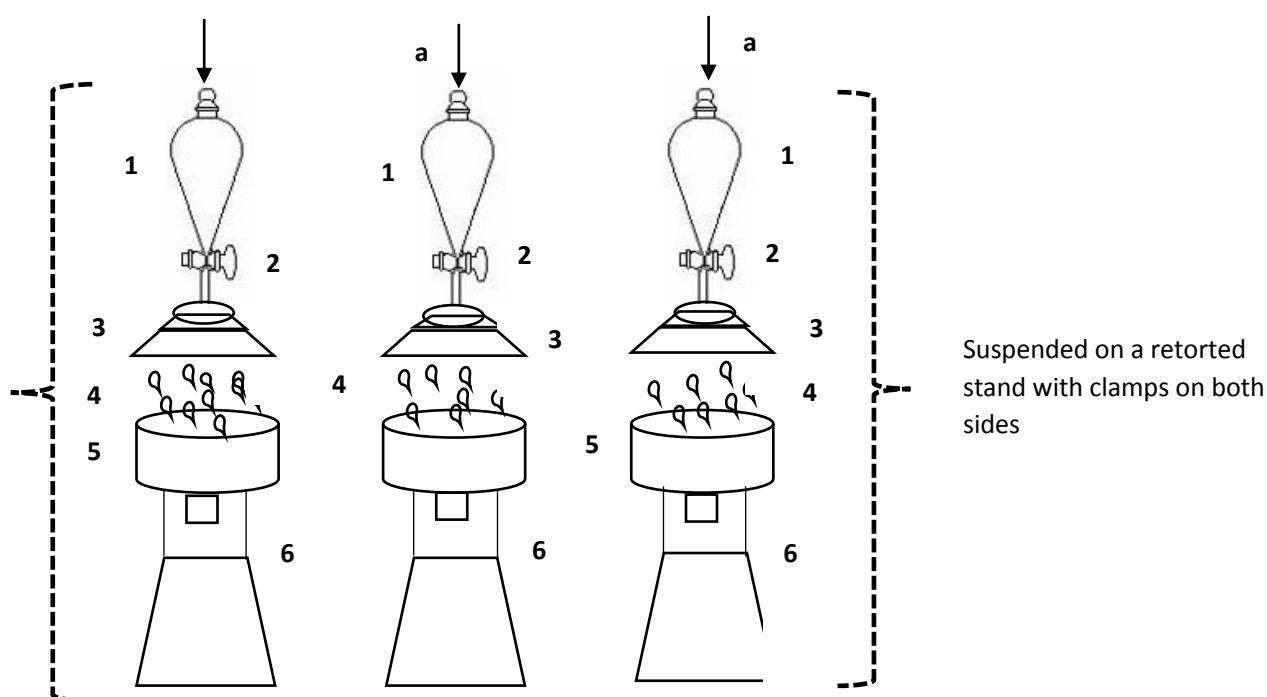
Figure 3 5 Schematic sketch of experimental set-up used for in-situ heap leaching. Key: 1, glass separating funnel (1, reservoir; 2, stopper; 3, improvised rain maker; 4, drip irrigation (leaching substance); 5, Buchner funnel; 6, beaker. Flow stream; a, recharge leaching substance

The (column and heap) dynamic processes described in Figs. 3.4 and 3.5 involves systematic study on movement of liquid flow in soil which takes into cognissance the hydraulic conductivity (K) of the system. The parameter K is generally used for evaluating water infiltration, run off, drainage, ground water recharge and importantly the movement of solutes in soils, which applies to the present study. The value of K can be calculated using Darcy's law.

Darcy's law is assumed to provide an accurate description and measurement of K in almost all hydro-geologic environment. It is applicable mainly to relatively homogenous and stable systems of intermediate scale and pore sizes, i.e. as long as flow is laminar and soil - water interaction does not result in a change of K with a change of gradient (Hillel 1998).

Existing laboratory methods of determining K are based on the development of a static or dynamic head over the infiltration soil column, regardless of whether the water enters into

the soil from the top or the bottom (Phogat and Horn, 2013). Darcy's law can be expressed as $J = \frac{Q}{A*t} = -K_t$

Where J is water flux (or flow of water) i.e the quantity of water (Q) moving through a cross-sectional area (A) per unit of time (t); K is hydraulic conductivity; and I is hydraulic gradient. The minus sign keeps K positive and maintains directional integrity. Hydraulic gradient describes the effectiveness of the driving force behind water movement and is defined as : $i = \frac{\Delta H}{l}$ $where$

ΔH is the difference in hydraulic head between points in the soil and l is the distance between the points. Darcy's law demonstrates that influx (J) is proportional to the hydraulic gradient (i).

The hydraulic gradient is the difference in total hydraulic head per unit distance. K is the constant that defines the proportionate relationship of flux to hydraulic gradient equal to unity. Therefore, it is a quantitative measure of a saturated soil's ability to transmit water when subjected to a hydraulic gradient.

3.9   ICP-OES analysis parameters

The ICP-OES used for this research was a Varian Thermo Scientific iCAP 6300 duo ICP-OES with the torch operated horizontally, to enable measurement of targeted metals in the axial view (end-on viewing). Argon (99.999%) was used as the carrier gas and 1% HNO_3 (aq) was used as the rinse agent. Some specifications of the ICP-OES system used are given in section 3.2.

3.10   Statistical analysis

All mathematical computations were made using both Microsoft office 2013 and SPSS 23. Data treatment and statistical analysis were then applied to compare the obtained results. Where applicable, experimental data were subjected to a normality test (parametricity) to check if the data set followed a normal distribution (Kolmogorov-Smirnov test). Two-Anova, Box and Whisker plots were used for comparisons.

The influence of the different constituents of our simulated soil on the leaching behaviour of metals of interest will be presented and discussed in chapter four.

Chapter 4

Predictive potential of individual soil components on leaching behaviours: Batch process

4.1   Introduction

Soil behaviour is influenced by the dominating properties (pH, particle size, cation exchange capacity, etc.) of its distinct components. This in turn affects numerous processes such as adsorption/absorption and desorption processes that takes place in the soil (Peters, 1999). In the light of this, the influence that the individual components, constituting a simulated soil (SS), will have on desorption or leaching processes were studied by using a batch process. In addition, the synergism and antagonism of single metal (SM) and multi-metal (MM) artificial contamination would have on metal leaching and recovery from the SS, were investigated.

4.2   Substrates characteristics

Characterisation of the individual components (Quartz Sand [QS], Bentonite Clay [BC] and Peat Moss [PM]) and the simulated soil (SS), as described in Section 3.1.2.1 in terms of pH, CEC, SSA, LoI and mineralogy, were conducted to provide information on the physical and chemical properties of the substrates. In turn, these were compared and contrasted with selected published data of natural soils. The findings are summarized in Table 4.1.

The pH values of SS (9.44) and BC (10.55) indicate alkaline substrates, whilst the QS and PM with similar pH values of 4.2 and 5.0, respectively, are described as acidic. SS was observed to compare well with mined and treated soil (Chen et al 2015). In principle, it is anticipated that alkaline substrates (BS and SS) and the acidic substrates (QS and PM) would exhibit dissimilar behaviour considering their opposing pH values. The different pH values observed by the four substrates may influence their metal retentive capacity, which in turn may affect metal leaching efficiency of the soil matrix.

The Cation Exchange Capacity (CEC) of QS (the main component of the SS) is typically low and in the range of 2 meq/100g. The CEC of the SS is in agreement with a loam type soil from France (Sun et al., 2001) and lies in the accepted range of 15 – 20 meq/100g taking the basicity of the soil in consideration, since the CEC is anticipated to increase with pH. This proportion also reflects the relatively low clay content and its perceived contribution on the properties of the SS, since clay and organic matter have much larger values than what we report here for the SS.

The SSA value (31m^2/g) is typical of what can be expected for ≈20% clay content soil and correlates well with the observed CEC reported by Peterson et al. (1996). However, the SSA of the SS was slightly lower than the value reported by other researchers (Kovo et al., 2015). This variation may be attributed in part, to the soil forming, soil processes and soil morphology of the natural soil (Sokolov, 1996; Buol et al., 1996).

Secondary electron images (SEI), as shown in Figure 1, describes the QS, BC, PM, and SS morphologies. The QS grains show varying degrees of sphericity and roundness. The BC displayed agglomerated structures characteristic of small particle sizes. The PM appears broad and elongated in structure with variegated spine edges, and the presence of plant material. The SS is composed of agglomeration of the three constituents albeit dominated with QS grains.

The major minerals, identified through XRD pattern recognition, were α-quartz and montmorillonite (a smectite clay and the main component in bentonite clays). The presence of montmorillonite partly suggest the alkaline behaviour exhibited by SS. The bulk geochemistry of the SS was observed to be laden with traces of potentially heavy metals of interest in varying concentrations; however, these concentrations were substantially below the target values of the Department of Petroleum Resources (DPR, 2002) of Nigeria. The extent of metal contamination was in the descending order Zn >> Cu > Pb > Ni >> Cd. This trend suggest that Zn should be present in greater proportion in the SS when compared to the other metals, but slightly higher than values reported in literature for natural soils (Sun et al., 2001).

Table 4 1 Physicochemical properties of the simulated soil as well as its constituents compared with selected published data

Properties		Simulated soil This Study		References (soil name used in original paper), soil taxonomic description
pH	[a] SS	9.44 ± 0.03		9.6 Chen et al.(2015) (Mined soil, Treated soil)
	QS	4.15		
	BC	10.55		
	PM	4.97		
[b]CEC (meq/100g)		17 ± 0.63		17.6 Sun et al.(2001) (Northern France, loam)
[c]SSA (m^2/g)		31 ± 1.38		55.8 Kovo et.al.(2015) (soil, clayey)
[d]LOI (%)		14		13.6 Kovo et.al.(2015) (soil, clayey)
Mineralogy of SS		Montmorillonite $(Na_{0.2}Ca_{0.1}Al_2Si_4O_{10}(OH)_2(H_2O)_{10}$ Quartz (SiO_2)		Montmorillonite, Quartz, Kaolinite. Kovo et al.(2015) (soil, clayey)
[e]Base-line acid-soluble metal concentrations in SS (mgkg^{-1})	Cd	0.2 ± 0.1	0.8*	0.2 Sun et al (2001) North France, loam)
	Cu	9.6 ± 1.1	36*	na
	Ni	1.7 ± 0.7	35*	na
	Pb	12.4 ± 0.1	85*	na
	Zn	55.4 ± 2.38	140*	49.4 Sun et al.(2001) (North France, loam)

[a] 1: 10 soil/deionized water ratio, [b] Cation exchange capacity (meq/100g), [c] Surface area (m^2/g), [d] Loss on ignition (%)

[e] Concentration determined after digestion with nitric acid (mgkg^{-1}). Values shown are means ± standard deviation, na: not available * denotes target values for Department of Petroleum Resources (DPR) Nigeria (2002)

a) Quartz sand   b) Bentonite clay

c) Peat moss   d) Simulated soil
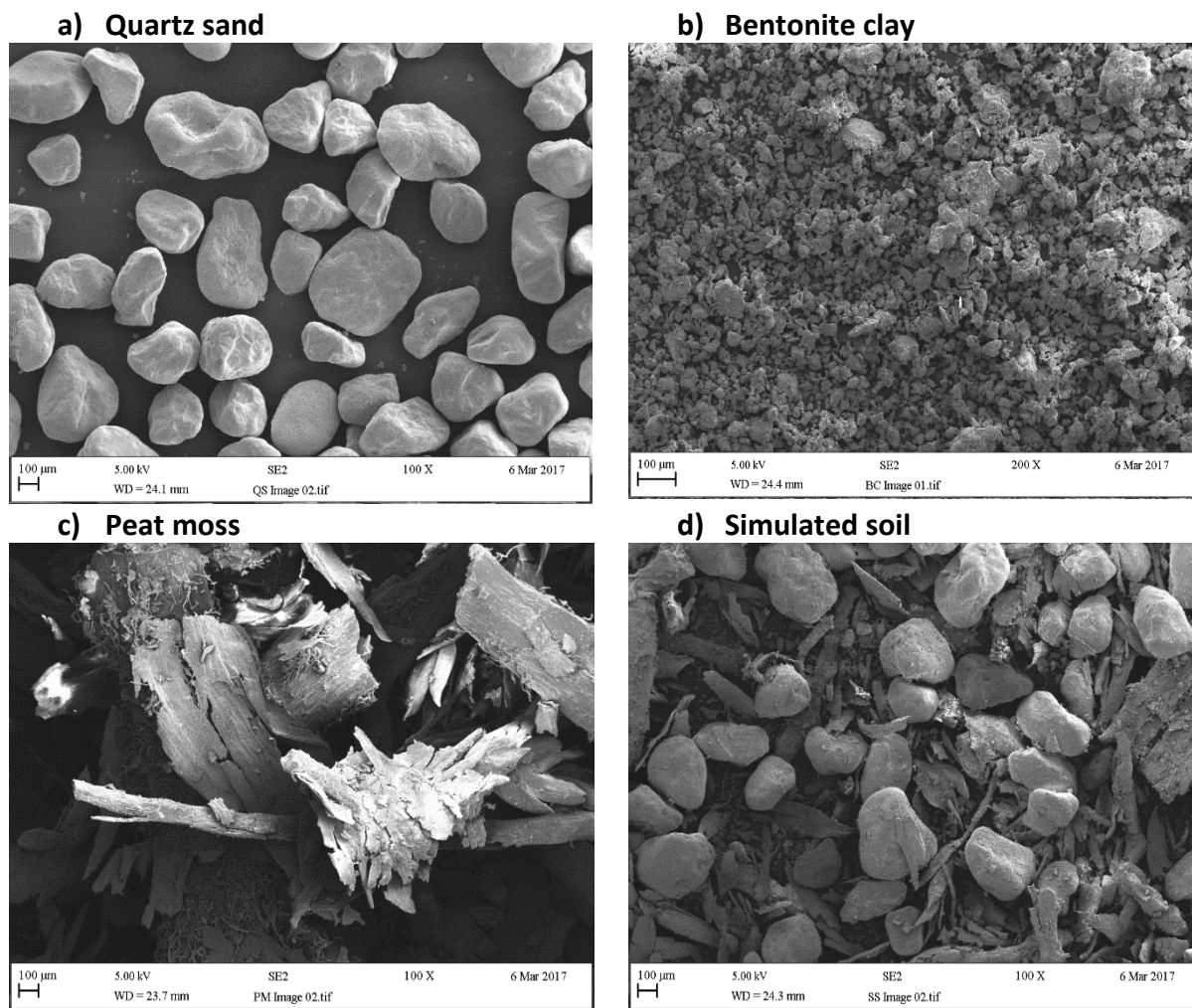
Figure 4 1 SEI micrographs of SS as well as its constituents (BC, PM, QS) at x100 magnification

4.3   Influence of the substrate and metal concentration on extraction efficiency

Using a batch approach and a 1:10 solid liquid ratio, the leaching behaviour of the 5 metals of interest (Cd, Cu, Ni, Pb and Zn) from the single soil components (QS, BC and PM) and the compiled SS were investigated. To illustrate the general leaching profile over time, the leaching concentrations arbitrary constant concentration [ACC], intermediate constant concentration [IMC], intervention concentration [IVC] and three times intervention concentration [3 times IVC] (all in mgkg^{-1}) of metals from single-metal-contaminated substrates, as well as the compiled SS, over time (5, 10, 20 and 30 minutes) with organic solvents (EDTA, EDDS, Hacac, CA and TA) have been investigated. This section focuses on the influence of the different components (excluding QS), single (SM) and multi-metal (MM) contamination, and different concentrations across all extractants. This will be illustrated as box plots as given in Figures 4.2 and 4.3 to indicate the variation in extraction efficiency that was observed. The exclusion of QS as a potential predictive tool for metal

removal efficiency was based on the fact that it's loading as well as contribution in the retention of metals of interest were significantly lower than the other two components.

4.3.1 Constant metal contamination

In order to investigate the contributory effects of the different soil components on the leaching behaviour of metals of interest using the different extractants, a constant metal concentration was used (200 mgkg^{-1}). Figure 4.2, representing the whisker plots, provides some insight in the variation of the extraction efficiency across the five extractants, after 30 minutes contact time. The extraction efficiency for the five metals were similar (taken as an average value across all five extractants), irrespective of whether it is SM or MM contamination, for the BC and the SS. The efficiency varied from 10.4% for Ni to 27% for Cd in the SS system, and 10.6% to 29% for the MM system in the case of BC. For the SS, however, the efficiency was much higher, varying from 34% for Pb to 68% for Ni in the SM system and 33% for Ni to 61% for Cu in the MM system. Ni seemed to be negatively influenced by the presence of other metals in the MM system and was the only metal that showed a significant difference between SM and MM. However, for the PM there is a significant difference between SM and MM, averaging a 12 % (ranging from 6 – 24%) difference. The MM contaminated PM showed synergistic behaviour in comparison with the SM leaching efficiency. The PM seemed to contribute the most to the extraction efficiency of the SS across the five extractants explored, with an average efficiency closest to that of SS. It varied from 11% for Pb to 27% for Cu in the SM system and 17% for Pb to 44% for Cu in the MM system.

4.3.2 Influence of varying concentrations of contamination

Section 4.2.1 documents the exploration of the influence of substrates on the average leaching efficiency where the metal contamination was held constant. Evidently, this did not focus on the effect that different concentrations of the different metals will have on the extraction efficiency. To determine the influence that different metal concentrations had on the leaching efficiency, varying metal concentrations (SM and MM systems), as described in Table 2 of section 3.2.1, were investigated. It is observed that the metal concentration plays a significant role in the metal recovery, and the discussion will be focussed around the MM systems, as this is more representative of natural soils. To consider the influence of the varying concentration displayed in Figures 4.3. 4.4 and 4.5, the metals will be discussed separately using the data in the following tables (Table 4.2).

Cadmium (Cd)

The extraction efficiency of Cd across the different extractants at various contamination regimes from different substrates are summarized in Table 4.2. Cd release across the four different metal concentrations investigated are the same in the order SS > PM > BC for the different substrates. Given the results, it can be inferred that the highest Cd release was observed in SS followed by PM and the least in BC. It is further evident that the higher the Cd concentration the higher the extraction efficiency. Therefore, with the release phenomenon exhibited it is possible to conclude that amongst other release controlling parameters, concentration drive influenced the process the most.

Copper (Cu)

Table 4.2 indicates the Cu released in the decreasing order of magnitude: IVC, SS > PM > BC; ACC, SS > PM > BC; IMC, SS > PM > BC; 3 times IVC, SS > PM > BC. However, from the manner with which Cu is released, it is difficult to identify which of the release controlling parameters could play a fundamental role in the release of Cu from the different substrates. There seems to be a breakthrough concentration at 200 mgkg^{-1} for Cu after which there is a negative correlation between concentration loaded and leached. It may therefore be concluded that amongst other parameters, the leaching of Cu is also concentration controlled, and that concentrations higher than 200 mgkg^{-1} may result in reduced leaching. It has to be taken into account though that this study minimised variables and therefore we appreciate that other factors not investigated here may change this conclusion.

Nickel (Ni)

With respect to Ni release as shown in Table 4.2 and presented in their decreasing order of magnitude: IMC, SS > PM > BC; ACC, SS ≈PM > BC; IVC, SS ≈ PM > BC; 3 times IVC, SS > PM > BC, it can be deduced that the leaching concentration of Ni across the different contamination regimes were the highest from the SS as was the case with Cd and Cu. The same kind of phenomenon was observed for Ni than what was described for Cu, where there seemingly is a breakthrough concentration (210 mgkg-1), after which extraction decreases. This was more prominent for the BC and PM in comparison with the SS, indicating that factors other than concentration may be at play in the case of SS.

<u>Lead (Pb)</u>

For Pb, the determined extraction efficiencies are summarized in Table 4.2. The influence of the different contaminant regimes on the different substrates can be seen as relatively comparable. High extraction efficiency in Pb release was observed in SS followed by PM and with BC leaching the least, as has been the trend for Cd, Cu and Ni cations. As was the case for Cu and Ni, an increase or similar extraction was observed up to a specific concentration (200 - 530 $mgkg^{-1}$), after which a decline is observed. We therefore, once again can infer that concentration plays a significant role in the release of the metals. In addition, it is possible that complexation of Pb with PM and SS could play an important role considering the affinity Pb has for organic matter (PM).

<u>Zinc (Zn)</u>

The data for Zn release from the different substrates (averaged over the selected extractants) are summarised in Table 4.2. Zn seemed to display the same pattern in general, whereby extraction from SS was the highest, but in this case, some of the values were similar or even slightly lower than PM. In addition, the Zn release from PM and SS were always higher than from BC (1.5---4 times). This could be attributed to the fact that the BC substrate acted as a sink for Zn cation and therefore values for efficiencies are significantly lower than for PM and SS. It can be deduced therefore that Zn-release may be determined by the amount of organic matter in the sediment. Once again a breakthrough concentration of 200 $mgkg^{-1}$ is observed, after which there is a decline in concentration extracted from the SS. However, the PM is more resilient to an increase in concentration, therefore it could be concluded that a larger organic content in the sediment could work in favour of Zn extraction.
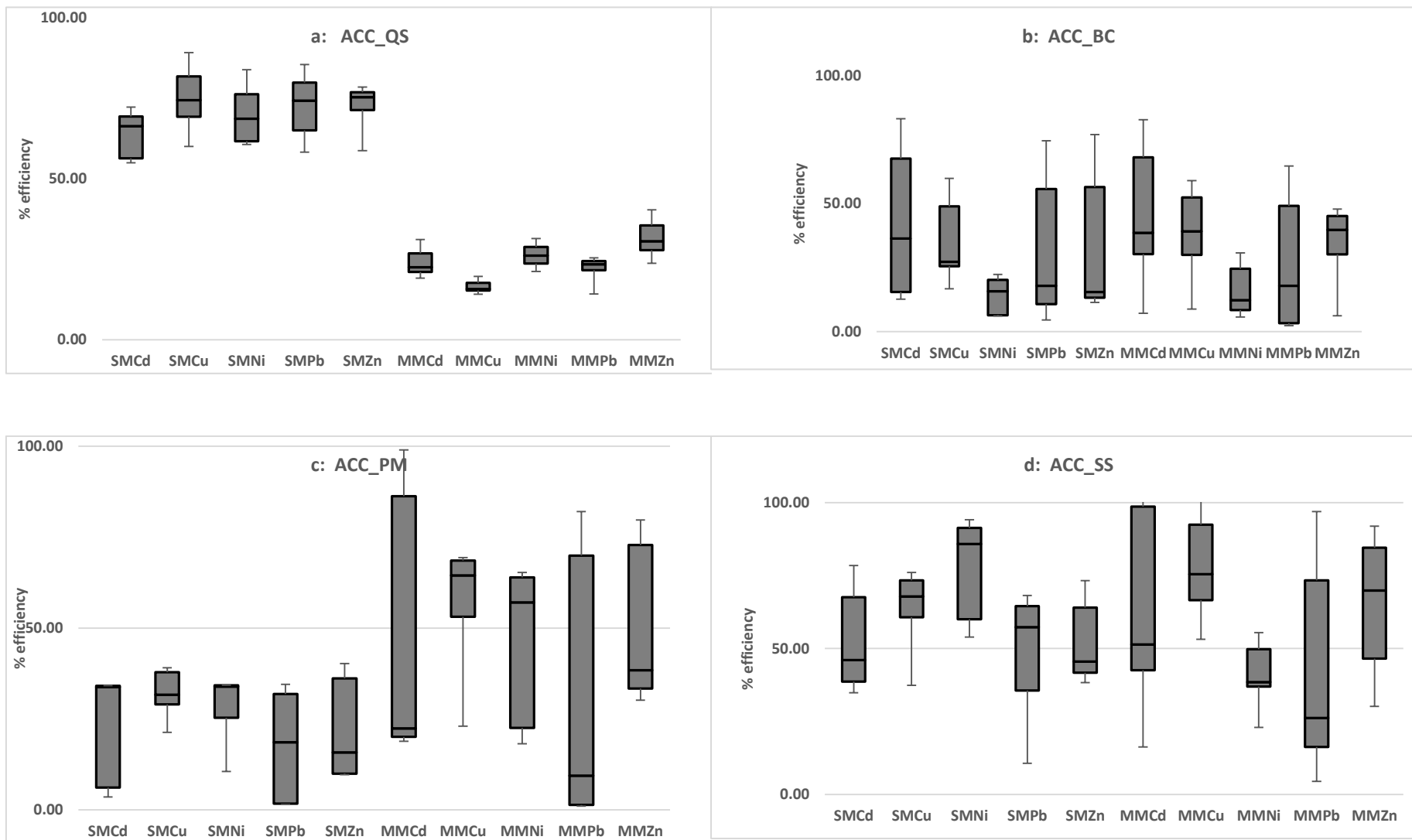
Figure 4 2 Influence of different soil components (at constant contaminant regime) on the leaching behaviour of target metals using specific extractants as a unit factor. The lower and upper boundaries of the box represent the 25 and 75% of the sample size (n=5). a, b, c and d represent quartz, bentonite , peat moss and simulated soil respectively.
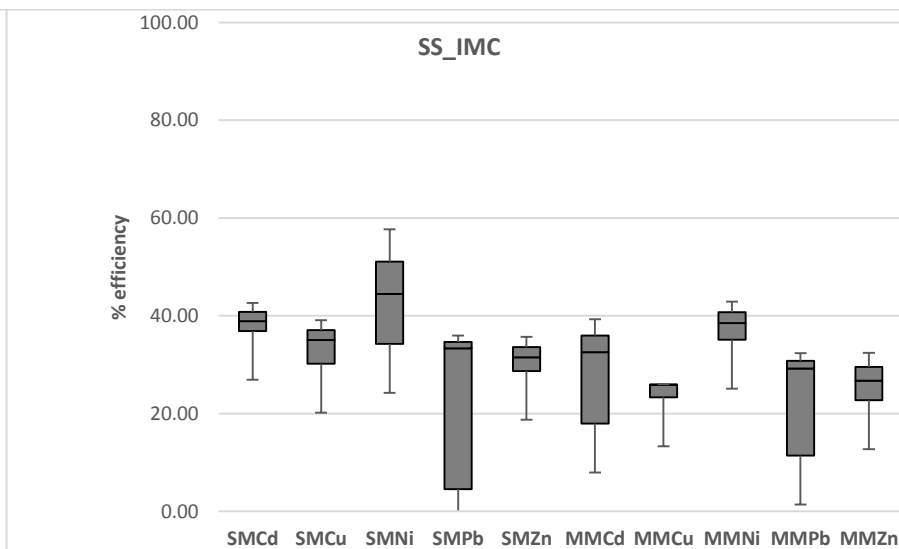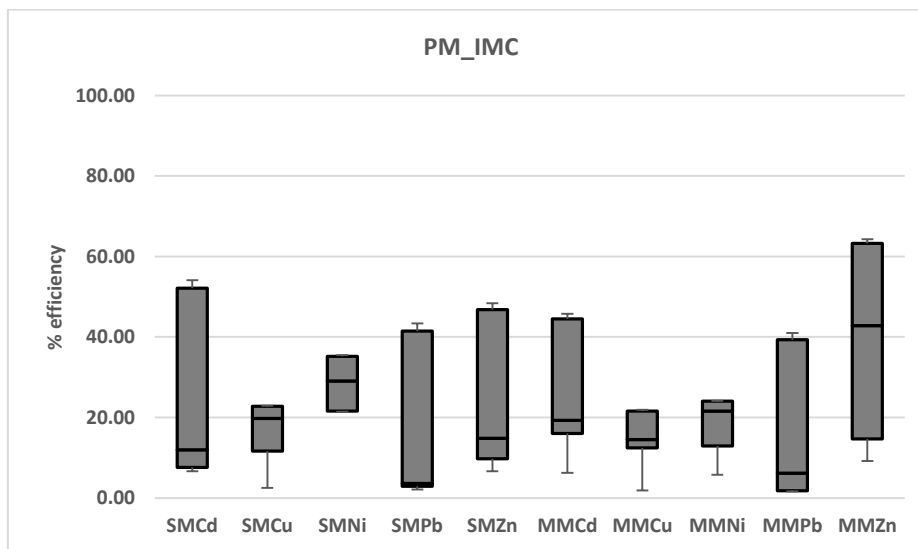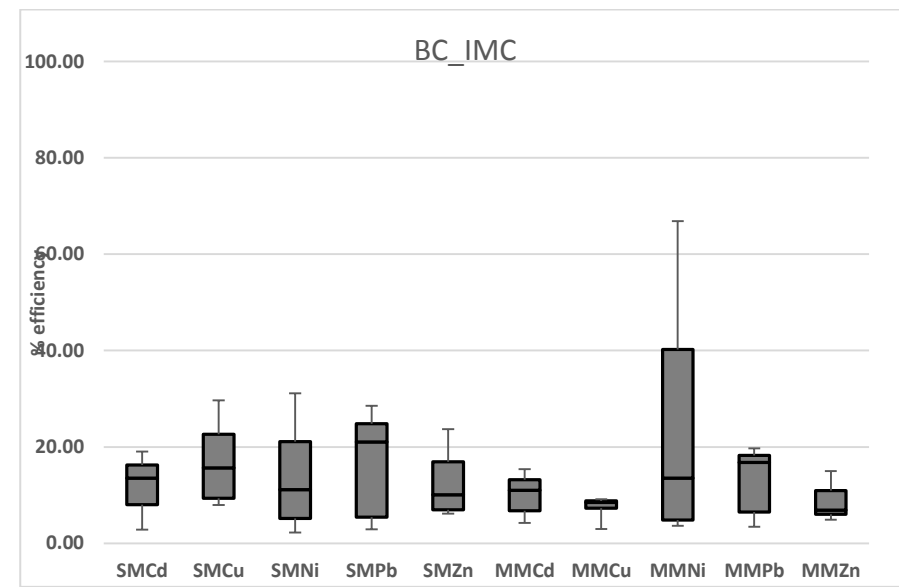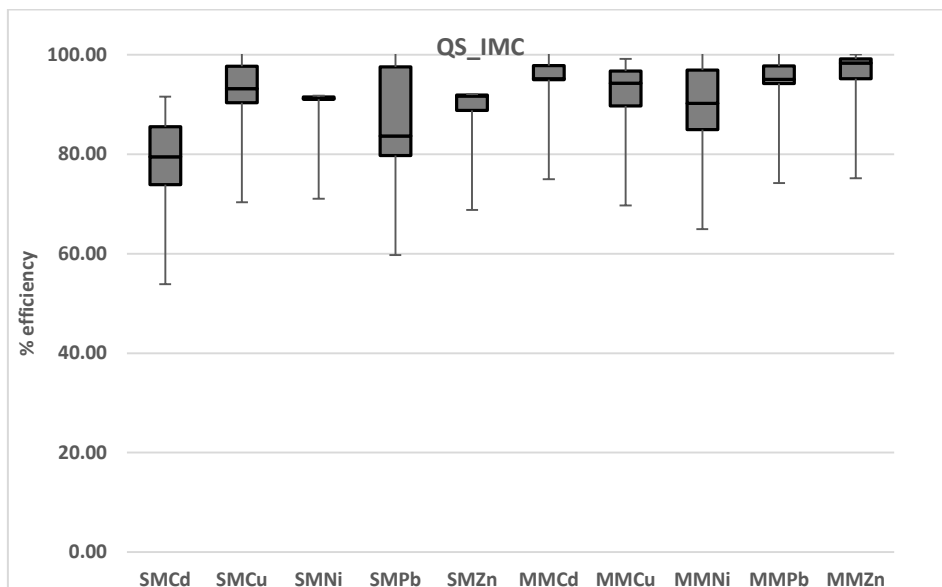
Figure 4.3 Influence of intervention concentration regime (IVC) on the leaching efficiencies of targeted metals from different substrates (BC, QS, PM, and SS) across the selected extractants as a unit factor. The lower and upper boundaries of the box represent the 25 and 75% of the sample size (n=5)
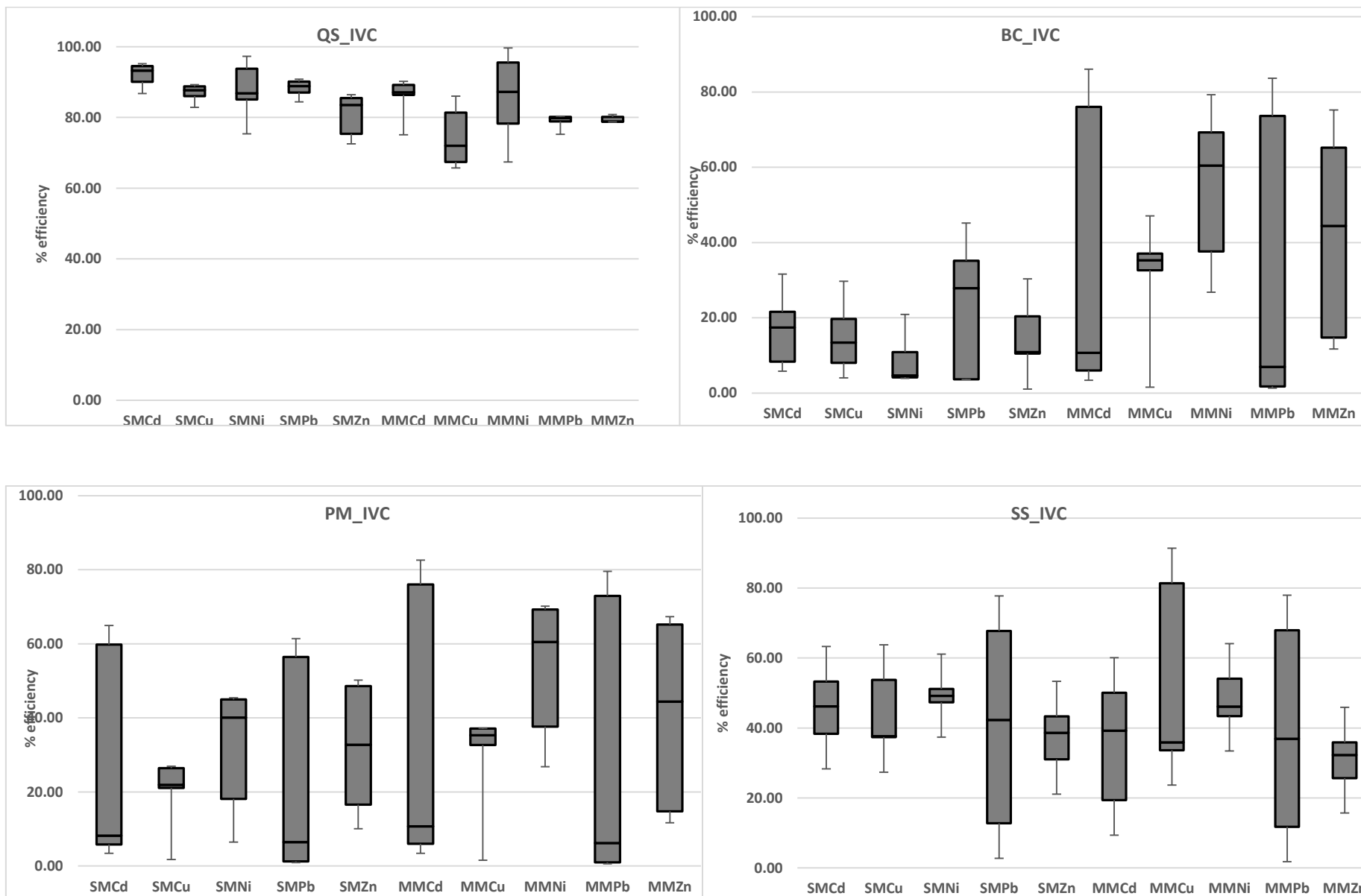
Figure 4.4 Influence of intervention concentration regime (IVC) on the leaching efficiencies of targeted metals from different substrates (BC, QS, PM and SS) across the selected extractants as a unit factor. The lower and upper boundaries of the box represent the 25 and 75% of the sample size (n=5)
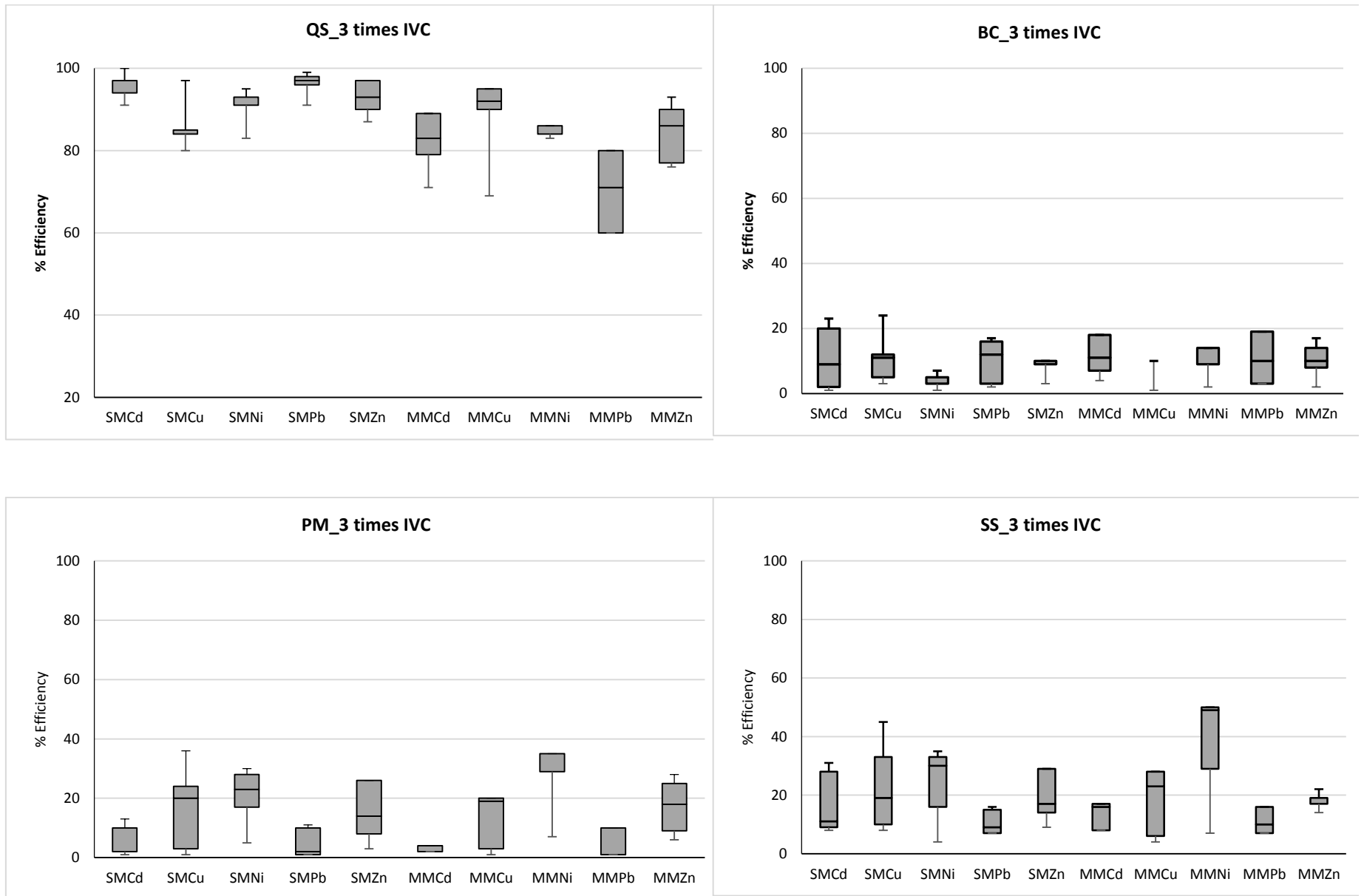
Figure 4 5 Influence of 3 X intervention concentration regime (3 X IVC) on the leaching efficiencies of targeted metals from different substrates across the selected extractants as a unit factor. The lower and upper boundaries of the box represent the 25 and 75% of the sample size (n=5)

Table 4 *2* Influence of varying contaminant regimes on the leaching efficiency of metals of interest (Cd, Cu, Ni, Pb and Zn) from different substrates across selected four extractants

Metal	Contamination regime (mgkg^{-1})	Average concentration extracted (mgkg^{-1})		
		BC	PM	SS
Cd	17 (IMC)	12	19.7	24.7
	20 (IVC)	7.3	18.2	21.3
	50 (3*IVC)	13.2	11.4	21.8
	200 (ACC)	29.3	32.6	44.3
Cu	385 (IMC)	5.9	10.3	21.9
	190 (IVC)	8.2	21.6	35.2
	570 (3 X IVC)	9.8	14.4	19.0
	200 (ACC)	16.1	26.5	38.0
Ni	40 (IMC)	5.7	13.5	23.8
	210 (IVC)	13.6	40.9	41.3
	630 (3 X IVC)	10.2	27.0	36.8
	200 (ACC)	10.7	32.8	32.7
Pb	1162 (IMC)	9.0	9.9	16.4
	530 (IVC)	11.3	16.2	24.1
	1590 (3 X IVC)	13.0	9.2	17.6
	200 (ACC)	14.6	16.5	24.3
Zn	824 (IMC)	6.1	27.2	23.4
	720 (IVC)	7.3	29.0	26.7
	2160 (3 X IVC)	10.4	17.6	17.6
	200 (ACC)	15.2	29.6	38.8

4.3.3 Influence of different extractants on metal recovery at constant metal concentration

The previous two sections dealt with the influence that variation in metal concentrations and substrates had on extraction efficiencies or profiles. This section will investigate the influence of the different extractants. In order to minimize the leaching variations associated with the different concentration regimes and substrates, the constant MM contaminated SS were considered for this discussion.

