ENVIRONMENTAL RISK ASSESSMENT FOR AN INFORMAL E-WASTE RECYCLING SITE IN LAGOS STATE, NIGERIA

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This thesis is submitted to Middlesex University in partial fulfilment of the requirements for the degree of Doctor of Philosophy

October, 2016

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Dedication

To my parents, Mr Abdul-Azeez Isimekhai and Mrs Zeenat Isimekhai for their unwavering love and support. You both gave me the foundation to hunger for excellence in education and all life's endeavours.

And my jewel of inestimable value Asmaa Imefa Ahmad-Ibrahim for making this experience worthwhile. I love you to bits.

Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this thesis are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other University. This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically indicated in the text. This thesis contains approximately 68,000 words including appendices, references, footnotes, equations and has about 40 figures and tables respectively.

Khadijah Ateda Isimekhai

October, 2016

Signature: ____

Date: ____

Acknowledgement

Alhamdulillahi rabbil alamin. All praises due to Allah the most gracious, the most merciful. Thee alone we worship, Thee alone we ask for help and Thee alone made this journey possible.

I would like to express my deepest sense of gratitude to my supervisors, Dr Diane Purchase, Prof Hemda Garelick and Dr John Watt for their supervision, their constructive criticisms, support and valuable suggestions and guidance from the onset of this research. Thank you for believing in me even in my most difficult time. Most importantly, under your tutelage, a fantastic researcher has been born and my writing skills have been honed.

My gratitude goes to Dr Oluseun Popoola and Dr Ahmed Adetoro for their constant support and also putting in place a team to make the site sampling possible.

A big thank you to the technical team for technical expertise, assistance in the laboratory techniques and sample analysis.

I would like to appreciate my parents, Mr Abdul-Azeez and Mrs Zeenat Isimekhai, thank you for being a constant source of support and encouragement all through my life. I really would not be here if not for your prayers, unconditional love and care. You have always given me reasons never to give up even when the going gets tougher. There will be no me without you both. I love you both.

I would like to thank my wonderful siblings, Zeenat, Nafisah, Rafat, Zulfah and Abdul-Hafeez for being there. Thank you for always believing in me and encouraging me in your own unique individual ways. You guys complete my world, I love you all.

I would like to appreciate my husband, Dr Ahmad Ibrahim; it’s been a long and tough journey, thanks a lot for your patience, encouragement and support. You have indeed made me a stronger woman and provided me a different perspective to life.

I cannot forget to mention Hajia Binta Mohammed, I appreciate your kindness. Thank you for being patient and strong when it matters. We have a lot to catch up on.

To my little but mighty daughter Asmaa, the research journey can never be complete without the mention of your name. Thank you for understanding sometimes that mummy had to get some work done. To my other children, Hannah, Ibrahim, Hauwa, Rabiah, Ailelota, Kamil, Nehitare and Ammaarah, we all have some serious catching up to do.

I started this research journey with Justin Okoli and Natasha Oyibo, and we grew closer than research buddies especially Natasha Oyibo, I appreciate we have been there for each other even outside the research world. This is just our stepping stone.

This acknowledgement would not be complete without appreciating other people I met on this research journey who have grown to be my friends, Ms Flora Agba, Okechukwu Madu, Anthony Futughe, your input in my life no matter how little is really appreciated.

To others who I might have not remembered to acknowledge at the spur of the moment, you are all appreciated.

Abstract

It has been recognised that the informal E-waste recycling may pose a risk to human health and the environment, this study aims to evaluate the e-waste contamination and the environmental and human health impact of informal e-waste recycling on the exposed population using the risk assessment framework. The distribution of a number of heavy metals in soil from an informal recycling site in the largest market for used and new electronics and electrical equipment in West Africa was investigated. The extent of pollution, potential bioavailability of heavy metals, potential risk due to the recycling activities and impact of external factors such as rainfall were assessed. In recent times, bioaccessibility has emerged as a testing tool used to accurately estimate the risk posed on human health by exposure to environmental contaminants, the oral bioaccessibility and inhalation bioaccessibility was also assessed. The concentrations of all the identified metals in the recycling site were consistently higher than values obtained from the control site, suggesting the impact of the recycling activities on the soil. The order of total metal concentration was Cu > Pb > Zn > Mn > Ni > Sb > Cr > Cd for both the dry and wet season. The total concentration of Cd, Cu, Mn, Ni and Zn where was significantly higher ($p \leq 0.001$) in the dry season than in the wet season. The concentrations of Cu (329-7106 mg kg^{-1}), Pb (115-9623 mg kg^{-1}) and Zn (508-8178 mg kg^{-1}) were consistently higher than the international soil guideline values. Using a sequential extraction method, the potential bioavailability of the metals was indicated as Cd > Sb > Zn > Cu > Ni > Pb > Cr, suggesting Cd was the most potentially available. Assessing the risk using the Potential Ecological Risk Index (PERI), Cu was found to contribute the most to the potential ecological risk and Cd the greatest concern due to its high toxic-response factor within the study site and the Risk Assessment Code (RAC) suggested Cd posed the most risk in this site. Furthermore, the oral bioaccessibility test showed that less than 40% of the total concentration of all the identified metals was potentially available for absorption in the gastrointestinal tract. In the inhalation bioaccessiblity, with the exception of Cd, the percentage bioaccessibility of the other metals was less than 35% after 120 hours. The health risk characterization indicated the adverse human health effect through the ingestion pathway and a relative lower probability of risk through the inhalation of pathway. This study established a high level of contamination as a result of the informal recycling activities, underscores the importance of applying speciation and bioaccessibility and bioavailability in risk assessment. Finally, in an attempt to evaluate the risk, the study proposed an integrated risk assessment framework which when tried and tested is aimed to positively influence the risk judgement and ultimately risk management decisions whereby providing valuable insights that would translate to an efficient and sustainable management system at the long run.

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List of abbreviations

ASTM	American Society for Testing and Materials
BAN	Basel Action Network
CalTOX	California environmental protection agency risk assessment model
CEC	Cation exchange capacity
CF	Contamination factor
CLEA	Contaminated Land Exposure Assessment model
CLR 11	Contaminated land risk model
CSOIL	Contaminated soil model
DETR	Department of the Environment, Transport and the Regions
DPPC	Dipalmitoyl Phosphatidylcholine
EDTA	Ethylene-diamine-tetra-acetic acid
EEE	Electrical and electronic equipment
E-waste	Electronic waste
EPR	Extended producer responsibility
ERA	Environmental risk assessment
ICP-OES	Inductively coupled plasma optical emission spectrometry
IRGC	International Risk Governance Council
ISO	International Organization for Standardization
LC_{50}	Median lethal concentration
NESREA	National Environmental Standards and Regulations Enforcement Agency

OMC	Organic matter content
PAHs	Polycyclic aromatic hydrocarbons
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzodioxin/furans
PVC	Polyvinyl chloride
PERI	Potential ecological risk index
PLI	Pollution load index
POPs	Persistent organic pollutants
RAC	Risk assessment code
RBCA	Risk-based corrective action model
SELF	Simulated epithelial lung fluid
SGVs	Soil guideline values
TI	Toxicity index
UBM	Unified bioaccessibility method

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CHAPTER ONE

1 Introduction

1.1 Background of study

Electronic waste (e-waste) is a generic term comprising electronic equipment that have either been disposed of by their original users or become obsolete; for example, mobile phones, televisions, computer monitors, laptops, printers, scanners, and associated wiring (Robinson, 2009; Luther, 2010). According to the StEP initiative 2014, “E-Waste is a term used to cover items of all types of electrical and electronic equipment (EEE) and its parts that have been discarded by the owner as waste without the intention of reuse.” This includes a wide range of products, which includes almost any household or business item with circuitry or electrical components with power or battery supply (Baldé et al., 2015).

E-waste is the fastest growing waste stream globally due to rapid advances and innovation in technology, increasing production of electronics and electrical equipment. The shortened life span of these products has all contributed to the growth and increase of e-waste (Robinson, 2009). An estimate of over 500 million computers were reported obsolete between 1997 and 2007 in the United States alone; approximately 48.9 million tonnes of e-waste was generated in 2012 and more than 50 million tonnes of e-waste produced annually worldwide (Wong et al., 2007; UNEP, 2009; Huisman, 2012).

E-waste is an emerging environmental problem, as it is composed of a heterogeneous mix of different metals, metalloid, glass and plastics. Some of these are valuable such as aluminium, copper, gold, silver and iron that are recovered by recycling thus contributing to sustainable environmental management. Additionally, e-waste contains hazardous substances such as cadmium, lead, nickel and flame retardants which could be detrimental to the environment and human health (Hoffman, 1992; Robinson, 2009).

Due to the high cost of safe recycling processes, approximately 80% of the waste generated annually is shipped to developing countries in Africa and Asia for disposal, where the capacity to manage the waste is lacking and there are no binding stringent environmental regulations (Adaramodu et al., 2012; Puckett et al., 2005). Nigeria is recognized as a dumping ground for e-waste from other countries (Figs 1.1 and 1.2); the import volumes it receives are significantly higher than all the neighbouring countries, including Benin and Ghana (Puckett et al., 2005; Manhart, et al., 2011; Efthymiou, et al., 2016).

In the hunt for valuable materials such as palladium, gold, silver, indium and germanium, rudimentary methods such as dismantling, chipping, melting and burning are used in disassembling and recycling different components of electronic equipment. Some of the valuable metals contained in e-waste are lost using these rudimentary methods since the method used is quite inefficient in the recovery of metals (Manhart, et al., 2011).

These informal recycling practices contribute to the release of toxic metals and persistent pollutants in the environment thereby contaminating the soil. The soil, being the main receptor of e-waste, it is a significant environmental medium that can provide information about the level, distribution, and fate of contaminants present in the terrestrial environment. Soils absorb, accumulate pollutants and can act as secondary contamination sources even long after the pollution has been controlled (USEPA, 2004; Wong et al., 2007; Leung et al., 2008).

Source: Greenpeace, Basel Action Network

Figure 1.1: The E-waste trail. Source: http://ewasteguide.info/europe-breaking [accessed 15th June, 2016].

There is currently no system for tracking legal or illegal (under international law) shipments of electronic waste, and therefore, there is no quantitative data on volumes or even all of the true destinations. Some electronic waste is shipped as "working equipment" only to end-up as waste upon arrival. This map indicates information collected through investigations by organizations such as the Basel Action Network, Silicon Valley Toxics Coalition, Toxics Link India, SCOPE (in Pakistan), Greenpeace and others.

Figure 1.2: Routes of e-waste dumping. Source: http://www.sustainelectronics.illinois.edu/policy/international.cfm [accessed 7th September, 2016]

1.2 Environmental risk assessment

The risk analysis process is divided into technically oriented risk assessment and a management oriented (decision based) risk management (Fig. 1.3) which deals with regulatory measures based on the risk assessment (VanLeeuwen & Hermens, 1995).

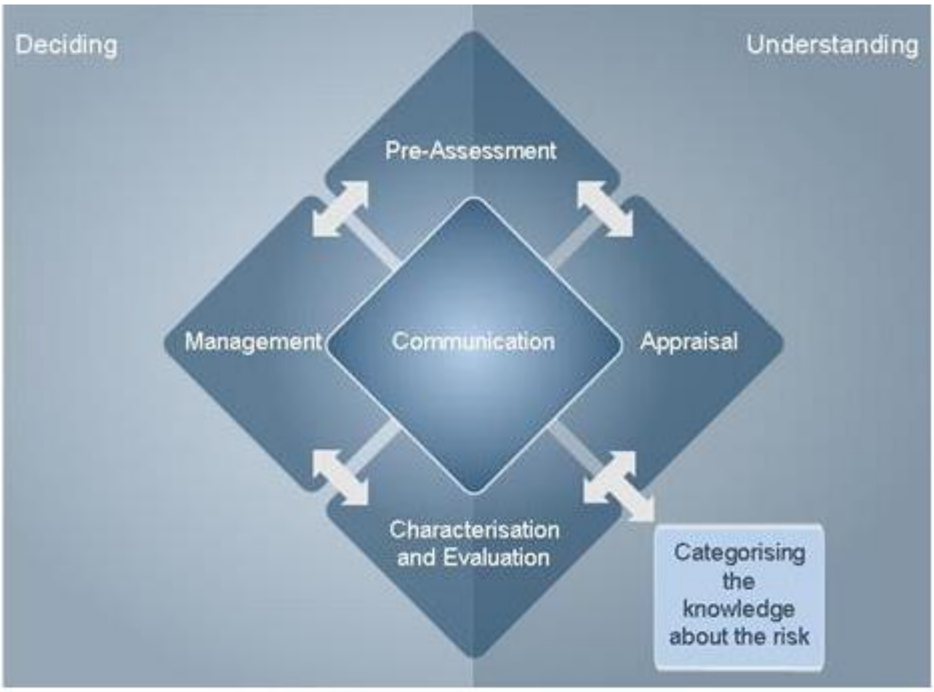


Figure 1.3: IRGC risk governance framework showing all the process entailed in risk analysis. (Source: Renn, 2008)

Risk assessment can be defined as the process of assessing severity of consequences and probabilities of occurrence to the adverse effects of anthropogenic activities and natural disasters (Suter, 1993). The aim of risk assessment is the generation of knowledge to link risk agents with uncertain but possible consequences. The risk could be assessed either by statistical data (actuarial extrapolation or Bayesian statistical tools); or experimental or epidemiological studies which are aimed at establishing statistically significant relationships between the exposure of a hazard and the adverse effect in a defined population sample (Graham & Rhomberg, 1996; Renn, 2008).

Environmental risk assessment (ERA), a theme in this thesis is technically oriented and falls into one half (understanding) of Fig. 1.3. ERA is a useful tool to estimate the possible adverse effects to human health due to contaminant exposure (Lopes et al., 2012). It is further defined by Depledge & Fossi (1994) and Oost et al. (2003) as “the process by which the likely or actual adverse effects of pollutants and other anthropogenic activities on ecosystems and their components are estimated with a known degree of certainty using scientific methodologies”. It comprises problem formulation, hazard identification, dose response assessment (effect assessment), exposure assessment, hazard evaluation and risk characterization (Fig 1.4).

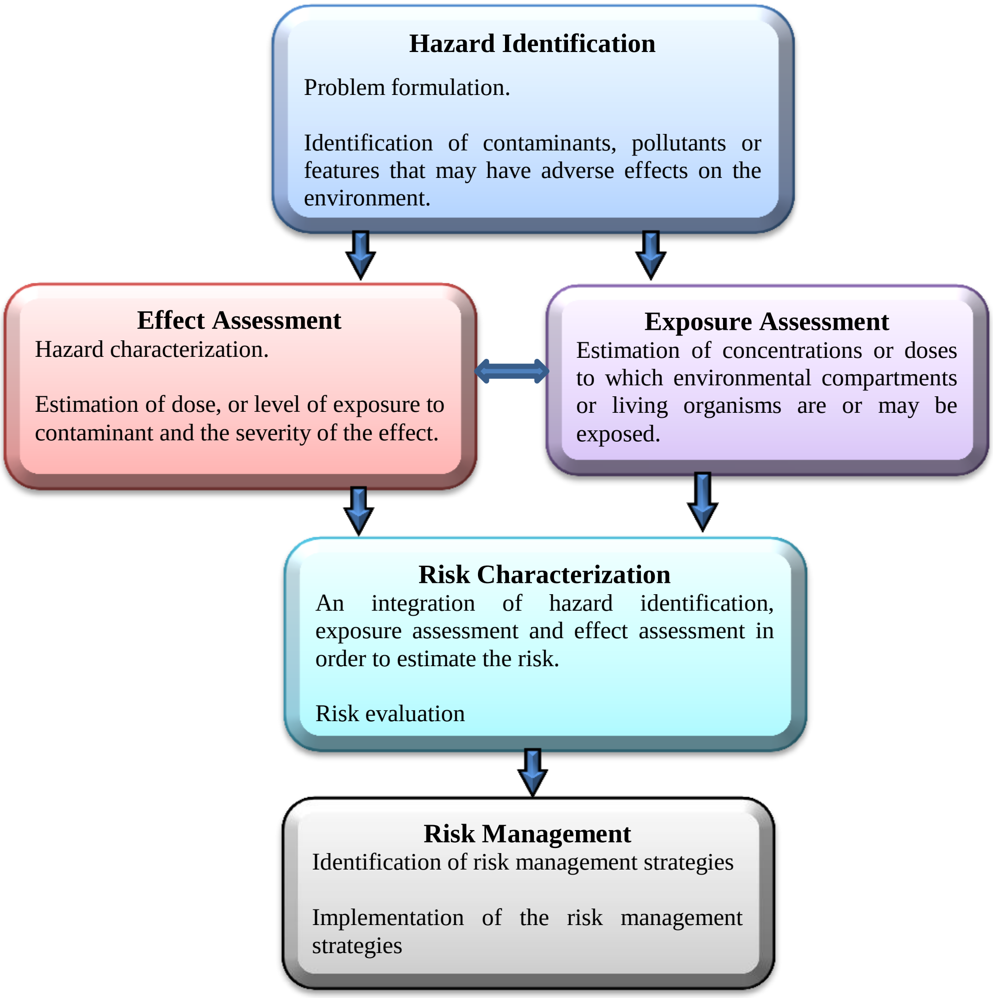


Figure 1.4: Environmental risk assessment framework. Modified from EPA's guidelines for risk assessment. Source: https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/ecological-risk-assessment-pesticides-technical [Accessed 11th March, 2014]

ERA has become very important since environmental scientists learnt that pollutants, which might not be toxic to humans, can have deleterious effects on the environment (Oost et al., 2003). ERAs primarily establish the potential relationship between a pollutant source and the effect caused by exposure of organisms to the pollutant (Fig 1.5) and bring to light the environmental consequences of decisions by indicating likely outcomes and their desirability (Suter, 1993).

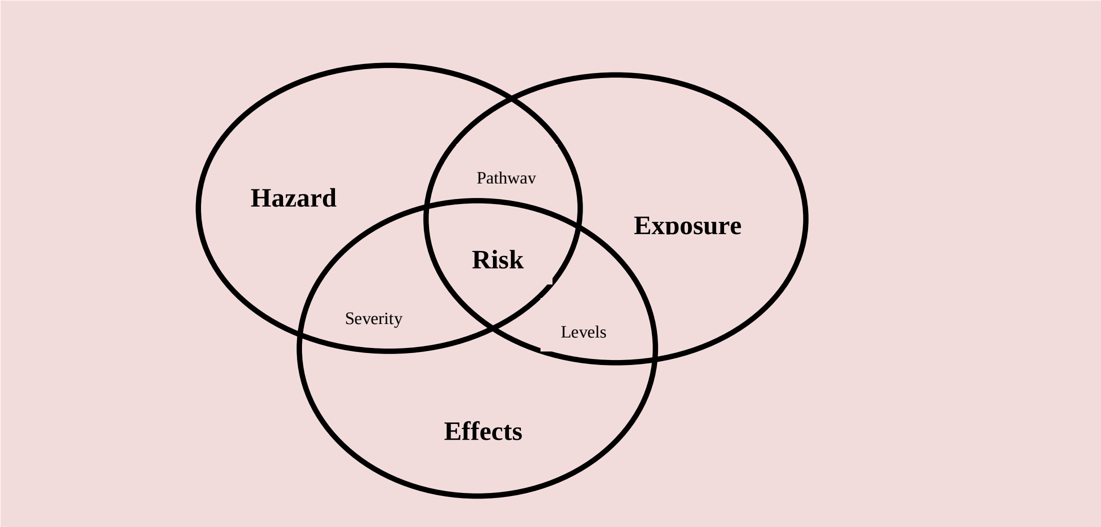


Figure 1.5: Relationship between source, exposure and effect of a contaminant.

1.2.1 Environmental risk assessment and (eco) toxicology

Contamination in soils is an important issue that can potentially affect both terrestrial and aquatic habitats owing to drainage and surface runoffs (Fernandez et al., 2005). Environmental risk assessments are used to identify the components that are most at risk from contaminants at a site and to quantify the magnitude of risk from those contaminants. In order to make these determinations, the relationships among organisms and between organisms and their physical environment need to be understood. Toxicity of contaminated soil is a focus for risk assessment as the effects of different soil components can be directly measured by exposure of organisms under set conditions mimicking the natural environment. Toxicity tests/assays are useful in establishing remedial goals because they demonstrate the bioavailability and effects of contaminants on exposed organisms in the given medium (USEPA, 1994).

1.3 Rationale and justification of study

E-waste has become an issue of major importance, as production technology rapidly develops and changes and more unknown components of the waste enter into the municipal waste stream. The absence of a structured management system and laxity in environmental laws and regulations in Nigeria has led to an increased influx of e-waste into the country. It has created an avenue for uncontrolled, crude method to recover valuable metals from the waste. These wastes are dismantled, and some are also burnt without prior knowledge of their composition and noxious matters are released into the environment. The effects of the informal crude recycling activities are not usually taken into consideration by stakeholders probably because the body of knowledge on the impact of e-waste recycling is still emerging. Although a number of studies have been carried out in several e-waste recycling sites in China and India on the composition of e-waste, the toxicity of e-waste as well as the risk to human health by the improper recycling of the e-waste (Leung et al., 2008; Li et al., 2011; Huo, 2013); only a few studies have been carried out in Nigeria to determine the concentration of the resultant contaminants from the e-waste activities (Adaramodu et al., 2012; Olafisoye et al., 2013; Ofudje et al., 2015) and most lack in-depth analysis. Currently, there is no comprehensive study on the pollution or contamination caused by e-waste in any environmental media in Nigeria, the exposure pathways have not been clearly identified nor understood, and the effects on environment and human health are relatively unknown.

1.4 Aim

To address the knowledge gaps identified above, this study aims to evaluate the e-waste contamination and the environmental and human health impact of informal e-waste recycling on the exposed population using the risk assessment framework.

1.4.1 Objectives

In order to achieve the aim of this study, the following objectives have been outlined:

I. Site characterization by identifying and characterizing the type of contaminants generated by the crude recycling process.
II. Investigation of the ecological impact of the recycling activities by quantifying the identified contaminants and establishing the potential ecological risk.
III. Investigation of the possible human health risk by characterizing and estimating the impact of the recycling activities.
IV. Risk evaluation of study.

Finally, fulfilling the objectives will result in risk characterization and evaluation of the informal recycling site and the development of a risk-based approach to improve the understanding of the e-waste challenge and provide evidence based management options.

1.5 Thesis outline

Chapter 2 gives a review of the sources and influx of e-waste in Nigeria, followed by a discussion on the socio-economic impact on e-waste. The ecological and human health impact of improper recycling processes, exposure routes and risk approaches used in investigating land contamination studies will be reviewed with the purpose of justifying the research context.

Chapter 3 gives an overview of the study area, a conceptual model of study identifying the possible pollution and exposure pathways and sample collection and preparation. The chapter will further explain the methodology detailing each quantitative analytical protocol utilized to achieve the research aim and objectives.

For additional clarity, the results have been organised into 3 chapters with detailed explanation and discussion in each.

Chapter 4 presents the distribution and concentration of the contaminants that will be identified in the study; the pollution level of the site and the potential ecological risk. The significance of soil properties in relation to the findings in the study will also be discussed.

Chapter 5 builds on the concept of bioavailability and bioaccessibility in the study; the results will establish the relationship between chemical speciation and bioaccessibility. The chapter will contain experiment data to demonstrate and characterize the human health risk on the exposed populace using two scenarios: using the total metal concentration only and with the integration of bioaccessibility factor.

Chapter 6 focuses on risk evaluation which is basically the introduction of societal values and norms into the scientific evidence obtained in the study. In this chapter the perception of the informal recyclers will be discussed, the factors that influence the identified perceptions, and conclusions will be drawn calling for the integration of a risk based process in evaluating and decisions making regards to the e-waste challenge in Nigeria.

Finally, chapter 7 concludes the thesis by discussing the implication of the study, the limitations of the study, recommendations and an outlook for future research.

CHAPTER TWO

2 Literature review

2.1 E-waste in Nigeria

Information technology (IT) is one of the largest and fastest growing industries on the globe having penetrated almost every aspects of modern life (Oliveira et al., 2012). The positive impacts of the technology are felt even in remote areas of developing countries such as Nigeria. The Nigerian information technology sector in the last decade has significantly benefited from the digital growth experienced worldwide. New electronics as well as second hand electronic appliances provide the populace with more comfort and easy access to information. With the growth of the Nigerian economy and increased access to mobile communication there is strong demand for high-quality electronics (Ejiogu, 2013). Due to high volume of importation (both legal and illegal), the electronic business booms in Lagos State; this is concentrated in Computer Village, Alaba International market, and Westminster market. The Basel Action Network (BAN) estimates that in the Computer Village alone, there are 3,500 registered businesses engaged in all manner of sales and repair of electronic equipment (BAN, 2011). Alaba International market features over 2,500 shops carrying out refurbishment and sale of used electrical and electronic products; whilst the Westminster market is the smallest of the three, has about 300 shops dealing with sale of used electrical and electronic appliances (Puckett et al., 2005; Manhart, et al., 2011; Ogungbuyi, et al., 2012).

Figure 2.1: Refurbished electronics for sale at Alaba international market, Nigeria. Source: http://www.theecologist.org/News/news_analysis/886532/uk_company_implicated_in_toxic_ewaste_trail_from_london_to_west_africa and http://www.allgoodfound.com/2015/08/used-electronics-a-booming-business-at-nigerias-alaba-international-market [accessed 10th July, 2016]

2.2 Sources and quantities of e-waste in Nigeria

Determining the volume of e-waste generated is complicated, largely due to the fact that there are no official records. The constraints to obtaining reliable data on the sources and quantities of e-waste generated in Nigeria include: unreliable data keeping and uncontrolled importation, lack of historical sales data of electrical/electronic equipment, e-waste being dumped in landfills without any assessment of quantity and quality, and difficulty in tracking data related to recycling as the majority of the e-waste items are informally dismantled to recover materials of economic value (Adediran & Abdulkarim, 2012). However, various authors as mentioned below have provided rough estimates and made predictions based on the advancement of technology, population growth as well as estimated number recorded importations per month.

2.2.1 External generation of e-waste

In 2005, an estimate of 500 containers of used electronic scrap of various ages and conditions were imported into Nigeria on a monthly basis. Each container was said to have had approximately 800 computers or monitors (amounting to about 400,000 units or 60,000 metric tons arriving each month) of which approximately 75% was not economically reusable or resalable (Puckett et al., 2005; Ejiogu, 2013). From the tags/labels on the electronics, it was concluded that 45 percent of the electronics came from the EU, 45 per cent from the USA and 10 per cent from other countries such as Japan, Korea, Malaysia and (Puckett et al., 2005; Benebo, 2009). In 2012, Ogungbuyi, et al. reported a statistical estimate for the importation from different countries; approximately 60% from United Kingdom, 16% from Germany, 9% from China, 3% from USA and 12% from other countries.

The Consumer International (2008) reported the estimates of broken electronics that entered Nigeria had gone up to about 500,000 units. Nnorom & Osibanjo, (2010) estimated that 468,000 metric tons of electronic scrap was imported into Nigeria between 2005 and 2010; and further predicted an annual increase of 10 percent if the practice went unchecked.

In 2011, the UK based Environmental Investigation Agency (EIA) published a report, indicating that e-waste from the UK was being dumped in Nigeria, although the quantity was not mentioned. The report details an investigation in spring 2010 where EIA undercover investigators visited two civic amenity sites in the London boroughs of Croydon and Merton respectively; whose waste management was overseen by a company known as Environmental Waste Control Limited (EWC). They watched as electronics were separated according to types and quality and purchased by another company (Sanak Ventures Limited) who shipped them to Nigeria. Since there were claims at the site that the electronics were tested and only electronics in good working conditions were being shipped off, the EIA investigators hid trackers inside TVs, which were broken beyond repair to confirm if only working electronics were being exported. The signal from the trackers was monitored till arrival at the final destination, with the precise location as Olojo Road, close to the Alaba International Market, Lagos State, Nigeria (EIA, 2011).

Furthermore, Ogungbuyi, et al, 2012 examined the major routes of importation of E-waste in Nigeria and reported it was mainly through the seaports (Tin can port) and land border (Seme border) with the Republic of Benin. They reported that approximately 77% of imported used electronics came in with 40 Ft. containers weighing 9,158kg and about 23% in 20 Ft. containers weighing 4805kg. They also reported of large quantities of unusable electronics loaded into what they termed “ironically un-reusable” vehicles which were then locked to avoid inspection. In August 2016, United Nations University organized an e-waste academy for scientist (EWAS 2016) bringing together doctoral and postdoctoral researchers from around the world to discuss the e-waste problem from different viewpoints which the author of this thesis participated in. A study visit to Dublin port, Republic of Ireland was organized as part of the e-waste workshop; the findings of Ogungbuyi, et al, 2012 were corroborated and confirmed during the study visit (Fig 2.2). The same scenario was observed at the port; the unusable electronics were disguised and hidden within other goods in the container. Although some shipments were detected and intercepted, it was confirmed by port staff that some still found their way to West Africa especially Nigeria due limited manpower at the Dublin ports authority.

The erstwhile Director-General of the National Environmental Standards and Regulations Enforcement Agency (NESREA) in Nigeria estimated that about 2 percent of the used electronics and electrical equipment imported could be directly reused without repairs, 5 percent could be put to use with minimum repairs, 20 percent could have their components used for local repairs, while the rest are unusable junk (Benebo, 2009). However, there are no official figures as to how much e-waste is imported into Nigeria.

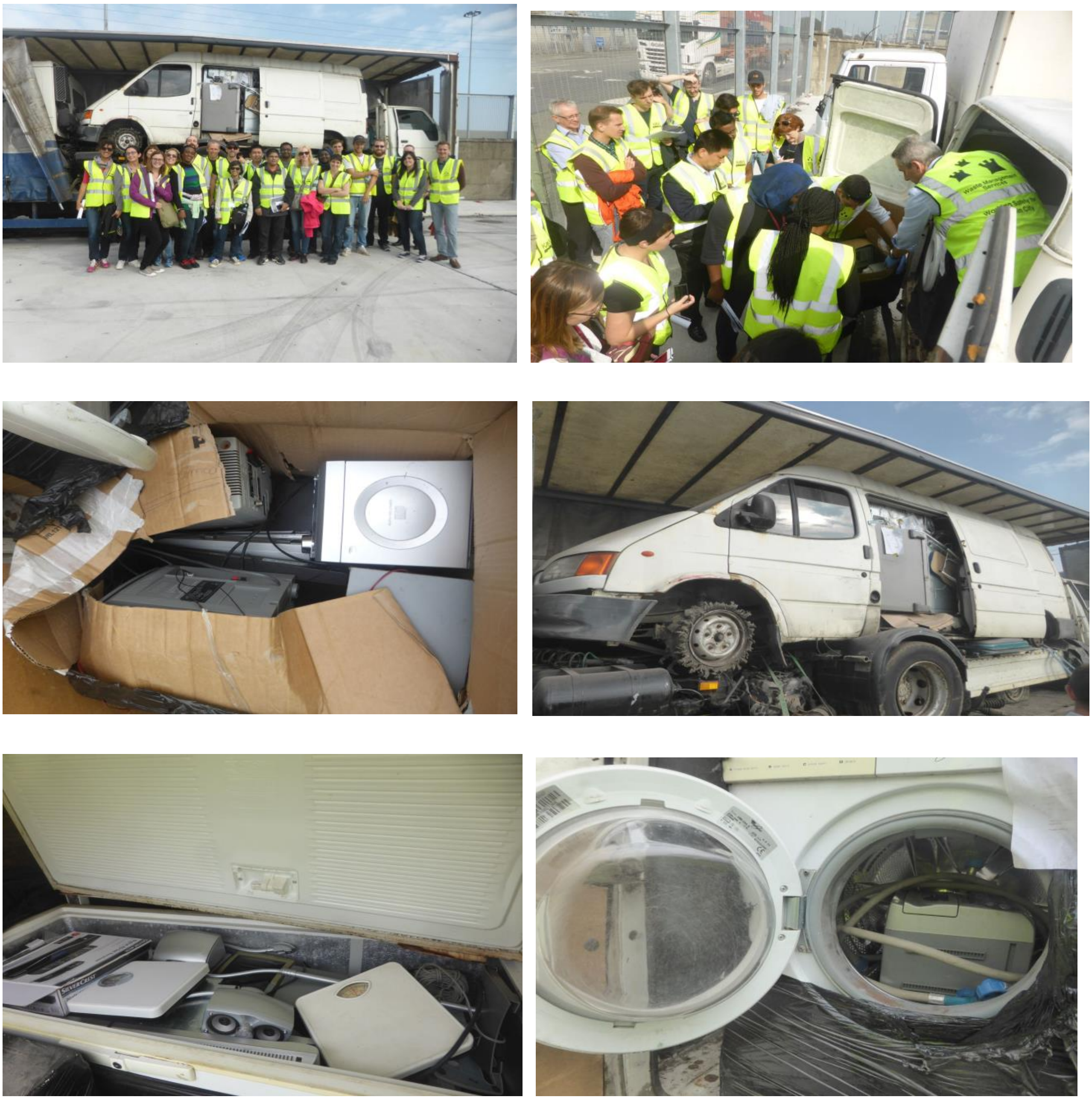


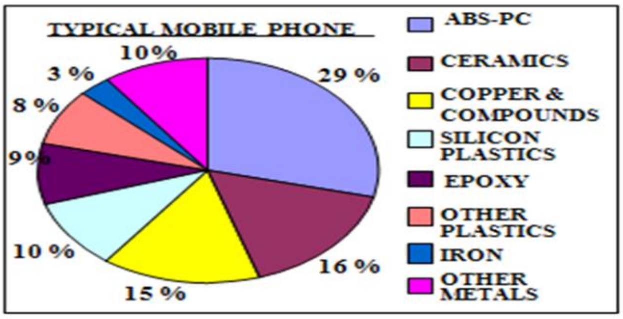
Figure 2.2: Intercepted disguised unusable electronics at Dublin port meant for shipment to Nigeria.

2.2.2 Internal generation of e-waste

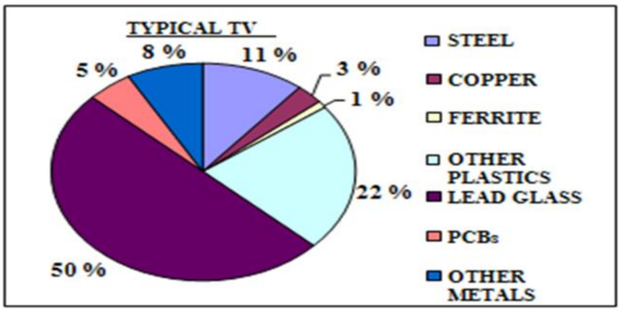
The main source of internally generated e-waste in Nigeria, are the government, public and private (industrial) sectors, which account for the bulk of the total e-waste generated. The contribution of individual households is relatively small at about 15 percent. Although individual households are not being identified as large E-waste contributors, they are large consumers and hence potential waste creators (Nnorom & Osibanjo, 2010).

2.3 E-waste: An environmental concern

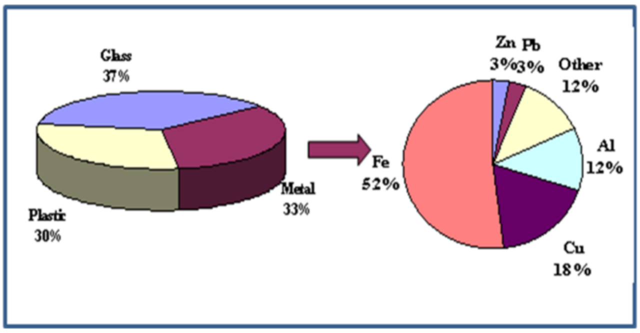
E-waste contains a complex mixture of potential contaminants that are distinct from other forms of waste; the changing composition of the e-waste due to technological development makes it distinct from other potential contaminants (LaDou & Lovegrove, 2008; Li et al., 2008). According to Baldé et al. (2015), e-waste comes in different categories which include: small IT and telecommunication equipment; screens and monitors; lighting equipment and large and small household appliances. They explained that the material composition and the weight for each category differs introducing additional complexity to the e-waste stream; thus causing environmental issues through the lack of characterization of e-waste, its low collection rates and unknown disposal methods. The material composition of e-waste consists of approximately 60% iron, copper, aluminium, gold and other metals; 15% plastic; and the remaining consists of cables and printed circuit boards amongst other parts (Cui & Forssberg, 2003; Widmer et al., 2005; Cui & Zhang, 2008). Although the amount of hazardous substances in e-waste is relatively small (Bandyopadhyay, 2008), they do have significant impact due to the concentration levels and their persistence in the environment. These may have long-term effects on the environment and public health at large.



Composition a typical mobile phone



Composition of a typical television



Composition of a typical computer

Figure 2.3: Material constituent of some equipment that end up as e-waste. Source: Ari, 2016.

Table 2.1: Some constituents of e-waste and their impact

Substance	Source in E-waste	Impact
Lead (Pb)	Printed circuit boards, lead-acid batteries, monitors, cathode ray tubes, fluorescent tubes and light bulbs	The accumulation of Pb in the environment results in both acute and chronic effects on human health. Can cause damage to the brain, nervous system, kidney and reproductive organs as well as blood disorders. May hinder development in children.

Cadmium (Cd)	Rechargeable Ni-Cd batteries, cathode ray tubes, semiconductor chips, infrared detectors, printer inks and toners, phones	Long term exposures can pose a risk of irreversible lung and kidney disease and cancers. Short term exposures can cause flu-like symptoms, weakness, fever and muscular pain
Nickel (Ni)	Batteries, computer housing, cathode ray tube and printed circuit boards	Can cause allergic reaction, bronchitis, reduced lung function and lung cancers
Chromium (Cr)	Anticorrosion coatings, plastic computer housing, cables, hard discs, floppy disks	Extremely toxic in the environment, cause DNA damage and permanent sight impairment
Antimony (Sb)	Cathode ray tube, plastic computer housings and a solder alloy in cables	Exposure through ingestion can lead to stomach pain, vomiting, diarrhoea and stomach ulcers over a long time period
Mercury (Hg)	Monitors, printed circuit boards, fluorescent lamps	Bioaccumulates causing brain and liver damage if ingested or inhaled.
Zinc (Zn)	Batteries, cathode ray tubes,	Exposure can cause stomach cramps, skin irritations, vomiting, nausea and anaemia. Long term exposure can cause respiratory disorders
Copper (Cu)	Cables, plugs and sockets, microprocessors and terminal strip	Exposure can cause nose, mouth and eyes irritation; headaches, stomach aches, vomiting and diarrhoea. High intake may cause liver and kidney damage.
Arsenic (As)	Light emitting diodes	Exposure can cause skin disease, lung cancer and impaired nerve signalling.
Beryllium (Be)	Power supply boxes, motherboards, relays	Exposure to beryllium can lead to beryllicosis, lung cancer and skin disease.
Barium (Ba)	Cathode ray tube, spark plugs and fluorescent lamps	Causes brain swelling, muscle weakness, damage to the heart, liver and spleen through short-term exposure.
Polyvinyl chloride (PVC)	Monitors, keyboards, cables and plastic computer housing	The incomplete combustion of PVC releases hydrogen chloride gas which forms hydrochloric acid (HCl) after combination with moisture. HCl can cause respiratory problems.

Brominated flame retardants (BFRs): polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol-A (TBBP-A)	Printed circuit boards, plastic housings, keyboards and cables	During combustion printed circuit boards and plastic housings emit toxic vapours known to cause hormonal disruption, damage to the immune system
Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)	Released during combustion of printed circuit boards and plastic housings, keyboards and cables	Reproductive, immune system damage and neurobehavioral disorder.
Polycyclic aromatic hydrocarbons (PAHs)	Released during combustion of printed circuit boards and plastic housings, keyboards and cables	Mutagenicity, teratogenicity and carcinogenicity

Sources: Brigden, et al., 2008; Frazzoli, et al., 2010; Kiddee, et al, 2013; Perkins, et al., 2014

2.3.1 Description of some constituents in e-waste

The constituents and the complex composition of e-waste may pose a threat to the environment and human health if they are not disposed of in the correct manner. The composition includes metals; persistent organic pollutants (POPs) such as flame retardants; plastics among other components (table 2.1). Heavy metals are natural constituents of the Earth’s crust (Shivakumar et al., 2012); some act as micronutrients such as Mn, Fe, Cu and Zn which are useful at certain low doses. However, anthropogenic activities have altered the balance of some heavy metals in the environment, causing these metals to be toxic to organisms and human health (Luoma, 1983).

Persistent organic pollutants (POPs) are a group of chemical compounds with different origins but similar characteristics such as semi-volatility, persistence and bioaccumulation in the environment, and bio magnification in food chain (Schwarzenbach et al., 1993; Gavrilescu, 2005; Betianu & Gavrilescu, 2006). These include polybrominated diphenyl ethers (PBDEs); polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs); polycyclic aromatic hydrocarbons (PAHs). Some POPs can be introduced into the environment through natural processes such as forest fires and volcanic eruptions, however, high concentrations of POPs are usually associated with anthropogenic activity such as vehicular emissions; industrial waste disposal; thermal process in the ferrous industry and waste and fuel combustion (Bargagli, 2008; Vallejo, et al., 2015). They are of concern due to their toxic effects on living organisms and the environment (Semple et al., 2003; Ahmad, 2011).

2.3.1.1 Antimony

Antimony is a silvery, white, brittle, crystalline solid that exhibits poor conductivity of electricity and heat with an atomic number of 51, an atomic weight of 121.8 and a density of 6.697 g cm^{-3} at 26°C (ATSDR, 1992). It is a semi-metal chemical element which can exist in two forms: the metallic form is bright, silvery, hard and brittle and the non-metallic form is a grey powder. Antimony is seldom found in nature as a native metal because of its strong affinity for sulphur and metals such as copper, lead and silver (Anderson, 2012). The main applications of antimony are industrial. It is used for producing semiconductors, infrared detectors and diodes. It is also mixed into alloys for manufacture of lead storage batteries due to its relative inflexibility (Sundar & Chakravarty, 2010). Antimony trioxide, Sb_2O_3, the most important antimony compound, is used in halogen compound flame retarding formulations for plastics, paints, textiles and rubber (Anderson, 2012); whereas antimony trisulphide is used in the production of explosives, pigments, antimony salts and ruby glass (Sundar & Chakravarty, 2010). Antimony is known to accumulate in soils, but, there is limited knowledge on its long term exposure to man but it is suspected to be a carcinogen. Short term exposure to high concentrations of antimony can cause diarrhoea, nausea and vomiting (ATSDR, 1992). Antimony also shows many chemical similarities to arsenic (Andrewes et al., 2004); like arsenic, it can form its trimethyl derivative (called trimethylstibine) as a result of microbial activities but at slower rates than arsenic, and also exhibit similar toxic effects to skin cells. (Patterson et al., 2003; Brigden et al., 2008)

2.3.1.2 Cadmium

Cadmium is a soft silver-white metal found naturally in the earth's crust, although, the most common forms of cadmium found in the environment exist in combinations with other elements (ATSDR, 2012) e.g. Zn. Cadmium is located at the end of the second row of transition elements with atomic number 48, atomic weight 112.4, density 8.65 g cm^{-3}, melting point 320.9°C, and boiling point 765°C. It is usually a by-product of zinc, lead and copper extraction in smelting. Cadmium is used in manufacture of batteries (Ni-Cd batteries), as rechargeable or secondary power sources exhibiting high output, long life, low maintenance, and high tolerance to physical and electrical stress. Also, cadmium is used in coating to vessels and other vehicles which provide good corrosion resistance (Wuana & Okieimen, 2011).

In the environment, cadmium can be taken up by plants and thus, becomes a danger to herbivores as they are plant dependent for survival. Cadmium thus accumulates in the bodies of the animals. Cadmium is taken up by humans through ingestion; it could cause health effects such as diarrhoea, damage to the immune system and nervous system amongst other ailments (ATSDR, 2012).

2.3.1.3 Copper

Copper is a reddish crystalline structure metal which reflects red and orange light and absorbs other frequencies in the visible spectrum (ATSDR, 2004). Copper is a transition metal with atomic number 29, atomic weight 63.5, density 8.96 g cm^{-3}, melting point 1083°C and boiling point 2595°C. Copper has a low chemical reactivity, it is a good conductor of heat and electricity and it is ductile and malleable. Copper is used for electrical equipment, in roofing and in alloys.

Copper is an essential micronutrient in the growth of both plants and animals. It is useful in seed production in plants; in humans it assists in the production of haemoglobin. However, in high doses, it can cause anaemia, kidney and liver damage as well as stomach irritation in man (Wuana & Okieimen, 2011). When present in the soil, copper accumulates in plants and animals. Copper disrupts the soil activity by influencing microbial and invertebrate activities, therefore reducing the survival rate of flora and fauna (ATSDR, 2004).

2.3.1.4 Chromium

Chromium is a silver-grey coloured, lustrous, brittle, hard metal. It has an atomic number of 24, atomic mass 52, density 7.19 g cm^{-3}, melting point 1875°C, and boiling point 2665°C. It is one of the less common elements and does not occur naturally in elemental form, but only in compounds (Wuana & Okieimen, 2011) as it is very unstable in oxygen. Chromium is used in alloys, electroplating and chrome plating. Chromium (VI) is the form of Cr mainly found at contaminated sites, however it can also occur in the +III oxidation state, depending on pH and redox conditions of the soil (Wuana & Okieimen, 2011). The mobility of chromium depends on the soil characteristics such as the quantity of organic matter present. Chromium(VI) is the more toxic form of chromium and is also more mobile (Chrostowski et al., 1991). Humans are exposed to chromium through ingestion, inhalation and dermal contact. The exposure could cause health effects such as skin rashes, respiratory disorder and kidney and liver damage.

2.3.1.5 Lead

Lead is a heavy, low melting, bluish-grey metal, of atomic number 82, atomic mass 207.2, density 11.4 g cm^{-3}, melting point 327.4°C, and boiling point 1725°C It occurs naturally in the Earth's crust, usually found combined with two or more other elements to form lead compounds. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air (ATSDR, 2007). Lead is combined with other metals to form alloys. Lead and its alloys are used in pipes, batteries and ammunition. Lead compounds are used in paints, dyes and ceramic glazes (ATSDR, 2007).

Concentration of lead in the environment is as a result of anthropogenic activities such as metal smelting. Lead accumulates in the soil and also in the food chain. According to Wuana & Okieimen (2011), lead does not readily accumulate in the fruiting parts of vegetable and fruit crops (e.g., corn, beans, squash, tomatoes, strawberries, and apples). However, higher concentrations are found in leafy vegetables (e.g. lettuce) and in root crops (e.g. carrots). There is no known essential function of Pb to humans and other organisms (Baldwin & Marshall, 1999). Ingestion and inhalation are the main routes of exposure. It accumulates in body organs and leads to poisoning. Lead can result in injuries to the brain, nervous system and red blood cells. There are also reports of memory loss, insomnia and weakened joints as a result of lead poisoning (Baldwin & Marshall, 1999) together with documented effects on the developing brain at sub-clinical doses (Brigden, et al., 2008; Frazzoli, et al., 2010).

2.3.1.6 Manganese

Manganese is a naturally-occurring metal which in pure form is silver-coloured without any smell or taste with atomic number 25, density 7.21 $g\,cm^{-3}$, boiling point 2061°C and melting point 1246°C. It is usually found in the environment as a compound with oxygen, sulphur, or chlorine (ATSDR, 2000). There are two forms of manganese in the environment. Inorganic manganese compounds used in the production of steel, batteries, ceramics, and dietary supplements and the organic manganese compounds are used in some pesticides, fertilizers, and in a gasoline additive called methlcyclopentadienyl manganese tricarbonyl (ATSDR, 2000; USEPA, 2007).

Manganese is an essential nutrient, required in trace amounts for human health. Intake is normally sufficient with a balanced diet; however, adverse effects occur when in high concentrations (USEPA, 2007). In other words, it is a toxic essential micronutrient. Anthropogenic activities increase the concentration of manganese in the environment. The routes of exposure include ingestion and inhalation. Uptake by human is mainly by food and in high concentrations; it could cause some nerve damage, hallucination, insomnia amongst other ailments.

2.3.1.7 Nickel

Nickel is a hard, silvery-white abundant metal with atomic number 25, density 8.91 $\mathrm{g\,cm^{-3}}$, boiling point 1455°C and melting point 2730°C. Nickel can be combined with other metals, such as iron, copper, chromium, and zinc, to form alloys. These alloys are used to make coins and jewellery. Nickel compounds are used for in making batteries. Nickel when released in the soil binds to particles containing iron and manganese. However, nickel is not known to accumulate in plants. Presence of nickel in the soil results in growth decline in microorganisms. Human studies examining the effect of nickel on new-borns and foetuses have been inconclusive but studies showed harm in new-borns of animals. Long term exposure of nickel has been shown to cause skin irritation as well as heart and liver damage. The International Agency for Research on Cancer (IARC) has determined that some nickel compounds are carcinogenic to humans and also the possible carcinogenicity of metallic nickel to humans (ATSDR, 2005).

2.3.1.8 Zinc

Zinc is a transition metal with atomic number 30, atomic mass 65.4, density 7.14 $\mathrm{g\,cm^{-3}}$, melting point 419.5°C, and boiling point 906°C. Zinc occurs naturally in the earth crust. In its pure elemental form, zinc is a bluish-white, shiny metal. It is used in galvanization iron, steel and other metals to prevent corrosion. Metallic zinc is also used in dry cell batteries.

Zinc enters the air, water, and soil as a result of both anthropogenic and natural processes. Most zinc enters the environment as the result of mining, metals purification, and steel production, coal burning, and burning of wastes. Ingestion, inhalation and dermal contact are exposure routes for zinc. Zinc is also a trace micronutrient essential for growth in humans, plants and animals, high doses could however be toxic. High concentration of zinc in the soil impacts negatively on soil microorganisms and invertebrates. Zinc is also accumulated in plants. In humans, high concentration of zinc in the body can cause damage to the pancreas and disrupt the protein metabolism. Respiratory disorders can be caused by exposure to zinc chloride. There are no known carcinogenic effects of zinc (ATSDR, 2005).

2.3.1.9 Polybrominated diphenyl ethers (PBDEs)

PBDEs are a class of brominated hydrocarbons used as flame retardant additives in plastics and foams, including plastic casings of electronic equipment (OECD, 2003; ASTDR, 2004; USEPA, 2014). They include different congeners differing in the numbers and positons of the bromine atoms in the molecule. There are three commonly available and commercially in use PBDE homologs: pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE) and decabromodiphenyl ether (decaBDE). DecaBDE is the most widely used PBDE globally (ASTDR, 2004; Brigden, et al., 2008).

PBDEs may enter the environment through emissions from manufacturing processes, volatilization from various products that contain PBDEs, recycling wastes and leachate from waste disposal sites. Their behaviour in the environment is a function of their molecular properties, largely governed by the number and character of the bromine atoms substituted. The lower brominated congeners of PBDE which are more persistent in the environment tend to bioaccumulate more than higher brominated congeners (ATSDR, 2004). Their mobility in the atmosphere has been established as they are known to attach to airborne particulate matter (USEPA, 2014).

2.3.1.10 Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are commonly known as dioxins and furans. PCDD/Fs are a group of 210 different structural congeners, (75 PCDD and 135 PCDF congeners) that are not intentionally produced but are by-products resulting from anthropogenic activities, including waste incineration, chemical manufacturing, petroleum refining, wood burning, metallurgical processes, fuel combustion, electric power generation, among other activities (ASTDR, 1998; Canadian Environmental Quality Guidelines, 2001).

PCDD/Fs are ubiquitous and persistent contaminants in the environment that are found in all primary (air, soil, water, sediment) and secondary (food and consumer goods) media. PCDD/Fs are released to the receiving environment and are moved away from their emission sources by atmospheric transport, as such, they can be transferred from one matrix to the other. They have been found in the aquatic environment, where they enter mainly from atmospheric deposition, despite their low water solubility (Vallejo et al., 2015).

2.3.1.11 Polycyclic aromatic hydrocarbons (PAHs)

PAHs are non-polar organic compounds with two or more fused benzene rings (Oluseyi et al., 2011); which are highly lipophilic and are ubiquitous in the environment (Sun et al., 2009; Wang et al., 2012). Over a hundred PAHs have been identified in nature (Sun et al., 2009) of which sixteen are listed as priority pollutants by the United States Environmental Protection Agency (USEPA, 2002). These include: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene (USEPA, 2002), of which seven of them are considered probable carcinogens (Cai et al., 2007; Wang et al., 2012). PAHs originate from both natural and anthropogenic sources. The anthropogenic sources include combustion and pyrolysis of fossil fuels or wood (pyrolytic sources) and from release of petroleum products (petrogenic sources) (Kowalewska & Konat, 1997; Oluseyi et al., 2011). Soil has been reported to be the primary reservoir for PAHs (Tang et al., 2010), as they are sparingly soluble, easily adsorbed by soil particles, difficult to degrade and tend to accumulate in soils (Ping et al., 2007; Tang et al., 2010). The activities of PAHs depend on their individual chemical structure and are of great environmental concern because of their mutagenic and carcinogenic activity.

2.4 The possible impacts of informal e-waste recycling

Many developing countries around the globe are faced with the e-waste problem. The informal recycling of e-waste could result in both positive and negative impacts; which could be a lucrative business for recovery of valuables such as copper, aluminium and gold or could impact on human and environmental health adversely.

2.4.1 Environmental impact

In developing countries such as in Nigeria; e-waste may be either dumped in landfills or recycled informally. This may lead to soil acidification and production leachates that pollute surface and ground water (Borthakur & Singh, 2012). Tsydenova & Bengtsson (2011) stated the primitive methods used in the treatment of e-waste have resulted in adverse environmental and human health impacts; the methods include open burning of wires and other parts of the waste to obtain copper, acid stripping and finally dumping of parts that cannot be further broken down.

Dismantling activities release dust particles loaded with heavy metals and POPs such as flame retardants into the atmosphere. These particles either re-deposit (wet or dry deposition) near the emission source or can be transported over long distances depending on their size. Similarly, dust together with compounds found in wet and dry depositions can leach into groundwater or react with the biota (Fig 2.4). The environmental fate of particles, ashes and fumes containing heavy metals and PBDEs released by burning activities is similar to that of the emissions released by dismantling activities (Sepúlveda et al., 2010).

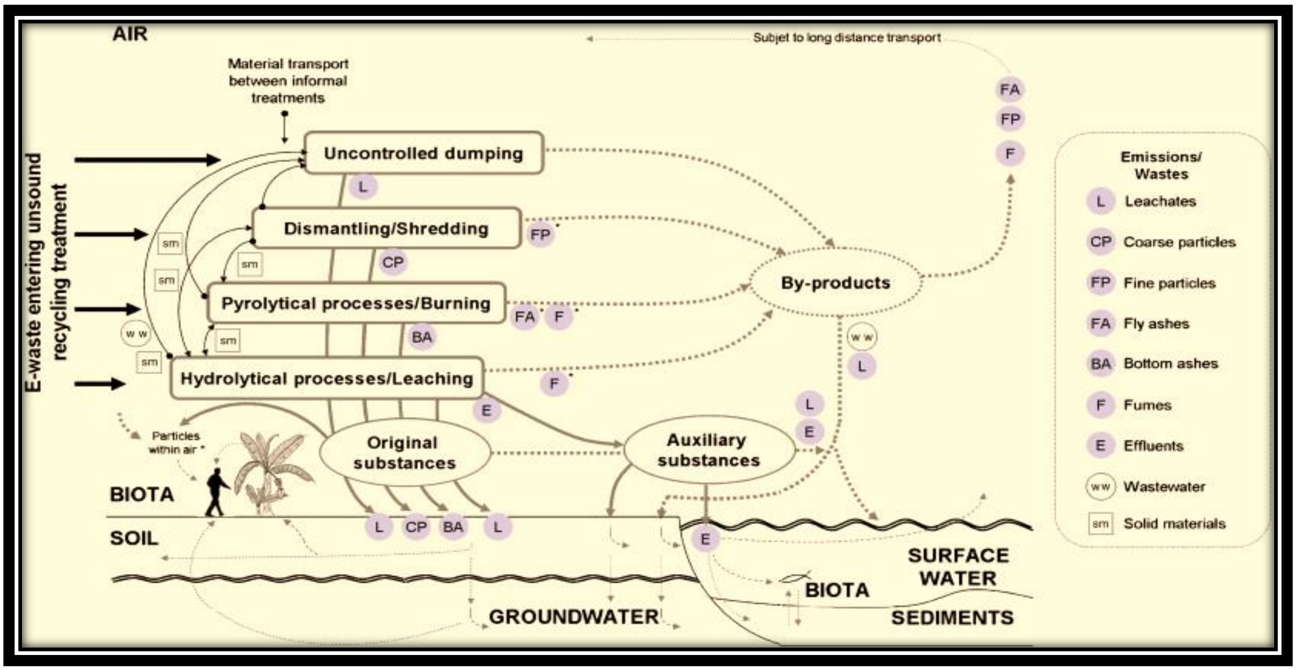


Figure 2.4: Environmental impact of informal recycling process. Source: Sepúlveda et al., 2010

A number of studies have reported the effects of e-waste processing activities especially in China, and results showed contamination in air, soil, surface water and sediments could be attributed to the direct effects of e-waste recycling operations (Luther, 2010). Leung et al. (2008), Sepúlveda et al., (2010), Luo et al., (2011), Otsuka et al., (2011) and Caravanos et al., (2011) all reported contaminant levels higher than the permissible values in soil and water and also confirmed the relationship between the environmental contamination and the informal e-waste recycling practices in China, India and Ghana.

2.4.2 Health impact

As indicated in Table 2.1, informal recycling releases most of the constituents of e-waste that have negative impacts and the potential to cause harm on human health. Different studies on e-waste recycling have reported an increased level of contaminants in the human body and damage to different organs including the DNA (Table 2.2). Zhang et al., (2016) reported higher blood Pb levels and lower percentages of natural killer cells in children exposed to informal e-waste recycling in Guiyu, China. In addition, Huo, (2013) reported significantly elevated blood lead, cadmium, chromium, manganese, nickel, PBDEs and PAHs in children and neonates from the same Chinese province. He further observed the children had impairment of neurobehavioral development, temperament alterations, damage of lymphocyte DNA and changes of antioxidant enzymatic activities. Li et al., (2008) also reported a strong correlation between the increased Pb concentrations in the umbilical cord, blood and meconium of neonates with the maternal involvement in e-waste recycling in Guiyu before and during the pregnancy.

Elevated levels of barium, manganese, selenium and zinc were found present in the urine, while in the blood serum, significantly elevated levels of barium, cobalt, chromium, copper, iron, selenium and zinc were found in workers at an e-waste recycling site in Ghana when compared to a control group (Caravanos et al., 2013).

Table 2.2: Some reported health impacts from informal e-waste recycling.