Therefore, to investigate the influence of the selected extractants on the leaching efficiency of metals of interest, the substrates were discussed individually below except for QS following the reason stated previously.

The BC contaminated with multi-metals (at ACC values) were exposed to five extractants in a batch leaching process. The data is reported in Table 4.3

For the MM-contaminated BC, the average efficiency over all metals and extractants were ~16% and ranged from 1.7 – 52.8%. By comparing the selected extractants for metal recovery efficiencies, it was observed that EDTA significantly outperformed the other extractants by a range of 2 to 10 times (on average 31% compared to the 19%, 18%, 4% and 3% for EDTA, Hacac, EDDS, CA and TA, respectively). Overall, the performance efficiency of the different extractants followed a decreasing order of magnitude of EDTA > EDDS ≈Hacac > CA > TA. The high leaching potential of EDTA over the other extractants could partially be attributed to the strong chelating ability (formation constants) for different heavy metals when compared to the other extractants used see (Table 4.6). However, the stability constant is not the only factor determining the leaching efficiencies of the extraction process. For example, in the case of EDDS, the poor efficiencies observed over EDTA could be associated with its dissociative tendency, whereby the metal in the complex is exchanged and readsorbed onto the soil surface, as described by Tsang et al. (2009).

Cd extraction followed the order EDTA>>EDDS~Hacac>CA>TA. EDTA extracted twice as much as the EDDS and Hacac, whilst it extracted 10 and 30 times more than CA and TA, respectively. For Cu and Ni the order of extraction was Hacac>EDTA~EDDS>CA~TA. Extractions with Hacac outperformed EDTA by 1.2 and 2.0 times. This phenomenon was to be expected considering the complexing affinity Hacac have for Cu and Ni (Podyachev et al., 2006). Extraction of Pb followed the order EDTA>>EDDS>>Hacac~CA~TA. EDTA extracted nearly three times more than the EDDS, while Hacac, CA and TA leached similar amounts and the least (about one-sixteenth of the EDTA extraction). The poor performance exhibited by Hacac, CA (Log K = 4.1) and TA (Log K = 5.5) were to be expected because of their poor complexing affinity for Pb compared to EDTA (Log K = 18.8) and EDDS (Log K = 12.7) (Table 4.6). The extraction trend for Zn was also observed to be higher in EDTA, followed by EDDS and Hacac with the least and similar performances exhibited by CA and TA. This leaching trend in Zn was also to be expected considering the decreasing order of their formation constants with: EDTA > EDDS > Hacac > CA > TA.

Table 4 3 Extractability of Cd, Cu, Ni, Pb and Zn from multi-metal contaminated Bentonite Clay with an initial loading capacity of 200 mgkg^{-1} subjected to batch study using selected extractants (EDTA, EDDS, Hacac, CA, and TA) at a total contact time of 30 minutes. The standard deviation on the values reported are in the range ± (0.1-0.7) (n =3)

Metal	EDTA		EDDS		Hacac		CA		TA	
	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency
Cd	105.7±0.1	52.8	59.9±0.2	30.0	47.0±0.2	23.5	11.1±0.1	5.5	3.4±0.2	1.7
Cu	45.7±0.1	22.9	35.0±0.2	17.5	61.2±0.5	30.6	10.3±0.1	5.2	8.7±0.1	4.4
Ni	19.7±0.3	9.9	13.5±0.1	6.7	39.6±0.0	19.8	9.3±0.1	4.6	3.7±0.0	1.8
Pb	80.7±0.7	40.4	29.5±0.1	14.7	2.7±0.5	6.4	6.4±0.2	3.2	5.4±0.2	2.7
Zn	59.4±0.3	29.7	45.1±0.1	22.6	16.7±0.1	9.0	9.0±0.4	4.5	5.4±0.5	2.7

*± *Values indicate Standard Deviation*

Similarly, the extraction efficiencies of metals from MM contaminated PM as influenced by the various extractants are summarized in Table 4.4.

In general, the efficiency over all metals and extractants were ~25% and ranged from 1.7 – 66.9%, suggesting higher extraction efficiency from PM than BC. However, the extraction trends remained similar for both BC and PM. EDTA once again outperformed the other extractants (on average 54% extraction compared to the 27%, 23%, 13% and 10% for EDTA, EDDS, Hacac, CA and TA, respectively) and followed the order EDTA > EDDS > Hacac > CA > TA.

Cd extraction followed the order EDTA>>EDDS≈Hacac≈CA≈TA, where EDTA extracted four and a half times as much as the rest of the leaching agents used. The EDDS, Hacac, CA and TA all extracted within experimental error the same mass of Cd. For Cu the order of extraction was the same as from the BC: Hacac>EDTA~EDDS>CA~TA, where Hacac outperformed EDTA again by 1.2 times. Ni however, did not display a similar extraction profile than with the BC and followed the order EDTA>EDDS>Hacac>CA>TA. Extraction of Pb followed the order EDTA>>EDDS≈Hacac≈CA>TA. EDTA extracted nearly 7.5 times more Pb than the other extractants. The extraction trend for Zn was also observed to be higher in EDTA, followed by the rest of the extractants, displaying similar performances but extracting half as much. As before, this leaching trend in Zn may partially be explained by

the decreasing order of their formation constants with the ligands: EDTA > EDDS > Hacac > CA > TA.

In conclusion, it is evident that based upon extraction efficiency, EDTA is the preferred extractant for Cd, Ni, Pb and Zn, and Hacac for Cu.

Table 4 4 Extractability of Cd, Cu, Ni, Pb and Zn from multi-metal contaminated Peat Moss (PM) with an initial loading capacity of 200 mgkg^{-1} subjected to batch study using selected extractants (EDTA, EDDS, Hacac, CA, and TA) at a total contact time of 30 minutes. The standard deviation on the values reported are in the range ± (0.0-0.8) (n =3)

Metal	EDTA		EDDS		Hacac		CA		TA	
	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency
Cd	133.8±0.2	66.9	29.3±0.9	14.6	24.1±0.0	12.1	31.2±0.8	15.6	3.4±0.2	17.4
Cu	80.1±0.2	40.0	75.3±0.3	37.6	92.1±0.2	46.0	10.3±0.1	6.8	8.7±0.1	1.8
Ni	102.8±0.1	51.4	91.7±0.3	45.9	56.3±0.1	28.2	9.3±0.1	14.7	3.7±0.0	1.8
Pb	115.0±0.2	57.5	15.4±0.4	7.7	23.3±0.3	11.7	6.4±0.2	6.4	5.4±0.2	1.9
Zn	108.8±0.1	54.4	57.4±0.1	28.7	35.0±0.0	17.5	9.0±0.4	22.5	5.4±0.5	24.9

*± *Values indicate Standard Deviation*

For the MM-contaminated SS (a combination of QS, BC and PM and ratio 70:20:10) as extractions summarized in Table 4.5, the average efficiency over all metals and extractants were ~33% and ranged from 1.2 – 77.1%, suggesting higher extraction efficiency when compared to PM and BC alone. The increased phenomenon may be due to changes in physicochemical parameters in the SS, thereby altering the redistribution of metal pool from less labile (reducible/Fe-Mn oxides) sites to a more mobile (exchangeable, organic and carbonate) sites (Bourg and Loch**,** 1995; Jean et al., 2007). As mentioned before, the increase may also be due to the contribution of the quartz. The order of extraction overall followed: EDTA > EDDS > CA > Hacac > TA. EDTA in general outperformed the other extractants by a range of 1.3 to 5.1 times (averaged across all metals: 61% compared to the 48%, 28%, 16% and 12% for EDTA, EDDS, CA, Hacac and TA, respectively). The efficiency of EDTA over other extractants is comparable to studies found in literature (Steele and Pichtel, 1998; Xie and Marshal, 2001).

Cd extraction followed the order EDTA>>EDDS>>CA>TA≈Hacac, where EDTA extracted between 1.5 and 7.5 times as much as the rest of the extractants. Different to the data from PM and BC extraction, the Hacac performed the poorest. For Cu the order of

extraction was not the same as from the BC and PM on their own and followed EDTA~EDDS> Hacac>CA>TA, where EDTA outperformed Hacac by 1.5 times. Ni, however, did not display a similar extraction profile than the Cu, as was observed before and followed the order EDDS>EDTA> CA>Hacac>TA. EDDS outperformed Hacac by 2.5 times. Extraction of Pb followed the order EDTA>>EDDS>CA>TA>Hacac. EDTA extracted up to 2.5 times more metals than the other extractants. The extraction trend for Zn was similar in EDTA and EDDS, followed by the rest of the extractants, where Hacac displayed the poorest extraction efficiency.

Overall, data suggests that based upon extraction efficiency, EDTA is the preferred extractant for Cd, Cu, Pb and Zn, while Ni will be best extracted with EDDS. It has to born in mind that variation in metal concentration (as described in section 4.2) has an effect on leaching efficiency, which is, at least in part, concentration driven. This prediction may therefore change in a different concentration regime, or soil composition.

Table 4 5 Extractability of Cd, Cu, Ni, Pb and Zn from multi-metal contaminated Simulated Soil (SS) with an initial loading capacity of 200 mgkg^{-1} subjected to batch study using selected extractants (EDTA, EDDS, Hacac, CA, and TA) at a total contact time of 30 minutes. The standard deviation on the values reported are in the range ± (0.1-0.9) (n =3)

Metal	EDTA		EDDS		Hacac		CA		TA	
	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency	mgkg^{-1} leached	% efficency
Cd	154.1±0.2	77.1	104.3±0.2	52.2	19.4±0.8	9.7	66.1±0.1	33.0	25.3±0.6	12.6
Cu	115.2±0.3	57.6	105.0±0.3	52.6	77.8±0.3	38.9	66.2±0.3	31.0	20.2±0.1	10.1
Ni	75.1±0.2	35.8	95.5±0.5	47.7	36.9±0.6	18.4	59.4±0.2	29.7	24.8±0.7	12.4
Pb	133.9±0.1	67.0	58.1±0.7	29.1	2.4±0.3	1.2	26.8±0.8	7.4	7.4±0.9	3.7
Zn	138.3±0.2	69.2	117.8±0.1	58.9	19.0±0.8	9.5	69.5±0.1	45.0	45.0±0.5	22.5

*± *Values indicate Standard Deviation*

Comparison to Other Results: As far as the author's knowledge goes and an internet search indicated, no studies are comparing the behaviour of metal leaching from the individual components of soil to those from a SS, using the various extractants. Although this contributes to the novelty of this research, it makes it difficult to obtain and compare results of the present study to any published work. However, some existing literature on the leaching behaviour of metals from both artificial soil (Lim and Chui, 2005; Zhang and Lo 2006) and natural soils (Wasay et al 2001; Di Palma and Ferrantelli 2005; Papassiopi et al. 1999) using chelating agents such as EDTA are available to compare with the leaching behaviour found in this investigation for the SS. For instance, according to a batch study

conducted by Lim and Chui, (2005), to investigate the recovery of heavy metals using the following process conditions: pH 4.7-8.0; extraction times, 15-240 min and EDTA, it was found that relative extractabilities followed the sequence Cd ≥ Pb >> Ni. This result compares favourably to some of the findings in this study.

Table 4 6 Complexation formation constants (Log K_{ML}) with cations (Qui et al., 2010; Tandy et al., 2004; Pettit and Powell, 2001; Schecher and McAvoy, 2001; Vaxavanidou et al 2008; Koopmans et al., 2008; Elliot and Shastri, 1999)

Chelant	$LogK_{mL}$ (T=25°C, I = 0.1M)				
	Cd	Cu	Ni	Pb	Zn
EDTA	16.5	18.8	20.1	18.8	17.5
EDDS	10.8	18.4	16.8	12.7	13.4
Hacac	NA	8.2	5.5	NA	NA
CA	4	5.9	6.6	4.1	6.2
TA	4.8	5.1	3.9	5.5	2.8

*NA means not available

4.4 Metal leaching kinetics from SS

Metal release from the soil matrix is dependent on many factors, such as the various constituents of the soil, its morphology, its environment and natural conditions. It is a slow process that influences the equilibrium condition between the soil matrix and leaching solutions (Amacher et al., 1998). In batch studies, the kinetics of the leaching process is of importance, as it provides valuable information on the leaching process and gives an indication of when maximum efficiency is reached. One reason for this research is to provide guidelines for the economic and sustainable urban mining and remediation of contaminated soil. As such, the fastest and less expensive method of extraction should be discerned. Therefore, to understand the general leaching profile of metals of interest over time, the leaching concentrations (mgkg^{-1}) of metals from multi-metal-contaminated substrates (BC, PM and SS) after 5, 10, 20 and 30 minutes of contact time with EDTA was explored. EDTA was chosen because it provided the best overall leaching efficiency as discussed in the earlier sections. It was observed (Figure 4.4) that for BC the maximum leaching is reached within 5 minutes. By contrast, for SS and PM, the maximum is reached after 10 minutes (although Pb and Zn did show a small increase after 10 minutes). This trend was followed irrespective of multi-metal (MM) contamination or extractant used. The leaching trend exhibited by the different substrates could be described as

instantaneously approaching equilibrium conditions in a relatively short contact time as shown in Figure 4.4. However, to be more empirical rather than depend only on equilibrium assumptions, it becomes essential to quantitatively and systematically study kinetics of the various metal releases from SS as a potential predictive model for natural soil processes. To study the kinetics, three mathematical equations, i.e First Order, Elovich, and Power Function equations, were used to describe the leaching of Cd, Cu, Ni, Pb, and Zn from SS, as well as the single component substrates BC and PM. These functions were selected because of their common use in the literature (Havlin et al., 1985; Sparks et al., 1980). To determine the equation(s) that best described the leaching process, a standard error of estimate (SE) was calculated for each equation to determine their spread or variability with experimental data. A relatively high value of the coefficient of correlation (R^2) and low SE were used as criteria for the best fit (Chien and Clayton, 1980). The experimental data was fitted to the various kinetic equations discussed in Potgieter-Vermaak et al. (2017) to obtain their rate constants a, b, k_1, and $1/\beta$. The First Order and simple Elovich equations yielded low values of R^2 and high SE estimates and as such, are not discussed further (The values of interest for these two models can be found in Appendix 1). Conversely, the Power Function equation appeared to give a better description of the leaching behaviour of the various metals as inferred from its R^2 and SE values and the relevant data are given in Table 4.7. The values of a ranged from 0.01 to 5.73 with a mean of 3.41, and b from 0.04 to 0.46 with a mean of 0.18, while (a x b) ranged from 0.15 to 0.83 with a mean value of 0.53 (Table 4.7). Similar values for b have been reported in the study by Motaghian and Hosseinpur (2014) and references therein, where they reported on DTPA extraction of Cu from calcareous soils. However, Motaghian and Hosseinpur (2014) reported a lower range for a (0.42 – 2.30), where the values for Cu extracted with EDTA from SS, PM and BC in our study ranged from 2.83 – 3.82. This points to a faster release rate and may be a reflection of the different properties of the substrates between the two studies. Furthermore, following the reasoning of Motaghian and Hosseinpur (2014) it can be concluded that the rate of release of all the metals will decrease exponentially as b < 1 across all substrates and extractants. As the equation of the power function indicates there was a direct correlation between the product of a and b and mass of metal leached (expressed as percentage leached), with correlation coefficients of 0.977, 0.907, 0.811, 0.806 and 0.703 for Cd, Ni, Cu, Pb and Zn respectively.
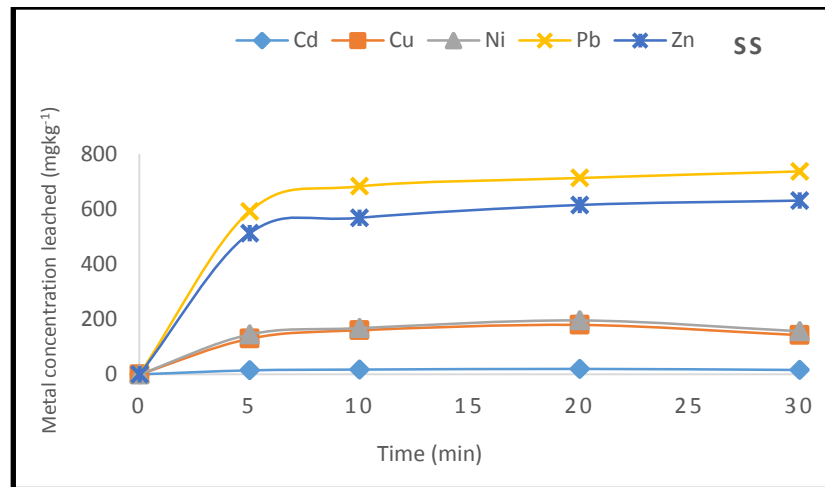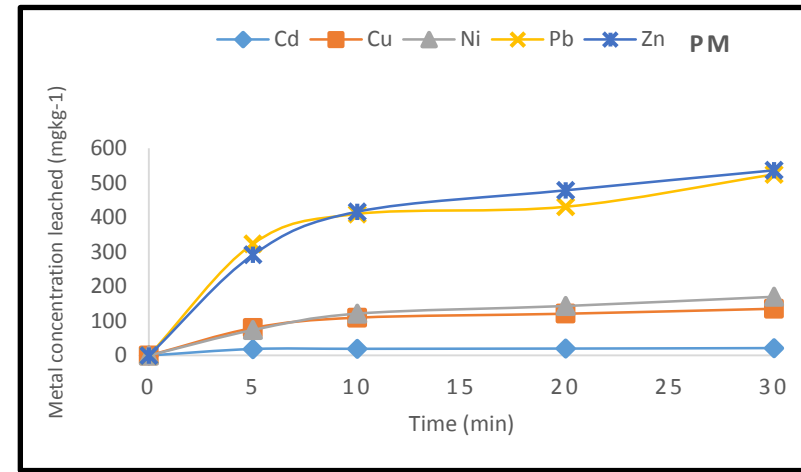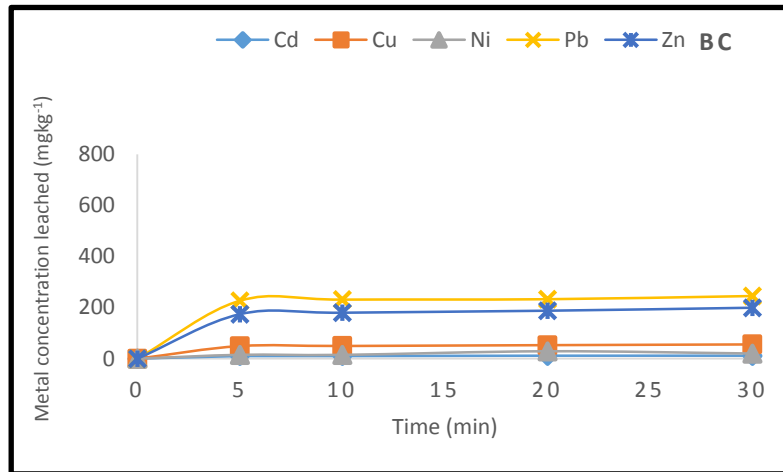
Figure 4 3 Leaching profile of single-metal-contaminated substrates (at three times intervention concentration) exposed to EDTA over time

Although the data fitting for the three equations used in this study yielded a straight line for all the metals leached, the First Order and simple Elovich equations were not as effective as the Power Function equation to describe the leaching of the metals from the various substrates. To illustrate the fitting of the three models to the data, the extraction of Pb from SS using the 5 different extractants are illustrated in Figure 4.5.

Therefore, the use of small batch rate coefficient a (0.42 – 2.30) is an indication of fast reaction process and which invariably could be described as a diffusion-controlled process (Motaghian and Hosseinpur 2014).

Table 4 7 Kinetics parameters for Cd, Cu, Ni, Pb, and Zn leached from SS, BC and PM using selected chelating agents (EDTA, EDDS, ACAC, CA, and TA).

	EDTA			EDDS			Hacac			CA			TA		
	SS	BC	PM	SS	BC	PM	SS	BC	PM	SS	BC	PM	SS	BC	PM
Cd															
a	1.52	2.91	2.54	1.03	1.73	1.3	0.38	0.14	1.3	1.96	1.16	0.49	1.14	0.89	0.37
b	0.21	0.05	0.07	0.21	0.08	0.18	0.18	0.09	0.18	0.48	0.05	0.14	0.04	0.18	0.09
a*b	0.32	0.15	0.18	0.22	0.14	0.23	0.07	0.01	0.23	0.94	0.06	0.07	0.05	0.16	0.06
R^2	0.99	0.99	0.99	0.99	0.99	0.90	0.9	0.9	0.9	0.99	0.99	0.90	0.99	0.99	0.90
SSE	0.94	0.94	0.93	0.94	0.94	0.93	0.94	0.94	0.93	0.94	0.94	0.93	0.94	0.94	0.93
Cu															
a	3.82	2.87	2.83	1.34	2.87	2.48	4.06	2.44	1.71	3.21	2.6	1.44	3.47	1.43	1.25
b	0.2	0.17	0.28	0.35	0.17	0.3	0.14	0.21	0.45	0.91	0.09	0.17	0.06	0.23	0.07
a*b	0.76	0.49	0.79	0.47	0.49	0.74	0.57	0.51	0.77	0.61	0.23	0.24	0.21	0.33	0.09
R^2	0.99	0.91	0.94	0.99	0.91	0.94	0.99	0.91	0.94	0.99	0.91	0.94	0.99	0.91	0.94
SSE	1.64	1.21	1.44	1.64	1.21	1.44	1.64	1.21	1.44	1.64	1.21	1.44	1.64	1.21	1.44
Ni															
a	3.31	0.01	3.32	3.31	0.1	3.32	3.62	0.8	0.84	3.31	0.1	3.32	3.03	0.36	2.72
b	0.25	0.46	0.17	0.25	0.35	0.17	0.29	0.33	0.56	0.25	0.35	0.17	0.2	0.2	0.08
a*b	0.83	0.01	0.56	0.83	0.04	0.56	1.05	0.26	0.47	0.83	0.04	0.56	0.61	0.07	0.22
R^2	0.99	0.84	0.91	0.99	0.84	0.91	0.99	0.84	0.91	0.99	0.84	0.91	0.99	0.84	0.91
SSE	1.61	3.19	1.56	1.61	3.19	1.56	1.61	3.19	1.56	1.61	3.19	1.56	1.61	3.19	1.56
Pb															
a	5.73	5.12	4.42	3.35	5.12	3.26	2.74	0.4	3.26	3.38	4.93	1.74	4.51	3.0	4.42
b	0.12	0.08	0.04	0.21	0.08	0.25	0.12	0.38	0.25	0.27	0.05	0.16	0.02	0.1	0.04
a*b	0.69	0.41	0.18	0.7	0.41	0.82	0.33	0.15	0.82	0.91	0.25	0.28	0.09	0.3	0.18
R^2	0.92	0.87	0.93	0.97	0.87	0.93	0.83	0.87	0.93	0.95	0.87	0.93	0.87	0.87	0.93
SSE	2.22	0.99	1.94	2.22	0.99	1.94	2.22	0.99	1.94	2.22	0.99	1.94	2.22	0.99	1.94
Zn															
a	5.57	3.24	3.86	5.17	3.24	5.05	3.32	4.04	1.02	5.17	5.69	3.76	4.56	3.24	3.1
b	0.12	0.15	0.33	0.07	0.15	0.18	0.38	0.17	0.56	0.07	0.08	0.26	0.16	0.15	0.18
a*b	0.67	0.49	1.27	0.36	0.49	0.91	1.26	0.69	0.57	0.36	0.46	0.98	0.73	0.49	0.56
R^2	0.98	0.99	0.96	0.98	0.99	0.96	0.98	0.99	0.96	0.98	0.99	0.96	0.98	0.99	0.96
SSE	2.16	1.81	1.88	2.16	1.81	1.88	2.16	1.88	1.88	2.16	1.81	1.88	2.16	1.81	1.88
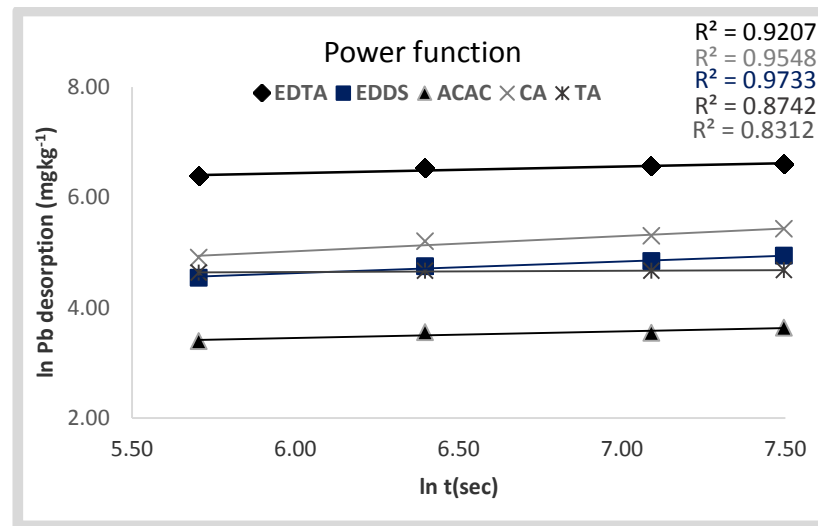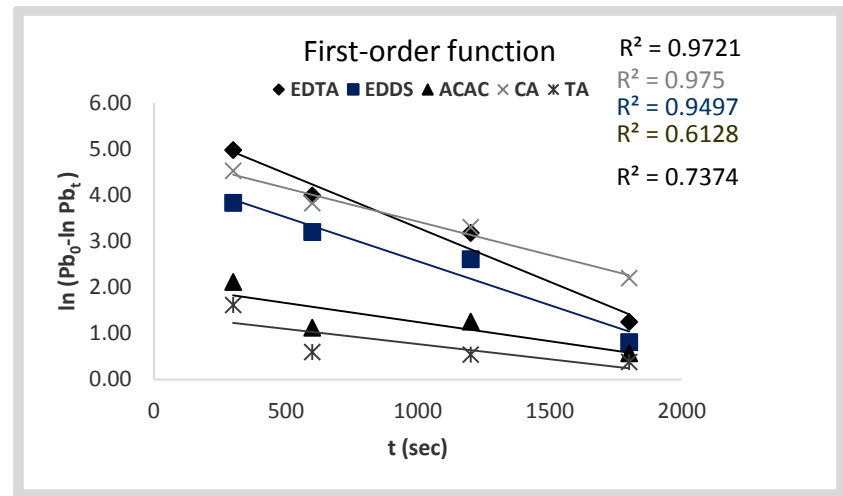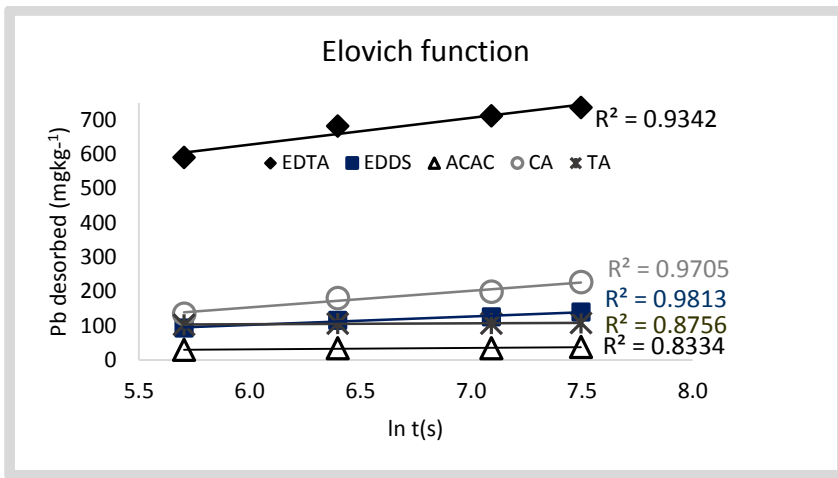
Figure 4.5 comparison of Pb leaching from SS when applying the power function, Elovich and first order equation and using five different extractants

4.5   Conclusions

The influence of different constituents of the SS on the leaching behaviour of single metal and multi-metal systems were studied using batch-leaching experiments with solid/liquid ratios of 1:10 across five extractants over a 30 min interval time. During the batch experiments, the effects of three variables on the leaching behaviour of targeted metals, the influence of varying contaminant regimes on the leaching efficiency of the substrates and the influence of selected extractants on the potential recovery of targeted metals at constant contaminant regime were measured. Firstly, it was observed that BC and SS behaved similarly in contrast to PM with respect to the leaching of their SM and MM contaminants. Secondly, it was observed that concentration fundamentally influenced metal release efficiencies. It was the strongest influence in the SS, followed by PM and BC which leached the least. Thirdly, that metal recovery was specifically influenced by the different extractants (e.g. Cu-Ni-Hacac; Cd-CA). EDTA outperformed all the other extractants evaluated. TA performed the least effective of the extractants. The kinetic equations studied indicated that Power Function equation gave the best descriptions of the leaching behaviour of the targeted metals as inferred by its R^2 and SE parameters. Overall, metal releases from SS can be described as a diffusion controlled process.

The influence of different leaching methods on metal recovery from SS is discussed in Chapter Five.

Chapter 5

Evaluation of the application of batch, column and heap leaching processes of contaminated simulated soil, to recover metals of interest.

This chapter presents the data obtained after a simulated soil (artificially contaminated with a multi-metal mixture of Cd, Cu, Ni, Pb and Zn) were washed with four different leaching agents (EDTA, EDDS, Hacac and CA) using three different leaching processes (batch, column and heap leaching). As this section of the work presented itself ideally as a scientific article, the data will be described here in paper format.

5.1   Introduction

Urban mining is becoming more attractive as economically essential metals used for current and future green technologies are rapidly being depleted due to global industrialization and demand (Kesler, 2010; Gordon et. al., 2006). Depletion in this context could imply that the amount of available metals is limited, due to extraction currently being either, economically prohibitive, or technically demanding. For example, copper (Cu) ore, is typically present in the earth's crust as copper-iron-sulphide and copper sulphide minerals, e.g. chalcopyrite $CuFeS_2$, or CuS_2 (Henckens et al., 2016; Brierley, 2008). However, reserves are such that, it is now rare to find a large copper deposit averaging more than 1 or 2% Cu, making their concentration in an ore body inevitably low (Kostov et al., 2008). Furthermore, there are predicted shortages in ore reserves for metals playing a significant role in technological progression. This shortfall can be overcome by utilizing waste repositories. Studies (Sapsford et al., 2016) have shown that many of these metals are present in significant concentrations in the wastes residue amenable to leaching, as well as in contaminated soils (Sapsford et al., 2016; Johansson et al., 2013). Presently, approximately 2 million potentially polluted sites have been identified in Europe and in the United States, with 40-50% of these sites (EEA, 2007; Fedje et al. 2013) impacted with heavy metals. In Sweden alone, more than 80,000 historically contaminated industrial sites have been reported (Dermont et al., 2008a; Sepa, 2009a). Research reported steep increases (up to 2040%) of heavy metals in soils and dumpsites in Nigeria and other African countries (Anikwe and Nwobodo, 2002). In Ghana, Odai et al. (2008) reported levels of Cd and Pb far higher than the WHO/FAO recommended values. This figure, although of environmental concern, offers a potential 'resource hub' for future recovery. The recovery of metal resources from secondary sources is regarded as a beneficial approach, extending the

efficient use of metals (Hultman and Corvellec, 2012), reducing pressure on virgin resources (Sadhukhan et al., 2016; Kesler, 2010) and resulting in major energy savings relative to the level of energy inputs required to produce metals from primary sources (Grathwohl and Susset, 2009). The effectiveness of any recovery process is usually characterized by the ability of the chemical reagent to potentially solubilize and extract the elements bound in, or associated with, a particular soil phase. This is commonly evaluated in the laboratory through dynamic (column and heap) and static (batch) (Jackson et al. 1984; Garrabrants and Kosson, 2005) studies.

In static studies, mixtures are vigorously stirred during the entire reaction time to enhance homogeneity and reactivity. This method has been noted for its ease of operation and provide qualitative predictive information on the leaching behaviour of metals from a soil matrix (Al-Abed et al., 2008; Ham et. al., 1979) on a larger scale. However, the efficiency of the batch approach is somewhat compromised because the soils are often subjected to excessive mobilization of dissolved organic carbon and/or colloids that is uncharacteristic of field scenarios (van der Sloot et al. 2003; Kendall, 2003). Dynamic studies, involve a percolation process that is characterized by a continuous flow of liquid through a fixed bed of feedstock (soil), which invariably presents a better simulation to a leaching process that occur under field conditions (Wasay, 1992; Dijkstra et al. 2006).

In this study, two dynamic (column and heap) leaching systems as well as a batch system were used as potential techniques to investigate the leaching of heavy metal from polluted simulated soil (SS) with various organic solvents. We have reported in Potgieter-Vermaak et al. (2017) what the influence on leaching profiles of synthetically contaminated individual soil components and its composite (a simulated soil) are, using a batch approach. The objective of this investigation is to evaluate metal leaching behaviour as influenced by the selected extractants (EDTA, EDDS, Hacac and CA), the process of leaching (batch, column or heap) and the combined interactive effects of these two factors. These findings will feed into the third phase of this investigation, during which the processes will be applied to industrially impacted environmental samples, to evaluate its use as predictive tool.

5.2   Experimental

5.2.1   Chemicals and materials

To minimise variables during this comparative study, use was made of a simulated soil (SS), consisting of kaolinite clay (KC), peat moss (PM) and quartz sand (QS) (all sourced from local shops) mixed in a ratio of 70:20:10 for QS: BC: PM according to standard guidelines (OECD, 1984; ISO 1998). In chapter 4, use was made of bentonite clay. This clay proved to be problematic when the column process was used, as it caused a water log and the desired flow rate could not be achieved. The clay content of the SS was therefore replaced with kaolonite, which did not present the same problem as benotinte clay. An important conclusion could however be drawn from this i.e. that if the clay content of a natural soil is mainly bentonite, column leaching will prove to be ineffective for metal recovery purposes. The contaminated SS were prepared as described in section 3.1.2.1.

5.2.2   Experimental methods

The SS was analysed for its physical and chemical properties, using standard techniques and approaches, as described in section 3.2.2. All metal concentrations were determined by ICP-OES and sample concentrations were corrected for matrix effects by procedural blanks, normalized to sample mass and reported as mgkg^{-1} dry weight, as described in section 3.3.1.7.

5.2.3   Contamination protocol

For this section of the work, accurately weighed (20± 0.0005 g) SS was contaminated with a multi-metal (MM) solution containing Cd, Cu, Ni, Pb and Zn of concentrations 50, 570, 650, 1590, and 2160 mgkg^{-1}, respectively. These concentrations are three times the intervention values set as regulatory limits by the Department of Petroleum Resources in Nigeria (DPR, 2002). The motivation behind these concentrations were to simulate heavily contaminated land in Nigeria, with the specific aim of showing the potential of the 3 methods of washing / leaching and the 4 leaching agents, discussed further on in this chapter, to remediate the soil and recover the metals of interest in an economically sustainable way. The metals investigated in this study were chosen based on their potential to generate revenue when recovered, as well as their toxicity potential to both the environment and humans. SS was used is to minimise the variability that a natural or industrially impacted soil will create in the data set so that the data could be used as predictive tool. The MM loading achieved was 96 ± 2.37 %.

5.2.4 Batch leaching test

As described in section 3.3.4, a standard batch leaching test at liquid-to-solid ratio (L/S) of 10:1 was used to determine the leaching potential of the metals in the contaminated SS. For reader convenience a brief description is given here. 20 ± 0.0003 g of dried contaminated substrate was added to 200 cm^3 of leaching solution (EDTA at 0.034 moldm^{-3} or EDDS at 0.034 moldm^{-3} or Hacac at 3.0 moldm^{-3} or CA at 0.026 moldm^{-3}) to maintain a solid/liquid ratio of 1:10. These concentrations ensured an excess of extractant. The mixtures were agitated at 3000 rpm for 30, 60, 90, 120 and 150 min and then centrifuged to achieve separation. A procedural blank was carried out by using deionized water as extractant on all substrates, to determine the contribution of the respective substrates. The changes in pH upon exposure to the leaching agent, as well as after 150 minutes were monitored. After each run, an aliquot of the supernatant (1cm^3) solution was filtrated with a syringe filter (0.45μm) into a plastic vial of 15 cm^3 capacity and later made up to 10 cm^3 with deionized water (or industrial methylated spirit in the case of Hacac). Subsequently, the filtrates were analysed by ICP-OES and the selected metal concentrations retained in the adsorbent phase (mgkg^{-1}) were calculated. The percentage metal leached from the soil were calculated using Equation (1).

$$\% \ metal \ leached = \frac{mass \ of \ metal \ in \ supernatant}{mass \ of \ metal \ originally \ loaded \ on \ substrate} \times 100 \qquad (1)$$

To ensure repeatability, this procedure was carried out in triplicate. Procedural blanks and matrix-matched standards ensured rigorous QA and QC.