Exposure scenario	**Pollutant**	**Health impact**	**Reference**
Blood from children (4-6 years old) from an e-waste dismantling site in Guiyu, China	PBDEs, Pb, Cd	Thyroid hormones alterations Elevated blood Pb	(Xu et al., 2014)
Pregnant women in an e-waste recycling site in China	PBDEs, PCDD/Fs, and PCBs	Thyroid hormones homeostatis	(Zhang et al., 2010)
Hair samples and urine from men in e-waste dismantling site in LQ area in east China	PBDEs, PCDD/Fs, and PCBs	High cancer risk due to oxidative damage to DNA	(Wen et al., 2008)
Blood from workers in an e-waste dismantling region, Guangdong, China	PBDEs	Elevated blood levels	(Qu et al., 2007)
Exposed populace close to e-waste recycling site in China	BFR	Altered levels of thyroid hormone (THs) and thyrotropins (TSH	(Wang et al., 2010)
School children (8-13 years) from an e-waste recycling area in China	Cr, Mn and Ni	Decreased pulmonary action	(Zheng et al., 2013)
Children (3-8 years old) in an e-waste processing area in Guiyu, China	Pb, Cd	Increased blood Pb affecting physical development of bone r	(Yang et al., 2013)
Pregnant women in e-waste processing area in Guiyu, China	Pb, Cr, Cd, Ni	Increased Pb in placenta which could threaten neonates	(Guo et al., 2010)
Children (11-12) in Luqiao e-waste recycling area, China	Pb	Increased blood Pb levels	(Wang et al., 2012)
Blood from children (3-7) in Guiyu, China	Pb	Increased levels affect immune system	(Zhang et al., 2016)
Placenta samples from pregnant women in Guiyu, China	Pb, Cd	Foetal growth retardation due to high placenta Cd.	(Xu et al., 2016)
Semen from men	Pb	Reduced sperm motility, poor morphology	(Li et al., 2013)
Blood from workers in Benin city, Nigeria	Pb, Cr, As, Cd, Hg	Elevated levels which establish synergistic toxicity	(Igharo, et al., 2014)

2.4.3 Socio-economic impact

In developing countries, the demand for second hand electronics is quite high reflecting the demand from the less wealthy consumers. As a result of the high demand, organizations and individuals use the opportunity to export both functional and non-functional electronics to developing countries (Ladou & Lovegrove, 2008). The non-functional equipment starts the e-waste chain from collection to recycling. The recycling activities lead to environmental and health impacts are discussed in sections 2.4.1 and 2.4.2.

In contrast, e-waste recycling generates employment for a group of people. These activities range from collection, dismantling, sorting to the actual burning of the wastes. As at 2012, in Nigeria, this sector created job opportunities and income source for approximately 80,000 people, impacted economically on the nearby communities by job creation for residents close to the recycling sites such as selling food and water to the workers on the sites (Ogungbuyi et al., 2012). In spite of the environmental and health risk posed by the activities, a number of people are still willing to join the sector because the wages received is commensurate with either the volume of waste collected or recycled, hence the motivation. However, due to the informal nature of the e-waste recycling sector in Nigeria, there are no official figures of the income of the workers (Manhart et al., 2011).

Furthemore, Manhart et al., (2011) reported that the informal recycling sector in Nigeria has a contribution to the national budget, although informal, the recyclers in a fixed site pay tax on daily basis to the local government and agencies collecting tax on behalf of the state government. They also reported that the informal recycling sector in Nigeria plays an important role in some conflict resolution; the recovery of some metals from the activities reduces the pressure to mine for raw materials and the fight for loss of land and properties by the affected people. In addition, Ogungbuyi et al., (2012) reported that the metal/steel sector in the country have been a beneficiary of the informal e-waste sector as they can source some materials from the recyclers and avoid costs spent on the importation of materials.

2.5 Ecological risk assessment

Ecological risk assessments adddress the risk to the environment and the biota in it and mainly refer to contaminated land and surface water where there is interaction between organisms of different trophic levels. Organisms absorb contaminants from different environmental media by ingestion, absorption from their food, contact with external surfaces and inhalation of the vapour phase or airborne particles. Due to the proximity between the organisms and the contaminated environmental media, many interactions such as acute and chronic toxicity, bioaccumulation, reproductive effects, genetic mutation and loss of species may occur. These processes usually encompass all tiers in the food web and are very complex due to variations in the exposure routes and number of species and population diversity and size (WHO, 1999; Suter et al., 2000; ITRC, 2003). It is often argued that ecological risk assessments are of more importance than any health risk assessment because ecological receptors experience a greater exposure and are more sensitive to contaminants in relation to human (Suter et al., 2000; Bartell, 2010).

Ecological risk assessment is a tiered process which begins with a site investigation to evaluate the physical and chemical characteristics of the site in order to establish whether the contamination concentrations are sufficient to pose a risk to the ecological receptors compared to the screening values. Screening values are concentrations of a contaminant in the environment (soil, water, sediment, air) which if exceeded may prompt further risk assessment. Screening values afford a level of protection to organisms/ species and critical ecological functions (Fishwick, 2004).

This is followed by a quantitative biological and ecological assessment which measures the toxicity and bioaccumulation of a contaminant to ascertain if the ecological receptors are being harmed, and finally, by characterization of the causes and effects which will facilitate decision making (Ashton et al., 2008).

2.6 Human health risk assessment

Human exposure to the hazardous components of e-waste is most likely to occur through ingestion, inhalation and dermal contact. Informal e-waste recycling has direct and indirect effects on human health conditions. Direct impact could be occupational exposure through the dismantling and burning process and indirect impact through soil, air and water contamination as well as through food sources (Grant et al., 2013). Some forms of exposure include: drinking water which may contain contaminants leached from the soil to groundwater or discharged through surface runoff. In other instances, contaminants may vaporize from the groundwater and inhaled (Shayler et al., 2009). In dusty environments, it has been estimated that adults could inhale up to 100 mg of dust a day (Hawley, 1985). However, Song & Li (2014) and Zhang et al., (2016) argued that children and neonates are a particularly sensitive group in the informal recycling sector due to additional indirect exposure routes such as placental exposures and breastfeeding.

2.6.1 Exposure via ingestion

Exposure of contaminants through ingestion is argued to be the most important. Oral ingestion of soil may occur knowingly or unknowingly as soil easily adheres to clothing and body parts, and may be ingested as a result of hand to mouth activity. Children may accidentally ingest soil as part of their day-to-day activities (Shayler et al., 2009). Adults may also ingest soil or dust particles that adhere to objects, food, cigarettes, or their hands, ingestion of cosmetic products and food packaging amongst other items (Christopher et al., 2007). Subsequent to soil ingestion, digestion may lead to the release of contaminants from the soil to the body.

This process begins from the mouth with chewing and combination with saliva (Vander et al., 2001). The ingested substance then moves to the stomach through the oesophagus and is subjected to low pH as a result of hydrochloric acid secretion from the stomach cell wall. The acidic stomach environment (pH 1–4) allows for dissolution of labile mineral oxides, sulphides and carbonates, thus releasing metals. The process in the stomach can last from a few minutes up to about 3 hours with an average of an hour (Dean, 2007; Ng et al., 2010).

The partially digested food (chyme) moves from the stomach to the small intestine where bicarbonates in the pancreatin and bile neutralise the pH. The small intestine is composed of three parts: the duodenum, jejenum and iluem. From the duodenum, the chyme passes through the ileum and jejunum respectively. The chyme is retained in the duodenum between 30 minutes and 45 minutes (at pH 4-5.5), in the jejunum for about 2 hours (at pH 5.5-7.0) and in the ileum for about 5 hours (at pH 7.0-7.5) (Dean, 2007). The small intestine is the major site of absorption by an electrogenic process involving a proton gradient and also where final digestion occurs (Diamond et al., 1997; Ratnaike, 2003). While passing through the small intestine, the chyme is in contact with epithelial cells which are responsible for absorption (Hillgren et al., 1995). Following absorption, contaminants may be metabolized to other products or accumulated in certain organs or tissues. Through this process, metals can bring to bear their toxicity by imitating essential elements and attaching to their physiological binding sites. For instance, Cu, Cd and Ni are known to mimic Zn; Mn behaves like Fe and Pb interacts with enzymes involved in the haem synthesis pathways, and alters porphyrin profile (HERAG, 2007). On the other hand, some metals can produce free radicals during metabolism which can result in oxidative stress and mutagenesis (Ng et al., 2010). Materials not absorbed in the small intestine are further moved to the large intestine and colon, where water and electrolytes are absorbed and the waste materials are moved to the rectum and passed out.

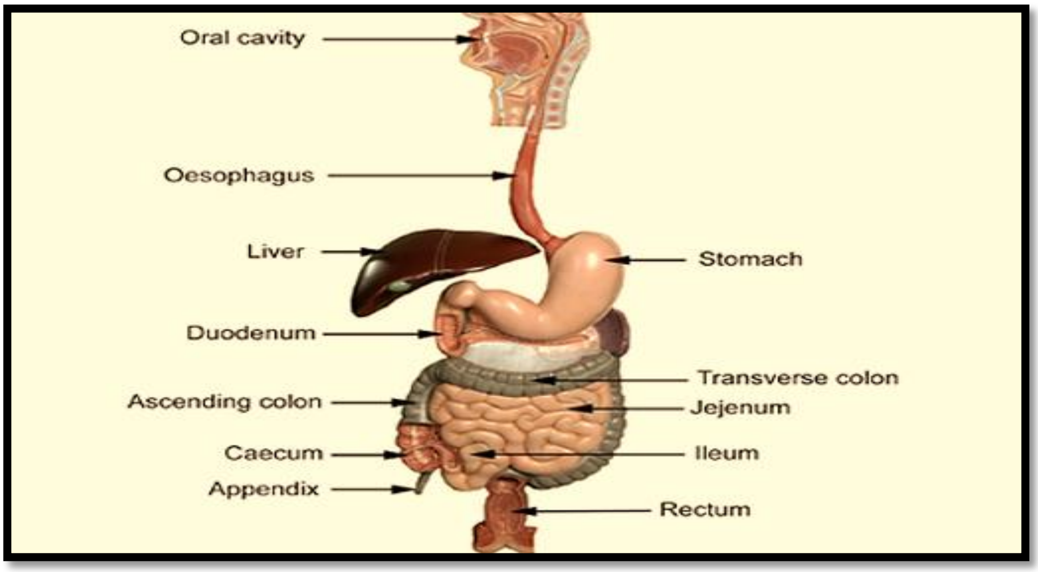
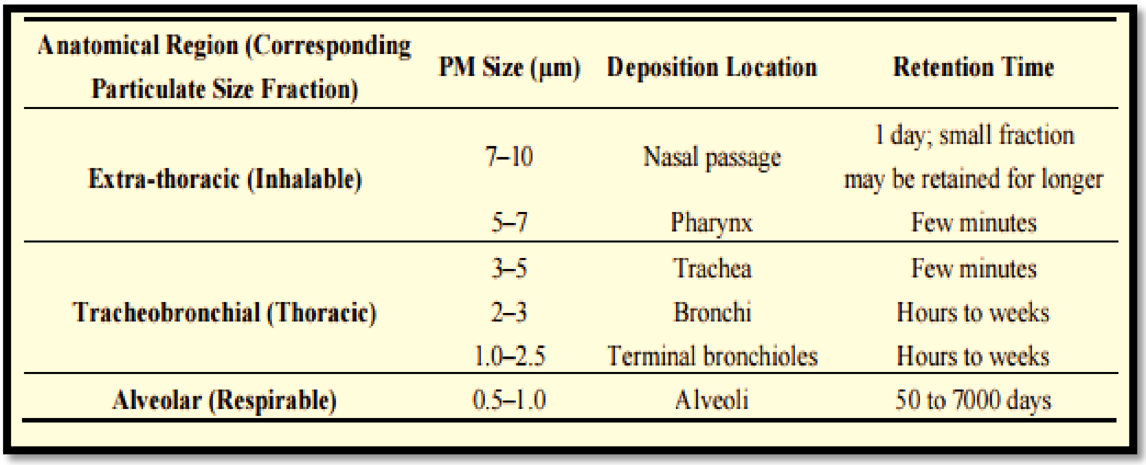


Figure 2.5: Anatomy of the human digestive system. Source: https://www.hud.ac.uk [Accessed 19th February, 2016]

2.6.2 Exposure via inhalation

Particulates get into the human respiratory tract through inhalation. These usually vary in source, composition and size. Physicochemical characteristics of particulates influence the distribution of airborne materials in the respiratory tract and the position of particulates settling in the respiratory tract determines the toxicological fate of inhaled compounds (Bakand et al., 2012).

The inhalation of particles is known to have negative health effects, depending on the nature of the material, exposure duration, and dose. The inhalation of some metal fumes (e.g. zinc, copper) may lead to metal fume fever, metal dusts (e.g. nickel, chromium) can lead to asthma while inhalation of other metallic dusts can cause pulmonary fibrosis and lung cancer (Ratnaike, 2003). During inhalation, particles mixed with the airstream get into the respiratory tract. A portion of the inhaled particles are retained while the remainder is exhaled. The retained particles are deposited in different areas of the respiratory tract according to size. Larger particles usually are settled in the nasopharyngeal region (5–30 µm) by the inertial impaction mechanism. Inertial impaction occurs when airflow changes direction and the particles close to the airway wall, follows their original direction instead of adjusting to the airflow. Smaller particles (1–5 µm) are settled in the tracheobronchial region, mainly due to sedimentation, which may be further absorbed or removed by mucociliary action (Siegmann et al., 1999). The tracheobronchial region is lined with cilia covered by a mucous layer. The cilia are in continuous and synchronized motion, which causes the mucous layer to have a continuous upward movement. Large and insoluble particles deposited on the ciliated epithelium are moved towards the epiglottis, and then swallowed or spat out within a relatively short time (WHO, 1999). The smaller the particle, the deeper it will travel into the respiratory tract; PM_{10} represents the upper limit for tracheobronchial and alveolar deposition in the human lung (Martin et al., 2014). The remaining particles with the smallest size distribution (< 1 µm) penetrate deeply into the alveolar region. The deeper the particles are deposited, the longer it takes to remove them from the lung and the higher the probability of adverse health effects (Martin et al., 2014; Siegmann et al., 1999; Bakand & Hayes, 2010).



Anatomical Region (Corresponding Particulate Size Fraction)	**PM Size (µm)**	**Deposition Location**	**Retention Time**
Extra-thoracic (Inhalable)	7–10	Nasal passage	1 day; small fraction may be retained for longer
	5–7	Pharynx	Few minutes
Tracheobronchial (Thoracic)	3–5	Trachea	Few minutes
	2–3	Bronchi	Hours to weeks
	1.0–2.5	Terminal bronchioles	Hours to weeks
Alveolar (Respirable)	0.5–1.0	Alveoli	50 to 7000 days

Figure 2.6: Deposition of particulate matter in the human respiratory system. Source: Martin, et al., 2014

The human respiratory tract consists of three regions, assisting the filtration effect. It is noteworthy that the regions of the respiratory system are named differently according to authors and sources as evident in Figures 2.5 & 2.6; however, the classification remains the same. The nasopharyngeal (extra-thoracic) consists of the nose, pharynx and larynx. The majority of particles deposited in this region are removed via a combination of sneezing and nose-blowing while the remainder is slowly cleared into the gastrointestinal tract (Smith et al., 2002). The tracheobronchial segment consists of the trachea, bronchi and terminal bronchioles. In this region, particles trapped in the mucus produced by the bronchial epithelial cells are typically cleared by mucociliary transport into the throat, and then expectorated or swallowed (Asgharian et al., 2001; Martin et al., 2014). Although the mucociliary transport is the principal clearance mechanism in the first 24 hours, the rate of clearance depends on the particle size, shape as well as the clearance velocity of the mucous. Other ways of clearance from the tracheobronchial region include coughing, absorption through airway epithelium into the blood or lymphatic system, and phagocytosis (Asgharian et al., 2001; Bakand et al., 2012). However, particles could be retained for longer in the respiratory tract depending on the clearance method as particle solubility plays a role in retention and clearance mechanism (Martin et al., 2014). In the pulmonary region, particles (≤1 μm) may be phagocytosed and cleared by alveolar macrophages, and either absorbed into regional lymph nodes via lymphatic vessels or transported into the ciliated airways and cleared via mucociliary transport (Asgharian et al., 2001; Martin et al., 2014). The process may take a long time to complete. The epithelial lining fluids found within the nasopharyngeal and tracheobronchial region form an interface between the respiratory epithelial cells and the outer environment protecting the pulmonary region (Cross et al., 1994). Dust and particulate matter inhalation from different sources pose potential health risks to man as studies have shown a correlation between inhaled particulate matter and adverse health effects (Shab et al., 2012).

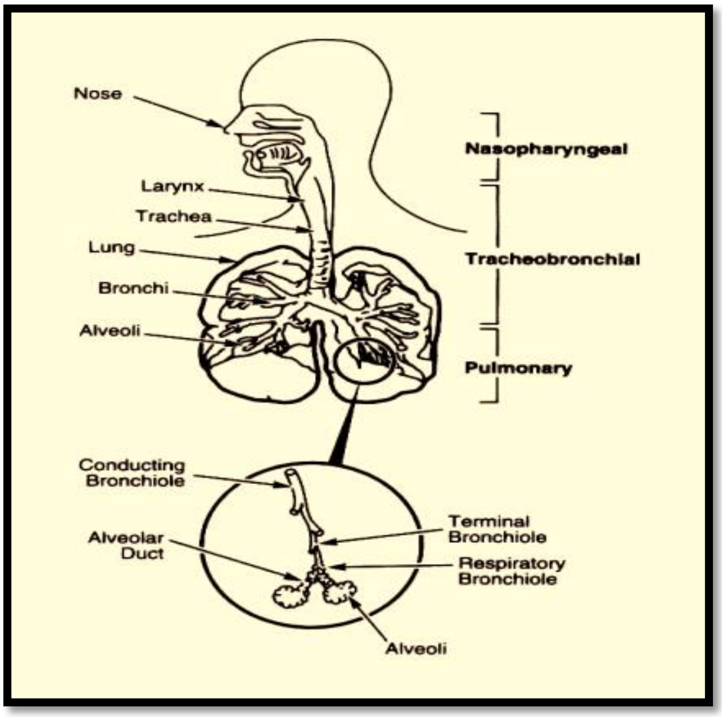


Figure 2.7: : Anatomical regions of the respiratory system. Source: Caponecchia, 2014

2.6.3 Exposure via dermal contact

Exposure through dermal contact is of great importance in the workplace as the skin may be exposed to hazardous substances. The skin acts as a physical barrier, preventing loss of body fluids and penetration of chemical substances. It also controls body temperature which is regulated by sweating as well as provides defence and repairs, wound healing, and cutaneous metabolism. Structurally, it is divided into three layers: the epidermis, the dermis and the hypodermis. The outer layer, which contains cells known as keratinocytes, covers the entire outside of the body and connective tissues. It provides protection against physical trauma, radiation and xenobiotics. The dermis is made up of fibrous protein mainly collagen and elastin which provides the skin flexibility. The dermis is home to the blood vessels, sensory nerves and lymphatic vessels. The hypodermis is similar to the dermis but consists of larger blood vessels and nerves, fat stores, the hair follicles, sweat glands, sebaceous glands and their associated erector muscles. The hypodermis provides lubrication, insulation and energy metabolism (Wiechers, 1989; Schneider et al., 2000; Berard et al., 2003; Hoet et al., 2004; WHO, 2006; Du Plessis et al., 2013; Poland et al., 2013).

The skin is permeable to many substances, with dermal absorption dependent on the physiological condition of the skin, hydration, density of hair follicles and sebaceous glands, thickness at the site of exposure, physiochemical properties of the substance, chemical exposure concentration and duration of exposure (Wiechers, 1989; Anderson & Meade, 2014). When a contaminant is in contact with the epidermis, interactions can occur with viable keratinocytes and trigger an inflammatory reaction or interaction with Langerhans cells from the immune system that initiate an allergic reaction such as contact dermatitis. However, when a contaminant penetrates the epidermis and becomes accessible to the dermis and potentially accessible to the systemic circulatory and lymphatic systems, the effects can be observed in distal organs within the body either by translocation through the circulatory system or by triggering systemic reactions. These can potentially lead to a wide range of toxicological effects and disease (Poland et al., 2013).

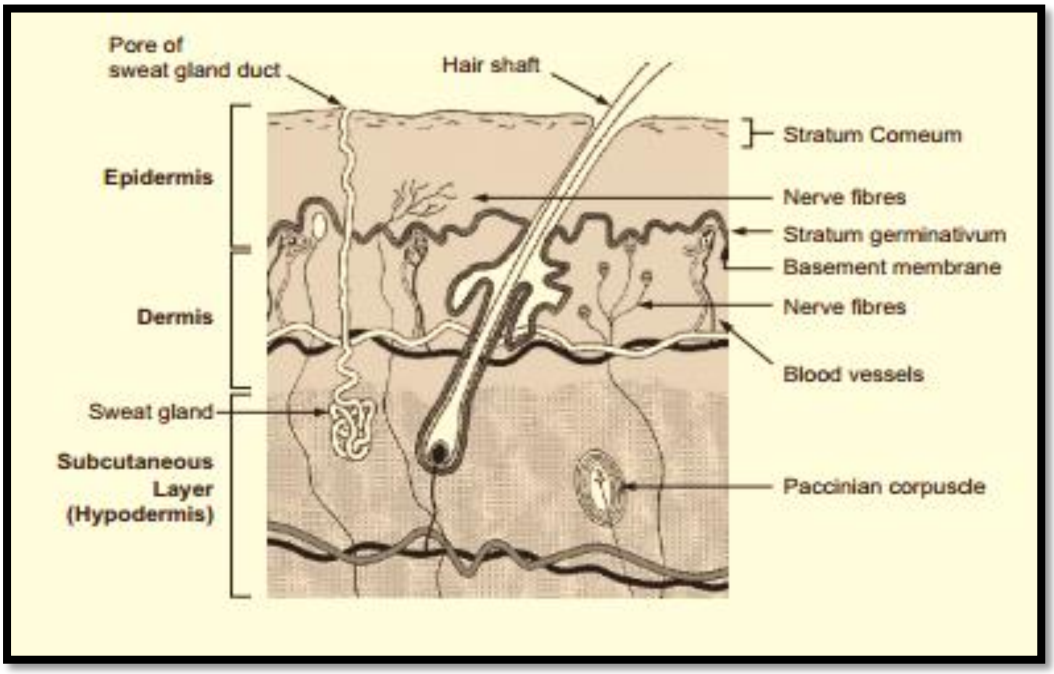


Figure 2.8: Anatomical regions of the skin. Source: WHO, 2006

2.7 Environmental risk assessment methods and tools

Sections 2.1 to 2.6 provide a critical review on the source, constituents, impacts and exposure routes and pathways, however the assessment of the reported impacts have not been carried out. Hence, this section seeks to critically explore the assessment tools and models used in the assessment of human health and ecological risk from contaminated sites.

Over the years, there has been an increase in the use of a risk-based approach (ERA) to manage contaminated land which has focused on the identification and mitigation of unacceptable risk to human health and the environment. ERA deals with assessment and management of effects caused by anthropogenic activities as most routes by which the ecosystem is polluted are related to human activities (Manuilova, 2003). Based on this fact, approaches for assessing risks from contaminated sites with the ability to identify the links between the source, pathways and receptors were developed. Contaminated sites can be assessed either by comparing the measured levels of contamination with established guideline values or by applying site-specific criteria where exposure and effect on receptors can be estimated for specific exposure scenarios. Estimating and utilizing the potential exposure and toxicity data generated during an environmental assessment is quite difficult as both components are needed to evaluate the potential adverse effect. Hence, models with a variety of mathematical equations have been used to estimate the potential risk in different environmental media (Pastorok et al., 2003).

A number of risk assessment tools exist, which could be human exposure, ecotoxicological or transport models. These include CLR 11, CLEA, CSOIL, CalTOX, RBCA, which aim to quantify the exposure of site contaminants and the transfer to humans, using bioassays and microcosms to establish the impact in the ecosystem which usually involves extrapolation of bioassay results and application of safety factors as in the case of the ecotoxicological model (Ferguson et al., 1998). The suitability of a method or model for a risk assessment depends on the desired outcome, contaminant of interest, types of receptors and available input data.

2.7.1 CLR 11

The model procedure for management of contaminated land, the contaminated land risk model (CLR 11) is a framework that focuses on individual contaminated sites for risk assessment. It was developed to provide the technical structure for applying a risk process when dealing with contaminated lands. It reflects a three tiered approach for assessing environmental risk as developed and described in the DETR, Environment Agency and Institute for Environment and Health publication (Environment Agency, 2004). Tier 1 involves hazard identification, preliminary risk screening and the development of a site conceptual model with the aid of site reconnaissance and desk study; Tier 2 is a generic quantitative risk assessment which involves the identification of the consequences of the hazard indicated in Tier 1; and Tier 3 involves the use of site specific risk information that correspond to relevant criteria in relation to the contamination for deciding if the risk is acceptable or not. The generic assessment criteria are derived using largely generic assumptions about the characteristics and behaviour of sources, pathways and receptors and these assumptions are conservative in a defined range of conditions.

2.7.2 CLEA

The Contaminated Land Exposure Assessment (CLEA) model is a frame work used to assess human health risks from contaminated sites and is modelled for three scenarios namely: industrial/commercial, allotment and residential. CLEA was developed by the UK government and uses generic assumptions about the fate and transport of contaminants in the environment and a generic conceptual model for site conditions and human behaviour to estimate child and adult exposures to soil contaminants for those potentially living and working on contaminated sites over a long period of time. It is a deterministic tool that can be used to derive assessment criteria for human health and allows contaminant concentrations of the exposure to be compared with health criteria values to assess risk posed (Environment Agency, 2009c).

2.7.3 CSOIL 2000

This model, developed by the Dutch National Institute for Public Health and the Environment (RIVM) Netherlands, is a very similar tool to CLEA but has more exposure routes, calculates the risks posed to humans when in contact with contaminated soil. The model considers exposure through soil ingestion, crop consumption, inhalation of indoor air, soil particles, and inhalation of air during showering, groundwater consumption and dermal absorption. It calculates the maximum concentration of a contaminant in the soil at which it is still safe for humans by determining the human toxicological risk limit and can be used to derive intervention values (Brand et al., 2007).

2.7.4 RBCA

The Risk Based Corrective Action was designed to meet the requirements of the ASTM (E-2081) standard guide for Risk Based Corrective Action for Tier 1 and Tier 2 evaluations for chemical release sites in addition to traditional risk assessment calculations developed in the United States. It combines contaminant transport models and risk assessment tools to calculate baseline risk levels and derive risk-based clean-up standards for a full array of soil, groundwater, surface water, and air exposure pathways. Exposures are modelled for residential, commercial, and user-defined receptors from groundwater, surface water, surface soil, outdoor air and indoor air, taking account of groundwater ingestion, surface water recreational contact and fish consumption, combined direct contact with soils (incidental ingestion, dermal absorption) and outdoor and indoor inhalation of vapours from soil or groundwater sources (Searl, 2012).

Environmental risk assessments are important in determining what action should be carried out at contaminated sites. In an attempt to minimize the uncertainties, the CLEA, CSOIL and RBCA models encourage the use of site specific parameters. However, their being deterministic models, as with most risk assessment tools, implies that single estimates of each parameter entered into the model generate point estimations of the exposure. This can overestimate the risk as the worst case scenarios parameters in the model accumulate. Also, default risk assessment methods frequently overestimate exposure by assuming that a chemical will be equally bioavailable in all media, irrespective of the properties of the environmental media or the chemical form of the contaminant. To this effect, section 2.8 examines the concept of bioavailability in risk assessments.

2.8 Bioavailability and risk assessment

In order to characterize a risk, a dose-response assessment is carried out to determine what is taken up from the environmental media; the actual absorption from the environmental media is often lower than the measured absorption in laboratory studies. This led to the introduction of bioavailability studies to determine absorption as a result of the exposure.

Bioavailability as defined by ISO (2005) is the degree to which chemicals present in the soil may be absorbed or metabolised by man or ecological receptors or are available for interaction with biological systems. For environmental risk assessments involving soil and sediment, bioavailability is the extent to which a substance can desorb, dissolve, or dissociate from the environmental medium in which it occurs to become available for absorption (Schoof, 2003). In pharmacology, it is the fraction of the chemical that can be absorbed by the body through the gastrointestinal system, the pulmonary system and the skin.

2.8.1 Sequential extraction procedure: a method of evaluating bioavailability in risk assessment

Bioavailability can either be determined by models that quantify scenarios or by chemical extractions. Chemical extraction is a straightforward method for determining the potential bioavailability of a contaminant, which involves leaching contaminated soil with a solution for a period of time and then analysing the concentration of contaminants in the solution such extractions are known as sequential extractions.

The theory behind the sequential extraction process is that the most mobile metals are removed in the first fraction and the process continues in order of decreasing of mobility till the end of the chemical process. The process facilitates fractionation, which is often referred to as exchangeable, weakly absorbed, hydrous-oxide bound, organic bound, and residual material components (Maiz et al., 2000; Zimmerman & Weindorf, 2010). A number of procedures have been established; the Tessier procedure (Tessier et al., 1979), the Community Bureau of Reference (BCR) procedure (Rauret et al., 1999) and the short extraction procedure by Maiz (Maiz et al., 2000). Irrespective of the procedure used, sequential extractions are an effective tool to determine the affinity of heavy metal to the soil and study metal distributions in various soil fractions (Silveira et al., 2006; Arenas-Lago et al., 2014). It is an important tool for predicting the potential effects of the contaminants, as contaminants that are more bioavailable are readily leached out and as such, a useful tool in risk assessment (Hodson et al., 2011).

2.8.2 Bioaccessibility testing a tool in risk assessment

Charlesworth et al., (2011) reported that toxicity values used in human health risk assessments are usually expressed in terms of absorbed doses and are often derived from assays that employ soluble salts or other easily-available chemical forms of trace elements. As a result, human health risk assessments assume that the concentration used to quantify the exposure represents the total amount available for absorption (i.e. bioavailable) in the human system. On the other hand, studies using animals turned out to be complicated, expensive, time consuming, and have raised a lot ethical issues thus stalling the evaluation of bioavailability.

In order to accurately assess the risk posed to human health by exposure to environmental contaminants, bioaccessibility testing was developed. This is an emerging testing tool which aims at eliminating differences that exist during extrapolation from test organisms applied in the process of obtaining health criteria values for humans by mimicking the human exposure routes (Nathanail, 2005). Bioaccessibility is used to describe the fractional dissolution of a metal in soil from *in vitro* study. It is the proportion of total intake of contaminant in the soil that is extracted in the human system and is available for absorption measured as a percentage (Wragg et al., 2011; Matos et al., 2015). The bioaccessible fraction is usually taken as a substitute and predictive proportion of bioavailability since the bioavailable fraction is the proportion of the bioaccessible fraction which can be absorbed and taken up by the blood system and circulated to other organs and can only be measured *in vivo* (Ruby et al., 1999).

The oral bioaccessibility mimics the chemical changes and movement in the human digestive system, simulating the leaching of the contaminant to determine the total concentration available for absorption in the intestine using simulated digestive fluids. Several *in vitro* models have been developed and approved; these include the physiologically based extraction test (PBET), the simplified bioaccessibility test (SBET) and the Unified BARGE method (UBM) that have been validated for As, Cd and Pb. However, the UBM stands out as it has been validated against a swine model for relative bioavailability (Ruby et al., 1996; Drexler & Brattin, 2007; Wragg et al., 2011).

Since inhalation is potentially an important exposure pathway, a number of *in vitro* measures using simulated lung fluid have been developed that are simple and practical. The *in vitro* methods are used to simulate the physiological condition in human lungs as they mimic the process after particulate matter enters the lungs (Li et al., 2016). Gamble's solution is one of the commonly used simulated lung fluids in the *in vitro* assay. It mimics the surfactant fluids released by Type II alveolar cells and acts to reduce the surface tension of the water in the lungs, facilitating gas exchange (Daniels & Orgeig, 2003). It was first developed in 1942 as an *in vitro* method for determining compound toxicity in the lungs and has been validated for radioactive compounds using *in vivo* tests (Damon et al., 1984). However, in recent times, the solution has undergone modification by the addition of organic acids, proteins and surfactants a number of researchers to enhance bioaccessibility estimations (Takaya et al., 2006; Wragg & Klinck, 2007; Gray et al., 2010; Boisa et al., 2014).

Although there are a number of *in vitro* bioacessibility methods and studies show substantial differences in quantitative comparison between the methods (Oomen, et al., 2002; Van de Wiele, et al., 2007), the aim of the *in vitro* bioaccessibility testing in demonstrating the concept of potential bioavailability is achieved. The inclusion of bioaccessibility in risk assessment produces data that can be used in adjusting estimates of the risk from the contaminants in the contaminated site. Hence, bioavailability and bioaccessibility are pivotal in the risk assessment process as they assess the proportion of a contaminant available for uptake by organisms and the potential ability of the contaminant to cause harm. It is also useful in the establishment of management goals that would be protective of the human health and the environment.

2.9 Risk assessment in informal E-waste recycling sites

Over the last decade, a large body of knowledge has emerged on the risk posed to the environment in e-waste recycling sites. Several studies have focused on the chemical composition and concentration of contaminants (metals, PBDEs, PCDD/Fs, PAHs) in soil and dust in these sites (Brigden et al., 2008; Otsuka et al., 2012; Amfo-Otu et al., 2013; Ofudje et al., 2015). Others compared the level of contamination with established regulatory benchmarks and relatively uncontaminated sites around the e-waste site to establish the risk (Leung et al., 2008, 2015; Ha et al., 2009; Pradhan & Kumar, 2014) whilst several studies evaluate the risk using pollution indices (Wang et al., 2012; Tue et al., 2013; Zhao et al., 2015; Kyere et al., 2016).

Furthermore, a number of health risk assessment studies using risk models to examine different exposure pathways and routes have been carried out on informal recycling sites report very high risk posed by the contaminants (metals, PBDEs, PCDD/Fs, PAHs) to the exposed populace (Man et al., 2011, 2015; Adaramodu et al., 2012; Zheng, et al., 2016; Huang, et al., 2016). A few studies using risk models assessed the risk posed to populace nearby an informal e-waste recycling site using soil samples and vegetation (Wang, et al., 2011, 2012). The results and conclusion drawn from all the above mentioned studies suggest that the informal recycling activities pose a high risk to all aspects of the environment.

Although the listed studies did not introduce the concept of bioavailability and bioaccessibility as discussed in section 2.8, this does not invalidate their observations, the potential to identify the contaminants of concern and the different pathways and routes of exposure. Indeed, bioavailability and bioaccessibility studies are being carried out in different aspect of urban contamination (Wragg & Cave, 2003; Farmer et al., 2011; Luo et al., 2012; Pelfrêne et al., 2012; Denys et al., 2012; Palumbo-Roe et al., 2013; Das et al., 2013; Izquierdo et al., 2015; Xia et al., 2016); however, there are very few bioaccessibility studies carried out on e-waste recycling sites (Tao et al., 2015).

The subsequent chapters in this thesis will address the risk in relation to bioaccessibility, putting site specific uptake values and the matrix type into consideration thereby addressing the knowledge gap identified. Farmer et al., (2011) and Walraven et al., (2015) reported that although evidences suggested bioaccessibility is dependent on the soil matrix, type and composition, relatively little research has been carried out on these factors. The following chapter focuses on the phases and analytical process that will be used to address the aims and objectives of this research and address a number of issues highlighted in this chapter.

CHAPTER THREE

3 Methodology

3.1 Scheme of work for study

Environmental risk assessment (ERA) is usually a complex process with many variables to put into consideration; thus, using a stepwise approach becomes useful in overcoming the complexity of an ERA. Each step could lead to a decision to either to proceed or to stop (Mesman et al., 2006). In view of this fact, this study will be carried out in phases to ensure the data gathered at every point is relevant to proceed in the ERA (Fig 3.1)

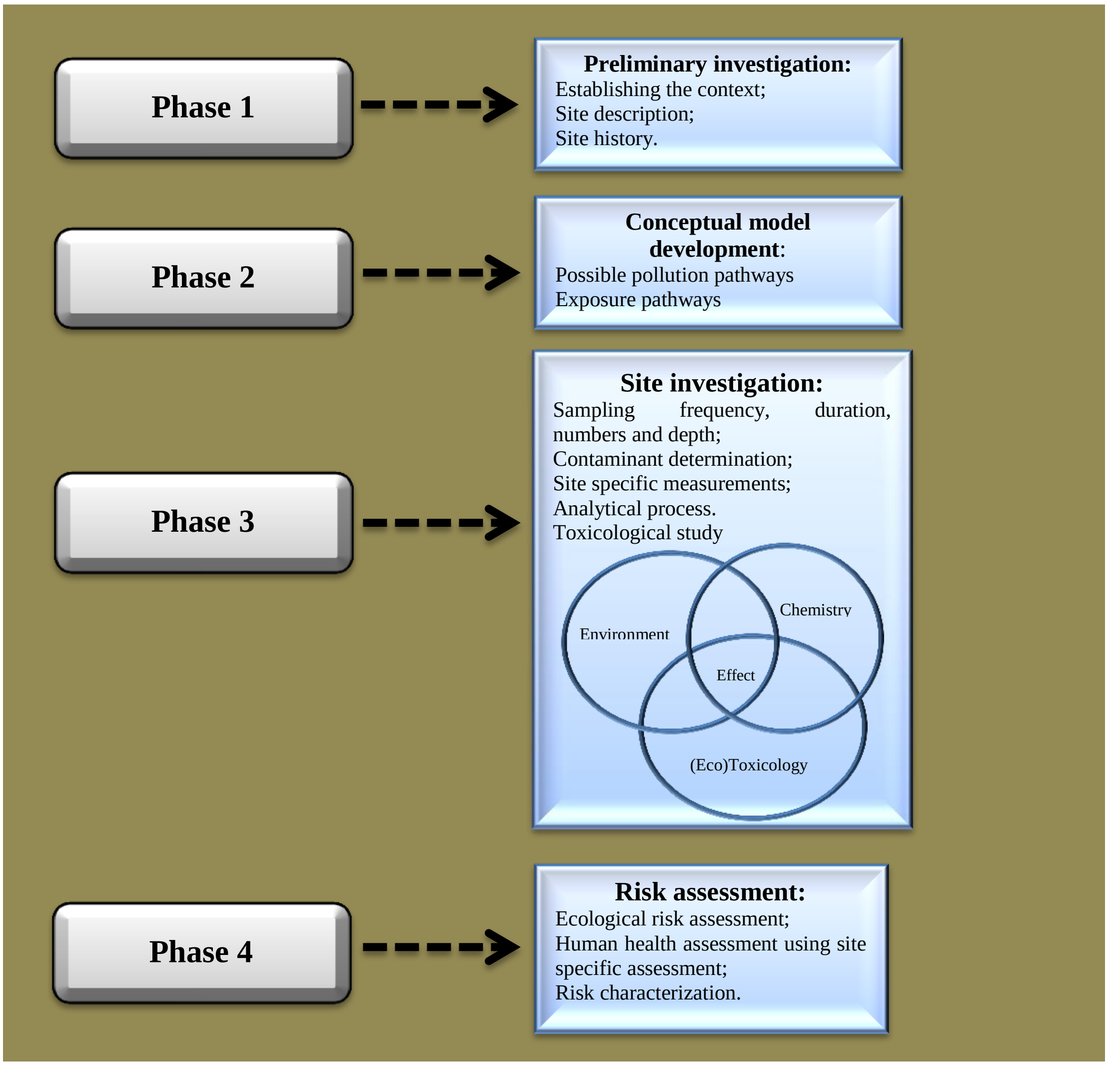


Figure 3.1: Work flow of study

Phase 1 focuses on defining the scope, aim and objectives of the research, obtaining an understanding of the site and characterizing the site. Phase 2 is the conceptual model development to determine whether potential source-pathway-receptor relationship can be established in the study site. The information gathered from phase 2 will lead to phase 3 which is an in-depth site investigation. In phase 3, the environmental medium to sample, the sampling strategy and frequency is determined. Site specific properties will be put into consideration and the analytical processes (such as extraction techniques and toxicological analysis to establish the concentration of the contaminants) and the effects of the contaminant concentration on receptors will be put in place. According to Rutgers et al., (2002), Mesman et al., (2006) and Niemeyer et al., (2015), in order to provide a very strong evidence of effects of the ERA, site-specific chemical and toxicological assessment should be integrated to reduce the uncertainty. The multidisciplinary approach of the three different fields as indicated in Fig 3.1 will attempt to establish coherent expression of assessment result, to support decision making. The environment is important for field observation of the contamination, chemistry is used to determine the concentration of contaminants in the environment (totals, potential bioavailable), and the toxicology uses bioassay to establish the toxicity of the environmental samples. Finally, in phase 4 the risk posed to exposed receptors will be characterized and evaluated.

3.2 Study area

Alaba International Market was founded in 1978. Located in Ojo Local Government Area of Lagos State, it is the largest market for used and new electronics and electrical equipment in West Africa. The market features over 2,500 shops refurbishing and selling used electrical and electronic equipment. A lot of waste reaches the market as a result of refurbishment of electronics, disposal of electronic components that cannot be refurbished. Within the market, there is an e-waste dismantling and recycling site known as Alaba rago. The study site was Alaba rago, Alaba international market situated on latitude 06^{0}27.731'N and longitude 03^{0}11.492'E. The control area, Lagos State University (LASU) is located on latitude 06^{0}27.770'N and longitude 03^{0}12.145'E. The control site is approximately 500m away from the study site; separated by a major road and has the similar geology as the study site (Fig 3.2).

Figure 3.2: Study area with a clear indication of the sampling locations. Source: Google Earth. Accessed 16/04/2017

This particular site has been in existence and actively recycling e-waste since 2010 after the previous site within the market used for informal recycling was built upon. A chain of processes occur before the e-waste is recycled. There are the scavengers otherwise known as collectors, the sorters, the dismantlers then the recyclers. The activities which occur at the site involve manual dismantling of electronics to isolate metals such as copper, aluminium and other precious metals. Also, there is open burning of some electronic components, wires and cables. These activities are carried out by young and adult men between 7 and 35 years old. They carry out these processes using rudimentary methods without any personal protective equipment (Fig 3.3). The majority of people engaged in the e-waste business ranging from the waste scavengers, the sorters, the waste dismantlers to the recyclers are from northern Nigeria.

Figure 3.3: Cross section of activities carried out in the e-waste recycling site

3.3 Exposure pathway

The exposure pathway is the route that an environmental contaminant takes from its source to exposed population, forming a link between the contamination and the potentially exposed population. Risk assessments involve investigating the different components in the link by projecting concentrations along the pathway between sources and receptors. An exposure pathway is complete when a contaminant moves from its source to the exposed populace directly or indirectly (Benjamin & Belluck, 2001; Simon, 2014). Fig 3.4 describes a conceptual model of a typical informal e-waste recycling site. Fig 3.5 describes the possible pollution pathways in the study site; due to some site limitations, all the pathways could not be explored. An unplanned resistance from workers on the site due to some superstitious beliefs as well as poor site security hindered sampling process of different environmental media. According to WHO, (2013), the presence of pollutants in different environmental media, their diffusion between media and diffusion by different exposure pathways vary greatly, as such, soil was decided as the environmental media of study. Soil samples were collected from the recycling and dismantling site within the study site. Fig 3.6 outlines the exposure pathway used in the evaluation of this study.

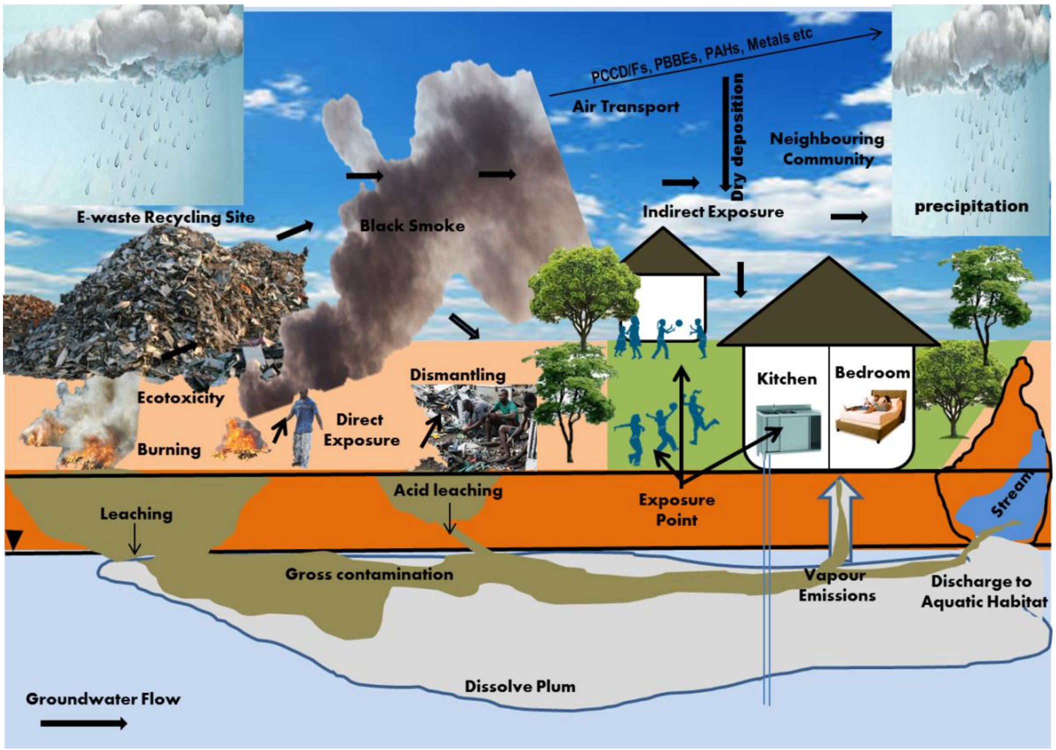


Figure 3.4: Conceptual model of a typical e-waste recycling site.

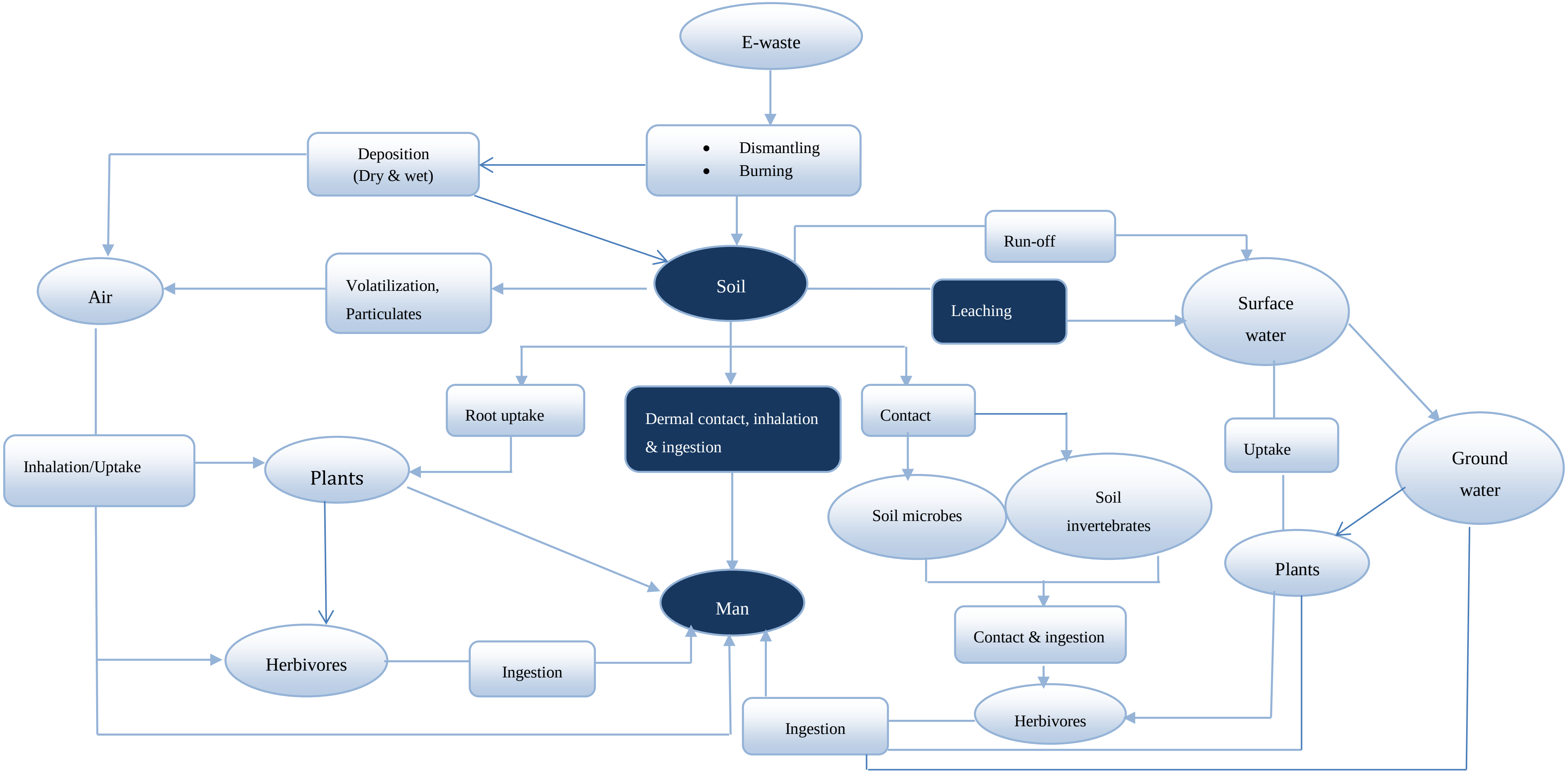


Figure 3.5: Site conceptual model (possible pollution pathway)

*highlighted pathways are examined in this study

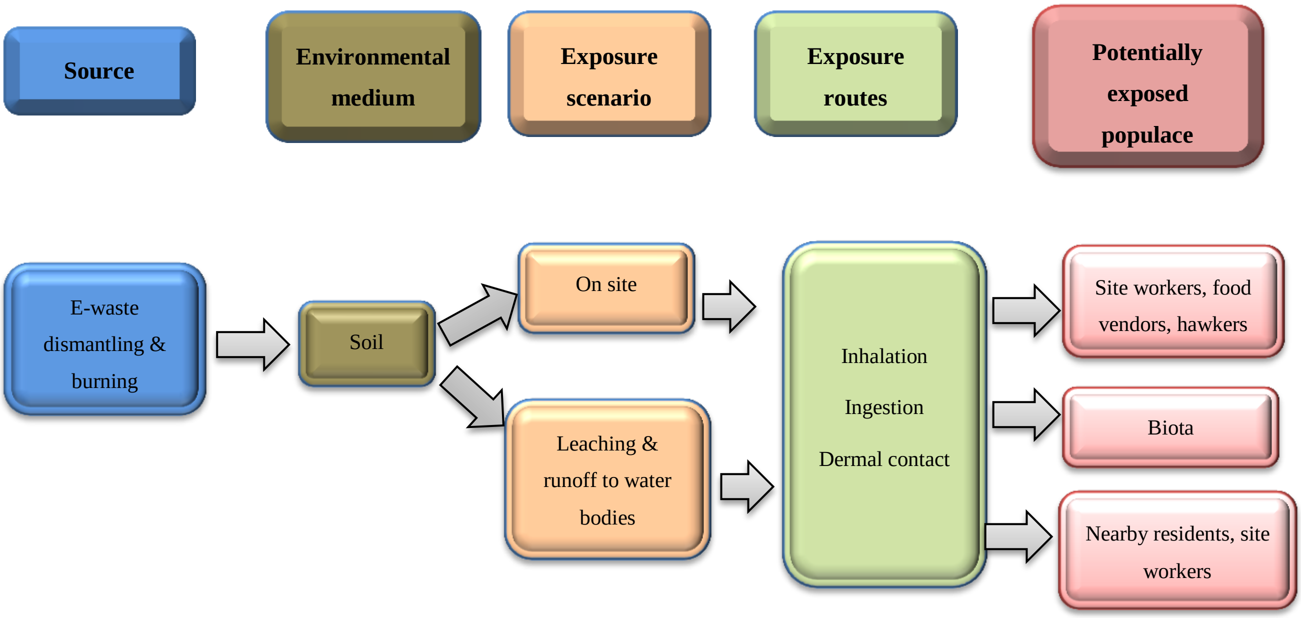


Figure 3.6: Exposure pathway evaluation of study

3.4 Sample collection and preparation

Soil samples were collected both in the wet (rainy) season and dry season in the year 2013. The wet season lasts from April till November with a brief dry spell in August known as the August break and the dry season starts from December to March. The site on which the activities occur measures approximately 4500 square meters. The site was further divided into two unequal parts by the site workers; with the smaller area for dismantling and the larger was used for burning to recover materials. A start point was specifically chosen and marked for future reference, and the systematic square grid sampling strategy was adopted for the recycling portion. The area was partitioned into equal sub areas and an equal distance of 10 metres was measured at intervals between each sampling location. Approximately 21 points were sampled at the recycling section with depths up to 30 cm in the ground at each point. Surface soil (0-5cm) samples only were collected randomly at the dismantling section of the site since digging the soil generated protest from the site workers, which hindered collection and 10 points were sampled in the dismantling section. A total of seventy three sub-samples from each season were collected, air dried and stored in the refrigerator.

Soil samples were collected for pilot studies on 14th August 2012. For the main study, samples collected were collected 13th and 14th March, 2013 and 21st and 22nd, October, 2013 representing the wet and dry season respectively.

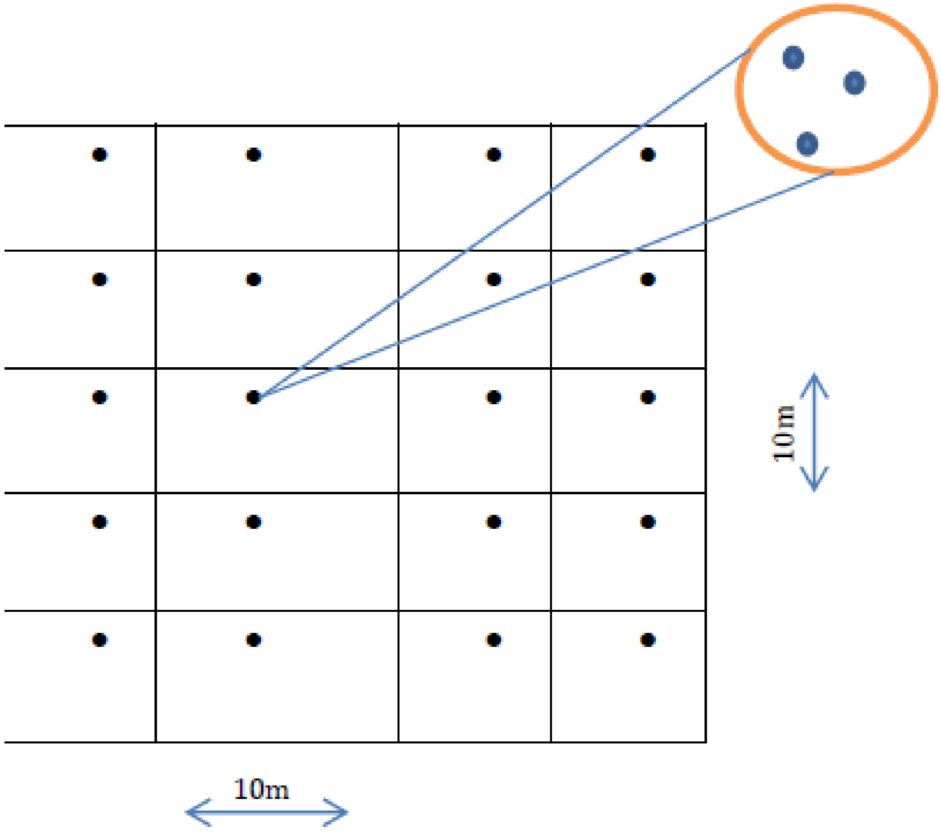


Figure 3.7: An illustration of the sampling strategy used in the recycling portion of the study site.

Soil samples were collected from the topsoil to the depth of 30cm with the aid of a soil auger (which was used to till the ground) and a narrow stainless steel trowel (used to transfer the soil from the auger) into labelled sampling/storage bags. The labelling was done according to the sampling points and depth from which the soil was collected. For example; $A_{0\text{-}10cm}$, $A_{10\text{-}20cm}$, $A_{20\text{-}30cm}$, $B_{0\text{-}10cm}$, $B_{10\text{-}20cm}$, $B_{20\text{-}30cm}$. The soil samples were then transported to the laboratory and air dried at room temperature for 5 days to reduce soil moisture before sieving. The samples were sieved using a standard test sieve with aperture size of 1mm -2mm. Sterilized sample bags were used in the packaging and the samples were stored in the refrigerator at 4°C pending further analysis.

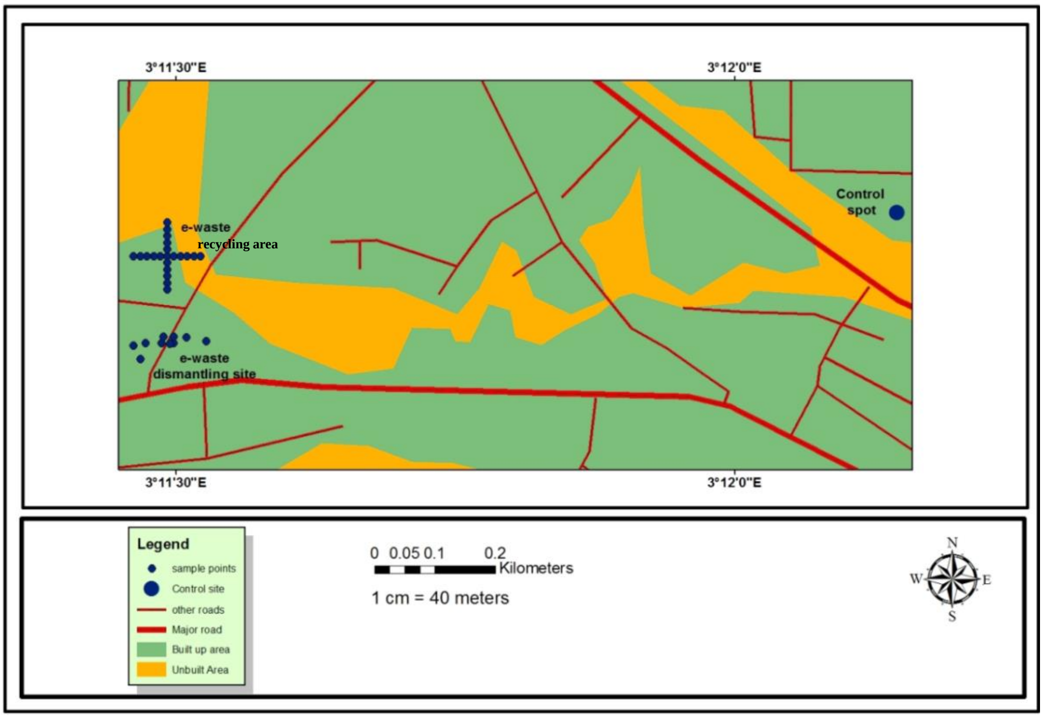


Figure 3.8: Sampling spots in the study site. Generated using ArcGIS 9.2

3.4.1 Data quality

All field sampling, field processing, and laboratory sample processing activities were carefully carried out. The soil auger was soaked in 10% HNO_3 overnight prior to sample collection; the trowel used in scooping the soil was cleaned with a brush between each replicate sample and cleaned thoroughly with wet wipes between each new sample point. Samples were transported to the laboratory following recommended protocols and proper laboratory principles were adopted and followed. The use of sterilized equipment was encouraged to avoid cross contamination; all glassware used was washed with alkaline laboratory detergent (Fisher Scientific), soaked overnight in 10% HNO_3 solution, rinsed with deionised water thrice and allowed to air dry.

3.5 Analytical process

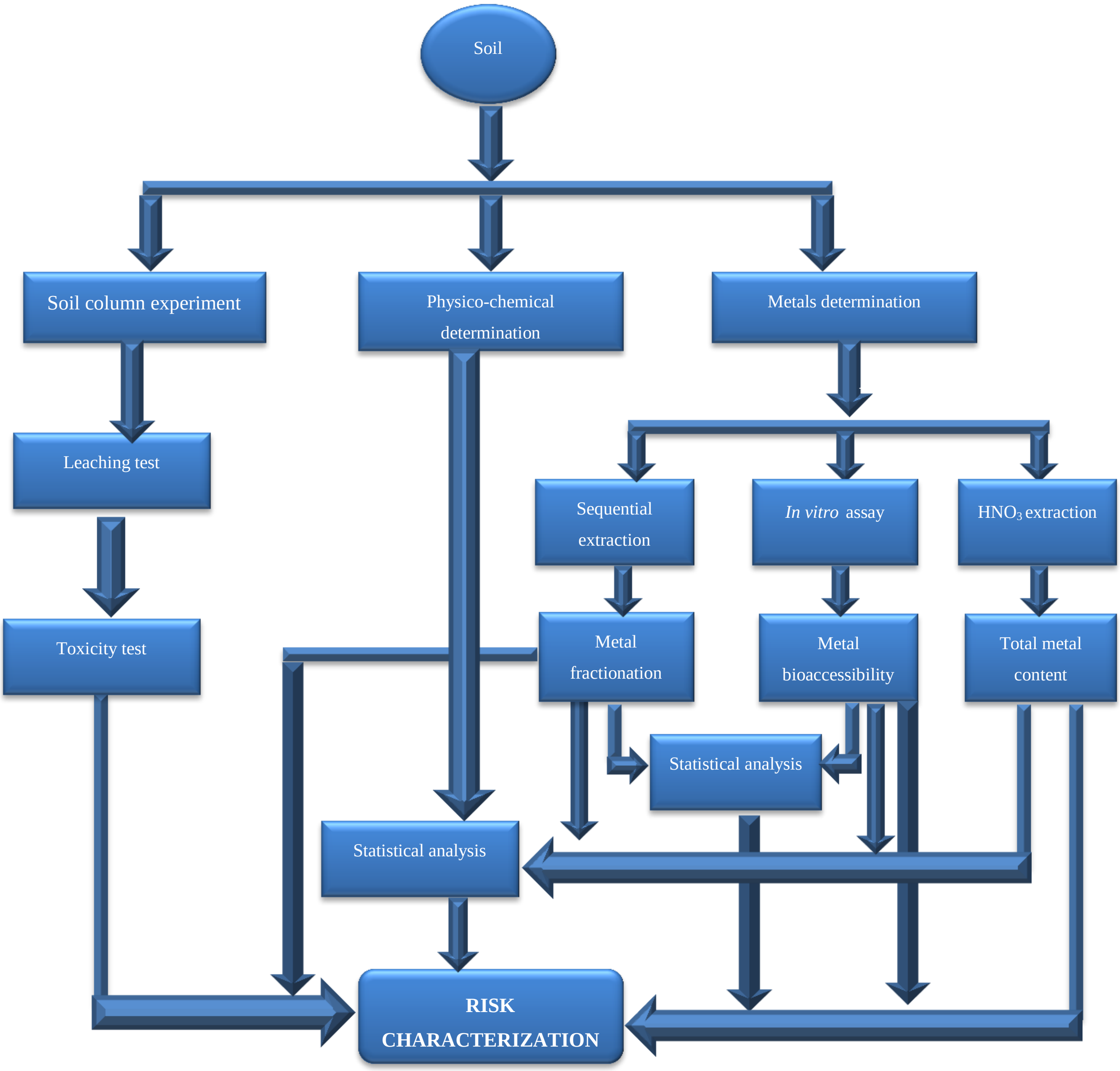


Figure 3.9: Flow diagram of analytical process

3.5.1 Physico-chemical assessment of the soil

Triplicate measurements of individual samples were carried out for all analysis to ascertain and measure variation in the experiment, increase analytical precision and detect possible outliers.

3.5.1.1 Soil texture

Soil samples large enough to make into individual balls were collected and ultra-pure deionized water 18.2MΩ from a Milli-Q analytical reagent grade water purification system (Millipore) was added drop by drop till the soil got to a sticky point. The step by step instruction on the ‘key for finger assessment of soil texture worksheet was followed to determine the soil texture (Thien, 1979).

3.5.1.2 pH

Sieved soil sample (1g) was placed in a beaker and mixed with ultra-pure deionized water 18.2MΩ from a Milli-Q analytical reagent grade water purification system (Millipore) in the ratio 1:10. The mixture was placed on a mechanical shaker for twenty minutes adopting the USEPA method 9045D (2004). Jenway 3505 pH meter was calibrated with buffer solution at pH 7 and pH 10. The calibrated pH electrode was placed in the suspension and the pH readings were taken immediately.

3.5.1.3 Organic matter content (OMC)

This was determined by Loss on Ignition (LOI) (ASTM, 1993). Firstly, the moisture content was determined; soil (5g) was heated to 105°C for 24 h in a muffle furnace then cooled in the desiccators and weighed. The samples were then heated to 440°C for 6 h or (till completely ashed), allowed to cool in desiccators and weighed. The percentage organic matter content was then calculated as:

% Moisture content= $\frac{\mathbf{A-B}}{\mathbf{A}} * \mathbf{100}$ --------------------Equation 3.1

% Ash content= $\frac{\mathbf{C*100}}{\mathbf{B}}$ ---------------------------------Equation 3.2

% Organic matter content = 100- % Ash content-----------Equation 3.3

Where; A= pre ignition weight (g), B= post ignition weight (g), C= weight of ash (g).

3.5.1.4 Cation exchange capacity (CEC)

The method used was adopted from Chapman (1965) and the USEPA method 9081. 5g of air dried soil was measured into 50 ml centrifuge tubes and 1M sodium acetate (30 ml) was added. The samples were agitated in an ultrasonic bath for 10 mins then centrifuged at 1500 *x g*[1] for 5 minutes. The resultant supernatant was decanted and discarded, and then 30 ml of ethanol was added to the samples, agitated, centrifuged and then decanted again. This procedure was carried out twice to ensure the removal of excess sodium acetate. The washed soil samples was extracted thrice using 20 ml portions of ammonium acetate using the ultrasonic bath and centrifuged each time. The supernatant from each extraction was filtered and collected in a 100 ml volumetric flask then made up to the mark.

Data analysis and calculation

Sample concentration = $\frac{\mathbf{C*D*V}}{\mathbf{S}}/\mathbf{R}$ ---------------Equation 3.4

Where: C= concentration in extract (mg l^{-1}), V = volume of extract (ml), D = dilution factor, S = dry weight of the sample (mg), R = relative atomic mass of element (Na=22.99, Mg=24.3, K=39.1, Ca= 40)

Cation exchange capacity ($\mathrm{cmol_c Kg^{-1}}$) = Na+Mg+K+Ca--------------Equation 3.5

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[1] Where g is the relative centrifugal force. It depends on the revolutions per minute (RPM) and radius of the rotor.

3.5.2 Chemical parameters assessment of the soil

Triplicate measurements of individual samples were carried out for all analysis.

3.5.2.1 Heavy metals determination

3.5.2.1.1 Total heavy metals content

The total metal concentration was determined according to the EPA 3051a protocol (US EPA, 2007). 0.5g of dried soil sample was weighed in Teflon microwave tubes, 20 ml of 70% nitric acid (HNO_3) added, tubes were placed microwave apparatus (CEM, Model MARS Xpress) at 175°C for 10 min. Cooled samples were centrifuged for 5 min at 1500 *x g*, filtered using Whatman's No 42 into 50 ml volumetric flasks and the extract was made up to the total volume of 50 ml with deionised water, placed in the fridge at 4 °C till ready for analysis.

ICP-OES analysis

A Thermos ICP-OES (iCAP 1600) was used for triplicate readings of blank sample, nitric acid solution, deionised water and soil sample extract. The instrument was calibrated and profiled using a mixed metal standard solution with concentrations ranging from 0.2 mg kg^{-1} to 1.0 mg kg^{-1}. The system was rinsed for one minute with 3% nitric acid solution in between the analysis of each sample. Details of the QA/QC are given in section 3.10 below.

3.5.2.1.2 Chemical speciation of heavy metals

The speciation of the total heavy metals was determined by sequential extraction. The sequential extraction process used in this analysis is a three-step method adopted from Carapeto and Purchase (2000).

Step 1: Exchangeable fraction (F1)

Approximately 4g of dried soil sample was weighed using an analytical balance and transferred into centrifuge tubes. 1M magnesium chloride of pH 7 was added to the soil in the ratio 1g of soil to 10ml magnesium chloride. The soil was extracted at room temperature for 1 hour using a sonication bath. After an hour, the mixture was centrifuged and filtered with filter paper (Whatman's No 48) and decanted into 50ml volumetric flasks. The residual soil was rinsed with deionised water and allowed to air dry.

Step 2: Organic bound fraction (F2)

The air dried soil residue was reweighed and put in centrifuge tubes. 0.05M 0f EDTA was added to the soil in the same ratio as above (1g of soil to 10 ml EDTA). The soil was again extracted at room temperature for 2 hours using a sonication bath. At the end of 2 hours, the mixture was centrifuged and filtered with filter paper (Whatman's No 48) and decanted into 50ml volumetric flasks. The residual soil was rinsed with deionised water and allowed to air dry.

Step3: Residual fraction (F3)

This step was carried out according to the EPA 3051a protocol (EPA, 2007). The dried soil residue was treated as in explained in section 3.5.2.1.1.

The extracts from each extraction step was analysed using a Thermos ICP-OES (iCAP 1600) after proper calibration. The concentrations determined in the extract are reported on the basis of the dry weight of the sample.

Sample concentration = $\frac{C*V}{S}$ ---------------------Equation 3.6

Where: C= concentration in extract (mg l^{-1}), V = volume of extract (ml), S = dry weight of the sample (mg).

3.6 Exposure assessment

For all assays carried out in the exposure assessment, a composite sample was prepared for each depth using a ceramic mortar and pestle. This was carried out in order to ensure representativeness and reduce variability in the sampled area because according to Ramsey & Argyraki, (1997) and Taylor et al., (2005), the soil matrix, being very heterogeneous, has uncertainty in environmental investigations as the main downside as measurements of contaminant concentration taken from same location can vary greatly. Also, the dry mixing with the mortar and pestle reduced the range of particle size, thereby promoting representativeness and reducing spatial heterogeneity sampling USEPA (2012). The samples were sieved using a standard test sieve with aperture size of 1mm-2mm. Sample bags were used in the packaging and the samples were stored in the refrigerator at 4°C pending further analysis.

3.6.1 Ecotoxicological study

The analysis in this section seeks to demonstrate the concept of bioavailability and bioaccessibility as discussed in section 2.8.

The soil samples used in this experiment was carefully homogenized. The soil from the different depth were mixed together to form a single sample. Soil columns were set up in a laboratory with controlled environmental conditions of air temperature 20 ±2°C and adopted OECD guidelines for soil leaching (OECD, 2004). Poly vinyl chloride (PVC) columns with internal diameter of 5cm and length 50cm were used for the test. Glass wool was placed in the bottom of the soil column and wrapped with muslin cloth to keep the soil in the column. A filter layer of 50g uncontaminated quartz sand was placed above the glass wool and the contaminated soil placed above the layer of quartz sand. The columns were filled with approximately 300g of air dried homogeneous soil samples to the height of 35 cm. To ensure uniform packing of the soil and avoid the formation of preferential flow pathways, soil was added in the column in small quantities and pressed down with a pestle under gentle vibration until the top of the soil column did not sink further. Before the start of the experiment, prewetting was carried out with artificial rain (0.01M $CaCl_2$) and left to equilibrate for 24 h. The system was replenished with 200 ml of artificial rain on a daily basis for 28 days. Leachates were collected on days 1, 7, 14, 21 and 28 and the pH, dissolved oxygen and metal concentration was determined. Garden soil purchased from Homebase was used as control for the leaching process.

3.6.1.1 *Daphnia magna* acute immobilization test

Daphnia magna are well established test species for ecotoxicological studies and risk assessment as they are primary consumers in the food web, have a short life cycle, are cost effective and are easy to maintain in the laboratory (Tatarazako & Oda, 2007).

3.6.1.1.1 Culturing conditions of the *Daphnia magna*

Single clones of B1, B2 and RD *Daphnia* strains were obtained from University of Birmingham. The daphnids where maintained in 1l beakers containing 500ml of ISO 6341 artificial freshwater (ISO, 2012) (Appendix 2). The strains were put in the media and allowed to reproduce. The reproduced neonates of less than 24 hours old were transferred to fresh culture media and maintained at approximately 20 daphnia per beaker at a temperature of 20±2°C and a light: dark photoperiod of 16:8 h. The animals were cultured in a static system with the media changed twice weekly and the beakers were covered with cling film to avoid contamination. Marinure, a seaweed extract, was added to the culture media at the start and at subsequent renewal of the media. 1 ml and 2 ml of the extract was added to 500 ml of culture media for neonates and adults respectively. The daphnids were fed daily with 1 ml-2 ml *Chlorella vulgaris* algal suspension and 0.5 ml-1 ml dry baker’s yeast suspension depending on their age. However, at a later stage, the daphnids were maintained on only yeast suspension as there was a contamination in the *Chlorella vulgaris* culture. Neonates were removed daily to avoid overcrowding.

3.6.1.1.2 Acute toxicity exposures

Prior to toxicity test, the *Daphnia magna* were examined against a dark background with tangential lighting, and any daphnid observed as inactive was discarded. The acute tests were carried out in accordance with OECD 202 guidelines (OECD 2004). Tests were maintained for 48 hrs at 20±2°C in a 16:8 h (light/dark) cycle. The tests were carried out in 250 ml beakers with 100 ml of culture media in the absence of food or supplements. Treatments included triplicates of five dilutions of leachates (collected on days 1, 7, 14, 21 and 28) with ISO artificial water: 10%, 20%, 40%, 60% and 100% respectively and the control of artificial water. pH, dissolved oxygen and temperature were monitored before the commencement, during the test and at end of the test. The endpoint examined was immobilization, after 48 hrs each beaker was gently agitated, animals that did not resume swimming after approximately 15 s were considered to be immobilised.

3.6.2 Simulated human study

3.6.2.1 Bioaccessibility via ingestion

The Unified Bioaccessibility Method (UBM) developed by the Bioaccessibility Research Group of Europe (BARGE) is used for the analysis. The UBM is a physiological *in vitro* simulation of the digestive system modified from a previous method used by the Netherlands National Institute for Public Health and the Environment (RIVM) (Oomen et al., 2002) and validated by inter-laboratory trials (Wragg et al., 2011).

The simulation aims to represent the main three stages of the digestive system: the mouth, stomach and small intestine with the stomach pH of 1.2 and an intestinal pH of 6.3 under fasting conditions with the aid of four simulated fluids (saliva, gastric, duodenal and bile). The constituents of the simulated fluids (Table 3.1) represent the physiological conditions in the human digestive system. The simulation consists of two phases; the gastric phase which is removed from the system after simulation of the mouth and stomach compartments and the gastro-intestinal phase which is a simulation of the mouth, stomach and the small intestine. The test is carried out at body temperature (37°C) as temperature affects enzyme activity and chemical characteristics such as solubility (Broadway et al., 2010; Wragg et al., 2011; Pelfrene et al., 2012).

The fluids were prepared individually a day prior to carrying out the extraction and stored in the refrigerator at 4°C. Each fluid was prepared from 500 ml solutions of organic and inorganic compounds, which were combined with enzymes in a 1l media bottle. The pH of each fluid was checked to ensure they were within the required limits: saliva 6.5±0.5, gastric fluid 1.1±0.1, duodenal fluid 7.4±0.2 and bile 8.0±0.2. The simulated body fluids were removed from the fridge an hour before the analysis and placed in a water bath at 37°C to bring the temperature up to mimic body temperature.

Table 3.1: Constituents of the simulated body fluids for the UBM bioaccessibility test

Reagents	**Saliva**	**Gastric**	**Duodenal**	**Bile**
	mg	**mg**	**Mg**	**mg**
Inorganic (500 ml)				
KCl	896	824	564	376
NaH_2PO_4	888	266		
KSCN	200			
Na_2SO_4	570			
NaCl	298	2752	7012	5260
$CaCl_2$		400	100	222
NH_4Cl		306		
$NaHCO_3$			5607	5786
KH_2PO_4			80	
$MgCl_2$			50	
NaOH (1M)	1.8ml			
HCl (37%)		8.3ml	180µL	180µL
Organic (500 ml)				
Urea	200	85	100	250

Glucose		650		
Glucuronic acid		20		
Glucosamine hydrochloride		330		
Enzymes (1000 ml)				
Alpha amylase	145			
Mucin	25	3000		
Uric acid	7.5			
Bovine serum albumin		1000	1000	1800
Pepsin		1000		
Pancreatin			3000	
Lipase			250	
Bile				6000
pH	6.5±0.5	1.1±0.1	7.4±0.2	8.0±0.2

3.6.2.1.1 UBM bioaccessibility procedure

Triplicate sets of 0.6 g of the contaminated soil samples were weighed into labelled extraction tubes, for the gastric and the gastrointestinal phases. Saliva (9.0 ml) was added by pipette for both gastric and the gastrointestinal phases to the tubes, tubes were capped and were quickly shaken manually for 10 s. To each test aliquot, 13.5 ml of gastric fluid was added by pipette and manually agitated again for 10 s. The pH of each test aliquot was checked to ensure they were 1.2±0.05. The pH was adjusted with dropwise addition of 1M NaOH and/or 37% HCl where necessary. The tubes were capped, placed in an end-over-end rotator at 37°C for 1 hour. At the end of 1 hour, both the gastric and gastrointestinal extracts were removed from the incubator and the pH of the resulting mixtures was measured. The pH ranged from between 1.22-1.45, the gastric phase was deemed complete and the gastrointestinal phase is continued. (According to the UBM protocol, if the pH is > 1.5, the procedure has to be restarted from the beginning See Fig 3.10). The gastric samples were centrifuged for 5 minutes at 1500 *x g* and the supernatant was carefully collected, acidified with HNO_3 and stored in the refrigerator at 4°C prior to analysis with ICP-OES.

The gastrointestinal phase is continued with the addition of 27 ml duodenal fluid and 9 ml of bile by pipette, tubes are recapped, shaken manually for 10 s and pH checked to ensure it is 6.3±0.5. The pH was adjusted with dropwise addition of 1M NaOH and/or 37% HCl were necessary. The tubes were placed in the end-over-end rotator at 37°C for 4 h. At the end of 4 h, the pH of the samples was measured and they ranged between 6.35-6.7. The gastrointestinal samples were centrifuged for 5 min at 1500 *x g* and the supernatant was carefully collected, acidified with HNO_3 and stored in the refrigerator at 4°C prior to analysis with the ICP-OES.

The residence and emptying time used in this analysis represent the average time it takes for the stomach to empty into the small intestine and digestion to complete in the human system.

Data analysis and calculation

BF (%) = $\frac{\mathbf{BMC}}{\mathbf{TMC}} * \mathbf{100}$-------------------------Equation 3.7

Where; BF= Bioaccessible fraction, BMC = bioaccessible metal fraction (mg kg^{-1}), TMC = total metal concentration (mg kg^{-1}).

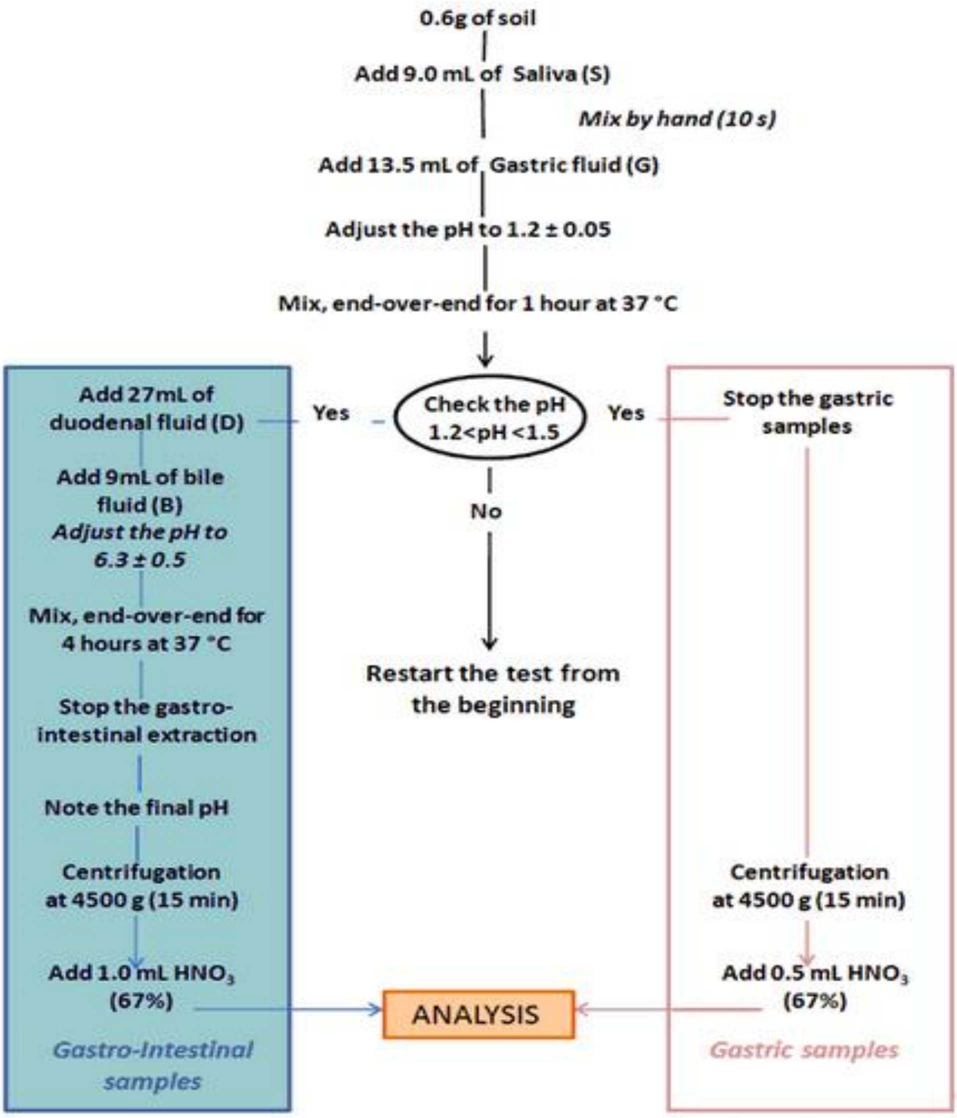


Figure 3.10: Flowchart of the UBM procedure. Source: https://www.bgs.ac.uk/barge/ubm.html

3.6.2.2 Bioaccessibility via inhalation

According to Boisa et al. (2014), inhaled particles may reside in either the extracellular environment typified by lung fluid of neutral pH or the more acidic environment within macrophages. In order to simulate the extracellular environment of the deep lungs, Gamble's solution, a simulated lung fluid designed to mimic the composition of human interstitial lung fluid was developed. The original formulation, which was a mixture of water and inorganic salts including chlorides, carbonates and phosphates, it has been modified by different researchers either by the substitution of acids, salts, buffers, proteins and other organic compounds that are found present in the alveolar fluid (Takaya et al., 2006; Wragg & Klinck, 2007; Gray et al., 2010). In this study, the simulated epithelial lung fluid (SELF) developed by Boisa et al. (2014) was used because the formulation contains inorganic salts, antioxidants, surfactant lipids, large molecular-mass proteins and organic acids that are all representative to the epithelial lung fluids of healthy non-smoking humans and the concentration of each individual constituents making up the SELF are of equal concentration reflecting documented in *in vivo* concentrations (Table 3.2).

For this experiment, a portion of the soil samples were pooled together to make a composite sample to ensure representativeness; sieved and ≤10 µm fraction of the soil samples was extracted from the soil, several studies (e.g. Ajmone-Marsan et al., 2008; Luo et al., 2011) have reported that this fraction (≤10 µm) holds the highest amount of metals in the soil. This fraction has also been categorized as the size that gets deep into the lungs as well as respiratory tract and correlates with respiratory infections in inhalation exposure (Parker et al., 2009; Drysdale et al., 2012).

3.6.2.2.1 Generation of PM_{10} fraction from soil

A process for PM_{10} generation by sedimentation technique according to Stoke's law has been described by a number of researchers (Wang et al., 2006; Ljung et al., 2008; Luo et al., 2011; Boisa et al., 2014) was modified in this study. Homogenized soil samples were put in an oven at 105°C for 4 h to dry. After which the samples were milled using a mortar and pestle then passed through a sieve of mesh size 35 µm. Ten gram soil sample (<35 µm) was suspended in 100 ml of deionised water and dispersed with the aid of a magnetic stirrer for 10 min. The resulting suspension was allowed to stand for 10 min. The top 50 ml was decanted into a centrifuge tube and centrifuged for 10 min at 1500 *x g* to obtain the <10 µm fraction. The resulting supernatant was filtered with ashless Whatman No 42 filter paper and the particles

(≤10 μm fraction) settled on the filter paper. Repeated gravitational sedimentation and decantation was carried out (50 ml deionized water was added to the remaining suspension and process repeated to obtain particulate matter) until the resulting suspension was clear. The extracted particulate matter had its moisture reduced in desiccators and dried in the oven at 105°C for 3 h prior to use for analysis.

Table 3.2: Constituents of the simulated lung fluid

Reagents	**Mg**
Inorganic (1 l)	
NaCl	12040
$CaCl_2$	612
Na_2HPO_4	300
KCl	596
$MgCl_2$	400
Na_2SO_4	144
$NaHCO_3$	5400
Organic (1 l)	
Ascorbic acid	36
Uric acid	32
Glutathione	60
Proteins/ Lipid (2 l)	
Bovine serum albumin	520
Cysteine	244
DPPC	200
Glycine	752
Mucin	1000
pH	7.4±0.2

3.6.2.2.2 Inhalation accessibility procedure

Prior to extraction, the simulated lung fluid was taken out of the fridge, warmed in a water bath for 2 hours at 37°C to mimic body temperature. The pH was checked to ensure it was 7.4±0.2. Triplicate sets of 0.2 g of the generated re suspended soil samples were weighed into labelled extraction tubes; 20 ml of simulated lung fluid was added to leach the samples. The samples were agitated for 10 s and pH was checked. The pH was adjusted with dropwise addition of 1M NaOH and/or 37% HCl where necessary. The samples were rotated at 37°C and resulting leachates were collected at 0.5, 1, 2, 3, 4, 6, 12, 24, 48, 72, 96 and 120 h intervals to determine the dissolution of metals. The extraction time was carefully considered as studies carried out by Wragg & Klinck (2007) indicated residence time of particulates in the lungs should be put into consideration; they reported a time frame of 100 h is required to have a reasonable estimate of metal bioaccessibility in the lungs. However, in this study, 120 hours was adopted as endpoint to include a 20% safety factor to the established 100 h to ensure full saturation. The percentage bioaccessibility will be estimated at the end of the analysis (120 h). The extracts were centrifuged at 1500 *x g*. Supernatant was collected acidified in HNO_3, stored at 4°C till ready for analysis using the ICP-OES.

Data analysis and calculation

BF (%) = $\frac{\mathbf{BMC}}{\mathbf{TMC}} * \mathbf{100}$-------------------------Equation 3.8

Where; BF= Bioaccessible fraction, BMC = Bioaccessible metal fraction (mg kg^{-1}), TMC = Total metal concentration (mg kg^{-1}).

3.7 Ecological risk assessment

3.7.1 Assessment of soil contamination

Pollution assessment indices are used to compare pollution rate of different parts of the environment (Tomlinson et al., 1980). The methods used in determining contamination intensity in this study include contamination factors (CF), pollution load index (PLI).

The CF is the ratio between the concentration in the sample and the background concentrations; in this case the values obtained from the control samples. Hakanson (1980) suggested CF values to be interpreted as CF < 1 indicates low contamination; 1 < CF < 3 is moderate contamination; $3 < CF < 6$ is considerable contamination and $CF > 6$ is very high contamination.

$CF = \mathbf{Csample / Cbackground}$ -------------------Equation 3.9

Where: C_{sample} = concentration of the pollutant in the sample (mg kg^{-1}), $C_{background}$ = baseline concentration of the pollutant in an unpolluted environment (mg kg^{-1}).

PLI reflects the impact of contaminants on the soil. It gives an indication of the level of heavy metal toxicity in a particular sample. PLI is calculated by multiplying the contamination factors and deriving the root of the n factors. PLI values greater than 1 indicate pollution while values less than 1 indicate that the metal loads are close to background levels (Tomlinson et al., 1980; Liu et al., 2005). The higher the value of PLI, the more polluted the site is said to be. However, according to Angulo (1996), a PLI value of ≥100 indicates an immediate intervention to stop pollution; a PLI value of ≥50 indicates a more detailed study is needed to monitor the site, whilst a value of <50 indicates no drastic measures are needed at the site.

$PLI= [CF_1 x CF_2 x CF_3 x \ldots\ldots x CF_n]^{1/n}$ -------------------Equation 3.10

Where n= number of factors (metals), CF= contamination factor.

3.7.2 Potential ecological risk assessment

Potential ecological risk index (PERI) is used to quantitatively express the potential risk of the measured metals in the soil. PERI is the sum of the ecological risk factors (Er) of the individual measured metals. It represents the sensitivity of the biological community to the toxic substance and illustrates the potential ecological risk caused by the overall contamination. The PERI guideline to determine environmental risk levels is presented in Table 3.3.

Er = $\mathbf{Tr} * \mathbf{CF}$ ----------------------------------Equation 3.11

PERI = $Er_1+Er_2+Er_3+\ldots\ldots Er_n$ ------------------------------Equation 3.12

Where Tr = is the biological toxic factor of an individual element, CF= contamination factors, Er = the individual ecological risk factor

Based on the standardized heavy metal toxic factor developed by Hakanson (1980), the toxic response factors for Cd, Cr, Cu, Mn, Ni, Pb, Sb and Zn are 30, 2, 5, 1, 5, 5, 1 and 1 respectively (Islam et al., 2015).

Table 3.3: Potential ecological risk index guidelines

$\mathbf{E_r^i}$	**Single pollutant degree of environmental risk**	**PERI**	**Comprehensive environmental risk level**
$E_r^i \leq 40$	low ecological risk	PERI ≤150	low ecological risk
$40 < E_r^i \leq 80$	moderate ecological risk	150 < PERI ≤300	moderate ecological risk
$80 < E_r^i \leq 160$	considerable ecological risk	300< PERI ≤600	considerable ecological risk
$160 < E_r^i \leq 320$	high ecological risk	PERI >600	very high ecological risk
$E_r^i > 320$	very high ecological risk		

3.7.3 Risk assessment code (RAC)

The risk assessment code (RAC) as proposed by (Perin et al., 1985), mainly applies to the percentage binding strength of metals in various geochemical phases which establishes their bioavailability and associated risks in soils (Sarkar et al., 2014). The RAC works with the fractionation from the sequential extraction; the most bioavailable and mobile leaches out first. According to the RAC, any metal, for which less than 1% of the total metal is released in the exchangeable fractions, will be considered safe for the environment (Table 3.4).

Table 3.4: RAC guidelines

% Exchangeable fraction	Risk
<1%	No risk
1-10%	Low risk
11-30%	Medium risk
31-50%	High risk
>50%	Very high risk

3.8 Human health risk assessment model

3.8.1 Exposure model

Exposure of man to heavy metals in soils can occur through three main pathways namely: oral ingestion of particles, inhalation of re suspended particles from soil through the mouth and nose and dermal absorption of heavy metals in particles adhered to exposed skin (Miguel, et al., 2007). However, in this study, only two routes were studied: the oral ingestion and the inhalation of re suspended particles. According to Huang et al., 2016, these two routes are the most difficult to ignore in comparison to dermal contact as putting on clothes considerably reduces the uptake of contaminants through the skin.

According to US EPA (2002), there are screening exposure scenarios: residential, commercial/industrial, and construction and each exposure scenario uses a similar modelling approach for a given exposure pathway. However, the input parameters differ based on the scenario. In this study, the study site falls into the category of “commercial/industrial”, and the receptor is “outdoor worker”. A number of studies have shown that inadvertent ingestion of soil is common and possible among children 6 years old and younger (Calabrese et al., 1989, 1997; Wijnen et al., 1990; Doyle et al., 2012) hence, an age-adjusted factor takes into account the difference in body weights, and exposure duration for children from 1 to 6 years old and others from 7 to 30 years old. The US EPA suggests that children are not considered in the risk assessment in commercial/industrial areas, as such, exposures are limited to adults. However, due to the distinctive conditions in this study, children as young as 7 years old were found on the site and were also found to be living in the makeshift houses on the site. It has been recommended that children aged 7 and above found in “commercial/industrial” sites should be classed as adults in risk assessment as a health-protective approach (Brewer, 2012). In lieu to this, the exposure assessment in this study has the assumption that the exposed populace are adults

In assessing the exposure, the dose received (chronic daily intake) through each pathway (the oral ingestion and the inhalation of re suspended particles) is calculated with the equations below as adopted from US EPA (1989; 1996; 2002).

$$\mathrm{CDI}_{\mathrm{ingestion}} = \frac{\mathbf{C*IR*EF*ED}}{\mathbf{BW*AT}} * \mathbf{CF} \text{ ------------ Equation 3.13}$$

$$\text{CDI}_{\text{inhalation}} = \frac{\mathbf{C*InhR*EF*ET*ED}}{\mathbf{PEF*AT}} \text{ ------------- Equation 3.14}^{2}$$

3.8.2 Toxicity assessment/Dose response assessment

Toxicity values for human health risk assessment, such as the Oral Slope Factor (SF), Inhalation Unit Risk Factor (IUR), and Oral Reference Dose (RfD) and inhalation reference dose (RfC) for each metal was obtained from the US EPA Regional Screening Level (RSL) Composite Worker Soil Table, 2015 (Table 3.5). The toxicity values for carcinogens are slope factors and non-carcinogens are reference doses.

The toxicity value used in describing the dose-response relationship for non-cancer health effects is the reference dose (RfD). It is defined as: ". . . an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human populations (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime" (US EPA, 1989). The oral RfD is generally expressed mg/kg/day. RfDs for effects associated with inhalation of a particular chemical are given as a reference concentration (RfC) (mg/m^3). The toxicity value to establish a dose-response relationship for cancer effects is expressed as a slope factor (SF) for ingestion and inhalation unit risk (IUR) for inhalation.

---

[2] Where; CDI is chronic daily intake; C is concentration; AT is averaging time (lifetime in yrs.* 365 days/yr); ED is exposure duration (25 yrs.); EF is exposure frequency (225 days/yr.); PEF is particulate emission factor (1.36*109 m3/kg); ET is the exposure time (8 h/day); IUR is the inhalation unit risk; RfC is inhalation reference concentration, RfD is ingestion reference dose, and SF is slope factor; CF is conversion factor(10^{-6} kg/mg); HQ is hazard quotient; HI is hazard index; IR is ingestion rate; InhR is inhalation rate, BW is body weight (70 kg).

Table 3.5: Toxicological characteristics of the investigated metals used for health risk assessment

Metals	RfD (mg/kg/day)	RfC (mg/m^3)	SF (mg/kg/day)	IUR (ug/m3)
Cd	1.00E-03	1.00E-05		1.80E-03
Cr	3.00E-03	1.00E-04	5.00E-01	1.20E-02
Cu	4.00E-02	1.20E-04		
Mn	2.40E-02	5.00E-05		
Ni	2.40E-04	1.10E-02	1.70E+00	2.40E-04
Pb	2.00E-02	2.00E-04	5.00E-01	1.50E-01
Sb	4.04E-04	1.00E-03		
Zn	3.00E-01	3.60E-04		

3.8.3 Risk characterization

The human health risk is characterized by non-carcinogenic and carcinogenic risk. The non-carcinogenic effects for each exposure route and metal are evaluated by comparing the chronic daily intake over a specified time period with the RfD. The ratio of the chronic daily intake or (average daily dose as some authors refer to it) to RfD for ingestion and RfC for inhalation is the hazard quotient (HQ). The HQ assumes that there is a dose below which adverse health effects are unlikely to occur (EPA 1989). If the chronic daily intake is below the threshold RfD or RfC, it is unlikely that non-carcinogenic effects would occur.

$$HQ= \frac{\mathbf{CDI}}{\mathbf{RfD\ or\ (RfC)}} \text{---------------------------Equation 3.15}$$

To assess the overall potential for non-carcinogenic effects from an exposure scenario with multiple contaminants, the HQ for the individual contaminants for each exposure pathway is summed up to get the hazard index (HI). The HI less than 1 signifies the threshold at which adverse health effects are unlikely to occur.

The quantitative risk estimates for carcinogenic effects are evaluated by the product of the chronic daily intake and the SF for ingestion and IUR for inhalation for each contaminant and exposure pathway.

Cancer risk =$\mathbf{CDI} * \mathbf{SF}\ \mathbf{or}\ (\mathbf{IUR})$---------------------Equation 3.16

Again, to assess the overall potential for carcinogenic effects from an exposure scenario with multiple contaminants, the cancer risk for the individual contaminants for each exposure pathway is summed to get the total cancer risk, which represents the cumulative predicted cancer risk for the contaminants at a site. The total cancer risk greater than the threshold (10E-04 - 10E-06) signifies high cancer risk probability.

3.8.4 Uncertainty approach

With every step in the risk assessment process, uncertainties are bound to occur; from the environmental sampling, the exposure pathway, the sample analysis to the risk characterization. Uncertainties were minimized all through the sampling and analytical process (section 3.10); with the risk assessment model, uncertainty was minimized using by using parameters for the exposure scenario and using site specific values to evaluate the risk posed by the informal recycling activities.

3.9 Statistical analysis

Statistical analysis was carried using MINITAB version 16. Normality and equal variance assumptions were carried out on the outcome of all analytical process, to ensure the appropriate statistical test was used. Analysis of differences in the soil parameters was carried out using Mann-Whitney test, T-test or one-way analysis of variance (ANOVA). The Mann-Whitney and T-test was used to determine if there were any differences between varying concentrations in the experiments and the time the samples were collected (difference between dry season and wet season). ANOVA was used between the soil depths and distances to determine any significance in varying concentration within different soil depths and the distance from the recycling area of the site.

Correlation was used to establish relationships between physical properties and chemical properties of the soil; identify the relationship between soil properties and metal concentration as well as provide an effective way to reveal the relationships and understand the influencing factors.

Probit analysis, commonly used in toxicology to determine relative toxicity of chemicals to living organisms, was used to analyse the of dose–response relationship between leachate concentration and *Daphnia magna*. Probit analysis transforms from sigmoid relationship to linear relationship and then runs a regression on relationship.

ArcGIS 9.2 was used in geostatistical analysis for distribution of metals within the study site using kriging as the tool for interpolation of spatial data. Kriging quantifies the correlation of the measured points through a variogram and produces predictions of unobserved values from weighted linear combinations of the known observations at nearby locations. The prediction derived by kriging is more accurate than polynomial interpolation (Van Beers & Kliejnen, 2003; Adeoti et al., 2014).

3.10 Quality assurance/quality control (QA/QC)

Rigorous QA/QC procedures were adopted to avoid errors where possible and to evaluate reproducibility and accuracy. The glassware used in the analysis was acid washed with 10% HNO_3 solution prior to usage; analytical grade reagents and deionised water were used throughout each analysis. Soil samples were analysed in triplicate; procedural blanks were prepared with the omission of soil samples and used in all extraction processes at a frequency of after every 9 unknown samples (3 batches) to ensure accurate results from instrumentation.

Proper calibration of the instrument and use of certified standards within the ICP-OES analytical run to avoid drifts in the instrument was carried out to ensure reliability, accuracy and precision of the analysis. On switching on the instrument, it was allowed to run on blanks for approximately 20 min to ensure the removal of any residuals in the instrument before sample analysis.

Certified reference material [SQC001-050G (lot 011233) Resource Technology Corporation, USA] was used to evaluate the reliability and accuracy of the analytical procedure. Mass balance of the three fractions in the sequential extraction procedure was also carried out (see Appendix 6). The BGS 102 oral bioaccessibility guidance material was used for the bioaccessibility test although it had been certified for only As in the gastrointestinal phase and Pb in the gastric phase.

CHAPTER FOUR

4 Metal distribution and potential ecological risk in study

Earlier studies carried out in Ghana, China and India presented results showing that illegal recycling activities caused metal pollution in soils (Li et al., 2011; Luo et al., 2011; Otsuka et al., 2011; Pradhan & Kumar, 2014). Based on this information, this study proposed to further assess the environmental impact of informal recycling of e-waste in Lagos State, Nigeria, using the risk assessment paradigm. As part of this assessment, this chapter presents and discusses the physico-chemical properties, total metal concentrations and spatial distribution of metals in the study site. The extent of contamination and potential ecological risk caused by the rudimentary practices will also be reported and discussed.

4.1 Physico-chemical properties of the soil

The mean values of the soil properties of the individual samples are presented in Table 4.1 below; the raw data is available in Appendix 4. Using the finger assessment, the soil texture was established to be loamy sand. The pH of the soil samples ranged from slightly acidic to slightly alkaline with most of the soil samples falling into the neutral range. The pH of the soil in the recycling area during the dry season ranged between 6.1 to 9.38 while in the wet season, it ranged from 6.5 to 8.11. The cation exchange capacity (CEC) in the study site ranged between 3.15 and 15.88 $\mathrm{cmol_c kg^{-1}}$ and the organic matter content (OMC) in the soil ranged from 6.20- 26% in both the dry and wet season respectively.

Table 4.1: Physicochemical parameters of soil samples within the study site

	pH	**%OMC**	**CEC (cmol$_c$ Kg^{-1})**	**pH**	**%OMC**	**CEC (cmol$_c$ Kg^{-1})**
		Dry season			**Wet season**	
			Recycling area			
0-10cm						
Mean	7.52±0.18	15.49±0.86	10.55±0.61	7.11±0.07	24.13±0.96	10.09±0.49
Minimum	6.45	6.20	4.33	6.86	15.75	5.35
Maximum	9.38	22	14.79	8.05	33.4	13.08
10-20cm						
Mean	7.34±0.15	20.27±0.57	10.10±0.63	7.08±0.06	25.69±0.77	9.45±0.515
Minimum	6.1	15.8	4.1	6.5	21.4	3.98
Maximum	8.29	25.2	15.57	7.88	35.4	14.08
20-30cm						
Mean	7.44±0.15	20.28±0.58	10.51±0.62	7.08±0.06	25.67±0.76	9.90±0.49
Minimum	6.27	16	3.15	6.76	20	3.6
Maximum	8.54	25	15.88	7.97	29.6	14.66
			Dismantling area			
Mean	8.32 ±0.15	15.69 ±1.22	9.57 ±0.66	7.71 ±0.11	12.61 ±0.89	10.00 ±0.7
Minimum	7.48	9.00	4.88	7.2	7.8	5.74
Maximum	9.03	19.8	12.62	8.11	16.8	13.12
Control	7.03±0.02	5.8±0.08	8.63±0.6	7.03±0.01	6.2±0.04	10.17±0.72

Values are presented mean ± S.E. (n= 63 for RA (21 sampling points * 3 determinations), n=30 for DA (10 sampling points *3 determinations)). Where RA is recycling area and DA is dismantling area.

4.2 Significance/interdependence of soil physico-chemical properties

The topography of the site was undulating with the recycling area of the site being more elevated than the dismantling area. The soil in the recycling area was observed to be very dark (black) in colour and in the dismantling area, to be brown with fine reflective particles. This could be explained by the fact that burning occurs in the recycling area whereas the breaking down of numerous fragments of electronics takes place in the dismantling area.

Furthermore, the surface at which the contamination occurs is loose and friable between (0-5cm), from depths below about 10 cm (typically), the soil structure was much more coherent and strongly formed and quite difficult to till using the soil auger.

Soil is a heterogeneous medium due to local variations in physical, chemical and biological factors (USDA-NRCS, n.d). The soil texture, pH, organic matter content and cation exchange capacity affect the presence and behaviour of contaminants and nutrients in soil (Illera et al., 2000). Soil texture is an important factor that influences the pH, cation exchange capacity, organic matter content, distribution of minerals as well as the microbial biomass (Scott & Robert, 2006). The soil texture has a significant effect on the soil air, water holding capacity and drainage properties of a soil. The CEC indicates the ability of the soils to absorb or release cations, the pH determines regulate the redox properties of the soil and the OMC is known to improve soil structure and permeability. According to the results in Table 4.1 above, the CEC concentrations in both dry and wet soil samples ranged from very low to slightly low based on the criteria described in Table 4.2. Since loamy sands have high leaching characteristics and also a rapid drainage rate, the soil texture, coupled with the soil CEC, suggests a potentially high leachability of nutrients and contaminants at the study site. Studies have shown that the CEC is reliant on the soil texture and organic matter content (Ashraf et al., 2012) which is confirmed in this study as a strong positive relationship between the soil percentage OMC and soil CEC ($r= 0.843$; $p< 0.001$) is established. This indicates that an increase in the OMC will lead to an increase in the CEC and improve the buffering capacity of the soil.

A significant difference was observed in the pH ($p< 0.005$) between the wet and dry seasons with the pH values in the dry season being significantly higher than in the wet season. Climatic conditions such as rainfall and temperature, as well as the soil texture, affect the physicochemical parameters of the soil since they control leaching intensity and soil mineral weathering (USDA-NRCS, n.d.). The high amount of rainfall in the wet season with a daily average of 169.5mm (NiMET, 2014) could result in the decrease in the pH of the soil. Increased precipitation results in displacement of ions in the soil, which in turn causes increased leaching of basic ions such as Ca, Mg and replacement with acidic ions such as H and Al. Water combines with CO_2 producing a weak acid which ionizes to release hydrogen and bicarbonate. Calcium ions in the soil are replaced by hydrogen ions and thus results in decreased pH (Ritter, 2012). The results also indicate that, at the recycling area, the %OMC was higher in the wet season than in the dry season with 1% significance ($p<0.01$). At the dismantling area, however there was no statistically significant difference ($p >0.05$) between the values of the dry season and the wet season. The higher OMC in the wet season in the recycling area may be attributed to the high amount of rainfall as well as the topography of the recycling area, which is undulating and poorly drained with visible pockets of water. Studies have shown that poorly drained areas have higher organic matter levels as the reduced oxygen levels slow down decomposition (Lancrop, 2013).

Table 4.2: Typical CEC levels in different soil types. Source: Lancrop, 2013

Rating	**CEC ($cmol_c/Kg$)**	**Comment**
Very low	0 – 10	Very low nutrient holding capacity indicating sandy soils with little or no clay or organic matter. Nutrients will easily be leached.
Slightly low	10 -15	Slightly low nutrient holding capacity indicating a more loamy mineral soil. Nutrients will still be leached.
Normal range	15 – 40	Adequate to high nutrient holding capacity indicating soils with increasing clay content.
High	+ 40	Very high level normally found in very heavy soil with high clay content or soils with a high organic matter level. Nutrients can be bound very tightly to the soil particles and therefore unavailable.

4.3 Soil total metal concentration

It is important to note that the selected metals reported in this study were chosen after a preliminary study of the site where a wide range of metals were analysed. The concentrations of heavy metals within the study site were highly varied (Table 4.2). For both seasons, the abundance of metals was consistently in this order: Cu > Pb > Zn > Mn > Ni > Sb > Cr > Cd. Overall, the concentration of Cd ranged between 2.92 mg kg^{-1} and 70.2 mg kg^{-1} and between 0.88 mg kg^{-1} and 29.4 mg kg^{-1} in the dry and wet season respectively. Cu ranged between 329-7106 mg kg^{-1} in the dry season and 1335-9277mg kg^{-1} in the wet season; Pb, 115-9623 mg kg^{-1} and 585-4069 $mgkg^{-1}$; Cr, 7.42-103.2 mg kg^{-1}, and 8.8-89.17 mg kg^{-1} in the dry and wet seasons respectively (see also appendix 5). The samples from the dry season and wet season differed significantly ($p<0.001$) in the total concentration of Cd, Cu, Mn and Zn, whereas no statistical difference was found in concentrations of Cr, Pb and Sb ($p>0.05$).

4.2.1 Quality control

The calibration curves used in the instrumentation presented a good linearity with correlation coefficients above 0.997. The certified reference material [SQC001-050G (lot 011233) Resource Technology Corporation, USA] used for the extraction of the total concentrations for the metals have certified values for Cd, Cr, Cu, Mn, Ni, Pb, Sb, Zn ranging between of 96-102 % recovery rate after 5 replicates (Appendix 6).

Table 4.3: Measured concentration (mg kg^{-1}) of metals in the study site (Mean ± S.E)

	Cd	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Zn**	**Cd**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Zn**
Recycling area																
	Dry season								**Wet season**							
0-10cm																
Mean	26.39±2.57	35.45±3.59	3277±277	115.35±8.86	40.80±4.87	2418±289	38.46±3.70	2195±180	12.69±1.27	23.04±2.51	4858±318	92±11.6	23.27±2.54	1969±157	35.36±3.30	915±42.7
Minimum	5.04	7.42	1730	53.50	4.07	1117	20.07	1000	3.94	8.80	2643	14.6	6.00	1052	10.34	508
Maximum	70.20	103.20	7106	202	149.60	9623	86	4884	24.50	47.30	7775	256	59.66	4069	66.38	1356
10-20cm																
Mean	26.09±3.87	33.23±3.14	3341±281	139.3±11.8	45.31±3.79	2280±282	33.63±3.25	2472±300	15.72±1.21	26.4±2.17	4938±263	92.33±9.79	55.5±3.0	2006±110	40.77±5.72	1012±53.1
Minimum	5.59	8.05	1561	59.9	4.32	1028	8	1568	9.03	11.78	2963	11.4	10.6	980	11.42	763
Maximum	69.94	87.8	5727	520	158.3	9260	81.55	8178	29.4	48.44	7600	206.55	65.38	2759	98.6	1504
20-30cm																
Mean	21.70±2.49	33.59±2.46	3380±340	148.9±14.4	40.88±3.67	1764±175	31.37±2.86	2440±217	13.48±0.99	26.65±2.01	5114±291	97.04±6.75	35.42±4.77	2202±173	33.33±5.4	1064±66.3
Minimum	4.92	10.2	780	78.3	5	753	13.96	1173	4.54	9.23	1335	21.86	11.84	902	8.45	621
Maximum	53.93	75.47	6022	316.4	88.1	3687	73.92	5904	24.7	42.71	7580	174.2	92.9	3880	107.15	1705
Dismantling area																
Mean	10.29±1.87	36.78±2.68	3165±502	254.9±24.4	77.4±10.7	911±111	22.51±2.68	862.6±42.1	8.67±2.4	49.6±4.72	5880±636	120.8±23.3	23.91±2.3	1823±230	58.4±13.6	1921±200
Minimum	2.82	24.18	329	90.4	10.6	115	5.37	661.2	0.88	13.52	2217	26.4	1.37	585	4.8	509
Maximum	21.39	50.17	6005	438.1	200	1610	65.37	1074.8	25.63	89.17	9277	376	56.13	3723	141	4471
Control																
	0.87±0.02	0.3±0.01	14.7±0.08	1.88±0.02	0.7±0.02	20.62±0.14	0.22±0.01	24.53±0.86	0.45±0.02	0.19±0.01	9.64±0.06	1.26±0.04	0.29±0.01	10.58±0.07	0.15±0.02	17.34±0.45

(n= 63 for RA (21 sampling points * 3 determinations), n=30 for DA (10 sampling points *3 determinations)). Where RA is recycling area and DA is dismantling area.

The type of metals found in the contaminated site is directly related to the type of activities carried out. The metals identified in the study site are synonymous with the metals identified in study carried out by Li et al., (2011) in a similar e-waste recycling site. Comparing this study with similar studies in other e-waste sites, a wide variation of the total metal concentration was observed between this study and previously reported studies. This disparity could be attributed to the type of recycling activities on the site, the length of time the recycling activities have occurred before soil sampling and the sampling strategy, sampling distance from the recycling site as reported by Olafisoye et al., (2013). Concentrations in this study were similar concentration ranges quoted in studies carried out by Li et al., (2011) and Luo et al., (2011) in Guiyu and Guangdong, China, respectively but interestingly, higher than another Nigerian study carried out in 2014 (Ofudje et al., 2015). They reported the presence of Cd, Cr, Cu, Pb and Zn (Table 4.4), comparing their reported concentrations with observed concentration in this study, Cd was 2.5 times higher, Cr was about 4 times higher, Cu was at least 35 times, Pb and Zn were about 10 times higher than their reported maximum concentration.

Table 4.4: Comparison on total metal concentration (mg kg^{-1}) in E-waste recycling sites

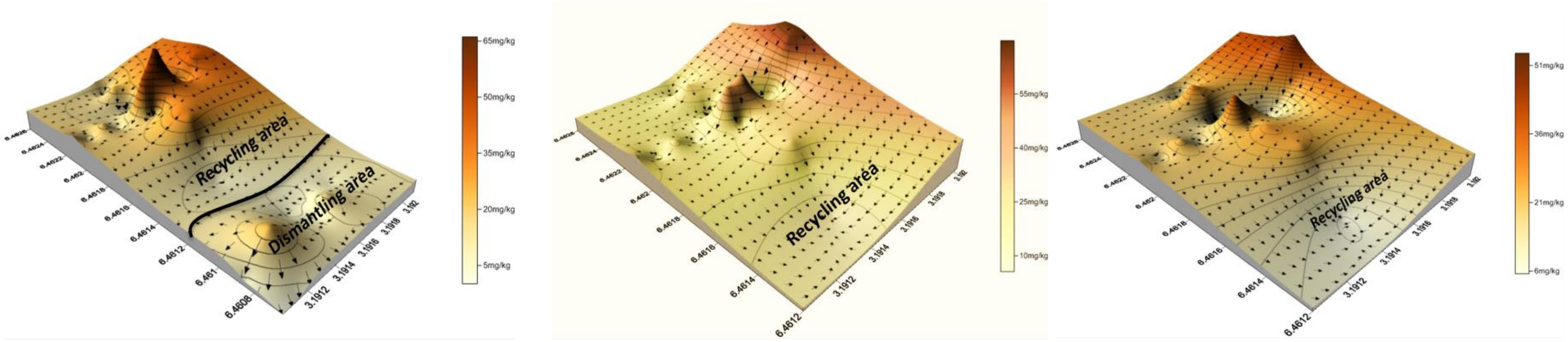
Location	Sample description	Sample collection date	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn	References
Lagos, Nigeria	Soil (0-30cm) dry & wet season	March-Oct 2013	0.88-25.3	8.8-89.17	1335-9277	11.4-438	1.37-158.3	115-9623	8-107.5	508-5904	Own study
Lagos, Nigeria	Indoor & outdoor dust	Nov 2009-Jan 2010	1.80-19.00	0.1-0.35	-	-	-	15.9-22.4	-	213-295.5	Adaramodu et, al 2012
Lagos, Nigeria	Soil (0-30cm) dry & wet	Oct 2011-May 2012	2.55-9.99	19.11-46.58	-	-	35.15-85.43	200-630	-	31.54-73.21	Olafisoye, et al, 2013

	season										
Guiyu, China	Soil	May 2009	1.21-10.02	320-2600	4800-12700	300-500	480-1100	150-480	1100-3900	330-3500	Li ,et al, 2011
Tema, Ghana	Soil (0-30cm	2013	1.40-2.60	-	1688-7834	-	-	-	-	-	Amfo-otu et al, 2013
Guangdong, China	Soil (0-15cm)	Sept 2007	3.05-46.8	23.6-122	1500-21400	-	122-132	629-7720	-	632-8970	Luo et,al, 2011
Lagos, Nigeria	Soil	2014	1.1-28.2	0.5-30.4	11.2-100.2	-	-	20.2-180.4		10.2-150.4	Ofudje et al, 2015
Agbogbloshie, Ghana	Soil (0-20cm)	Aug 2010	-	-	50-22000	-	-	-	-	200-16000	Otsuka et al, 2011

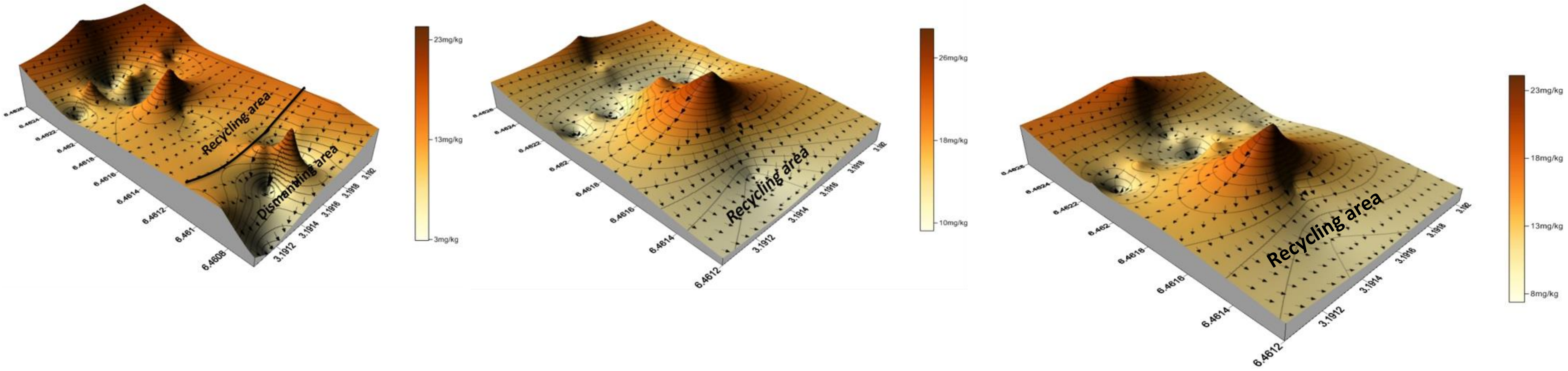
4.4 Spatial distribution of heavy metals.

The range of contaminant concentrations on the site depends on the activities, the land use for the disposals, the dispersion patterns and also the heterogeneity of soil on the study site. This potential variability makes it interesting to examine the spatial distribution, which revealed hot spots for a number of metals. GIS is a valuable tool for visualizing and interpreting spatial variability and contamination. In recent times, studies (Lee et al., 2006; Lu et al., 2010; Zou et al., 2015) used GIS to digitally present the distribution of contaminants in the environment.

Figures 4.1 to 4.8 illustrate the spatial distribution of metals vertically and horizontally. The distribution figures show that contamination was uneven across the site with clear hotspots at the locations where burning occurred.