5.2.5 Column leaching test

To compare the in-situ leaching with a dynamic process, a column leaching approach was used, as described in section 3.3.5. In short, a glass chromatographic column equipped with a sintered disc frit was used, so that the flow rate could be controlled. Various experimental set-ups were tried and tested (not shown here) and the following set-up shown in Figure 3.4 delivered the best results. The soil was uniformly packed (8 cm) using a slurry technique and the SS was sandwiched between two layers of sand (0.5cm each). The sand bed on the frit was to ensure no clogging or loss of sample and at the top, it ensured that the introduction of the sample did not disturb the soil bed. After packing, the column head was brought to a minimum before the leaching agent (EDTA, EDDS, Hacac, CA) was introduced, using a separating funnel as a reservoir and a head of 10 cm^3 was maintained. The flow rate was maintained at 0.8 cm^{3}min^{-1}. The leachate was collected every 30 minutes over a total

leaching time of 150 minutes and the volume measured to the nearest 0.5 cm^3. The Cd, Cu, Ni, Pb, and Zn concentrations leached from the SS by the different leaching agents were determined using ICP-OES as described in section 3.3.1.7, after the pH of the leachate was measured. Each extractant was run in triplicate.

5.2.6 Heap leaching test

Heap leaching, as a dynamic process, was also considered for comparison to the in-situ leaching method. The heap configuration was simulated as illustrated in Figure 3.5, and as described in section 3.3.6. In short, a perforated Buchner funnel (70 mm) with a filter paper (0.45 um) was used to contain the heap and facilitate collection of the leachate over time for metal analysis. The SS (20 ± 0.0004 g) was irrigated with the respective leaching agents, which was supplied a continuous flow from a reservoir, for which a 250 ml separating funnel has been used. An average flow rate under gravity of 11.2 cm^{3}min^{-1} was maintained and the leachate collected over time intervals of 30, 60, 90, 120, and 150 min. The leachate was analysed for Cd, Cu, Ni, Pb, and Zn, as described in section 3.3.1.7. Each extractant run was done in triplicate. The pH measurements of the leachate samples was taken before metal analysis on the ICP-OES.

5.3   Results and Discussion

5.3.1 SS characteristics

The ultimate goal of the work reported here is to use artificially contaminated simulated soil (SS) of known composition as a model to determine leaching efficiencies of impacted environmental samples. Selected physicochemical properties of SS were determined and are compared with those reported for some natural soils in literature. This was summarized in Table 4.1, Chapter 4, page 53.

5.3.2 Batch process

The leaching behaviour of the 5 metals of interest were investigated by subjecting the solid SS sample to an in-situ leaching process that is characteristic of a batch configuration. The leaching trend for these metals were monitored over leaching time intervals of 30, 60, 90, 120, and 150 min using selected extractants (EDTA, EDDS, Hacac and CA). The results, indicating the mass of metal per kg SS extracted after 150 min, as well as the % extraction efficiency for each metal, are summarised in Table 5.1. From the data it is evident that

specific metals reported different extraction efficiencies across the 4 extractants investigated.

For Cd the order of leaching efficiency was EDTA=CA>EDDS>>Hacac, with an average efficiency of 24.4 % (range: 34.6 – 4.4). EDTA and CA leached the most Cd (17 mgkg^{-1}), followed by EDDS (12 mgkg^{-1}) and Hacac (2.1 mgkg^{-1}). EDTA and EDDS are strong chelating agents that form multidentate ligands with metal cations. It is expected that molecules with more carboxyl groups have higher extracting capacity than a molecule with less carboxyl groups (Zaleckas et al., 2013), which could explain the higher efficiency of EDTA and CA (four and three carbonyl groups, respectively). However, this would suggest that EDDS (4 carbonyl groups) should behave similar to the EDTA, which is not the case (12 mgkg^{-1}). This phenomenon could partly be attributed to the influence of acid dissolution in the CA. CA will reduce soil pH by releasing hydrogen ions and forming soluble complexes by a complexation reaction (Evangelou et al., 2007). In our study, we have shown that CA lowered the pH to 3.64 in comparison to 5.45 and 5.54 by EDTA and EDDS, respectively. Peters (1999) and Schwab et al. (2008) also reported a higher extraction efficiency for Cd during the application of CA and EDTA as compared to EDDS and Hacac. In addition, higher mobilisation of targeted metals are observed for EDTA compared to EDDS (Xie and Marshall 2001; Steele and Pichtel, 1998). The effectiveness is related (or part related) to the fact that the metal complexes with EDDS are somewhat lower in stability than the corresponding complexes with EDTA (Table 5.3).

For Cu the order of extraction efficiency was completely different to that of Cd (Hacac>EDTA>EDDS>CA; with an average efficiency of 30.1 % and a range of 41.8 to 11.7). The Hacac leached the highest amount of Cu (226.8 mgkg^{-1}), followed by EDTA (204 mgkg^{-1}) and EDDS (131 mgkg^{-1}). CA leached only 65 mgkg^{-1} of Cu. The high extraction of Cu leached by Hacac over other extractants was observed before (Potgieter-Vermaak et al., 2017) and was expected, as Hacac is known to preferentially form complexes with Cu ion (Podyachev et al., 2006). Cu mobilisation by EDDS was significantly lower than what was observed for EDTA, even though EDTA (Log$K$ = 18.8) is about similar to EDDS (Log$K$ = 18.4) (Table 5.2). According to Orama et al.(2002), the metal complexes with EDDS are somewhat lower in stability than the corresponding complexes with EDTA. This phenomenon could be attributed to the dissociative tendency of CuEDDS to exchange its metal in the complex and readsorb onto the soil surface (Tsang et al., 2009).

The Ni had a very similar profile to Cu and only differed slightly in that the EDDS and CA exchanged places in the order of extraction efficiency. The average extraction efficiency percentage for Ni was 27.1 % (37.3 – 16.4). EDTA leached the highest amount of Ni (227.7 mgkg^{-1}), followed by Hacac (215.1 mgkg^{-1}) and CA (97.9 mgkg^{-1}). Surprisingly, EDDS (88.4 mgkg^{-1}) leached the least amount of Ni.

In contrast, Pb had the leaching agent profile EDTA>>EDDS≈CA>>Hacac with an average of 17.7 % and a range of 45.4 to 1.9 mgkg-^{1} leached. EDTA (702 mgkg^{-1}) leached the most Pb followed by EDDS (207 mgkg^{-1}) and CA (150 mgkg^{-1}) with Hacac (30 mgkg^{-1}) leaching the Pb least. EDTA extracted between 4 times and 20 times as much Pb as the rest of the extractants. This result was to be expected due to the much stronger complexation of PbEDTA compared to other metal complexing extractants (Tandy et al ,2004 and references therein).

Finally, Zn displayed a profile that was similar to Cd, but the EDTA extracted Zn about 1.5 times better than CA and the Hacac and EDDS arbitrarily changed places. The average extraction efficiency was 16.8% and ranged from 26.9 down to 6.0%.

It is further noted from Table 5.1, that overall EDTA outperformed the other extractants and an average extraction efficiency of 36.4 ± 6.7% was calculated across the 5 metals of interest. The other extractants had similar efficiencies overall (20.2, 18.6, 17.7 % for Hacac, CA and EDDS, respectively). The extraction behaviour observed indicated a possibility to recover certain metals, using sequential extraction approaches, due to preferential leaching. For example, Cu and Ni can be separated from the rest using Hacac because of their structure, acidic properties and ability to form complexes (Podyachev et al., 2006 and references therein). This can be followed by a CA leach which will preferentially remove Cd. The Pb and Zn can then be separated from the matrix by an EDTA leach.

Table 5.1 Extractability of Cd, Cu, Ni, Pb, and Zn in artificially contaminated SS by a batch extraction with selected extractants. The standard deviation on the values reported are in the range ± (0.1 – 13.4) (n =3).

Metal	EDTA		EDDS		Hacac		CA	
Loading (mgkg^{-1})	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency
Cd (50)	17.0±3.0	34.5	12.0±0.1	24.1	2.1±0.1	4.4	17.0±0.2	34.6
Cu (550)	204.6±5.6	37.9	131.6±9.6	28.9	226.8±9.9	41.8	66.5±0.6	11.7
Ni (650)	227.7±4.7	37.3	88.4±5.5	16.4	215.1±10.1	36.7	97.9±1.1	18.1
Pb (1590)	702.1±15.2	45.4	207.0±0.8	13.1	30.1±1.0	1.9	150.2±0.6	10.3
Zn (2160)	567.7±9.1	26.9	26.9±10.2	6.0	327.0±13.4	16.4	356.2±1.9	18.2

*± *Values indicate Standard Deviation*

Table 5.2 Complexation formation constants (Log K$_{ML}$) with cations (Qui et al., 2010; Tandy et al., 2004; Pettit and Powell, 2001; Schecher and McAvoy, 2001; Vaxavanidou et al 2008; Koopmans et al., 2008; Elliot and Shastri, 1999)

Chelant	LogK$_{mL}$ (T=25°C, I = 0.1M)				
	Cd	Cu	Ni	Pb	Zn
EDTA	16.5	18.8	20.1	18.8	17.5
EDDS	10.8	18.4	16.8	12.7	13.4
Hacac	NA	8.2	5.5	NA	NA
CA	4	5.9	6.6	4.1	6.2
TA	4.8	5.1	3.9	5.5	2.8

5.3.3 Column leaching

In-situ extraction leaching was performed on SS by using a column approach and a solid liquid ratio of 1: 10 to investigate the extraction of the metal species of interest. To illustrate the elution trends, the leaching concentrations (mgkg^{-1}) of metals from SS after 30, 60, 90, 120, and 150 minutes contact time with extractants (EDTA, EDDS, Hacac and CA) were chosen. The results (indicating the mass of metal per kg SS extracted after 150 min as well as the % extraction efficiency for each metal) are summarised in Table 5.3. From the data, it is evident that specific metals reported different extraction efficiencies across the 4 extractants investigated.

For Cd the order of leaching efficiency was different to the batch study: EDTA ≈ EDDS > CA >Hacac, with an average efficiency of 19.8 % (23.8 – 12.4%) which is significantly lower than what was observed for the batch process. EDTA and EDDS leached the most Cd (11.9 mgkg^{-1}), followed by CA (10.2 mgkg^{-1}) and Hacac (6.2 mgkg^{-1}).

Cu leaching data showed very little difference between the extractants, with Hacac and CA reporting slightly lower extraction efficiencies and significantly different from the batch process, as can be seen from the data in Table 5.3. The leaching efficiency was observed to follow the order EDTA ≈ EDDS > Hacac ≈ CA with an average efficiency of 19.0% (20.8 - 17.3%). EDTA and EDDS leached 114.4 mgkg^{-1}and Hacac 97.3 mgkg^{-1}.

For Ni, the extraction efficiency differed considerably from Cd and Cu and was observed to follow the order EDDS ≈ EDTA > Hacac > CA, with an average efficiency of 39.3% (47.3 − 26.9%), which was much higher than the batch process average. EDDS leached 307.2 mgkg^{-1} and CA 174.6 mgkg^{-1} of Ni

For Pb, the extraction efficiency was in the order of CA >> EDTA > EDDS > Hacac, with an average efficiency similar to the batch process of 19.6% (50.8 − 3.2%). CA (807.7 mgkg-1) leached the most, followed by EDTA (211.5 mgkg^{-1}) and EDDS (173.1 mgkg^{-1}) with Hacac (51.2 mgkg^{-1}) leaching the least.

Zn displayed a leaching profile that was similar to Cu. However, CA leached Zn much better than Hacac and as such, the extraction efficiency followed the order EDTA ≈EDDS ≈ CA > Hacac, with an average efficiency similar to the batch process of 15.9% (18.4 -10.7%). EDTA (397.2 mgkg^{-1}) leached the most with Hacac (231.3 mgkg^{-1}) leaching the least amount of Zn.

Over all, the extraction efficiencies of EDTA, EDDS and CA (24 ± 12; 24 ± 13; 26 ± 14%, respectively) across the 5 metals of interest, were nearly double that of Hacac (16 ± 13%). The data suggest a specificity of the metals for extractant as well as process, if we compare it with the batch process. For example, CA extraction of Pb by batch process was only 10.5% effective, but with the column process the extraction efficiency was 5 times higher and outperformed the highest extraction efficiency obtained by the batch process (EDTA at 45 %). On the otherhand, Cd showed similar extraction efficiencies with EDTA and CA, but extraction in the batch process was 1.5 times higher, indicating that the process plays a significant role in determining extraction efficiency. These findings therefore suggest that these metals may be removed from contaminated soil, using a combination of processes and different extractants.

Table 5 3 Extractability of Cd, Cu, Ni, Pb, and Zn in artificially contaminated SS by a column extraction with selected extractants. The standard deviation on the values reported are in the range ± (0.1 – 21.7) (n =3).

Metal	EDTA		EDDS		Hacac		CA	
Loading (mgkg^{-1})	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency
Cd (50)	11.9±0.1	23.8	11.3±0.25	22.6	6.2±0.5	12.4	10.2±0.3	20.4
Cu (550)	114.4±2.1	20.8	110.7±3.8	20.1	97.3±10.8	17.7	95.1±2.0	17.3
Ni (650)	290.4±1.4	44.7	307.2±3.5	47.3	248.9±6.5	38.3	174.6±0.5	26.9
Pb (1590)	211.5±1.8	13.3	173.1±15.4	10.9	51.2±3.6	3.2	807.7±21.7	50.8
Zn (2160)	397.2±3.1	18.4	389.0±7.9	18.0	231.0±17.3	10.7	355.0±1.0	16.4

*± **Values indicate Standard Deviation**

5.3.4   Heap leaching

To further compare a dynamic perculating process with the batch process reported in 3.2, a heap leaching experiment with a solid liquid ratio of 1: 10 were used to investigate the leaching behaviour of Cd, Cu, Ni, Pb and Zn bound to SS as well. As before, the elution profile over time intervals (30, 60, 90, 120, and 150 minutes) was monitored with the selected extractants (EDTA, EDDS, Hacac, and CA). The results (indicating the mass of metal per kg SS extracted after 150 min, as well as the % extraction efficiency for each metal) are summarised in Table 5.4. It was observed that the specific metals reported distinctly different extraction efficiencies across the four extractants examined.

For Cd, the leaching efficiency followed the order EDTA ≈ EDDS > CA >Hacac, with an average efficiency of 36.3 % (48.2 – 21.4%) across all extractants, exceeding both previous processes by 33 and 46%, respectively. EDTA and EDDS leached the most (24.1 mgkg^{-1}), followed by CA (16.2 mgkg^{-1}) and Hacac (10.7 mgkg^{-1}). The data suggests, as seen for the column leaching, that Cd extraction is mainly dependent on by the process, with heap leaching outperforming the other two processes.

For Cu, the extraction efficiency was similar to the batch process, with Hacac > EDTA ≈ EDDS > CA but with a lower average efficiency of 20.6% (28.7 – 15.4%). Hacac leached the most (157.7 mgkg^{-1}) CA the least (84.6 mgkg^{-1}). Based on formation constants, this result is unexpected (see Table 5.2). The enhanced Cu extraction efficiency by Hacac is only observed for the batch and heap leaching processes. Therefore, it seems as though the process again plays a significant role in the recovery of the metals.

Contrary to the other processes, the Ni extraction efficiency was in the order Hacac > EDTA ≈ EDDS > CA, similar to the Cu, with an average efficiency of 27% (30.5 – 22.4%). There was however, not a big difference in the efficiency of the Hacac, EDTA and EDDS. Hacac (198.2 mgkg^{-1}) leached the most and CA leaching the least (145.7 mgkg^{-1}). The effectiveness of the three leaching agents, Hacac, EDTA and EDDS, is seemingly not dependent or only partially dependent on their respective formation constants (displayed in Table 5.2), since this is in the order of Ni-EDTA > Ni-EDDS > Ni-acac. Clearly other factors are also at play here.

For Pb, the extraction efficiency did not follow the order of the column process and resembled that of the batch process, namely EDTA > CA >> EDDS > Hacac with an average efficiency of 14.2% (24.6 – 5.1%). This is a bit lower than what was reported in the two previous processes. EDTA leached the most (24.6 mgkg^{-1}) and Hacac leached the least (5.1 mgkg^{-1}). The efficient removal of Pb by EDTA treatment can be explained considering the much higher stability constant of Pb-EDTA (Log k = 18.8) if compared to the rest of the extractants (Pb-EDDS [Log K = 12.7], Pb-CA [Log K = 4.1] (Orama et al., 2002) and Pb-Hacac [not available]). However, this assumption is not applicable for the perceived efficiency of CA over EDDS if one considers their formation constants. Such a result maybe due to lower stability of Pb-EDDS complexes (Yip et al., 2010) or better still, the acid effect of the CA, which can reduce the soil pH and form soluble complexes with Pb (Evangelou et al., 2007). Hacac is less efficient for Pb recovery because of its poor complex stability.

Zn extracted noticeably poorer with this process, regardless of the extractants used. The extraction efficiency was similar in magnitude for all extractants used and was in the order EDTA ≈ EDDS ≈ CA ≈ Hacac, with an average efficiency of 6.5% (7.3 - 5.5%) which is much less (about 3-fold) than with the other two processes. The low extraction efficiency of this process on Zn contaminated soil is in line with previous findings by Tandy et al. (2004). It can be said that in the case of Zn, the extraction process is the main factor in determining its recovery.

Overall, it was further observed from Table 5.4 that EDTA (25 ± 15%) and EDDS (22 ± 15%) had similar efficiencies, calculated across the 5 metals of interest, and marginally outperformed the other extractants. The other extractants yielded 18 ± 12% and 19 ± 10% for Hacac and CA, respectively.

Table 5.4 Extractability of Cd, Cu, Ni, Pb, and Zn in artificially contaminated SS by a heap extraction process with selected extractants. The standard deviation on the values reported are in the range ± (0.1 – 8.9) (n =3).

Metal	EDTA		EDDS		Hacac		CA	
Loading (mgkg^{-1})	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency
Cd (50)	24.1±2.1	48.2	21.5±0.1	43.0	10.7±0.4	21.4	16.2±0.2	32.4
Cu (550)	104.5±0.3	19.2	105.9±1.3	19.3	157.7±2.6	28.7	84.6±2.6	15.4
Ni (650)	175.7±0.1	27.0	183.3±0.2	28.2	198.0±1.7	30.5	145.0±1.1	22.4
Pb (1590)	390.4±0.7	24.6	155.3±8.9	9.8	81.0±3.9	5.1	274.0±5.9	17.3
Zn (2160)	158.2±0.9	7.3	155.7±0.6	7.2	119.0±3.6	5.5	127.8±3.4	5.9

*± *Values indicate Standard Deviation*

5.3.5 Comparison of the three processes

To investigate the leaching process efficiency of the 5 metals of interest at three times their respective intervention value concentrations from a SS, a static (batch) and two dynamic (column and heap) processes were investigated We appreciate that direct comparison between the three processes are influenced by technical and dynamic differences (for example, velocity variations), however, by keeping other parameters (pH, solid/liquid ratio) constant, a relative comparison of the leaching tests could give insight in formulating a predictive leaching trend for the targeted metals and their released from a contaminated soil.

5.3.5.1 Extractant efficiency vs metal release

In order to compare the potential recovery of the metals of interest, using the 4 leaching agents (extractants) and the three different processes of batch leaching (BS), column leaching (CS) and heap leaching (HS), data presented in Table 5.5 and Figure 5.3 were used. The important observations will be noted for each metal in the section below.

The efficiency trends of the three processes shown in Figure 5.3, displayed significant differential behaviour for the different metals extracted. This can be expected due to the different properties of the metals and their different mechanisms during soil washing (Sun et al., 2001; Zhang et al., 2010). The process efficiency for the three processes followed the order BS ≈ CS > HS with average efficiency of 22.3% (range: 23.2 – 20.9%). The lower process efficiency exhibited by HS was also reported previously in literature by other scholars

(Acevedo, 2002; Brierley, 2008). However, the process efficiencies of CS and BS appeared to be similar when calculated across the 4 extractants. This is contrary to a study reported by Hauser et al. (2005) where it was found that column leaching, using the chelating agent EDTA was better suited, especially for Zn and Pb removal, from contaminated soils than batch leaching.

Cd: HS showed a higher average process efficiency (36.0 ± 12%) taken across all the extractants, than BS (24.5 ± 14.6%) and CS (20.3 ± 5.0%). It has to be borne in mind that a large variation in the data was observed. In the same vain, the highest efficiency is reported for leaching with EDTA. We can therefore conclude that Cd may be best extracted with EDTA using the heap leaching process.

Cu: Cu extraction was favoured by the BS with an average process efficiency across the extractants of 30.3 ± 13.3%, while for the CS and the HS it were 19.3 ± 2.1 and 21 ± 5.6, respectively. Table 5.5 also indicates that Hacac was the leaching agent that achieved the highest extraction efficiency.

Ni: The highest process efficiency, calculated across all leaching agents, as for the CS and was 45 ± 7.7%, while the BS and HS were 27 ± 11.6% and 26.6 ± 2.4%, respectively. The leaching agent providing the highest efficiency was EDTA. Therefore, the data suggested that a column leaching with EDTA will provide the best recovery for Ni.

Pb and Zn: The average process efficiency for these two metals were the highest with the BS and CS (BS_{Pb} 17.5 ± 18.9%; CS_{Pb} 19.8 ± 21.2%) and (BS_{Zn} 16.8 ± 8.6%; CS_{Zn} 15.8 ± 3.3%). For Pb the highest extraction efficiency was with CA and for Zn with EDTA. This suggests that Pb be best extracted by column perculation and CA, while Zn would be best extracted with the batch process and EDTA.

5.3.5.2 Extractant efficiency vs process used

In order to compare the influence of the 4 leaching agents (extractants) on the process efficiency of the batch study (BS), column study (CS) and heap study (HS), the data presented in Table 5.5 and Figure 5.4 were used.

Figure 5.4 provides a graphical data summary, including the median, quartiles, skewness of distribution as well as the mean percentage extraction in a comparison with the different processes (BS, CS and HS) studied. The data were averaged over all the metals. It is firstly noticed that the HS showed the most variation for EDTA and EDDS, but for Hacac and CA the variation was most for the BS and CS, respectively. For the EDTA plot, each of the

operations illustrated different trends in their skewness patterns. The batch operation is skewed to the left, the heap operation is skewed to the right, and the column operation appeared to be fairly symmetrical.

The EDDS plot showed similar trends than the EDTA, except that the average efficiency for the BS was lower. Hacac as leaching agent showed the largest 50 percentile variation for the batch process data, which may point to lower confidence as a predictive tool. On the otherhand, large variability lends itself to selective leaching. The three processes are skewed to the right. The mean values for the batch (20.3%) and HS (21.2%) were comparable, while CS (14.2%) differed by a factor of 1.5. For CA, both the column and heap systems were skewed to the right as well as displaying a larger variability when compared to the batch system that remained fairly symmetrical with minimal variability. However, the BS had a mean value of only 8.6%, while the HS (32.4%) and CS (24.2%) were significantly more efficient. Following the extraction trends, the data suggests that EDTA on average provides the highest extraction efficiency across all metals, using the heap leaching process. Due to the large variations observed across the metals for each of the leaching agents for one or two of the processes, selective leaching can be achieved by designing a multi-step contaminant specific process.
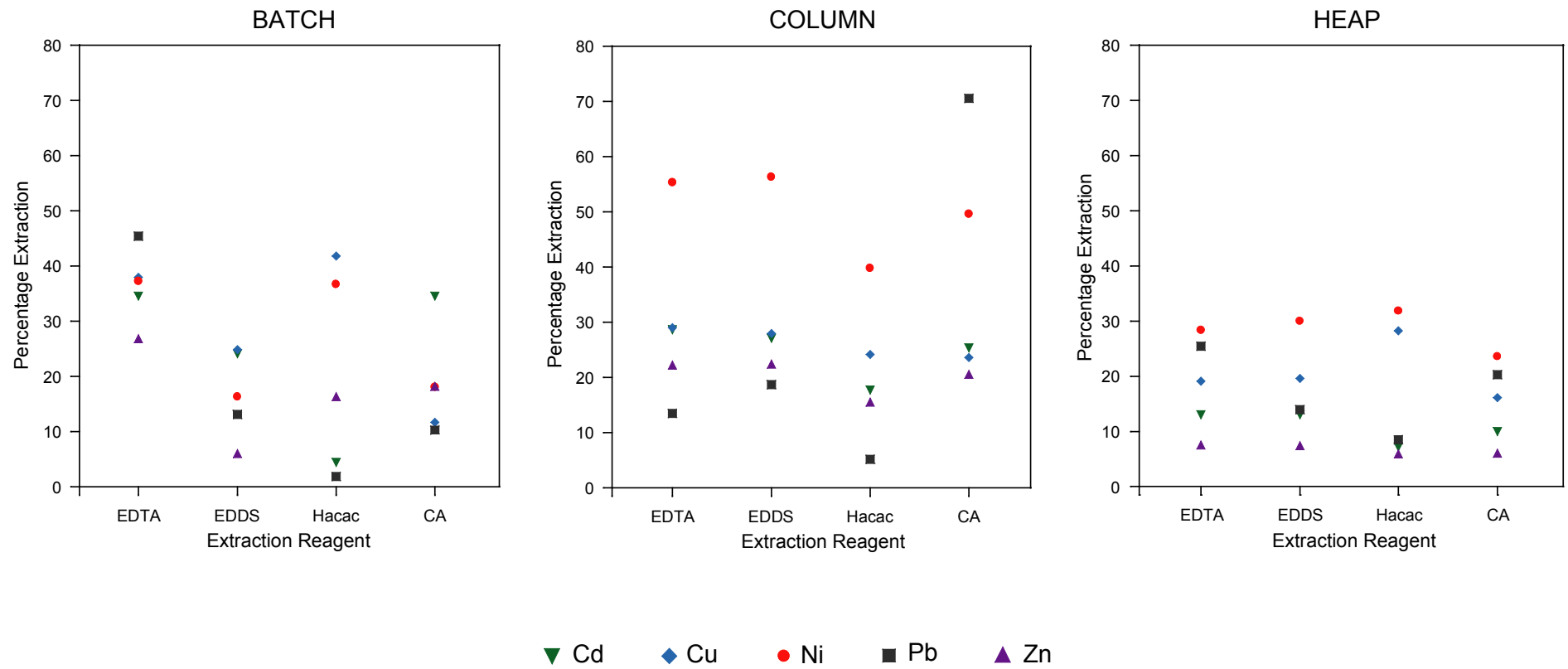
Figure 5.1 Influence of the three process techniques (BS, CS and HS) on the leaching efficiencies of metals of interest (Cd, Cu, Ni, Pb and Zn) calculated across the four selected extractants (EDTA, EDDS, Hacac and CA)

Table 5.5 Comparison of process efficiency for metal leached by selected chelating agents. The standard deviation is ± (0.03 – 5.69)

Metal	EDTA						EDDS						Hacac						CA					
	Batch		Column		Heap		Batch		Column		Heap		Batch		Column		Heap		Batch		Column		Heap	
	mgkg^{-1}	%	mgkg^{-1}	%	mgkg^{-1}	%	mgkg^{-1}	%	mgkg^{-1}	%	mgkg^{-1}	%	mgkg^{-1}	%	mgkg^{-1}	%	mgkg^{-1}	%	mgkg^{-1}	%	mgkg^{-1}	%	mgkg^{-1}	%
Cd	17	35	12	24	24	***48***	12	24	11	23	22	43	2	4	6	13	11	21	17	35	10	21	16	32
Cu	205	38	114	21	105	19	132	29	111	21	106	20	227	***42***	97	18	158	29	67	12	95	17	85	16
Ni	228	37	290	***55***	176	28	88	16	307	47	183	28	215	37	249	40	175	27	98	18	249	38	146	23
Pb	702	45	212	13	390	25	207	13	173	11	155	10	30	2	51	4	81	5	150	10	808	***51***	275	17
Zn	568	***27***	397	18	158	8	130	6	389	18	156	7	327	16	231	11	120	6	356	18	355	16	128	6

(Highest leaching efficiency for each metal indicated in bold)
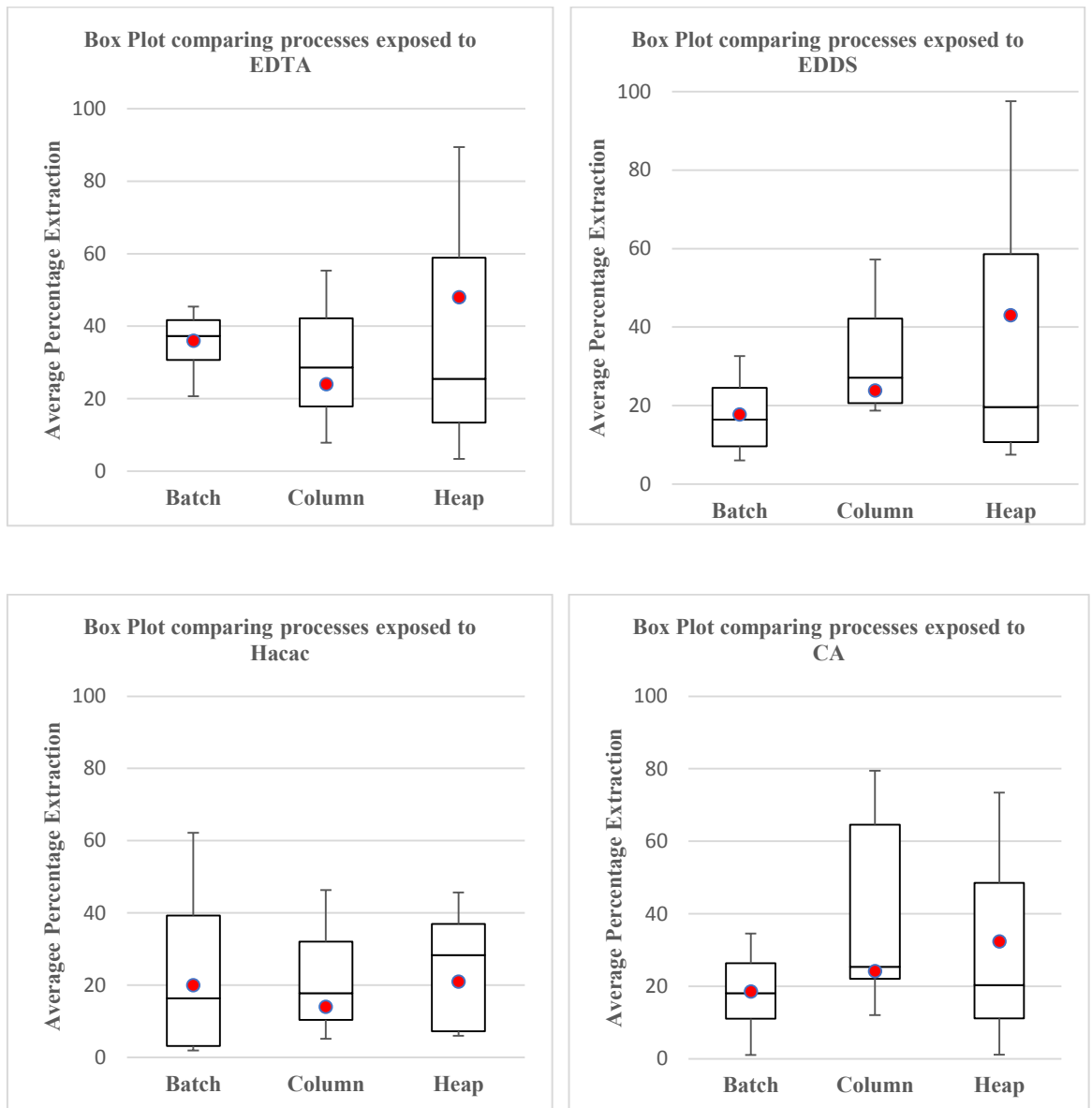
Figure 5.4. Box plots comparing BS, CS, and HS processes for percentage metal (Cd, Cu, Ni, Pb, & Zn) leaching using selective extraction reagents as a unit factor and calculated across 5 metals. The lines inside the boxes represent the median values; the red dots represent the mean values; and the lower and upper boundaries of the box indicate 25 and 75 percentiles of the sample size (n=5)

5.4   Conclusions

1.   Generally, the leaching test results showed that the mobilization of the five metals of interest were substantial and differently influenced by both the leaching process as well as the extractants used.This was evidenced with CA leaching a high efficiency of Pb using column and heap operations, than was obtained for the batch, by a factor of five and two respectively. By contrast, EDDS yielded similar efficiencies for all the three processes.

2.   It was observed that no leaching process demonstrated superiority over the other. However, EDTA was identified as the most efficient extractant in the mobilization of the targeted metals when compared to the other extractants

3.   The batch study revealed that better metal mobilization across the metals investigated from SS was prominently enhanced by EDTA when compared to the other extractants. The capacity of CA to extract Cd was comparable to EDTA, but showed lower efficiencies for the other metals. This invariably implies that preferentially, much better Cd will be recovered by CA. Equally, reasonable efficiencies in Cu and Ni were reported for Hacac using same process. On a practical scale the batch process could be wortwhile for sequential metal recovery by first using CA, followed by the Hacac and finally EDTA for efficient metal recovery and separation.

4.   It can be concluded that, with respect to extraction efficiencies of EDTA, EDDS and CA,) across the five metals leached, the column leaching process behaved in a similar way as the BS although yielding lower efficiencies than the BS. The extraction efficiency of Pb with CA was, however, the highest in comparison to all other processes and extractants and it could be therefore concluded that Pb recoveries will be best performed with a column process and CA as extractant. Ni showed preferential recovery with Hacac and was comparable to the recovery using the batch method.

5.   The heap leaching gave results similar to the column, with CA's performance less efficent but comparable to Hacac across all the metals. Cd was recovered with the highest efficiency with this process compared to the other processes. This finding suggest that a battery of the 3 processes may be considered, however, this will be solely dependent on a sustainable and economic viable plant design, to recover and separate metals from soils.

6.   Since our study has demonstrated that metals may be removed from contaminated soils using a battery of processes and different extractants, an efficient selective leaching process that takes into consideration optimal recovery of specific metal using a process type could be developed if a multi-step contaminant specific process for full scale recovery purposes is designed.

7.   The results could now be used to predict a suitable design for environmental soils of similar composition to that of SS.

The leaching capacities of three environmental soils sourced from Nigeria (Nig-S) and Romanian (Ro-SB and Ro-HP) will be compared and contrasted with the our simulated soil (SS) in chapter six, to test the predictive power of our earlier work to date.

Chapter 6

Influence of selected extractants on the leaching potential of target metals from soils: real soils versus simulated soil

6.1   Introduction

Soil contaminated with potential toxic elements (PTEs) constitutes a serious environmental problem throughout the world. The scale of its impact is potentially both long-term and far reaching due to their mobility, toxicity and persistence in the environment. Metal-bearing solids at contaminated sites vary significantly depending on the type of soil, geographic region and anthropogenic input in a manner that is above defined background values capable of causing threat to biodiversity and ecosystem. However, if properly harnessed, could potentially serve as an alternative source of metal resource.

This chapter aims at evaluating the metal leaching efficiencies of selected extractants when applied to Real-world scenarios, using soils from Romanian origin (Copşa Mica (Ro-SB) and Campîna (Ro-PH)) and Nigerian origin (Nig-S). In addition, the leaching behaviour of these natural soils is compared to the SS with the purpose of evaluating its use as a predictive tool.

6.2   Soil description

The soil parameters of colour (Munsell), CEC, mineral profile, pH and SOM were used to characterize the three real soils and were in turn compared and contrasted with the soil parameters of SS. The findings are summarized in Table 6.1.

Physical observation confirms that all the natural soils investigated are characterized as sandy loam. However, assessment of the colour parameter using the Munsell colour chart, shows that whilst Ro-PH and Nig-S exhibited a similar reddish brown colour (Munsell 5YR.5/1), attributed to the presence red earths characterized of oxidized ferric iron oxide, Ro-SB soil appeared dark and brownish grey, indicating the presence of black carbon (5Y 2.5/1), and be more precisely defined as humic-rich sandy loam, reflecting high organic matter content. The classification of these soils for colour and texture could assist in the description and prediction of the behaviour of the soil. For example, it is expected that Ro-SB will have a higher cation exchange capacity capable of holding exchangeable cations as well as buffer against soil acidification. The presence of iron oxides in Ro-PH or Nig-S will modify the surface properties of the soils.

The CEC of soils is an important property in terms of the leaching and adsorption behaviour of PTEs and is reported in Table 6.1. It is observed that Ro-SB displayed the highest CEC (16.7 meq/100g) as reported in literature by Floarea et al. (2008), and therefore is only. This value is close to that of the SS (17.0 meq/100g). An increased CEC will increase the retention of metal (Msaky and Calvet, 1990) in a system. Therefore, it is expected that Ro-SB and SS will have the capacity to provide a higher charge density per unit surface area or enhanced surface area for cation adsorption sites, or a combined effect of both. It is believed that black carbon enrichment could be the main contributor to the higher CEC in Ro-SB, as stated or showed by Glaser et al., (2001). It becomes interesting to know if the two systems would behave alike, as their CEC indicates, especially since the SS has been modified with the metals of interest in their cationic state and Ro-SB, an industrial synthetic soil, has been naturally modified and the metals are present in a more complex material. Conversely, Nig-S shows a CEC of approximately half that of the SS and Ro-SB, therefore it is expected that Nig-S will have reduced surface area available for metal exchange capacity, a phenomenon, likely to influence the leaching dynamics of Nig-S in comparison to that of the SS.

Comparison of the mineral profiles, determined using XRD, for each of the four soils considered, identified that whilst quartz is found to be the dominant crystalline phase in all soils, differences in other contributing mineral phases exist. Quartz sand (QS) is identified as a key mineral phase in the three soils and plays a subsidiary role in the retention of metals, as previously discussed and concluded based on behaviour of SS in Chapter 4. It remains to be determined whether the mineral phases identified in the XRD analysis will have an overt influence over the leaching efficiencies of a given extractant.

The kandite clay, kaolinite and the titanium oxide, anatase, are known to contribute to the mineralogy of Nig-S. Due to the presence of highly weathered clay minerals such as kaolinite in the Nig-S, their ability to retain cations will be solely influenced by surface area, which is a reflection of its CEC content. Differences in mineralogy of the two Romanian soils are noted, with calcite and the iron (oxy) hydroxide, goethite being found in higher concentrations than the others in Ro-PH soil matrix. The presence of goethite (α-FeOOH) can play important roles in chemical and physical attributes of Ro-PH, such as aggregate stability and particle dispersion (Pinheiro-Dick and Schwertmann, 1996). For instance, Fe^{3+} make bridging with clay particles and increases their aggregate stability (Bronick and Lai, 2005).This phenomenon may reduce the solubility of Ro-PH soil which invariably affects its

leaching ability. Goethite, are known to exhibit low solubility at the pH range of soils, a phenomenon that influences the efficiency of the extractants. However, this greatly depends on the particle size, crystallinity and percent of Al substitution (Schwertmann, 1991).

Graphite is reported as a crystalline phase of the Ro-SB soil probably due to a sustained input of black carbon production from industrial processes that was on going from 1935-1993 in the vicinity. The presence of graphite as earlier eluded, may also be part of the reason for the substantial increase in CEC characteristics of the Ro-SB, and may influence the way in which metals leach from this soil considering their ability to retain cations by electrostatic force. Furthermore, although clays such as montmorillonite identified in the SS are not observed in the mineralogical profile of the Ro-SB soil, the CEC reported for the soil suggests that it is likely clays may be present but are either in an non-crystalline, amorphous state and, or the crystalline form is below the instrumental limits of detection.