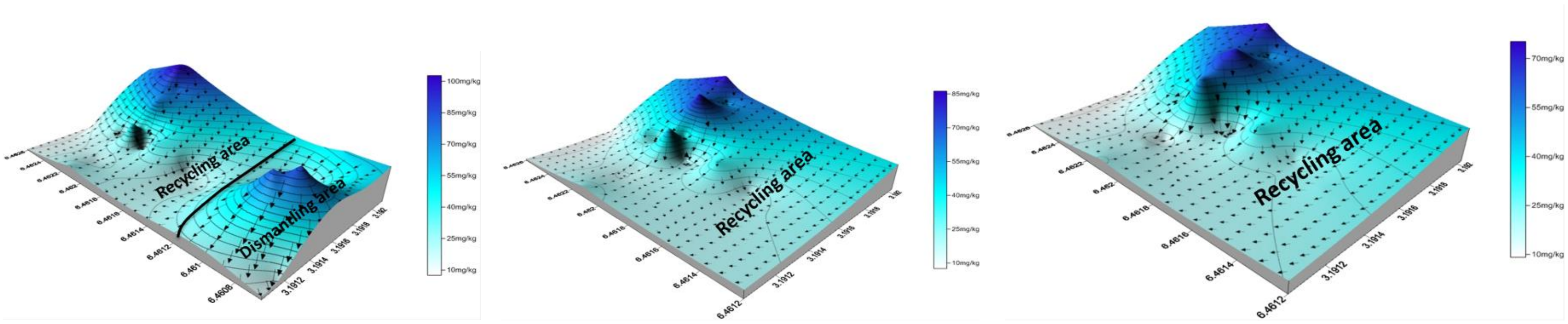


Cd distribution (dry season) in 0-10cm depth Cd distribution (dry season) in 10-20cm depth Cd distribution (dry season) in 20-30cm depth



Cd distribution (wet season) in 0-10cm depth Cd distribution (wet season) in 10-20cm depth Cd distribution (wet season) in 20-30cm depth

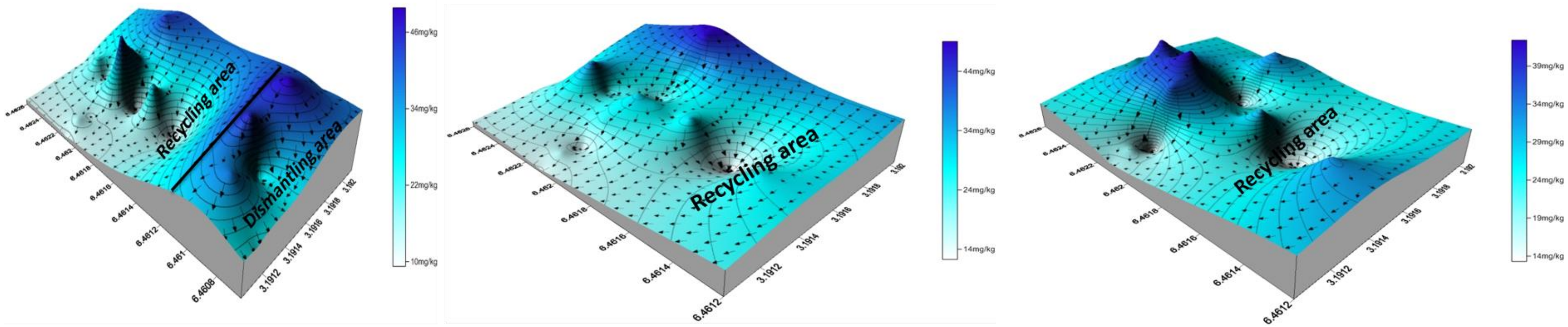
Figure 4.1: Spatial distribution of Cd in the study site (including the recycling area and dismantling area)



Cr distribution (dry season) 0-10cm depth

Cr distribution (dry season) 10-20cm depth

Cr distribution (dry season) 20-30cm depth

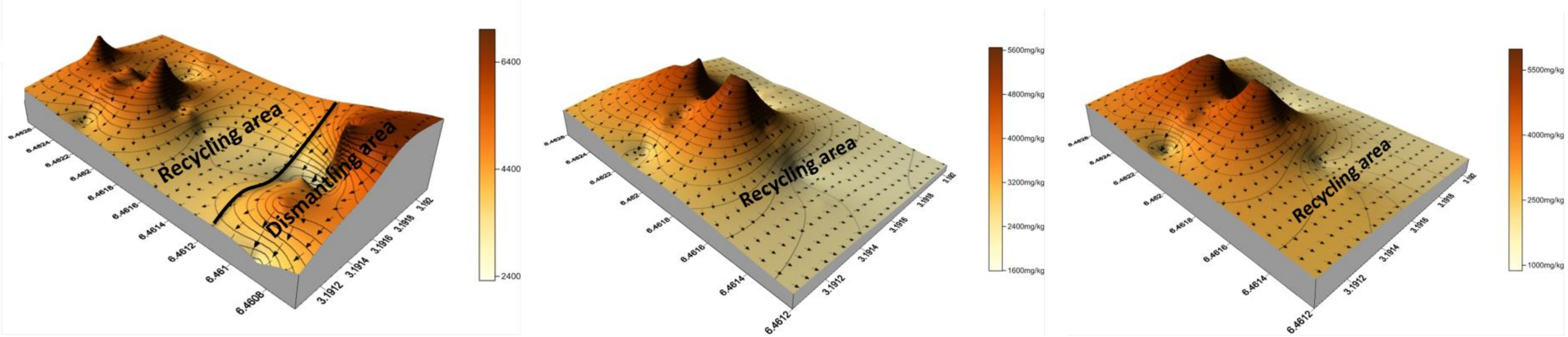


Cr distribution (wet season) 0-10cm depth

Cr distribution (wet season) 10-20cm depth

Cr distribution (wet season) 20-30cm depth

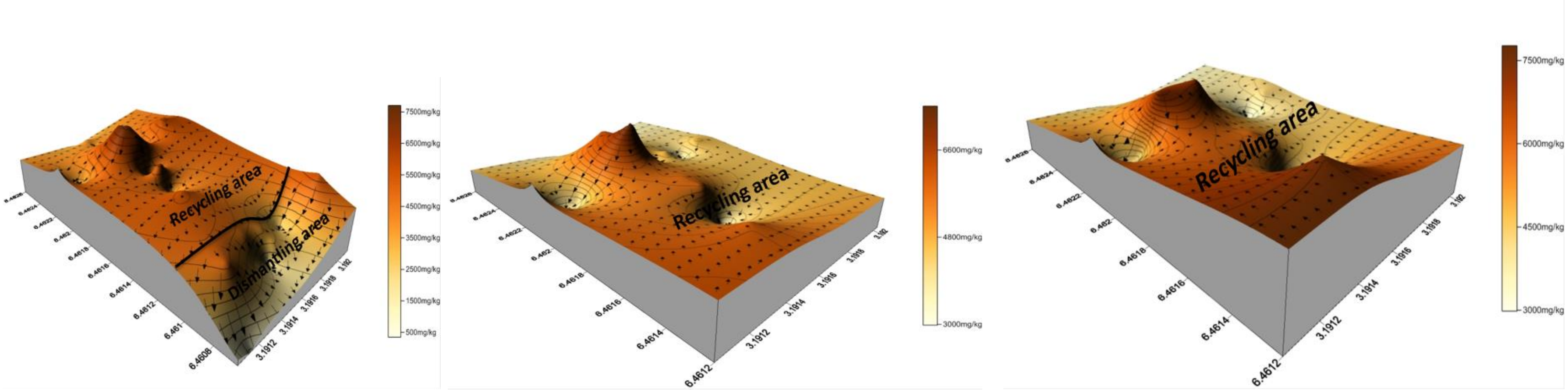
Figure 4.2: Spatial distribution of Cr in study site (including the recycling area and dismantling area).



Cu distribution (dry season) 0-10cm depth

Cu distribution (dry season) 10-20cm depth

Cu distribution (dry season) 20-30cm depth

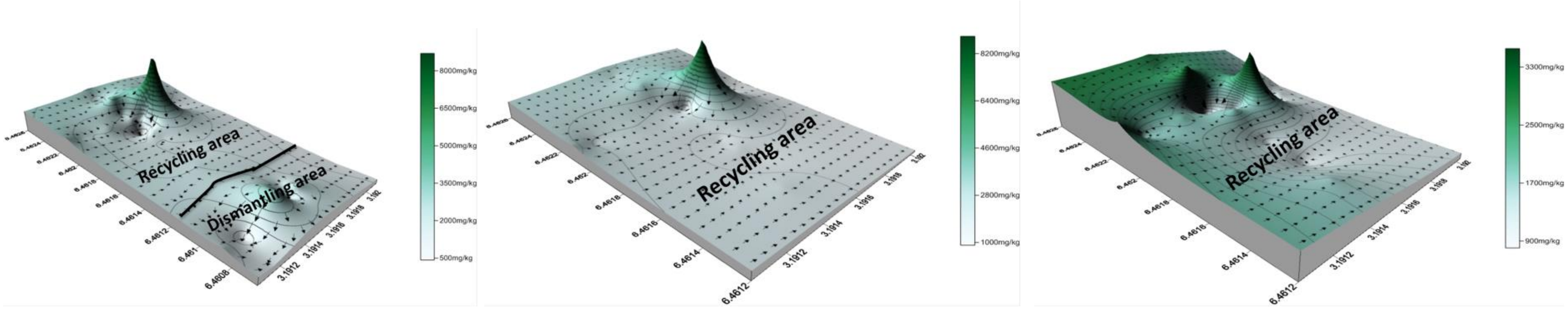


Cu distribution (wet season) 0-10cm depth

Cu distribution (wet season) 10-20cm depth

Cu distribution (wet season) 20-30cm depth

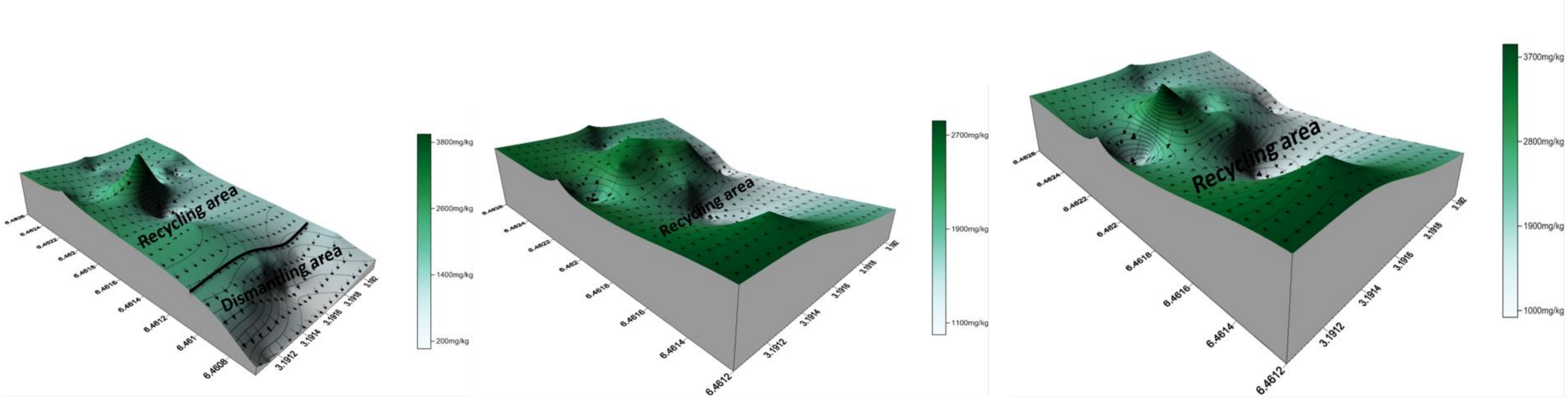
Figure 4.3: Spatial distribution of Cu in study site (including the recycling area and dismantling area).



Pb distribution (dry season) 0-10cm depth

Pb distribution (dry season) 10-20cm depth

Pb distribution (dry season) 20-30cm depth

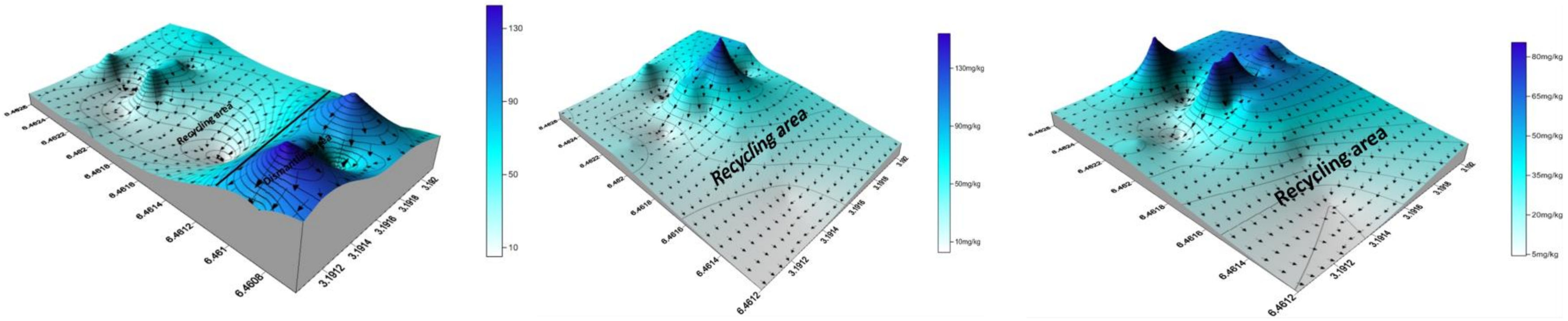


Pb distribution (wet season) 0-10cm depth

Pb distribution (wet season) 10-20cm depth

Pb distribution (wet season) 20-30cm depth

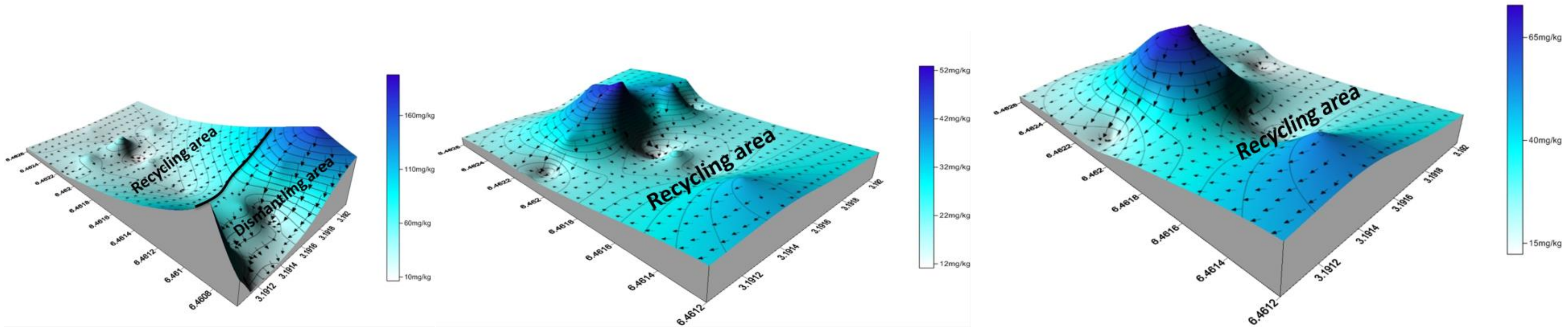
Figure 4.4: Spatial distribution of Pb in study site (including the recycling area and dismantling area).



Ni distribution (dry season) in 0-10cm depth

Ni distribution (dry season) in 10-20cm depth

Ni distribution (dry season) in 20-30cm depth

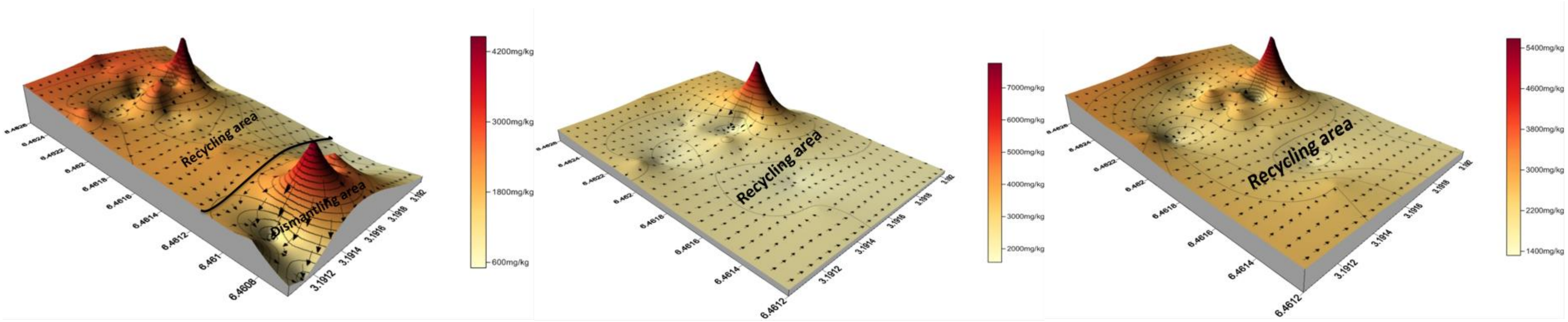


Ni distribution (wet season) in 0-10cm depth

Ni distribution (wet season) in 10-20cm depth

Ni distribution (wet season) in 20-30cm depth

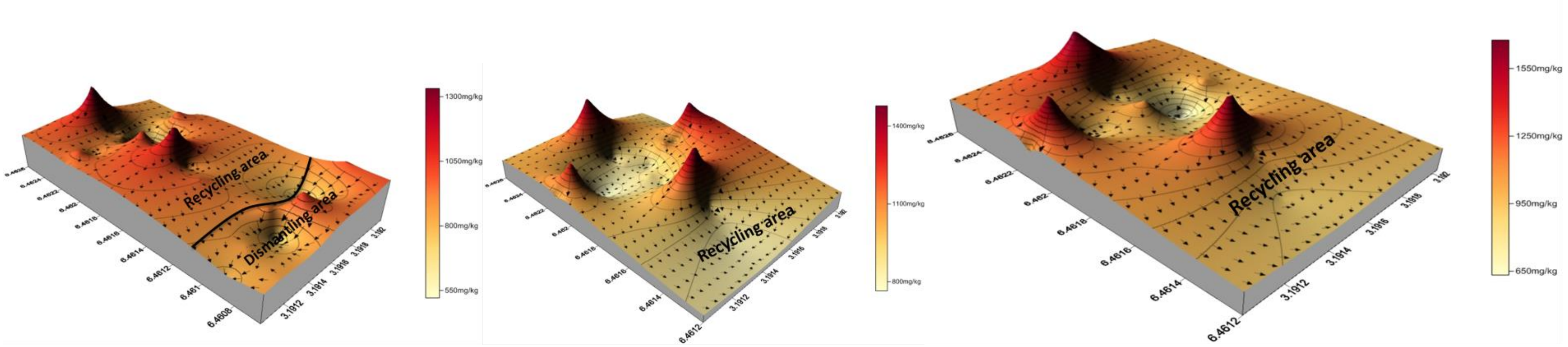
Figure 4.5: Spatial distribution of Ni in study site (including the recycling area and dismantling area).



Zn distribution (dry season) 0-10cm depth

Zn distribution (dry season) 10-20cm depth

Zn distribution (dry season) 20-30cm depth

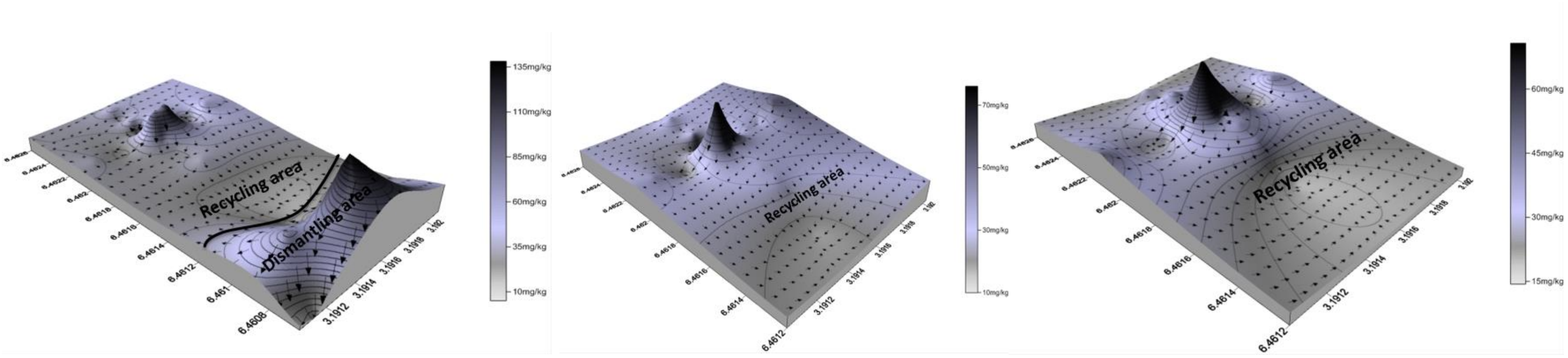


Zn distribution (wet season) 0-10cm depth

Zn distribution (wet season) 10-20cm depth

Zn distribution (wet season) 20-30cm depth

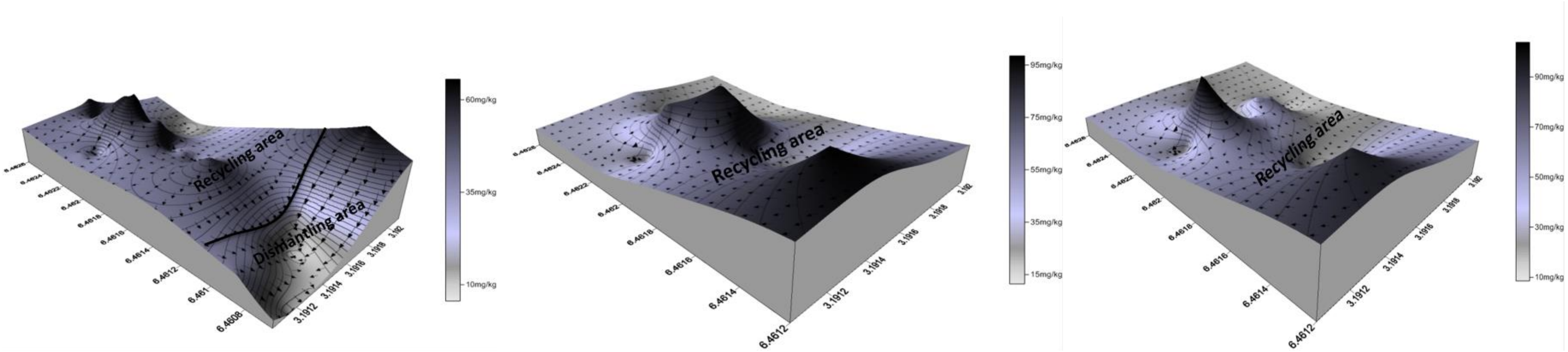
Figure 4.6: Spatial distribution of Zn in study site (including the recycling area and dismantling area).



Sb distribution (dry season) 0-10cm depth

Sb distribution (dry season) 10-20cm depth

Sb distribution (dry season) 20-30cm depth

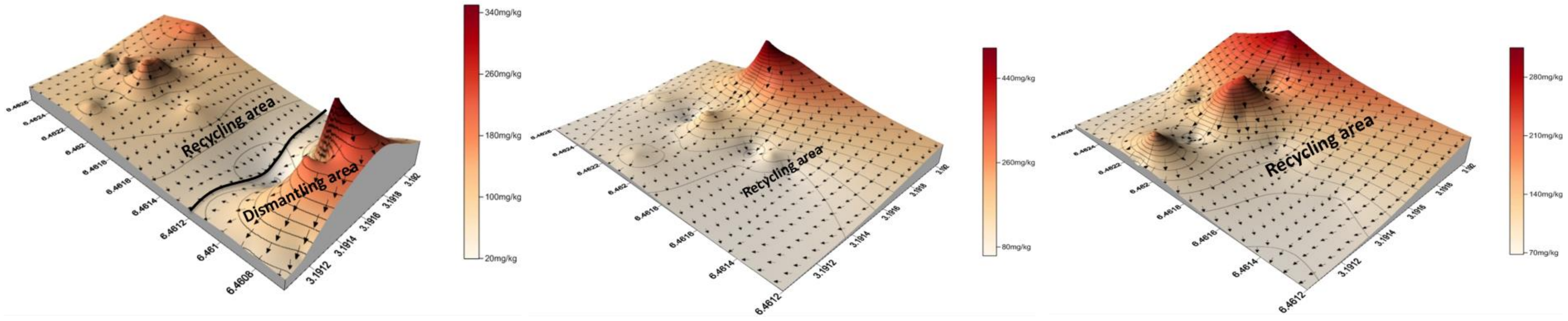


Sb distribution (wet season) 0-10cm depth

Sb distribution (wet season) 10-20cm depth

Sb distribution (wet season) 20-30cm depth

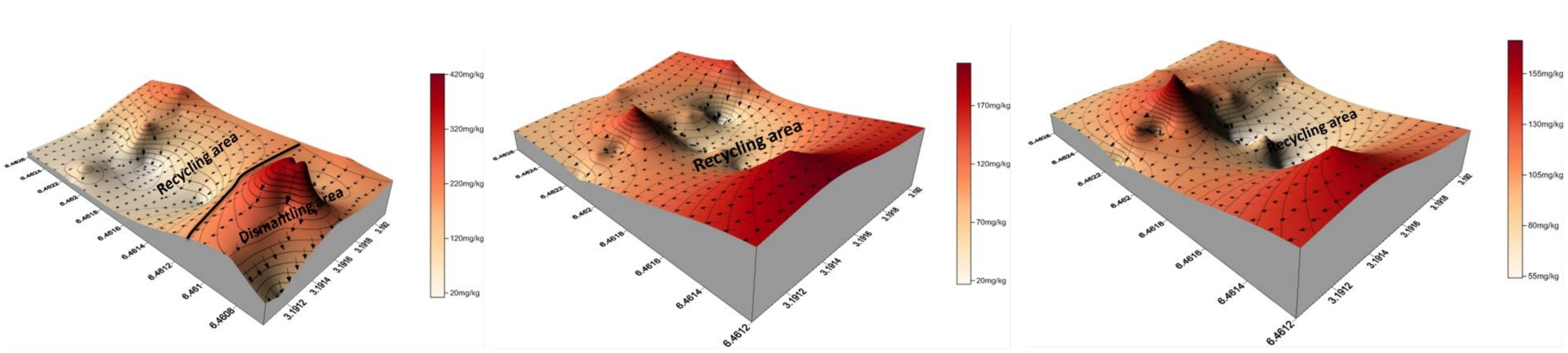
Figure 4.7: Spatial distribution of Sb in study site (including the recycling area and dismantling area).



Mn distribution (dry season) 0-10cm depth

Mn distribution (dry season) 10-20cm depth

Mn distribution (dry season) 20-30cm depth



Mn distribution (wet season) 0-10cm depth

Mn distribution (wet season) 10-20cm depth

Mn distribution (wet season) 20-30cm depth

Figure 4.8: Spatial distribution of Mn in study site (including the recycling area and dismantling area).

From Figs 4.1 to 4.8, a similar trend in the spatial distribution pattern was observed in Cd, Cu, Pb and Zn portraying hot spots clustered around the recycling sites. The distribution of Ni and Cr had the high concentrations with visible hotspots in the dismantling area. Sb and Pb had similar distribution pattern which is quite noticeable especially in the wet season maps but quite difficult to notice in the dry season maps especially 0-10cm because of the standalone hotspot which had the highest concentration of Pb when compared to other areas in the study site. The similarity in the distribution pattern could be attributed to the fact that Sb is usually alloyed with Pb to increase Pb durability in electronics (Sundar & Chakravarty, 2010) and when the informal recycling occurs both metals are released simultaneously in the environment. Furthermore, some metals are known to occur together in the environment as they compete for same binding sites in the soil such as Cd and Zn (ASTDR, 2004). It can be observed from the figures above, Zn and Cd have similar spatial distribution patterns, and the peaks where the highest concentrations are identified are similar.

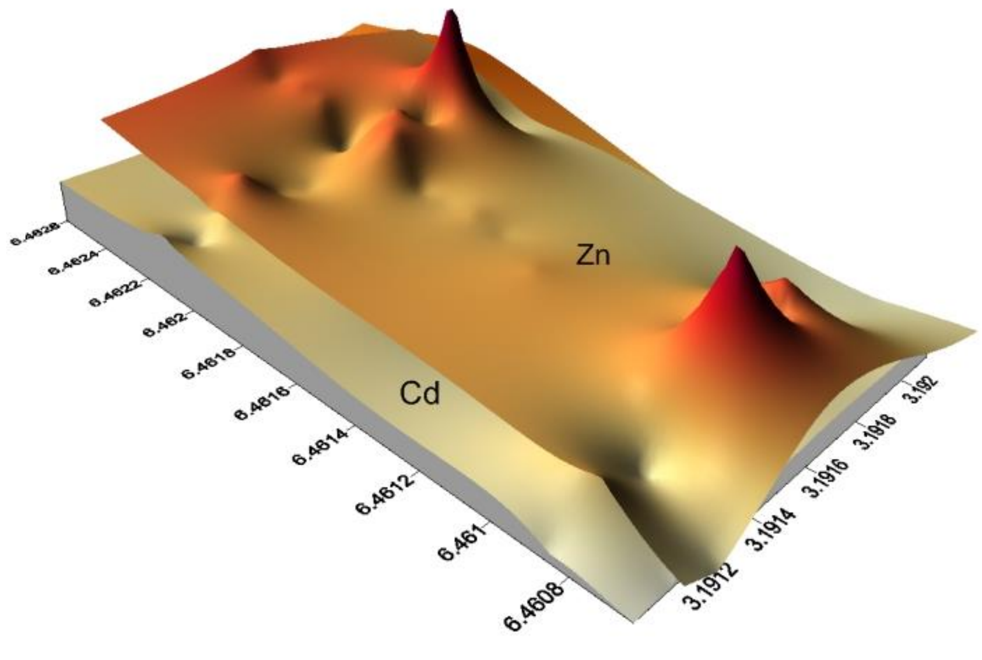


Figure 4.9: Overlay of dry season Cd and Zn spatial distribution maps showing the similarity in the spread pattern

Figs 4.9 and 4.10 give a clearer overview of the distribution pattern of Cd and Zn.

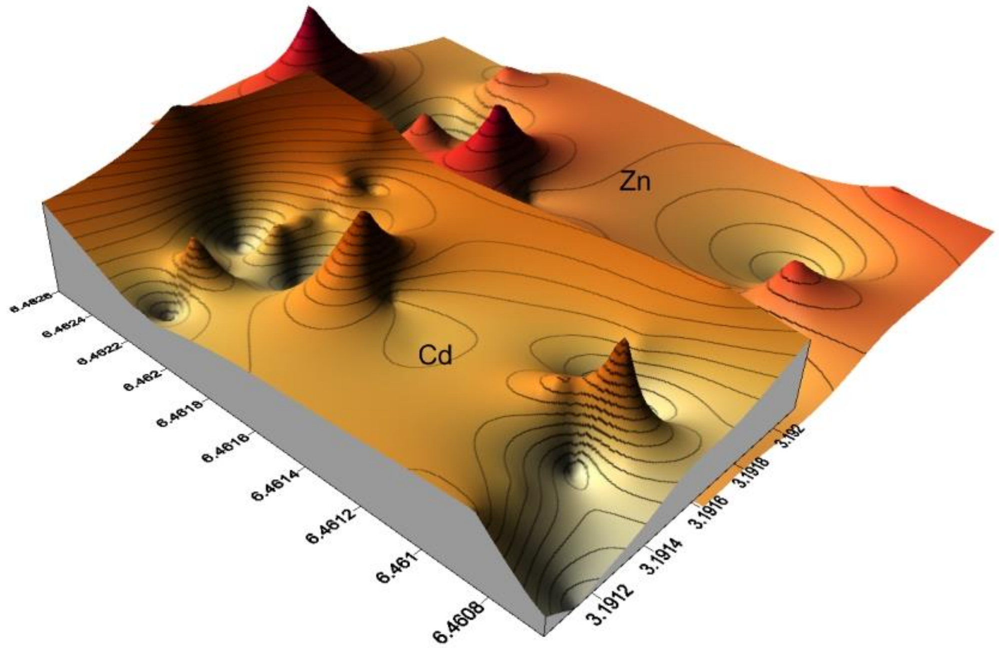


Figure 4.10: Break apart wet season maps of Cd and Zn showing similarities in the distribution pattern.

In the wet season, the hot spots were identified in slightly different locations from the dry season and could be attributed to temporal change, rainfall, surface runoffs, constant movement of people in and out of the site, particles movement due to wind and air movement and also the possible change in location of burning and other practices carried out on the site. This is in accordance with studies carried out by Rahman et al. (2014) who reported that spatial variability in heavy metals in the wet season is commonplace, especially for metals that are not complexed due to the heavy rainfall which causes runoff, with the soil or soil organic matter being flushed out to other positions.

A slight difference in the concentration and distribution of metals is observed in both seasons in the top surface, depth samples, although no significant statistical difference was observed between the metal concentrations in the different depths using the one way ANOVA. The presence of metals down the soil profile might be as a result of the soil properties (texture and CEC) which have been identified to promote leaching of contaminants. A significant difference ($p \leq 0.001$) in both seasons (dry and wet) was established between the Cd, Cu, Pb, Sb, Zn concentration at different distances from where most of the recycling occurs. The further away from the site activities, the lower the concentration of the metals found. The additional metal contamination may be occurring as a result of dispersion by air, water flow especially after rain and by movement of people in and out of the site.

4.5 Ecological risk assessment of the metal contamination at the study site

In assessing the potential risk posed by the e-waste recycling activities, different guidelines and indices as outlined in section 3.7 have been utilized and are discussed below.

4.5.1 Pollution assessment

In view of the potential pollution by metals, an assessment was carried out by comparison of measured mean metal concentration with guideline values of different regulatory bodies and also ranking the pollution with respect to background values. The mean concentrations of Cu, Pb, Sb and Zn are higher than the USEPA, ESDAT, DEFRA and Dutch guideline values. The mean values of Cd are higher than the target and intervention values of the regulatory bodies but not higher than the level for industrial sites according to DEFRA and the contaminated soil screening level by USEPA (Table 4.5).

Table 4.5: Comparison between the mean metal concentration (± S.D) in the site and SGVs

	Mean conc. (mg kg^{-1})	**Mean conc. (mg kg^{-1})**	**USEPA (mg kg^{-1})**	**ESDAT (mg kg^{-1})**		**DEFRA (mg kg^{-1})**		**Dutch (mg kg^{-1})**	
	Dry season	**Wet season**	**CSSL**	**TV**	**IV**	**Residential IV**	**Industrial IV**	**TV**	**IV**
Cd	**22.53±15.49**	**13.46±5.58**	70	0.8	12	1-8	1400	0.8	12
Cr	36.14±23.98	26.93±10.73	230	100	380			100	380
Cu	**3682± 1693**	**4723± 1485**		36	190			36	190
Mn	132.66±77.58	115.87±80.62							
Ni	39.81± 31.34	43.46±79.35	1600	35	210	50	5000	35	210
Pb	**2109±1460**	**1901.4±769.5**	400	85	530	450	750		
Sb	**37.76±22.25**	**34.57±22.36**		3	15			3	15
Zn	**2308±1108**	**978.6±245.9**		140	720			140	720

S.D= standard deviation, TV= Target value, IV= Intervention level, CSSL= Contaminated soil screening level, [3]DEFRA= Department for Environment Food & Rural Affairs, ESDAT= Environmental Data Management System, USEPA= United States Environment Protection Agency. Values highlighted exceed target values and intervention values.

Soil pollution is often assessed either by comparing total metal concentrations with guideline values or by ranking using pollution indices. The study found higher concentration of all metals in the e-waste site than that in the control site (Table 4.3). The results also indicate that the concentration of a number of metals (Cd, Cu, Pb, Sb and Zn) are significantly higher than the soil guideline values (SGVs) set by DEFRA, ESDAT and Dutch regulatory agencies (Table 4.5). SGVs, which are a screening tool for quantitative risk assessment of land contamination (DEFRA & EA, 2004), can be used as a starting point to evaluate long-term risks from contaminants in soil (Environment Agency, 2009). The evaluation of pollution using pollution indices has been established to be effective in determining the environmental

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[3] Values highlighted exceed target values and intervention values.

damage associated with the anthropogenic activities in comparison to control sites (Morton-Bermeaa, et al., 2009).

The contamination factors (CF) and pollution index (PLI) assess the extent of contamination (refer to section 3.7.1 for equations), using the suggested CF values by Hakanson (1980). This method for assessing pollution was initially developed for pollution of sediments (Tomlinson et al., 1980; Hakanson, 1980), but have since been applied to determine pollution of contaminated soils in a number of studies (Chen et al., 2005; Wei et al., 2009; Liang et al., 2011; Karim et al., 2015). With respect to background values, it is evident that the activities carried out on the site are the cause of the pollution as the contamination factors for each metal were elevated. Results presented in Table 4.6 establish the severity of the contamination using CF and PLI. In the dry season samples, using the mean values, Cd in the 0-10cm and 10-20cm soil samples were approximately 30 times and in the 20-30cm soil samples 25 times higher than the those in the control soil. For Cr, Cu and Pb these increases ranged between 110-230 times higher than the control soil except for Pb that was approximately 86 times higher than the control soil at 20-30cm depth. The mean contamination values of the selected metals indicate the site is highly contaminated.

The extent of pollution increases with the increase of numerical PLI value. The combined pollution load index (PLI) suggests extremely high level of pollution (Table 4.6) when compared with the classification (section 3.7.1) according to Tomlinson et al. (1980), although, based on the PLI values devised by Angulo (1996), a detailed site study and intervention would be advised. As suggested by Angulo, PLI value of ≥100 indicates an immediate intervention to stop pollution; a PLI value of ≥50 indicates a more detailed study is needed to monitor the site, the mean PLI of the site ranged >50 and>100.

Analysing the contamination with the indices of Tomlinson et al., (1980) and Angulo (1996) suggests that there is very high soil contamination. The Angulo’s index is favoured in this study as it has a broader range when compared to the index proposed by Tomlinson et al. (1980). In the wet season, the PLI values in the study site suggest that an immediate intervention to stop the pollution is required (Table 4.6).

Angulo (1996) observed that the mean PLI of a contaminated site is usually higher in dry season than in the wet season due to leaching; on the contrary, in this study, the mean PLI was higher in the wet season than the dry season. This could be traced to the soil samples collected from the control site with the total metal concentration differing significantly in both seasons; the dry season had higher values than the wet season. The lower metal concentration (control) in the wet season samples could be as a result of leaching (soil property) or surface runoff, thus affecting the PLI.

In pollution assessment, the use of values obtained from a control site (relatively uncontaminated site) is recommended when there are no established baseline values of the contaminants. Although Nigeria has a national environmental agency and individual states also have their own environmental agency, there are no documented baseline values for heavy metals in soil, thus the use of samples obtained from a control site in this study. The variability in the values from the control samples resulting in the higher PLI values in the wet season could have been minimized if there were documented baseline values.

Table 4.6: Pollution assessment in the study site

CFs and PLI of metals across the study site																		
	Dry season									Wet season								
	Cd	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Zn**		**Cd**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Zn**	
Recycling area																		
	CFs								**PLI**	**CFs**								**PLI**
0-10cm																		
Mean	30.33	118.17	222.92	61.38	58.21	117.28	172.73	89.47	92.10	28.2	121.26	503.94	73.01	80.24	186.10	235.73	52.77	**111.2**
Minimum	5.79	24.73	117.69	28.46	5.81	54.17	91.22	40.77	29.43	8.76	46.32	274.17	11.59	20.69	99.43	68.93	29.3	39
Maximum	80.69	344	483.40	107.45	213.71	466.68	390.91	199.10	240.5	54.44	248.95	806.54	203.17	205.72	384.59	442.53	78.2	222.84
10-20cm																		
Mean	29.98	110.76	227.27	74.09	64.73	110.57	152.86	100.77	94.13	34.93	138.95	512.24	73.28	191.38	189.60	271.8	58.36	**134.15**
Minimum	6.42	26.83	106.19	31.86	6.17	49.85	36.36	63.92	28.35	20.1	62	307.36	9.05	36.55	92.63	76.13	44	50.03
Maximum	80.39	292.67	389.59	276.59	226.14	449.07	370.68	333.39	274.1	65.33	254.95	788.38	163.93	225.45	260.78	657.33	86.74	227.66
20-30cm																		
Mean	24.94	111.96	229.93	79.20	58.4	85.55	142.59	99.47	88.02	29.96	140.26	530.49	77.01	122.13	208.13	222.2	61.36	**152.66**
Minimum	5.65	34	53.06	41.65	7.14	36.52	63.45	47.82	27.6	10.1	48.58	138.49	17.35	40.83	85.25	56.33	35.81	41.18
Maximum	61.90	251.57	409.66	168.30	125.86	178.81	336	240.68	193.39	54.89	224.78	786.31	138.25	320.34	366.73	714.33	98.33	240.16
Dismantling area																		
Mean	11.82	122.6	215.30	135.58	110.57	44.18	102.32	35.16	72.26	19.26	261.05	609.95	95.87	82.45	172.31	389.33	110.78	**143.54**
Minimum	3.24	80.6	22.38	48.08	15.14	5.58	24.41	26.95	18.8	1.96	71.16	229.98	20.95	4.72	55.29	32	29.35	25.24
Maximum	24.59	167.23	408.5	233.03	285.71	78.1	297.13	43.82	135.51	56.96	469.32	962.34	298.41	193.55	351.89	940	257.84	325.73

PLI value of ≥100 indicates an immediate intervention to stop pollution; a PLI value of ≥50 indicates a more detailed study is needed to monitor the site, whilst a value of <50 indicates no drastic measures are needed at the site.

*Highlighted values indicate PLI values >100

Table 4.7: Potential ecological risk at the study site

Potential ecological risk index of metals in the study site																		
	Dry season									**Wet season**								
	Cd	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Zn**		**Cd**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Zn**	
Recycling area																		
	Individual risk factors (Er)								**PERI**	**Individual risk factors (Er)**								**PERI**
0-10cm																		
Mean	909.9	236.34	1114.6	61.38	291.05	586.4	172.73	89.47	3461.87	846	242.52	2519.7	73.01	401.2	930.5	235.73	52.77	5301.43
Minimum	173.7	49.46	588.45	28.46	29.05	270.85	91.22	40.77	1271.96	262.8	92.64	1370.85	11.59	103.45	497.15	68.93	29.3	2436.71
Maximum	2420.7	688	2417	107.45	1068.55	2333.4	390.91	199.1	9625.11	1633.2	497.9	4032.7	203.17	1028.6	1922.95	442.53	78.2	9839.25
10-20cm																		
Mean	899.4	221.52	1136.35	74.09	323.65	552.85	152.86	100.77	3461.49	1047.9	277.9	2561.2	73.28	956.9	948	271.8	58.36	6195.34
Minimum	192.6	53.66	530.95	31.86	30.85	249.25	36.36	63.92	1189.45	603	124	1536.8	9.05	182.75	463.15	76.13	44	3038.88
Maximum	2411.7	585.34	1947.95	276.59	1130.7	2245.35	370.68	333.39	9301.7	1959.9	509.9	3941.9	163.93	1127.25	1303.9	657.33	86.74	9750.85
20-30cm																		
Mean	748.2	223.92	1149.65	79.2	292	427.75	142.59	99.47	3162.78	898.8	280.52	2652.45	77.01	610.65	1040.65	222.2	61.36	5843.64
Minimum	169.5	68	265.3	41.65	35.7	182.6	63.45	47.82	874.02	303	97.16	692.45	17.35	204.15	426.25	56.33	35.81	1832.5
Maximum	1857	503.14	2048.3	168.3	629.3	894.05	336	240.68	6676.77	1646.7	449.56	3931.55	138.25	1601.7	1833.65	714.33	98.33	10414.07
Dismantling area																		
Mean	354.6	245.2	1076.5	135.58	552.85	220.9	102.32	35.16	2723.11	577.8	522.1	3049.75	95.87	412.25	861.55	389.33	110.78	6019.43
Minimum	97.2	161.2	111.9	48.08	75.7	27.9	24.41	26.95	573.34	58.8	142.32	1149.9	20.95	23.6	276.45	32	29.35	1733.37
Maximum	737.7	334.46	2042.5	233.03	1428.55	390.5	297.13	43.82	5507.69	1708.8	938.64	4811.7	298.41	967.75	1759.45	940	257.84	11682.59

Er <40 is low risk; 40 ≤ Er < 80 is moderate risk; 80 ≤ Er < 160 considerable risk; 160 ≤ Er < 320 high risk and Er ≥ 320 is very high risk.

PERI < 150 is a low ecological risk; 150 ≤ PERI < 300 is moderate ecological risk; 300 ≤ PERI < 600 considerable ecological risk; and PERI ≥600 is very high ecological risk.

4.5.2 Potential ecological risk assessment

The ecological risk is assessed using potential ecological risk index (PERI) which estimates the potential ecological risk based on the contamination factor and toxicity level of each metal (refer to section 3.7.2 for equation).

The analysis shows that the risk posed by individual metals in the soil samples varied (Table 4.7). Zn ranged between moderate risk and considerable risk, Cr was high risk ($160 \leq Er < 320$), Cd and Cu, very high risk ($Er \geq 320$). Mn ranged between moderate risk and considerable risk, and Pb ranged between high risk and very high risk. Based on the PERI, the study site presents a very high ecological risk from the cumulative impact of all the identified metals. Furthermore, the potential ecological risks of the metals in the soil samples from the e-waste recycling site were mainly contributed by Cu followed closely by Cd and Pb (Table 4.7). The advantage of potential ecological risk assessment lies in the consideration of the heavy metal toxicity, reflecting the impacts of the different contaminants (Song et al., 2015); it could be inferred that the input of Cd in the soil within the study site is of great concern because of its high toxic-response factor and its presence in the environment at concentrations higher than soil guideline values (SGVs) (Table 4.5).

The heavy metal contamination was also observed up to the 20-30cm depth within the soil, although not very deep, is an indication of heavy metal migration further down the soil profile, arising from long term and continuous recycling activities and thus, suggesting a risk of contaminating surface and groundwater around the study site. Overall, the evaluation of the results using the different indices for pollution assessment and assessing risk established the presence of pollution and high ecological risk irrespective of the season.

CHAPTER FIVE

5 Integrating bioavailability and bioaccessibility in risk assessment

Chapter 4 presented the total metal concentration, the level of pollution on the study area and evaluated the potential risks due to the presence of metals in the site. The usefulness of bioavailability and bioaccessibility in risk assessment as against the use of total contaminant concentration was outlined in Section 2.8; this chapter presents results and discusses the potential bioavailability and bioaccessibility and implication in risk assessment, the relationship between fractions in chemical speciation and bioaccessibility and the influence of soil properties on bioaccessibility.

The term ‘bioavailability’ has been used extensively in scientific literature; however, its definition may vary depending on discipline-specific designation (Ng, et al. 2015). Environmental scientists consider bioavailability to represent the accessibility of a solid-bound chemical for possible toxicity (Alexander, 2000). In the environment, only a portion of the total concentration of a chemical present is potentially available for uptake by organisms. For instance, in the case of metals, the potentially bioavailable fraction could be the freely dissolved ion of the metal while other forms of the metal bound in precipitates or covalent or hydrogen bonded to other ions would not be available (USEPA, 2000). Bioavailability processes describe a chemical’s ability to interact with the biological world and they are quantifiable through the use of multiple tools such as sequential extraction as described in section 5.1 below. On the other hand, bioaccessibility is usually evaluated by *in vitro* digestion procedures, simulating gastric and small intestinal digestion and respiration procedures using simulated lung fluids, this is because a good estimation of bioavailabilty *in vivo* is difficult. Semple et al. (2004) suggest that contaminant bioavailable fraction in soil represent the freely dissolved compounds in pore water while the bioaccessible fraction is that available to enter the human system from the environment which is potentially absorbable.

5.1 Chemical characterization, bioavailability and potential mobility of metals in the study site

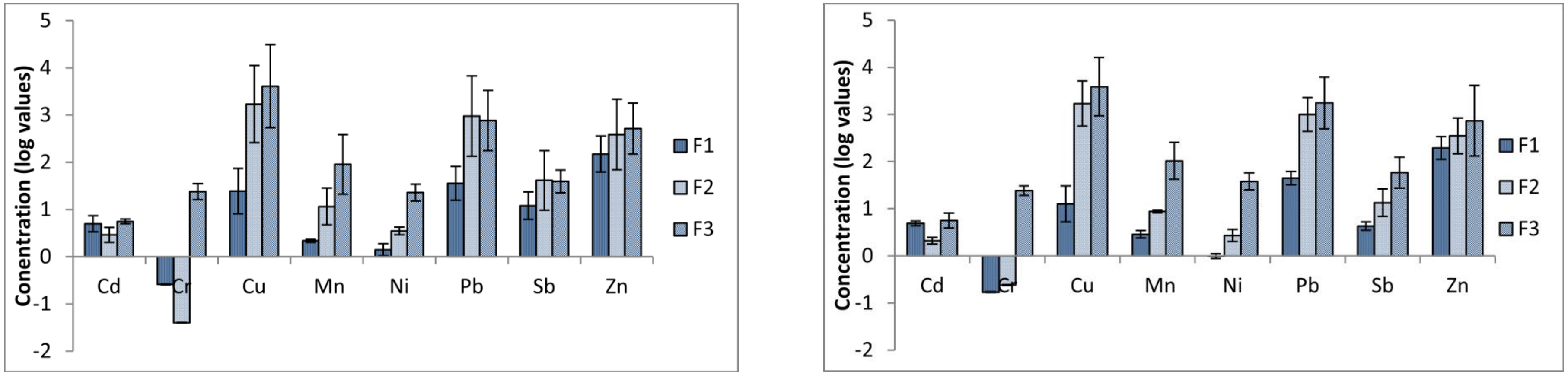
The sequential extraction method detailed in section 3.5.2 fractionates the heavy metals in the soil in the order of decreasing solubility into different operationally defined geochemical phases: F_1 is the easily exchangeable fraction, which represents the readily available fraction was leached out using a neutral salt solution without pH buffer capacity; F_2 represents the organically bound fraction extracted with EDTA and F_3, represents the residual fraction digested using a strong acid. Heavy metals have different speciation patterns, the concentration of the different fractions are represented in Figs 5.1 and 5.2 and the percentage mean metal associated with each fraction is presented in Fig 5.3. The results of this study show the percentage association with F_1 in descending order: Cd > Sb > Zn > Cu > Ni > Pb > Cr. The second fraction (F_2) is bound to organic matter and, under oxidizing conditions, degradation of organic matter leads to the release of the metals bound to this fraction. The mean percentage association with F_2 occurred in the order: Pb > Sb > Zn> Cu > Cd > Mn > Ni > Cr. The third fraction (F_3) is associated with alumino-silicate minerals and the mean percentage association with F_3 in descending order is as follows: Cr > Ni > Mn > Cu > Zn > Pb > Sb > Cd.

5.1.1 The importance of speciation in assessing risk of metals in the study site

As shown in Figs 5.1 – 5.3, metals may occur in different chemical forms as they either interact chemically or physically with other compounds or may also be partitioned into different fractions such as exchangeable, dissolved, organic and crystalline fractions. These fractions are usually associated with the bioavailability and mobility of the metals in soil.

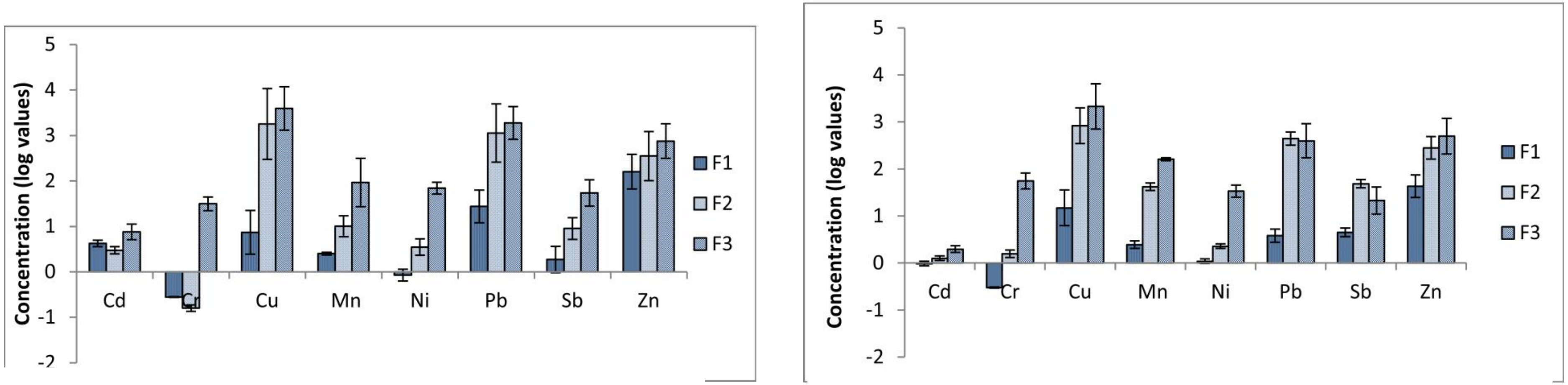
Mobility is a concept used in soil science to estimate the risk of contamination of other environmental compartments (Domergue & Védy, 1992). This means the distribution of metals in different phases, their contamination risk in the environment, and subsequently to plants, water bodies and humans can be determined (Krishnamurti, 2008). The exchangeable fraction, also known as the non-specifically adsorbed fraction, can be released by the action of cations displacing weakly bound metals; is easily dissolved and easily mobilized and taken up by biota. The organic fraction consists of metals bound to organic matter and can be mobilized with time, oxidation or decomposition. The crystalline fraction, which is also known as the residual fraction, is not usually available to biota as the metals are tightly bound within the structures of the soil (Salomons, 1995; Gleyzes et al., 2002).

Sequential extraction provides detailed information on the partitioning of the metals by their associations with phases or fractions allowing characterisation into exchangeable, carbonates, organic-bound and residual forms (Sahuquillo et al., 2003). The procedure by Tessier et al., (1979) is the commonly used protocol; however, have been modified over the years as outlined above (section 2.8.1). The protocol adopted (Carapeto & Purchase, 2000), characterised the metals into 3 phases which are of importance in this study; the potential bioavailable fraction being the most important.



Concentration (mg kg^{-1}) in different fractions in 0-10cm depth in the recycling

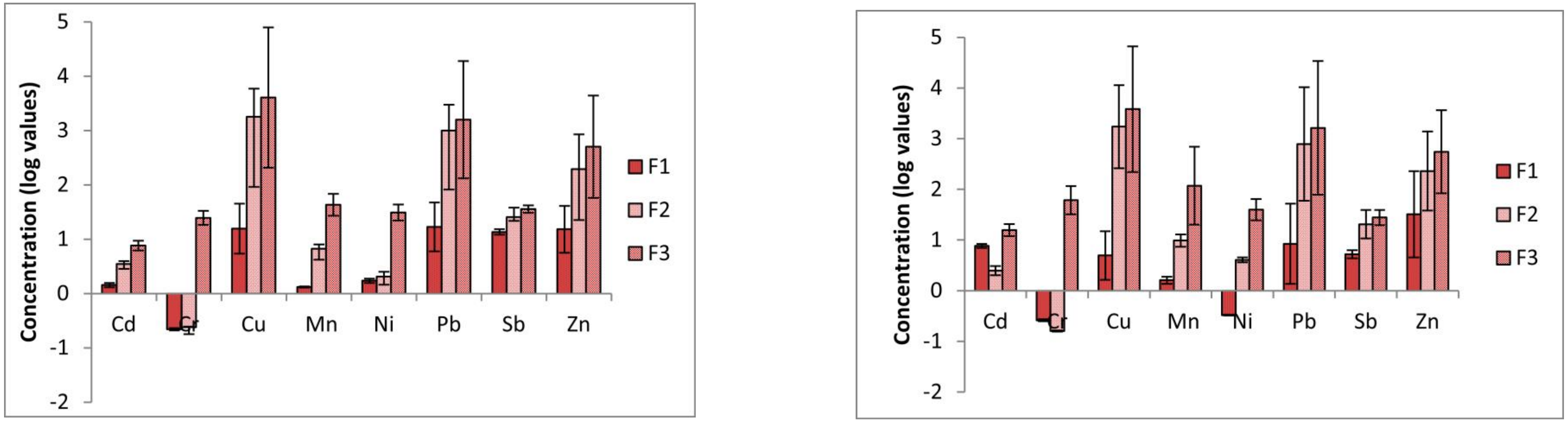
Concentration (mg kg^{-1}) in different fractions in 10-20cm depth in the recycling area



Concentration (mg kg^{-1}) in different fractions in 20-30cm depth in the recycling area

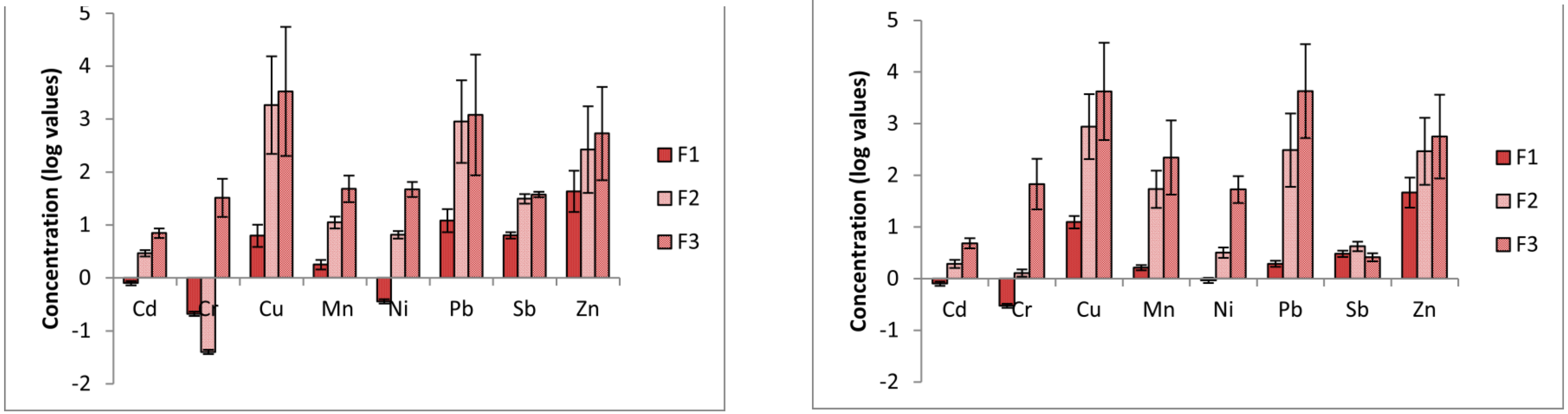
Concentration (mg kg^{-1}) in different fractions in 0-5cm depth in the dismantling area

Figure 5.1: Mean metal concentration ± S.D (dry season) in different chemical fractions



Concentration (mg kg^{-1}) in different fractions in 0-10cm depth in the recycling area

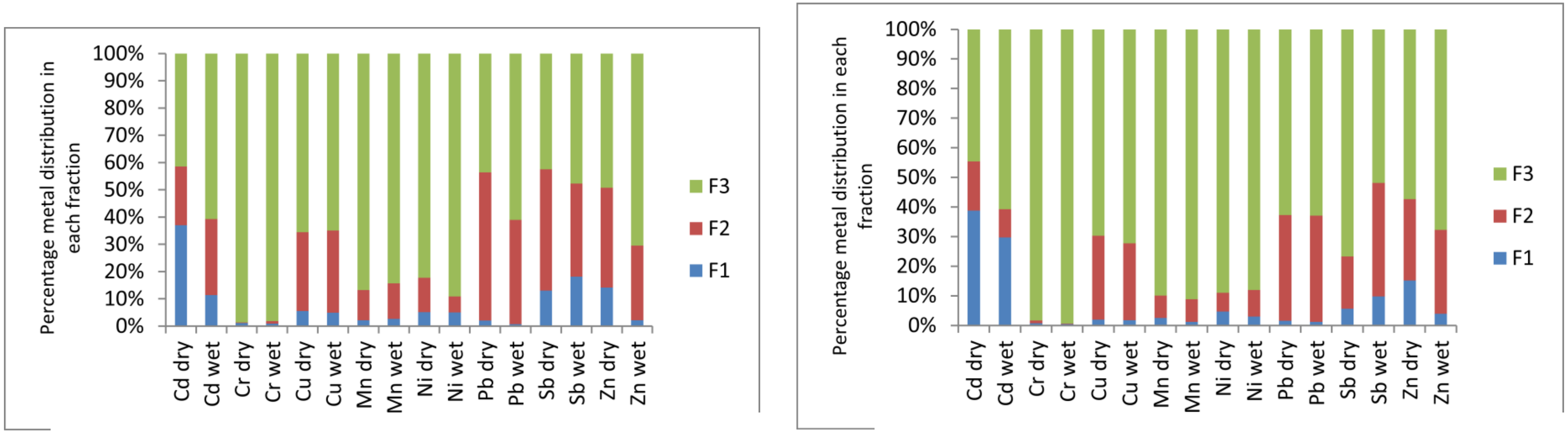
Concentration (mg kg^{-1}) in different fractions in 10-20cm depth in the recycling



Concentration (mg kg^{-1}) in different fractions in 20-30cm depth in the recycling area

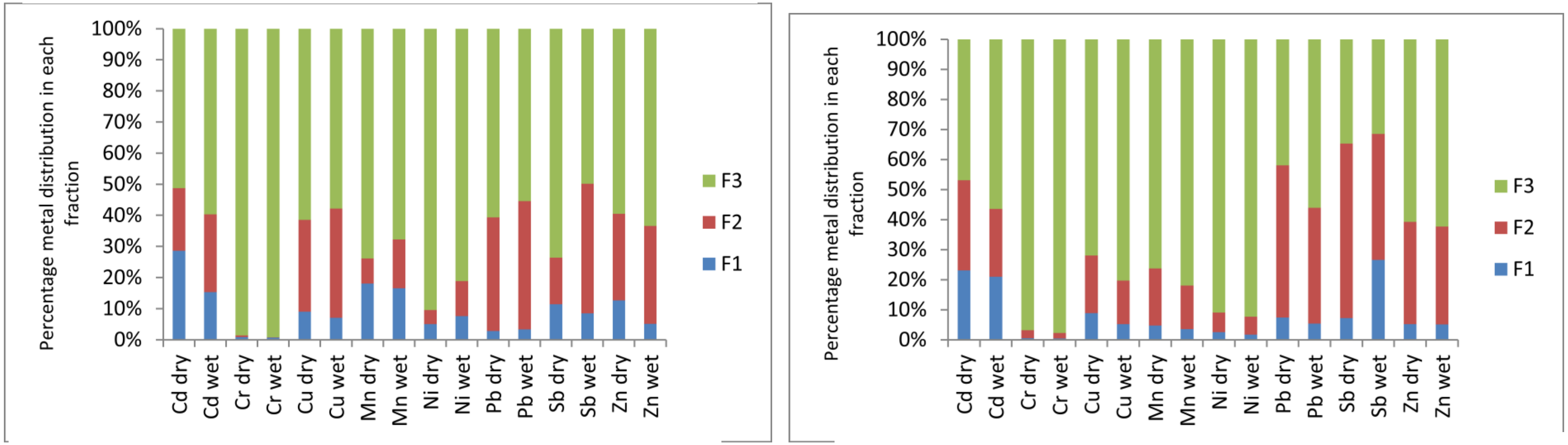
Concentration (mg kg^{-1}) in different fractions in 0-5cm depth in the dismantling area

Figure 5.2: Mean metal concentration ± S.D (wet season) in different chemical fractions



Percentage mean of the metals in different fractions in the 0-10cm soil of the recycling area

Percentage mean of the metals in different fractions in the 10-20cm soil of the recycling area



Percentage mean of the metals in different fractions in the 20-30cm soil of the recycling area

Percentage mean of the metals in different fractions in the soil of the dismantling area

Figure 5.3: Percentage metal fractionation in the study site

From the speciation analysis, Cr is largely associated to the residual fraction (95%); 10% of Cu was in the exchangeable fraction and between 20% and 30% was bound to organic matter. Approximately 30% of Sb was associated with the exchangeable phase and 40% was bound to organic compounds. Sb binds very well with organic matter to form other complexes. This differs from studies carried out by Casado et al. (2007) and Flynn et al. (2003) who reported that, although the total concentration of Sb in the soil may be high, Sb has low availability and mobility. However, a study carried out by Baroni et al. (2000) highlighted that Sb can be readily available and absorbed.