The pH values for the three real soils show the following order of increasing pH: Nig-S< Ro-SB<Ro-PH, with the most alkaline pH being for Ro-PH (pH=8.3), which is the closest in alkalinity to that of the SS. By contrast, the pH of the Nig-S (pH=3.7) is six times of magnitude more acidic than the SS. As seen in Chapter 4, pH is found to influence the metal retention ability of a soil, with metals typically being less likely to be leached from an alkaline soil than acidic counterparts. This phenomenon is explained by the protonation and deprotonation of surface hydroxyl groups in the crystal edges of the soil. Such concept is in agreement with findings of Fontes et al. (2000). Therefore, it is anticipated that metals in the Nig-S will be more readily leached than those associated with the more alkaline soils of Ro-PH, Ro-SB and SS.

The SOM data for the three environmental soils reported in Table 6.1 shows that SOM values ranged from 0.3 % and 3%. However, in comparison to the SS, these values are significantly lower (between 5 and 50 times) than that for SS. This fact does such that metal retention characteristics and consequently the extractant efficiencies of the different soils may differ (de Matos et al., 2001; Fontes et al., 2000; Gomes et al., 2001).For instance, as initially discussed in section 2.1.1, SOM, can act as organic immobilizing agents to chelate metals and form stable complexes (Datta., 2001). Depending on the stability complex, this phenomenon can influence the leaching potentials of the metals in the SS or undermine the efficiency of the selected extractants.

On reflection, given the acidic pH, low CEC and SOM, it is anticipated that Nig-S is less likely to mimic the leaching profile of the SS in comparison with the two Romanian soils (Ro-PH and Ro-SB)

6.3 Soil bulk geochemistry

Table 6.1 displays the metal concentrations for the different soils, as well as the regulatory /intervention standard concentrations for the different geographical areas. It is observed that the metal concentrations vary with site (Table 6.1), reflecting the differences in anthropogenic activities and inputs between individual sites, as previously explained. The Cd concentrations in the different soils varied significantly, ranging from 8 – 52mgkg[-1] and follow the order Ro-SB ≈ SS >> Nig-S >> Ro-PH. However, all the soils investigated were Cd enriched, with values well above the regulatory values (Table 6.1). A review by Chao et al. (2014) to investigate Cd enrichment in urban and agricultural soils revealed that the average content of Cd in urban soil and agricultural soil are 1.5 mgkg[-1] and 0.3 mgkg[-1] respectively. These values are substantially lower compared to Cd concentrations observed in any of the natural soils under investigation. Overall increased concentration of Cd observed in Nig-S is probably influenced by activities associated with spent batteries and vehicle repairs whilst atmospheric depositions, construction rubbles, and foundry waste could be responsible for the sustained input observed in Ro-SB and Ro-PH sites respectively.

For Cu, the concentrations in the soils varied substantially, and followed the order of magnitude, SS > Ro-PH >> Nig-S ≈ Ro-SB. Only the Ro-PH soil had concentrations higher than the respective intervention values. The average Cu content found in urban and agricultural soils were found to be 49.6 mgkg[-1] and 38.0 mgkg[-1], respectively by Chao et al. (2014). As was the case with Cd, the Cu concentrations of the natural soils under investigation are higher than the literature values cited. Higher concentration of Cu observed from the Ro-PH site could be attributed to construction rubbles that has been abandoned over time.

For Ni, the concentration in the different soils differed greatly, from the SS (8.4, 12.4 and 20 times for Nig-S, Ro-PH and Ro-SB, respectively), and followed the order of magnitude, SS >> Nig-S > Ro-PH > Ro-SB. The average concentration of Ni content in urban and agricultural soils are 29.1mgkg[-1] and 26.1 mgkg[-1] (Cao et al., 2017). However, the concentration of Ni in the natural soils was lower than the stipulated values for their

respective domain and slightly higher for the European standard, with the exception of Ro-SB.

For Pb, the concentration in the soils differed significantly, and assumed the order of magnitude, Ro-SB >> SS > Ro-PH >> Nig-S. However, Pb concentration in Nig-S is lower than the stipulated value for its domain while Ro-SB and Ro-PH are more than order of a magnitude higher than their respective domain. According to Chao et al. (2014), the average concentrations of Pb in the urban and agricultural soil are 1733.9 mgkg^{-1} and 51.2 mgkg^{-1}respectively. These values are lower than what is observed for the natural soils under investigation (Table 6.1). Increased Pb observed from Ro-SB and Ro-PH soils is likely to reflect atmospheric deposition from a non-ferrous (Pb) smelter site in close proximity to the site and inputs of construction and iron foundry waste respectively.

The Zn concentration in Nig-S was also much lower than the two Romanian soils, similar to the Pb and followed Ro-SB >> SS >> Ro-PH >> Nig-S. However, in all cases the Zn concentration were higher than the threshold specified for their respective domains as well as that stipulated for the European Union. Zn concentration in urban and agricultural soils are 289.78 mgkg^{-1} and 117.35 mgkg^{-1}(Chao et al., 2014) However, these values are much lower than what is obtained in the natural soils under investigation (Table 6.1). Increased Zn observed from Ro-SB and Ro-PH soils is likely to reflect atmospheric deposition from a non-ferrous (Zn) smelter site in close proximity to the site and inputs of construction and iron foundry waste respectively.

Table 6 1 Selected physicochemical properties and the elemental concentrations of the metals Cd, Cu, Ni, Pb and Zn in three real soils used in the comparative column and heap extractions

Soil type	Mineral composition	Characterization				Elemental concentration (mgkg^{-1})				
		Texture	pH	SOM (%)	CEC (meq/ 100g)	Cd	Cu	Ni	Pb	Zn
Nig-S	Kaolinite, Anatase and Quartz	Sandy loam	3.7	0.3	7.3	26.3	155.0	75.0	210.0	350.0
Ro-PH	Quartz, calcite and Goethite	Sandy soil	8.3	2.9	na	8.1	431.7	50.7	1482.1	1279.7
Ro-SB	Quartz and Graphite	Humic sandy loam	7.2	3.0	16.7	51.9	147.8	31.5	1940.9	3169.2
S-S	Montmorillonite and Quartz	Sandy loam	9.4	14.0	17.0	51	570	630	1590	2160
The European Union Standard (MEF, 2007)						1.0	100.0	50.0	60.0	200.0
Romania Intervention value (Harmanescu et al. 2011)						5.0	200.0	150.0	100.0	600.0
Nigerian Intervention value (DPR, 2002)						17.0	190.0	210.0	530.0	720.0

CEC, cation exchange capacity; SOM, soil organic matter; na: not available

6.4   Column studies

The leaching behaviour of the five metals of interest were investigated by subjecting the different soil (Nig-S, Ro-PH and Ro-SB) samples to an in-situ leaching process that is characteristic of a column configuration (described in section 5.3.3). The leaching trend for these metals were monitored over leaching time intervals of 30, 60, 90, 120, and 150 minutes using selected extractants (EDTA, EDDS, Hacac and CA) as was used for the SS study. It was observed that the targeted metals generally reached their maximum leaching potentials (breakthrough point) at different leaching times due to the influences of extractants and soil types (Appendix B, Figure 1). In the Nig-S, Cd, Cu, Ni and Pb, reached their maximum leaching potential after 90 mins of leaching times whilst for Zn it was reached after 150 mins regardless of extractants used. For Ro-PH, Cd, Cu, Ni and Pb reached breakthrough point after 90 mins; however, it appears as though an extended time beyond 150 min would be needed for Zn to achieve a breakthrough curve (Appendix B, Figure 2). For Ro-SB, the maximum leaching potential for the targeted metals except for Zn was reached after 60 mins (Appendix B, Figure 3). It appears as though Zn would leach beyond 150 mins to achieve breakthrough point, as was the case in Ro-PH. For SS, leaching potential for the targeted metals was reached after 90 mins regardless of extractants used (Appendix B, Figure 1). Cd and Ni in Hacac and Pb in CA however, did show different leaching potentials, as breakthrough curve could not be achieved after 150 mins. The results expressed the mass of metal per kg soil extracted after 150 min, and the percentage extraction efficiencies for each metal are discussed below.

6.4.1   Nig-S soil

From the data summarized in Table 6.2, it is evident that specific metals showed different extraction efficiencies across the four extractants investigated. For instance, the order of extraction efficiency of Cd was EDTA > CA > Hacac > EDDS (52.4%; 16.2%; 12.3% and 11.2%, respectively). The extraction margin between the most and the least efficient was discernibly large with EDTA extracting between 4.7 and 3.2 times as much as the rest of the extractants. As such, only EDTA gave a satisfactory efficiency for Cd. This effectiveness of EDTA over other extractants for cationic Cd may not be limited to its binding capacity (Sun et al., 2001b; Lim and Chui, 2005) but may be attributed to its reaction kinetics as well as the biodegradation of the complexing agent (Ylivainio, 2010). For instance, equilibrium condition between EDTA and Cd was achieved in a short while when compared to the steady-state condition of other extractants and Cd (Appendix B). EDDS and CA are

susceptible to rapid biodegradation when compared to EDTA, though this could be influenced by the type of metal being complexed (Thomas et al., 1998; Vandevivere et al., 2001). For Cu extraction, the order of efficiency was EDDS > Hacac > EDTA > CA. Although significant differences for Cu leached by the selected extractants were observed, the fact remains that Cu was poorly extracted by all the extractants as leaching efficiency did not yield more than 40%. For Ni, the leaching efficiency was EDDS > EDTA > Hacac > CA, with EDDS (54.94 mgkg^{-1}) leaching the most, followed by EDTA (38.9 mgkg^{-1}), Hacac (36.9 mgkg^{-1}) and CA (22.28 mgkg^{-1}) with an average efficiency of 18.7% (34.7 − 9.7). Hacac (26.04 mgkg^{-1}) yet leached the most, followed by EDTA (17.78 mgkg^{-1}) and EDDS (7.30 mgkg^{-1}) with CA (22.28 mgkg^{-1}) leaching the least. For Pb, the order of efficiency was EDTA > CA > EDDS > Hacac with an average efficiency of 22.9% (37.21 − 1.86%). EDTA (78.14 mgkg^{-1}) leached the most, followed by CA (63.12 mgkg^{-1}) and EDDS (46.80 mgkg^{-1}) with Hacac (3.91 mgkg^{-1}) leaching the least. For Zn, the order of efficiency was EDTA > EDDS > Hacac > CA, with an average efficiency of 23.34% (40.2 − 11.62). EDTA (140.59 mgkg^{-1}) leached Zn the most, followed by EDDS (84.1 mgkg^{-1}) and Hacac (61.29 mgkg^{-1}) with CA (40.67 mgkg^{-1}) leaching the least.

From the observed targeted metals released by the selected chelants, it is evident that the Pb extraction is average and similar for all extractants, except for Hacac that did not mobilize the metal in the soil profile. The lower efficiency of Hacac can be attributed to its poor chemical combination (low affinity) with Pb and Cd (Table 5.2).

On average, Ni (51%) showed highest extraction efficiencies overall, irrespective of extractants used. The leaching efficiency of Ni was higher compared to the other metals calculated across the four extractants used. The other metal contaminants leached differently but not more than 23% each for Cd, Cu, Pb and Zn. However, the greater efficiency of Ni by the extractants over the other metals could be attributed to synergy or due to the greater share of exchangeable Ni out of the total Ni in the soil matrix.
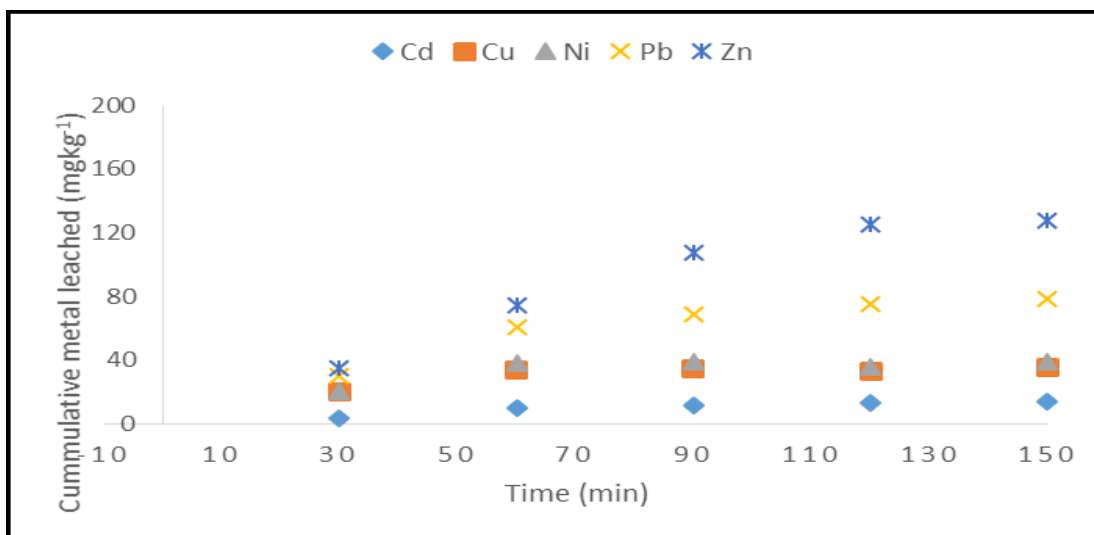
Figure 6.1. Breakthrough curves of selected metals leached from Nig-soil using EDTA as an efficient extractant

Table 6 2: Extractability of metals (Cd, Cu, Ni, Pb and Zn) of interest from industrially impacted Nig-S soil by a column extraction with selected extractants. The standard deviation on the values reported are in the range ± (0.8 – 15.0)

Metal	EDTA		EDDS		Hacac		CA	
Loading (mgkg^{-1})	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency
Cd (26.3)	13.8±13.2	52.4	3.0±10.1	11.2	3.2±2.3	12.3	4.3±9.3	16.2
Cu (155.0)	35.1±8.0	22.7	51.0±4.4	32.9	43.7±5.2	28.2	12.9±4.1	8.3
Ni (75.0)	38.9±15	51.8	54.9±0.4	73.3	36.9±7.2	49.2	22.3±2.6	29.7
Pb (210.0)	78.1±0.8	37.2	46.8±9.7	22.3	3.9±1.5	1.9	63.1±5.0	30.1
Zn (350.0)	140.6±3.0	40.2	84.1±6.8	24.0	17.5±3.8	17.5	40.7±3.9	11.6

*± *Values indicate Standard Deviation*

6.4.2 Ro-PH soil

The extraction efficiencies of specific metals as summarized in Table 6.3 were observed to be different across the four extractants investigated. The release of Cd was of similar magnitude with EDTA (0.96 mgkg^{-1}) and Hacac (0.91 mgkg^{-1}), followed by EDDS (0.72 mgkg^{-1}), where CA (0.46 mgkg^{-1}) displayed the lowest efficiency (Table 6.3). The order of leaching efficiency was EDTA ≈ Hacac > EDDS > CA, with an average efficiency of 9.4 % (11.9 – 5.7). For Cu, the order of leaching efficiency was Hacac > EDTA > EDDS ≈CA, with average efficiency of 15.8% (20.9 – 13.4). Hacac (90.31 mgkg^{-1}) leached Cu the most followed by EDTA (66.14 mgkg^{-1}), with EDDS (59.09 mgkg^{-1}) and CA (58.04 mgkg^{-1}) being leached the least and with a similar magnitude. For Ni, the order of leaching efficiency was Hacac >>

CA> EDTA ≈ EDDS, with average efficiency of 6.3% (18.9 – 1.6). Hacac (9.63 mgkg^{-1}), leached the most followed by CA (1.50 mgkg^{-1}), where EDTA (0.93 mgkg^{-1}) and EDDS (0.80 mgkg^{-1}) significantly leached the least and in similar magnitude. For Pb, the order of leaching efficiency was EDTA > EDDS > Hacac > CA with average efficiency of 1.2% (2.6 – 0.04). EDTA (39.08 mgkg^{-1}) leached the most followed by EDDS (29.94 mgkg^{-1}) and Hacac (3.85 mgkg^{-1}) with CA (0.52 mgkg^{-1}) leaching the least. EDTA generally outperformed the other extractants by a range of 78 to 1.3 times (on the average 3% compared to the 2%, 0.3% and 0.1% for EDTA, EDDS, Hacac and CA respectively). For Zn, the order of leaching efficiency was Hacac > EDTA > EDDS ≈ CA with average efficiency of 11.3% (14.8 – 9.7). Hacac (189.31 mgkg^{-1}), leached Zn the most, followed by EDTA (147.22 mgkg^{-1}), where EDDS (119.59 mgkg^{-1}) and CA (124.02 mgkg^{-1}) leached the least and similar magnitude.

The metal concentrations leached from Ro-PH soil were observed to be considerably lower compared to Nig-S. The poor leaching efficiency observed could partly be attributed to the presence of goethite, which is known as strong absorbent for metals such as Ni, Pb and Cd onto soil surfaces (Roussel et al., 2000; Lee et al., 2005). Nevertheless, general mobilization trends shows that EDTA and Hacac outperformed the other extractants, and specifically Hacac were often the extractant with the highest efficiency. EDTA notably leached most of the metals with the exception of Ni (≈ 2%) and Pb (≈ 3%) that were poorly leached, despite their (Ni-EDTA (log K = 20.1) and Pb-EDTA (log K = 18.8) formation constants. The reason for the poor efficiency observed for Pb may be partly explained by soil properties. The lower organic matter content as observed in Table 6.1 may affect enhanced solubility of Pb. In addition, poor efficiency of Ni may be attributed to low solubility of Ni that is often associated with soils (Uren, 1992). Other palpable reasons could be attributed to their presence in a chemical state that is bound to reducible/Fe-Mn oxide fraction as observed in data (not shown), making it difficult for extractants, especially EDTA less efficient to access (Abumaizar and Smith, 1999; Wasay et al., 2001; Papassiopi et al., 1999). Furthermore, the poor efficiency of Pb-Hacac (< 1%) was to be expected because of the poor complexation of Hacac for Pb as observed in our previous studies. Similarly, the poor performance of EDDS and CA as observed maybe partly due to metal exchange tendencies and lower formation constants to form stable metal complexes respectively (Luo et al., 2005; Tsang et al., 2009).

Overall, the average mobility of metals leached are in the decreasing order Cu (15.8%) > Zn (11.3%) > Cd (9.4%) > Ni (6.3%) > Pb (1.2%), with Pb exhibiting the least average percent

(1.2%), and as such, can be considered immobile in this soil. Generally, the leaching for all metals were extremely low, irrespective of extractant, in contrast to the Nigerian soil. In addition, the Hacac showed the most promise with this soil, except for Pb extraction, the reason for which has been discussed before.
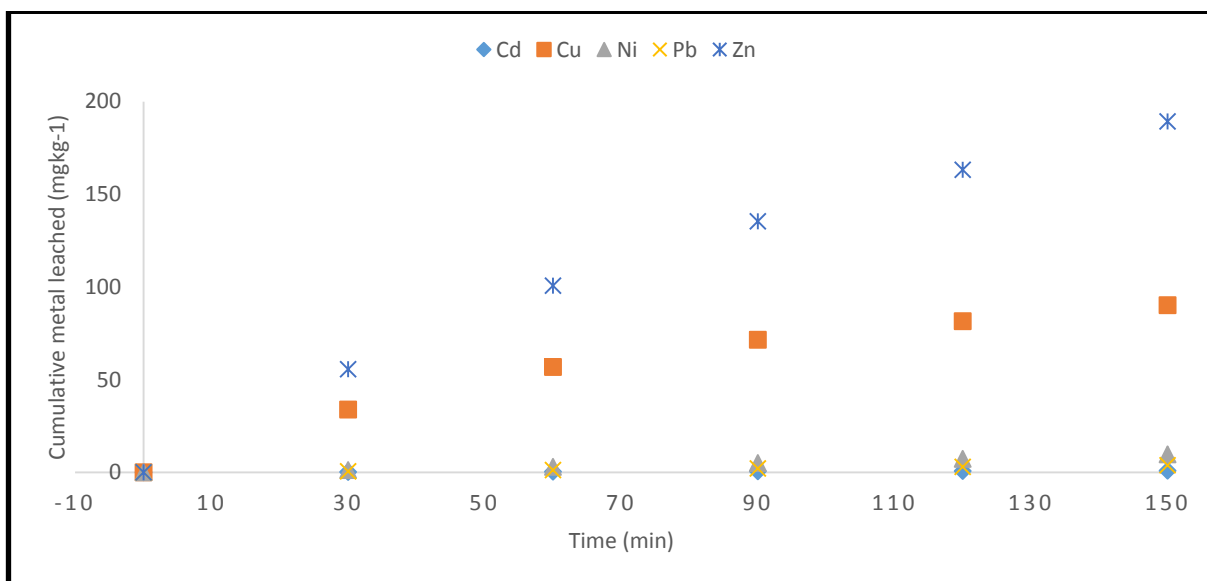

Figure 6.2. Breakthrough curves of selected metals other than Zn leached from RO-PH using Hacac as extractant

Table 6 3 Extractability of metals (Cd, Cu, Ni, Pb and Zn) of interest from industrially impacted Ro-PH soil by a column extraction with selected extractants. The standard deviation on the values reported are in the range ± (0.1 – 8.6)

Metal	EDTA		EDDS		Hacac		CA	
Loading (mgkg^{-1})	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency
Cd (8.08)	1.0±0.1	11.9	0.7±0.1	8.9	0.9±0.1	11.3	0.5±0.1	5.7
Cu (431.71)	66.1±0.5	15.3	59.0±0.7	13.7	90.3±0.1	20.9	58.0±2.5	13.4
Ni (50.73)	0.9±0.1	1.8	0.8±0.1	1.6	9.6±0.1	19.0	1.5±0.1	3.0
Pb (1482.09)	39.1±1.7	2.6	29.9±0.3	2.0	3.9±0.1	0.3	0.5±0.1	0.5
Zn (1279.74)	147±0.9	11.5	119.0±1.5	9.3	189±0.5	14.8	124.0±8.6	9.7

± Values indicate Standard Deviation

6.4.3 Ro-SB soil

The extraction efficiencies of the specific metals across the four extractants investigated is summarized in Table 6.4. For Cd the order of leaching efficiency was CA > EDTA >> EDDS > Hacac with an average efficiency of 31.4% (64.4 – 7.8%). CA (33.46 mgkg^{-1}) leached Cd the greatest, followed by EDTA (22.93 mgkg^{-1}) and EDDS (4.73 mgkg^{-1}), where Hacac (4.04

mgkg^{-1}) leached the least. Interestingly, CA outperformed the other extractants, including the preferred EDTA by a range of 8 to 1.3 times (on the average 64% compared to the 44%, 9% and 8% for CA, EDTA, EDDS and Hacac respectively). For Cu, the order of leaching efficiency was EDDS > EDTA ≈ Hacac > CA with average efficiency of 42.5% (48.6 – 30.0%). EDDS (71.9 mgkg^{-1}) leached Cu the most. It was observed that EDTA (66.86 mgkg^{-1}) and Hacac (67.98 mgkg^{-1}) leached similar amounts, whilst CA (44.4 mgkg^{-1}) leached lowest. The order of leaching efficiency for Ni was Hacac > CA > EDTA > EDDS with average efficiency of 13.4% (21.8 – 8.1%). Hacac (6.86 mgkg^{-1}) was found to leach the most, followed by CA (4.37 mgkg^{-1}) and EDTA (3.30 mgkg^{-1}) with EDDS (2.54 mgkg^{-1}) performing the least efficient. In the case of Pb, the order of leaching efficiency was EDTA >> CA >>EDDS >Hacac with average efficiency of 15.5% (45.4 -03). EDTA substantially leached Pb by a range of 159 to 4 (on the average of 45% compared to the 12%, 4% and 0.1% for EDTA, CA, EDDS and Hacac respectively). Zn followed the order CA > EDDS> Hacac > EDTA, where CA extracted between 1.8 and 1.5 times as much as the other extractants.

Interestingly, it can be observed that metals were prominently leached across the selected extractants used. The average potential metal mobilized from Ro-SB soil could be as a result of high abundance of some of the metals bound to the more labile phase such as exchangeable and carbonate phases where they are easily mobilized by the extractants (Jain et al., 2008). Conversely, poor leaching observed for Cd, Ni, and Pb (Table 6.4) may be attributed to extractant-metal specificity and affinity. For instance, Cd and Pb having poor complexing affinity for EDDS and Hacac. In addition, the processes of metal mobilization may be partly influenced by the nature of the soil properties such as mineralogy, pH and metal type (Jones and Jarvis, 1981). For instance, presence of some minerals (e.g. graphite, goethite) in the soil can influence the leaching efficiency of extractants while the solubility of some elemental cations (Ni^{2+}) in the can be significantly low. The presence of targeted metals in the geochemical phase where they can be easily leached from the soil matrix makes recovery efficiently appealing. The effectiveness of EDTA and CA leaching capacity could be commonly attributed to formation constant and acid dissolution effect respectively. The poor efficiency of EDDS and Hacac notably for Pb and Cd could also be attributed to their poor complexation stability (See chapter 5), whilst the enhanced extraction efficiencies observed for EDDS and Hacac in the case of Cu and Ni has been previously studied by Yip et al. (Yip et al., 2010) and Podyachev et al. (Podyachev et al., 2006) respectively.

Overall, the average leaching potential of the metals (calculated across the four extractants) are in the decreasing order 42.5% > 38.5% > 31.4% > 15.5% > 13.4% for Cu, Zn, Cd, Pb and Ni respectively. CA extracted the metals in Ro-SB much higher than its performance with other soils and showed the highest efficiencies for Cd and Zn. Cu was extracted satisfactorily by all extractants, although lower with CA. Ni showed lowest extraction efficiencies overall, in contrast to the other Romanian soil with Hacac as the best extractant. Pb extraction is satisfactorily with EDTA only, while Zn showed satisfactory extraction with all extractants with the highest efficiency with CA (53%).
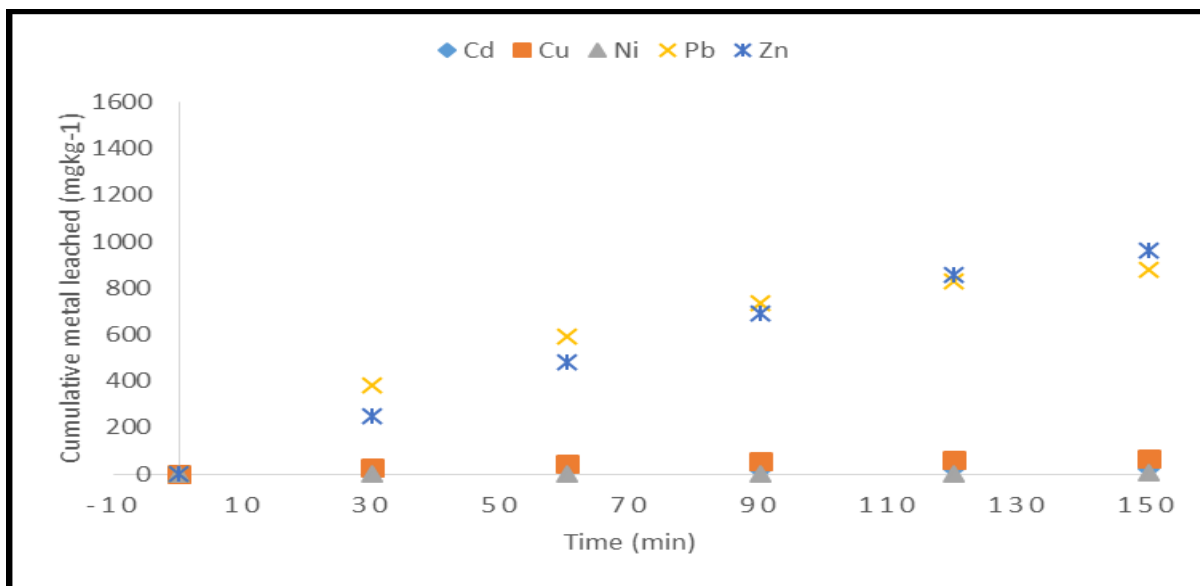

Figure 6.3. Breakthrough curves selected metals leached from RO-SB using Hacac as an extractant

Table 6 4 Extractability of metals (Cd, Cu, Ni, Pb and Zn) of interest from industrially impacted Ro-SB soil by a column extraction with selected extractants. The standard deviation on the values reported are in the range ± (0.1 – 17.1)

Metal	EDTA		EDDS		Hacac		CA	
Loading (mgkg^{-1})	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency
Cd (50)	22.9±0.1	44.2	4.7±0.1	9.1	4.0±0.5	7.8	33.5±0.2	64.4
Cu (550)	66.9±0.6	45.2	71.0±0.1	48.6	68.0±0.6	46	44.4±0.4	30
Ni (650)	3.3±0.1	10.5	2.5±0.1	8.1	6.9±0.1	21.8	4.4±0.1	13.9
Pb (1590)	881±5.5	45.4	76.0±4.4	3.9	5.5±0.4	0.3	238.0±3.2	12.3
Zn (2160)	959±17.1	30.3	1157.0±3.1	36.5	1066±8.67	33.7	1691±10.7	53.4

*± *Values indicate Standard Deviation*

6.4.4 Real Soil versus SS

The leaching potential of three different environmental soils (Nig-S, Ro-PH and Ro-SB) were compared and contrasted with the simulated soil (SS) used in Chapters 4 and 5 for establishing a predictive behaviour that was earlier hypothesized in Section 4.4. The metal enrichment for these environmental soils are entirely influenced by different anthropogenic inputs as discussed in section 6.3 and therefore are likely to differ in metal concentrations, composition, process and period (Jiang et al., 2011). However, the potential leaching efficiency of these soils when compared and contrasted may give credence on the suitability of using SS (Table 6.5) as proxy for predictive purposes. In order to facilitate such an assessment, the leaching efficiency of five metals of interest (Cd, Cu, Ni, Pb and Zn), as determined from the column extraction using four selected extractants (EDTA, EDDS, Hacac and CA) are presented graphically in Figure 6.1.

Visual comparison of the four soils considered in Figure 6.1 shows that the three different environmental soils' displayed significant differences in leaching behaviour for the different metals extracted. This phenomenon was expected because of the heterogenous nature of the soils and pollution sources as well as the metal contaminants and applied extraction method (Rao et al., 2008). However, when these soils were individually compared to the SS, it was observed that whilst Ro-SB compared favourably with SS, the other two soils (Nig-S and Ro-PH) behaved differently. The important findings are noted for each soil and extractants in the section below.

The average leaching efficiencies of the metals extracted in Ro-PH and Nig-S were below 25% and 50% respectively, when compared with the SS that has an average leaching efficiency of 50% and above (Figure 6.1). This result implies that the metal leaching capacity of Ro-PH was about two times lower than Nig-S and up to three times lower than RO-SB and SS respectively. It was also noted that although the actual metal varies with the individual soils, the highest extraction efficiencies of metal was observed from Ro-SB and SS and was notably extracted by CA. Leaching efficiency between group shows that Ro-SB and SS extracted the highest metals when compared to the other soils (Ro-PH and Nig-S). The duo also exhibited similar leaching profile for the different metals extracted (Figure 6.1). The leaching potentials of these soils is in the order Ro-SB > SS > Nig-S >> Ro-PH.

However, when extracted metals were compared within group for the selected extractants, CA appears to outperformed the rest of the extractants for the different soils investigated

except for Ro-PH where Hacac slighlty outwit it (Figure 6.1). The extraction efficiency is in the order CA > EDTA > EDDS ≈ Hacaca , CA > EDDS ≈ EDTA > Hacac, Hacac > CA ≈ EDDS ≈ EDTA and CA > Hacac ≈ EDTA > EDDS for Ro-SB, SS, Ro-PH and Nig-S, respectively.

This result implies that the metal leaching capacity of Ro-PH was about two times lower than Nig-S and up to three times lower than RO-SB and SS respectively. Higher metal extraction as observed for SS was anticipated, because leaching of the metals bound to historically contaminated soils are not easily amenable to leaching when compared to metals bound to artificially or newly contaminated soils due to some factors like ageing effect, associated with soil processes (Kim et al., 2003; Scheidegger and Sparks, 1996). However, the presence of minerals, e.g. goethite reflected the low immobilization capacity of Ro-PH because, goethite and metals such as Pb and Ni form stable complexes (Evans, 1989). Conversely, the leaching trends of Ro-SB compared reasonably with SS.This phenomenon was anticipated considering the close similarity in their physicochemical properties The average metal leached for both soils were above 50% with most of the metals (such as Cd, Cu, Pb and Zn) displaying similar leaching behaviour, except in the case of Ni, where marginal variations greater than 50% were observed for SS soils. The similarity in leaching behaviour observed for SS and Ro-SB could be attributed to similarity in their chemical (pH and CEC, Table 6.1) properties. Enhanced leaching efficiency observed for Ro-SB could be due to the greater share of exchangeable metals out of the total metals in the soil than in Ro-PH and Nig-S (Table 6.1). As such, most of the metals are potentially bound to geochemically labile phases (exchangeable and carbonate) that are considered to be weakly bound, readily and potentially mobile (Jain et al., 2008). The fractionation of metals using Tessier extraction method to test speciation of metals in soils was not part of this study, and as such, was not investigated. However, this is proposed for future work.
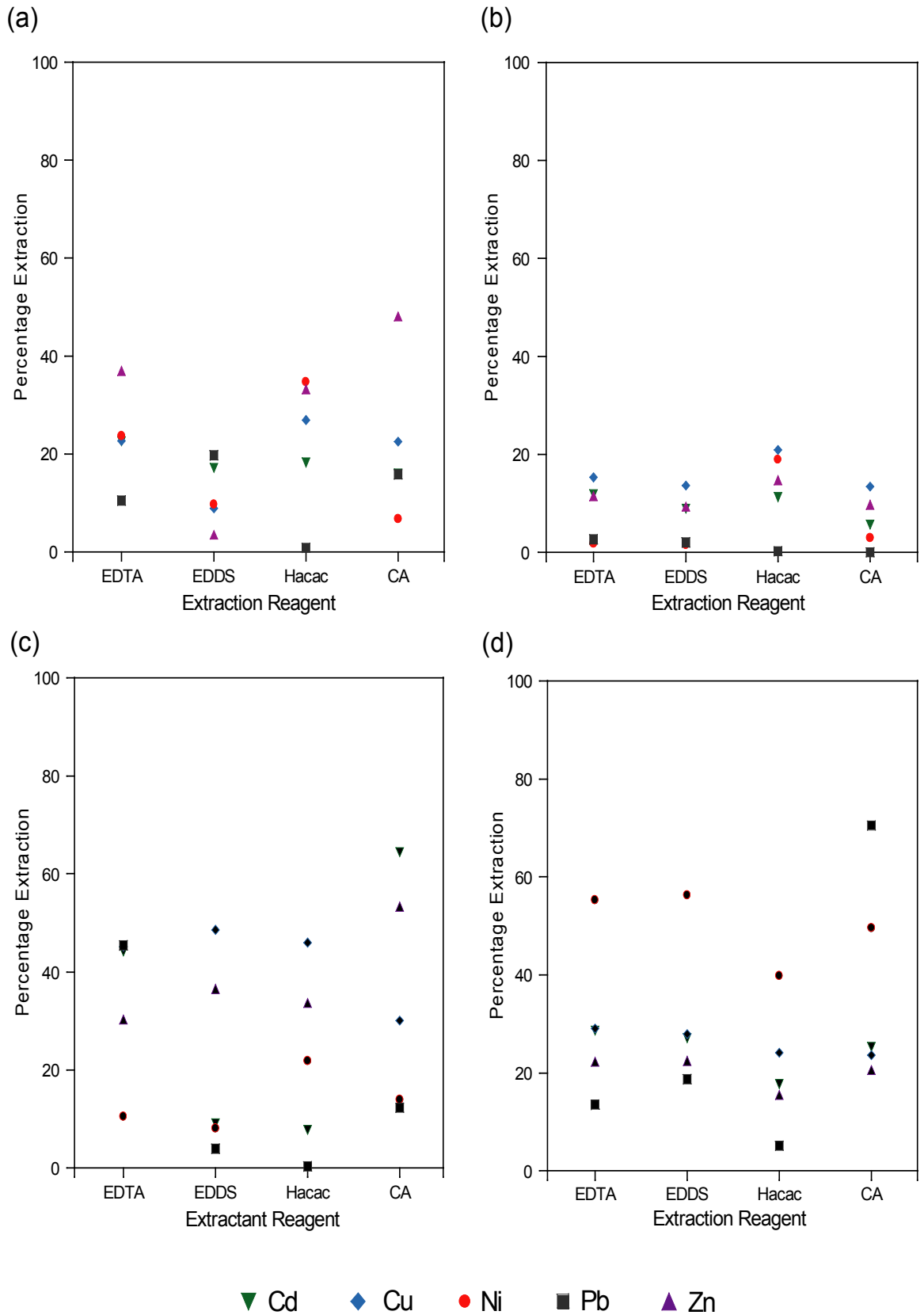
Figure 6 1 Percentage extraction of metals of interest (Cd, Cu, Ni, Pb and Zn) from contaminated soils as influenced by selected extractants (EDTA, EDDS, Hacac and CA) studied with a column and used for comparing and contrasting of environmental soils (Nig-S, Ro-PH and Ro-SB) with SS for predictive purposes, where a) Nig-S; b) Ro-PH; c) Ro-SB; d) SS.

6.5   Heap studies

In situ heap leaching experiments with a solid liquid ratio of 1: 10 were used to investigate the leaching behaviour of Cd, Cu, Ni, Pb and Zn bound to different soil matrices (Nig-S, Ro-PH and Ro-SB). To illustrate the leaching trend over time, the leaching concentration of metal (mgkg^{-1}) bound to contaminated soils after 30, 60, 90, 120, and 150 minutes contact time with selected extractants (EDTA, EDDS, Hacac, and CA) were considered. It was observed that for Nig-S, most of the targeted metals reached a breakthrough point after 150 mins regardless of extractants used (Appendix B, Figures 5). However, the breakthrough point was occasionally observed at different leaching times especially for Zn and Pb extractions (Appendix B). For Ro-PH, maximum leaching potential for all the targeted metals other than Zn was reached after 90 mins (Appendix B, Figure 6), with the later not reaching breakthrough point after 150 minutes of leaching. For Ro-SB, breakthrough point was achieved after 30 and 90 mins of leaching time for most metals and extractants (Appendix B, Figure 7). Zn in EDDS and Pb in CA however were extended beyond 150 mins leaching time. For SS, maximum breakthrough point for targeted metals extracted in EDTA, Hacac and CA was achieved after 30 mins (Appendix B, Figure 8), though Pb in Hacac and CA behaved differently from the rest as their breakthrough was reached after 120 mins. By contrast, targeted metals in EDDS reached their maximum leaching potential after 90 mins. The results expressing the mass of metal per kg soil extracted after 150 min and the percentage extraction efficiency for each metal are discussed below.

6.5.1   Nig-S soil

Assessment of the extractant data for the heap leaching of the Nig-S in Table 6.5, shows that for the specific metals, considerable differences in the extraction efficiencies are observed across the four extractants examined. In the case of Cd, the order of leaching efficiency was EDTA > CA> EDDS > Hacac with average efficiency of 35.32% (61.58 − 11.91%). The magnitude of extraction by EDTA was in the range of 5.2 to 1.4 times greater than the other three extractants (on the average 62% compared to the 43.9%, 23.8% and 11.9% for EDTA, CA, EDDS and Hacac respectively). For Cu, the order of leaching efficiency was EDDS > EDTA > CA > Hacac with average efficiency of 26.7% (34.3 − 19.7%). Hacac extracted between 1.7 and 1.3 times less than the rest of the other extractants. For Ni, the order of extraction efficiency was observed to be EDDS >> CA > EDTA > Hacac with average efficiency of 43.5% (88.9 − 19.7%). EDDS extracted between 4.5 and 2.3 times more than the rest of the other extractants. For Pb, the leaching efficiency was observed in the order

of EDTA >> CA > EDDS >> Hacac with average efficiency of 40.9% (80.7 – 2.4%). EDTA outperformed the other extractants by a range of 33.1 to 1.8 times, with an average efficiency 80.7% compared to 44.8%, 35.5% and 2.4% for EDTA, CA, EDDS and Hacac respectively. In the case of Zn, the leaching efficiency was observed in the order of EDTA >> CA > EDDS >> Hacac with average efficiency of 22.5% (38.2 – 9.4%), where EDTA extracted 4.1 to 1.7 times more in comparison to the other extractants (38.2% compared to 22.2%, 20.1% and 9.4% for EDTA, CA, EDDS and Hacac, respectively). Overall, Cd extraction was better extracted by EDTA and CA. Cu and Zn were poorly leached. Pb however, efficiently leached with EDTA and acceptable with CA. This implies that CA could be 2-4 times better in heap, Hacac could be 1.5 to 2 times better in heap in similar circumstance with EDDS, while EDTA could be 2 times better in heap with Pb. The high leaching potential of EDTA over other extractants is likely to be attributed to its strong chelating ability for targeted metals (Peters, 1999; Sun et al., 2001a; Sun et al., 2001b; Lestan et al., 2008). This phenomenon suggests that extraction processes could influence the leaching behaviour of Cu and Ni in Hacac.
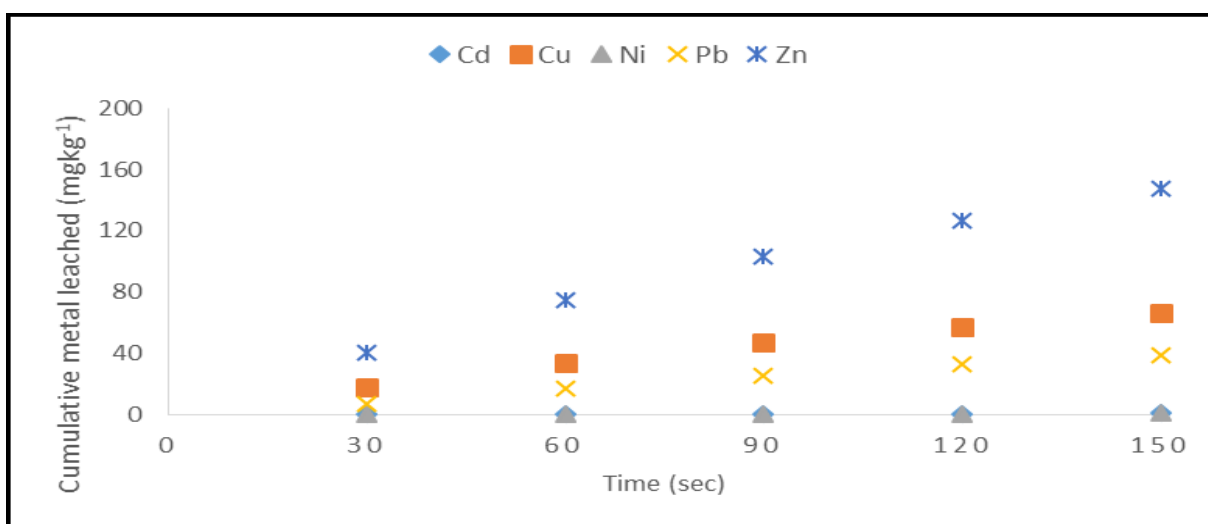

Figure 6.4. Breakthrough curves of metals leached from Nig-S using EDTA as extractant

Table 6 5 Extractability of metals (Cd, Cu, Ni, Pb and Zn) of interest from industrially impacted Nig-S soil by a Heap extraction with selected extractants. The standard deviation on the values reported are in the range ± (0.2 – 7.8)

Metal	EDTA		EDDS		Hacac		CA	
Loading (mgkg^{-1})	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency
Cd (26.3)	16.2±0.2	61.6	6.3±0.8	23.9	3.1±1.6	11.9	11.6±3.1	43.9
Cu (155.0)	42.4±0.2	27.4	53.2±0.2	34.3	30.6±2.4	19.7	39.4±1.2	25.4
Ni (75.0)	19.6±0.8	26.2	66.7±1.0	88.9	14.8±2.7	19.7	29.4±0.3	39.3
Pb (210)	169.5±7.8	80.7	74.5±1.1	35.5	5.1±0.2	2.4	94.1±0.1	44.8
Zn (350.0)	133.8±2.1	38.2	70.4±0.9	20.1	33.0±0.5	9.4	77.8±2.4	22.2

*± *Values indicate Standard Deviation*

6.5.2   Ro-PH soil

The extraction efficiencies of the targeted metals in the RO-PH soil as across the four extractants investigated as summarized in Table 6 6 ,show significant differences in the extraction trends. In the case of Cd, the order of extraction efficiency was EDTA > CA > EDDS > Hacac with average efficiency of 20.6% (36.1 – 1.7%); EDTA outperformed the other extractants by a range of 21.2 to 1.3 times. For Cu, it is noted that the extraction trend was highest and similar in EDTA and CA, followed by the rest of the extractants, where EDDS displayed the lowest efficiency. The order of extraction efficiency was EDTA ≈ CA > Hacac > EDDS with average efficiency of 35.3% (42.7 – 26.1). In the case of Ni, the order of extraction efficiency was CA > EDTA > EDDS > Hacac with average efficiency of 5.7% (11.8 – 0.71). CA extracted between 16.9 and 1.9 times as much as the rest of the extractants. For Pb, the order of extraction efficiency was CA > EDTA > Hacac > EDDS with average efficiency of 6.9% (12.39 – 3.21). CA extracted between 3.9 to 1.6 times as much as the rest extractants. For Zn, the order of extraction efficiency was CA > EDTA > EDDS > Hacac with average efficiency of 30.1% (42.9 – 18.7%). CA again, outperformed the other extractants by a range of 2.4 to 1.2 times. Further scrutiny of the data shows that with the exception of CA that showed most promise for Cu and Zn with the Ro-PH, the other extractants performed poorly for all metals extracted. It maybe hypothesized that most of these metals were sorbed onto iron (oxy) hydroxide surfaces of the soil matrix, thereby limiting the efficiencies of the extractants. Overall, higher extraction of Cu is best extracted with heap and was on the average of 2 times better than column.
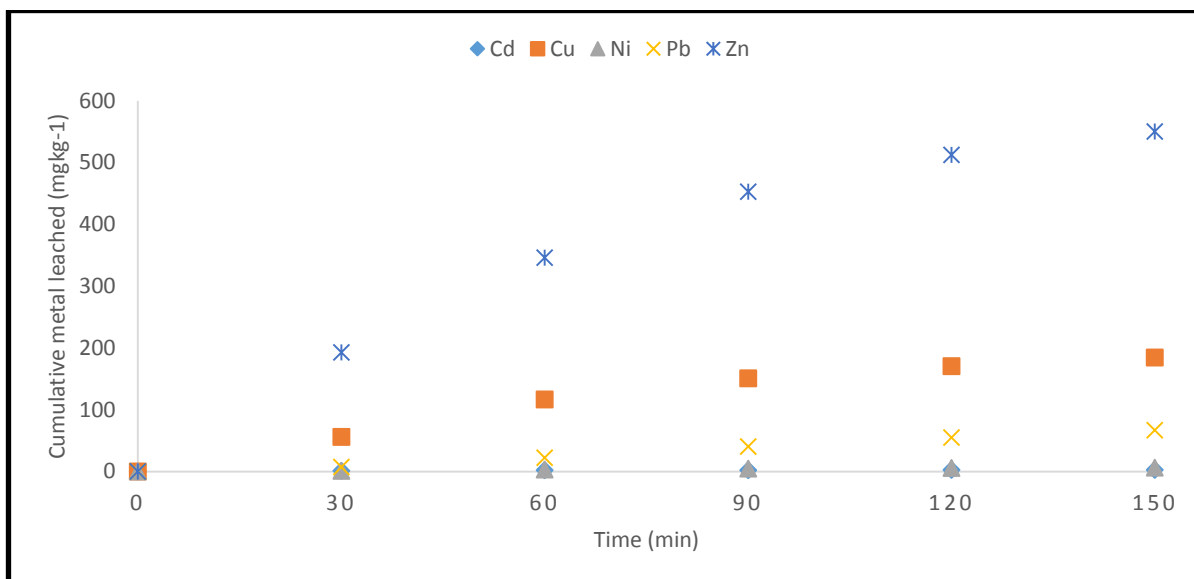
Figure 6.5 Breakthrough curves of selected metals leached from RO-PH using CA as the extractant

Table 6 6 Extractability of metals (Cd, Cu, Ni, Pb and Zn) of interest from industrially impacted Ro-PH soil by a heap extraction with selected extractants. The standard deviation on the values reported are in the range ± (0.1 – 6.3)

Metal	EDTA		EDDS		Hacac		CA	
Loading (mgkg^{-1})	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency
Cd (8.08)	2.9±0.1	36.1	1.4±0.1	16.7	0.2±0.5	1.7	2.3±0.0	27.8
Cu (431.71)	179±2.3	41.5	112.0±1.3	26.1	134.0±0.9	31.1	184.0±2.4	42.7
Ni (50.73)	3.2±0.1	6.3	2.1±0.1	4.1	0.4±0.5	0.7	6.0±0.1	11.8
Pb (1482.09)	115.0±7.8	7.8	47.5±0.2	3.2	66.9±0.9	4.5	183.6±2.4	12.4
Zn (1279.74)	474.7±6.3	37.1	274.0±0.7	21.5	239±4.7	18.7	550.0±6.1	43.0

*± Values indicate Standard Deviation

6.5.3   Ro-SB soil

The data for the heap leaching of the Ro-SB soil is summarized in Table 6.7, and shows that the specific metals reported different extraction efficiencies across the four extractants examined. In the case of Cd, the order of extraction efficiency was EDTA > CA > EDDS > Hacac with average efficiency of 60.8% (86.6 – 28.9). EDTA outperformed the other extractants by a range of 3 to 1.2 times. For Cu, it was observed that all extractants efficiently mobilized Cu, although, Hacac extracted the most, with less than 10% as much as the other extractants. The order of extraction efficiency was Hacac > EDDS > EDTA > CA

with average efficiency of 68.9% (71.4 – 65.4). For Ni, Hacac in general, outperformed the other extractants by a range of 6.3 to 5.7 times. It is however, noted that EDTA, EDDS and CA extracted similar amounts of Ni. In the instance of Pb, the order of extraction efficiency was EDTA >> CA >> EDDS >> Hacac with average efficiency of 38.1% (81.4 – 2.0). EDTA extracted between 40 to 2 times more than the rest of the extractants. For Zn, the order of extraction efficiency was EDTA > EDDS > CA > Hacac with an average efficiency of 69.9% (77.2 – 60.3%). Although, EDTA extracted Pb the most, the percentage efficiency with the exception of Hacac (22%) was less than 10% for the other extractants. Overall, it is observed that Cu and Zn were efficiently extracted irrespective of the extractants applied. Only EDDS gave a satisfactory efficiency for Ni. Cd was extracted satisfactorily by all extractants except for Hacac that displayed poor efficiency for the metal. EDTA and CA showed reasonable extraction efficiency for Pb, while EDDS and Hacac extracted the metal poorly. The high efficiencies in metals extracted suggests the availability of these metals in a more labile phase (exchangeable and carbonate) where they are easily mobilized (Jain et al., 2008). The poor extraction observed for Pb using Hacac and EDDS may be attributed to poor complexation preferences and metal exchange reaction due to metal ion dissociation (Tsang et al., 2009) as discussed in previous chapters.
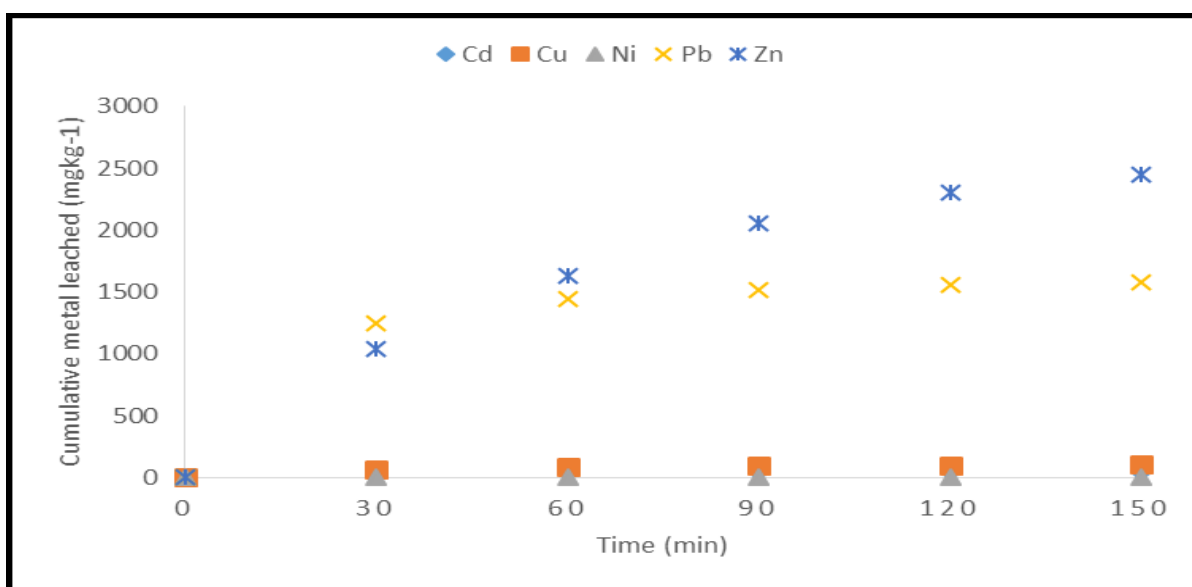

Figure 6.6. Breakthrough curves of selected metals leached from RO-SB with Zn and Pb optimally extracted using EDTA as extractant

Table 6 7 Extractability of metals (Cd, Cu, Ni, Pb and Zn) of interest from industrially impacted Ro-SB soil by a heap extraction with selected extractants. The standard deviation on the values reported are in the range ± (0.1 – 22.5)

Metal	EDTA		EDDS		Hacac		CA	
Loading (mgkg^{-1})	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency	mgkg^{-1} leached	% efficiency
Cd (51.93)	45.0±0.5	86.6	26.4±0.3	50.8	15.0±0.2	28.9	40.0±0.1	76.9
Cu (147.83)	102.0±0.7	69.0	103.5±0.3	70.0	105.5±0.4	71.4	96.6±1.8	65.4
Ni (31.46)	5.3±12.1	16.7	4.7±0.2	14.9	29.8±0.8	94.6	5.3±0.4	17.0
Pb (1940.91)	1578.2±8.2	83.4	339.1±5.8	17.5	38.8±1.0	2.0	1003.4±2.9	51.7
Zn (1279.74)	2446.2±3.8	77.2	2283.0±18.4	72.1	1911.0±22.5	60.3	2222.0±13.1	70.1

*± **Values indicate Standard Deviation**

6.5.4 Real soil versus SS

A similar comparison undertaken in Section 6.3.4 was carried out for the heap study. The data is displayed in Figure 6.2. Investigation of the three environmental soils shows that the extraction trends as shown in Figure 6.2, displayed significant differences in the leaching behaviour of the different metals extracted. However, when the soils were individually compared with the the SS, notable similarities and differences in the metals leached to natural soils were observed. Significant variation was observed when SS was compared to Ro-PH leaching capacity, and most especially for Ni and Pb that were poorly leached. Significant findings are noted for each soil in the section below.

The average leaching efficiencies of the metals extracted in Ro-PH, Nig-S and Ro-SB were approximately 30%, 50%, and 70% respectively. The leaching potential of the natural soils are compared with the SS soil. It was observed that Ro-SB, Ro-PH and Nig-S soils were in the range of 1.2, 2.0 and 3.0 times higher than SS respectively. The sequence for average leaching potential of the soils are in the order Ro-SB > Nig-S > Ro-PH > SS (Figure 6.2).

However, when extracted metals were compared within group for the selected extractants, EDTA appears to outperformed the rest of the extractants for the different soils investigated (Figure 6.1). The extraction efficiency is in the order EDTA > EDDS > CA > Hacaca ; EDTA ≈ CA > EDDS > Hacac ;EDTA > CA ≈ Hacac > EDDS ;EDTA > EDDS > Hacac≈ CA for Nig-S, Ro-PH, Ro-SB and SS respectively.

The enhanced extraction of metals observed in Nig-S and Ro-SB soils could be attributed to the same reason alluded for similar soils studied under column extraction in Section 6.3.4.

However, lower extraction efficiency of metals observed for SS (25.3%) in section 6.2 (d) was not to be expected, considering the fact that, SS is an artificial soil therefore, should be anticipated to have most of its metals loosely bound to geochemical phase(s) (exchangeable/carbonate) that is easily amenable to leaching (Jain et al., 2008) as was observed for SS in column extraction. However, these differences maybe attributed to the reaction kinetics associated with the process configuration of the leaching systems (Ylivainio, 2010).

In addition, lower metal extraction in Ro-PH as was previously observed with the column extraction in Section 6.3.4 which, could be as a result of the presence of goethite previously explained. Moreso, it was observed that the presence of goethite in Ro-PH soil influenced the dynamics and leachability of the extractants used (reaction kinetics) and showed dissimilar trends in the order in which metals are extracted in most soils. For instance, Hacac and EDDS do have preferential affirnity to complex Cu and some trace metals in most of the soils investigated (SS, Ro-SB, Nig-S) in this study. However, in the case of Ro-PH soil, CA seem to perform better than Hacac and EDDS compounds in the presence of goethite. The explaination to this phenomenon could be explained by the presence of the three carboxylate groups (COOH and four phenolic groups (OH) that enables a greater capacity to increase solubities of most minerals (goethite).
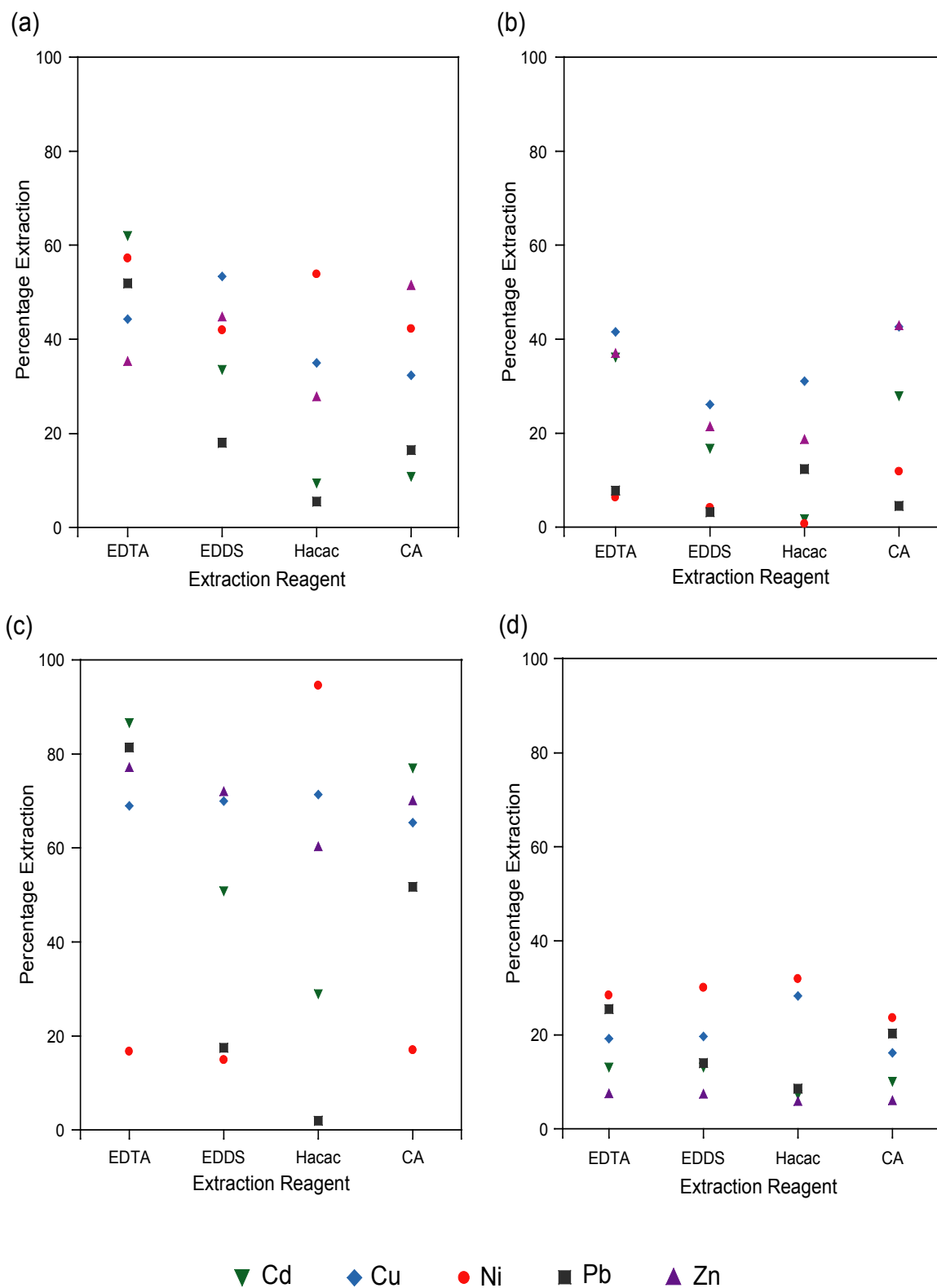
Figure 6 2 Percentage extraction of metals of interest (Cd, Cu, Ni, Pb and Zn) from contaminated soils as influenced by selected extractants (EDTA, EDDS, Hacac and CA) studied with heap leaching and used for comparing and contrasting of environmental soils (Nig-S, Ro-PH and Ro-SB) with SS for predictive purposes, where a) Nig-S; b) Ro-PH; c) Ro-SB; d) SS.

6.6   Extraction profiles and trends

The description of base metal releases from column and heap processes over time using appropriate models (First-order, Elovich and Power function models) was previously covered in section 4.4. Such information became vital to better understand desorption mechanisms associated with chemical reactions and diffusion processes in a dynamic system (Riahi et al., 2017). Three common models were used to describe the desorption process that occurred over a period of 150 min (Table 6.8). All parameters were evaluated by a non-linear regression using excel software 2013 version. The experimental data for the metals of interest (Cd, Cu, Ni, Pb and Zn) from different soils (Nig-S, Ro-PH, Ro-SB and SS) using EDTA as the preferred extractant was fitted to these same three models. The reaction rate parameters and the simple regression analysis for the different equations tested are listed in Table 6.8. The goodness of fit of these models were evaluated by the coefficients of correlation (r^2) and standard error of estimate (SSE) and graphs displayed in Figure 6.3. However, for the purpose of convenience, only the data for the column leaching process was shown here, although it was compared with the heap leaching studies (calculated elsewhere) afterwards.

For the first-order model, the correlation coefficients are unacceptably low between 0.546 and 0.952. In addition, the difference between the experimental (measured) and theoretical (calculated) masses released at equilibrium is large (between 0.5 -436.9 and 0.70 - 673.0). The experimental values are five to ten times higher than the theoretical ones. This shortfall suggests that targeted metals release kinetics did not follow a first-order mechanism (Figure 6.3).

The power function equation, which has been used to describe Cd, Cu, Ni, Pb and Zn release from simulated soil studied in section 4.4, fitted the experimental data reasonably well, as judged by its r^2 (Table 6.8) and S.E values. Based on the r^2 values (0.908 – 0.993) and relatively low SSE (0.599-6.347), the metal extractions from Nig-S, Ro-PH and Ro-SB natural soils were best described by the Elovich model (Jang et al., 2005; Li et al., 2001; Shirvani et al., 2007). According to Saha et al. (2005), an increase in α or β^{-1} would increase the reaction rate. For the Elovich model, the mean metal release after 90 mins ranged from (4.04 to 1.28) for Cd, (5.33 to 2.79) for Cu, (62.36 to 7.90) for Ni, (14.69 to 3.45) for Pb and (6.79 to 2.79) $mgkg^{-1}$ of soil min^{-1} for Zn with SS and Ro-SB having the capacity to release more metals when compared with Ro-PH and Nig-S. The suitability of this model for natural soils

can be attributed to its usefulness in describing desorption of metals on highly heterogeneous surfaces (Saha et al., 2005). Conversely, this was not the case for the SS as the r^2 was low for most metals when compared to the natural soils (Figure 6.5). The parameters α and $β^{-1}$ of the Elovich model varied substantially with soils and concentration of specific metals. Therefore, the soils in which a fast release of metals occurred had relatively large α values. These were observed in Cd, Pb and Zn extractions in Ro-SB and Cu and Ni in SS (Table 6.8).

The comparison of the column leach process with the heap leach process indicates that the kinetics of the different metals leached from the different soils, shows significant variations in the mean rate of metals as judged from the Elovich equation released. This variation was clearer in the SS than in the natural soils (Ro-SB, Ro-PH and Nig-S). In fact, the mean metal leaching rate of Cu, Ni, Pb and Zn in the column process was about 9.4, 12.3, 3.2 and 15.5 $mgkg^{-1} min^{-1}$soil higher than in the heap leaching process. The natural soils showed slight variations of kinetic data between the column and heap processes. This phenomenon may indicate that the desorption behaviour in the natural soils is a heterogeneous diffusion process (Aharoni and Suzin, 1982a; b; Anju and Banerjee, 2010).

Table 6 8. Parameters of kinetic models calculated for the extraction of base metals of interest from soils as a function of time and 0.034M EDTA in a column leaching process

Extractant	Metals	Soils	Elovich $q_t = \left(\dfrac{1}{\beta}\right) ln(\propto \beta) + \left(\dfrac{1}{\beta}\right) ln(t)$			Power function $ln q_t = ln a + b ln(t)$			First order $ln(q_e - q_t) = a - k_1 t$		
			α	β	r^2	a	b	r^2	a	k_1	r^2
EDTA	Cd	Nig-S	11.104	0.171	0.963	1.475	0.778	0.949	1.200	0.0001	0.753
		Ro-PH	3.316	0.573	0.993	1.760	0.632	0.972	0.970	0.0001	0.623
		Ro-SB	14.209	0.129	0.979	0.348	0.500	0.955	4.460	0.0050	0.614
		SS	8.191	0.217	0.893	0.388	0.461	0.856	4.050	0.0500	0.639
	Cu	Nig-S	22.135	0.080	0.930	0.227	0.310	0.843	3.070	0.0005	0.911
		Ro-PH	42.245	0.043	0.993	0.999	0.756	0.973	5.420	0.0005	0.785
		Ro-SB	42.245	0.043	0.986	0.711	0.520	0.962	5.510	0.0050	0.659
		SS	117.961	0.016	0.826	1.631	0.573	0.866	6.340	0.0050	0.680
	Ni	Nig-S	24.753	0.071	0.981	0.445	0.340	0.881	2.380	0.0001	0.908
		Ro-PH	3.137	0.629	0.981	2.514	1.343	0.857	0.980	0.0005	0.983
		Ro-SB	3.137	0.629	0.981	2.079	1.007	0.974	2.310	0.0005	0.950
		SS	195.620	0.009	0.894	0.586	0.452	0.969	7.150	0.0050	0.686
	Pb	Nig-S	49.256	0.037	0.969	0.887	0.530	0.890	2.600	0.0050	0.904
		Ro-PH	36.094	0.055	0.987	1.635	0.962	0.973	4.780	0.0005	0.960
		Ro-SB	530.225	0.003	0.982	0.868	0.484	0.957	8.030	0.0050	0.867
		SS	153.762	0.012	0.858	1.103	0.637	0.789	6.650	0.0050	0.639
	Zn	Nig-S	118.768	0.016	0.836	0.601	0.744	0.985	4.150	0.0001	0.546
		Ro-PH	118.772	0.016	0.992	0.601	0.744	0.980	6.140	0.0050	0.952
		Ro-SB	806.058	0.002	0.987	1.275	0.783	0.968	8.030	0.0050	0.927
		SS	288.677	0.006	0.896	0.593	0.487	0.858	7.470	0.0500	0.690

Solid/liquid ratio (1:10)

q_e = base metals released (mgkg^{-1}) at equilibrium; q_t = base metals released (mgkg^{-1}) at time t (sec); k_1 = first order rate constant (sec^{-1}); a = constant; b = constant (rate coefficient value); β and α are Elovich constants obtained from the Elovich kinetic model, r^2 = coefficient correlation, SSE = standard error of estimates
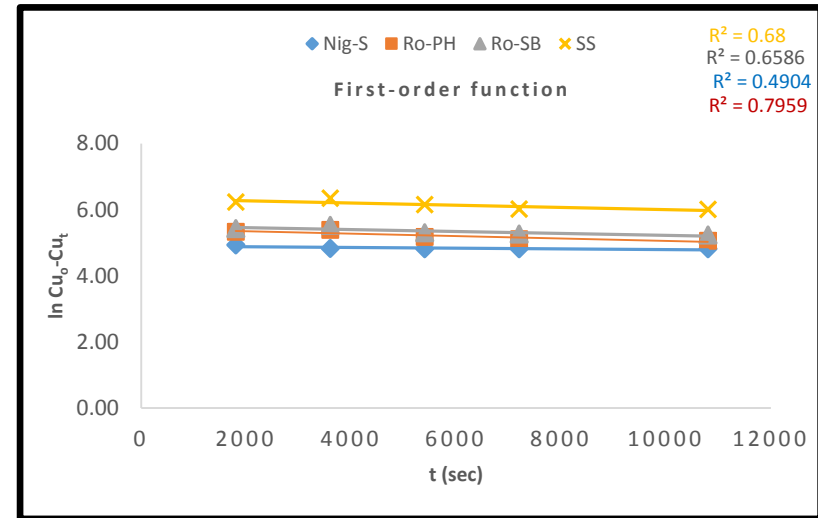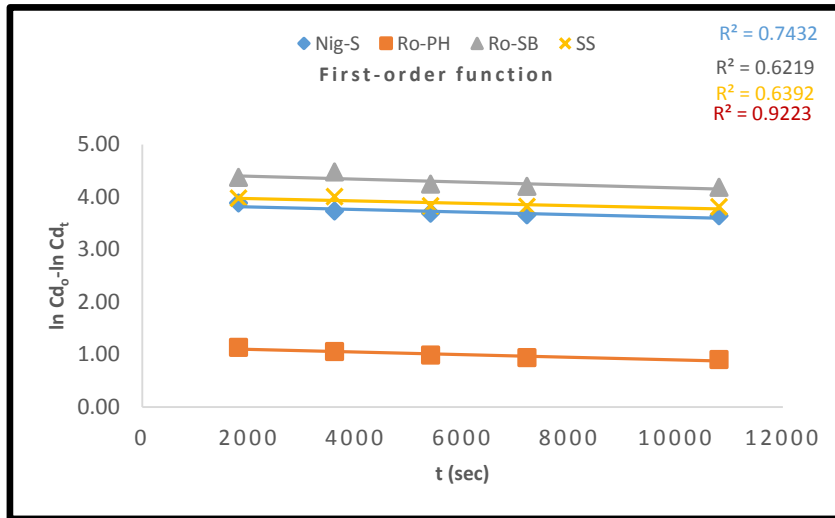
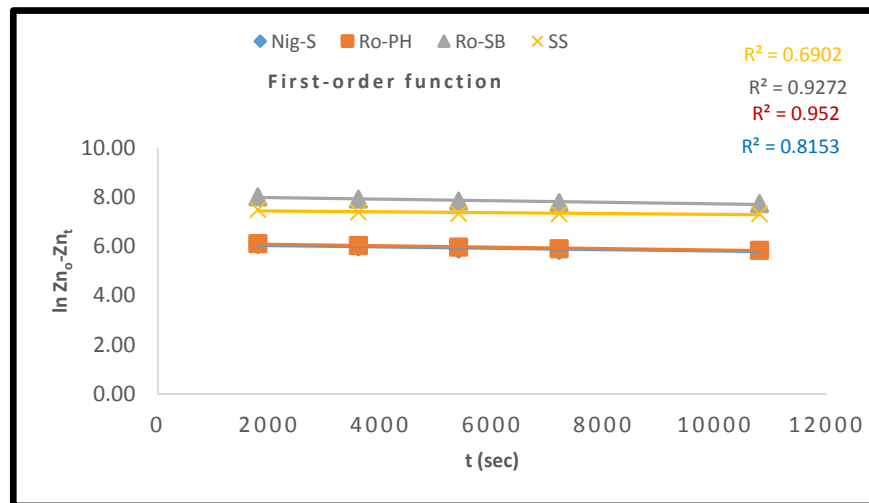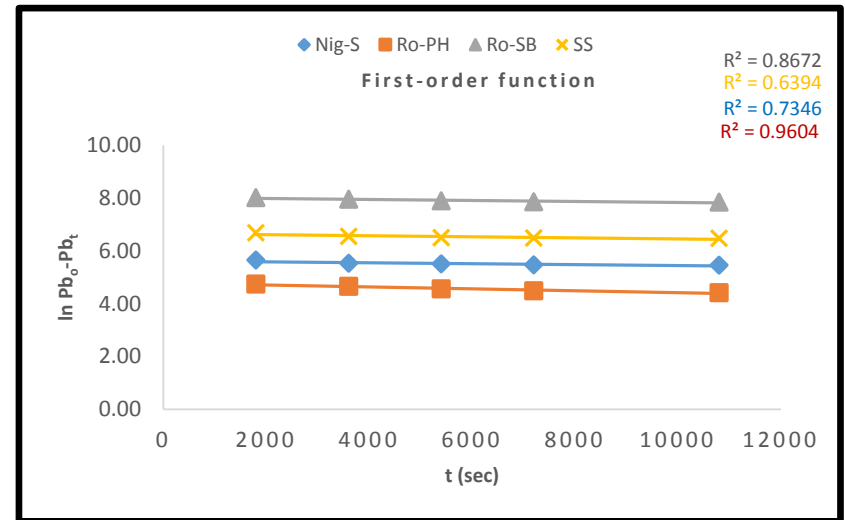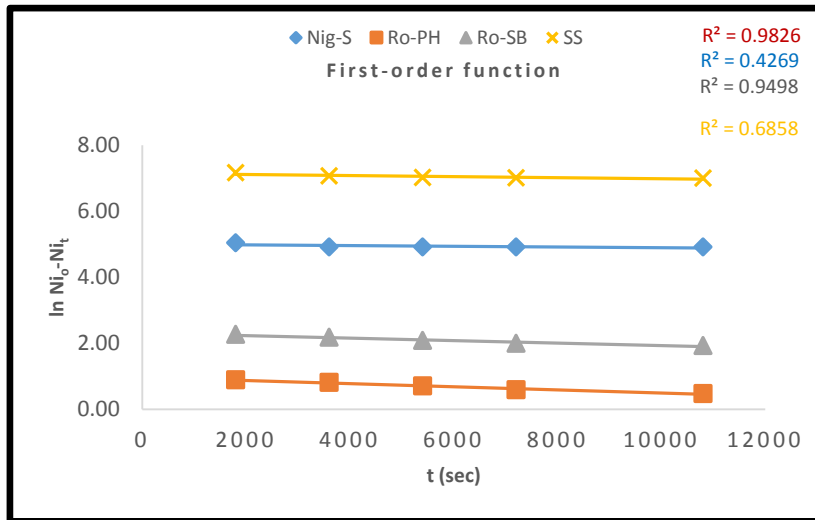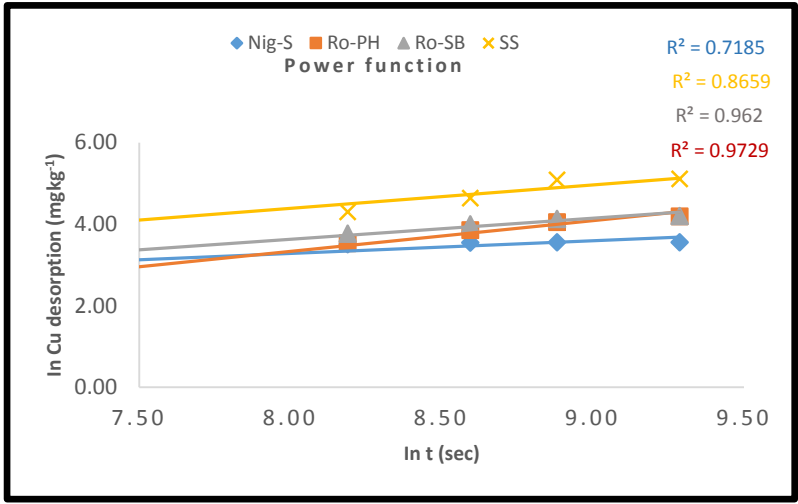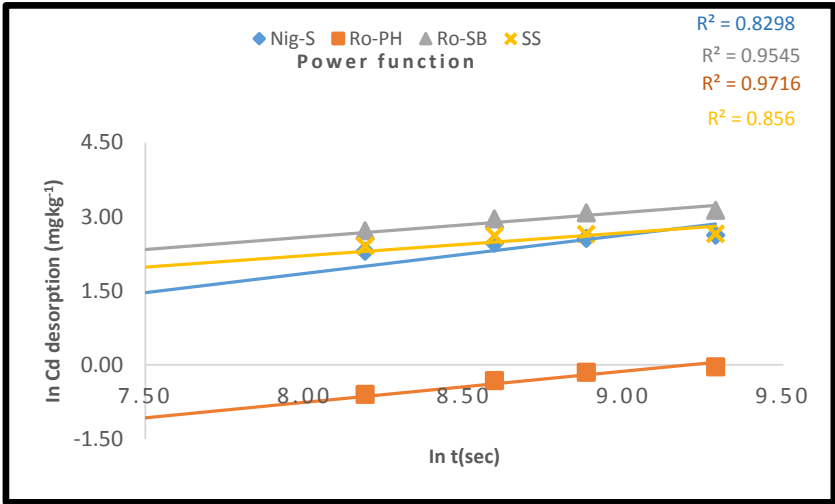Figure 6 3. Desorption kinetic curves of base metals (Cd, Cu, Ni, Pb and Zn) in the soil using fitting curves of First Rate Order equation