About 20% of the total Zn content was associated with the exchangeable fraction and approximately 50% bound to the residual fraction; Ni was bound to the residual fraction of the soil, between 8% and 20% of the total Ni was associated with the exchangeable phase. Ni has the ability to form soluble complexes with soil and is also known to bind with organic matter in the soil and form complexes which become mobile under appropriate conditions (ATSDR, 2005). Approximately 10% of Pb was in the exchangeable fraction; about 50% of the Pb content is associated with the organic matter as it is known to bind firmly with organic matter soil to form stable complexes (Halim et al., 2005; Santiago-Martín et al, 2014). Finally, between 20% and 40% Cd is associated with the exchangeable fraction.

The results imply that Cd is the most bioavailable metal in the site closely followed by Sb and Cr is least available for uptake. The results obtained in this study accord well with earlier research by Luo et al., (2011) and Damasceno et al., (2015); in the study by Luo et al., (2011), Cu, Cr, Ni and Pb were predominantly associated with the residual fraction and Cd attributed to the exchangeable fraction. Rivera et al., (2016) established Pb to be easily extracted with EDTA and Cd being associated with the exchangeable fraction. Also, studies carried out by Takáč et al., (2009) attributed metals extracted with EDTA as potential mobilizable fraction with up to 99.6% of Pb in their study associated with this fraction.

Furthermore, using a similar method as used in this study, Damasceno et al., (2015), found Cu, Ni, to be strongly associated with F2 and F3, 67% of Zn was attributed to F3 (the residual fraction), and 92% Pb associated with F2. They suggested that the high levels of Pb in F2 was as result of the complexation with humic substances formed by composting in presence of e-waste; Pb was attributed the most bioavailable metal in their study.

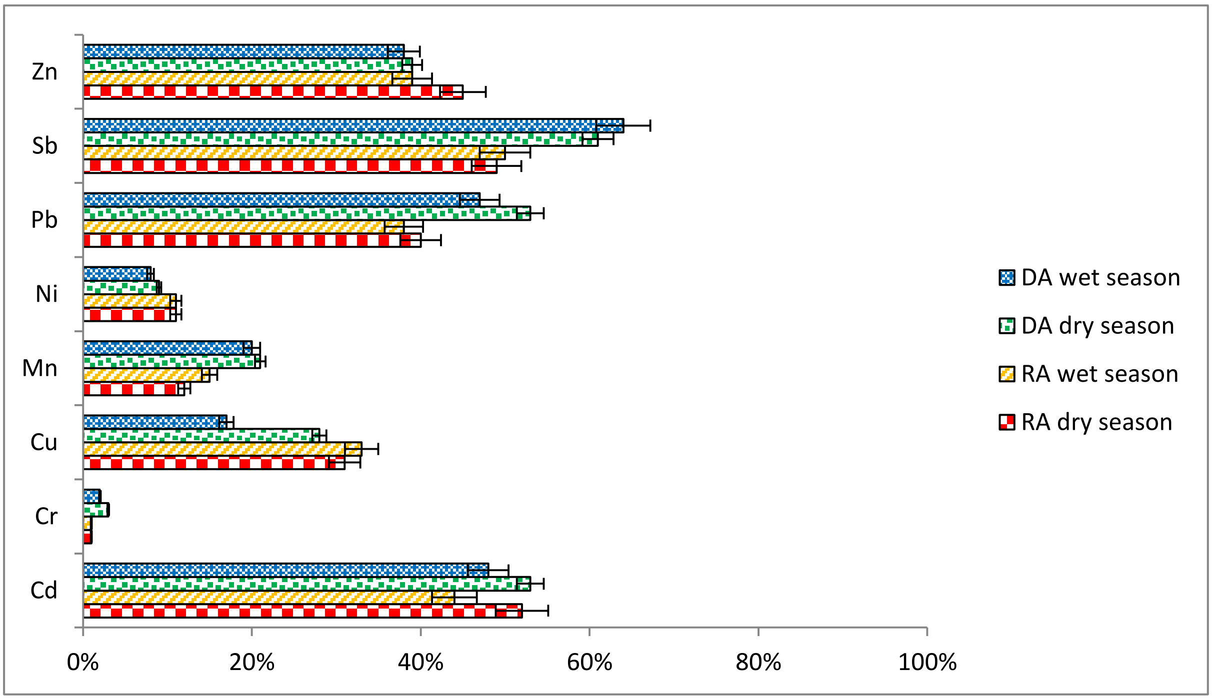
Olaniran et al., (2013) stated that EDTA is the most suitable solvent used in single-step extraction procedure for determination of the bioavailable fraction in soils according to the European Commission's standards, measurements and testing programme. According to Ure (1996), Rauret (1998) and Rivera et al., (2016), EDTA extracts metals from the exchangeable metal fraction, organic matter fraction, Fe and Mn oxy-hydroxides, and metals bound to carbonate fraction and thus environmentally available since the resulting bioavailability of the metals is demonstrated in the long term. Furthermore, Sahuquillo et al., (2003) also defined the fraction extracted by EDTA as being potentially mobile since the mobility has been demonstrated in plant root system. EDTA promotes high mobility, which may increase the potential migration of metals, thus leading to potential adverse environmental and health effects (Luo et al., 2005; Meers et al., 2005; Luo et al., 2006).

The use of EDTA and DTPA in extraction of metals such as Cd, Pb, Cu, Mn, Zn from soils has also been demonstrated to be positively correlated with the organic matter content in the soils (Dai, et al., 2004; Fanrong, et al., 2011). Although EDTA has also been widely used in different studies as a prediction of heavy metal bioavailability (Ghestem & Bermond, 1998; Manouchehri et al., 2006); used in increasing the extraction of soluble metals especially Pb in contaminated soils, subsequently enhance uptake by plants (Sun et al., 2001) and also used in the removal of metals from soil (Zeng et al., 2005). It is noteworthy that availability differs in organisms even in the same environment and bioavailability determination should be comparable to soil activities *in situ*; hence the conservative use of the term "potential mobility" in describing the fraction extracted with EDTA is used in this study.

According to Yang et al., (2014), the higher percentage of non-residual fraction the soils contain, the easier it is for metals to be released. The association of metals with the different geochemical fractions also represents the potential bioavailability and mobility of the metals. The potential mobile fraction in this study is classed as F_1+F_2 while the readily available fraction and bioavailable is F_1.

Potential mobility of metals = $\frac{F1+F2}{F1+F2+F3} * \mathbf{100}$------------------------Equation 5.1

From the sequential extraction, the potential bioavailability of metals within the study site in both seasons decreased in the following order: Cd > Sb > Zn > Cu > Mn > Ni > Pb > Cr while the observed potential mobility in the study site decreased in the order: Sb > Cd > Pb > Zn > Cu > Mn > Ni > Cr as summarized in (Fig 5.4).



Where DA is dismantling area and RA is recycling area

Figure 5.4: Mean potential mobility of metals in the study site

The sum of concentrations of metals in the non-residual (F_1+F_2) geochemical fraction can be used to express the potential mobility of metals (Fig 5.4). The percentage potential mobility for Sb ranged between 48% and 65%, Pb ranged from 40% to 55%, Cd from 44% to 55% and Cr ranged between 1% and 4% across both seasons. Sb has the highest mean potential mobility when compared to other metals while Cr has the least mobility. Although the order of potential mobility is quite similar to the potential bioavailability; Pb with a low availability has an increased potential mobility, because metals bound to the organic fraction tend to become potentially mobile as a result of organic matter degradation and strong redox conditions.

Potential bioavailability and mobility is an indication of the risk posed by metals in the environment. In terms of bioavailability, Cd poses the most risk as it is readily available for uptake in the environment. Sb also poses a risk as being most potentially mobile with the tendency of being taken up and released into the environment. The environmentally available (bioavailable and potential mobile fractions) metals can be transported through the soil profile by percolating water and eventually enter the groundwater system (Rivera et al., 2016). Cr poses least threat as it is bound tightly to the residual fraction. The metals bound to silicate and crystal lattice (residual fraction) are often considered to be of little risk because they are not easily released. However, interaction with the soil's physico-chemical parameters, geochemical changes and weathering could cause this fraction to be potentially mobile, thereby making it a fraction that should not be ignored. According to Okoro et al. (2012), the residual fraction is a useful tool in assessing the long term potential risk of metals in the environment.

5.1.2 Relationship between soil properties and metal speciation

A number of studies (ATSDR, 2004; Li et al., 2010; Matos et al, 2011; Wuana & Okieimen, 2011) have established that the potential bioavailability and mobility of metals in soils largely depends on their association with different phases; the association is in turn dependent on the soil properties. These studies have shown that the bioavailability and mobility of heavy metals are controlled by adsorption and desorption characteristics in soils which have been associated with the physico-chemical parameters of the soil such as texture, pH, OMC, CEC, redox potential, mineralogy, total metal concentration, amongst other parameters. Therefore, this section of the study seeks to establish if there is any geochemical control in the potential bioavailability and mobility of metals in the study site. It is noteworthy that only the metals that shared a significant relationship are discussed.

In F_1, an inverse relationship was established between the pH and Cd content ($r=-0.773$, $p \leq 0.001$). A decrease in the soil pH will increase the Cd content in that fraction. An inverse relationship was also established between the CEC and Cd ($r=-0.384$, $p \leq 0.001$) and a positive weak relationship between the %OMC and Pb ($r=0.38$, $p \leq 0.05$).

In F_2, a correlation was observed between pH and Cu, Mn, Pb and Sb in F_2 ($r=-0.544$, $p \leq 0.005$; $r=0.398$, $p \leq 0.01$; $r=-0.273$, $p \leq 0.01$; $r=-0.371$, $p \leq 0.05$ respectively). The relationship indicated that a decrease in pH will increase the concentration of Cu, Pb and Sb associated with F_2. Correlation was also observed between the % OMC and Cu, Mn, Pb concentration in F_2 ($r=0.613$, $p \leq 0.005$ $r=-0.43$, $p \leq 0.005$ 0.472, $p \leq 0.001$) respectively which could be interpreted as a decrease in % OMC content would increase the concentration of Mn associated with F_2, while an increase in the %OMC content would increase the concentration of Cu and Pb associated with F_2. Finally, a relationship between CEC and Cd in F_2 was also established ($r=-0.331$, $p \leq 0.005$) which indicates a small but significant correlation that decrease in the CEC level in the soil will increase the concentration of Cd associated with F_2.

The soil texture is dependent and can be described as a representation of the disposition of the particle size and the content of components which either promotes or inhibits the bioavailability and mobility of metals in soil. A high degree of metal extractability was reported in sandy soils and it was attributed to the low ionic binding strength in these soils (Rieuwerts et al., 1998). A study by Eriksson (1989) found that irrespective of the total Cd content in soils, it was more soluble and easily released in sandy soils than any other soil type which was observed in this study.

The soil pH is said to be most important factor because of its strong effect on solubility, sorption and mobility of metals in the different fractions; the mobility of metals (and thus the bioavailability) are enhanced at a low pH as a result of increased proton concentration (ATSDR, 2005; Rieuwerts, 2007; Shreene, 2010; Santiago-Martín et al., 2014). In this study, it can be inferred that the neutral to alkaline pH of the study site affected the potential mobility and bioavailability of most of the metals. It was established that a decrease in the soil pH would increase the bioavailibity of Cd and the mobility of Cu, Mn, Pb and Sb. It is important to mention that the change in mobility of the metals due to pH, is as a result of the pH dependence of some soil components adsorption sites, which become less negatively charged as pH decreases, favouring the adsorption of anions and the desorption of cations at these sites. To an extent, the CEC of a soil is not only dependent on the pH as previously mentioned but also on mineralogy and particle size, the finer particles contribute a larger surface area resulting in many more potential exchange sites (Ersahinet al. 2006). Therefore knowing the mineralogy and of the soils samples collected from the study site as sandy loam (coarse particles) may give some further understanding the on metal mobility.

Several studies (Finzgar et al., 2007; Shreene, 2010) have shown that the organic matter content decreases mobility and bioavailability as it retains metals by complexation, adsorption and ion exchange. The correlation in this study showed that an increase in the %OMC will lead to an increase in the concentration of Cu and Pb associated with the organic bound fraction while a decrease in the %OMC will lead to an increase in Mn associated with this fraction. Organic matter content also plays an important role in the mobility of metals within the soil as the break down products of organic matter contain acidic functional groups that are able to form metal complexes which can result in the metal being either bound to a solid state, or if the organic matter is dissolved, enhance metal mobility. This was observed with the use of EDTA as an extractant in this study, organic matter was dissolved and the mobility of the metals especially Pb was enhanced (section 5.1.1). The ability for organic matter to bind metals is also dependant on pH as the lower the pH the more likely functional groups will be protonated and unavailable for forming complexes with the result of releasing complexed metals into solution while an increase in pH will result in the functional groups being available and allowing the formation of metal complexes (McLean and Bledsoe 1992).

Furthermore, the concentration of Cd, Cr, Cu and Zn in F_1 and F_2 where significantly higher in the dry season than in the wet season ($p \leq 0.005$) while there was no significant difference in Mn, Ni, Pb and Sb. This could be as a result of the poor draining during the wet season as suggested by Hodson et al., (2011), who reported that since some metals can exist in more than one oxidation state and the lower oxidation state ions are more soluble, under reducing conditions the concentration of metals in the pore water often increases. As such, when soils are water-logged, they become anaerobic, the oxy-hydroxides of Fe, Al and Mn in the soil become unstable and dissolve, and so the release of metals initiated by waterlogging is partially offset by the precipitation of sulphides, which can reduce metal availability (Hodson et al., 2011).

5.1.3 Fate of heavy metals in soils

Heavy metals when accumulated in soils behave differently depending on the environmental conditions and soil properties. The fate of metals in the soil surface is dominated by soil process which depend on the soil properties because they cause interactions which can influence the metal distribution (ATSDR 2007; Finzgar et al., 2007; Shreene, 2010). In section 4.1 and 4.2 above, the basic soil characteristics (soil texture, pH, OMC and CEC) which govern and determine the behaviour of different metals have been investigated and discussed. Other physicochemical processes which influence the behaviour and transformation of metals in soil environments include sorption, solution complexation, oxidation-reduction, and precipitation-dissolution reactions. Interestingly, the adsorption/desorption reactions of metals on/from soil sorbents are influenced by pH, nature of soil components, and presence and concentrations of cations and inorganic anions (Caporale & Violante, 2016).

The distribution and behaviour of metals in soils is difficult to predict because the mechanisms of mobility through the different soils horizons diverse (Pontoni, et al., 2016). Sequential extraction which is widely used technique for understanding metal distribution in the solid phase (Rauret, et al., 1999) has been carried out in this study and discussed in section 5.1.1. However, heavy metals migrate differently in soil types because their metal adsorption capacity. For instance, in calcareous soils, the presence of carbonates is a major factor controlling the heavy metals availability because the carbonates control the pH (ATSDR, 2004). In this study, the soil type is loamy sand, sandy soil is coarser grained and has higher porosity, very low organic matter and carbonate content in comparison to other soil types, hence lower adsorption capacity which would promote migration. However, this was not the case in this study because metals can also be retained in the sand soil by specific adsorption of some Fe and Al, since the sand soil is rich in these oxides. The concentration of Al and Fe present in the samples were also measured and are attached in Appendix 5. Since it has been established that sandy soils have low carbonate content (Pontoni, et al., 2016), there is an indication that most of the Fe in the soil samples obtained from the study site might be in oxide or hydroxide forms. These oxides could bind the metals by adsorption and prevent migration of metals such as Cr, Cu, Pb in the soil. Also, it would be expected that precipitation (wet season samples) might have total control of the metals migration, but the amount of Fe oxides can cause adsorption of metals to occur in a slightly different space and slightly prevent total migration (Figs 4.1 to 4.8). The metals in this study are typically retained in the soil due to inner-sphere adsorption[4] between the metals and the Fe, Al and Mn oxides. These inner-sphere complexes are restricted to ions that have a high affinity for surface sites and in contaminated sites, metal ions compete for binding sites (ASTDR, 2007). Apart from the constant recycling and dismantling occurring at the study site making there conspicuous hot spots, the competition of metals for same binding sites could also be the reason for metals accumulating around same areas (Fig 4.1 to 4.8) since sorption is the dominant reaction, resulting in the enrichment of metals in soils. Since Fe and Al oxides in the soil influence the retention and release of metals by soil (Richter and Theis 1980), it can be inferred that this was a contributing factor to the potential bioavailability and mobility of metals in this study (Figs 5.4 and 5.5).

Apart from the Fe and Al content, the behaviour of metals in the soil is also influenced by the %OMC. According to ASTDR 2004, Cu and Pb binds strongly to soils with high organic content (14–34%, dry weight), when the organic matter content is low, the mineral content or Fe and Al oxides become important in determining the adsorption. In soil with high organic matter content and a pH of between 6 and 8, lead may form insoluble organic lead complexes, but at a pH between 4 and 6, the organic lead complexes become soluble and leach out or may be taken up by plants (USEPA 1986). The %OMC and pH in this study that the falls within this range (Tab 4.1) making these metals bound to the organic matter fraction (F_2) and a further confirmation from section 5.1.2, where correlation between the %OMC content Cu and Pb associated with F_2 was observed and discussed. Finally, Zn primarily tends to sorb more readily strongly onto soil particulates at a high pH ($pH \geq 7$) than at a low pH (USEPA, 1986). This explains why between 50% and 65% of the total Zn concentration in

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[4] Occurs when metal ions bind directly to the soil surface with no intervening water molecules.

the study site was bound to the residual fraction (Fig 5.4). Also, under anaerobic conditions, zinc sulfide is the controlling species, thus, the mobility of zinc in anaerobic soil is low. This can be observed in this study (Fig 5.4), the concentration of Zn leached out in the dry season is consistently higher than the concentration in the wet season.

In summary, the most important parameters controlling heavy metal behaviour and distribution in soil are soil type, metal speciation, metal concentration, soil pH (which have been investigated in this study) and sorption. As observed in this study, greater metal retention and lower solubility occurs at high soil pH.

5.1.4 Assessing ecological risk using the Risk Assessment Code (RAC)

In order to estimate the risk associated with heavy metals from e-waste recycling in the study area, the soil was classified according to RAC based on the bonding strength associated with the geochemical fractions in the soil and the ability of the metals to enter the food chain. In this study, the risk is based on metal percentage in the exchangeable fraction (F_1) as it is the readily available fraction. By applying RAC guidelines (Table 3.4) to the results obtained in this study, it was revealed that between 15%-40% of total Cd was present in the exchangeable phase; Cr ranged between 1%-3%; Ni, 3%-9%; Pb 2%-9%; Cu, 3%-12%; Zn, 7%-15%; Sb, 7%-25% and Mn, 5% -20% in the exchangeable phase. This translates to Cd being classified as the metal that poses most risk; its presence in the environment ranged between medium and high risk, the presence of Cu, Zn, Sb and Mn indicate the risk levels as ranging between low and medium risk and the presence of Cr, Ni and Pb in soil represents low risk.

Toxicity and risk, affected by mobility and bioavailability are better estimated using metal speciation data than total metal concentration. The extent of risk posed by the metals can thus be estimated by the fractions where the metals are found. RAC determines the toxicity and risk of the heavy metals by applying the availability of the metals in the environment (Perin et al., 1985; Hui-na et al., 2012; Sarkar et al., 2014). The potential ecological risk (PERI) as established in section 4.4.2 indicated Cu as the metal that contributed most to the risk to the environment followed by Cd; the risk was estimated based on the total metal concentration in the soil. However, from 5.1.1 above, it is evident that, since metals in soils are distributed in different fractions, using only the total metal concentration is a poor measure of assessing the risk as it does not give an understanding of the bioavailability and mobility of the metals.

5.2 Ecotoxicological availability/assessment

Though the soil type was identified as loamy sand, its structure from 10cm downwards was found to be coherent and tightly bound (section 4.2). It would be reasonable to expect any metal found below the 0-10cm depth would be as a result of downwards migration. However, a clear difference between the depths was expected owing to the fact that the informal recycling process at the site was relatively new (2 -3 years) at the time of sampling, there was no observed statistical significant difference (section 4.4). Since there is evidence of downwards migration which is typical of sandy soils (Rieuwerts et al., 1998; Eriksson, 1989; Chen et al., 2006), the rapid migration of the metals down the soil profile and into water bodies is of concern. Hence, the soil column experiment was used as a method to examine the soil leaching and determine the potential bioavailable and mobile fractions of the metals. Artificial rain (0.01M $Cacl_2$) was used as the extracting agent since it is known not to modify the soil pH (Sahuquillo et al., 2003).

Table 5.1 presents the metal concentration in the leachates up to 28 days. It can be observed that the concentration of metals in the leachate was highest after 7 days of leaching and the metal concentration on day 28 had lower concentration than the leachates collected on days 7, 14 and 21 with the exception of Zn, where the concentration in the leachate from the wet season samples was higher than the concentration leached out after days 14 and 21 (Table

5.1). The physicochemical parameters measured in the leachates collected at each sampling time did not differ greatly across assay ($p>0.05$). The pH and the oxygen saturation of the leachates ranged between 7.04-7.82 and 73-88% respectively (Table 5.2).

Table 5.1: Metal concentration (mg l^{-1}) in leachate

	Dry season					Wet season				
	Day 1	**Day 7**	**Day 14**	**Day 21**	**Day 28**	**Day 1**	**Day 7**	**Day 14**	**Day 21**	**Day 28**
Cd	1.05±0.16	8.53±0.41	5.76±0.27	3.87±0.08	3.74±0.21	0.94±0.15	2.01±0.05	1.62±0.15	1.06±0.10	1.12±0.01
Cr	0.002±0.00	0.13±0.01	0.21±0.01	0.82±0.19	0.58±0.08	0.001±0.00	0.1±0.00	0.13±0.01	0.13±0.03	0.08±0.02
Cu	1.86±0.40	48.11±1.38	30.32±1.26	15.07±1.62	11.12±0.76	1.56±0.24	28.88±1.91	19.76±1.75	11.79±0.65	9.11±0.42
Mn	1.28±0.18	32.93±1.50	23.51±1.39	16.24±0.47	12.48±0.98	1.06±0.10	20.66±2.10	12.57±0.83	8.6±0.48	8.17±0.69
Ni	0.96±0.04	3.07±0.17	2.92±0.11	1.93±0.10	1.91±0.23	0.73±0.09	3.16±0.30	2.51±0.13	2.49±0.29	1.87±0.23
Pb	1.38±0.18	22.50±1.80	18.06±1.26	6.01±0.47	6.05±0.33	1.19±0.10	12.42±0.85	9.45±0.32	6.58±0.36	4.04±0.67
Sb	0.87±0.03	4.23±0.19	2.79±0.11	2.68±0.20	2.34±0.24	1.28±0.13	10.42±0.39	8.31±0.25	8.30±0.38	6.67±0.54
Zn	10.29±0.51	309.67±15.42	269.62±11.92	199.2±5.29	136.8±9.49	9.14±1.6	77.97±5.73	58.25±2.58	50.64±3.04	69.28±11.68

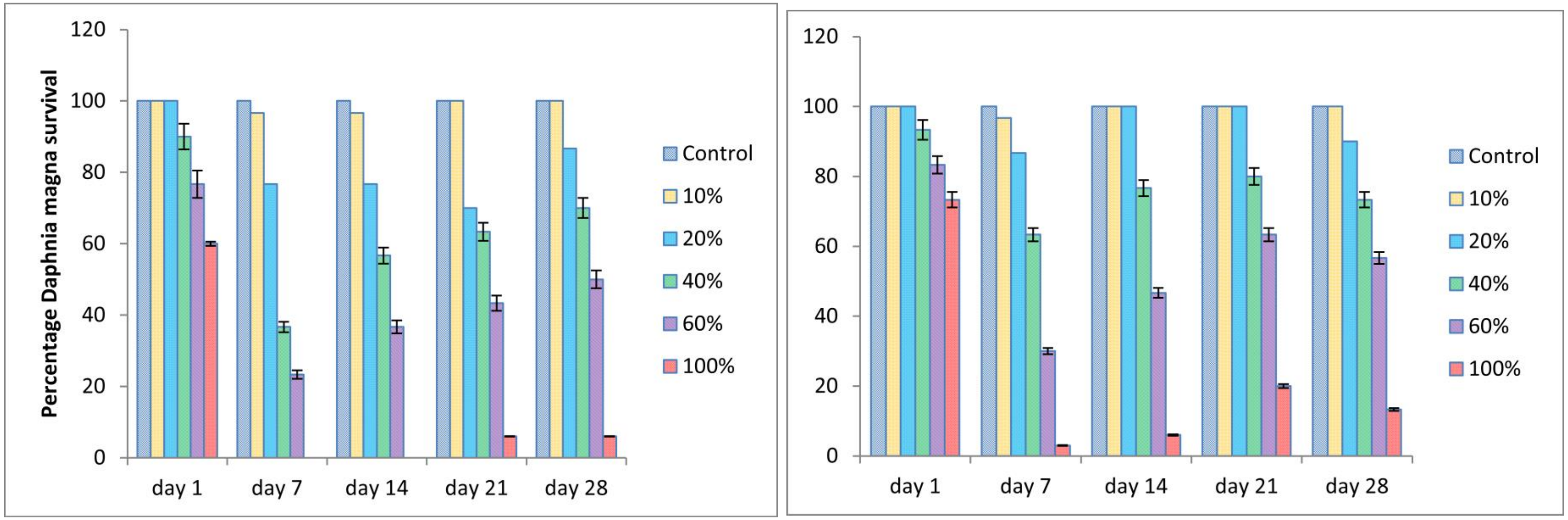
Table 5.2: Physicochemical parameters of the leachate (properties of the leachate from beginning to end of the toxicity test).

	Day 1	Day 7	Day 14	Day 21	Day 28	Day 1	Day 7	Day 14	Day 21	Day 28	Control
	Dry season leachate					**Wet season leachate**					
pH	7.04-7.13	7.15-7.32	7.38-7.25	7.22-7.47	7.64-7.82	7.67-7.32	7.25-7.25	7.43-7.46	7.47-7.39	7.82-7.54	7.04
DO (%)	87-82	82-78	85-88	87-81	88-79	83-75	78-80	81-81	75-73	79-75	88

5.2.1 Ecotoxicological response

In the acute toxicity tests survival of the control was 100% for *Daphnia magna* after 48 h. It can be observed that the percentage survival of the *Daphnia magna* was affected by leachates having between 40% and 100% of the total concentration at sampling days 7, 14, 21 and 28 days. 100% survival was observed in all the control (garden soil) leachates, 100% *Daphnia magna* survival was observed in mixtures with 10% and 20% leachates concentration collected on day 1 in both dry and wet season. In the dry season, there was no (0%) *Daphnia magna* survival in the mixture containing 100% leachate concentration on leachates collected on days 7 and 14 respectively, whereas, in the wet season, 2% and 4% survival was observed (Fig 5.5).

Using the probit analysis, it was observed that the leachate obtained from the dry season sample on day 7 was most toxic (LC_{50} =32.54) with approximately 32.5% (v/v) of the concentration needed to reduce the daphnids by half the population size (Table 5.3). An increase in the LC_{50} value corresponded to a decrease in leachate toxicity with time (sampling days) with the exception of leachates collected on day 1 in the dry and wet seasons. Although not statistically significant ($p>0.05$), leachates from the dry season samples were observed to be more toxic than leachates from the wet season.



a. Daphnids survival when exposed to leachates from dry season

b. Daphnids survival when exposed to leachates from wet season

Figure 5.5: Acute toxicity representing percentage *Daphnia magna* survival when exposed leachates (obtained from dry and wet season soil samples) collected on days 1, 7, 14, 21 and 28 respectively

Table 5.3: Toxicity (median lethal concentration) of leachate against *daphnia magna*

	Dry season leachate				**Wet season leachate**			
			Fiducial interval (CI 95%)				Fiducial interval (CI 95%)	
	LC_{50}(%)	Standard error	Lower limit	Upper limit	LC_{50}(%)	Standard error	Lower limit	Upper limit
Day 1	113.93	20.69	87.21	211.56	160.08	49.26	106.79	642.94
Day 7	32.54	2.71	27.31	38.33	42.02	3.48	35.51	49.77
Day 14	38.80	3.42	32.42	46.44	55.98	3.39	49.38	63.47
Day 21	43.10	4.13	35.58	52.72	66.74	4.94	57.94	78.98
Day 28	50.82	4.26	43.08	60.77	57.26	5.07	48.33	69.75

The leachate tested on the cladoceran *D. magna* had a complex mixture of metals which behave differently. From Fig 5.5 and Tab 5.3 above, a relationship between chemical concentration and toxicity of the leachate can be observed. As a result of such relationships, a Toxicity Index (TI) was proposed and used to justify the contaminants present in the mixtures and estimate the contribution of individual elements to mixture toxicity in bioassays (Vaj et al., 2011; García-Gómez et al., 2014). Toxicity indices are characterized by dividing the LC_{50} estimate from the bioassay by the individual metal estimate (Fikirdesici et al., 2012).

$TI=\frac{C}{LC50}$ ---- Equation 5.2

Where TI is Toxicity Index, C= concentration of individual metals in the leachate and LC_{50} is the median lethal concentration.

From Table 5.4, it can be observed that Zn is the highest contributor to the leachate especially in the dry season with a toxicity index ranging from 0.09 in dry season day 1 leachate and the highest toxicity index (9.52) obtained in dry season leachate collected on day 7.

Table 5.4: Toxicity index of metals in leachate.

	Day 1	Day 7	Day 14	Day 21	Day 28	Day 1	Day 7	Day 14	Day 21	Day 28
			Dry season					**Wet season**		
Cd	0.009	0.26	0.15	0.09	0.07	0.006	0.05	0.03	0.02	0.02
Cr	2.05E-05	0.004	0.005	0.02	0.01	8.33E-06	0.002	0.002	0.002	0.001
Cu	0.02	1.48	0.78	0.35	0.22	0.01	0.69	0.35	0.18	0.16
Mn	0.01	1.01	0.61	0.38	0.258	0.007	0.49	0.22	0.13	0.14
Ni	0.008	0.09	0.08	0.04	0.04	0.005	0.08	0.04	0.04	0.03
Pb	0.01	0.69	0.47	0.14	0.12	0.007	0.30	0.17	0.1	0.07
Sb	0.008	0.13	0.07	0.06	0.05	0.008	0.25	0.15	0.12	0.12
Zn	0.09	9.52	6.95	4.62	2.69	0.057	1.86	1.04	0.76	1.12

5.2.2 Ecotoxicological risk characterization

Daphnia magna are of ecological importance being primary consumers at a low trophic level and are sensitive to environmental contaminants (Tyagi et al., 2007), their short life cycle and their asexual reproduction makes them a very useful species in ecotoxicological assessment. According to OECD (2004), Daphnia is very sensitive to pH and changes in the pH levels outside the range 6.0 and 9.0 would affect the toxicity test. The pH was monitored from the start to the end of the assay (without being adjusted) to avoid interferences with the assay (Table 5.2).

The leaching test confirmed the migration of metals through the soil profile and demonstrated the role geochemical fractions and site specificity have to play in ecotoxicological assessment. It was observed that Cr was the least leached metal which corresponded with the chemical characterization in section 5.1.1. In ecotoxicological assessment, bioavailability of contaminants is very important; the ecotoxicity assay confirmed the acute toxicity of leachates obtained from the soil samples.

According to Fikirdesici et al., (2012), ecotoxicological assays with metal mixtures make environmental risk assessment difficult due to the possibility of chemical interactions. Despite of the difficulty of linking the concentration of a single contaminant in the leachate to the toxicity, Zn was identified as the highest contributor to the leachate, thus causing the toxicity. The total concentration of zinc in the leachate ranged between 9.14 and 309.67 mg/L which is much higher than the levels of Zn dissolved in water bodies given by WHO. According to WHO (2001), a dissolved zinc concentration of $20\mu gL^{-1}$ has been shown to have adverse effects on freshwater organisms in soft water while in hard water concentrations of $90\mu g\ L^{-1}$ have been reported to have adverse effects. In the marine environment, dissolved zinc concentrations of $100\mu g\ L^{-1}$ have been shown to have adverse effects.

The assessment of the e-waste recycling area based on indirect toxicity determined the toxic effect of the metals in the leachate and provided some degree of biological relevance to the risk assessment process. Although further assessment could be carried out to estimate the chronic effects of the leachate, it can be argued that for the scope of this study, the effect from the acute toxicity is appropriate to assess the hazard or risk posed by the e-waste recycling activity.

5.3 Human availability/bioaccessibility

In recent times, the use of *in vitro* bioaccessibility has been introduced as a screening tool in human health risk assessment. Although there are still some uncertainties associated with *in vitro* testing, the tools used for bioaccesibility test in this study (UBM for oral and SELF for inhalation bioaccessibility) were selected because they both have a proper representation of the human system mimicking the enzymes, inorganic salts and other composition in both the digestive and respiratory systems. Although, previous bioaccessibility studies (Broadway et al., 2010; Wragg et al., 2011; Pelfrene et al., 2012; Boisa et al., 2014) have focused on single contaminants, this study has taken multiple contaminants into consideration.

5.3.1 Oral bioacessibility

For this analysis, a portion of soil samples were pooled together to form composite soil as described in section 3.6 ($A_{0\text{-}10cm}+B_{0\text{-}10cm}+C_{0\text{-}10cm}$…., $A_{10\text{-}20cm}+B_{10\text{-}20cm}+C_{10\text{-}20cm}$…., $A_{20\text{-}30cm}+B_{20\text{-}30cm}+C_{20\text{-}30cm}$,). The composite samples were checked for the soil properties and metal content. Tables 5.5 and 5.6 below present the soil properties and metal content.

It is important to mention that Tables 5.5 and 5.6 are completely different from Tables 4.1 and 4.3 and should not be mixed up. Tables 4.1 and 4.3 presents the range (minimum and maximum) as well as the mean of the measured parameters of all the individual samples while Tables 5.5 and 5.6 present data of the bulked up (composite) soil samples.

Table 5.5: Physicochemical parameters of composite soil samples within the study site

Physicochemical parameters of the composite soil samples.

	Dry season			Wet season		
	pH	%OMC	CEC (cmol$_c$ Kg^{-1})	pH	%OMC	CEC (cmol$_c$ Kg^{-1})
Recycling area						
0-10cm	8.54 ±0.02	15.2±1.08	11.58±0.98	6.98±0.02	30.56±0.01	10.68±0.72
10-20cm	7.23±0.03	23.44±1.18	12.72±1.06	6.94±0.02	28.1±0.05	11.54±0.48
20-30cm	7.98±0.04	24.48±1.18	12.36±0.86	7.03±0.01	28.88±0.1	11.18±0.66
Dismantling area						
	7.99±0.05	15.44±1.02	10.14±0.54	7.28±0.02	13.38±0.78	10.36±0.8

Values are presented mean ± S.E. (n= 9 for RA (composite samples representing each depth * 3 determinations), n=3 for DA (composite sample *3 determinations)). Where RA is recycling area and DA is dismantling area.

Table 5.6: Concentration of metals in composite samples in study site

Metals concentration in composite samples of recycling and dismantling section of the study site.

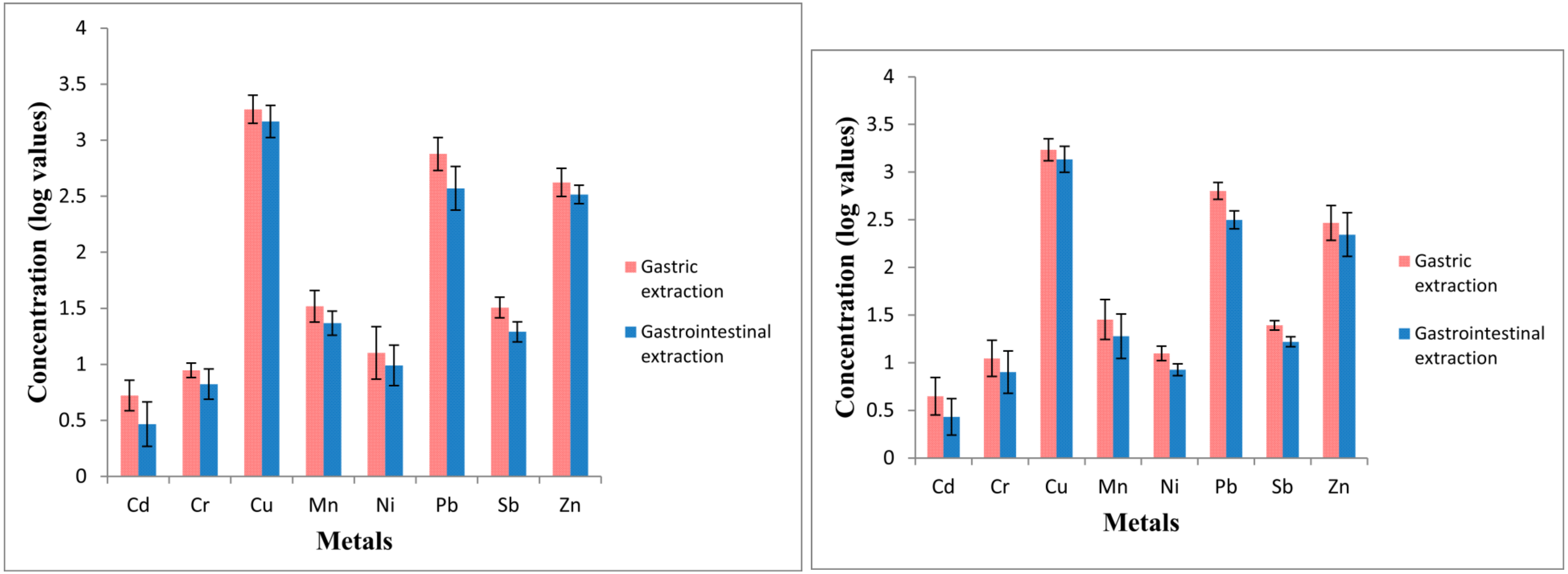
		Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
					Dry season				
Recycling area	0-10cm	10.61±1.85	22.86±0.61	5297±414	82.42±4.5	56.6±3.51	1504±241	88.2±10.9	976.8±97.4
	10-20cm	11.21±1.18	23.12±0.91	5676±137	95.92±5.02	37.34±1.35	2688.9±37.8	68.19±3.78	1178±44.2
	20-30cm	12.71±1.02	31.81±1.20	5801±258	81.07±5.83	72.24±4.14	2981±145	58.67±2.52	1290±63.6
Dismantling area	0-5cm	6.3±0.22	27.6±0.71	4166.67±39.52	149.4±0.79	31.53±0.64	1977.13±9.24	81.43±1.16	1873.87±51.24
					Wet season				
Recycling area	0-10cm	9.98±0.62	26.22±0.76	5140±507	49.98±2.00	43.98±5.91	2230±250	62.53±7.64	688.3±26.9
	10-20cm	15.19±2.96	54.97±8.21	4995±381	102.88±7.79	39.28±2.98	2145±231	50.61±5.80	751±47.8
	20-30cm	9.70±1.27	32.62±1.21	5026±337	68.60±9.75	50.9±2.90	1984±98.7	71.68±6.13	804±53.1
Dismantling area	0-5cm	5.21±0.58	24.89±1.62	3948.67±238	145±7.96	42.39±3.87	1908±94.32	65.41±1.71	1810±86.54

Values are presented mean ± S.E. (n= 9 for RA (composite samples representing each depth * 3 determinations), n=3 for DA (composite sample *3 determinations)). Where RA is recycling area and DA is dismantling area.

The measured concentration of metals in the gastric phase in both seasons ranged between 2.37-6.96 mg kg^{-1} for Cd; 1152-2204 mg kg^{-1} for Cu; Cr, 7.34-20.86 mgkg^{-1}; Ni, 7.16-21.67 mg kg^{-1}; Pb, 482.1-1028 mg kg^{-1}; Sb, 21.62- 42.22 mg kg^{-1} and Zn, 223-623.2 mg kg^{-1}. In the gastrointestinal phase, Cd varied between 1.48 and 4.08 mg kg^{-1}; Cr, 4.29 and 15.24 mg kg^{-1}; Cu, 858 and 1801 mg kg^{-1}; Pb, 195.5-556 mg kg^{-1} and Zn, 154-482.3 mg kg^{-1} (Fig 5.6).

It can be observed that the concentration of all metals in the gastro-intestinal phase is lower than the metal concentration in the gastric phase. This is can be linked to the fact that the solubility of metals increases with the low pH in the gastric region, while in the intestinal phase, at a higher pH, there will either be sorption of metals due to interaction with enzymes, precipitation of metals as insoluble compounds or stabilization of metals in solution as a result of complexation (Pelfrene et al., 2012; Wragg et al., 2011; Poggio et al, 2009). The bioaccessible fraction of interest is the gastro-intestinal phase as it represents the maximum proportion available for absorption and the main exposure route into the since little or nothing is absorbed from the stomach. The soluble metals may be absorbed and transported across the intestinal wall into the lymphatic system and distributed to different parts of the body were they can start to exert their toxicity.

In the dry season, the percentage bioacessibility of Cd ranged between 23-35%; Cr 16-32%; 22-34% for Cu and 22-26% for Mn. Bioaccessiblity ranges of 20-22%; 13-21%; 22-30% and 23-29% were obtained for Ni, Pb, Sb and Zn respectively. In the wet season, the percentage bioaccessibiliy ranged between 27-30% for Cd; 19-28% for Cr; 22-33% for Cu and Mn ranged between 21-25%. Ni ranged between 17-21%; Pb 12-21%; 25-28% for Sb and Zn ranged between 22-27% (Fig 5.7).



a. Metal concentration in gastric and gastrointestinal phase (dry season samples)

b. Metal concentration in gastric and gastrointestinal phase (wet season samples)

Figure 5.6: Metal concentration in *in vitro* bioaccessibility test indicating concentration in the gastric and gastrointestinal phases respectively in the dry and wet season samples.

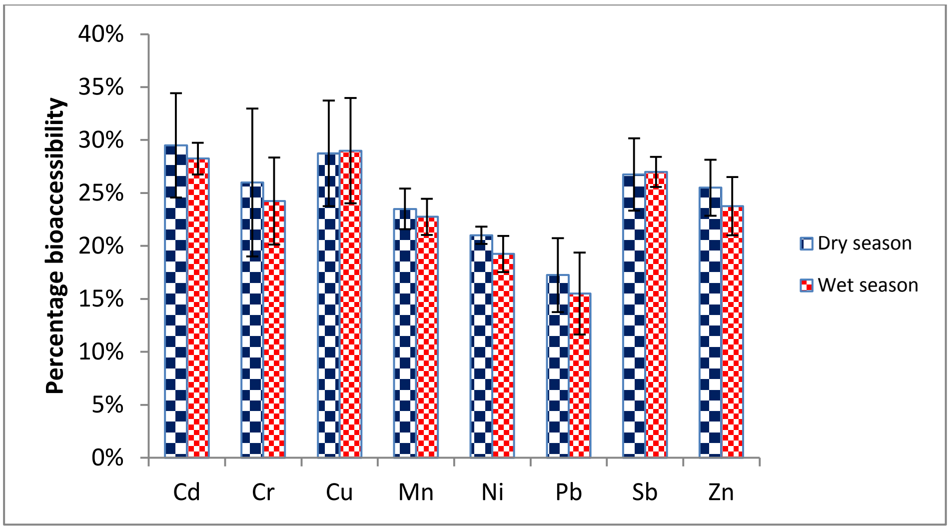


Figure 5.7: Percentage bioaccessibility in the gastrointestinal phase representing the concentration available for potential absorption in soil samples both seasons.

The order of percentage mean bioaccessibility in the gastro-intestinal phase decreases as thus: Cd > Cu > Sb > Zn> Cr > Mn> Ni > Pb. This implies that Cd is the readily bioaccessible for absorption thus being potentially bioavailable this also corresponds with the speciation analysis as discussed in section 5.1.1. Comparing the bioaccessiblity range (Fig 5.7) in the gastrointestinal phase obtained in this study with similar studies, a variation in the percentage range could be observed. Denys et al., (2006) reported a range of 5% and 25% of the total Pb content in two garden soil samples collected in South France. A range of 2–42% was reported by Farmer et al., (2011) as the bioaccessible Pb collected in 27 soil samples in Glasgow, Scotland. The bioaccessible Cd, Pb and Zn in soils collected in Northern France were 46± 19%, 21±9% and 9±4% respectively (Pelfrene et al., 2012). Xia et al., (2016) reported a range of 6.2-45% for Cd and 16-96% for As in soil samples collected in Australia.

The variability in bioaccessibility in the different studies could be attributed to the soil matrix, type, properties and composition in the different locations as suggested by Farmer et al., (2011) and Walraven et al., (2015). This variability as a result of the possible influence of the soil properties on the bioaccessible metal fraction is discussed in the next section.

5.3.1.1 Relationship between the soil properties and bioaccesible metal fractions.

Correlation analysis was carried out in order to establish the effect of physico-chemical properties of the soil and the bioaccessible metals (Table 5.7).

Table 5.7: Relationship between bioaccessible metals (in the gastrointestinal phase) and soil properties

Correlation between bioaccessible metals and soil properties								
	Cd GI	Cr GI	Cu GI	Mn GI	Ni GI	Pb GI	Sb GI	Zn GI
pH	0.042	-0.325	0.057	0.266	0.486	0.045	0.725*	0.30
%OMC	0.521	0.568	0.570	-0.821*	0.157	-0.093	-0.525	-0.883**
CEC	-0.781*	0.383	-0.757*	-0.401	0.534	0.256	0.064	0.078

Where GI is gastrointestinal phase, * is $p \leq 0.05$ and **is $p \leq 0.001$

A number of studies have shown that bioaccessibility can be influenced by soil properties and further established that the relationship between the soil properties and bioaccessibility may be site specific (Meunier et al., 2010; Das et al., 2013; Xia et al., 2016). Das et al., (2013) reported that total organic carbon had a negative relationship on As bioaccessibility in soil collected in India; and Xia et al., (2016) reported similar negative relationship between the total organic carbon, Fe oxide and Al oxide and bioaccessibility of Cd and As in soils collected in Australia. Li et al., (2014) also reported inverse relationships between organic matter, Fe oxide and Al oxide and bioaccessible Sb and As from soil samples collected in China. In the study carried out by Izquierdo et al., (2015), a relationship soil pH and bioaccesible metals studied could not be established but there was a positive correlation between the organic matter content and Mn in soil samples from Spain.

Although there are no published similar e-waste studies with which to compare results of this study, a negative relationship was observed between %OMC and bioaccessible Zn and Mn, which implies that a decrease in the %OMC content would increase the bioaccessible Zn and Mn respectively. A negative relationship was established between CEC, Cd and Cu which implies that the lower the CEC, the higher the bioacessible concentration of Cd and Cu. Similarly, in section 5.1.2, the results implied a decrease in CEC would lead to an increase in the potential bioavailable fraction of Cd. This reaffirms that influence of soil properties on bioaccessibility thus making it site specific and brings to fore the possible relationship between chemical speciation and bioaccessibility which will be discussed below.

5.3.1.2 Relationship between bioaccessible metals in the gastro-intestinal phase

According to Goyer et al., (2003) and Xia et al., (2016), there is a high likelihood of the ingestion of multiple contaminants and also the possibility of competitive antagonistic or synergistic interaction during absorption in the gastrointestinal tract which could result in an increase or decrease in bioaccessibility of the metals.

An inverse relationship was observed between Zn-Cd and Zn-Cu in the gastrointestinal tract and positive linear relationship between Cd-Cu, Cd-Cr and Zn-Mn (Table 5.8). An increase in the Cd concentration will result in an increase in Cu concentration and a decline in the Zn concentration results in the increased absorption of Cd and Cu respectively (and vice versa).

Table 5.8: Bioaccessible metal-metal interaction

Relationship between bioaccessible metals in gastrointestinal phase

	Cd GI	Cr GI	Cu GI	Mn GI	Ni GI	Pb GI	Sb GI
Cr GI	0.746*						
Cu GI	0.952**	0.562					
Mn GI	-0.615	-0.31	-0.785*				
Ni GI	0.605	0.161	0.65	-0.477			
Pb GI	-0.093	-0.137	-0.196	0.318	0.116		
Sb GI	0.057	-0.401	0.198	-0.026	0.332	-0.496	
Zn GI	-0.657*	-0.609	-0.738*	0.901**	-0.265	0.489	0.128

Where GI is gastrointestinal phase, * is $p \leq 0.05$ and **is $p \leq 0.001$

Studies (Torra et al., 1995; Reeves et al., 1996; Bzorska & Moniuszko-Jakoniuk, 2001) show that in the gut, an increased level of Zn can antagonize the toxicity of Cd and Cu by inhibiting absorption and reducing the bioavailability. The absorption of Cd is affected by Cu as increased Cd reduces the absorption of Cu. However in this study, both metals are mutually synergistic, the bioaccessible Cd increases with increase in bioaccessible Cu.

Potential genotoxicity has also been reported in joint action of Cu-Zn, Cd-Zn and Cu-Cd in aquatic organisms (Sunila, 1981; Obiakor et al., 2010) Cu has been shown to supress Mn absorption in the guts of rats (Adekalu, 2005), an interaction between Cu-Mn was identified in the urine of women in Japan, however joint action toxicity of metals have not been fully established (Watanabe et al., 1991).

Despite the synergistic and antagonistic interactions between the metals, it is evident that only a proportion of the total metal content is available for absorption from the intestine when measured against the total metal concentration.

5.3.1.3 Relationship between speciation and oral bioaccessibility tests

The potential bioavailability of the metals present in soil in relation to the bioaccessible metal in the gastrointestinal phase is established. In the F_1, the only significant relationship was with Cd; a strong and positive relationship was observed between Cd in the bioavailable fraction (F_1) and Cd in the gastrointestinal phase ($r=0.837$, $p \leq 0.01$). An increase in Cu bound to F2 will increase the bioaccessible Cu and a decrease in Pb bound to F_2 will increase the concentration of bioaccessible Zn (Table 5.9). A correlation was observed between potential mobile fraction (F_1+F_2) and bioaccessible Cd and Cu ($r=0.915$, $p \leq 0.001$; $r=0.682$, $p \leq 0.05$ respectively) (Table 5.10).

Table 5.9: Relationship between speciation and oral bioaccessibility

Correlation between bioaccessible metals and organic bound fraction (F_2)

	Cd F_2	Cr F_2	Cu F_2	Mn F_2	Ni F_2	Pb F_2	Sb F_2	Zn F_2
Cd GI	0.616*	-0.875**	0.862 **	-0.870 **	0.153	0.832 *	-0.162	0.211
Cr GI	0.343	-0.575	0.567	-0.558	0.316	0.360	-0.167	-0.270
Cu GI	0.744*	-0.937**	0.937**	-0.947	0.137	0.938**	-0.070	0.219
Mn GI	-0.885**	0.843*	-0.901**	0.889 *	-0.257	-0.859*	-0.028	0.200
Ni GI	0.652	-0.610	0.591	-0.514	0.222	0.713	-0.140	0.501
Pb GI	-0.337	0.338	-0.269	0.240	-0.388	-0.041	-0.558	0.182
Sb GI	0.122	-0.145	0.047	-0.044	-0.040	0.145	0.451	0.658
Zn GI	-0.782*	0.831*	-0.874**	0.872**	-0.397	-0.706*	-0.123	0.404

Where GI is gastrointestinal phase, * is $p \leq 0.05$ and **is $p \leq 0.001$

Table 5.10: Relationship between speciation (potentially mobile) and oral bioaccessibility

Correlation between bioaccessible metals and potential mobile fraction (F_1+ F_2)

	Cd (F_1+ F_2)	Cr (F_1+ F_2)	Cu (F_1+ F_2)	Mn (F_1+ F_2)	Ni (F_1+ F_2)	Pb (F_1+ F_2)	Sb (F_1+ F_2)	Zn (F_1+ F_2)
Cd GI	0.915**	-0.781*	0.575	-0.843*	0.130	0.607	-0.141	0.261
Cr GI	0.847*	-0.445	0.407	-0.506	0.168	0.271	-0.102	-0.188
Cu GI	0.828*	-0.744*	0.682*	-0.843*	0.194	0.746	0.006	0.335
Mn GI	-0.521	0.341	-0.842*	0.546	-0.395	-0.868*	-0.341	-0.146
Ni GI	0.435	-0.410	0.459	-0.417	0.303	0.595	-0.034	0.524
Pb GI	-0.277	-0.110	-0.409	-0.055	-0.524	-0.245	-0.698	0.009
Sb GI	-0.005	-0.148	0.022	-0.062	0.148	0.110	0.292	0.512
Zn GI	-0.690*	0.284	0.845*	-0.503	-0.461	-0.765*	-0.423	0.040

Where GI is gastrointestinal phase, * is $p \leq 0.05$ and **is $p \leq 0.001$

Assessing bioaccessibility of metals in soil could present some difficulties since metals occur in varying concentrations and chemical forms; and the chemical form may be interchangeable depending on the soil properties, conditions and history. The assessment of bioaccessibility for metals reflects the geochemical conditions in soil (Grøn & Andersen, 2003). Studies show that the concentration of metals in the gastro-intestinal phase represents the proportion entering systemic circulation and the bioavailable fraction is dependent on soil properties, speciation of the metals, which in turn affects human bioaccessibility (Casteel et al., 2001; Denys et al., 2006; Das et al., 2013; Xia et al., 2016). Caboche et al., (2010) found a relationship between the bioaccessible Pb and Pb in organic matter fraction while Denys et al., (2012) and Palumbo-Roe et al., (2013) associated the bioacessible Pb to Pb in the carbonate fraction.

In this study, there was no significant correlation between the bioaccessible Pb and the different fractions from the sequential extraction. However, a significant correlation was established with other metals such as the strong positive relationship between Cd in the exchangeable fraction (F_1) and bioaccessible fraction. There is a high possibility for the metals bound to the organic fraction to become potentially bioavailable due to pH changes and other complex chemical and biological interactions in the soil (Gleyzes et al., 2002) and this can alter the bioaccessibility the metals, having a potential secondary effect on the magnitude of risk posed to human health (Wragg & Cave, 2012), which could be a reason for the relationship between bioaccessible and organic bound (F_2) Cu and Cd. Other relationships were established between some bioaccessible metals and different fractionated metals in different fractions which is an indication of the interaction of metals and their chemical forms during the *in vitro* test and could further affect the bioaccessibility positively or negatively in the human gut.

From this study, it can be inferred that the bioaccessibilty of metals can be dependent on the geochemical fraction of the metals in the soil and possibly the properties of the soil.

5.3.1.4 Quality Control

It is noteworthy that certified reference materials for oral bioaccessibility are not readily available. However, BGS 102 was kindly provided by Dr Johanna Wragg of the British Geological Survey for this study. The oral bioaccessibility guidance material is certified for only As in the gastrointestinal phase and Pb in the gastric phase and good mass recovery were observed 108% and 124% respectively after five replications. (Appendix 6)

5.3.2 Inhalation bioaccessibility

In this study, the size of the particle was put into consideration because of the possibility of the finer particles to remain suspended for longer period than larger particles and has the potential to cause harm to human health by their penetration into the lungs (Witt et al., 2014). The soil samples used for this analysis were bulked together to produce samples representing the recycling and dismantling area respectively. The total metal content in the samples are presented Table 5.11.

Table 5.11: Total metal concentration in ≤10µm composite soil samples

Metal concentration (mg kg-1) of ≤10µm composite samples. Mean±S.E.								
	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
RA dry	9.8±0.12	32.17±0.62	5858.58±77.07	84.01±1.11	58.15±1.01	3059.85±16.26	75.04±2.03	3101.83±20.86
DA dry	9.78±0.58	93.2±0.40	3791.78±48.08	394.29±1.30	105.1±0.78	2297.89±76.37	43.29±1.72	2358.71±56.92
RA wet	9.04±0.25	30.2±2.31	7046.35±132.94	73.7±2.03	63.58±0.43	2811.56±28.99	87.33±0.98	1323.96±4.35
DA wet	11.76±0.43	103.46±0.11	4445.31±108.54	550.72±1.99	130.79±1.61	1902.61±67.07	43.92±1.79	2723.35±24.75

Where RA is recycling area and DA is dismantling area

The inhalation biaccessibility test ran for 120 hours with a gradual increase of metal dissolution by the simulated lung fluid was observed at the start of the experiment at 30 minutes till the end at 120 hours. Table 5.12 presents the bioaccessible metal concentration at 120 hours.

Table 5.12: Metal concentration (mg kg^{-1}) at the end of the experiment

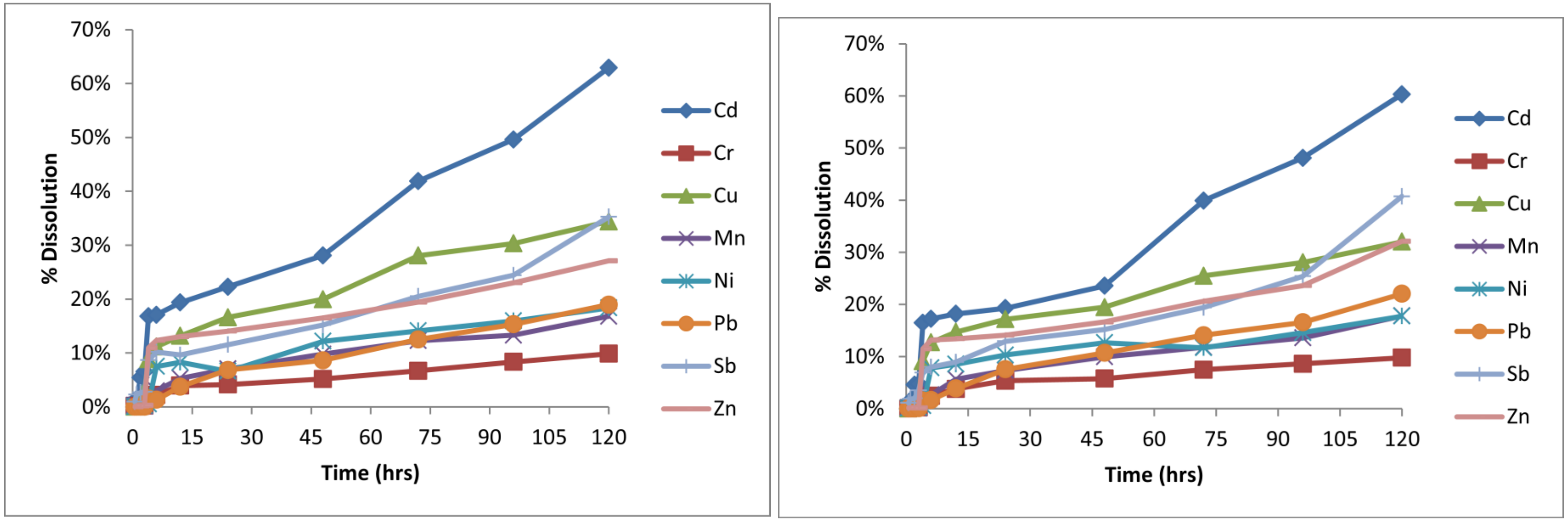
Bioaccessible metal concentration (mg kg-1) ≤10µm. Mean±S.E. n=3

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
RA dry	6.65±0.08	5.45±0.04	1984±42.3	23.02±0.88	9.25±0.52	586.24±11.44	27.75±0.78	916±21.64
DA dry	5.67±0.04	6.72±0.07	1325±56.12	24.54±0.92	21.88±0.84	432±14.5	14.52±0.46	582±15.8
RA wet	5.64±0.04	5.12±0.05	2165±64.2	21.4±0.64	11.85±0.06	506.4±23.5	34.82±1.14	464±6.4
DA wet	6.84±0.02	8.56±0.06	1482±58.6	36.24±1.04	22.12±0.88	506.44±25.6	18.27±0.58	793.64±33.3

Where RA is recycling area and DA is dismantling area

The mean percentage dissolution of the metals after 3 hours of extraction was less than 1% except for Cd and Sb. Cr rose from 1.6% to approximately 10%; Pb, from1.5% to 20%; Cd, from 16% to 60% (Fig 5.8). It can be observed that Cd closely followed by Sb had the highest percentage dissolution in the simulated lung fluids in relation to its total concentration at all time intervals, while Cr demonstrated the lowest dissolution.

At the end of 120hrs, percentage bioacessibility ranged between 58% and 68% for Cd; 7%-13% for Cr; 31-34% for Cu; and 6-27% for Mn. Ni ranged between 16-21%; Pb ranged between 18%-26%; 34-42% for Sb and Zn ranged between 25-30% (Fig 5.9). The response of Cd, Sb and Cr in the inhalation bioaccessibility test was similar to the results obtained in the potential bioavailable fraction in the chemical speciation results discussed in section 5.1.1.



a. Percentage dissolution of metals at each time interval (dry season samples)

b. Percentage dissolution of metals at each time interval (wet season samples)

Figure 5.8: Percentage mean metal dissolution at different time intervals.

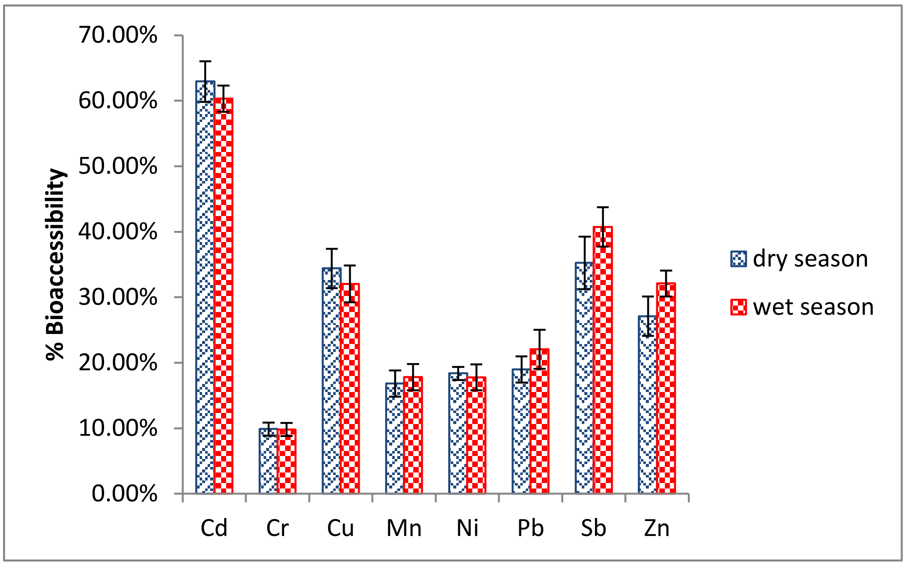


Figure 5.9: Percentage inhalation bioaccessibility after 120 hours

When inhaled, the particles can get dissolved in the lung fluids and are retained in the lungs for a couple of weeks (Hoffman & Asgharian, 2003). Studies have reported short term retention as a day (Julien, et al., 2011) and long term retention ranging between 4 days to 15 days (Wragg & Klinck, 2007; Drysdale et al., 2012; Boisa et al.,2014; Wiseman & Zereini, 2014; Li et al., 2016). In this study, a maximum retention period of 5 days (120 h) was studied with samples being analysed at given time intervals. The pH was measured at each time interval as indicated in section 3.6.2.2 and no significant pH fluctuation was observed. The time frame used in this study was chosen to represent acute toxicity since it is quite difficult to determine the exact retention time when particles are inhaled.

A comparable study by Boisa et al., 2014, using certified reference material, soils and tailings from a mining site, reported the leaching of Pb peaked at 100 hrs. Using a different extracting agent from Boisa et al., (2014), Wragg & Klinck, (2007) reported a peak of Pb in less than 100 h of leaching. However, in this study, unexpectedly, it was observed that despite including an additional 20% margin of safety over published saturation times, a number of metals, especially Cd was still being taken into saturation. A percentage (2%) of Pb was still extracted at 120 hours which coincided with the study on Ni by Drysdale et al., (2012) who reported Ni still being extracted at 168 h. Since the simulated lung fluids used in the studies were different, the peak of Pb and other metals could be due to the sorptive dynamics of particles during the extraction period (Wiseman & Zereini, 2014).

Cd had the highest percentage solubility in the simulated lung fluid followed by Sb, Cu then Zn. Comparing the percentage bioaccessibility with other studies might be difficult since there are different composition of lung fluids used in different studies. A study carried out by Li et al., (2016), comparing the percentage bioaccessibiliity of Pb using different simulated lung fluids including the method used in this study, found that the percentage inhalation bioaccessibility to be between 23-43% which is higher than the percentage bioaccessiblity obtained in this study (18-27%). Different studies reported different percentage bioaccessibility in different time frames; Wiseman & Zereini, (2014) reported mean perecentage bioaccessibility of Cr, Cu, Pb and Sb using artificial lysosomal fluid (ALF) as 37, 83, 96 and 82% after 24 h. However, using Gamble's solution, they reported the mean perecentage bioaccessibility of 21. 40, 26 and 52 % for Cr, Cu, Pb and Sb respectively. Li et al., (2016) also observed the percentage bioaccessibility of Pb to be higher when extracted with ALF than Gamble's solution, which was attributed to the differences in pH (ALF, 4.5 and Gamble's solution, 7.4) and the chemical components in the two lung fluids. Furthermore, they reported the presence of organic compounds, proteins and surfactant used in the lung fluids enhances the bioaccessibility suggesting the surfactant (DPPC) improved contact between the particles and the simulated lung fluid. Although, Drysdale et al., (2012) reported low bioaccessibility in Ni (1.5-3%), they reported the presence of organic compounds enhanced the bioaccessibility of Ni from the soil particles.

Although there may be disparities in the percentage bioaccessibility in the *in vitro* method using different simulated lung fluids, the bioaccessble metal fraction may be more realistic in risk assessment than the total metal concentration in assessing the risk posed to human health.

5.3.2.1 Speciation of ≤10µm soil particles.

Comparing with the total metal concentration in the re suspended particles (≤10µm), the speciation analysis showed the percentage association with the exchangeable fraction (F_1) as 28%-35% for Cd; Cr 3%-5%; Cu 8%-10%; and 7%-9% for Mn. The percentage metals in F_1 ranged between 8-9%; 6-9%; 17-20%; and 9-14% for Ni, Pb, Sb and Zn respectively.

Table 5.13: Metal concentration (mg kg^{-1}) in F1 fraction of the resuspended soil particles (≤10µm)

Metal concentration (mg kg-1) in F_1 fraction of the ≤10µm soil particles. Mean±S.E.								
	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
RA dry	3.39±0.02	1.22±0.01	522.54±15.28	7.65±0.06	4.52±0.03	272.86±11.64	14.66±0.82	339.42±15.62
DA dry	2.92±0.01	2.96±0.01	693.8±33.62	34.16±1.16	9.54±0.06	181.38±9.38	7.22±0.06	214.28±17.24
RA wet	2.86±0.01	1.38±0.01	312.16±26.04	5.95±0.02	5.48±0.04	192.29±14.25	15.88±0.09	148.56±11.08
DA wet	3.27±0.01	3.18±0.01	397.42±32.4	36.45±2.28	11.42±0.06	116.46±7.46	7.27±0.04	389.12±22.54

Where RA is recycling area and DA is dismantling area

5.3.2.2 Comparison between F1 fraction in sequential extraction and inhalable bioaccessible fraction.

As with the oral bioaccessibility analysis in section 5.3.1.3, the speciation of the metals is of importance. A correlation analysis was carried out to determine the relationship between the potential bioavailable metals (F_1) present in soil and the bioaccessible inhalable metal fraction. A strong relationship was established between the F_1 fraction of ≤10μm and the bioaccessible inhalable fraction after 120 hours in all metals except Mn and Pb (Table 5.14).

Table 5.14: Relationship between the inhalable bioaccessible fraction and F1 in sequential extraction

Relationship between F_1 and inhalable bioaccessible fraction at 120 h								
	Cd F_1	Cr F_1	Cu F_1	Mn F_1	Ni F_1	Pb F_1	Sb F_1	Zn F_1
Cd IBF	0.949*	0.1	-0.166	0.17	0.195	-0.053	-0.166	0.973*
Cr IBF	0.129	0.979*	-0.980*	0.984*	0.979*	-0.781	-0.973*	0.496
Cu IBF	-0.001	-0.938	0.974*	-0.966*	-0.876	0.569	0.984*	-0.318
Mn IBF	0.424	0.751	-0.726	0.742	0.829	-0.769	-0.703	0.735
Ni IBF	-0.19	0.993*	-0.975*	0.979*	0.975*	-0.83	-0.965*	0.95
Pb IBF	0.708	-0.741	0.700	-0.702	-0.687	0.656	0.692	0.405
Sb IBF	-0.107	0.895	0.948*	-0.936	-0.825	0.474	0.964*	-0.395
Zn IBF	0.988*	-0.027	-0.067	0.056	-0.015	0.294	-0.089	0.908*

Where IBF is inhalable bioaccessible fraction, F_1 is exchangeable fraction in sequential extraction.

In recent times, the determination of the inhalable bioaccessible metals fraction has been encouraged; for instance, by leaching out with water (Wiseman & Zereini, 2014). Weak salt solutions have also been used to leach out bioaccessible metal fraction in studies involving respiratory nickel toxicology (Drysdale et al., 2012). The salt solutions represent lung fluid and also the exchangeable fraction in the sequential extraction process. In the inhalation assay, Cd presented a high bioaccessibility and Cr a low bioaccessibility, the same trend was observed in the speciation analysis reported in section 5.1.1. As such, this study compares the result of bioaccessible metal fraction after 120 hours and the exchangeable fraction (F_1) from the sequential extraction. According to Wragg & Cave (2012), the bioaccessibility of metal is dependent on the speciation of metal in the soil. With the exception of Pb and Mn, a correlation was observed between the bioaccessible metal fraction and the exchangeable fraction (F_1), which could either be due to the association of Pb and Mn to different geochemical phases as discussed in section 5.1 or the percentage fraction extracted in the bioaccessibility and chemical speciation are not proportional with each other.

According to Wiseman & Zereini (2014), although studies using water and weak salt solutions for the inhalation assay obtained results reported a relationship, the use of simulated lung fluid in simulating inhalation bioaccessibility is encouraged as it reflects the human system.

5.4 Analogy of analytical processes and outcome

In order to evaluate the impact of the informal e-waste recycling activity in the environment, soil from the top 30cm sectioned in 10cm intervals were collected from the study site and analysed as detailed in Chapter 3. In chapter 4, the impact of evaporation in the dry season saw the concentration of metals in the dry season samples higher than that in the wet season with the exception of Cu. The vertical distribution of metals in the soil profile established possible accumulation and migration of metals under combining influence of edaphic factors and environmental conditions. The total concentration of all metals in both seasons (dry and wet) was consistently higher than levels in the control sample, and the concentration of Cd, Cu, Pb, Sb, Zn all exceed various SGVs. Further analysis using pollution indices confirmed the poor environmental quality as a result of the e-waste recycling activities. The CF and PLI reflected the degree of disturbance of the recycling activity on the environment while the PERI put into consideration the total metal concentration, sensitivity of metal contamination to the environment, toxicity level and multi-metal synergy. The pollution indices especially the PERI are widely used in environmental risk assessments as this index is useful from the perspective of the health of crops and soil organisms.

However, the persisting need for improved assessment of risk from heavy metal contamination of the environment has prompted scientific interest in quantifying and predicting metal lability because metal toxicity in soil is related to their availability, which in turn depends on the specific forms of metals in soil.

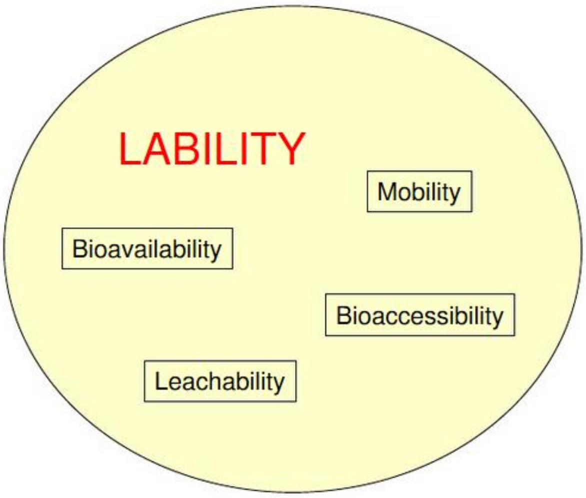


Figure 5.10: Establishing the lability of metals in this study

The lability studies (Fig 5.10) carried out required the use of different extractants to release metals from the soil matrix. The ability to release these metals from soils is particularly important in managing environmental risk as it can allow prediction of potential availability and mobility. This understanding led to the use of different methods and techniques in this study to evaluate the lability of metals (Tab. 5.15).

A combination of analysis (sequential extraction, one step leachability, bioaccessibility), carried out in this study has proven to be a powerful combination of techniques to understand metal lability in soils. Whilst the total concentration of the metals (Cd, Cr, Cu, Ni, Pb, Sb and Zn) is elevated due to the recycling activities, the bioaccessibility testing, which mimics the conditions in the human gastrointestinal system, shows that only a small proportion of the total concentration is available for absorption into the human body, so also the sequential extraction and the one-step leaching test show the proportion readily available in the environment.

Considering the first step of the sequential extraction procedure, the data obtained for each metal provides bioavailability for plants, soil organisms as well as for deposit-feeder organisms. While it is possible for the data obtained from the first step of sequential extraction to be used in predicting for humans, this will underestimate the impact on human as the values obtained from the human bioaccessibility test were quite higher. The results highlight the fact that toxicological and environmental risks depend on the chemical species and on its "availability/accessibility" to target organisms.

Table 5.15: Comparison between methods used to establish metal lability and results obtained

Analysis	Results	Inference
Sequential extraction This provides an estimation of the different fractions of metal present in soils.		
1M Mgcl Neutral salt solutions are often used to extract exchangeable metals which are usually retained mainly by electrostatic attraction on charged surfaces in soils. This fraction is understood to represent the 'bioavailable' metals in soils, controls metal uptake by plants and soil organisms as well as the toxic response of the metals on the organisms.	Cd>Sb>Zn>Cu>Mn>Ni>Pb>Cr	Cd is the potentially most bioavailable metal in the environment.
0.05M EDTA EDTA, a known chelant, is able to dissolve metals not	Pb>Sb>Zn>Cu>Cd>Mn>Ni>Cr	The results represent the concentration of metals associated with the weakly

only in the exchangeable fraction but also metals forming complexes with organic matter, fixed within soil Fe and Al (hydr)oxides or bound to carbonates making it a more powerful extractant and a good choice in trying to estimate lability (potential bioavailability and mobility).		bound organic matter fraction. The extraction with EDTA suggests the migration ability (mobility) of the metals in the soil; metals bound to the organic fraction tend to become potentially mobile as a result of strong redox conditions and organic matter degradation.
70% HNO_3 Nitric acid can dissolve metals associated with a range of fractions and also mobilize the non-labile metal fraction.	Cr>Ni>Mn>Cu>Zn>Pb>Sb>Cd	The metals in this fraction are bound to silicate and crystal lattice and are not easily released in the environment.
Leachability The basis of this test is to estimate the potential of the contaminant to mobilize into different environment compartment(ground water and surface water) and impact on receptors		
0.01M Cacl2	(a) Zn>Cu>Mn>Pb>Sb>Cd>Ni>Cr (b) When concentration leached out is expressed in relation to the total metal concentration in soil, the results become similar to the potential bioavailable fraction from the sequential extraction process. Cd>Sb>Zn>Mn>Cu>Ni>Pb>Cr	The order (a) illustrates the concentration of metals leached out in descending order which signifies potential bioavailability. However, this does not invalidate the results from the sequential extraction. The results from the sequential extraction are in ratio with the total metal concentration. When the metal concentration leached out are used in ratio with the total metal concentration in the soil, a similar result (b) is obtained with the potential bioavailable fraction in the sequential extraction

Bioaccessibility		
The bioaccessible fraction is that available to enter the human system from the environment prior to absorption		
Oral bioaccessibility	Cd >Cu>Sb>Zn>Cr>Mn>Ni>Pb	Cd had the highest solubility in the digestive fluids making it the most bioaccessible metal. In comparison with the sequential extraction. The low pH (1.5) in the gastric region increased the solubility of metals in the digestive fluids. This explains the increase of the concentration of metal e.g Cr in solution which is was shown to be tightly bound to residual fraction in the sequential extraction process. this also supports studies that report the potential bioavailability and solubility of metals increase in low pH.
Inhalation bioaccessibility	Cd>Sb>Cu>Zn>Pb>Ni=Mn>Cr	Cd presented a high bioaccessibility and Cr a low bioaccessibility, a similar trend as was observed in the potential available fraction (F1) in sequential extraction. The result is similar with the sequential extraction process which could be attributed the similarity in the pH of the extractant.

5.5 Human health risk characterization

All the identified metals in this study have been recognized to be potentially hazardous with respect to human health. As such, the health risk characterization is based on an estimation of both of the non-carcinogenic and the carcinogenic risk due to the intake of contaminated soils with the risk indices as the reference dose (RfD/RfC) for non-carcinogenic characterization and the slope factor (SF/IUR) for carcinogenic risk characterization (refer to section 3.8.2). Current risk characterization in environmental risk assessment does not consider bioavailability of heavy metals (Poggio et al., 2008). In this study, the risk characterization was carried out using two different scenarios: the total metal concentration and the bioaccessible fraction. It is important to mention that in assessing the risk of metals in contaminated soils, it is assumed that the metals have additive effect (US EPA, 2002), thus making it possible to calculate the cumulative non-carcinogenic hazard expressed as the hazard index and carcinogenic risk expressed as the total cancer risk.

The values obtained from the composite soil samples were used in evaluating the human health risk. From Table 5.16, using the total metal concentration, it is observed that the non-carcinogenic hazard index (HI) is above the threshold (HI>1) which indicates high risk through ingestion. The cumulative hazard quotient (HQ) for ingestion which is the HI ranged between 5.52 and 7.55 in the dry season and 5.33 and 5.88 in the wet season. The HQs for Cd and Cr were less than 1 and greater than 1 for Cu, Ni, Pb and Sb, the data indicates the contributory effects of the metals to the perceived risk. Cr, Ni and Pb have been identified by the US EPA (1989; 2002) as carcinogenic when ingested; high cancer risks have been identified with the individual metals and also the total cancer risk of the metals (Table 5.17).

Table 5.16: Non cancer risk characterization (ingestion) of metals in study site using total metal concentration

Non cancer risk characterization via ingestion									
Dry season									
	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn	
	HQs individual metals								HI
Recycling area									
0-10cm	0.10	0.075	1.30	0.034	2.31	0.736	2.14	0.032	6.72
10-20cm	0.11	0.075	1.39	0.025	1.52	1.31	1.65	0.038	6.12
20-30cm	0.12	0.14	1.42	0.033	2.95	1.46	1.42	0.042	7.55
Dismantling area									
0-5cm	0.062	0.09	1.02	0.061	1.29	0.967	1.97	0.061	5.52
Wet season									
	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn	
Recycling area									
0-10cm	0.098	0.086	1.26	0.02	1.79	1.09	1.51	0.022	5.88
10-20cm	0.15	0.18	1.22	0.042	1.60	1.05	1.23	0.025	5.49
20-30cm	0.095	0.11	1.23	0.028	2.08	0.039	1.74	0.026	5.34
Dismantling area									
0-5cm	0.051	0.081	0.966	0.059	1.73	0.93	1.58	0.059	5.46

Where HI is hazard index; HI>1 signifies high non cancer risk

Table 5.17: Cancer risk characterization (ingestion) of metals in study site using total metal concentration

Cancer risk characterization via ingestion								
	Dry season				**Wet season**			
	Cr	Ni	Pb		Cr	Ni	Pb	
Recycling area								
	Individual cancer risk			TCR	Individual cancer risk			TCR
0-10cm	5.0E-04	4.21E-03	3.29E-02	3.76E-02	5.73E-04	3.27E-03	4.88E-02	5.26E-02
10-20cm	5.06E-04	2.78E-03	5.84E-02	6.17E-02	1.20E-03	2.92E-03	4.69E-02	5.10E-02
20-30cm	6.96E-04	5.37E-03	6.52E-02	7.12E-02	7.13E-04	3.78E-03	4.34E-02	4.79E-02
Dismantling area								
0-5cm	6.03E-04	2.34E-3	4.32E-02	4.62E-02	5.44E-04	3.15E-03	4.17E-02	4.54E-02

Where TCR is total cancer risk; cancer risk >threshold signifies high cancer risk Threshold =10E-04-10E-06)

On the other hand, the non-carcinogenic risk and cancer risk posed to human health due to the inhalation of re-suspended particles where found to be below the threshold level (Tables 5.18 and 5.19). The HQs of the metals were less than 1 and the cumulative effect (HI) was also less than 1, which indicated little or no adverse health effect through the inhalation of re-suspended soil particles. Although Cd, Cr, Ni and Pb are identified as possible carcinogens when inhaled, the individual risk and total cancer risk were also found to have little or no adverse effect on human health.

Table 5.18: Non cancer risk characterization (inhalation) of metals in study site using total metal concentration

Non cancer risk characterization via inhalation of re suspended particles									
	Dry season								
	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn	
	HQs of individual metals								HI
Recycling area	1.58E-04	5.19E-05	7.88E-03	2.71E-04	8.53E-07	2.47E-03	1.21E-05	1.39E-03	1.22E-02
Dismantling area	1.58E-04	1.50E-04	5.10E-03	1.27E-03	1.54E-06	1.85E-03	6.99E-06	1.06E-03	9.60E-03
	Wet season								
Recycling area	1.46E-04	4.87E-05	9.48E-03	2.38E-04	9.33E-07	2.27E-03	1.41E-05	5.94E-04	1.28E-02
Dismantling area	1.90E-04	1.67E-04	5.98E-03	1.78E-03	1.92E-06	1.54E-03	7.09E-06	1.22E-03	1.09E-02

Where HI is hazard index; HI>1 signifies high non cancer risk

Table 5.19: Cancer risk characterization (inhalation) of metals in study site using total metal concentration

Cancer risk characterization via inhalation of re suspended particles										
	Dry season					**Wet season**				
	Cd	Cr	Ni	Pb		Cd	Cr	Ni	Pb	
	Individual cancer risk				TCR	Individual cancer risk				TCR
Recycling area	1.22E-12	2.67E-11	9.66E-13	3.18E-08	3.18E-08	1.13E-12	2.51E-11	1.06E-12	2.92E-08	2.92E-08
Dismantling area	1.22E-12	7.74E-11	1.75E-12	2.38E-08	2.39E-08	1.46E-12	8.59E-11	2.17E-12	1.97E-08	1.98E-08

Where TCR is total cancer risk; cancer risk >threshold signifies high cancer risk (Threshold =10E-04-10E-06)

5.5.1 Integration of bioaccessibility in human health risk assessment

The results in section 5.3 indicated that the total metal content in soils is not completely bioaccessible/bioavailable, and so the assumption of total metal would result in an overestimate of health risks at the site. Since the site-specific bioaccessibility values were obtained, the risk posed by ingestion and inhalation of re-suspended particles are adjusted by including the % bioaccessibility factor.

$$CDI_{ingestion} = \frac{\mathbf{C*\%BAF*IR*EF*ED}}{\mathbf{BW*AT}} * \mathbf{CF} \text{ ------------- Equation 5.3}$$

$$CDI_{\ inhalation} = \frac{\mathbf{C*BAF*InhR*EF*ET*ED}}{\mathbf{PEF*AT}} \text{ ------------- Equation 5.4}^{5}$$

---

[5] Where; C is concentration; AT is averaging time (lifetime in yrs.* 365 days yr^{-1}); ED is exposure duration (25 yrs.); EF is exposure frequency (225 days yr^{-1}.); PEF is particulate emission factor (1.36*109 m^3 kg^{-1}); ET is the exposure time; IUR is the inhalation unit risk; %BAF is the percentage bioaccessbility factor; IR is ingestion rate; InhR is inhalation rate; CF is conversion factor (10-6 kg mg^{-1}).

Incorporating the bioaccessible factor, it is observed that the HQs of the individual metals are all less than 1 and lower than the HQs when evaluated with the total metal content. The HI ranges between 1.16 and 1.81 (Table 5.20) which is above the limits (HI≤1). The individual cancer risk through ingestion for Cr and Ni fall within the threshold level (Table 5.21), although the total cancer risk and non-cancer risk posed from ingestion exceeds the threshold limits, the levels of risk is lower than the risk assessed using the total metal content.

Table 5.20: Non cancer risk characterization (ingestion) of metals in study site including the bioaccessibility factor

Non cancer risk characterization via ingestion									
					Dry season				
	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn	
				HQs of individual metals					HI
Recycling area									
0-10cm	0.036	0.024	0.44	0.009	0.51	0.096	0.64	0.009	1.76
10-20cm	0.033	0.022	0.41	0.009	0.32	0.21	0.45	0.009	1.45
20-30cm	0.038	0.028	0.43	0.008	0.62	0.27	0.4	0.01	1.81
Dismantling area									
0-5cm	0.015	0.014	0.22	0.014	0.25	0.21	0.43	0.014	1.16
					Wet season				
Recycling area									
0-10cm	0.03	0.023	0.4	0.004	0.37	0.15	0.42	0.005	1.41
10-20cm	0.04	0.05	0.41	0.009	0.32	0.16	0.34	0.006	1.33
20-30cm	0.026	0.025	0.35	0.006	0.4	0.12	0.43	0.005	1.36
Dismantling area									
0-5cm	0.015	0.015	0.21	0.015	0.29	0.2	0.43	0.016	1.19

Where HI is hazard index; HI>1 signifies high non cancer risk

Table 5.21: Cancer risk characterization (ingestion) of metals in study site including the bioaccessibility factor

Cancer risk characterization via ingestion								
	Dry season				**Wet season**			
	Cr	Ni	Pb		Cr	Ni	Pb	
Recycling area								
	Individual cancer risk			TCR	Individual cancer risk			TCR
0-10cm	3.56E-05	2.07E-04	9.57E-04	1.20E-03	3.48E-05	1.53E-04	1.52E-03	1.70E-03
10-20cm	3.25E-05	1.30E-04	2.09E-03	2.25E-03	7.46E-05	1.30E-04	1.59E-03	1.79E-03
20-30cm	4.20E-05	2.53E-04	2.72E-03	3.02E-03	3.69E-05	1.63E-04	1.18E-03	1.38E-03
Dismantling area								
0-5cm	2.10E-05	1.02E-04	2.01E-03	2.14E-03	2.28E-05	1.19E-04	2.00E-03	2.14E-03

Where TCR is total cancer risk; cancer risk > threshold signifies high cancer risk. (Threshold =10E-04-10E-06)

The non-cancer and cancer risk posed by inhalation of re-suspended particle all fall below threshold level and integrating the bioaccessible factor also reduced the risk when compared to the risk evaluated using the total metal content (Tables 5.22 and 5.23).

Table 5.22: Non cancer risk characterization (inhalation) of metals in study site including the bioaccessibility factor

Non cancer risk characterization via inhalation of re suspended particles									
Dry season									
	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn	
	HQs of individual metals								HI
Recycling area	1.07E-04	8.80E-06	2.67E-03	7.43E-05	1.36E-07	4.73E-04	4.48E-06	4.11E-04	3.75E-03
Dismantling area	9.15E-05	1.08E-05	1.78E-03	7.92E-05	3.21E-07	3.49E-04	2.34E-06	2.61E-04	2.58E-03
Wet season									
Recycling area	9.11E-05	8.27E-06	2.91E-03	6.91E-05	1.74E-07	4.09E-04	5.62E-06	2.08E-04	3.70E-03
Dismantling area	1.10E-04	1.38E-05	1.99E-03	1.17E-04	3.25E-07	4.09E-04	2.95E-06	3.56E-04	3.00E-03

Where HI is hazard index; HI>1 signifies high non cancer risk

Table 5.23: Cancer risk characterization (inhalation) of metals in study site including the bioaccessibility factor

Cancer risk characterization via inhalation of re suspended particles										
	Dry season					**Wet season**				
	Cd	Cr	Ni	Pb		Cd	Cr	Ni	Pb	
	Individual cancer risk				TCR	Individual cancer risk				TCR
Recycling area	8.28E-13	4.53E-12	1.54E-13	6.08E-09	6.09E-09	7.02E-13	4.25E-12	1.97E-13	5.26E-09	5.26E-09
Dismantling area	7.06E-13	5.58E-12	3.63E-13	4.48E-09	4.49E-09	8.52E-13	7.11E-12	3.63E-13	5.26E-09	5.26E-09

Where TCR is total cancer risk; cancer risk > threshold signifies high cancer risk (threshold =10E-04-10E-06)

As stated in section 3.8, the exposure scenario in this study focused on workers on the e-waste recycling site which were mainly adults. Although children aged between 7 and 11 years were found working on the site, the US EPA recommended that in occupational composite sites aged 7 and above should be categorized as adults (US EPA, 2002).

The individual HQ of Cu indicated that it was the highest contributor to the non-cancer risk through the exposure pathways (ingestion and inhalation). This was also observed in section 4.4.2, where the potential ecological risk identified Cu as the highest contributor in the ecological risk. Some metals in this study such as Cu and Zn are essential micronutrients to man, but their high level in soils have adverse health effects. Pb and Ni have no known biological importance, they are also identified as high contributors to the non-cancer and cancer risk through ingestion; the individual HQs where higher found higher than the threshold for acceptability for the additive effect of all metals in the exposure pathway.

The risk posed by inhalation of re-suspended particles either through the mouth or the nose, or both, is almost negligible compared with the risk posed through ingestion (Tables 5.15 - 5.18). The associated risk posed either cancer or non-cancer was all found below the limits of acceptability. Many risk assessments often do not estimate the risk associated with the inhalation of re-suspended soil particles, because it is assumed that ingestion is typically the dominant exposure pathway as regards soils (James et al., 2012). This study indicated that although the carcinogenic and non-carcinogenic risks on inhalation of the studied metals were non-significant in comparison to the ingestion route, this exposure pathway should not be overlooked.

Furthermore, when comparing the risk using the total metal content and the percentage bioaccessible fraction, it was observed that the use of bioaccessible fraction had a significant impact on the magnitude of risk and indicated that using the total metal content might overestimate the potential risk posed (Tables 5.19 - 5.22). The results obtained in this study is in accordance with Wragg & Cave (2003), Luo et al., (2012), Pelfrêne et al., (2012) and Izquierdo et al., (2015), their studies highlighted the fact that assessing human health risk based on total metal concentration may overestimate the risk and may be suitable for worst case scenarios or long term risks. Therefore, the integration of bioavailability is important in more realistic assessment of short term to medium term risk.

In assessing the risk according the risk model used in this study, the presence of uncertainties should be put into consideration. The risk model has some elements of conservatism built into it, and so, caution should be taken in interpreting the quantitative results obtained.

Firstly, the effects of the intake of the combined metals were assumed to be additive, but based on the findings presented in section 5.3, metals could have either synergistic or antagonistic effect.

Secondly, due to the recycling activities carried out daily, there is a probability of bioaccumulation when the contaminants are accidentally taken in, and can occur by metals attaching to binding sites in the human system. Studies have reported that metals can bring to bear their toxicity by imitating essential elements, attaching to their physiological binding sites and utilizing their transport mechanism. For instance, Cu, Cd & Ni are known to mimic

Zn; Mn behaves like Fe. Pb enters the body through the Ca transport mechanism and also interacts with enzymes involved in the haem synthesis pathways, and alters porphyrin profile (HERAG, 2007). The risk assessment model used does not create room to include the possibility of a bioaccumulation factor; again being very conservative.

Finally, according to Izquierdo, et al., (2015), the exposure frequency and ingestion rates influence the output of the risk assessment. In this study, the values used in estimating the risk were the standard values in assessing risk of an outdoor worker, which are also conservative since the working behaviour of the populace could be population specific.

Irrespective of these uncertainties in the risk assessment process, the results obtained in this study suggest that the recycling activities at the site have negative human health impact.

CHAPTER SIX

6 Integration of the scientific evidence into strategic management of risk: the case of informal e-waste recycling.

Strategic risk in this study is defined as the uncertainties embedded in the informal recycling of e-waste process. Managing the risk includes adopting the uncertainties and opportunities in the informal recycling process which gives a clear understanding on developing an integrated and effective risk management measure. Strategic risk management involves five main processes: pre-assessment, risk appraisal, tolerability and acceptability judgement, risk management and communication (Fig 6.1). The pre-assessment phase places importance on the need of understanding the risk and selects major assumptions, conventions and procedural rules for assessing the risk. The risk appraisal phase provides knowledge base comprising of the scientific assessment (which seeks to link a potential source of harm, a hazard, with likely consequences, specifying probabilities of occurrence) and the social and economic implication (understanding the knowledge of stakeholders' concerns and questions). The tolerability and acceptability judgement phase involves the characterization and evaluation of the risk with the aim of judging the tolerability of the risk. The risk management phase designs and implements the actions required to tackle risks with an aim of risk reduction. Finally, the risk communication requires the exchange of information between all the phases (Renn, 2007). The results obtained in this study so far fits perfectly into the first half (risk assessment) of the risk appraisal phase.

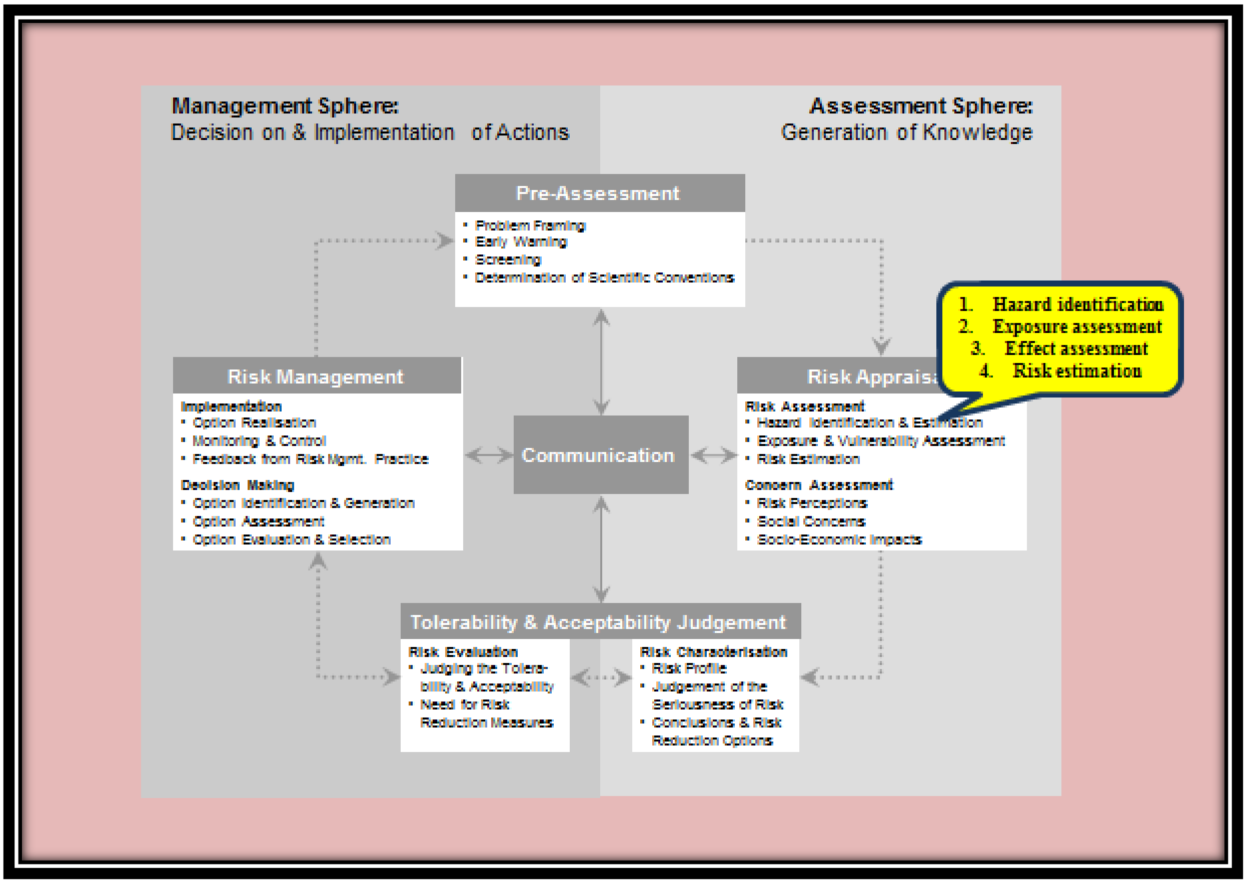


Figure 6.1: Detailed IRGC framework for risk management. Source: (Renn, 2007)

6.1 Risk evaluation

The results obtained and discussed in chapters 4 and 5 provide evidence that the site not only has ecological implications but it is also risky to human health, as a result, it would be rational to suggest potential solutions to improve the site conditions. On intuition, the suggestion to ban the workers and activities and implementation of policies would arise. However, these potential solutions could be marred by challenges and barriers and in order to reduce risks, institutions are required to evaluate risks and manage risk. Although this study is not based on risk management, the risk evaluation is required in order to make an appropriate judgement that will feed into the management phase as described in Fig 6.1.

From the framework, the results obtained from the risk appraisal which consists of both risk assessment (chapter 4 and 5) and concern assessment will be fed to the next stage which is the acceptability and judgement stage. This stage entails risk characterization and risk evaluation.

Risk characterization and evaluation are interrelated; each depend on the other and are often referred to as an entity, but, risk characterization determines the evidence-based component while risk evaluation determines the value-based component for making necessary judgement (Löfstedt & Vogel, 2001). Risk characterization involves collecting and summarising all relevant evidence useful for making an informed decision and potential options of the risk in question from a scientific perspective. On the other hand, risk evaluation involves the application of societal values and norms in determining the need for risk reduction measures (Renn, 2008).

Risk is conceptualized into three approaches: objective, subjective, and perceptive (Crawford-Brown, 1999). The objective approach refers to risk as an outcome of scientific methods and experimental research conducted; the subjective approach believes risk is not entirely objective as it varies depending on the uncertainties, social norms and the experience of the individuals involved. The perceptive approach on the other hand, relates risk to the exposed individuals who have evidence on the effects or severity of the risk (Crawford-Brown, 1999).

In recent times, a lot of questions are being raised on risk assessment carried out based on science alone because the risks to society are exhibiting far more diverse aspects beyond the scope of scientifically estimated risks (Janmaimool & Watanabe, 2014). According to Ropeik (2011), although scientific risk assessment is thoroughly conducted by using reliable methods and are usually accurate, the interpretation of the results obtained might be conflicting with socio-economic conditions, the way humans perceive and why they are willing to undertake the underlying risk. Ropeik’s assertion was supported by Péry et al., (2013), Wilks et al., (2015) and the Science for Environment Policy (2015), who all agreed that including the perception and socio-economic conditions in risk assessment provides an overall view of the negative impacts on human and environmental health, the value of the activity in the society as well as reasons to stop, ban and manage the informal e-waste recycling activity.

In other words, risk evaluation may be used to assist risk management decisions, and to make proper judgement and manage risks, it is not enough to consider only the results of scientific risk assessment, the concerns of the various stakeholders, perceptions and the further implications of the direct consequences of a risk is required (Renn, 2008).

6.2 Risk perception

Risk means different things to different individuals, groups of people and society; the majority of people react based on intuitive risk judgement known as “risk perception”. Risk perception is the subjective judgement people make on the severity of a risk they might be exposed to (Slovic, 1987; Schmidt, 2004). Risk perception is dependent on individual attitude, beliefs, value system and analytical way of thinking. In other words, it can be formed based on both belief and self-appraisal (Sjöberg et al., 2004).

6.2.1 Risk perception and risk decisions

According to Slovic et al., (2004) individuals have two ways of thinking in decision making: the intuitive and the analytical. Intuitive decisions are made quickly and rely on mental shortcuts which may introduce bias, while decision made analytically gives room to analyse data and assess the best options. Risk perception is seen as an obstacle to rational decision making, because people may see risks where a more scientific approach may suggest that there is little risk and vice versa (Sjöberg et al., 2004). There are four main approaches in understanding risk perception; the cultural theory (Peters & Slovic, 2000; López-Navarro et al., 2013) social amplification of risk framework (SARF) (Kasperson et al., 1988; Renn et al., 1992), the axiomatic measurement paradigm (Slovic & Weber, 2002) and the psychometric paradigm (Fischhoff et al., 1978), which is most dominant in the field of risk.

The psychometric paradigm has been the most influential model in the field of risk analysis. The “cognitive maps” of hazards produced by the paradigm seem to explain how laypeople perceive the various risks they face which unveil the factors that determine risk perception (Siegrist, et al., 2005). The psychometric paradigm addresses risk perception of people as being significantly influenced by the physical properties of risks (voluntariness, familiarity, and catastrophic consequences), as well as psychological and cognitive factors (dread, experience, benefits associated with the risks, controllability, and knowledge (Fischhoff et al., 1978, 1993; Slovic, 1987; Slovic & Weber, 2002; Sjöberg et al., 2004; Schmidt, 2004).

6.2.2 Risk attitude

Risk attitude is people's tendency to evaluate a risk in either a favourable or unfavourable manner and to act according to underlying traits of risk propensity or risk aversion (Fig 6.2). In order words, risk attitude is an individual’s generic orientation towards taking or avoiding a risk when deciding how to proceed in situations with uncertain outcomes (Rohrmann, 2008, 2011). People’s risk attitudes are neither stable, nor homogeneous across different types of hazard; rather, people tend to hold domain-specific attitudes regarding physical, financial and social risks (Weber et al., 2002; Gattig & Hendrickx, 2007).

Since people have different attitudes to risk, risk attitudes can be chacterized into risk averse, risk seeking, risk tolerant and risk neutral which represent actions to an uncertain hazard (Hillson & Murray-Webster, 2007; Fig 6.2).

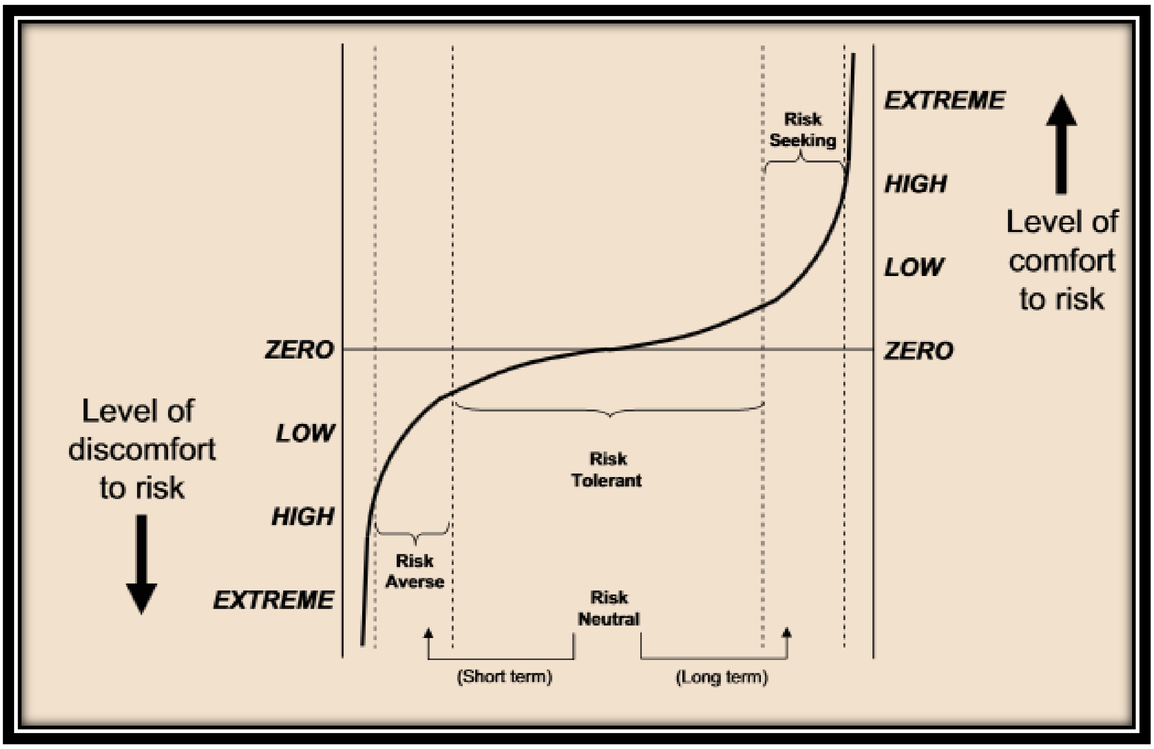


Figure 6.2: Risk attitude spectrum. Source: (Hillson & Murray-Webster, 2007)

Furthermore, Hillson & Murray-Webster (2007) reported that people's risk perception and risk attitude are influenced by similar factors and both concepts (risk perception and attitude) are interrelated. They summarized these factors as conscious, subconcious and affective. The conscious factors are based on rational assessment founded on the visible and measurable characteristics of the risk before decision making. The subconscious factors include mental short-cuts made to facilitate decision-making, which can introduce bias, and the affective factors are based on emotions or deep underlying feelings rather than rational assessments.

In summary, sections 6.2.1 and 6.2.2 are indicative of some factors that could influence the perception and decision making of individuals in evaluating the environmental risk especially in the informal e-waste recycling site. From Fig 6.1, the aim of a risk evaluation is to arrive at a judgement on tolerability and acceptability based on balancing the potential impacts, concerns and evidence. In order to make the judgement, the risk appraisal phase has to be complete. The evidence of the risk assessment has been reported in chapters 4 and 5; however, there have been no reports on the concern assessment. Hence, the next section provides information on the risk perception of the informal e-waste recyclers in the study site.

6.3 Risk perception of the informal e-waste recyclers in the study site.

During field investigation, a chain of activities involving collection, dismantling, sorting and burning was revealed (section 3.2); the informal recyclers had enough manpower and manual skills to ensure the process continued on a day-to-day basis. Armed with the scientific evidence and the state of the workers and study site, a pilot study was carried out with the consent of the informal e-waste recyclers to find out their understanding of the risk and impact associated with their various activities.

A series of open ended questions which covered demographic information (Tab 6.1), knowledge of environmental impacts and perceived health risks related to improper recycling activities were administered on twenty two willing informal e-waste recyclers. The interviews were recorded with a Sony ICD- PX333 digital voice recorder for an average of 20 minutes for each participant. The interviews were transcribed verbatim, and analysed thematically to identify major themes. Thematic analysis involves the searching across a data set either a number of interviews or focus groups, or a range of texts to find repeated patterns of meaning (Braun & Clarke, 2006). The interview which was designed to evaluate the perceived environmental and health risks by informal recyclers to build upon the outcome of the risk characterization was conducted in the local pidgin English language and then translated into English.

6.3.1 Responses from the informal recyclers

Although the interview was not intended as a detailed study, the outcome of the interviews gave an insight to why people are willing to undertake risk, which is one factor necessary to input in risk assessment according to Ropeik, (2011).

Table 6.1 gives the profile of the informal recyclers interviewed. The participants were all men and represented a wide range in age (9 – 40 years) and the youngest interviewed was aged 9. The participants all claimed to have formal education, only 1 of them reached achieved tertiary level, 4 of them stopped at primary school education while 3 (the under 10 years old) claimed to still be in primary education. The 3 boys still in primary school said they scavenge after school hours, weekends on days they do not have to be in school.

Majority of the participants claimed to have over 3 years job experience and they multi-tasked, carrying out both dismantling and burning.

Table 6.1: Demographic profile of workers at the informal e-waste recycling site in Lagos State, Nigeria, (October 2013).

		Number	**Percent**
Gender	Male	22	100%
	Female	0	
Age	0-10	3	13.64%
	11-20	3	13.64%
	21-30	11	50%
	31-40	5	22.73%
Ethnicity	Hausa	17	77.27%
	Yoruba	2	9.09%
	Igbo	0	0%
	Other tribes	3	13.64%
Marital status	Single	14	63.64%
	Married	8	36.36%
Educational background	None	9	41%
	Primary	7	31.82%
	Secondary	5	22.72%
	Tertiary	1	4.55%
	Postgraduate	0	

Job description	Scavengers/collectors	3	13.64%
	Dismantlers	5	22.73%
	Sorters	2	9.09%
	Burners	12	54.5%
Job experience (years)	<1	0	0%
	1-3	9	40.9%
	3-5	10	45.45%
	>5	3	13.64%
Average daily income (Naira)	<1000	0	0%
	1000-3000	6	27.27%
	3000-5000	13	59.1%
	>5000	3	13.64%

1 Nigerian Naira= 0.006 U.S dollar; 1 U.S dollar =150 Nigerian Naira * was correct as at October 2013 at the time the data was obtained, but as at 1st October 2016, 1 Nigerian Naira= 0.003 U.S dollar; 1 U.S dollar =450 Nigerian Naira

The major themes identified after analysing the interviews were lack of knowledge/poor awareness, socio-economic conditions and financial benefits.

6.3.1.1 Socio-economic conditions

It was observed that that majority of participants (82%) migrated to Lagos State seeking better livelihood. Lagos State was once the capital of Nigeria and a thriving commercial hub. The cities in Nigeria have experienced rapid urbanization due to population migration and growth. The population explosion in Nigerian cities has outstripped the government capacity to provide adequate jobs and services, hence, the high rate of unemployment in the country.

"I left my family in Nassarawa since no work there, so I can get money to feed them or do you want them to eat sand?"(James, 31years old, burner)

"There are a lot of job opportunities in Lagos, like this our job now, even if we do it in my State, it will not move as it is moving here because big customers all buy from Lagos" (Kelly, 24 years old, burner)

Improper recycling of electronic waste has become a thriving business due to unemployment. This finding is similar to studies reported by (Manhart, et al., 2011) who reported the migration from the northern part of Nigeria during non farming seasons to seek livelihood through e-waste recycling.

6.3.1.2 Financial benefits

E-waste is known to contain considerable quantities of valuable and reusable materials as reported in chapters 1 and 2, which recyclers try to recover through rudimentary methods. The recovered materials are sold according to the rates in the international market. For instance, copper sold at 5.50 dollars per kilogram (825 Nigerian naira) while aluminium sold at 1.50 dollars per kilogram (225 Nigerian naira)[6] in October 2013. These workers claim to have a huge market for their thriving business as many manufacturers buy these products from them.

"We have big customers that buy all this copper and aluminium from us and they always give us something[7] after every transaction" (Mike, 17 years old, dismantler)

They claim their customers prefer to buy from them because their products are free from impurities and also the customers avoid paying duty and fees when they have to import the materials themselves. The high demands coming in from the customers of the recyclers, keeps the business booming and more youths are willing to go into the business.

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[6] Prices correct as at October 2013

[7] Something refers to tips

"Our customers buy copper according to international trading prices of the day. So they call us first and ask how much for copper then come to buy. Only one person can buy all the copper we have gathered in the market because they buy in bulk. Like now, I have up to 15kg, if I sell it today or tomorrow, I will rest till next week before I start work again"(Solomon, 35 years old, burner)

"They like to buy from us because they don't have to pay tax or port clearance fee and we know that so we always ask them to give us something. Even if I don't work that day, the tip I get from the customers will feed me" (Anthony, 21 years old, dismantler)

Furthermore, the participants are not keen on leaving their jobs because of lack of any incentives offered by the government. The average minimum wage is 18,000 naira monthly, which is equivalent to 110 U.S dollars monthly and 3.54 U.S dollars on a daily basis[8]. This amount is barely enough to cater for a person's daily needs let alone a family.

"God forbid I work for government or anybody, how much will they pay me? I am already building house in my State, how many of my mates can boast of building a house? When I finish building the house, I will gather money to start another business then I will leave this one" (Job, 28 years old, burner)

"On the days I work, I get between 1000 -1200 naira and sometimes I also find useful things I can sell to get money while scavenging" (Dore, 9 years old, scavenger/collector)

From the interviews, the least paid worker at the site earns an average of 10 U.S dollars on a daily basis. The workers, being aware of this fact, have no incentive to leave their jobs despite the risks involved. Although the workers claim these earnings, there are no data to confirm the earnings since they are not documented. These findings are also in line with

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[8] Value correct as at October 2013

studies by Manhart, et al., (2011), they reported that financial benefits received by the recyclers keep the informal recycling business thriving.

6.3.1.3 Poor awareness/lack of knowledge

From the interview, all participants did not recognise that their recycling activities were informal, improper and could cause harm to the environment. Fifteen of them argued that they paid tax on a daily basis to the Local Government Council in which the recycling site was located (Ojo Local Government Area), further arguing that they could have been banned from their informal recycling activities if it had any environmental impact.

"Please, there is nothing wrong with this our job. How can you say it is bad? If it is bad, why do the council boys collect 200 naira tax from us every day? If it is bad, council could have driven us away from here since. Please, our job is not bad, we are not causing any environmental problem". (Faruk, 23 years old, dismantler and burner).

The remaining seven maintained that they were earning a daily living by hard work, without causing harm to people or breaking the law.

"Madam, nothing is wrong in our job, nobody has come to complain that we are causing problem, after all we did not kill anybody or steal from anybody. It is the work of our hands we are using to feed ourselves" (Thank God, 16 years old, Sorter)

On their knowledge of the environmental and health impact of their activities, nineteen had no prior knowledge of the impact while the remaining three people had little knowledge of the impact based on hearsay. However, they all argued that they do not fall ill frequently hence their bodies had developed some resistance to the "claimed health impacts" despite being exposed to it on a daily basis.

"My parents told me what you do not know can never kill you". (Robbie, 10 years old, scavenger/collector)

"Madam, you said this is your project, what is written in book is not what happens on ground. I have heard it before that this work can cause sickness but no proof, so I don't believe it, we have not had complain from any of our members here. As for the environment, is the erosion not spoiling the environment too? Since I finished from the polytechnic, no job, nothing to do, the government cannot even provide employment or do anything right and you are here telling me of protecting the environment. Tell government to stop erosion and flooding or provide jobs to protect the environment". (Steve, 33 years old, dismantler and burner and also leader of the informal recyclers at the site).

"*It is normal, when all of us just started the job, we were coughing and sneezing because our body was not used to it but now, none of us here can get any cough. We now have odeshi*[9] *to any sickness you claim can be contracted from this work. Even you madam, if you go to a new place, your body will change first now before it adjust" (Gary, 25 years old, burner)*

"I have never been sick because of this job. It is only malaria that I used to have because you know our job is always outside now and mosquito will bite you. Then I will buy amalar[10] *and paracetamol from chemist, the next day, I am ready to hustle again" (Dayo, 20 years old, dismantler)*

A significant number, (91%) admitted they had coughed and sneezed a lot when they were new on the job and the longer they spent on the jobs, the stronger their immune system became and they no longer had the symptoms. None of the participants had visited a

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[9] Odeshi in local parlance refers to resistance

[10] Amalar is a brand name for an antimalarial drug (combination of Sulfadoxine 500 mg and Pyrimethamine 25 mg) in Nigeria

physician in a period of twenty four months prior to the study; they rather bought medication over the counter without prescription.

"*What I'm I going to do in the hospital? You will waste your whole time there waiting to see the doctor and at the end, it is the same drug chemist boy give you in 1 minute that doctor will use the whole day to prescribe. I cannot remember when last I went to the hospital, maybe when I was 6 or 7 years" (Ade, 35 years old, dismantler and burner)*

"Hospital? When our agbo[11] *is there. Nobody has ever had any sickness from this job. Dirt does not kill a black man. Besides, something must kill a man, it is better I die in the course of work than been shot down dead" (Jude, 28 years old, dismantler and burner)*

All participants stated a belief that they could not contract any ailment on the job and the worst ailment they could have was catarrh and cough which they claim they were now resistant to.