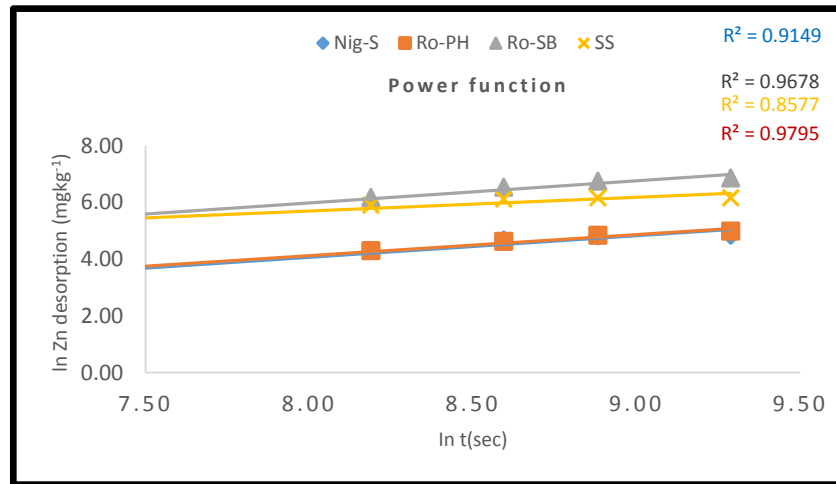Figure 6 4. Desorption kinetics curves of base metals (Cd, Cu, Ni, Pb and Zn) in the soil using fitting curves of the Power Function equation

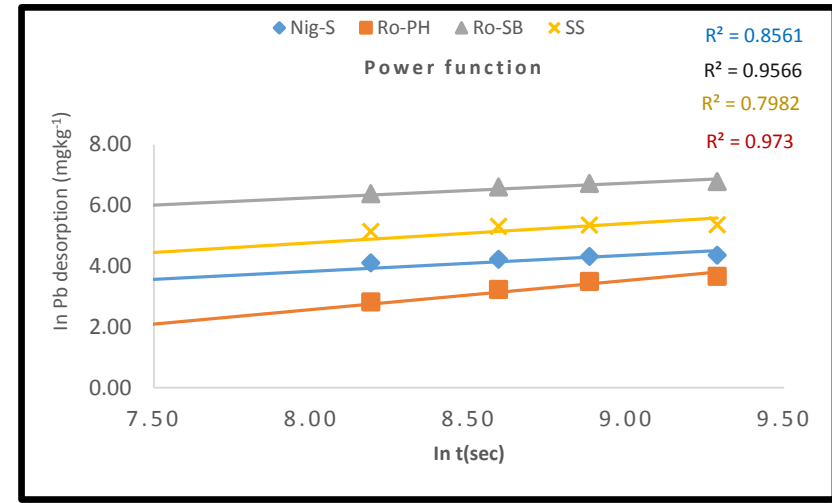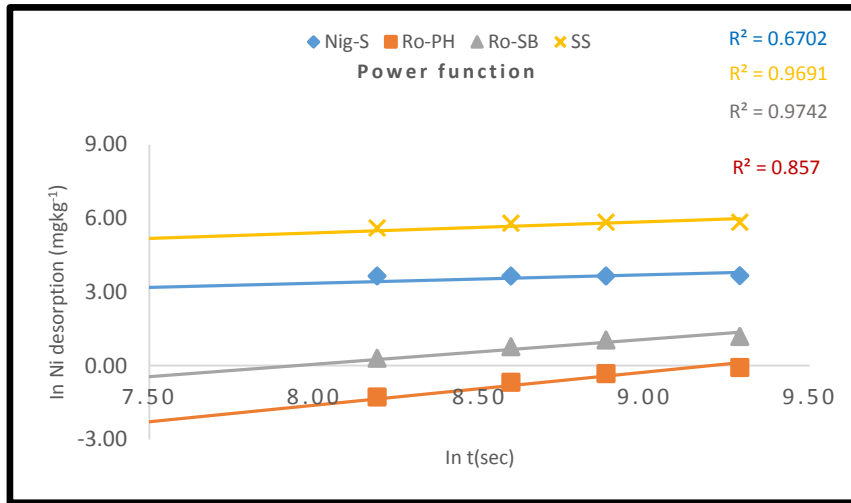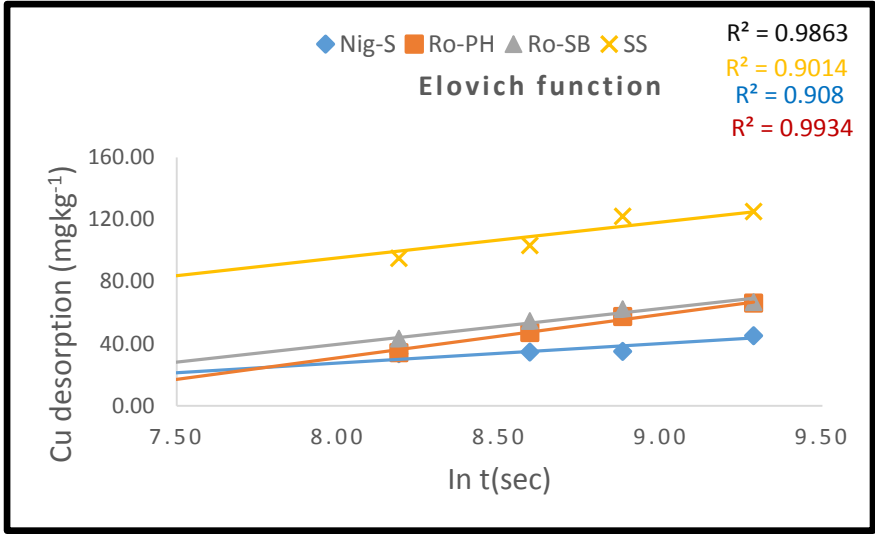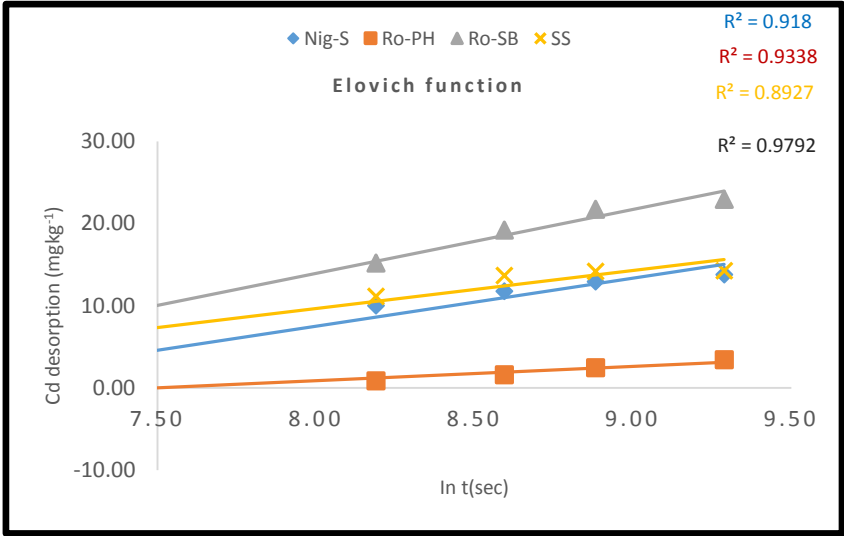Elovich function (Cd desorption vs ln t)

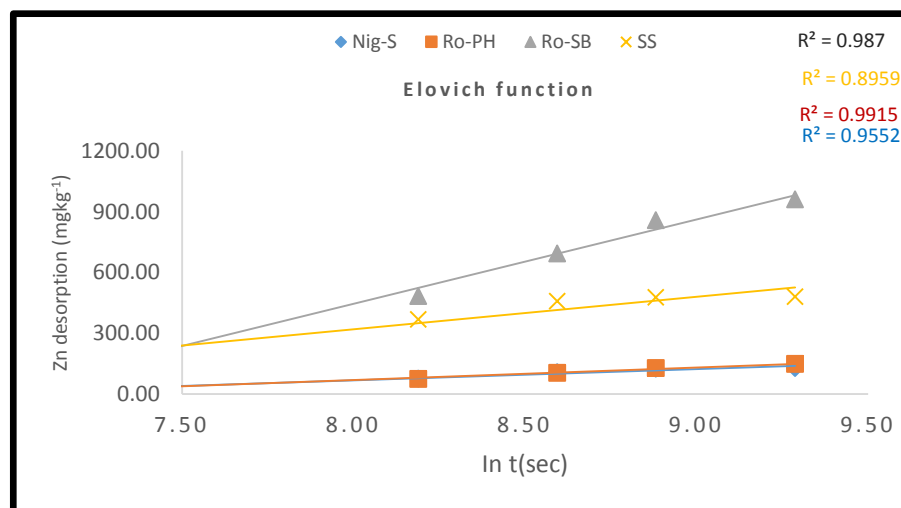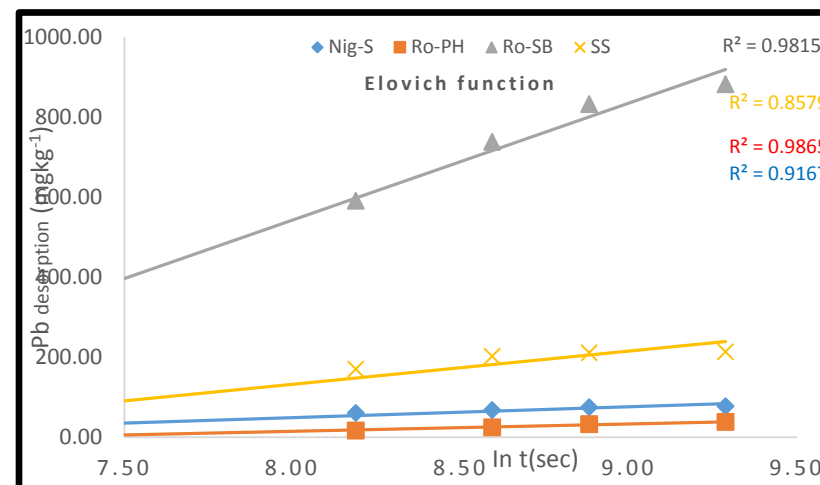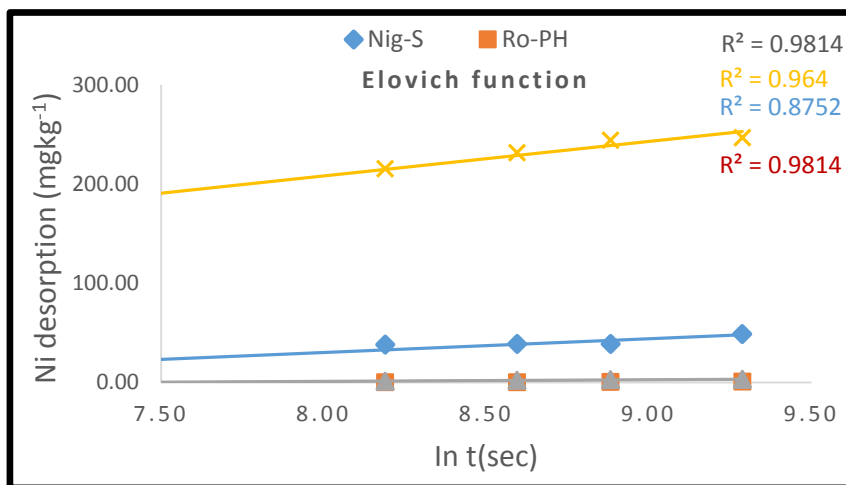Elovich function (Cu desorption vs ln t)

Figure 6 5. Desorption kinetic curves of base metals (Cd, Cu, Ni, Pb and Zn) in the soil using fitting curves of Elovich equation

6.7   Conclusion

The behaviour of SS appeared comparable with the leaching behaviour exhibited by Ro-SB. The leaching potentials of three environmental soils of a multi-metal system was studied using dynamic column and heap leaching experiments with a solid/liquid ratio 1:10 across five extractants for 150 min. During the dynamic experiments, the behaviour of the three environmental soils as influenced by the process as well as the extractants were compared and contrasted with the simulated soil (SS) for predictive purposes. Some of the important findings are summarized below:

- The desorption trends of the base metals from the different soils (both natural and simulated) were studied by using first-order, power function and Elovich rate equations. For all heterogeneous soil systems evaluated, the Elovich equation provided the best correlation and the least SSE of the experimental data. The rate parameter of the Elovich showed that the rate of metal release was higher for the SS and Ro-SB soils than for the Nig-S and Ro-PH soils.

- A comparison of the heap leach and column leach processes for metal extractions from the different soil matrices indicated significant differences. However this was more influenced in the SS than in the natural soils.

- When considering result obtained in column leach study, it was observed that the leaching behaviour of the three environmental soils (Nig-S, Ro-PH and Ro-SB) differed noticeably from one another. For the Nig-S soil, the amount of metal leached decreased in the order Zn > Cu > Ni ≈ Cd > Pb. Cd and Pb leached better with EDTA, whilst Cu and Ni efficiently leached with Hacac. Zn however, showed the best leaching efficiency with CA. For Ro-PH, It was observed that the metals leached in decreasing order Cu > Zn > Cd >Ni > Pb, with EDTA and Hacac yielding the best leaching results when compared to the other extractants. Cd and Pb were efficiently leached with EDTA, while Cu, Ni and Zn were better extracted with Hacac. For Ro-SB, it was observed that Cd and Cu were preferentially leached compared to the other two environmental soils. However, no individual extractant was most efficient for the respective metals leached. However, based on a comparison with SS studied under similar conditions, it was observed that the Ro-SB leaching profile compared

reasonably well, with the SS one. In addition, the total metal removal efficiency was over 50% for both soils. By contrast, Nig-S and Ro-PH behaved differently with total metal removal efficiencies of less than 50% and 20% respectively.

- In the application of the heap leach studies, it was observed that the three different environmental soils displayed notable differences in their individual leaching behaviour. For Nig-S, it was observed that the metals leached decreased in order Ni > Cu ≈ Zn > Cd > Pb. The individual extractants performed differently, during the process with EDTA giving the best extractions. Cu extractions, however was with Hacac. For Ro-PH, Ni and Pb were poorly extracted by less than 10% in EDTA, EDDS and Hacac. However, a higher leaching efficiency was observed by with CA, followed by EDTA > EDDS > Hacac. For Ro-SB, it was observed that metals were extracted from the soil matrix much better and in higher quantities than the other two environmental soils, except in the case of Ni where the Nig-S leached better. It is observed that EDTA generally outperformed the other extractants. However, Cu showed better leaching efficiency with Hacac. Overall, the amount of metal leached from the different soils decreased in the order Ro-SB > Nig-S > Ro-PH. In order to appreciate the variations in the different extraction profiles from the different environmental soils, one should evaluate their economic feasibility for revenue generation to make a practical selection for their treatment. This aspect will be explored in more detail in chapter 7 where the laboratory generated extraction data will be utilized in an economic estimation based on certain assumptions.

Table 6.9 Stability sequence of metals for different environmental soils studied with column leach and heap leach studies

Soil	Column leached	Heap leached
Nig-S	Zn > Cu > Ni ≈ Cd > Pb	Ni > Pb > Cd > Cu > Zn
Ro-SB	Cu > Zn > Cd > Pb > Ni	Ni >> Zn ≈ Cu > Cd >> Pb
Ro-PH	Cu >> Zn > Cd > Ni > Pb	Cu > Zn > Cd >> Pb ≈ Ni

-

Table 6.10 Evaluation of performance indicator for the different soils, extractants and processes measured

Soil	Extractant	Column leached	Heap leached
Nig-S	EDTA	Cd, Pb, Zn	Cd, Pb, Zn
	EDDS	Ni	
	Hacac	Cu, Ni	
	CA		Cu, Ni
Ro-PH	EDTA	Pb	Cd, Cu
	EDDS		
	Hacac	Cu, Ni, Zn	
	CA		Cu, Ni, Pb, Zn
Ro-SB	EDTA	Pb	Cd, Pb, Zn
	EDDS	Cu	
	Hacac	Ni	Cu, Ni
	CA	Cd, Zn	

Chapter 7

Economic evaluation of the remediation of real soils

In chapter 6 displayed a comparative study of the leaching behaviours of metals from the different contaminated natural soils and an artificially contaminated simulated soil. Not only was the leaching profiles of different leaching agents (ethylene diamine tetraacetic acid [EDTA], ethylene diamine disuccinic acid [EDDS], acetylacetone [Hacac] and citric acid [CA]) compared, but also two different leaching processes (column vs heap leaching). When considering an industrial process and making a recommendation as to the effectiveness of a remediation approach (which is potentially also profitable), various economic factors have to be considered. These include, but are not limited to, the price of the leaching agent and its reuse potential; the price of the metals, it's leaching and recovery efficiency; the process type; the environmental impact of the process, and any other operating and raw material costs. This chapter investigates the influence of some of these factors on the economics and evaluates some of the process alternatives based on the experimental results from the column and heap leaching tests.

Ultimately, the following question will be addressed: "Can one of these remediation processes be financially profitable (self-sustaining) and if not, to what extent can the leaching and recovery of heavy metal contaminants from contaminated soils be sustainable."

7.1   Process Description

A process block flow diagram of the soil remediation process was conceptualised and is presented in Figure 7.1. The process comprises two main process steps, namely soil cleaning/ metal extraction and metal recovery from the leach liquor.
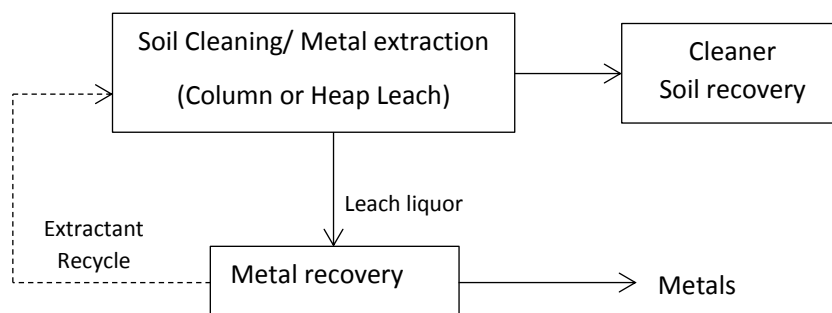

Figure 7 1 Block Flow diagram of the proposed soil remediation/recovery process

Included in this diagram is an extractant recycle stream as recycling of the extractant might have a significant effect on the economics of the process. A more detailed process flow diagram will be presented in a later section of this chapter.

7.2 Economic factors and its influence on the process economics

The study considered the remediation of three soils, namely Nigerian soil [Nig-S] and two Romanian (Copsa-Mica [Ro-SB] and Campina [Ro-PH]) soils. It was previously stated that metal contaminants can be an alternative source of metals and consequently it is important to determine the potential maximum revenue that can be obtained from these soils.

Revenue from the remediation of soils is generated by selling the extracted and recovered metals in the metal market. The prices of the metals contaminants were obtained from the most relevant websites (e.g. https://www.lme.com/; Metalprices.com; Infomine.com), in the period between March to August 2017, and is presented in Table 7.1. From the table it can be seen that metal contaminants, Nickel, Copper and Zinc offer the highest potential revenue if it is recovered and sold.

Table 7. 1 Metal market Prices ($/kg)

Metal	Price $/kg
Cadmium (Cd)	1.157
Copper (Cu)	6.418
Nickel (Ni)	11.26
Lead (Pb)	1.028
Zinc (Zn)	2.993

These values were used to calculate the potential revenues from the different soils under investigation. Three cases are presented in Table 7.2. In the first case, it is assumed that all the metals are extracted and recovered from the soils. In the second case, extraction values from previous researchers were used to calculate potential revenue, once again assuming that the total mass extracted are recovered. The last case uses the experimental extracted values (as given in Chapter 6) and assumes total metal recovery. However, as initially stated, soil type and extractants are two major factors that have influenced the recovery of targeted metals and as such will significantly affect the economics of metal recovery. For instance, the presence of minerals (goethite) in Ro-PH and an extractant's preferential affinity as it relates to the different metals, was shown to be significant in chapter 6 of this study. The values in Table 7.2 are calculated on the basis of 90% metal recovery and is given as cumulative of total mass extracted for each metal multiply by both the metal price and 90% recovery.

$$Revenue\ from\ soil\ = (x_i * mp_i + x_{ii} * mp_{ii} + x_{iii} * mp_{iii} + x_{iv} * mp_{iv} + x_v * mp_v) * 0.9$$
EQ 1

Where

$x_i, x_{ii}, x_{iii}, x_{iv}$ and x_v are Cd, Cu, Ni, Pb and Zn leached in $(mgkg)$ and mp_{i-v} represent current price for each of the metal leached.

Table 7.2 Revenue from metals in contaminated soils presented on three case instances of values generated from a) an ideal system, b) adopted from literature c) experimental system

Description	Revenue from Ro-SB Soil ($/tonne)	Revenue from Ro-PH Soil ($/tonne)	Revenue from Nigerian Soil ($/tonne)
All metals extracted (a)	19.01	8.71	3.13
Literature - Column EDTA(b)*	12.73	5.83	2.10
Experimental – Column EDTA (c)	3.84	0.92	0.84
Experimental – Column EDDS (c)	3.64	0.78	0.26
Experimental – Column Hacac (c)	3.35	1.26	0.92
Experimental – Column CA (c)	5.11	0.76	0.82
Experimental – Heap EDTA (c)	8.74	2.46	1.29
Experimental – Heap EDDS (c)	7.14	1.46	1.26
Experimental – Heap Hacac (c)	6.11	1.59	1.00
Experimental – Heap CA (c)	7.57	2.67	1.13

EDTA values from literature source: Irene and Yang (1999).

If one compares the theoretical maximum amount of revenue from literature that can be obtained from extracting, recovering and selling all the metals present in the soils with that obtained for the column and heap experiments conducted in this study, then the values are very low. From the heap leaching experiments, EDTA and citric acid leaching appears to be the most promising extractants for maximum metals leached. A similar trend is seen for column leaching. However, the potential revenue generated by the heap leaching is more than that of column leaching for the experimental conditions used in this study. It is also clear that one Romanian soil (Ro-SB) has the potential to generate the most revenue compared with Nigerian soil (Nig-S) and Romanian soil (Ro-PH).

If we compare the potential revenue based on EDTA column leaching values obtained from literature (references) with the experimental values from this work, then it is clear that there might be scope for improving the existing leaching processes proposed in this study. It should be noted that soil characteristics can play a significant role in the extraction and that previous studies were performed on different types of soils (Herbert et al., 2002).

Revenue is however not the only criteria that should be used to make a conclusion as to which method of extraction to use (heap or leach), and which chelate is the most economical. Therefore, the raw material cost of the leaching process was also considered and a maximum possible profit was calculated for each soil based on column or heap leaching using different chelates. This is presented in Tables 7.3 to 7.5. The term maximum profit refers to the revenue less raw material costs and presents the maximum possible profit that one can make. In general, costs such as operating expenses and utility costs (water and electricity) will also have an effect on the profitability of a process. The elemental cost analysis for the recovered metals is highlighted below

Cost Analysis

The project evaluation for the laboratory-generated data was based on the following assumptions:

Maximum metal recovered 50% and 90%

Maximum chelate recycled 50% and 90%

Cost of energy consumed 283.9 KWh (Sadhukhan et al., 2016)

Components of initial fixed investments like building, machinery and equipment where not considered at this phase because the scheme is a laboratory based exercise at the moment. Potential scale-up to both pilot and commercial phases are possibilities in the future.

Operating Cost

The operating cost for the different components are as follows; here, the raw material is the effluent that is to be disposed of during remediation as such no cost is attached to it. However, cost of other inputs like utilities (energy, water and extracting chemicals are calculated as

Utilities per process type (column or heap) are as follows;

Cost of extracting chemicals (EDTA, EDDS, Hacac and CA) per column/heap ($/kg) are calculated with respect to the unit price of each extractant as 2.9, 5.65, 3.13 and 2.8 respectively and presented in Table 7.3.

Cost of energy (KJ) as applicable to a laboratory process = 283.9 KWh

Total cost per process (column or heap) type for the Ro-SB, Ro-PH and Nig-S soils are presented in Tables 7.3, 7.4 and 7.5 respectively.

Therefore, Operating Cost for the selected extractants cum different soils = Cost of (Utilities + laboratory reagents) as presented as presented in Appendix D

Benefits

The benefits were calculated on the basis of the following data:

Average volume of effluent processed per heap = 1500 M^3

Average volume of effluent processed per column = 250 M^3

Average multi-metals recovered in mgkg per heap for Ro-SB, Ro-PH and Nig-S are 800, 155 and 80 mgkg respectively

Average multi-metals recovered in mgkg per column for Ro-SB, Ro-PH and Nig-S are 400, 51 and 42 mgkg respectively

Cost of multi-metals recovered in mgkg per heap/column for Ro-SB, Ro-PH and Nig-S are calculated from EQ.1 and represented in Table 7.2.

Revenue Return per column/heap in Tables 7.3, 7.4 and 7.5 = metal income (Table 7.2) – operating cost (utilities)

Present Value of Expenditure

The calculations of present values of expenditure and returns are calculated by applying the relationships:

Expenditure: Initial Fixed Investment + Operating Cost   EQ 2

Present Value of Operating Cost ($/t) (EDTA) for Ro-SB, Ro-PH and Nig-S per column and heap

Column = 8.64, 16.93 and 10.20 (calculated as chelate usage kg/t * concentration of chelant (mol/L* recycled %) respectively and represent the **Present Value Cash outlays** for column

Heap = 368.48, 117.51 and 291.68 (calculated as chelate usage kg/t * concentration of chelant (mol/L* recycled %) respectively and represent the **Present Value Cash outlays** (cost) for heap

Present Value of Revenue Returns

Present Value of Return (cash flow) for Ro-SB, Ro-PH and Nig-S per column or heap are represented in Tables 7.3, 7.4 and 7.5

$$Benefit: Cost\ (B:C)ratio = \frac{present\ value\ of\ B}{present\ value\ \ of\ C} \qquad\qquad \text{EQ 3}$$

$$B:C = \frac{8.74}{368.48} = 0.02\ for\ EDTA\ heap\ process$$

$$Net\ Present\ Value$$
$$= Present\ Value\ Cost - Present\ Value\ of\ Benefit\ for\ the\ soils \quad \text{EQ 4}$$

These values were all negatives when calculated and are presented in Tables 7.3, 7.4 and 7.5

The Pay Back Period (PBP) is calculated by applying the Equation;

$$PBP = \frac{Total\ investment}{Annual\ Return} = \frac{368.48_{edta}}{8.74x12_{edta}} = 3.5\ (approx = 4\ years) \qquad \text{EQ. 5}$$

 Thus, the Payback Period will be 4 years.

As can deduce above, the **Benefit to Cost ratio**, **Net Present Values** and **payback period** are indicators used to evaluate if a project is non-profitable, profitable or socially acceptable within the context of techno-economic studies. The indicators are defined on certain decision criteria. For example, the decision rule for B/C ratio is such that the value must be more than 1 for the project to be profitable, and non-profitable if it is less than 1.

For the Net Present Value (NPV), the decision rule is that the project is acceptable if NPV is positive depending upon how much is the expectation of the investor. However, if the values of NPV is negative, then the project is rejected provided it does not fall in the category of social obligations. Social obligation in this context refers to general social benefits such as soil remediation, creation of employment opportunity, community/public safety, etc.

The payback Period from our calculations in EQ 5 shows that PBP is potentially recoverable in 4years. Included in the tables are three cases where the unreacted and regenerated chelant is either not recycled or recycled back to the extraction section at 50 and 90 % recycling rates. Once again, it was assumed that all the extracted metals could be recovered and sold.

Table 7. 3 Maximum Profit for metal recovery from Copsa-Mica (Ro-SB) soil at different chelate recycling rates using heap and column leaching.

Method & Extractant	Max Profit 0% Recycling ($/t soil treated)	Max Profit 50% Recycling ($/t soil treated)	Max Profit 90% Recycling ($/t soil treated)
Column - EDTA	-82.17	-38.95	-4.37
Column - EDDS	-673.36	-334.66	-63.70
Column - Hacac	-213.93	-105.11	-18.05
Column - Citric Acid	-326.07	-160.20	-27.50
Heap - EDTA	-3605.11	-1797.70	-351.77
Heap - EDDS	-2731.67	-1361.87	-266.03
Heap - Hacac	-1234.11	-613.66	-117.30
Heap - Citric Acid	-3481.77	-1736.68	-340.61

It can be seen from the data that for the column leaching EDTA gives the highest potential maximum profits. The column leaching process consumed far less leachant solution than the heap leaching. It can also be observed that recycling of the chelate is essential to reduce the costs of the process. For each experimental scenario shown here a loss is being made. If other costs were to be included such as operating costs and utilities then this loss per tonne of soil treated will increase even more. It therefore seems that at these experimental conditions the process is not profitable, but that you actually pay to treat the soil. One would of course always pay to treat soil, the question is just how much. If the cost paid is high, it may still be sustainable and profitable to adopt this route of treatment.

Table 7 4 Maximum Profit for metal recovery from Campina (Ro-PH) Soils at different chelate recycling rates using heap and column leaching.

Method & Extractant	Max Profit 0% Recycling	Max Profit 50% Recycling	Max Profit 90% Recycling

	($/t soil treated)	($/t soil treated)	($/t soil treated)
Column - EDTA	-168.38	-83.73	-16.01
Column - EDDS	-456.76	-227.99	-44.97
Column - Hacac	-249.61	-124.17	-23.83
Column - Citric Acid	-116.09	-57.66	-10.92
Heap - EDTA	-1172.34	-584.81	-114.78
Heap - EDDS	-3387.23	-1692.80	-337.26
Heap - Hacac	-1180.50	-589.37	-116.46
Heap - Citric Acid	-2428.19	-1212.61	-240.15

From the Table 7.4, it can be deduced that maximum profit was given by citric acid treatment on a column study, while the least profit was made by EDDS treatment on a heap study. It can also be observed that recycling of the chelate at 90% as in the case of the Ro-SB is significant to reduce the costs of the process. However, for each experimental scenario observed, a loss is being made.

Table 7 5 Maximum Profit for metal recovery from Nigerian Soils at different chelate recycling rates using heap and column leaching.

Method & Extractant	Max Profit 0% Recycling ($/t sand treated)	Max Profit 50% Recycling ($/t sand treated)	Max Profit 90% Recycling ($/t sand treated)
Column - EDTA	-101.21	-75.7	-9.36
Column - EDDS	-670.60	-502.9	-66.83
Column - Hacac	-221.45	-165.9	-21.32
Column - Citric Acid	-314.48	-235.7	-30.71
Heap - EDTA	-2915.35	-1456.96	-290.25
Heap - EDDS	-3364.15	-1681.38	-335.16
Heap - Hacac	-1222.68	-610.79	-121.27
Heap - Citric Acid	-2943.16	-1470.95	-293.18

From the Table 7.5, it can be deduced that EDTA gave maximum profit on a column operation while the minimal profit was given by EDDS used in a heap leaching operations. It can also be observed that recycling of the chelate at 90% as in the case of the Ro-SB and Ro-PH is essential to reduce the costs of the process to reasonable levels. However, for each experimental scenario observed, a loss is being made.

If one compares the economic potential of each of these soils then all of them indicate a net loss up to 90% recycling of the extractant. The Ro-SB shows economic promise if one can increase the recycling on the column and heap leaching. Even though the heap leaching is much more expensive, however, from a soil remediation point of view, it appears to be more efficient than column leaching. If one can recycle the extractant multiple times before metal recovery, then it might be possible to reduce the cost of extractant, which is in large excess. The most economic potential of this soil lies, however, in its nickel content (650 mg/kg), but the leaching of nickel is poor for all the extractants under investigation. This is the reason why Hacac performs better economically than EDTA for heap leaching, as more nickel can be leached, 29.8 g/tonne compared with 5.3 g/ tonne.

It can therefore be concluded that the economics are strongly dependant on the type of metals present in the contaminated soil, and the value metal that one is able to recover from it.

In practice 100% recovery of the metals is not a sensible assumption and so a more realistic value would be 90-95% (Irene and Yang 1999) recovery as some of the metals in the metal complexes might be lost or unrecoverable. It is worthwhile to look at the influence of the prices of the metals and the chelate costs on the overall process economics assuming 90% recovery of metals. Hence, a sensitivity analysis was performed by assuming that the prices of the metals increase and decrease by 25 and 50% as shown in Figures 7.2, 7.3 and 7.4. This assumption on changes in the metal price did not yield any significant impact, as this was relatively similar for the different soils (Ro-SB, Ro-PH and Nig-S) and different processes (heap and column) when compared to the current metal price. The insignificant change observed could be attributed to the amount of metal leached for one-step (cycle) leaching. However, it is anticipated that if multiple steps (e.g. 2-cycles) were adopted in the leaching scheme, reasonable changes in metal values would be achieved to compare to our current metal value.

An additional sensitivity analysis was performed assuming that the prices of the chelates increase and decrease by 25 and 50% as shown in Figures 7.5, 7.6 and 7.7. In these scenarios, it was also assumed that it is possible to recycle 90% of the chelate. The assumption on changes in extractant price significantly influenced the entire process and soil type. The change observed was more in the heap leaching process than the column leaching process, as could be expected due to the volume of extractants used during the leaching study. In addition, significant change in the price of extractant that could improve the profit margin of the process is at -25% and -50% price changes.

7.2   Process Description

As EDTA is the most widely used chelate for soil washing and showed the most promise as a chelating agent during the experimental studies, it was decided to conceptualise a process that utilises EDTA as a chelate. In the previous section, it was also shown that from an economic point of view, column leaching led to a smaller loss than heap leaching under the experimental conditions of this study. It was therefore decided that column leaching would be the preferred process of leaching.

The process flow diagram of a metal recovery process from contaminated soils is presented in Figure 7.2.using Aspen Plus software. Contaminated soil is loaded in one of two columns, which are placed in parallel. Two columns are used, as the column leaching is a semi-batch process. Soil is loaded and unloaded after certain time intervals and so while soil is being unloaded from the one column, leaching from the other column occurs allowing the recovery process to be a continuous process.

While leaching occurs, the leach liquor is stored in an agitated storage tank until the leach is complete. The fluid is then transferred to an intermediate storage tank. In this way, it is possible to maintain the composition of the feed to the recovery section.

Sulphur precipitation was chosen as the preferred method of metal recovery from the chelate. It was chosen because metals have a great affinity to precipitate in the presence of sulphur anions (sulphides), ensuring high levels of recovery from the chelate. The source of sulphur anions was chosen to be H_2S. Gaseous H_2S was chosen for several reasons. Firstly, the H_2S can be recycled by burning the precipitates of metal-sulphur in a hydrogen flame. This extraction ensures recycling of H_2S, thus resulting in less running costs. If a solid source of Sulphur was used e.g. Na_2S, the cation from the compound (Na^+) would be difficult to recycle and would accumulate in the system. The sulphide in the metal-sulphide-compound would also have to be recovered in a separate process. Secondly, gaseous H_2S can be handled in a closed system easily. Thirdly, H cations in the chelating agent should not have an effect on the amount of metals extracted from soil once the chelating agent is recycled. Further investigation can be conducted on this aspect of the process.

Using H_2S as a precipitating agent, studies have found recoveries of 99.7 % Cadmium, 99.8 % Copper, 47.8 % Nickel, 100% for lead and 92 % - 100 % Zinc (Tabak et al., 2003; Alvarez et al., 2007). Although the studies were conducted on waste mine water, it is expected that similar results would be obtained for recovery from contaminated soils considering the extracting potentials of the chelating agents used. These amounts of recovery were used in the economic analysis to assess the cost of the system.