6.3.2 Factors influencing the risk perception of the recyclers

No enterprise thrives without taking risks; the risk appetite and risk attitude of individuals at the informal recycling site could be identified and quantified by the way their aims and goals are achieved. Based on the psychometric paradigm discussed in section 6.2.1, it can be inferred that their voluntariness, controllability, familiarity, delayed effect, and their financial benefit influenced their perception, attitude and appetite to the risk.

The financial benefits may thus make them ignore the health risks. Risks perceived to have benefits are more accepted than risks with little or no benefit; the benefit serves as compensation (Schmidt, 2004). Although there are no confirmed data on the earnings of the informal recyclers, their income serves as a motivation for the activities. Manhart et al., (2011)

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[11] Agbo refers to local herbs taken on a weekly basis with the belief that it flushes out any ailment

and Ogungbuyi et al., (2012) both reported that the informal recyclers' income is much higher than usual earnings for an average Nigerian despite the recyclers' educational background (little or no education) and this is another reason the informal recycling business thrives.

Their willingness to carry out their activities and the autonomy to do what they needed to do without being tied to a specific time (i.e. not tied to the usual 9 to 5 job) gave them personal freedom and encouraged them to accept the risk. An excerpt from the interview confirmed this fact. "*….Like now, I have up to 15kg, if I sell it today or tomorrow, I will rest till next week before I start work again".* According to Renn, (1992) and Schmidt, (2004) risk perception is attenuated if the risk is chosen, as it is a wanted risk probably because of some of the expected benefits. Similarly, risks under an individual's control are perceived to be more acceptable than risks controlled by others. The individual affected by the risk is convinced that he/she could stop at any time and convinced he/she has chosen the best available option. Familiarity with the risk also affects the perception and attitude to the risk. According to Slovic, (1987), known risks are more accepted than unknown risk.

Although the workers at the site are exposed to various hazards, they do not see it in the same light. There are claims that there were no reported case of any chronic ailment has being made in two years prior to the study carried out apart from malaria (which is endemic to Nigeria). This could be characterized as a delay effect, which is the period of latency between the initial event and the actual impact of the event. The delay effect poses a problem in recognizing the effects of some risks since the impact is not immediately apparent (Schmidt, 2004). Based on the data presented in section 5.4, the health risk as a result of the activities is high but probably the health impacts have not been manifest, or because of the poor medical attitude of the site workers, there has been no diagnosis, hence the workers believe there is no health risk posed. It could also be due to cherry picking of health evidence by blocking their hearing to health reports in order to avoid the health scare.

Finally, it has been established that risk perception is a social construct and psychological elements guide people’s response to a hazard as against technical risk estimates from experts, one such element is trust (Frewer, 1999). Trust is defined as a psychological state comprising the intention to accept vulnerability based upon positive expectations of the intentions or behaviour of another (Rousseau et al., 1998). The lack of trust in the government and cooperate bodies and agencies due to broken promises on improving the socio-economic condition of its citizens could fuel the workers risk perception. “*….Since I finished from the polytechnic, no job, nothing to do, the government cannot even provide employment or do anything right and you are here telling me of protecting the environment”* Over the years, there have been un-kept promises by the different governing dispensations on improving the conditions of an average Nigerian. The recyclers, having lost hope and trust in the government, have decided to seek a livelihood in order to survive irrespective of the consequences.

6.4 Integrating risk process in e-waste recycling in Nigeria

The ERA characterized the risk posed by the informal recycling and then initiated the process of risk management (evaluation) which will eventually lead to a choice of action that will achieve the desired level of "safety" by the determination of the "acceptability" or "tolerability" of risk. Acceptability is not only based on scientific data, but also on social, ethical and economic considerations (Lammerding, 1997). From Fig 6.1, the process of characterization ends the assessment sphere and feeds into evaluation which begins the management sphere and according Renn, (2007), these entities are the most controversial part in handling risk. The main aim of evaluation is to make a judgement which will assist in the development of effective and feasible management plans (Klinke & Renn 2002). By so doing, existing infrastructures need to be put into consideration. In Nigeria, the e-waste challenge has been managed with a number of policies discussed in section 6.4.1

6.4.1 Legislation, policies and regulations

The evidence gathered in this study (Chapters 4 and 5), and similar studies carried out in China, India, Ghana (Chi et al., 2011; Oteng-Ababio 2012; Perkins et al., 2014; Annamalai, 2015), revealed the ecological and human health impact informal recycling of e-waste. Some of these same studies have reported the use of laws, regulations and policies as one of the steps in controlling the impact of e-waste on the environment. According to Perkins et al. (2014), most e-waste regulations were initially focused on environmental protection only without the enforcement of human health concerns, although in recent times, human health concerns have been added.

In Nigeria, the high demand for second-hand electronics, the high influx of e-waste and the weak environmental regulations make the informal e-waste sector thrive (Nnorom & Osibanjo, 2008; Ejiogu, 2013). In order to regulate the activities, the Federal Government ratified several international conventions and put in place a number of national policies and regulations.

6.4.1.1 International conventions

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was created in 1989 and entered into force in 1992 to address concerns over the management, disposal and transboundary movements of hazardous wastes that are toxic or inflammable and these include e-waste. The main principles of the Convention include: the transboundary movements of hazardous wastes should be reduced to a minimum, consistent with environmentally sound management; hazardous wastes should be treated and disposed of as close as possible to their source of generation; and hazardous waste generation should be reduced and minimized at source. Nigeria was the first African country to sign and ratify the agreement and was also a signatory to the 2008 Bamako Convention, which is a treaty among African countries that prohibits the import of hazardous wastes into member countries (Nnorom & Osibanjo, 2008; Ejiogu, 2013). The Bamako Convention on the ban on the import into Africa and the control of transboundary movement and management of hazardous wastes within Africa was negotiated at the Organization of African Unity at Bamako, Mali in January, 1991 by twelve African nations and came into force in 1998.

6.4.1.2 National regulations

The federal government passed the NESREA Act which is tasked with the responsibility of enforcing compliance with regulations on the environment. On 25th May 2011, the National Environmental (Electrical/Electronic Sector) Regulation, (S.I. No 23 Gazette No. 50, Vol. 98) was passed to prevent or minimise pollution from all operations and ancillary activities of the electrical and electronic sector. Furthermore, in May 2011, "The National Environmental (Electrical/Electronic Sector) Regulations 2011 for E-waste management in the Federal Government Gazette No. 5, Vol. 98 was expanded from 3Rs to 5Rs namely: Reduce, Repair, Reuse, Recycle and Recover. The Extended Producer Responsibility (EPR) program was put in Schedule VIII of the Regulations. The Eko Declaration, which encourages and enforces collection, reduce, recovery and recycling (3Rs) of E-waste, was made in the Eko international summit, Lagos in February 2011. Fines and punishment for both individual and corporate offenders were all put in place in the regulations (Obaje, 2013).

Despite these actions, Nigeria still faces considerable threats from E-waste importation and informal recycling which might not be unconnected to the factors discussed in section 6.2.2. Based on the responses of the recyclers in the interview, mitigation strategies could be recommended to design awareness programmes to educate them on behavioural change and the impacts and management of e-waste or establish effective e-waste collection points or even suggest management plans that have been successful in other societies. However, according to Klinke & Renn, (2002) and Renn, (2007), many management measures might prove to be effective but may turn out to be inefficient or unfair to the public and community involved, and in order to have sustainable and effective management options which will be accepted by the public, it is important to incorporate stakeholders perspective into decision making.

6.4.2 Stakeholders involvement in risk process

Renn, (2008) defined stakeholders as socially organised groups that are, or will be, affected by the outcome of the event or the activity from which the risk originates and/or by the risk management options taken to counter the risk. Ejiogu, 2013 identified some stakeholders in the e-waste sector as importers, scavengers, dismantlers, repairers and government. From the definition of stakeholder by Renn, 2008, the stakeholders identified by Ejiogu, 2013 are incomplete. With respect to this study, the stakeholders should also the members of community in which the recycling occurs, the “customers” as mentioned by the recyclers, experts, and the media. The community will have first-hand experience on the effect of the recycling; the customers will have a reason why they prefer to buy from the recyclers since their high demands fuel the recycling activities. On the other hand, the experts will present the results from their studies just like the results of this study and finally, the media will be required to communicate the risks and impact of the recycling activities.

The role and involvement of stakeholders is very important in risk evaluation and possible management of e-waste as it cuts across all factors identified to fuel the informal recycling of e-waste in Nigeria. The purpose of stakeholder involvement is to ensure that all values and preferences are made clear to the decision-makers with the aim of achieving a balanced view on the positive and negative sides of the informal e-waste sector. This balance is best accomplished if the stakeholders who will have to live with the consequences of the management decisions can add their trade-offs and preferences to the final judgment (Renn, 2015). In other words, the different stakeholders identified in the informal recycling site in this study would bring in different views which would integrate to reach an agreement. The stakeholders evaluate the scenario and any alternatives by linking back to the original goals, thus ensuring greater acceptance by all stakeholders (Briggs, 2008).

It is important to understand that the risks to the informal recyclers are incurred as a result of their activities which are geared towards achieving human needs, hence prudent judgements need to be made. So far, this study has identified some gaps by answering some key questions which will feed into the tolerability and acceptability judgement phase (Fig. 6.3) and enhance risk evaluation of the study. The pre-assessment phase in Fig 6.3 deals with the existing legislation and policies, putting in context why they are not effective, introducing the concept of stakeholders' opinions which could end up being productive in the evaluation process. The appraisal stage is also complete with the risk assessment and concern assessment; the next step will be to evaluate the risk. However, before the risk evaluation process, it would be valuable to highlight the reasons for the identified gaps and try to mend the gaps. Hence, the next section seeks to proffer solution which bridge the identified gaps and improve risk judgement and decision making.

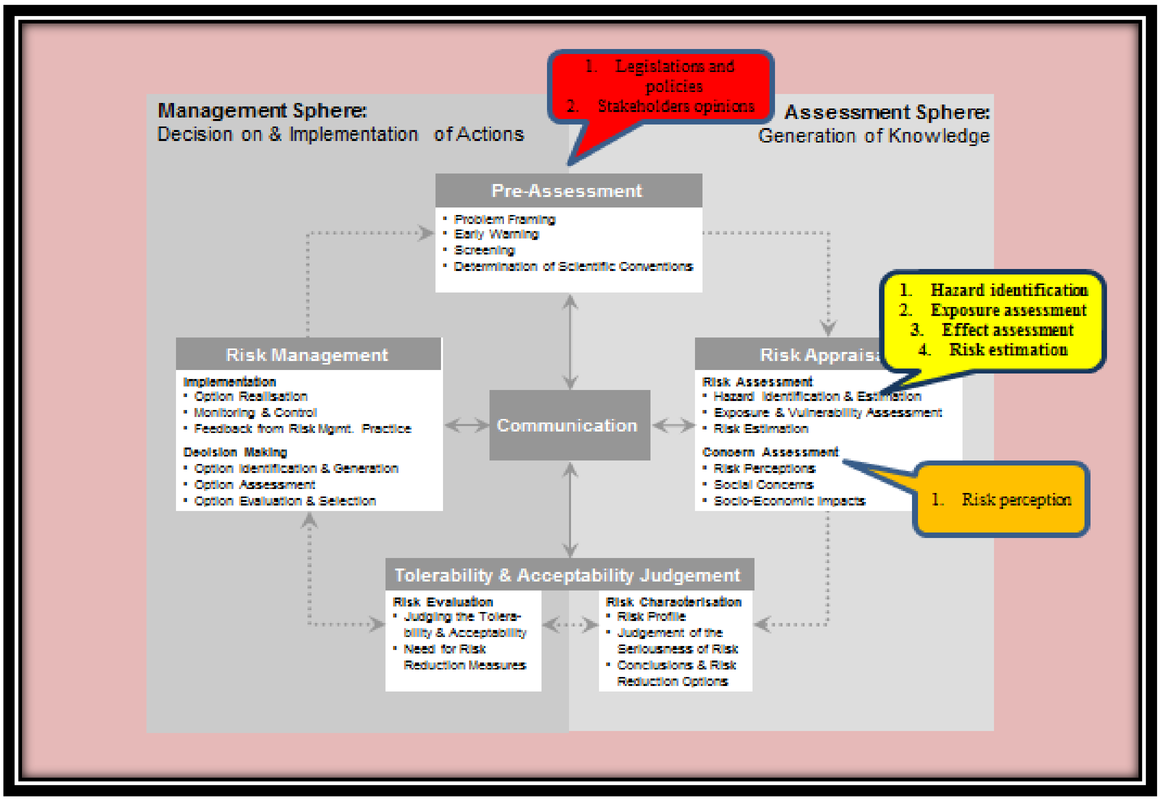

Figure 6.3: Detailed IRGC framework for risk management identifying processes carried out in this study.

6.5 Bridging the gap: the way forward

From the interviews with the informal recyclers, it was understood that the major personal driving force behind their activities was their perception and risk attitude which was fuelled as a result of the socio-economic situation in Nigeria, which included poverty and lack of jobs. Furthermore, a number of them believed the informal recycling process had no ecological or human health impact, while a few of them were aware of some impacts but felt that they had to get a means of livelihood, a finding that was similar with a study carried out by Ejiogu, (2013). Although the informal activity is driven as a result of socio-economic reasons as well as low perception to the underlying health risks as observed in this study, Manhart et al., (2011) and Ogungbuyi et al., (2012) argued that the socio-economic impact as a result of the informal activites is beneficial to the economy, thus making risk evaluation and decision making complex.

Taking into account the complexity involved in the informal recycling process and Fig 6.3, Fig 6.4 shows a Driving forces-Pressure-State-Impact-Response (DPSIR) Framework which identifies the causes and effects of the e-waste challenge. The DPSIR framework describes the relationships between the source and impacts of environmental problems putting all possible indicators into consideration (Kristensen, 2004; Xu, et al., 2015). The framework offers the potential to clarify environmental complexities, understand their dynamics and formulate mitigation stategies accordingly (Greyl, et al., 2010)

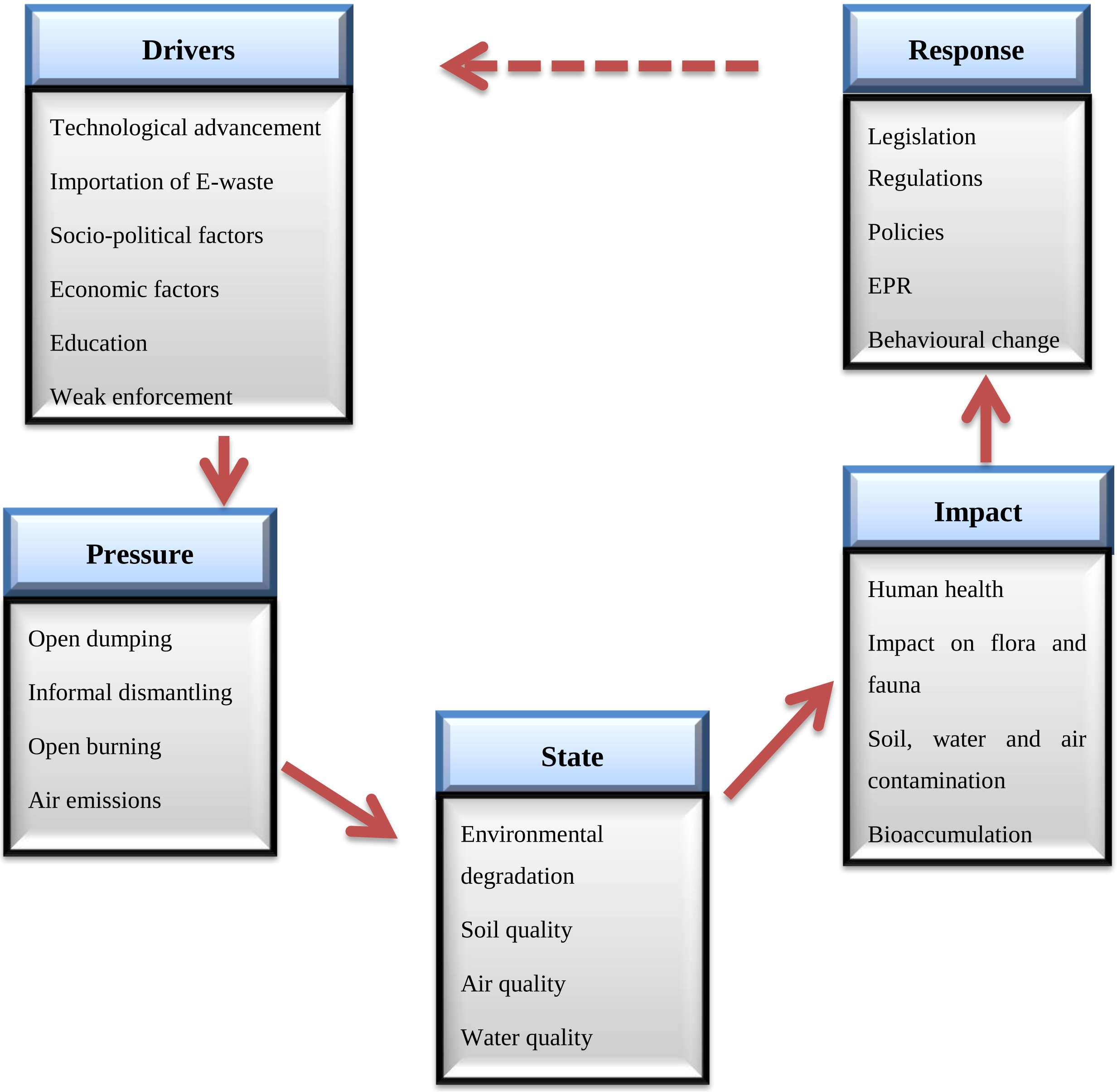

Figure 6.4: DPSIR framework for the informal E-waste recycling in Nigeria.

The general DPSIR framework lends itself to a system analysis approach and is useful in describing the relationships between the origins and consequences of complex environmental problems. The linkages or relationships between the different indicators are identified through the DPSIR chain, and the assessment provides information to support decision making process to ensure that the appropriate actions are carried out (Gobin, et al., 2004). According to Bone, et al., (2011), the DPSIR approach is commonly used to assess the pressures and risk of failing objectives and the effect of current management measures are reassessed and redefined.

The main driving force fuelling the generation of e-waste is technological advancement. This is a complex indicator that is related to different identified pressure indicators in developing countries such as in Nigeria. The pressures then result to environmental degradation and the impact is felt in all facets of life; affecting human health and the ecosystem. The response to the drivers, pressures, state and impact is the use of mitigation strategy which includes legislation, regulations and policies. However, the e-waste sector is not actually being effectively managed by the responses established by the government because it is a quasi-legal. The next section (6.5.1) proposes a framework which might be useful in tackling the informal e-waste challenge in Nigeria.

6.5.1 Integrated risk assessment framework

Fig 6.4 offers a presentation of the complex relationships in the informal e-waste sector in Nigeria. As observed during field investigation, socio-economic factors, the lack of education and awareness between the recyclers and consumers as well as the lack of enforcement of the legislation and standards fuelled the informal recycling process. These findings also corroborated with studies carried out by Obaje (2013) and Ejiogu (2013). Perkins et al., (2014), suggested the introduction of incentive-based policies would be more practical and proactive in reducing the informal recycling practice. Whilst in support with the recommendation by Perkins et al., (2014), this study proposes an interactive risk based approach to assist in the mitigation of the ecological and human health impact of the informal recycling process. This approach would put into consideration some factors that are not included in the traditional risk assessment process.

With the factors identified (socio-economic and socio-political conditions, lack of awareness and perceptions) as fuelling the informal recycling of e-waste, it might be impractical to ban the informal recycling activities due to the lack of recycling infrastructure or facilities, and the possibility of the recyclers relocating from place to place. This study adopts and modifies the integrated risk assessment (IRA) approach by WHO (2001) as a way of managing the informal recycling sector in Nigeria. According to the European Commission (2013), this process might produce a more effective risk evaluation, improve regulatory recommendations, facilitate the acceptance of risks amongst all stakeholders involved and create more relevance in policy making and sustainable management plans. The integrated risk assessment provides scientific and socio-economic answers; enabling stakeholders to postively influence environmental decision and policy making (Wilks et al., 2015).

An integrated risk assessment (IRA) framework takes into consideration scientific, economic, social and environmental factors in order to characterize and estimate the risk; the inclusion of these factors, provides the confidence, reliance and dependence of risk assessment and evaluation outcome and thus leads to establishment of better policies and regulations as a result of inputs from multiple sources (Suter II et al., 2005; Péry et al., 2013; Wilks et al., 2015; Xu et al., 2015).

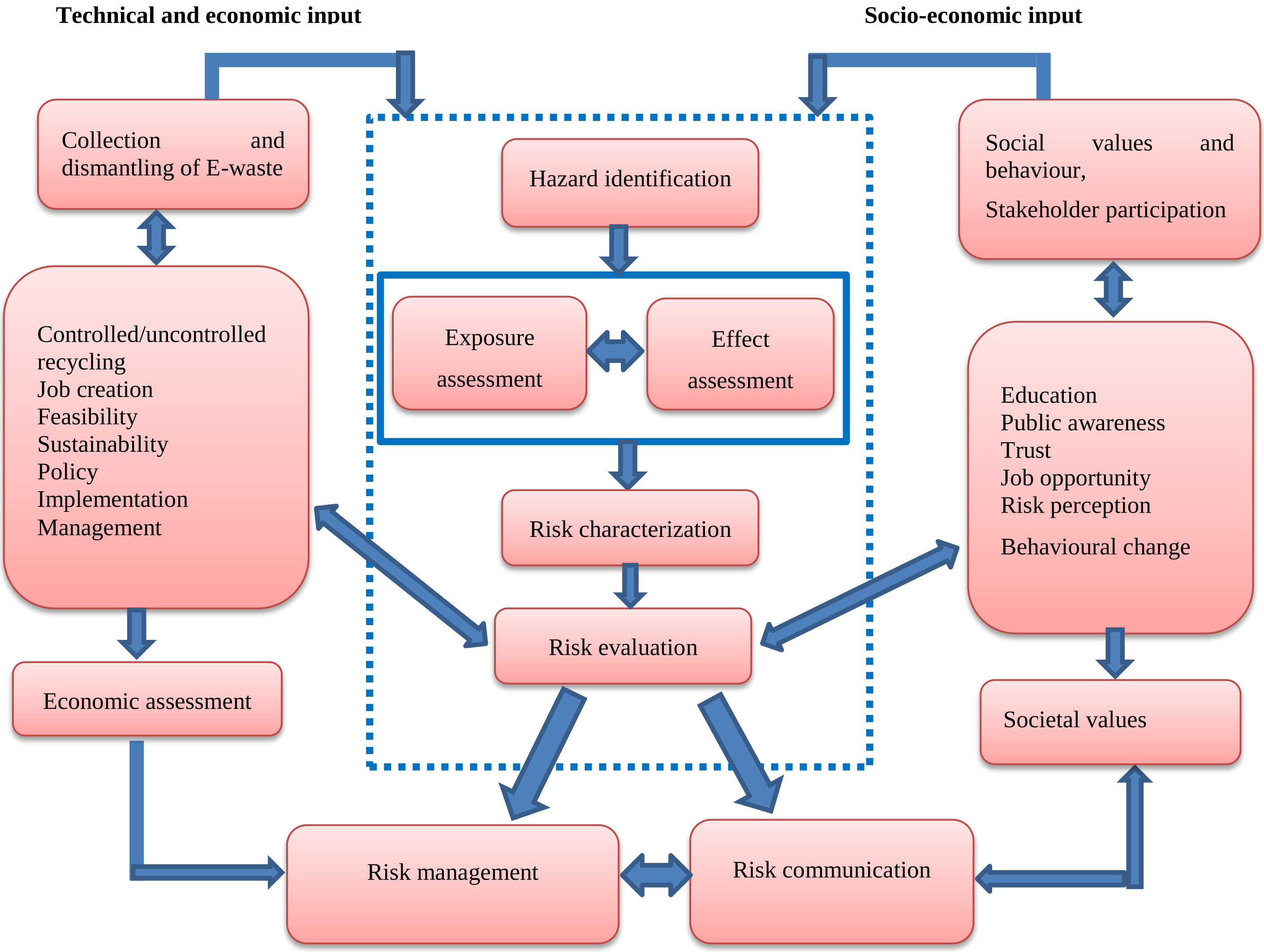

Figure 6.5: Proposed integrated risk assessment framework for managing informal e-waste recycling in Nigeria.

The framework (Fig 6.5) proposed in this study sets out to address the deficiencies identified by the DPSIR framework (Fig 6.4) by integrating the environmental fate and effects of contaminants obtained in this study, other evidence and the views of involved stakeholders prior to policy making and make informed sustainable decisions as regards E-waste management. The stakeholders' participation would assist in unmasking individual risk perceptions and build trust (Péry et al., 2013) through physical contact, persuasion, negotiation and integration of cultural and social values (Briggs, 2008).

From the proposed framework (Fig 6.5), the stakeholders' involvement will be integrated from the beginning of the risk process which is hazard identification through the evaluation phase up to the management and communication phase. This is to ensure that the drivers (Fig 6.4) as it concerns e-waste are not overlooked. Interaction and collaboration between stakeholders will be promoted and will complement existing knowledge, verify some unconfirmed information, and in the long run assist in evaluating the risks and making informed decisions regarding e-waste recycling in Nigeria.

6.6 Risk judgement of study

The main objective of risk evaluation is to arrive at a judgement on balancing the scientific results with societal values and norms, as to whether the risk is acceptable, tolerable or not (Renn, 2008). A risk deemed "acceptable" is usually limited in negative consequences so it is taken on without risk reduction or mitigation measures being envisaged. A risk deemed "tolerable" links undertaking an activity which is considered worthwhile for benefits it provides with measures to limit the adverse effects (Renn, 2007). According to HSE, 1998, "tolerability" does not mean "acceptability"; it refers to a willingness to live with a risk so as to secure certain benefits and in the confidence that it is being properly controlled. Making a judgement on risk reduction typically entails the reduction of some benefits, hence, decision makers are required to weigh the risk against the benefits. The question then becomes "how safe is safe enough"? (Fischhoff et al.,1978), which is ultimately the question that this study seeks to evaluate.

This study revealed the high level of contamination by evaluating with pollution indices, possibility of metals leaching into water bodies, toxicity to exposed organisms and also the human health probability of cancer and non-cancer risk as a result of exposure through ingestion. This scientific evidence suggests that there is risk posed as result of the recycling activities.

Making judgement based on both evidence from the risk assessment and evaluation of value based choices can be made using the tolerability of risk framework (Fig 6.6) to establish the level of risk, if it is tolerable or not, thus answering the questions"how safe is safe enough" for the health perspective or "how clean is clean enough" from the environment perspective.

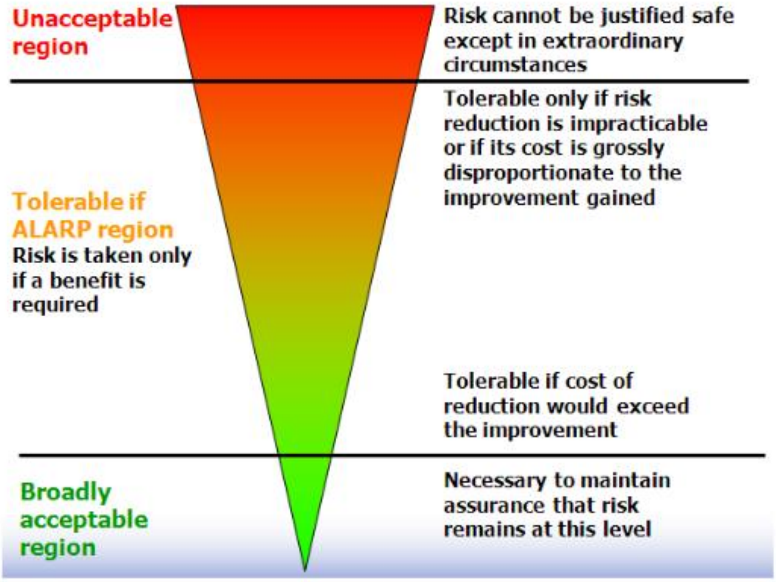

Figure 6.6: Tolerability of risk framework. Source: http://www.pdo.co.om/hseforcontractors/Health/Documents/HRAs/Risk%20Tolerability%20Framework.pdf [Accessed 26th October, 2016]

6.6.1 Challenges in making risk judgement

In a wider context, the scientific evidence in this study shows that the informal recycling process is an issue both to human health and the ecosystem. However, sections 6.4 and 6.5 addresses the issues and identified potential solutions. It will be reiterated here that although this study is not a risk management study, it recognises a number of barriers in the implementation of the proposed IRA framework and also making risk judgement. A few of the barriers as identified in Fig 6.7 (which shows the external challenges in making risk judgement and ultimately implementation of risk management plans)will be mentioned.

In making a risk judgement, the risk evaluation process will attempt to derive "acceptable" or tolerable risk on a case-by-case basis and this might raise the question of "acceptable to whom”? Answering the question would need proper engagement to find some common ground for characterising and qualifying the evidence and establish agreement about the appropriate values and their application (Renn, 2007).

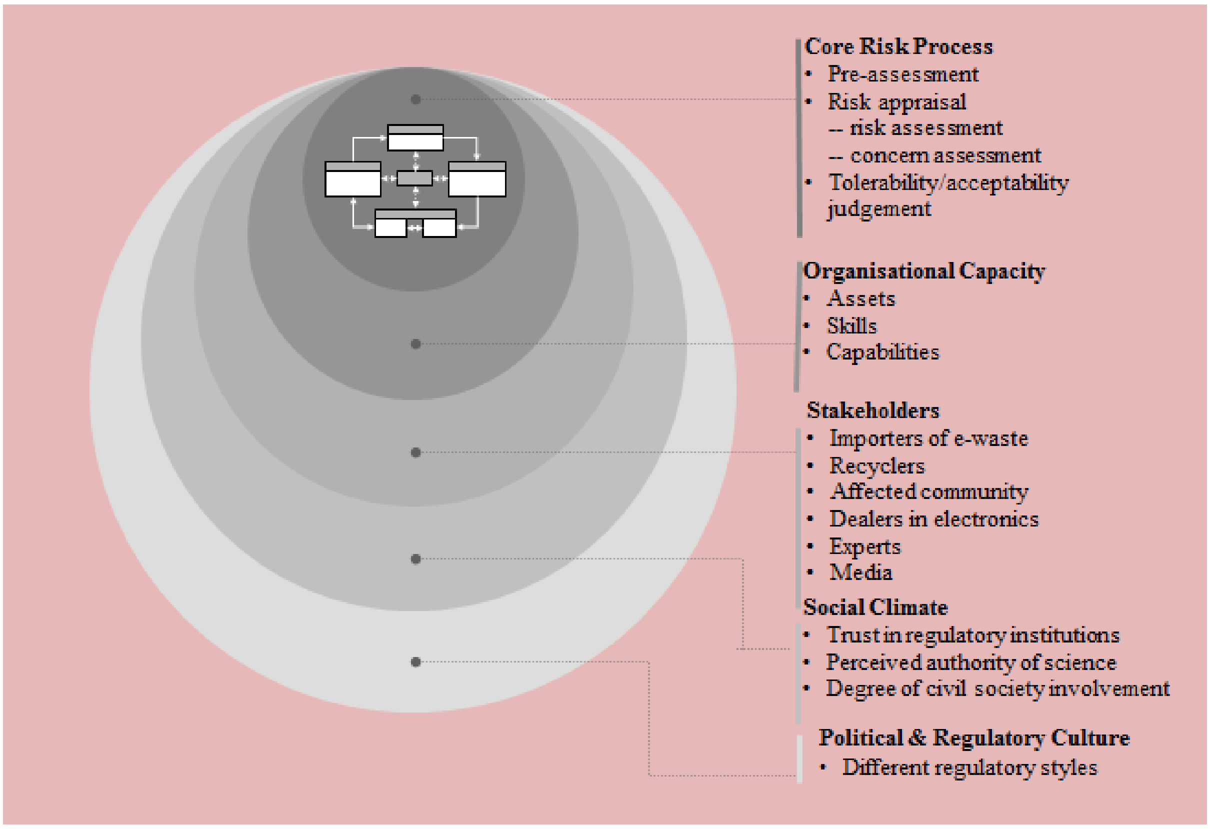

Figure 6.7: Modified and adapted IRGC risk governance overview for this study. Source: Renn, 2007

Putting Fig 6.7 into the context of this study, considering the uniqueness of the informal e-waste sector, the first challenge which is the organizational capacity will address the issues of if the assets, skills and capabilities are available to manage the informal sector before judgement is made. Are regulations in place effective enough? Are there facilities in place to make the informal sector formal? Secondly, the recognition of the different stakeholder involved is paramount as different stakeholders have very different agendas which would need to be addressed. The social climate represents the government, their goals, and the corruption within the system which might affect risk judgement due to vested interests. Finally, it is important to acknowledge that this study is unique as it is carried out in Lagos State, Nigeria which is a developing country, and generally, governments are used to laissez faire approach of dealing with some issues. This approach is also identified as a factor that could affect risk judgement. Furthermore, the possibility of political change in the process of decision making can affect the risk judgement and decision making.

Although the environmental risk assessment process uses scientific data to obtain the degree of risk posed, it cannot be a completely scientific process due to the influence of some social factors as discussed in this chapter. It is recognized that although this study tried to suggest potential solutions to combat the e-waste challenge and ease the risk judgement process in the informal e-waste recycling sector in Lagos State, a few barriers that could affect prudent risk judgement were identified, thus acknowledging the complexity involved in a risk process. In conclusion, the study did not try to find the solutions to the identified barriers or feed the management phase as identified as in Fig 6.1 because it is outside the study scope. However, the study emphasizes on the role of both the scientific evidence and social factors play in risk evaluation and decision making.

CHAPTER SEVEN

7 Conclusion and Recommendation

This study set out to evaluate the pollution impact due to informal recycling of e-waste in Nigeria using Alaba international market, Lagos State as a case study. In order to address the aim, the study explored the presence of contaminants and the relationship between the contaminants, the possible pathways and the receptors (Figs 3.5 and 3.6) and the potential risks posed by the exposure. Pollution indices, metal speciation, toxicity test were used to assess and establish the pollution impacts. Furthermore, risk assessment method was used to establish and assess risk from multiple sources, stressors, and routes of exposure for humans, biota and ecological resources. Risk assessment methods have been applied in the management of various contaminated sites; however, its application in e-waste recycling sites in Nigeria had not previously been utilized. The quantitative risk assessment carried out in this study included the use of site specific assessment criteria as a useful tool to demonstrate if there is any manifest or apparent risk.

7.1 Summary of study

The first approach in assessing the environmental contamination in this study was based on the soil's physical and chemical analysis of heavy metals. The soil properties (pH, %OMC, CEC) were assessed and the following metals (Cd, Cr, Cu, Ni, Mn, Pb, Sb and Zn) were identified in the study site. The extent of pollution due to the recycling activities and the impact of external factors such as rainfall were assessed. Soil samples were collected from the already demarcated (dismantling and recycling area by the workers) site to represent the dry and wet season in the year 2013 and establish if the seasonal rainfall had an impact on the physical and chemical properties of the soil. The total concentration of Cd, Cu, Mn, Ni and Zn where was significantly higher ($p \leq 0.001$) in the dry season than in the wet season, a variation in the soil pH was also observed between both seasons and was attributed to the leachability of the soil type (loamy sand). Furthermore, the concentrations of metals measured in the soil were compared to established guideline values; Cd, Cu, Pb, Sb, Zn were all found to be higher than established thresholds of UK, Australia and the Netherlands.

Using GIS as a tool for visualization, distribution maps revealed the spatial variability of the metals in the dry and wet seasons as well as the hotspots of the metals. Cd, Cu, Pb and Zn were found to be clustered around the recycling/burning area while Ni, Cr and Mn were associated with the dismantling area of the site.

To further assess the ecological impact of the recycling activities, the contamination factor (CF), pollution load index (PLI) and the potential ecological risk index (PERI) were employed. A severe contamination/pollution was confirmed to a depth of 20-30cm in the soil which could be explained as a contamination arising from long-term and continuous informal recycling activities. The PERI revealed that Cu closely followed by Cd then Pb were the major risk contributors to the environment.

7.1.1 Speciation: a tool for potential bioavailability assessment in contaminated soils.

In order to have a better understanding of the degree of pollution and the toxicity of pollutant present in the site, speciation analysis using a sequential extraction process and reflecting the site specific conditions was carried out. The extraction method used in this study was designed to provide an operational assessment for exchangeable metal fraction, the organic bound fraction and the residual fraction. Cd was found to have the highest association with the exchangeable fraction, making it the most potentially bioavailable metal for uptake. Pb had highest affinity to the organic bound fraction with the potential of it being mobile due to the strong redox conditions. Cr had the highest percentage association with the residual fraction and thus least likely to be released in the environment.

From the speciation studies, it was deduced that, although the total metal concentration in the soil can be used to indicate the environmental quality, the severity of the contamination does not depend only on the total concentration but also the potential bioavailability and mobility. The sequential extraction method gave a better understanding of the behaviour, bioavailability and mobility of metals with respect to the observed physico-chemical properties of the soil and identified Cd as the most potentially available metal. Furthermore, assessing the risk with the RAC guidelines which works with the fractionation from the sequential extraction showed Cd to have the highest potential environmental risk in the study site due to its potential bioavailability.

7.1.2 Significance of bioassays in assessing potential bioavailability and environmental impact of contamination

The soil leaching experiment confirmed the results obtained from the speciation; proving the possibility of potential mobility, bioavailability as well as toxicity. The leachates collected on day 7 of both dry and wet season soil had the highest toxicity [LC_{50} 32.5% and 42.0% (v/v) respectively] to the *Daphnia magna* species. The toxicity index (TI) of the leachates identified Zn as the highest contributor to the leachate and Cr the least. Despite Zn being identified as the highest contributor based on the toxicity index, it does not invalidate the observation from the speciation studies reported, because according to WHO, 2001, approximately 10% of total Zn in soils is potentially bioavailable. The concentration of Zn that leached out in the soil column experiment falls within the 10% range in comparison to the total Zn concentration in the soil which is similar to the results obtained from the speciation analysis.

The toxicity assessment of the leachates in this study further demonstrates the ecological impact of the informal recycling activities; and can contribute in estimating and predicting the contamination of groundwater and surface water as well as the potential risk posed to organisms which come in contact with the soil and the leachates.

7.1.3 Role of *in vitro* bioaccessibility in determination of potential human bioavailability and risk assessment

The human bioaccessibility test was carried out for both the ingestion and inhalation routes using simulated digestive fluid and respiratory fluid respectively. The percentage bioaccessibility fraction obtained for the metals in the study represented the fraction available for absorption in the human system. In the oral bioaccessibility, the study showed that less than 40% of the total concentration of all the identified metals was available for absorption in the gastrointestinal tract. In the inhalation bioaccessiblity, despite the addition of the 20% safety margin on the 100 hr published saturation time, the dissolution of metals especially Cd was still observed, however, with the exception of Cd, the percentage bioaccessibility of the other metals was less than 35% after 120 hours. Both bioaccessibility tests confirmed that only a percentage of the total metal content is available for uptake in the human system, as against the conventional risk assessment assumption that total metal content taken in is absorbed.

Furthermore, relationships were established between the different geochemical fractions in the sequential extraction and the bioaccessible fractions which inferred that the bioaccessibilty of metals could be dependent on the geochemical fraction of the metals in the soil and possibly the soil properties. This confirms that bioaccessibility is site specific as the lability of metals can be dependent on the soil properties and also the advantage of site specific risk assessment as against generic risk assessment. The results obtained in this study support the assertion that the inclusion of bioaccessibility assessment in risk assessment refines and increases the accuracy of the outcome, making it a better decision support tool for human health risk assessment.

7.1.4 Health risk characterization

The health impacts from the e-waste recycling were assessed by evaluating the carcinogenic and non-carcinogenic health risks posed by metals (Cd, Cr, Cu, Ni, Mn, Pb, Sb and Zn) exposure through ingestion and inhalation of re-suspended soil particles. The risk was evaluated using two scenarios: the total metal content and integrating the percentage bioaccessibility. The non-cancer risk expressed as hazard index (HI) for ingestion was between 5 and 50 times higher than the threshold (HI=1) when the risk was evaluated using the total metal content. With the integration of the percentage bioaccessible factor, the HI was between 1.19 and 1.81 times higher than the recommended threshold and thus the risk is accurately quantified. The cancer risk for ingestion followed a similar trend; the cancer risk with the total metal content ranged between 0.0454 and 0.0712; while with the percentage bioaccessible fraction ranged between 1.2E-03 and 3.02E-03. Although both assessments exceeded the threshold (10E-04-10E-06), the integration of the percentage bioaccessible fraction had an impact on the evaluated risk. The non-cancer and cancer risk posed by the inhalation of re-suspended soil particles for both scenarios (the total metal content and integrating the percentage bioaccessibility) were all within the threshold of acceptability.

The health risk characterization indicates adverse human health effect through the ingestion pathway and a relative lower probability of cancer and non-cancer risk through the inhalation of pathway. However, the inhalation of re suspended particles pathway should probably not be overlooked because of the possibility of finer particles lodging down the respiratory system and causing harm.

Although the health risk assessment model used in this study might be have a degree of uncertainty related to the exposure parameters, this does not dispute the integrity and the utility of the assessment results in this study. The results obtained in this study point to the fact that the recycling activities have adverse health effect to man. The aforementioned uncertainties notwithstanding, risk assessment has proven to be a very useful tool to reveal the implications for human health of the concentrations of metals found in soils.

7.1.5 Integrated risk assessment: a pathway to manage informal E-waste recycling

Lastly, the scientific evidence of the study revealed the pernicious ecological and human health impact of the informal recycling activities, also revealed was the fact that the management of e-waste and the informal recycling in Nigeria is almost non-existent despite the existing legislations and policies. The boom of informal recycling of e-waste could be attributed to the poor awareness of the dealers and recyclers involved, economic conditions of the country and the recyclers' perceptions and attitude to the impact of the activities. In an attempt to properly evaluate the risk posed by the informal e-waste recycling in Lagos State, the study proposed an integrated risk assessment framework (IRA) which would assist risk judgement and ultimately decision making. The structure of the IRA integrates stakeholders (experts, non-experts), socio-economic factors as well as the behavioural attitude of the public into the risk process, thus enhancing risk judgement. The stakeholders' involvement in the risk process cannot be overemphasized as they can enhance risk perception, trust and could advocate and stimulate integrity in the risk evaluation and decision making process. The framework when tried and tested is aimed to positively influence the risk judgement and ultimately risk management decisions whereby providing valuable insights that would translate to an efficient and sustainable management system at the long run.

7.2 Recommendation

i. Studies report the informal recycling of e-waste release contaminants including metals, PBDEs, PCCD/Fs in the environment; however, the kind of contaminants found in the recycling site is dependent on the kind of electronics recycled at the site. Although this study focused on some of the toxic metals released in the study site, the study of other contaminants such as PBDEs, PCCD/Fs and PAHs is recommended.

ii. The UBM method used for the oral bioaccessibility test had been validated for Sb, Cd, As and Pb individually; however, this study showed some metal-metal interaction in the gastrointestinal phase which could affect bioavailability and absorption. An *in vivo* validation of mixed metals and the joint action of the metals is recommended. This is because most land contamination such as an e-waste recycling site is not caused by an individual contaminant.

iii. The inhalation bioaccessibility method used has to be developed further especially with the timing. It was observed in this study that all metals do not attain saturation at the same time, furthermore *in vivo* validation of single metals and joint action of metals is required, as a result, in-depth study is recommended.

iv. Although the IRA was proposed as a management system, it might undeniably be a long term project; as a measure, the creation of a formal e-waste recycling sector is recommended. The formal sector could utilize the strength of the informal sector which would lead to a healthier environment.

v. Finally, in an attempt to evaluate the risk caused by informal E-waste recycling in this study, a gap was identified. The scientific evidence identified the risk posed, however the perception of the people identified no risk. The gap could be merged by proper risk communication; eliciting the opinions of all stakeholders (the lay people, experts, media, policy makers, affected community etc.) involved and the development of a risk communication protocol that would be sustainable in Nigeria is recommended.

7.3 Further research perspective

i. E-waste is made up of a heterogeneous and complex mix of metals, as such, during the informal recycling there is a possibility to lose some rare and critical metals. Since thermodynamics dictates what can be recovered together, would targeted dismantling of E-waste improve the recovery of rare metals? Would the impact of targeted recycling be less deleterious to environmental and human health?

ii. On August 23rd 2016, the BBC announced that Japan plans to use E-waste for 2020 Olympics in an attempt to take the sustainability theme a step further. Recent developments have included the use of microorganisms (bio mining/bioleaching) to recover metals of interest; however, current processes are faced with challenges associated with complex e-waste streams, speciation and competing side reactions. Following the sustainability theme, bio mining/bioleaching and bioremediation have the potential to make novel contributions due to the ever changing electronic technology, future research plans are to derive and apply a holistic understanding of microbial-metal interactions in order to develop effective processes to separate, recover, recycle metals (critical, rare earth metals and platinum group metals).

iii. Currently, most e-waste management strategies largely focus on the environmental aspects, leaving out underlying social and economic problems and barriers which could affect decision making as discussed in chapter 6. Future studies will develop a holistic management plans for e-waste including both the formal and informal sectors in developing countries.

7.4 Limitations of study

i. Environmental risk assessment is important as it establishes and investigates the potential effects of contaminants in the environment. Before the commencement of an environmental risk assessment, it is imperative to develop a site conceptual model. The site conceptual model visualizes the risk hypothesis; describes the relationship between the contaminant sources, pathways and receptors (Simon, 2010). From Figs 3.4 and 3.5, the possible pollution pathways and exposure pathways in the site conceptual model are visualized. However, due to the uniqueness of the site and the superstitious belief of the workers at the site, all pathways could not be explored, leaving the study only the option of using soil for analysis.

ii. The inability to obtain samples from further depth in soil profile to establish the extent of the contamination since downward migration of metals was observed up to 30cm depth with no significant difference between the different depths (section 4.4).

iii. One of the major challenges of risk assessment is complexity (Renn, 2008), which this study was faced with. Apart from the multiple causal risks by different exposure routes not explored in the study, the human health risk model estimated the metals as having same mode of action whereas, the different metals found in the medium have different characteristics. Their effects by the model were additive, however, there is high possibility for the effects to have synergistic and antagonistic effect as discussed in Section 5.3.

7.5 Conclusion

Electronic waste (e-waste) is an increasingly problematic issue arising from discarded electronic appliances. It is a source of opportunities due the high economic value of the components but is also generating attention due to the potential environmental problems resulting from the presence of hazardous substances released during informal recycling. The soil, the foundation of terrestrial ecosystems and environmental quality is also a sink and source of contaminants as a result of the informal e-waste recycling. Of the toxic components of informal e-waste recycling, this study focused on heavy metals; heavy metals continue to be relevant because of their fate and toxicological relevance to ecosystems and human health. Exposure to contaminated soil is an important pathway environmental health risk as contaminants can directly pose significant risks through contact. Risk assessment provides a framework for a structured review of information relevant to estimating health or environmental outcomes. However, the risk assessment tools for various contaminated lands assume the exposure is equivalent to the total soil concentrations of contaminants as well as extrapolation from test animals to humans and the risks are usually overestimated and associated with uncertainties. According to Ruby et al., (1999), an accurate risk assessment needs bioavailability embedded in it. The methodology adopted in this study estimated the potential bioavailability and bioaccessibility with respect to site specific parameters and incorporated it into the risk assessment.

The study reported the extent of contamination due to the informal recycling activities by comparing the observed concentration with reported studies, established guideline values and evaluating with different pollution indices. The fact that metal has the ability to sorb to soil constituents and also vary in solubility gave rose to the need for bioavailability and bioacessibility studies. The results obtained from the study imply that the informal recycling activity is detrimental to both ecological receptors and humans.

This study adds to the body of knowledge and literature in informal e-waste recycling in Nigeria, the extent of contamination, metal speciation and risk assessment. The metal concentration and distribution in the soil from this site, the understanding of the importance of potential bioavailability and bioaccessibility of metal in an e-waste site in Nigeria have not been previously reported. The study emphasizes on the need of site specific risk assessment due to the influence of physico-chemical parameters unique to the site. Furthermore, the study tried to evaluate the risk posed by the informal e-waste recycling activities by presenting evidence alongside the concern assessment. The concern assessment (risk perception) revealed some reasons why the informal recycling business thrived. In order to properly evaluate the risk posed, existent structures in managing the risk were examined and a possible structure (an integrated risk assessment framework) to deal with the risk as a result of the informal e-waste recycling was proposed, also, some barriers which could affect risk judgement and ultimately risk management and decision making were identified. On a final note, the proposed integrated risk assessment framework when tested, transcends the use in Nigeria, it can be considered suitable in other developing countries with similar informal e-waste recycling challenge.

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9 Appendix

Appendix 1: Operating parameters of ICP-OES (iCAP 1600)

Operating parameters of the thermos ICP-OES (iCAP 1600)	
Power (W)	1150
Auxiliary gas flow (L/min)	0.5
Nebuliser gas flow (L/min)	0.75
Coolant gas flow(L/min)	12
View	Axial
Purge gas flow	Normal
Flush pump rate (rpm)	100
Analysis pump rate (rpm)	50
Camera temperature	-47
Optics temperature	38

Wavelengths used on the ICP-OES of the elements investigated.

Elements	Wavelength (nm)
Cd	228.802
Cr	283.563
Cu	324.754
Fe	259.940
Mn	257.610
Ni	221.647
Pb	220.353
Sb	206.833
Zn	213.856

Appendix 2: Culturing of Daphnia magna

Constituent of ISO culture media for Daphnia magna

Compound	Concentration needed for 1L stock solution	Volume of stock solution added to 1L deionized water for culture media
Calcium chloride $CaCl\cdot 2H_2O$	11.76g	25ml
Magnesium sulphate $MgSO_4\cdot 7H_2O$	4.93g	25ml
Sodium bicarbonate $NaHCO_3$	2.59g	25ml
Potassium chloride KCl	0.23g	25ml

Ensure pH is between 7.5 and 8.2

Preparation of seaweed extracts for Daphnia magna cultures

Marinure, a standard organic extract, was purchased from Glenside Groups, Livingstone, West Lothian. Approximately 1ml of Marinure extract was dissolved in 100ml deionized water to make a stock solution. A 1:10 dilution of the Marinure stock was made and the extract was analysed for optical density using the Jenway 6705 UV/Vis spectrophotometer. Readings of the extract were measured at wavelengths 400nm. With a spectrophotometric reading of between 0.760 and 0.800, the extract can be used.

Preparation of baker’s yeast suspension for Daphnia magna cultures

10mg of of dry baker’s yeast was added to 100 ml of deionized water and mixed with a magnetic stirrer till all the yeast dissolved.

Culturing Chlorella vulgaris for Daphnia magna cultures

Chlorella vulgaris was cultured in a sterile in Bold’s basal medium (BBM) for the use of Daphnia feed. Individual stock solutions were prepared and autoclaved before the preparation of the BBM and BBM was autoclaved prior use. The culture was exposed to constant light.

Appendix 3: Constituent of BBM for culturing Chlorella vulgaris

Compound	Concentration needed for 1L stock solution	Volume of stock solution added to 1L deionized water for BBM
di-Potassium hydrogen orthophosphate $K_2 HPO_4$	7.5 g	10ml
Potassium dihydrogen orthophosphate KH_2PO_4	4.93 g	10ml
Magnesium sulphate $MgSO_4 \cdot 7H_2O$	7.5 g	10ml
Sodium nitrate $NaNO_3$	25 g	10ml
Calcium chloride $CaCl_2 \cdot 2H_2O$	2.5 g	10ml
Sodium chloride NaCl	2.5 g	10ml
EDTA tetrasodium EDTA-Na_4	50 g	1ml
Potassium hydroxide KOH	31 g	1ml
Ferrous sulphate $FeSO_4 \cdot 7H_2O$	4.98 g	1ml
Zinc sulphate $ZnSO_4 \cdot 7H_2O$	14.12 g	100µl
Manganese chloride $MnCl_2 \cdot 4H_2O$	2.32 g	100 µl
Sodium molybdate $Na_2MoO_4 \cdot 2H_2O$	1.92 g	100 µl
Copper sulphate $CuSO_4 \cdot 5H_2O$	2.52	100 µl
Cobaltous nitrate $Co(NO_3)_2 \cdot 6H_2O$	0.8 g	100 µl
Boric acid H_3BO_3	11.42 g	1ml
Sulphuric acid H_2SO_4	10ml	1ml

Appendix 4: Physicochemical properties of the soil

4.1: pH in recycling area

Measured values of pH in the recycling area of the study site Mean ± S.E n=3

	Dry season			Wet season		
	0-10cm	10-20cm	20-30cm	0-10cm	10-20cm	20-30cm
Pt 1	6.48±0.01	6.32±0.01	6.45±0.03	7.12±0.04	7.07±0.02	7.19±0.03
Pt 2	6.77±002	6.91±0.00	6.82±0.02	6.86±0.03	7.15± 0.02	7.01±0.01
Pt 3	6.69±0.01	6.72±0.02	7.3±0.02	6.89±0.02	7.17±0.01	7.03±0.03
Pt 4	7.31±0.01	7.38±0.01	7.75±0.01	6.92±0.01	7.34±0.03	7.14±0.04
Pt 5	7.24±0.00	6.99±0.01	6.77±0.03	6.99±0.01	7.01±0.02	6.92±0.01
Pt 6	9.38±0.02	6.47±0.03	6.83±0.04	8.05±0.02	6.5±0.02	7.02±0.00
Pt 7	7.91±0.01	7.46±0.02	7.54±0.02	6.89±0.03	6.93±0.00	6.91±0.02
Pt 8	8.07±0.01	8.04±0.03	7.98±0.00	6.97±0.02	6.99±0.01	6.89±0.02
Pt 9	8.05±0.00	8±0.00	7.97±0.02	7.01±0.01	6.94±0.02	7.07±0.01
Pt 10	7.27±0.01	8.01±0.00	8.17±0.04	6.87±0.04	7.13±0.02	7.26±0.00
Pt 11	7.54±0.01	8.15±0.01	8.54±0.01	7.32±0.02	7.88±0.03	7.97±0.01
Pt 12	6.45±0.02	6.75±0.02	6.81±0.00	6.94±0.03	6.96±0.01	6.97±0.02
Pt 13	6.96±0.02	6.64±0.03	7.33±0.03	6.94±0.03	6.95±0.02	7±0.01
Pt 14	7.36±0.01	7.92±0.02	7.79±0.01	6.96±0.01	7.02±0.01	7.06±0.02
Pt 15	8.02±0.01	8.11± 0.04	8.07±0.02	6.99±0.00	7.34±0.02	7.16±0.02
Pt 16	8.21±0.01	8.29±0.02	8.39±0.04	7.55±0.02	7.48±0.04	7.64±0.02
Pt 17	8.01±0.00	7.11±0.03	6.88±0.02	7.06±0.01	6.89±0.02	6.76±0.03
Pt 18	7.2±0.01	6.99±0.01	6.94±0.03	7.02±0.00	6.9±0.00	6.79±0.02
Pt 19	6.48±0.01	6.1±0.02	6.27±0.00	7±0.01	6.91±0.01	6.81±0.02
Pt 20	7.23±0.02	7.87± 0.04	7.74±0.00	7.01±0.02	6.91±0.01	6.8±0.02
Pt 21	9.27±0.03	7.81±0.02	7.98±0.03	7.93±0.02	7.24±0.01	7.35±0.01
Control						

4.1.1: pH in dismantling area

Measured values of pH in the dismantling area of the study site Mean ± S.E n=3

	Dry season	Wet season
Pt 1	8.27±0.03	7.95±0.02
Pt 2	7.83±0.02	7.26±0.02
Pt 3	7.89±0.02	7.24±0.01
Pt 4	8.44±0.04	7.86±0.02
Pt 5	7.48±0.02	7.2±0.00
Pt 6	8.42±0.02	7.96±0.02
Pt 7	8.34±0.02	7.89±0.03
Pt 8	9.03±0.04	8.11±0.03
Pt 9	8.88±0.03	8.02±0.02
Pt 10	8.61±0.02	7.59±0.01

4.2: Percentage organic matter content in recycling area

Measured values of % organic matter content in the recycling area of the study site

	Dry season			Wet season		
	0-10cm	10-20cm	20-30cm	0-10cm	10-20cm	20-30cm
Pt 1	15.6	19.6	17.6	18.8	25.4	26.6
Pt 2	16.8	20.4	18.8	33.4	29.8	29.6
Pt 3	19	21	22.8	32	31	23.4
Pt 4	15	22	19.6	22.4	21.6	20
Pt 5	20	13	19.8	18.8	21.4	22.5
Pt 6	14	19.2	16	20.6	21.8	21
Pt 7	11	21.2	23.6	29.5	24.7	29.2
Pt 8	15	21.3	22.1	26.6	26.8	28.8
Pt 9	17.6	19.8	20.3	30	24.8	24
Pt 10	17.7	17.9	18.2	25	22	23
Pt 11	17.2	16.5	18.3	19	22	23.2
Pt 12	6.6	18	17	23	23.8	20
Pt 13	17.4	22	25	25.2	27	28.5
Pt 14	15	23	24.2	23.2	24	28.2
Pt 15	16.7	19.6	21	21.5	28.2	26.4
Pt 16	14	15.8	19	21	24.6	26
Pt 17	6.2	12	18.2	15.75	23.2	20.74
Pt 18	18.3	16.7	20.2	23.6	25.4	24.2
Pt 19	18.2	22	21	25.6	24.6	28.4
Pt 20	12	17	18.2	26.2	27.6	28
Pt 21	22	23.7	25	25.6	26.8	28.4
Control						

4.2.1: Percentage organic matter content in dismantling area

Measured values of % organic matter content in the dismantling area of the study site

	Dry season	Wet season
Pt 1	16	14.8
Pt 2	18	14.6
Pt 3	19.2	16.8
Pt 4	18.9	13
Pt 5	19.8	15
Pt 6	15.4	11
Pt 7	17.6	13
Pt 8	10	7.8
Pt 9	13	9.9
Pt 10	9	10.2

4.3: Cation exchange capacity in recycling area

Measured values of cation exchange capacity (cmolcKg^{-1}) in the recycling area of the study site Mean ± S.E n=3

	Dry season			Wet season		
	0-10cm	10-20cm	20-30cm	0-10cm	10-20cm	20-30cm
Pt 1	14.79±0.04	12.31±0.20	13.11±0.64	12.82±0.84	12.96±0.88	12.85±1.16
Pt 2	12.14±0.35	15.57±1.08	15.88±1.03	13.08±0.62	14.08±1.02	14.66±1.07
Pt 3	9.24±0.02	10.8±0.46	10.56±0.44	11.38±0.72	10.92±0.85	11.02±0.66
Pt 4	8.31±0.05	8.1±0.04	7.05±0.05	9.47±0.08	8.57±0.05	7.98±0.04
Pt 5	9.32±0.01	11.04±0.33	10.89±0.45	9.63±0.1	10.84±0.52	10.62±0.72
Pt 6	4.33±0.02	4.1±0.02	3.15±0.03	5.47±0.04	3.98±0.01	3.6±0.01
Pt 7	12.14±0.21	11.32±0.58	14.23±1.04	11.79±0.52	10.46±0.38	11.27±0.33
Pt 8	9.87±0.05	7.88±0.06	10.32±0.62	10.12±0.07	8.23±0.06	9.86±0.04
Pt 9	13.44±0.61	13.03±0.45	12.96±0.24	12.56±1.02	9.66±0.04	10.55±0.12
Pt 10	8.77±0.07	7.78±0.03	8.32±0.06	7.29±0.04	7.52±0.02	8.01±0.03
Pt 11	6.74±0.03	5.35±0.04	8.04±0.04	7.07±0.03	6.16±0.02	9.78±0.06
Pt 12	12.1±0.18	11.46±0.72	11.89±0.58	11.18±0.82	10.63±0.45	9.63±0.05
Pt 13	13.2±0.08	10.64±0.36	9.86±0.07	11.78±1.01	9.88±0.05	10.75±0.82
Pt 14	11.04±0.65	9.21±0.08	10.33±0.16	10.68±0.75	9.02±0.03	9.85±0.04
Pt 15	5.57±0.03	4.64±0.02	6.89±0.04	5.35±0.03	5.03±0.02	6.31±0.02
Pt 16	10.37±0.55	10.94±0.49	10.88±0.32	10.12±0.62	10.38±0.62	10.33±0.72
Pt 17	12.06±0.82	11.9±0.78	11.42±0.18	11.57±0.88	11.13±1.02	10.48±0.61
Pt 18	9.65±0.92	9.77±0.04	9.4±0.03	9.28±0.03	9.55±0.07	8.93±0.05
Pt 19	13.34±1.01	11.87±0.15	13.08±0.23	9.88±0.06	10.24±0.57	10.82±0.64
Pt 20	14.63±1.15	12.75±0.26	12.66±1.02	11.87±0.53	9.85±0.08	10.36±0.73
Pt 21	10.56±0.44	11.72±0.15	9.88±0.07	9.4±0.08	9.25±0.04	9.64±0.03
Control						

4.3.2: Cation exchange capacity in dismantling area

Measured values of cation exchange capacity content (cmolcKg^{-1}) in the dismantling area of the study site Mean ± S.E n=3

	Dry season	Wet season
Pt 1	10.72±0.42	10.42±0.26
Pt 2	11.14±0.88	12.04±0.18
Pt 3	9.89±0.06	10.89±0.45
Pt 4	7.93±0.05	9.81±0.06
Pt 5	9.42±0.06	10.41±0.72
Pt 6	4.88±0.01	5.74±0.03
Pt 7	9.02±0.05	8.69±0.06
Pt 8	12.62±1.02	11.48±0.92
Pt 9	10.24±0.08	13.12±1.06
Pt 10	9.87±0.07	7.44±0.04

Appendix 5: Total metal concentration in the study site

5.1: Metal concentration (mg/kg) in 0-10cm layer of the recycling area of the study site (Dry season).