Leach liquor thus enters the recovery section where H_2S is used to precipitate the metals as sulphides. The chelating agent is recycled back into the process, while the metal sulphides are sent to a hydrogen burner. Burning of the metal sulphides in hydrogen releases H_2S and elemental metals are recovered. The H_2S is then recycled back to the metal recovery section of the plant.
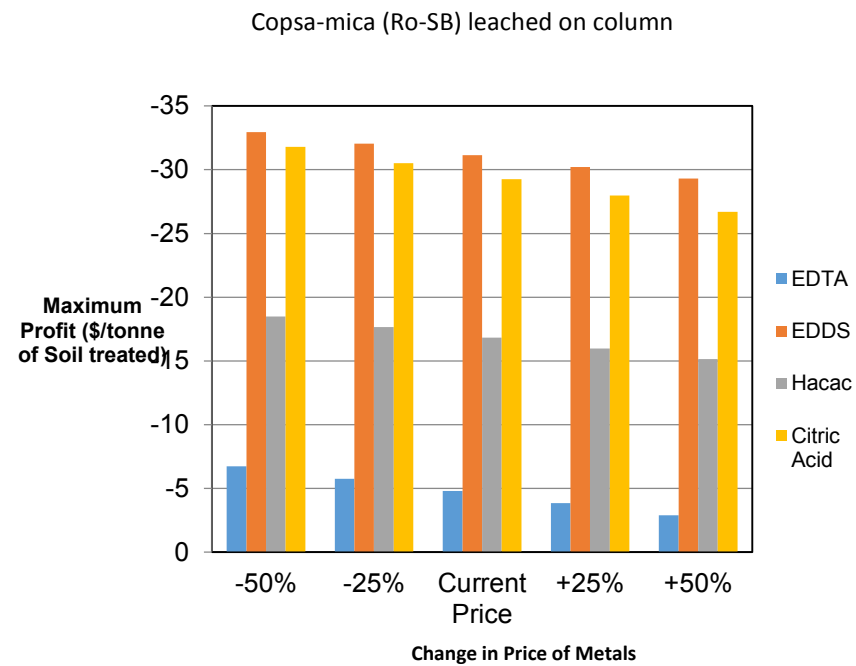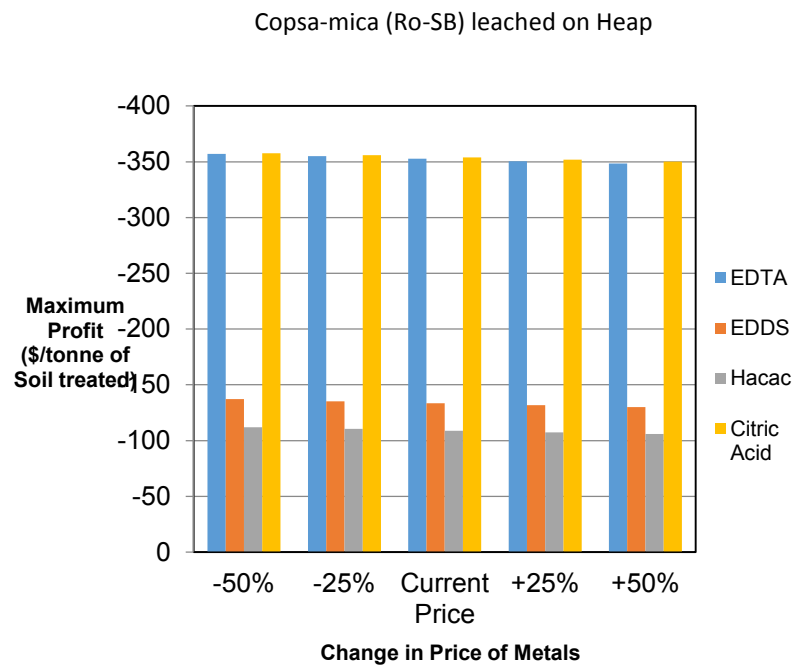
Figure 7. 2 Assumed sensitivity analysis for metal price changes by 25% and 50 % in Ro-SB studied on heap and column processes
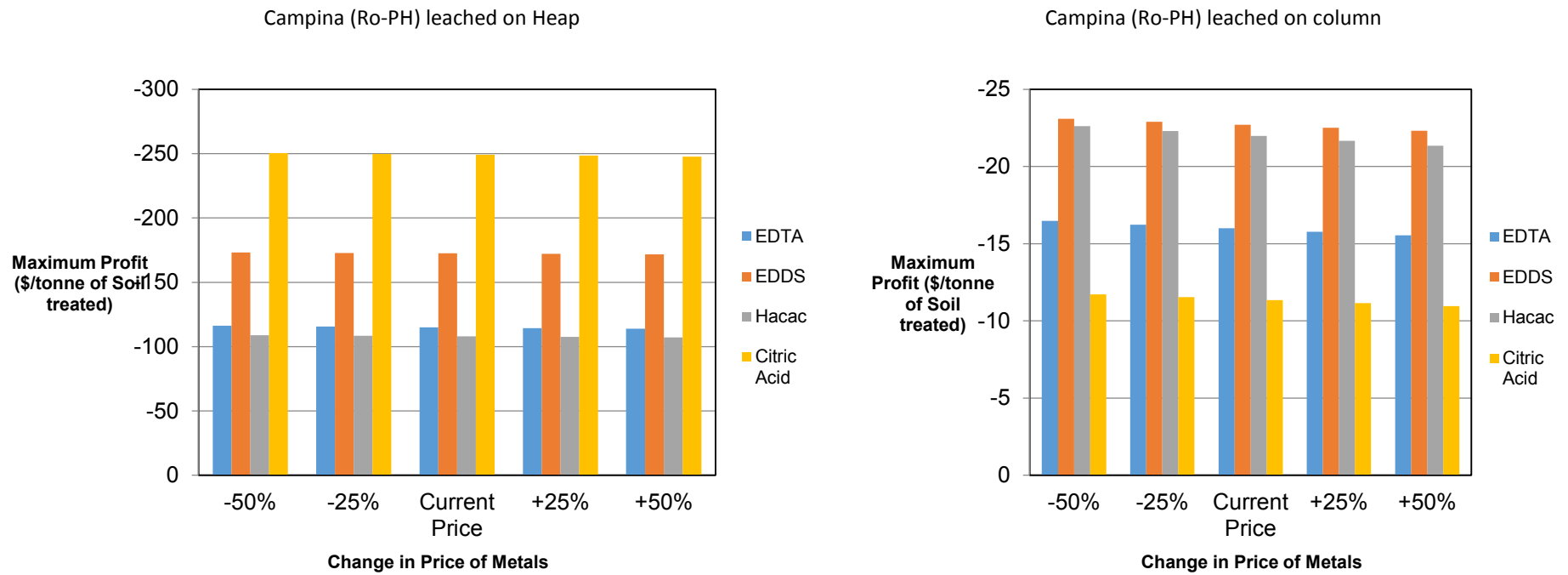
Figure 7 3 Assumed sensitivity analysis for metal price changes by 25% and 50 % in Ro-PH studied on heap and column processes
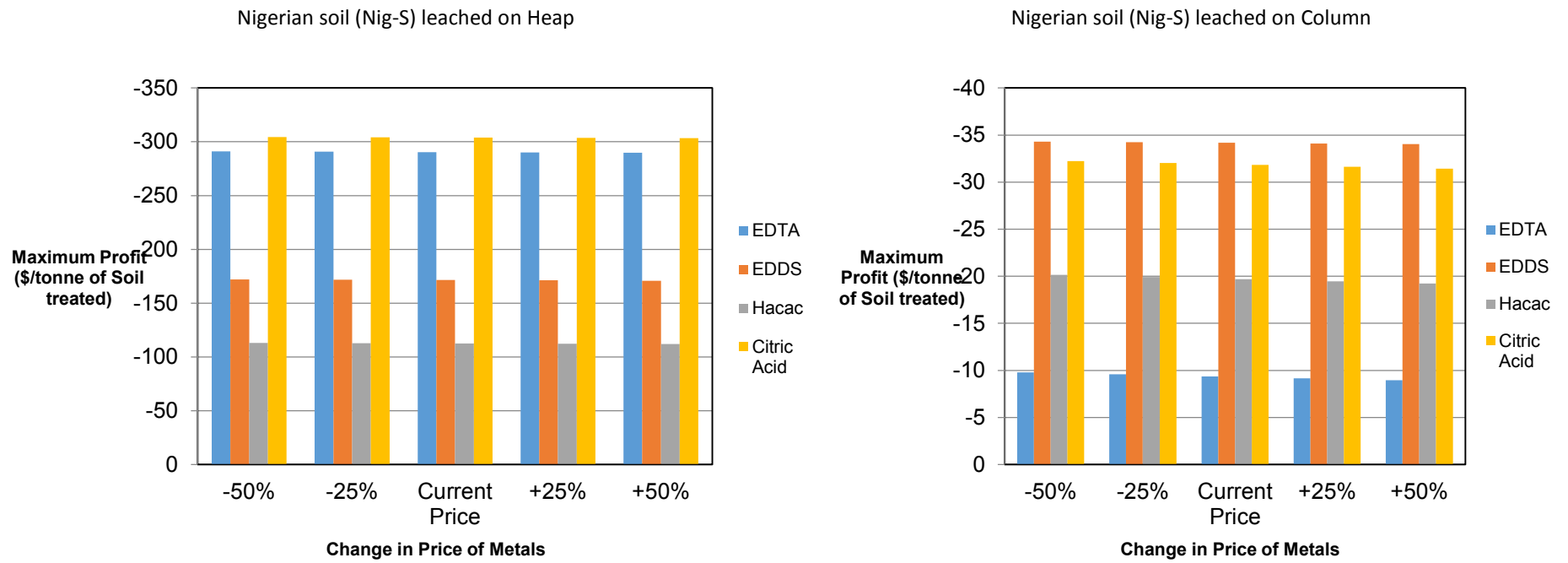
Figure 7.4 Assumed sensitivity analysis for metal price changes by 25% and 50 % in Nig-S studied on heap and column processes
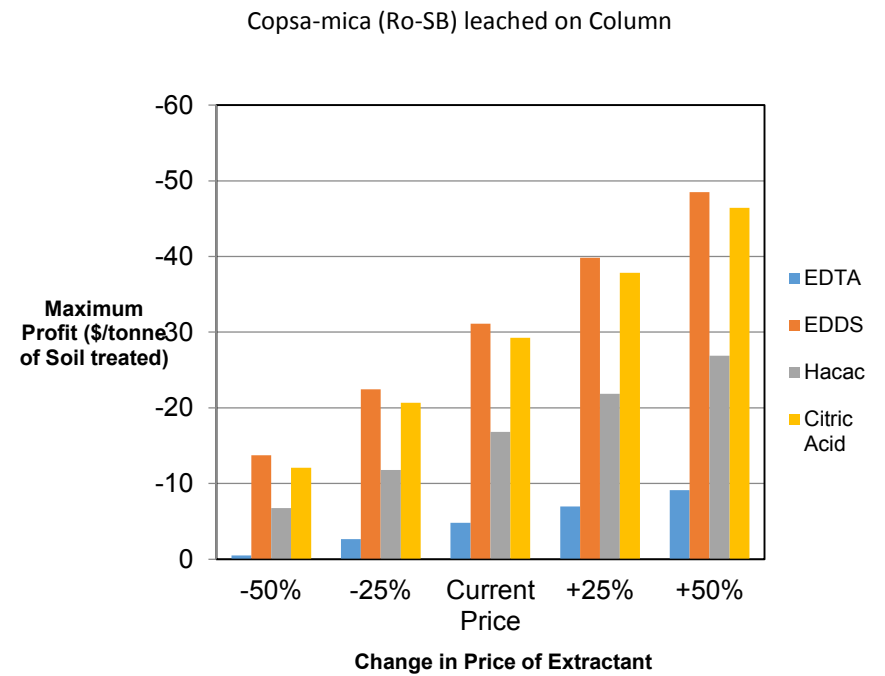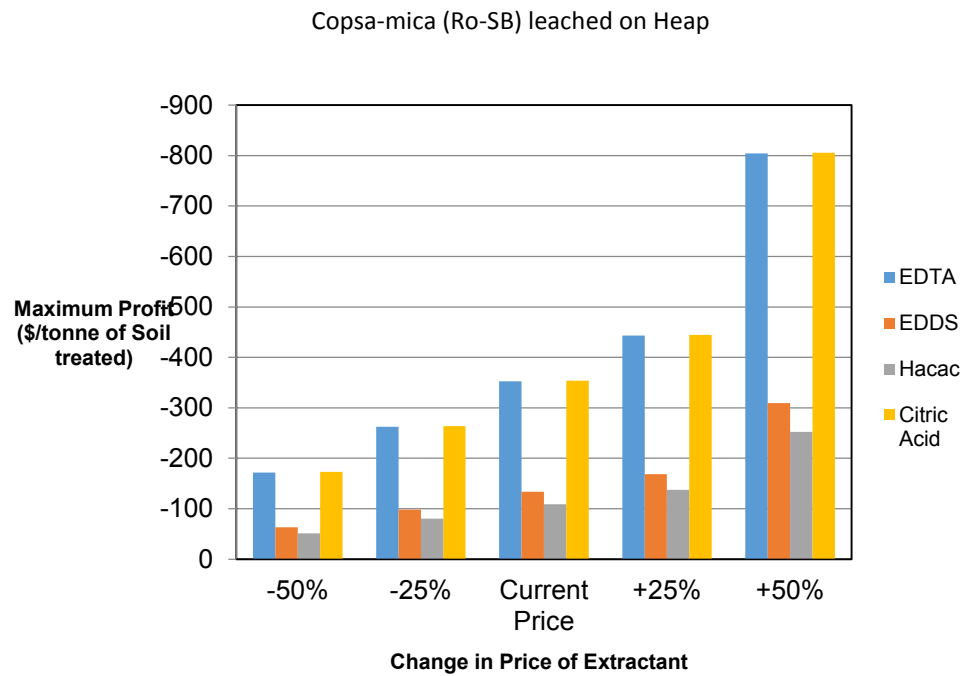
Figure 7. 5 Assumed sensitivity analysis for change in extractant price by 25% and 50 % in Ro-SB studied on heap and column processes
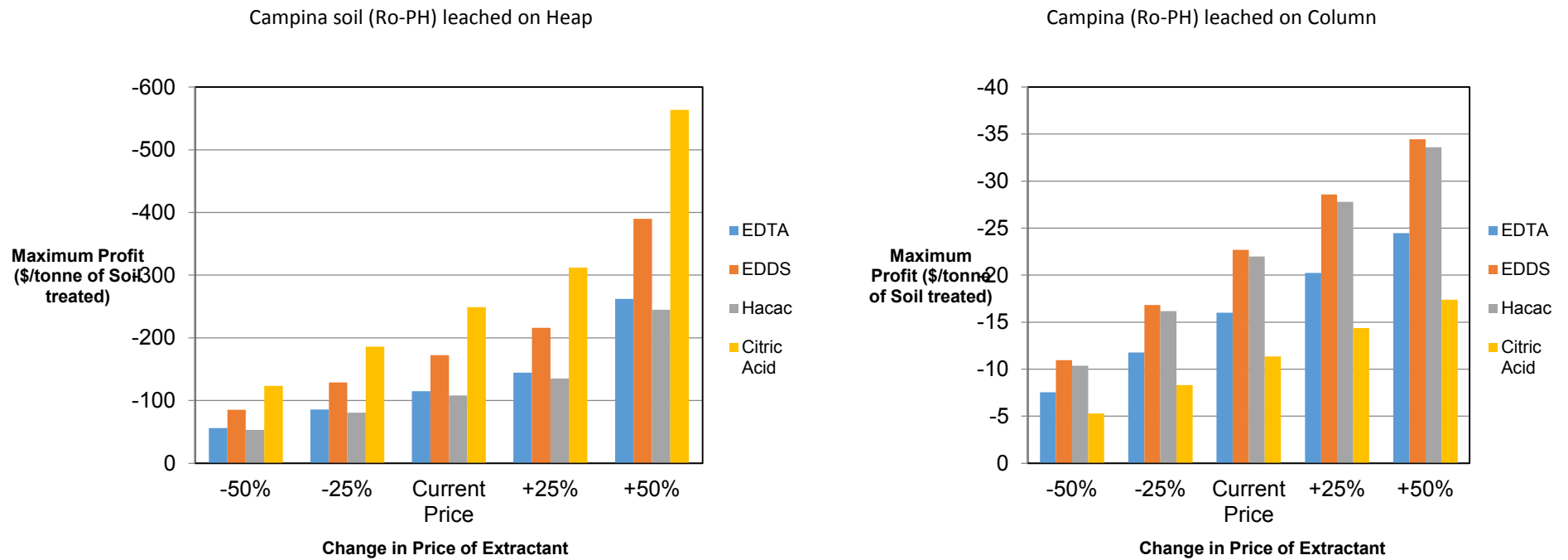
Figure 7. 6 Assumed sensitivity analysis for change in extractant price by 25% and 50 % in Ro-PH studied on heap and column processes
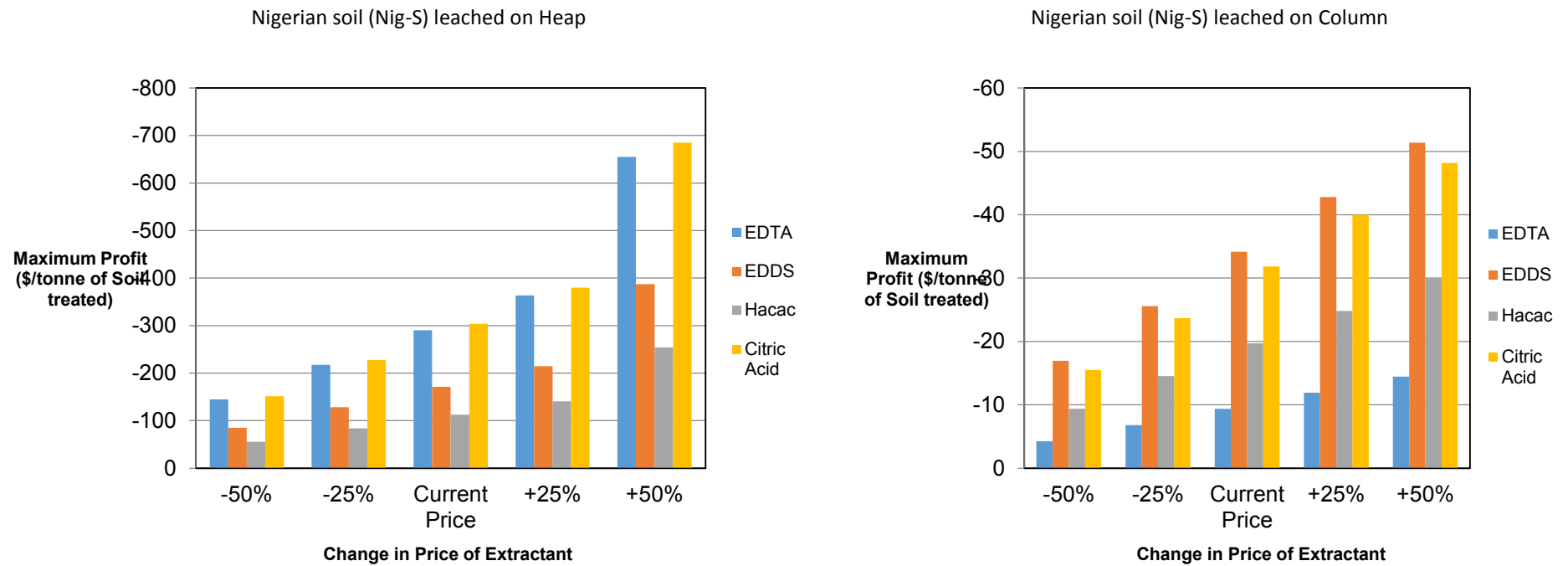
Figure 7. 7 Assumed sensitivity analysis for change in extractant price by 25% and 50 % in Nig-S studied on heap and column processes
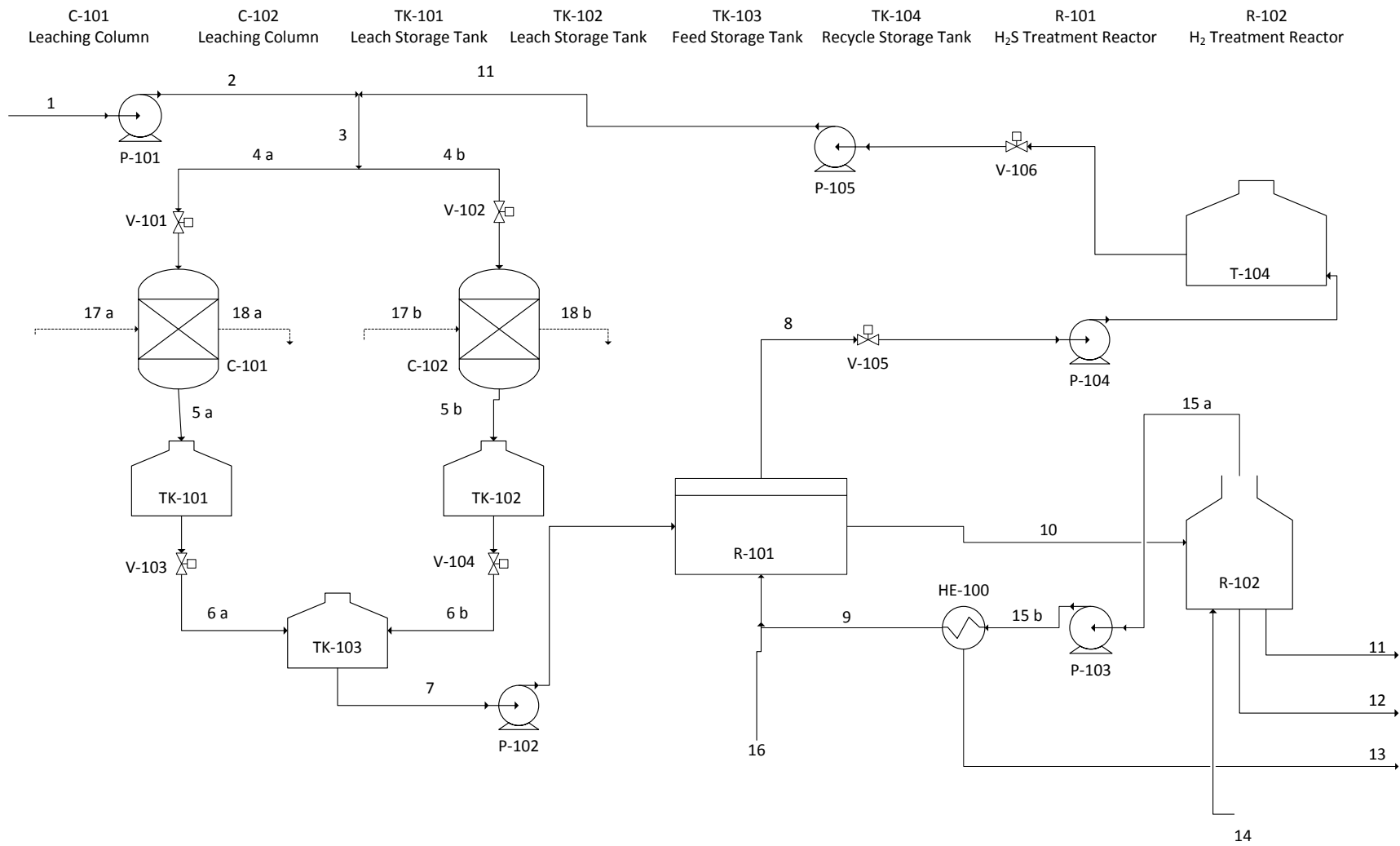
Figure 7. 8 Process Flow Diagram of EDTA treatment of contaminated soil

Chapter 8

Conclusions and recommendations

8.1   Introduction

Over the years, demand for base metals and their allied products used for economic development and social advancement has led to growing concern for global sustainable development in mining, minerals processing and primary metal productions. There is real doubt as to whether the earth has the capacity to support increasingly escalating demand for resource extraction and disposal. However, base metal production has been predominantly relying on primary mining which, in most cases, entail the conventional use of hydro- and pyrometallurgy for metal production processes. According to life cycle assessment (LCA) studies (Weidema, 1997), this conventional processes present some environmental impacts, which ranges from various gaseous emissions to global warming and acid rain. To protect the natural environment from imminent depletion of non-renewable metal ores, and ensure environmental sustainability, land reuse and resource conservation as well as secondary recovery of metals from wastes (e.g. contaminated soils) is a potential viable option for the future.

The broad aim of this study was to compare the extraction capability of various chelating agents for the removal/recovery of base metals from different environmental soil types and constituents with the ultimate goal of providing an economically sustainable solution to recover metals from contaminated soils. A further aim was to compare the treated soil with relevant applicable regulatory threshold (USEPA and DPR) for the purposes of land reuse for agricultural, residential or recreational purposes.

8.2   Achievement of objectives

The use of a simulated soil (SS) and its constituents (bentonite clay [BC], peat moss [PM] and quartz sand [QS]) of known composition and properties was successfully used to develop and describe metal leaching profiles for both single metal and multi-metal systems studied by a batch leaching process at a solid/liquid ratio 1:10 with five different extractants over a 30 min time interval.

The individual substrates that was contaminated with single and multi-metal systems at various concentrations of interest (Table 4.2) using a batch process approach yielded over 90% loading and 50% recovery efficiencies, respectively. The effect of the individual constituents on the leaching behaviour of the targeted metals (Figure 4.2) indicates that BC and SS behaved similarly, in contrast to PM, with respect to their SM and MM contaminants. Further evaluation of the process using varying contaminant regimes on the leaching efficiency of the substrates (Figure 4.3) and the influence of selected extractants on the potential recovery of targeted metals at a constant contaminant concentration (Figure 4.3) were investigated. It was observed that concentration drive amongst other release controlling factors such as complexation, pH and substrate type fundamentally influenced the metal extraction efficiencies from the SS. This was also observed for PM and BC leaching, with the latter showing the least amount of leaching. Overall, metal releases from SS, as influenced by the individual component substrates, seems to be a diffusion-controlled process.

The recovery efficiencies of the multi-metal contaminated SS using batch , column and heap processes, as well as different extractants used, showed that the mobilization of the five metals of interest were differently influenced. This was evidenced in Tables 5.1. 5.2 and 5.3.

The batch study revealed that EDTA, when compared to the other extractants, delivered better metal leaching from SS across the metals investigated. The capacity of CA to extract Cd was comparable to EDTA, but showed lower efficiencies for the other metals. It was also observed that with respect to extraction efficiencies of EDTA, EDDS and CA, although lower than the BS across the five metals leached, the column extraction process behaved in a similar way as the BS process. The extraction efficiency of Pb with CA was however the highest in comparison to all other processes and extractants. Equally, reasonable leaching efficiencies of Cu and Ni were reported for Hacac and was comparable to the recovery using the batch method. Cd was recovered with the highest efficiency using the heap leaching process, compared to the other processes.

These findings suggest that using a batch process could be used in a sequential process to yield metal recovery firstly by CA, followed by Hacac and finally EDTA. However, on a practical scale, a battery of the 3 processes should be considered. This will be dependent

on a sustainable and economic viable plant design, to recover and separate the different metals from a particular soil.

The results obtained from multi-metal leaching profile of the SS was used to predict the leaching capacities of the three environmental soils sourced from Nigeria (Nig-S) and Romanian (Ro-SB and Ro-PH), using column and heap leaching processes performed under similar experimental conditions as in the case of the SS. The findings suggests that the behaviour of SS compared well with the leaching behaviour exhibited by Ro-SB. The Elovich equation showed that the rate of metal release was higher for SS and Ro-SB soils than the Nig-S and Ro-PH soils.

A significant difference was observed in the comparison of the heap and the column processes for metal extractions from the different soil matrices. This was more visible in the SS than in the natural soils. With regard to the column study, it was observed that the leaching behaviour of the three natural soils (Nig-S, Ro-PH and Ro-SB) all behaved differently from another. For the Nig-S, the metals leached in the decreasing order of Zn > Cu > Ni ≈ Cd > Pb. Cd and Pb were better leached with EDTA, whilst Cu and Ni were efficiently leached with Hacac. Zn was best leached with CA. For Ro-PH, metals leached in the decreasing order Cu > Zn > Cd >Ni > Pb, with EDTA and Hacac giving the best leaching when compared to the other extractants. Cd and Pb were efficiently leached with EDTA, while Cu, Ni and Zn were better extracted with Hacac. For Ro-SB, it was observed that Cd and Cu were leached better compared to the other two natural soils. A comparison with SS, studied under similar conditions, showed that Ro-SB had a similar leaching behaviour and profile than the SS, with easy extraction of the metals of interest. In addition, the metal removal efficiency was over 50% for both of these soils. By contrast, Nig-S and Ro-PH behaved differently with typical total metal removal efficiencies of less than 50% and 20%, respectively.

Regarding the heap studies, it was observed that the natural soils displayed notable differences in their leaching behaviour. For Nig-S, it was observed that the metals leached decreased in the order Ni > Cu ≈ Zn > Cd > Pb. While the individual extractants each performed differently, EDTA overall provided the best leaching results. Cu, could best be extracted with Hacac. For Ro-PH, Ni and Pb were poorly extracted, in both cases by less than 10% with EDTA, EDDS and Hacac. However, better leaching efficiency for these metals was observed with CA. For Ro-SB, it was observed that metals were extracted from the soil

matrix much better than the other two environmental soils except in the case of Ni where the Nig-S leached better. It is observed that EDTA generally outperformed the other extractants; however, Cu showed better efficiencies with and a particular affinity for Hacac. Overall, metals recovery from the soils decreased in the Ro-SB > Nig-S > Ro-PH. The observed differences in the values of metal contaminants leached can be ascribed to differences in heterogeneity of the soils, pollution sources as well as the metal contaminants and the chosen applied extraction method.

The Economic evaluation indices has the B/C ratio at 0.02 and a negative NPV as presented in Tables 7.3, 7.4 and 7.5. Both indices are far below the criteria for decision to accept the project. This may be concluded that the project at this time is not economically viable. However, as the project falls in the social obligations of remediation studies to protect plant, environment and public health, it becomes imperative to encourage the pilot scale up of the studies even if it means investing without much expectation. Thus, the study advises that the project should be seen as a two-prong approach that seeks to achieve clean-up metal contaminated soils as well as recover metals for economic motives.

 A further sensitivity analysis performed based on 25% and 50% changes in the prices of the various metals and extractants shows that when 90% of the extractants could be recycled a significant change in the process economics can be achieved

8.3   Contribution of the study

The study has established that recovery of metals from contaminated sources using soil washing techniques could be achieved considering the similarities in attributes displayed for RO-SB and SS, and can assist to reduce loss of critical metals to landfill. In the long term it can minimize over dependency on conventional mining. The suitability of this study can be explored ex situ from two beneficial point of view. The potential for revenue generation, though not economically viable at this point with current metal prices, can assist to offset cost incurred for soil remediation activities. Secondly, the degree of metal removal achieved was high enough with well selected extractants for soil reclamation intended for agricultural and other recreational purposes. However, regulatory threshold that is globally applicable would need to be taken in consideration.

These findings indicates that by using a combination of different processes and different extractants, an efficient leaching process from contaminated sites could be proposed for full-scale recovery plant to be designed.

It is believed that information derived from this study may be useful to environmentalists and stakeholders involved in urban mining activities to predict the potential of metal recoveries from soil before critical decisions are taken on the mining and/or remediation of contaminated sites.

8.4   Limitations of the study

The economic evaluation of metal recovery from contaminated sites is essential to develop a long term strategy for urban mining with existing remediation techniques. However, the economic evaluation applied to this study showed that it is currently too early in the application of this methodology to be able to fulfil all of the criteria that must be satisfied for adoption in a typical industrial plant setting. For instance, several energy assumptions for sustainable management operations could not be estimated. Therefore, a robust economic evaluation has not been possible at present.

8.5   Recommendations and future work

The necessity to recover metals from contaminated soils is inevitable considering the increasing importance placed on environmental protection and human health, as well as predicted shortfalls in the primary metals production. Soil washing with chelating substances could be a viable option to potentially recover metals from contaminated sites, especially when the organo-metal complex produced during the washing exercise can be sustainably separated into a metallic form with minimal impact to the environment and the extractants recycled. The chemical extractants used in this study, with the exceptions of EDTA and Hacac, are environmentally friendly and their biodegradation status are widely documented. However, it will also be necessary to compare the soils before and after treatment for any significant changes in their mineral and microbial make-up (DNA sequencing) prior to commercial implementation in the field, aspect, which have not received any attention in this work. In addition, prior to commercialisation, the recovered metals will have been separated from its complex with hydrogen sulphide (H_2S), as a key proof of concept for the commercialisation of the laboratory methodology developed in this study.

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Appendix A: Initial concentrations (arbitrary constant concentration [ACC], intermediate constant concentration [IMC], intervention concentration [IVC], three times intervention concentration [3 X IVC]) of metals of interest loaded on SS and its constituents (BC, PM, and QS) for single metal (SM) and multi-metal (MM) systems

Simulated Soil (SS)

Metal	ACC		IMC		IVC		3 x IVC	
	SM	MM	SM	MM	SM	MM	SM	MM
	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %
Cd	198.9	187.6	19.7	19.8	17.9	18.0	47.7	49.1
	99.4	93.8	98.5	99.0	95.5	99.8	95.0	98.2
Cu	194.4	186.8	358.8	364.9	176.5	182.6	551.3	56.8
	97.2	93.4	93.9	95.5	92.9	96.1	96.7	98.4
Ni	186.7	180.6	33.7	36.7	196.4	196.4	588.5	586.3
	93.3	90.3	84.3	91.5	93.5	93.5	93.4	93.1
Pb	199.8	184.4	1146.6	1155.9	527.0	528.6	1502.0	1589.6
	99.9	92.2	98.8	99.7	99.4	99.7	94.4	99.7
Zn	198.1	184.5	820.8	808.3	718.4	719.6	2148.6	2109.8
	97.2	92.3	99.6	98.1	99.5	99.7	99.5	97.7

Bentonite Clay (BC)

Metal	ACC		IMC		IVC		3 x IVC	
	SM	MM	SM	MM	SM	MM	SM	MM
	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %
Cd	187.2	190.9	20.0	20.0	18.0	18.0	48.1	49.8
	93.6	95.4	100.0	100.0	99.9	99.9	96.2	99.6
Cu	198.0	198.0	381.9	381.4	189.5	189.5	558.2	568.7
	98.9	98.9	99.6	99.8	99.7	99.7	97.9	99.7
Ni	196.1	179.0	40.0	39.8	209.9	209.7	571.8	626.7
	98.7	89.5	99.5	99.5	99.9	99.9	90.8	99.5
Pb	198.8	199.9	1159.9	1159.9	530.0	530.0	1571.3	1580.8
	99.4	95.9	99.9	99.9	100.0	100.0	98.8	99.4
Zn	179.3	196.0	821.7	823.6	821.7	823.6	2153.2	2153.1
	89.6	98.0	99.7	99.6	99.9	99.9	99.6	99.5

Peat Moss (PM)

Metal	ACC		IMC		IVC		3 x IVC	
	SM	MM	SM	MM	SM	MM	SM	MM
	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %
Cd	192.2	186.5	19.2	18.8	17.8	17.7	49.3	47.3
	96.1	93.3	96.0	94.0	98.9	98.3	98.6	94.7
Cu	195.3	191.4	369.8	326.5	186.4	186.3	561.8	566.8
	97.7	95.7	96.8	85.5	98.1	98.5	98.6	99.5
Ni	186.3	186.2	31.6	33.3	202.4	202.6	570.3	568.9
	93.2	93.3	80.0	83.3	96.4	96.5	90.5	98.3
Pb	198.8	198.6	1151.2	1133.9	527.7	528.0	1578.5	1586.5
	99.4	99.3	99.2	97.6	99.2	97.8	99.3	99.7
Zn	183.2	185.6	777.1	768.5	688.0	695.6	2058.8	1965.3
	91.6	92.8	94.3	93.3	95.3	96.3	95.3	90.9

Quartz Sand (QS)

Metal	ACC		IMC		IVC		3 x IVC	
	SM	MM	SM	MM	SM	MM	SM	MM
	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %	ads (mgkg^{-1}) %
Cd	33.2	30.2	2.0	2.0	4.0	4.0	6.4	6.0
	16.7	15.1	9.0	7.5	23.3	20.6	12.7	11.5
Cu	30.1	36.0	155.0	112.0	47.0	4.7	19.5	18.7
	15.2	17.9	40.6	29.3	24.5	24.7	34.3	32.9
Ni	30.6	24.2	4.0	7.0	5.0	7.3	2.6	12.0
	14.9	12.2	10.8	16.5	2.2	3.2	3.8	4.6
Pb	26.0	26.5	184.2	82.0	18.3	17.4	14.8	12.0
	13.2	13.2	15.8	7.1	34.6	32.8	9.3	7.6
Zn	32.3	28.0	295.0	21.1	23.5	25.6	75.9	73.7
	15.9	13.8	35.8	25.6	32.5	35.1	35.1	34.1

Appendix B: Leaching profiles of column extracted metals from different environmental soils (Nig-S, Ro-PH, Ro-SB and SS) at varying contact times (30, 60, 90, 120 and 150 min) in the presence of EDTA, EDDS, Hacac and CA as selected extractants
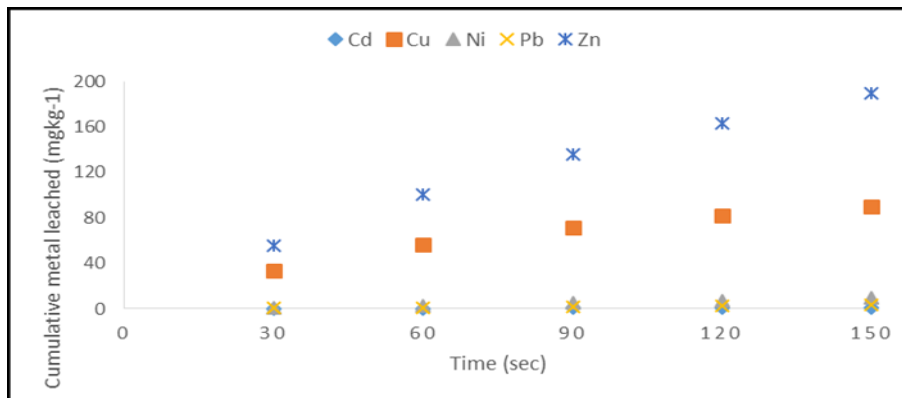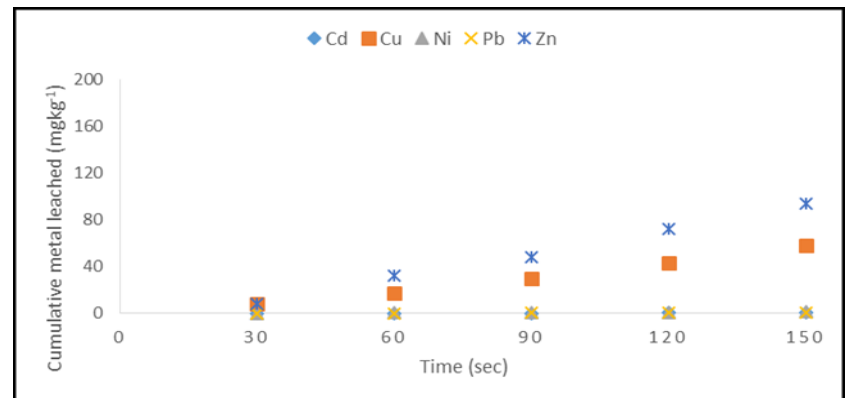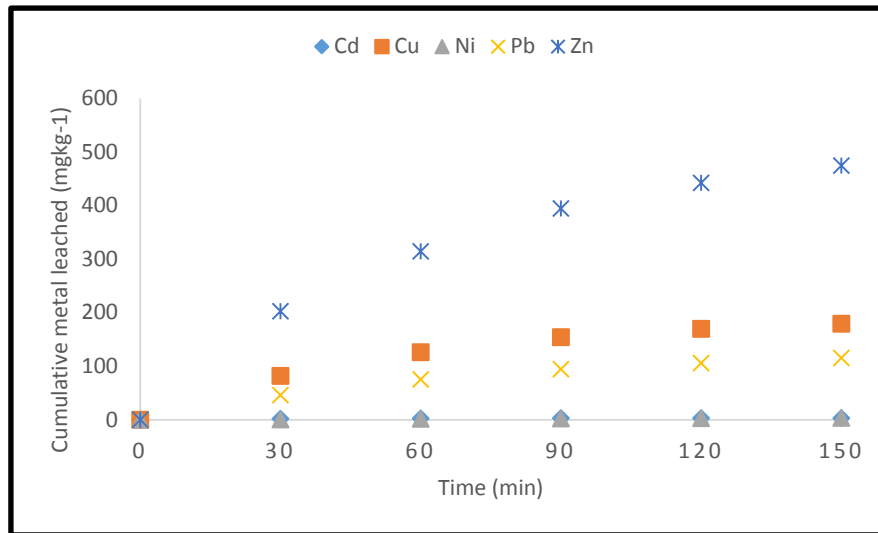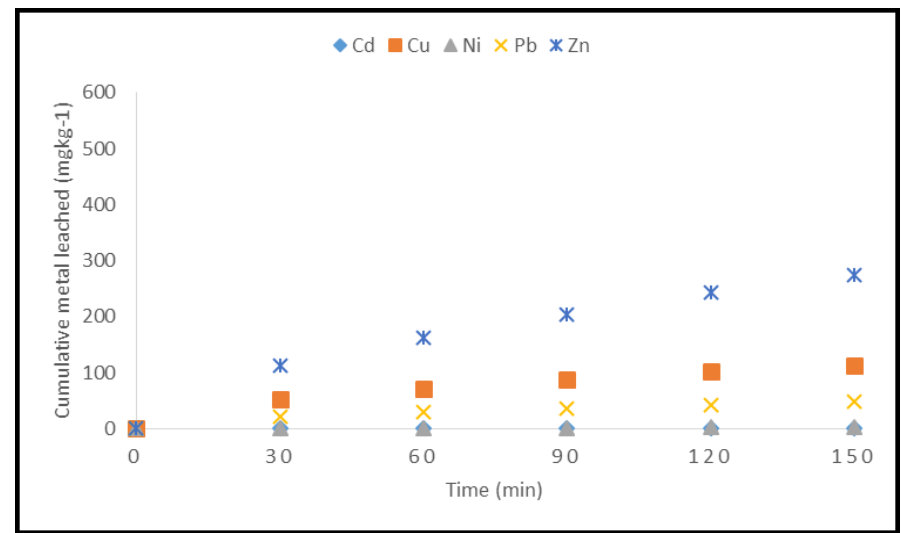
Nig-S

EDTA
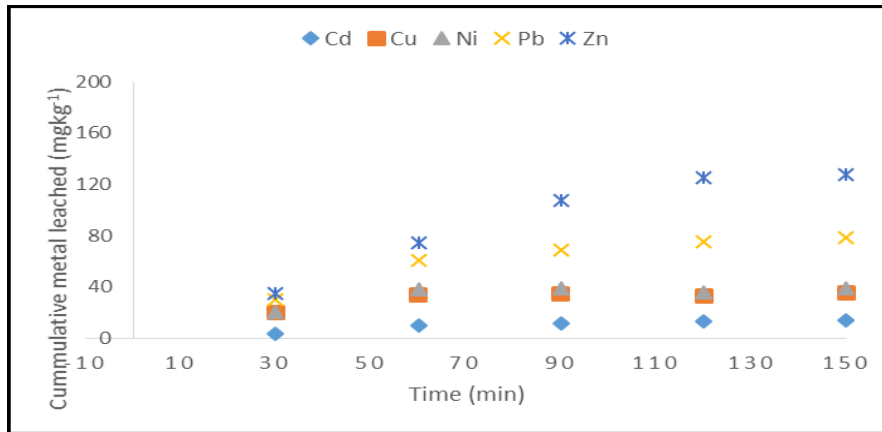
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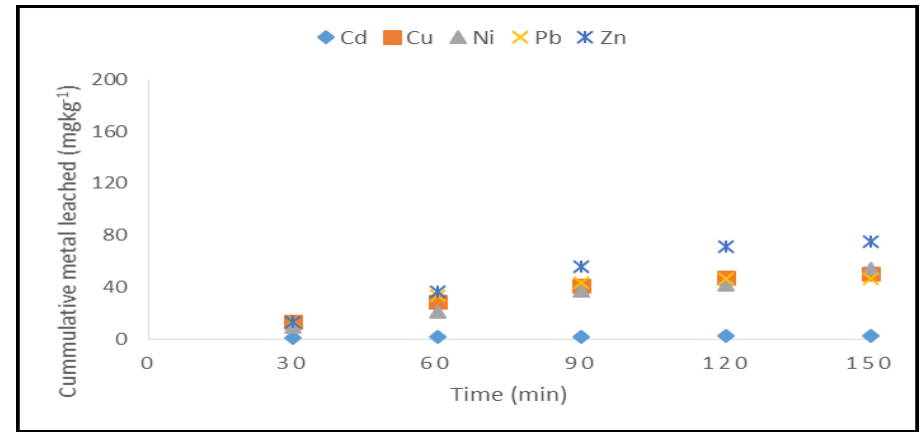
Hacac
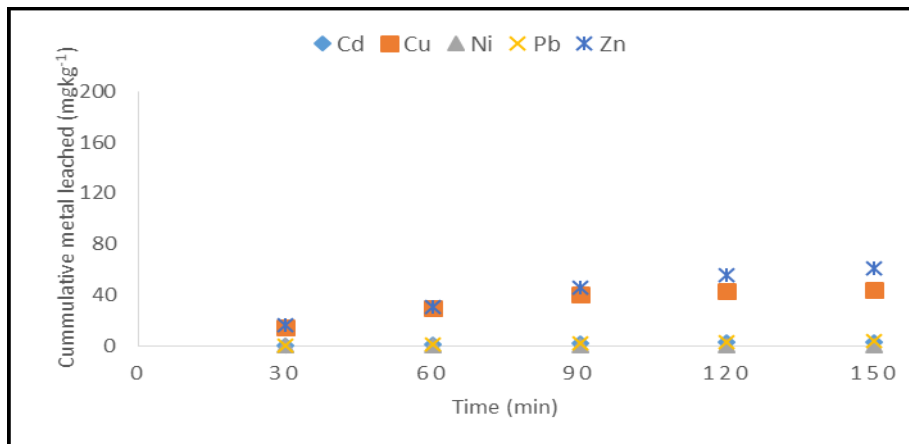
CA
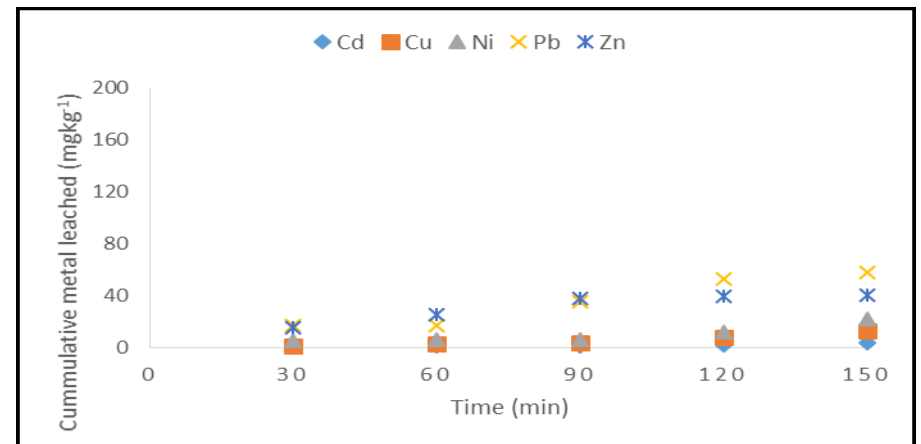
Figure 1 Leaching profiles of column extracted metals from Nig-S, at varying contact times (30, 60, 90, 120 and 150 min) in the presence of EDTA, EDDS, Hacac and CA as selected extractants
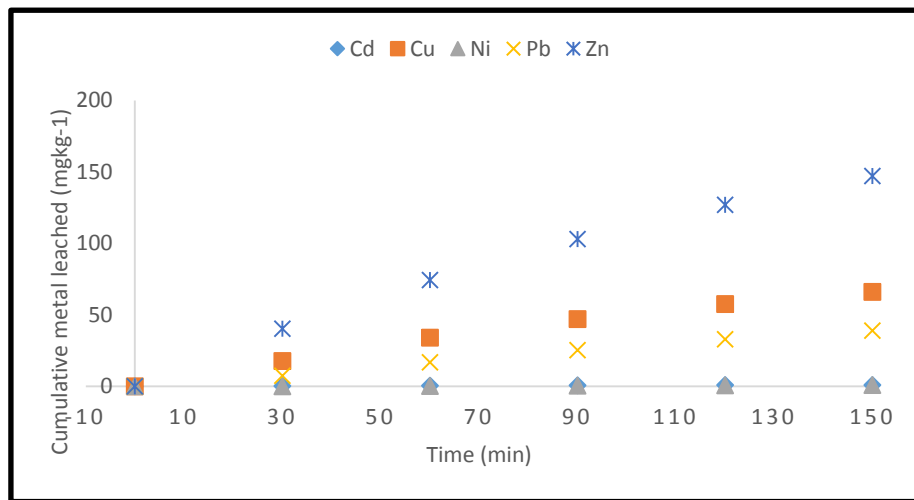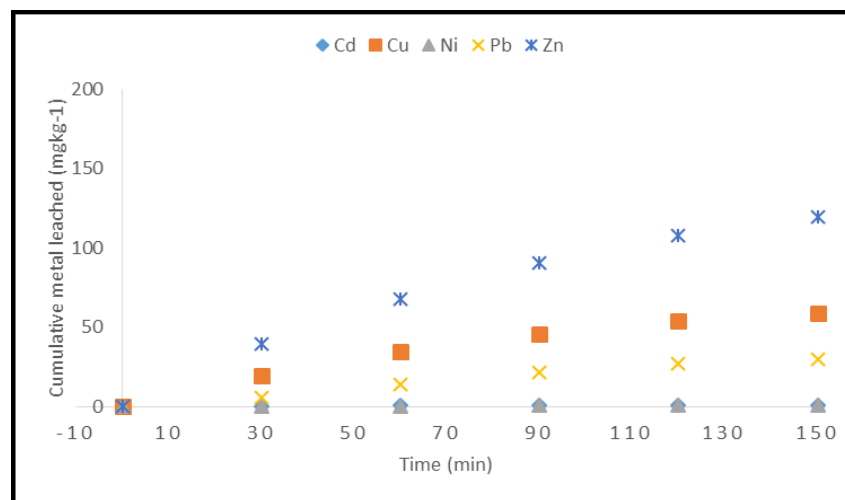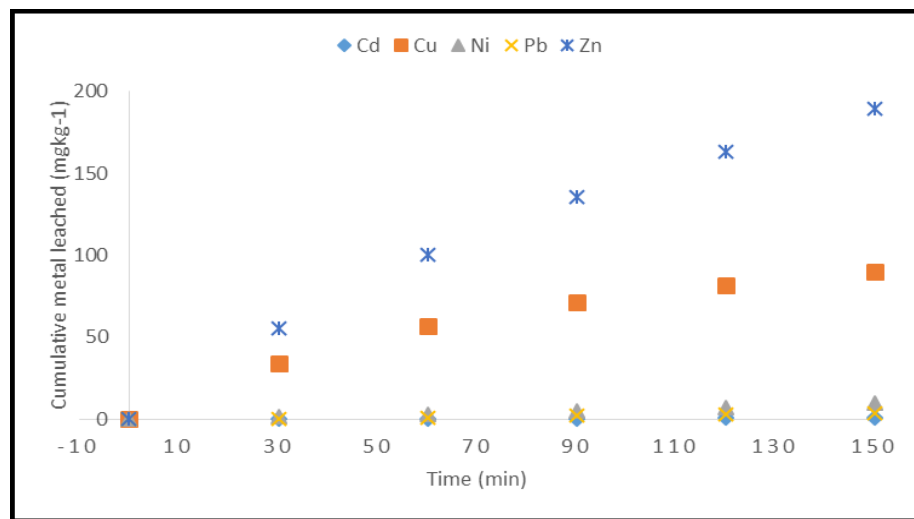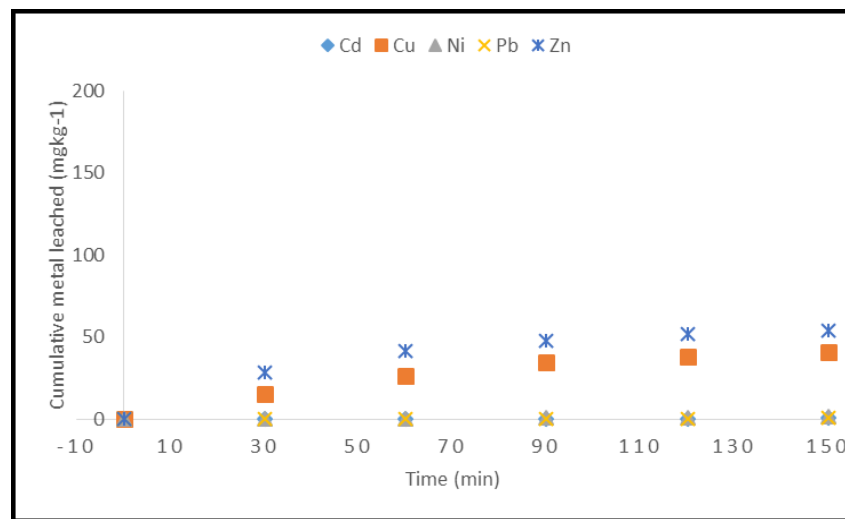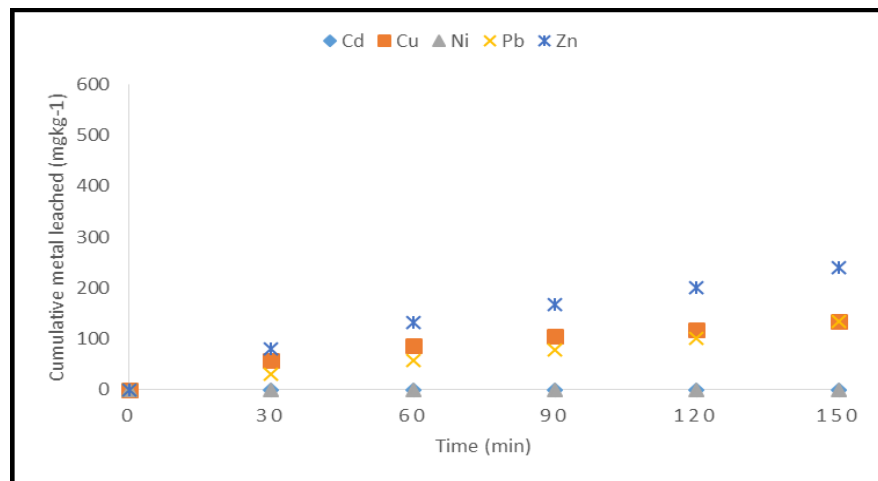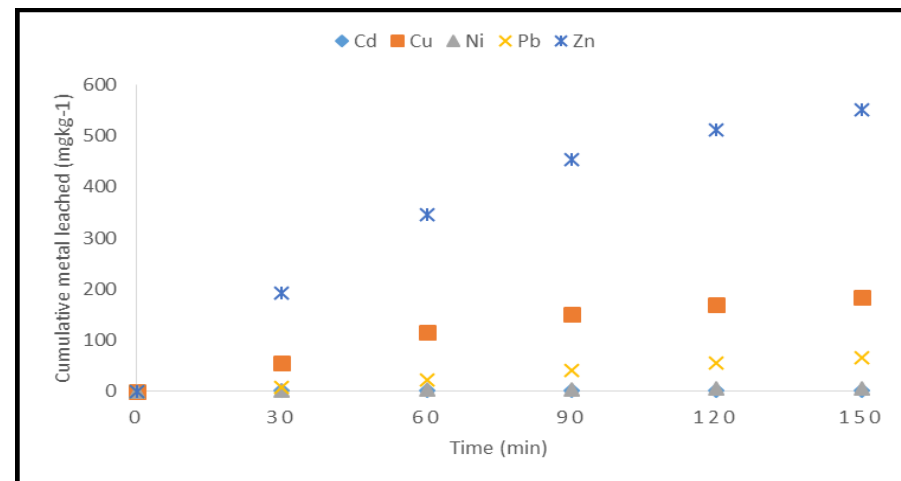
Figure 2 Leaching profiles of column extracted metals from Ro-PH, at varying contact times (30, 60, 90, 120 and 150 min) in the presence of EDTA, EDDS, Hacac and CA as selected extractants
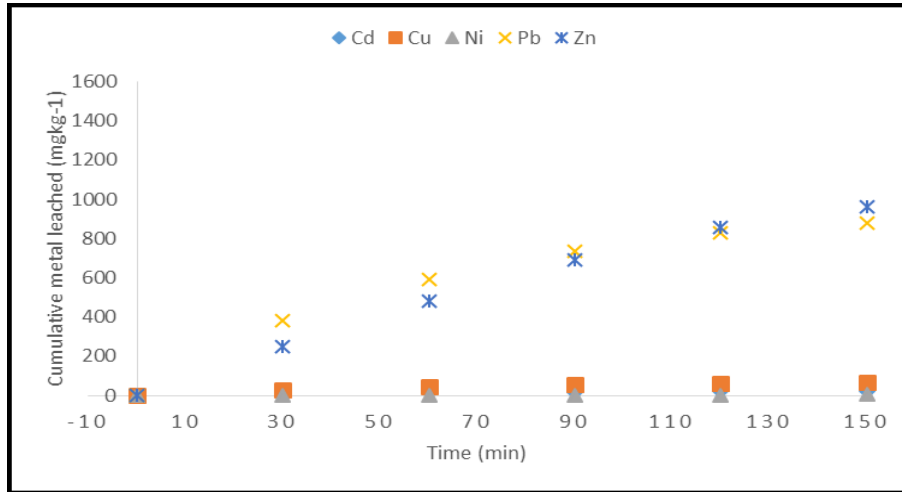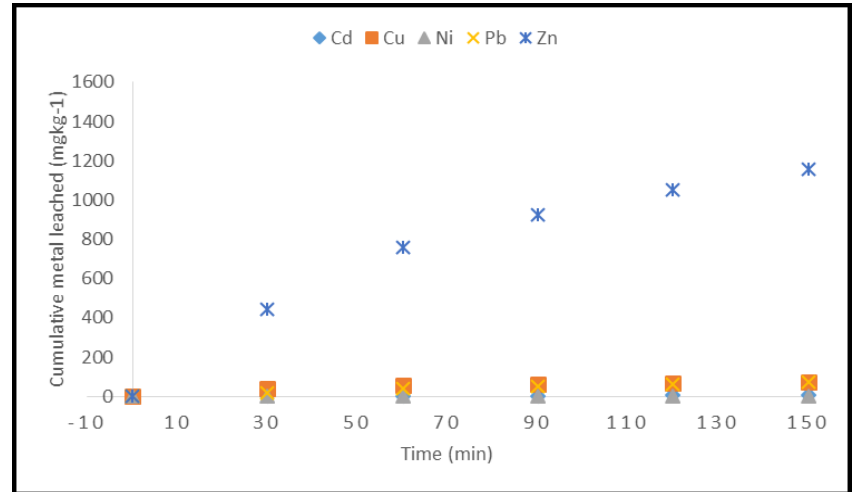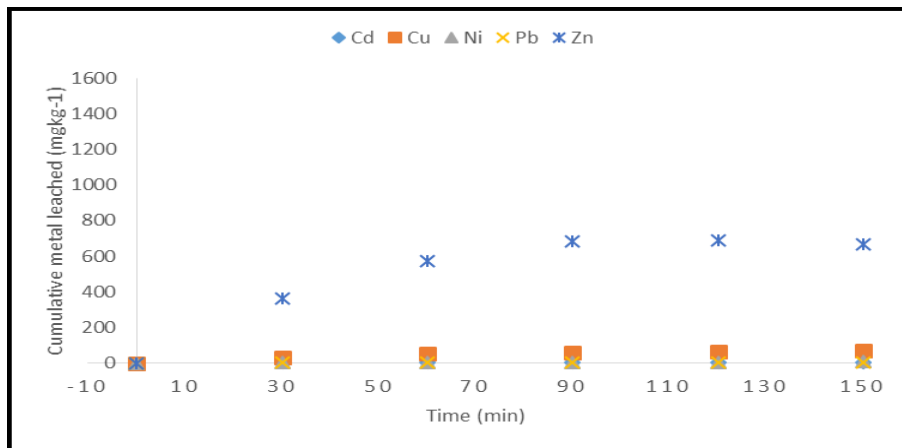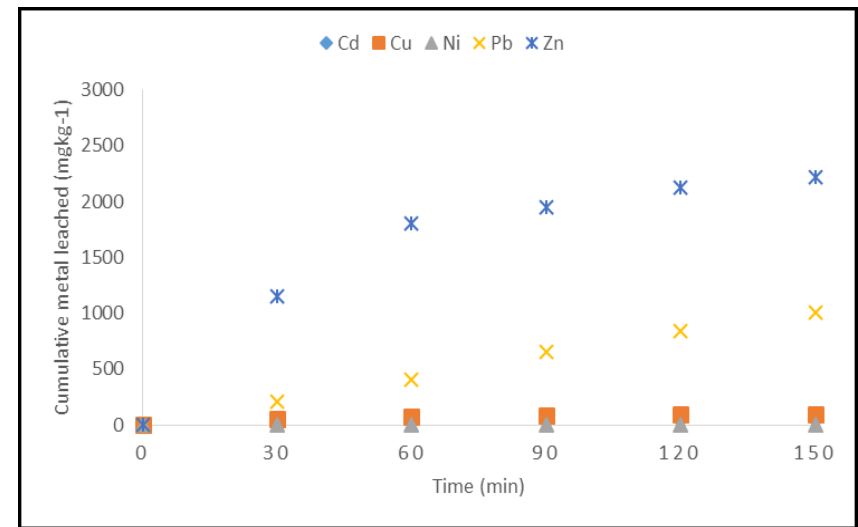
EDTA

EDDS

Haca

CA
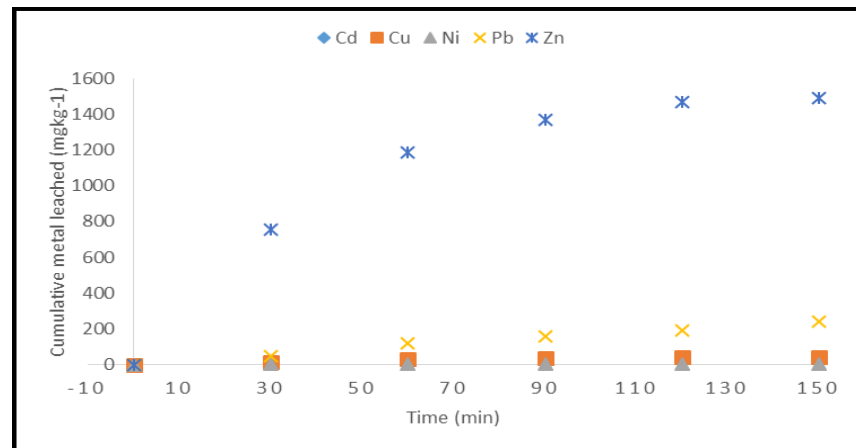
Figure 3 Leaching profiles of column extracted metals from Ro-SB, at varying contact times (30, 60, 90, 120 and 150 min) in the presence of EDTA, EDDS, Hacac and CA as selected extractants
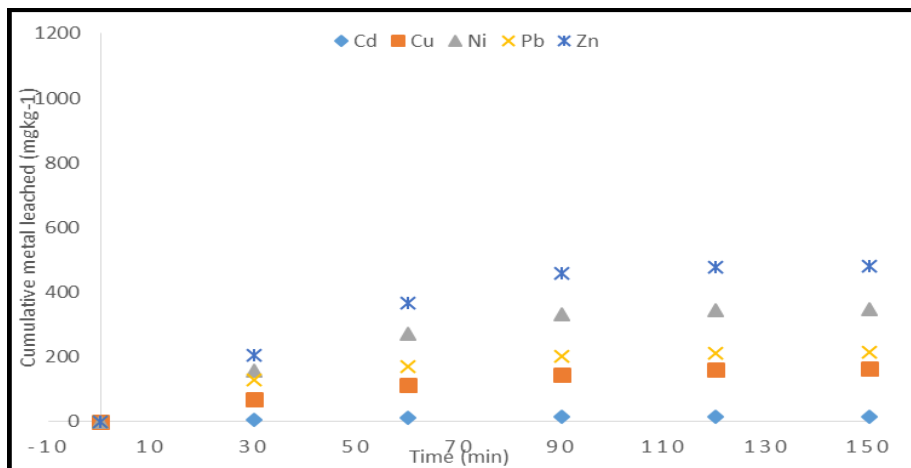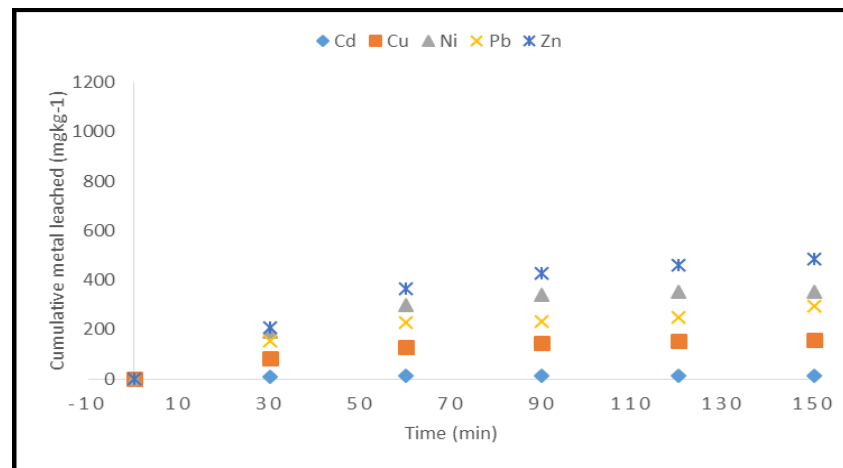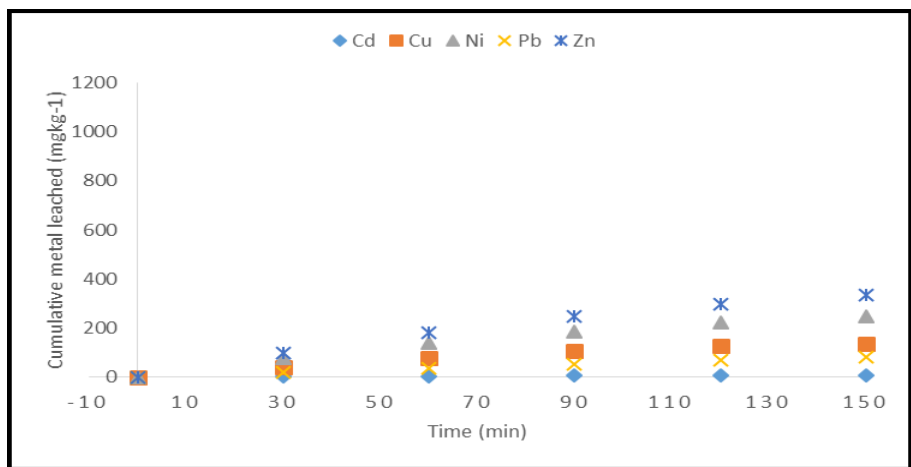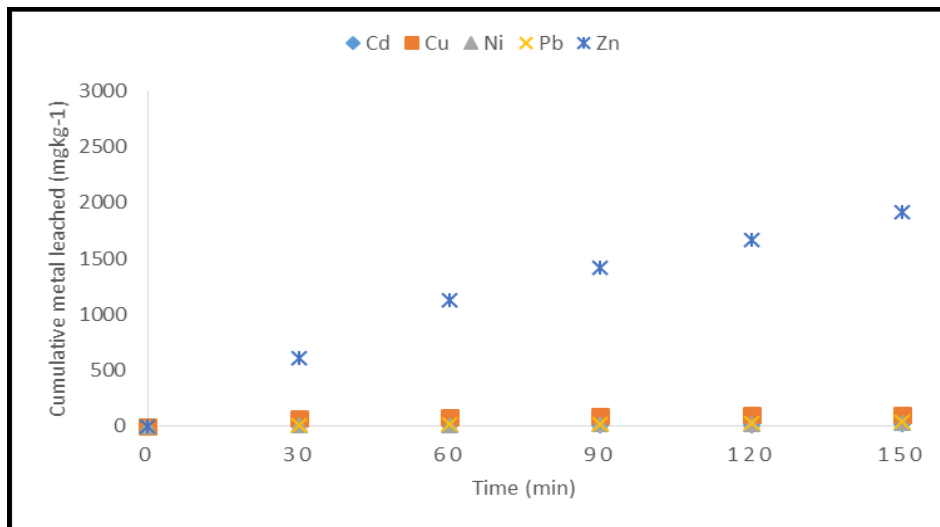
EDTA

EDDS

Hacac

CA
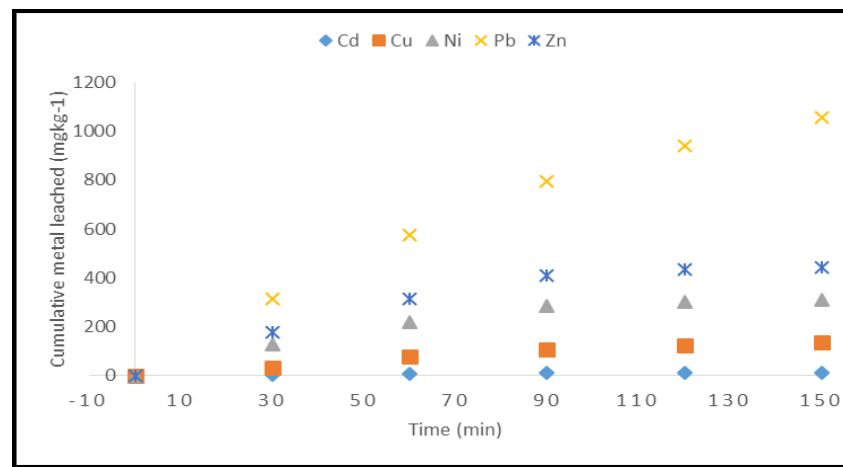
Figure 4 Leaching profiles of column extracted metals from SS, at varying contact times (30, 60, 90, 120 and 150 min) in the presence of EDTA, EDDS, Hacac and CA as selected extractants
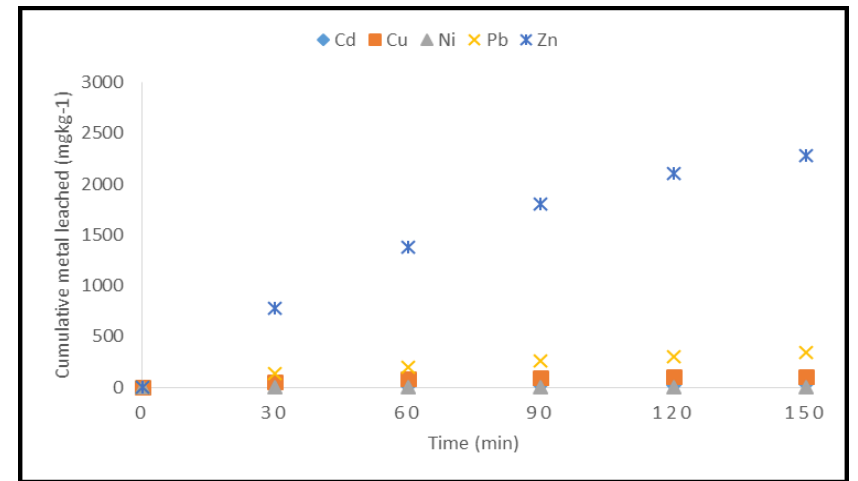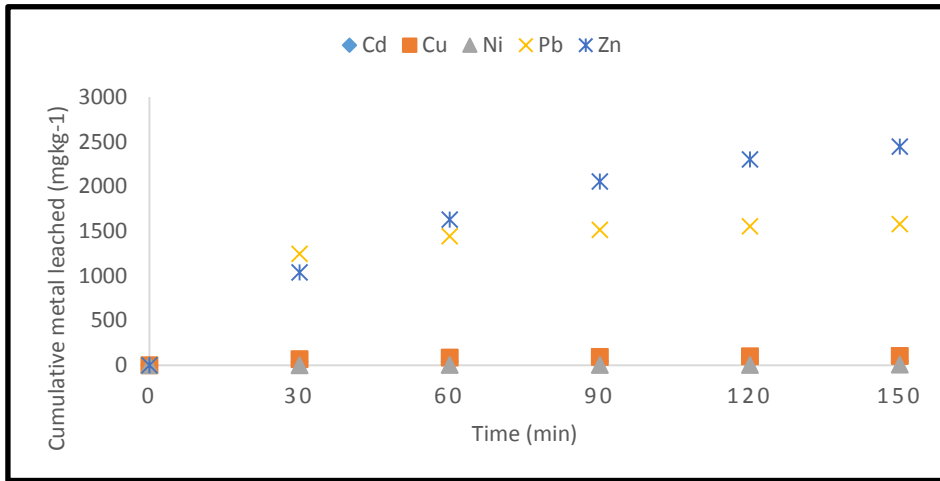
Appendix C: Leaching profiles of heap extracted metals from different environmental soils (Nig-S, Ro-PH, Ro-SB and SS) at varying contact times (30, 60, 90, 120 and 150 min) in the presence of EDTA, EDDS, Hacac and CA as selected extractants
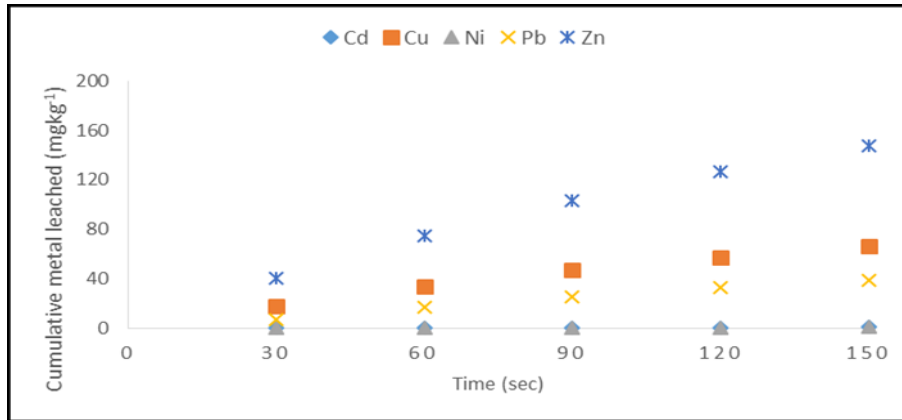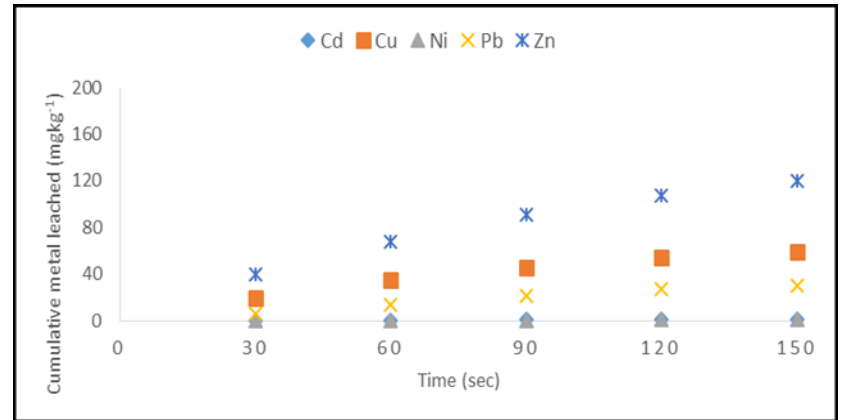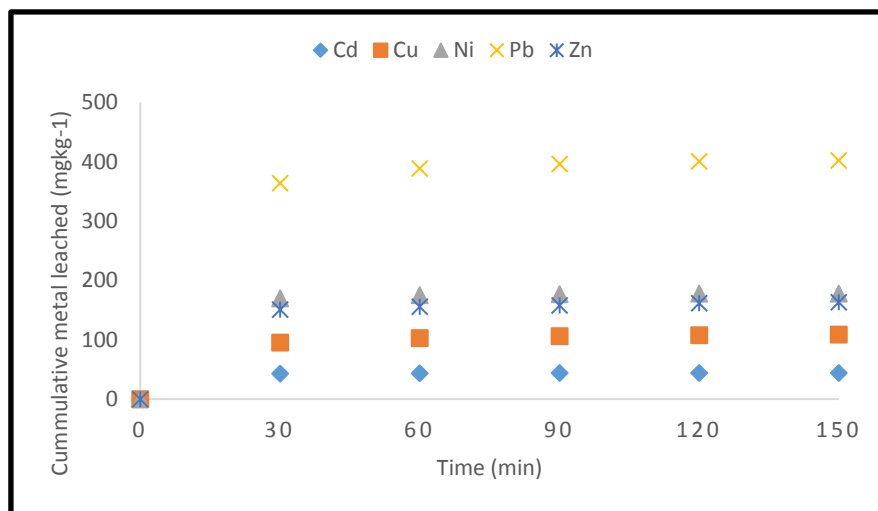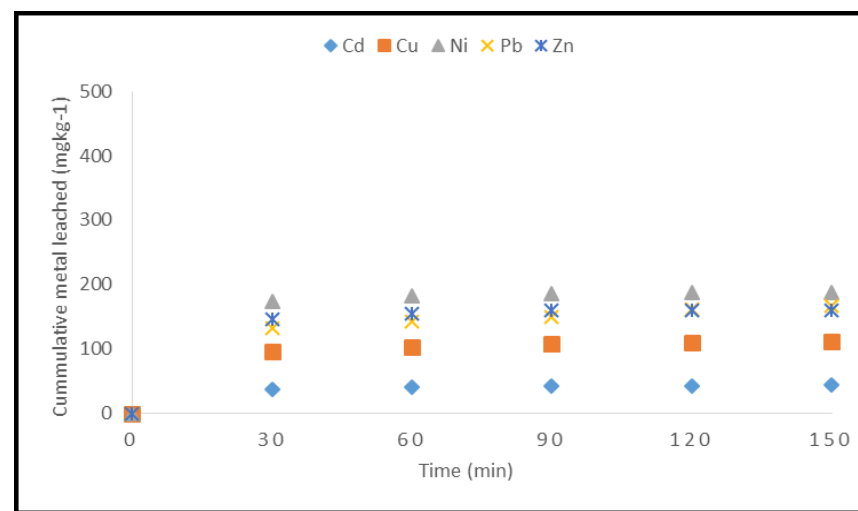
EDTA

EDDS

Hacac

CA

Figure 5 Leaching profiles of heap extracted metals from Nig-S, at varying contact times (30, 60, 90, 120 and 150 min) in the presence of EDTA, EDDS, Hacac and CA as selected extractants

EDTA

EDDS

Hacac

CA

Figure 6 Leaching profiles of heap extracted metals from Ro-PH, at varying contact times (30, 60, 90, 120 and 150 min) in the presence of EDTA, EDDS, Hacac and CA as selected extractants

Figure 7 Leaching profiles of heap extracted metals from Ro-SB, at varying contact times (30, 60, 90, 120 and 150 min) in the presence of EDTA, EDDS, Hacac and CA as selected extractants
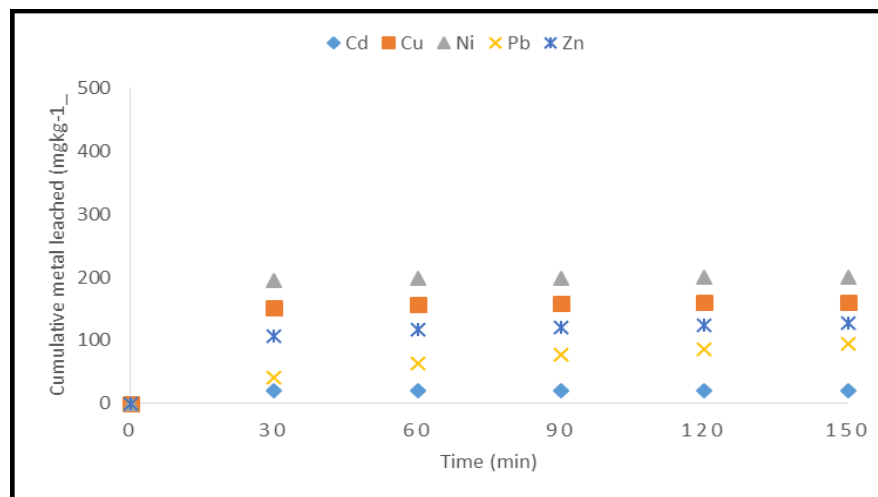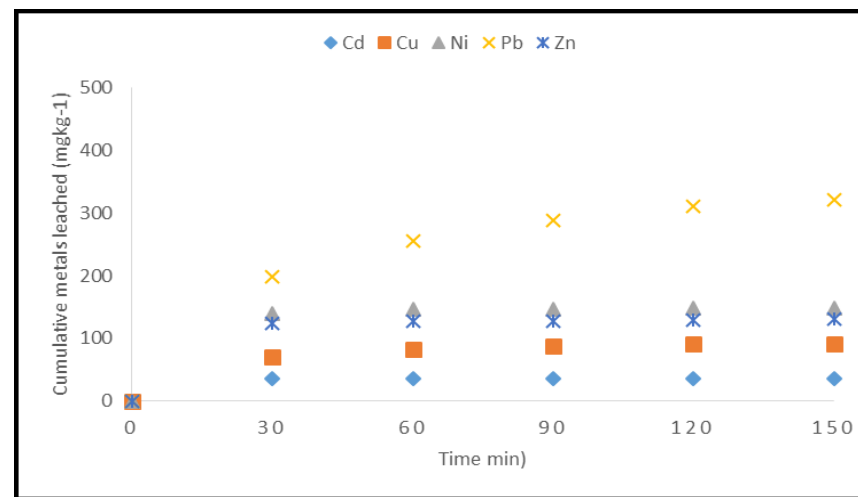

EDTA

EDDS

Hacac

CA

Figure 8 Leaching profiles of Heap extracted metals from SS, at varying contact times (30, 60, 90, 120 and 150 min) in the presence of EDTA, EDDS, Hacac and CA as selected extractants