Measured values of metals (mg/kg) in 0-10cm layer of the recycling area of the study site (Dry season). Mean ± S.E. n=3

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Pt 1	49.37±3.05	54.3±3.85	2825±236.4	202±9.7	84.7±5.2	2035±186	77.65±0.56	2451±117.5
Pt 2	70.2±6.78	35.4±1.99	3062±291.2	182.5±11.2	97.4±0.88	1625±66.6	86±2.45	2765±168
Pt 3	37.91±4.27	71.95±5.8	1730±88.4	114.5±6.8	85.7±3.7	9623±774	40.16±2.4	1528±85.8
Pt 4	22.89±0.88	74.5±6.64	3478±297.8	110.8±1.6	33.37±1.24	1117±88.3	29.58±1.42	4884±276
Pt 5	47.03±3.89	76.57±8.02	2532±205	114.9±9.4	49.8±1.21	1255±58	54.56±2.66	1000±43.4
Pt 6	45.93±5.01	103.2±9.34	2498±180.6	199.5±15.6	149.6±9.8	1374±66	49.7±2.12	1577±122.8
Pt 7	8.54±0.5	18.87±0.98	3043±310	99.67±7.5	9.93±0.56	1901±53	20.07±0.09	1483±76
Pt 8	16.22±0.92	27±1.5	7105.7±557.8	166.33±9.5	17.23±0.08	3853±212	42.73±1.88	2495±162.4
Pt 9	25.03±1.03	22.89±3.10	4162±372	74.71±2.7	25.84±0.77	2385.7±176	31.02±1.04	2674±148
Pt 10	9.67±1.1	19.63±0.86	3917±303	130.89±8.9	61.78±2.17	2395±154	42.7±1.55	2515.3±216
Pt 11	19.12±1.3	7.42±0.06	2643±250.6	79.73±1.86	28±0.88	3110±126	33.87±0.43	3063±228
Pt 12	18.5±0.9	13.92±0.78	3030±277	127.1±9.12	32.78±1.1	2521±93.5	40.26±0.65	2667±123.1
Pt 13	27.64±1.3	37.64±3.27	5972±492.35	94.5±6.4	31.38±1.7	1888.7±78.3	30.12±1.02	1672±97.4
Pt 14	33.11±2.2	34.65±2.8	3261±190	85.53±4.35	25.18±0.88	1503±64	29.61±0.47	1633±118
Pt 15	32.5±1.80	29.9±3.15	2729±165	107.57±15.2	26.23±1.05	1478±58.2	35.56±1.06	1743±142
Pt 16	16.07±0.98	16.19±0.68	1894±68.4	90.53±5.22	19.38±0.56	1365±58.4	29.45±0.52	1589±122
Pt 17	5.04±0.03	18.46±1.34	2637±142	53.5±3.6	4.07±0.08	1994.7±106	20.41±0.07	1965±105
Pt 18	9.76±0.04	19.72±0.92	3676±256	97.2±3.4	10.44±0.18	2175±112	22.73±0.07	1673±92
Pt 19	23.48±1.42	15.82±1.22	3833±196	86.25±5.3	14.67±0.45	1975±98.2	26.43±0.18	1823±124
Pt 20	12.37±0.87	20.56±0.86	2239±116	116.28±5.89	21.54±0.08	2154±152	33.04±0.66	2700±186
Pt 21	23.77±1.68	25.83±1.67	2547±76.5	88.43±4.6	27.87±0.66	3053±174	32±1.06	2204±118

5.2 Metal concentration (mg/kg) in 10-20cm layer of the recycling area of the study site (Dry season).

Measured values of metals (mg/kg) in 10-20cm layer of the recycling area of the study site (Dry season). Mean ± S.E. n=3

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Pt 1	47.03±0.74	56.66±3.5	2631±98.2	198±2.46	69.78±4.22	1841±105	81.55±5.32	2208±158
Pt 2	52.7±1.44	33.05±1.66	1575.7±55.6	147.23±8.05	78.33±3.75	1103±88.4	34.35±1.55	1664±118
Pt 3	15.3±0.09	87.8±3.8	1561±101	152.3±11.2	158.3±11.2	9260±742	37.2±1.06	2123±144
Pt 4	16.86±0.07	65.66±2.5	2582±166	245±16.8	57.2±3.7	1128±92.4	34.56±1.65	8178±622
Pt 5	63.4±2.16	57.07±1.34	2550±202	520±30.3	37.1±1.68	1028±88.2	53.08±2.42	1574±98.2
Pt 6	69.94±3.12	86.55±1.86	2206±136	194.5±11.4	87.4±4.22	1098±86.4	49.471.08	2568±234
Pt 7	10.37±0.07	23.94±0.82	5727±378	59.9±3.65	76.03±4.21	2267±131	8±0.07	2284±164
Pt 8	22±0.16	33.64±1.16	4732±225	101.43±8.72	10.67±0.08	3352±288	30.39±0.5	1928±132
Pt 9	28.24±1.08	19.48±0.74	4524±342	124.9±6.8	28.29±0.16	2974±204	26.79±0.72	2409±198
Pt 10	8.99±0.45	13.78±0.62	3900±112.2	119.36±13.6	69.65±3.77	2753±212	34.2±0.88	2707.7±174
Pt 11	17.06±0.66	8.05±0.06	2963±164	60.22±2.5	24.27±0.88	3134±292	25.433±1.14	3146±158
Pt 12	19.97±0.78	18.84±0.08	5627±384	148.85±12.6	39.99±1.48	1925±101	38.65±1.12	2662±206
Pt 13	25.9±1.1	20.35±0.76	5618±370	123.9±10.8	41.88±2.45	1639±116	34.37±0.82	2104±182
Pt 14	26.85±1.84	35.81±1.04	3575±252	68.54±5.74	39.83±1.44	1321±92	34.56±0.98	2052±220
Pt 15	28.87±1.36	27.25±0.83	3032±175	121.19±11.2	28.93±1.62	1460±78.6	31.66±1.24	1863±190
Pt 16	16.53±0.64	16.57±0.06	2069±88	68.72±4.92	25.84±1.05	1240±88.2	23.861.4	1568±132
Pt 17	5.59±0.08	20.74±0.82	2324±102	73±2.57	4.32±0.07	1760.7±101	16.79±0.78	2054±178
Pt 18	10.21±0.08	16.53±0.08	3586±147	92.58±4.56	5.75±0.03	2024±158	18.06±0.32	1761±124
Pt 19	22.39±1.03	14.44±0.08	3949±186	100±6.2	15.84±0.48	1945±126	25.68±0.88	1766±116
Pt 20	12.98±0.86	18.1±1.02	2623±92.4	118.75±9.8	26.13±0.16	1867±98.2	33.6±1.26	2753±202
Pt 21	26.62±1.12	23.43±1.13	2803±162	87.43±7.54	26±1.02	2759±128.5	34±1.06	2543±152

5.3: Metal concentration (mg/kg) in 20-30cm layer of the recycling area of the study site (Dry season).

Measured values of metals (mg/kg) in 20-30cm layer of the recycling area of the study site (Dry season). Mean ± S.E. n=3

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Pt 1	39.17±1.24	57.67±1.16	2523±116	222±10.78	82.7±4.2	1581±94.2	73.92±6.44	2312
Pt 2	24.88±0.98	63.23±3.84	2573.7±128	251.8±30.6	88.1±5.62	1138.7±82.4	48.46±2.84	2880
Pt 3	7.37±0.06	72.6±5.42	780±54.2	148.4±15.2	37±1.54	3687±128	25.9±1.24	1173±94
Pt 4	15.63±0.7	56.77±3.86	1590±86.4	172±11.4	82.22±6.14	753±48.4	20.62±0.96	5904±386
Pt 5	28.6±1.12	51.33±3.44	1785±132	253±18.72	49±2.16	1108±85	38.1±1.78	1417±120
Pt 6	53.93±2.15	75.47±4.82	1619±144	316.4±23.4	64.6±3.22	962.5±76.3	31.5±2.57	1656±108
Pt 7	4.92±0.64	28.96±1.04	6022±498	184.53±8.64	26.2±1.04	768±64.2	31.4±1.16	3104±274
Pt 8	23.43±0.84	32.89±0.82	5922±512	113.31±9.86	16.86±0.67	3011±178	38.34±2.08	1993±165
Pt 9	30.52±1.54	25.64±1.02	5170±384	146.12±12.4	41.93±1.98	2370±156	25.54±1.26	2201±114
Pt 10	10.95±0.06	14.02±0.64	4076±225	112.87±10.24	85.95±6.22	2426±182	28.31±1.68	2797.3±227
Pt 11	19.96±0.42	10.2±0.06	2960±128	85.11±6.12	21.05±1.42	2744.7±126	13.96±0.72	3517±284
Pt 12	20.66±1.24	26.67±0.98	5737±492	151.8±12.4	39.77±1.86	1926.7±175	37.14±0.88	2635±202
Pt 13	27.5±1.67	19.07±0.56	5473±550	126.5±8.48	48.52±3.66	1478±124	38.01±1.64	2166±125
Pt 14	25.63±0.88	33.48±1.84	3660±287	95.37±6.72	40.42±2.92	1125±88.4	32.69±1.12	2150±171
Pt 15	25.88±0.92	26.25±1.22	3111±170	96.14±8.14	32.75±2.54	1261±98	21.44±1.59	1907±128
Pt 16	16.19±0.08	20.04±0.88	2137±198	100.78±11.2	18.28±0.77	985.7±75	15.94±0.94	1655±114
Pt 17	5.41±0.84	23.68±1.07	2697±240	78.33±8.02	5±0.06	1641±148	18±0.07	2398±164
Pt 18	13.21±0.72	11.88±0.77	3835±306	86.2±6.32	9.22±0.72	1899±192	24.67±2.08	1943±136
Pt 19	24.17±1.02	16.99±0.62	4114±372	109±11.4	16.38±0.84	1771±138	25.17±1.89	1705±128
Pt 20	15.87±0.4	17.79±1.32	2254±148	186±14.4	27.52±1.10	1688±142	30.73±2.48	2800±184
Pt 21	21.85±0.64	20.79±1.44	2946±178	91.7±4.62	25±1.12	2718±212	39±1.84	2926±245

5.4: Metal concentration (mg/kg) in 0-5cm layer of the dismantling area of the study site (Dry season).

Measured values of metals (mg/kg) dismantling area of the study site (Dry season). Mean ± S.E. n=3

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Pt 1	17.79±0.67	61.6±4.82	7230±565	376±25.37	33.7±1.38	2763±184	113.6±13.4	3065±228
Pt 2	5.5±0.06	89.17±5.63	5919±422	117.2±9.54	44.87±2.86	1387±94.6	141±10.6	2154±284
Pt 3	8.7±0.08	73.1±3.81	4369±287	220.9±14.5	56.13±3.65	3723±192	81.5±5.88	4471±395
Pt 4	25.63±0.35	39±1.02	8143±679	125.7±10.92	25.24±1.58	584.6±35.6	72.9±5.76	825.8±70.8
Pt 5	3.37±0.02	19.44±0.32	9277±1012	58.2±3.42	14.38±0.91	1941±154	37.7±1.02	1986±147
Pt 6	5.22±0.64	21.95±0.48	5983±562	101±6.92	15.17±0.67	1345±86.4	38.4±1.48	805±72.5
Pt 7	10.33±0.82	56.27±3.24	5623±381	38.94±1.87	1.37±0.00	673±58.2	29.3±0.84	509±33.5
Pt 8	0.88±0.01	13.52±0.78	4470±286	65.43±5.24	15.97±0.58	1109±80.3	4.84±0.00	640±52.68
Pt 9	4.3±0.07	83.78±3.63	5564±488	26.44±0.92	22.96±1.04	3036±246	27.33±1.27	2196±196
Pt 10	5.03±0.6	32.73±1.09	2217±224	78.62±6.83	9.36±0.08	1667±132	37±2.64	2560±282

5.5: Metal concentration (mg/kg) in 0-10cm layer of the recycling area of the study site (Wet season).

Measured values of metals in 0-10cm layer of the recycling area of the study site (Wet season). Mean ± SE. n=3

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Pt 1	13.81±0.65	47.3±3.54	7359±550	107.98±9.76	59.66±4.42	1821.2±113	66.38±4.52	726.8±57.24
Pt 2	13.14±0.77	35.53±2.67	4746±404	195±11.6	22.17±1.41	1138±84.2	29.15±1.93	590±33.51
Pt 3	10.78±0.08	27.17±2.08	3945±216	158.6±12.63	18.44±1.04	1052±68.34	23.75±1.18	508±41.2
Pt 4	16.44±1.22	33.36±2.13	4674±235	159.4±8.76	31.44±1.12	2160±148	16.93±0.09	849±47.39
Pt 5	11.44±0.93	44.84±3.82	6186±412	160±11.4	19.38±0.08	1160±120	11.9±0.82	1019±76.4
Pt 6	19.61±2.02	39.48±2.15	5045±395	256±18.6	22.72±0.91	1968±200	10.34±0.31	784±54.27
Pt 7	7.14±0.06	20.32±1.07	5120±427	73.75±5.48	18.58±0.74	1724±132	60.2±4.48	866±61.07
Pt 8	6.18±0.04	17.18±0.92	4576±284	63.25±4.31	16.57±1.02	1665±154	50.55±4.67	825±51.54
Pt 9	13.75±0.81	25.41±1.47	3567±223	68.45±5.04	18.44±0.81	1885±148	31.02±1.83	1074±88.21
Pt 10	19.8±0.97	18.88±1.05	3917±272	108.3±8.36	19.38±0.43	1549±104	23.66±1.35	1356±154.61
Pt 11	24.5±1.09	16.5±0.84	2643±198	63.7±4.2	9.86±0.01	2210±192	43.1±3.14	870±63.14
Pt 12	5.79±0.07	13.19±0.78	7775±555	21.91±0.98	7.47±0.06	4069±312	44.26±2.13	1068±76.63
Pt 13	3.94±0.00	8.8±0.01	6890±585	14.56±0.73	6±0.07	3068±269	53.38±4.65	931±65.19
Pt 14	15.83±0.81	31.83±1.24	3030±217	51.5±2.51	33.56±2.61	1503±107	29.61±3.03	973±70.82
Pt 15	22.6±1.14	17.96±0.79	5972±550	63.52±4.75	22.2±0.89	1478±125	35.56±2.72	1304±142
Pt 16	10.85±1.17	9.85±0.03	3261±264	93.64±8.15	26.15±1.62	1365±118	29.45±1.78	859±68.34
Pt 17	10.43±0.73	20.04±0.52	5660±493	35.13±1.42	28.45±0.91	2229±220	51.35±3.55	954±72.1
Pt 18	8.63±0.09	16.33±0.48	5020±416	29.17±1.17	24.36±1.24	2117±172	40.56±2.28	903±62.51
Pt 19	17.27±1.24	13.34±0.87	3567±242	65.5±3.71	40.55±2.15	1975±152	26.43±1.56	853±53.42
Pt 20	5.12±0.06	15.8±1.01	3165±188	100±7.53	22.72±0.87	2154±172	33.04±2.42	1000±87.15
Pt 21	9.39±0.07	10.65±0.42	5894±303	43±2.50	20.55±1.41	3053±233	32±0.98	902±58.27

5.6: Metal concentration (mg/kg) in 10-20cm layer of the recycling area of the study site (Wet season).

Measured values of metals in 10-20cm layer of the recycling area of the study site (Wet season). Mean ± SE. n=3

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Pt 1	15.82±0.08	31.39±1.65	7600±535	65.37±2.13	53.8±2.93	2215±176	63.27±3.54	845.3±48.27
Pt 2	9.55±0.06	21.32±2.33	4185±288	94±5.40	30.86±1.04	2412±138	23.76±0.79	830±51.94
Pt 3	12.47±0.7	24.66±2.04	4821±304	82.5±4.12	27.97±1.65	2403±112	28.12±1.01	1088±74.42
Pt 4	9.38±0.06	32.35±2.71	3615±237	11.4±0.71	41.64±2.28	1620±86.52	19.62±0.45	961±55.28
Pt 5	14.51±1.05	48.44±2.92	4684±187	94.1±5.36	14.8±0.93	980±64.31	13.64±0.81	1460±96.22
Pt 6	17.46±1.10	48.31±3.15	4195±354	161.5±11.57	31.46±1.06	1431±96.42	11.42±0.33	913±62.84
Pt 7	12.47±0.82	24.66±1.72	6420±377	98.15±6.92	46.64±3.81	2556±184	37.42±1.45	861.5±53.2
Pt 8	11.45±0.95	23.06±1.18	6185±414	91.15±8.23	43.66±3.15	2473±142	34.28±1.52	847±36.68
Pt 9	15.69±0.18	37.8±2.76	4280±373	94.21±7.68	23.25±0.89	1794±193	23±0.91	1245±95.14
Pt 10	15±0.06	29.73±1.05	3900±185	112.6±8.44	18.41±0.54	1806±165	30.1±1.68	1504±107
Pt 11	22.76±1.14	18.24±0.77	2963±147	71.4±5.81	14.33±0.33	2341±154	33±2.04	896±73.24
Pt 12	21.7±1.62	29.02±1.63	5675±378	54.4±2.55	17.28±1.04	2076±116	94.8±5.84	895±52.71
Pt 13	19.23±0.77	25.97±1.55	5460±333	49.49±3.21	10.56±0.04	2001±95.6	81.2±4.72	855±64.26
Pt 14	24.67±1.58	30.68±2.41	5627±248	92±5.15	24.12±1.07	1321±86.46	34.56±1.35	1025±82.42
Pt 15	29.4±1.82	18.44±0.78	5618±381	58.3±3.27	17.85±0.84	1460±112	31.66±2.18	1498±116
Pt 16	19.36±1.14	11.78±0.84	3575±223	78.56±5.42	18.73±1.01	1420±92.7	23.86±0.84	899±71.42
Pt 17	10.54±0.48	28.88±1.83	5950±364	206.55±14.56	35.42±2.58	2694±313	98.6±6.23	805±62.31
Pt 18	9.03±0.06	24.53±1.08	5515±280	182.2±11.4	32.36±1.83	2543±202	80.55±5.35	763±44.2
Pt 19	15.45±0.57	13.98±0.72	4068±224	80±6.55	31.06±2.75	1945±148	25.68±1.51	766±57.24
Pt 20	9.54±0.42	17.5±0.51	3670±301	103±8.22	13.1±0.69	1867±133	33.6±2.54	1315±88.4
Pt 21	14.73±0.61	13.6±0.32	6321±550	58±2.46	18.75±1.08	2759±194	34±2.12	980±72.4

5.7: Metal concentration (mg/kg) in 20-30cm layer of the recycling area of the study site (Wet season).

Measured values of metals in 20-30cm layer of the recycling area of the study site (Wet season). Mean ± SE. n=3

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Pt 1	7.02±0.05	32.16±2.08	7123±556	92±7.42	72.9±5.74	1945±152	19.75±0.95	1109±85.3
Pt 2	12.83±0.09	18.98±0.78	4906±225	105±7.68	24.91±1.06	2478±202	48.61±3.52	689±45.8
Pt 3	10.64±0.16	15.78±0.94	4298±353	86.75±4.77	23.2±1.02	2234±108	39.55±2.65	621±33.83
Pt 4	11.84±0.34	29.45±1.19	3102±262	85.69±5.92	23.1±0.48	2000±125	8.45±0.07	1056±55.72
Pt 5	9.54±0.07	34.16±2.71	4301±248	76.4±3.11	11.84±0.06	902±52.15	9.45±0.04	970±62.14
Pt 6	10.41±0.81	24.1±1.92	4312±315	113±10.04	22.4±0.69	1330±82.44	13.01±0.06	1023±87.43
Pt 7	11.48±0.75	42.71±3.08	6000±365	118.8±7.85	63.45±3.12	2638±235	21.98±1.35	943±72.71
Pt 8	9.91±0.07	36.08±2.48	5620±382	104.55±8.12	56.25±2.72	2536±202	18.48±0.08	915±62.15
Pt 9	14±0.08	42.4±2.67	4532±314	112.46±6.55	25±0.77	2020±178	21.45±0.68	1486±95.4
Pt 10	21.85±1.11	24.18±0.88	4076±292	110.5±7.22	21.22±0.82	1996±145	28.2±1.15	1705±124
Pt 11	19.8±1.04	28.7±1.27	2960±183	75±4.28	16.7±0.08	2540±137	25.2±0.88	964±72.44
Pt 12	14.97±0.86	28.17±1.36	5785±305	59.2±3.16	59.75±3.45	2675±106	43.8±2.57	922±55.31
Pt 13	13.18±0.77	24.9±1.02	5450±286	53.6±2.12	53.1±2.68	2543±148	37.33±1.52	894±43.78
Pt 14	19.64±1.10	31.64±1.73	5737±550	96.42±6.31	25±1.12	1125±73.28	32.69±2.22	950±62.16
Pt 15	24.7±1.54	15.3±0.21	5473±422	55.6±2.23	19.38±1.04	1261±88.43	21.44±1.05	1675±95.42
Pt 16	13.19±0.69	13.3±0.46	3660±185	65.88±2.42	20.49±1.33	1687±114	15.94±0.82	1055±62.44
Pt 17	10.12±0.06	32.38±1.44	7580±481	156.4±9.88	55.4±2.65	3765±206	92.5±3.66	881±52.73
Pt 18	11.42±0.15	36.64±1.31	7360±612	174.2±10.43	61±4.82	3880±167	107.15±8.72	912±44.58
Pt 19	14.25±0.82	12.5±0.09	4390±274	91±4.88	34.88	1771±105	25.17±1.05	905±55.4
Pt 20	8.42±0.04	19.32±0.84	4040±308	126±6.82	15.3±0.05	1688±105	30.73±1.25	1650±92.42
Pt 21	13.85±0.08	16.9±0.04	6685±292	79.4±4.33	18.55±0.42	3218±265	39±0.89	1022±32.4

5.8: Metal concentration (mg/kg) in 0-5cm layer of the dismantling area of the study site (Wet season).

Measured values of metals (mg/kg) dismantling area of the study site (Wet season). Mean ± S.E. n=3

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Pt 1	3.7±0.00	38.01±1.33	2994±132	187.3±13.62	24.15±0.48	513.3±44.42	19.46±0.82	1074.8±72.5
Pt 2	21.39±0.42	34.68±0.92	1736±164	438.1±36.3	25.65±1.52	287.1±19.36	10.53±0.77	954.8±67.3
Pt 3	4.43±0.01	25.81±1.46	2952±236	238.6±16.22	52.18±4.62	751±38.92	6.99±0.54	682.2±26.73
Pt 4	9.72±0.04	38.18±3.24	4723±348	244.4±19.34	47.5±3.2	1610±88.28	20.47±1.57	852±58.35
Pt 5	12.24±0.06	29.88±1.62	2811±197	221.1±10.62	200±11.64	1404±102.1	26.3±1.24	779±73.4
Pt 6	11.68±0.54	50.17±3.82	2320±92.7	156.1±14.2	118.5±9.52	569.5±43.28	38.92±2.29	661.2±35.33
Pt 7	15.25±0.82	37.82±2.58	6005±482	224±17.5	175.5±15.08	1100.8±112	65.37±4.24	1010.5±75.42
Pt 8	2.82±0.00	24.18±1.41	328.5±22.4	90.38±10.41	10.64±0.84	114.9±9.84	5.37±0.07	843.8±57.93
Pt 9	14.41±0.38	47.02±3.04	4148±487	365.3±18.68	69.1±4.06	1595.3±126	15.82±1.07	922±71.44
Pt 10	7.28±0.06	42.08±2.88	3634±268	384.2±24.1	50.67±3.71	1161.8±92.1	15.89±0.14	846.17±38.72

5.9: Fe and Al concentration (mg/kg) in the recycling area of the study site (dry season)

	Fe			Al		
	0-10cm	10-20cm	20-30cm	0-10cm	10-20cm	20-30cm
Pt 1	3982	3991	4102	1538	1311	1517
Pt 2	4822	2538	2980	1358	1103.7	1715
Pt 3	12068	2716	3195	954.3	1124	978.7
Pt 4	9894	2314	2596	798.9	993.5	900
Pt 5	8488	4043	3728	940.7	1061	922
Pt 6	6654	4900	3208	1996	1077	1376
Pt 7	4776	5064	4952	1692	1535	1987
Pt 8	4119	4156	3764	2134	3943	4023
Pt 9	5343	4371	4713	4295	4147	4524
Pt 10	7643	5911	5980	2036	2288	2796
Pt 11	4598	4378	4419	1470.7	1788.7	1956.3
Pt 12	3427	5971	3780	2517	2406	2728
Pt 13	5869	5380	4258	1743	1573	1920
Pt 14	3894	3134	3587	1535	1901.7	2105
Pt 15	3388	3677	2709	1407	1070	1708
Pt 16	13220	10570	9040	1003	1077	1268
Pt 17	4043	3944	4131	967	1285	1293
Pt 18	3377	3559	3949	1167	1137	1157
Pt 19	8733	7998	8052	1761	1890	2357
Pt 20	2643	3810	2973	1052	1239	1850
Pt 21	5068	4994	5321	1281	1617	1615

5.10: Fe and Al concentration (mg/kg) in the recycling area of the study site (wet season)

	Fe			Al		
	0-10cm	10-20cm	20-30cm	0-10cm	10-20cm	20-30cm
Pt 1	5644	3347	4596	1358	1605	1105.2
Pt 2	4896	3153	3230	1698	1569	1249
Pt 3	9510	8852	7970	1646	1559	1554
Pt 4	12610	8813	8980	1941	1181	920
Pt 5	8109	6244	5681	1846	1984	1514
Pt 6	2840	3010	2809	1868	1090	903
Pt 7	7802	5647	3844	1468	1559	1227
Pt 8	5485	3530	3619	1447	1062	906
Pt 9	3243	3384	3653	1635.3	1201	1254
Pt 10	2985	2361	2876	1329	1404	1410
Pt 11	3898	4028	4291	950	785.5	814.3
Pt 12	6318.55	6641	5050	1370.5	902.5	1073
Pt 13	4498	2832	3284	1346.8	1275	1050
Pt 14	5187	5784	3995	1486	1520	1688
Pt 15	11056	9678	7045	1638	1393.67	1040.8
Pt 16	12008	9245	7670	1465	1601	1339.6
Pt 17	9214	6557	5143	1479.15	1205.5	613
Pt 18	3017	3239	3323	971	880	605
Pt 19	4875	3520	3531	995.35	871	816
Pt 20	2016	2566	2890	943	789	805
Pt 21	2206	2587	3030.58	925	818	895

5.11: Fe and Al concentration (mg/kg) in 0-5cm layer of the dismantling area of the study site (dry and wet season)

	Dry season		Wet season	
	Fe	Al	Fe	Al
Pt 1	12604	3281	8910	2402.58
Pt 2	15220	2821	7318.3	1418.1
Pt 3	7400	3463	7045	2379.52
Pt 4	15443	1649	6683.3	1575.83
Pt 5	9063	1565	5255	1530.8
Pt 6	9967	1515	4939	1504.8
Pt 7	10990	958	6224	920.5
Pt 8	8073	1447	6426	1372.3
Pt 9	10069	1535.8	7076.7	1508.17
Pt 10	6916	2462	6670.3	1488.18

Appendix 6: Percentage recovery of reference materials

6.1: Percentage recovery of metals in certified reference material SQC001-050G (lot 011233)

Measured values (mg/kg) and % recovery of metals in certified reference material SQC001-050G (lot 011233) Mean ± S.E. (n=5)

	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Certified total	134±2.57	176±4.08	56.1±1.20	183±3.74	65.1±1.54	134±3.02	73±10.5	473±9.21
Measured total	133.4±1.21	169.15±1.4	56.14±0.44	182.89±2.11	63.19±1.15	132.58±3.15	71.67±0.63	483±1.03
% Recovery	99.6	96.11	100.3	99.9	97.1	98.9	97.2	102.1

6.2: Percentage recovery of metals in BGS 102

	Microwave assisted digestion (BGS 102) mgkg^{-1} n=5			**In vitro oral bioaccessibility (BGS 102) mgkg^{-1} n=5**				
	Measured total	Certified total	% recovery	Gastric phase measured	Gastric phase Certified	Gastrointestinal Phase measured	Gastrointestinal phase certified	% accuracy
As	101.24	104	97.3	7.97	N/A	5.86	5.4	108 (GI)
Cd	0.277	0.275	100.73	0.11	N/A	0.06	N/A	
Cr	219.67	225	97.63	14.9	N/A	9.33	N/A	
Cu	24.56	26	94.46	12.48	N/A	5.9	N/A	
Mn	5391.33	7330	73.55	1528.75	N/A	1377.45	N/A	
Ni	75.88	80	94.85	2.15	N/A	1.45	N/A	
Pb	71.67	79.4	90.26	16.09	13±6	6.37	N/A	124 (gastric)
Sb	3.65			0.81	N/A	0.39	N/A	
Zn	189.29	191	99.1	43.29	N/A	32.11	N/A	

G= gastric phase; GI= gastrointestinal phase

6.3: Mass balance of the sequential extraction procedure of composite soil samples in the dry season.

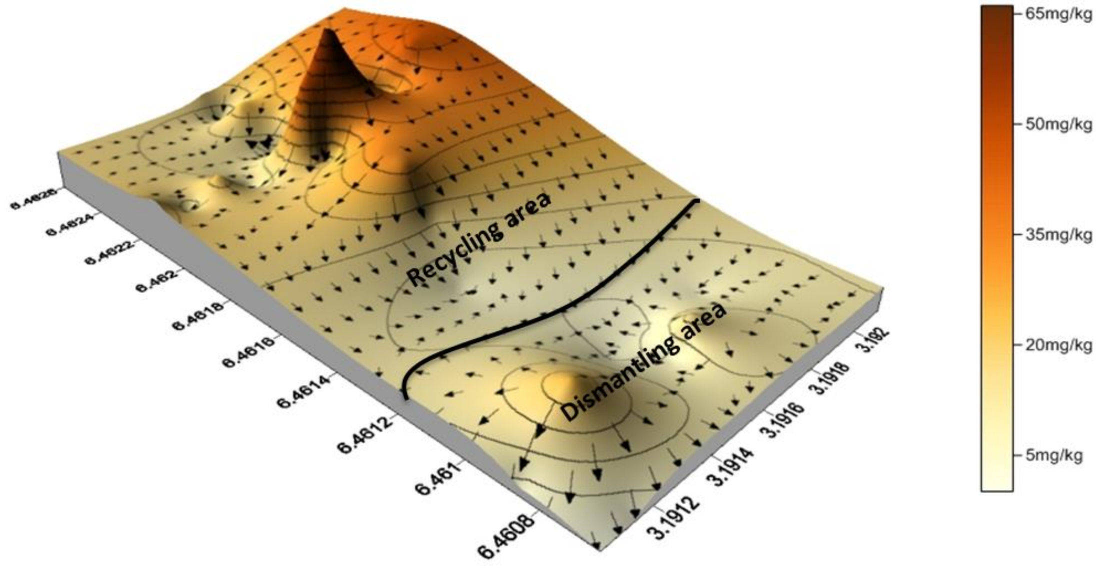
		Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Recycling area 0-10cm	F1	4.99	0.26	324.59	2.18	1.4	44.66	12.02	149.27
	F2	2.91	0.04	1712.5	11.59	3.51	1001	41.35	388.13
	F3	5.59	23.83	3880	90.82	32.82	1761.5	39.52	521.33
	F1+F2+F3	13.49	24.13	5917.09	104.59	37.73	2807.16	92.89	1058.73
	Total concentration	10.61	22.86	5297	82.42	56.6	1504	88.2	976.8
	Percentage recovery	127%	105.6%	111.7%	126.9%	66.7%	186.7%	105%	108%
Recycling area 10-20cm	F1	4.89	0.17	517.4	22.53	3.85	44.66	4.29	194.77
	F2	2.09	0.24	1687.5	10.02	3.51	1001	13.45	352.3
	F3	5.63	24.16	3523.3	92.09	49.83	1761.5	58.48	737
	F1+F2+F3	12.61	24.57	5728.2	124.64	57.19	2807.16	76.22	1284.07
	Total concentration	11.21	23.12	5676	95.92	37.34	2688.9	68.19	1178
	Percentage recovery	112%	106%	101%	130%	153%	104%	112%	109%
Recycling area 20-30cm	F1	5.61	0.28	517.4	6.53	5.95	97.51	6.87	159.97
	F2	2.97	0.16	1687.5	10.02	3.51	1030.9	8.98	352.3
	F3	7.26	31.35	3523.3	92.09	69.83	1781.7	44.28	753.73
	F1+F2+F3	15.84	31.79	5728.2	108.64	79.29	2910.11	60.13	1266
	Total concentration	12.71	31.81	5801	81.07	72.24	2981	58.67	1290
	Percentage recovery	125%	100%	99%	134%	110%	98%	102%	98%
Dismantling area 0-5cm	F1	1.27	0.3	364.91	10.44	0.89	164.81	8.47	43.02
	F2	1.26	1.56	769.8	41.63	2.28	542.2	35.61	379.46
	F3	1.87	55.47	2437.8	166.92	31.73	467.08	21.27	598.58
	F1+F2+F3	4.4	57.33	3602.51	218.99	34.9	1174.09	65.35	1021.06
	Total concentration	6.3	27.6	4166.67	149.4	31.53	1977.13	81.43	1873.87
	Percentage recovery	70%	208%	86%	147%	111%	59%	80%	54%

6.4: Mass balance of the sequential extraction procedure of composite soil samples in the wet season.

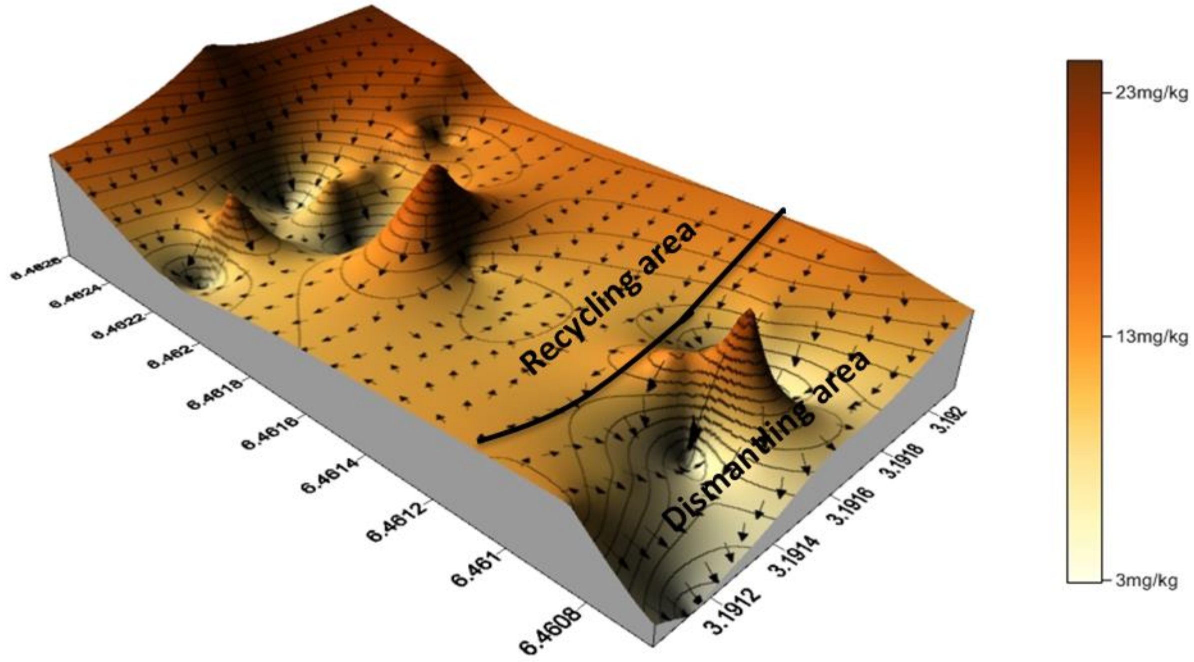
		Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
Recycling area 0-10cm	F1	1.43	0.22	285.61	1.32	1.72	16.86	13.53	15.2
	F2	3.5	0.24	1779.6	6.68	2.05	989.8	25.59	195.34
	F3	7.64	24.66	3828.3	43.01	30.94	1580.8	35.73	503
	F1+F2+F3	12.57	25.12	5893.51	51.01	34.71	2587.46	74.85	713.54
	Total concentration	9.98	26.22	5140	49.98	43.98	2230	62.53	688.3
	Percentage recovery	126%	96%	115%	102%	79%	116%	120%	104%
Recycling area 10-20cm	F1	7.69	0.26	84.94	1.61	1.33	28.43	5.25	32.1
	F2	2.48	0.16	1230.4	9.76	4.05	812.8	20.51	229
	F3	15.72	60.95	3426.7	117.72	39.43	1429.8	27.72	549.17
	F1+F2+F3	25.89	61.37	4742.04	129.09	44.81	2271.03	53.48	810.27
	Total concentration	15.19	54.97	4995	102.88	39.28	2145	50.61	751
	Percentage recovery	170%	112%	95%	125%	114%	106%	106%	108%
Recycling area 20-30cm	F1	1.8	0.21	366.27	11.79	4.36	72.06	6.4	43.06
	F2	2.94	0.04	1834.2	11.16	6.53	893.5	31.36	265.59
	F3	7.03	32.56	3024.2	48.19	46.87	1200.8	37.57	534.67
	F1+F2+F3	11.77	32.81	5224.67	71.14	57.76	2166.36	75.33	843.32
	Total concentration	9.70	32.62	5026	68.60	50.9	1984	71.68	804
	Percentage recovery	121%	101%	104%	104%	113%	109%	105%	105%
Dismantling area 0-5cm	F1	1.8	0.3	282.45	9.63	0.93	151.94	23.03	146.46
	F2	1.93	1.28	777.7	39.05	3.18	1080.92	24.78	392.55
	F3	4.84	37.6	4310	221.29	49.38	1572.5	13.59	660.2
	F1+F2+F3	8.57	39.18	5370.15	269.97	53.49	2805.36	61.4	1199.21
	Total concentration	5.21	24.89	3948.67	145	42.39	1908	65.41	1810
	Percentage recovery	164%	157%	136%	186%	126%	147%	94%	66%

Appendix 7: Spatial distribution of metals in the study area.

7.1: Cd distribution in 0-10cm depth

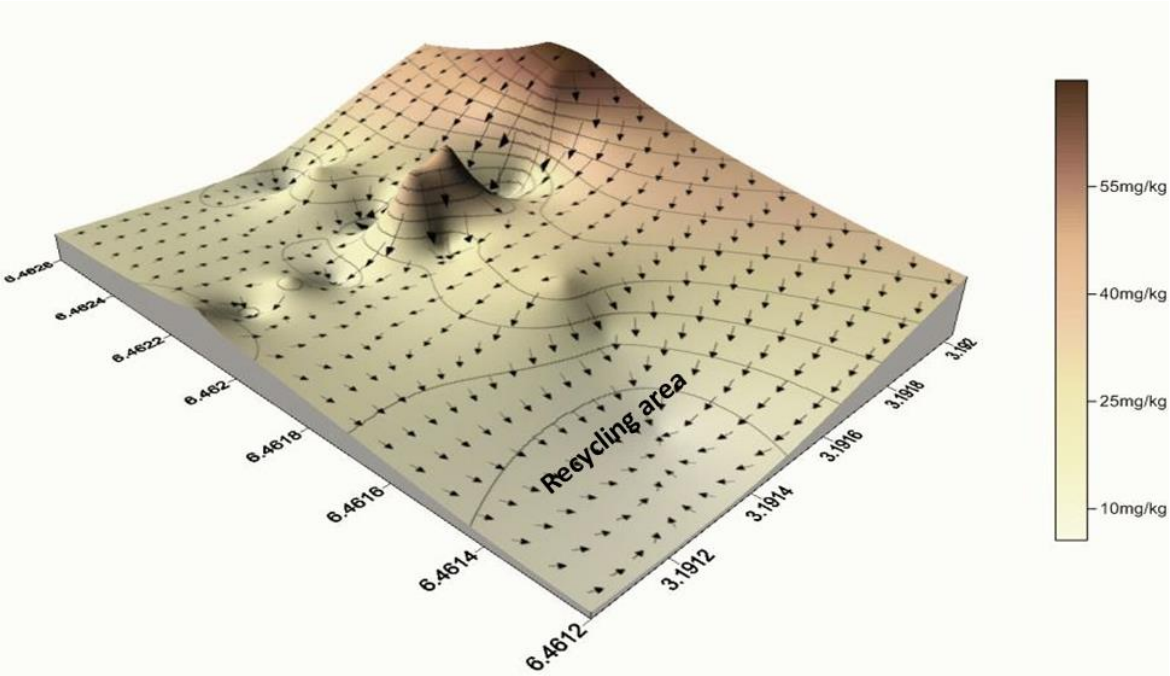


Cd distribution in the dry season.

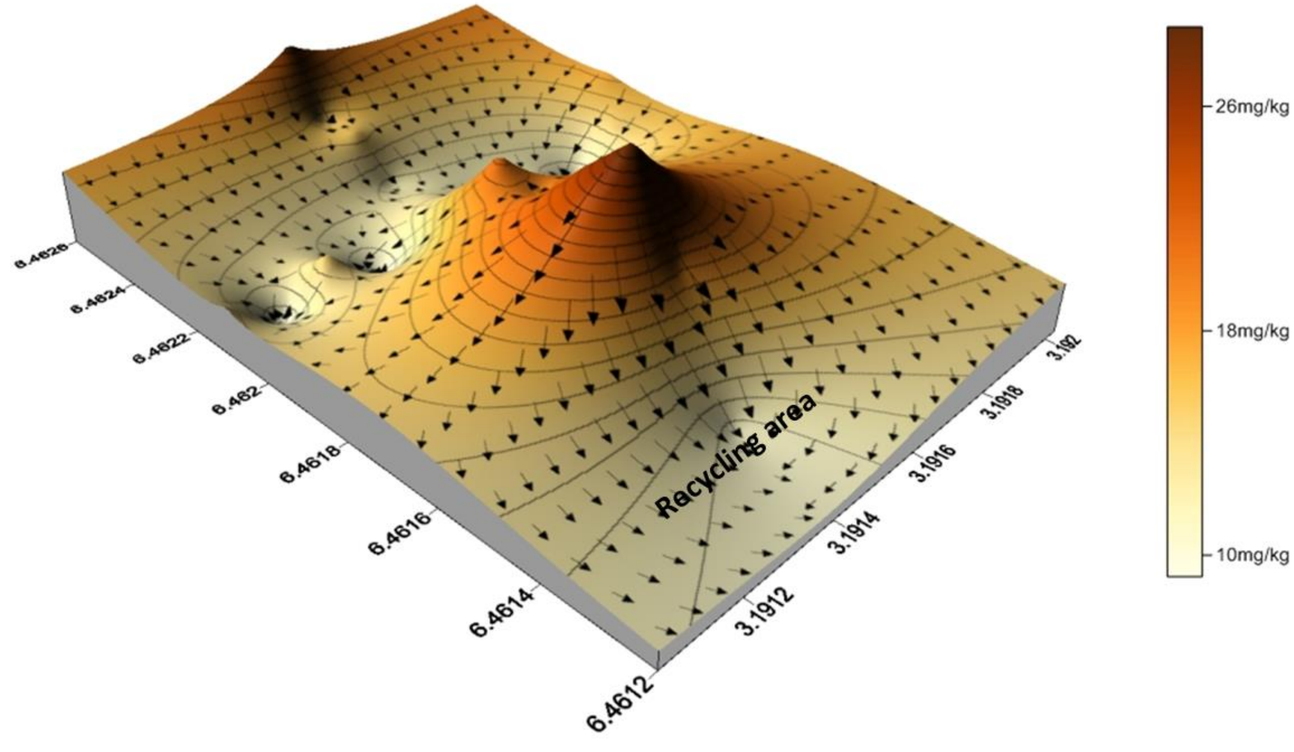


Cd distribution in the wet season.

7.2: Cd distribution in 10-20cm depth

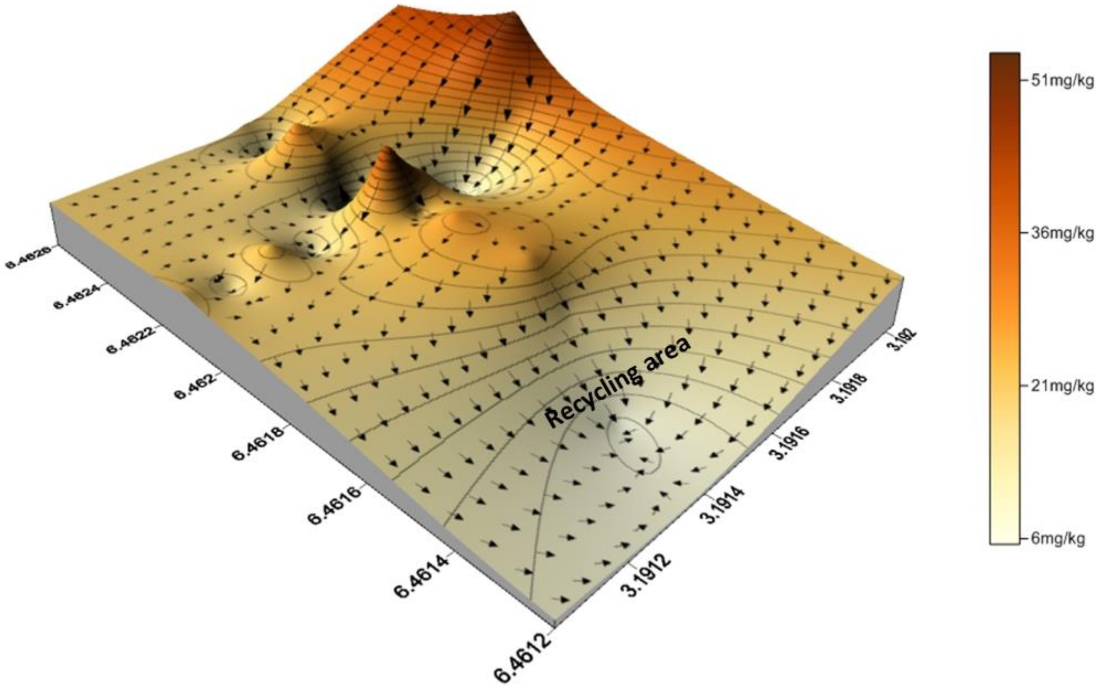


Cd distribution in the dry season.

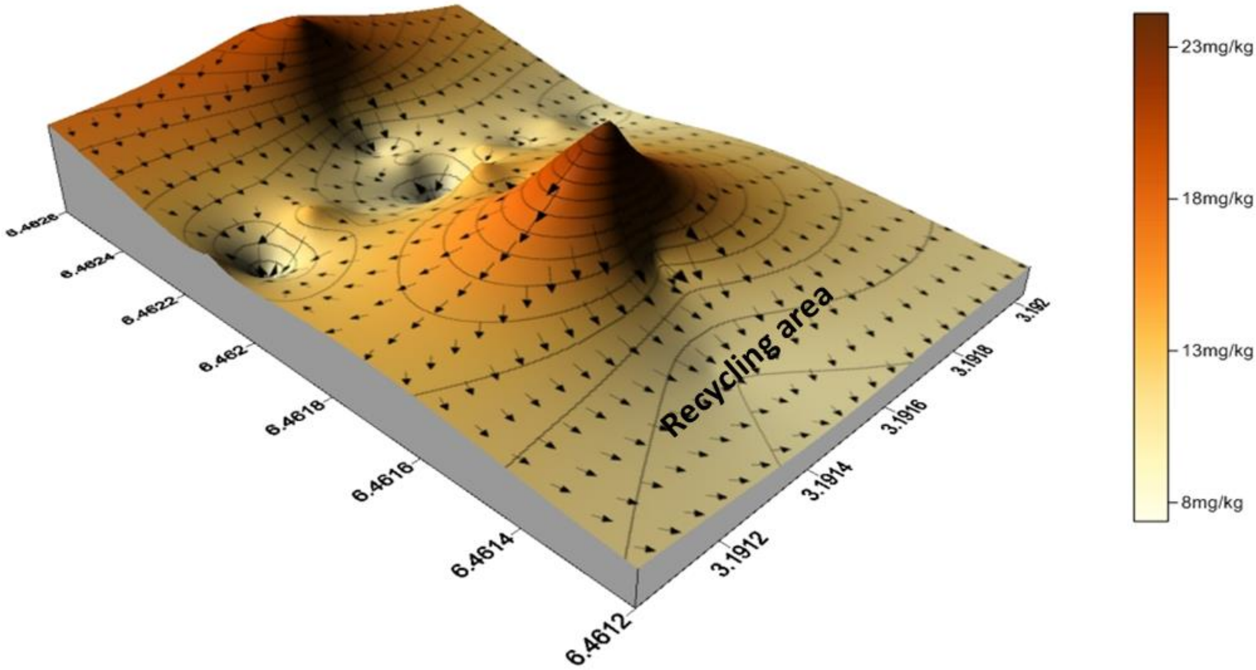


Cd distribution in the wet season.

7.3: Cd distribution in 20-30cm depth

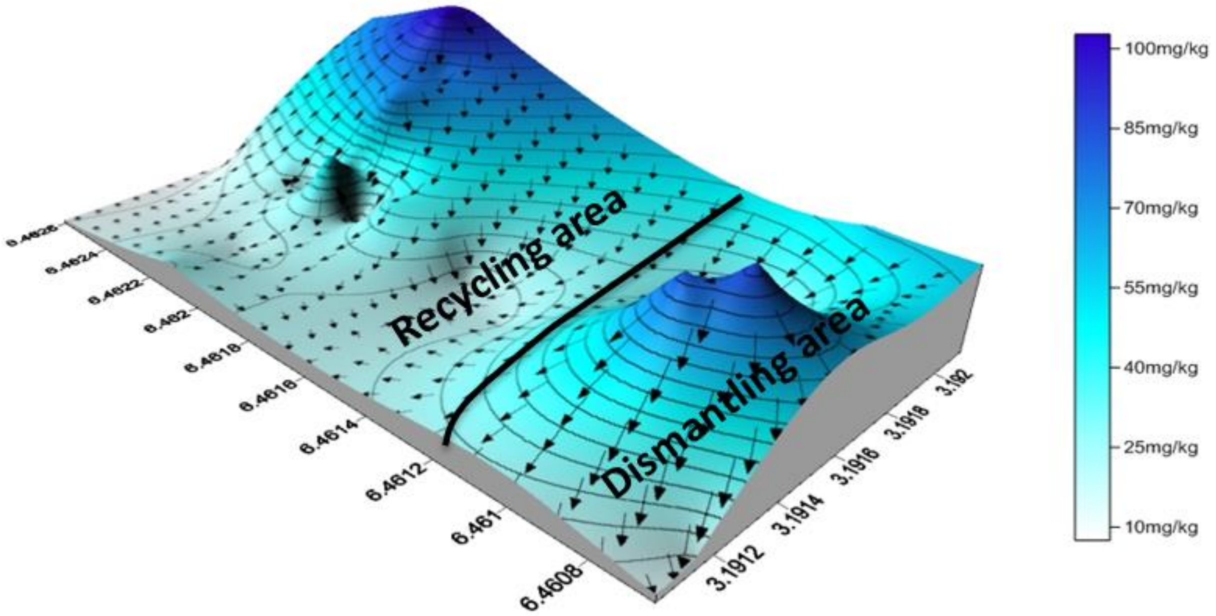


Cd distribution in the dry season.

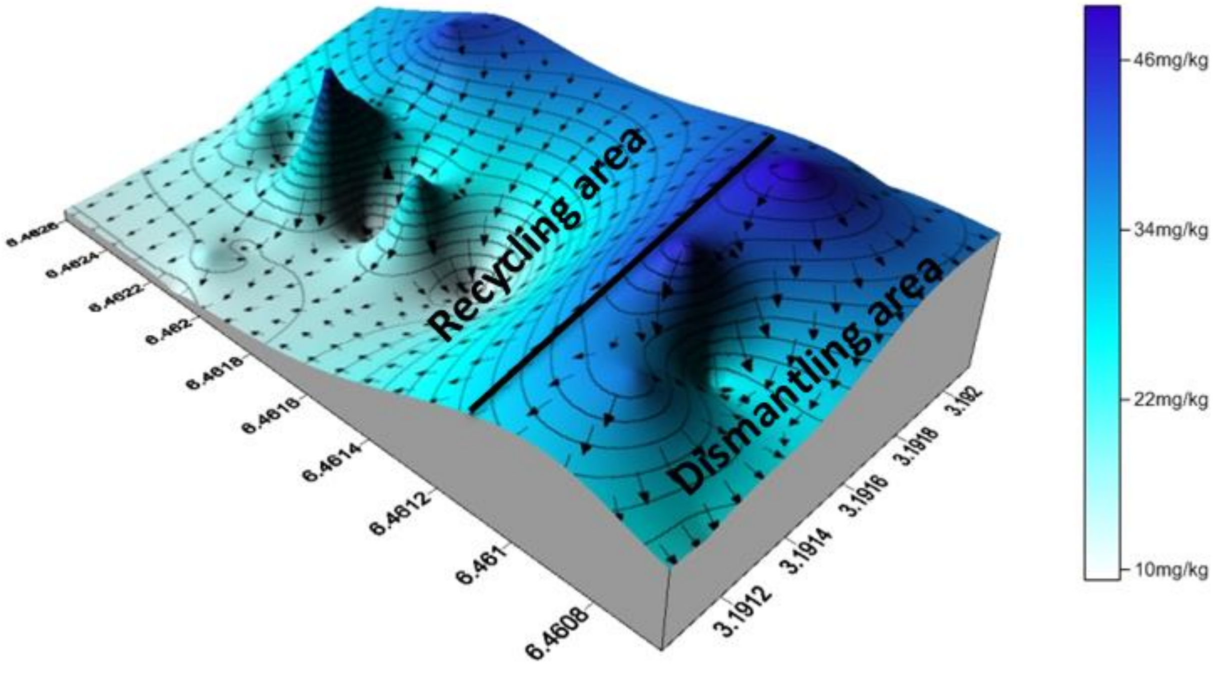


Cd distribution in the wet season.

7.4: Cr distribution in 0-10cm depth

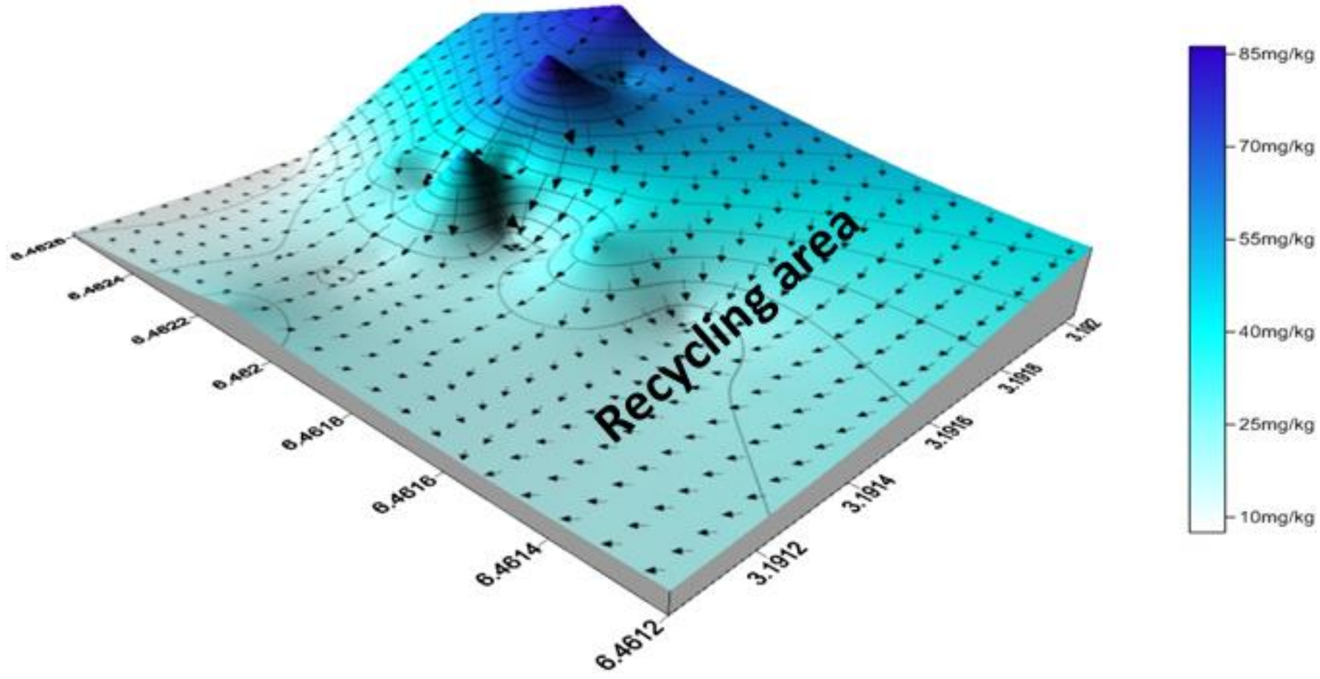


Cr distribution in dry wet season.

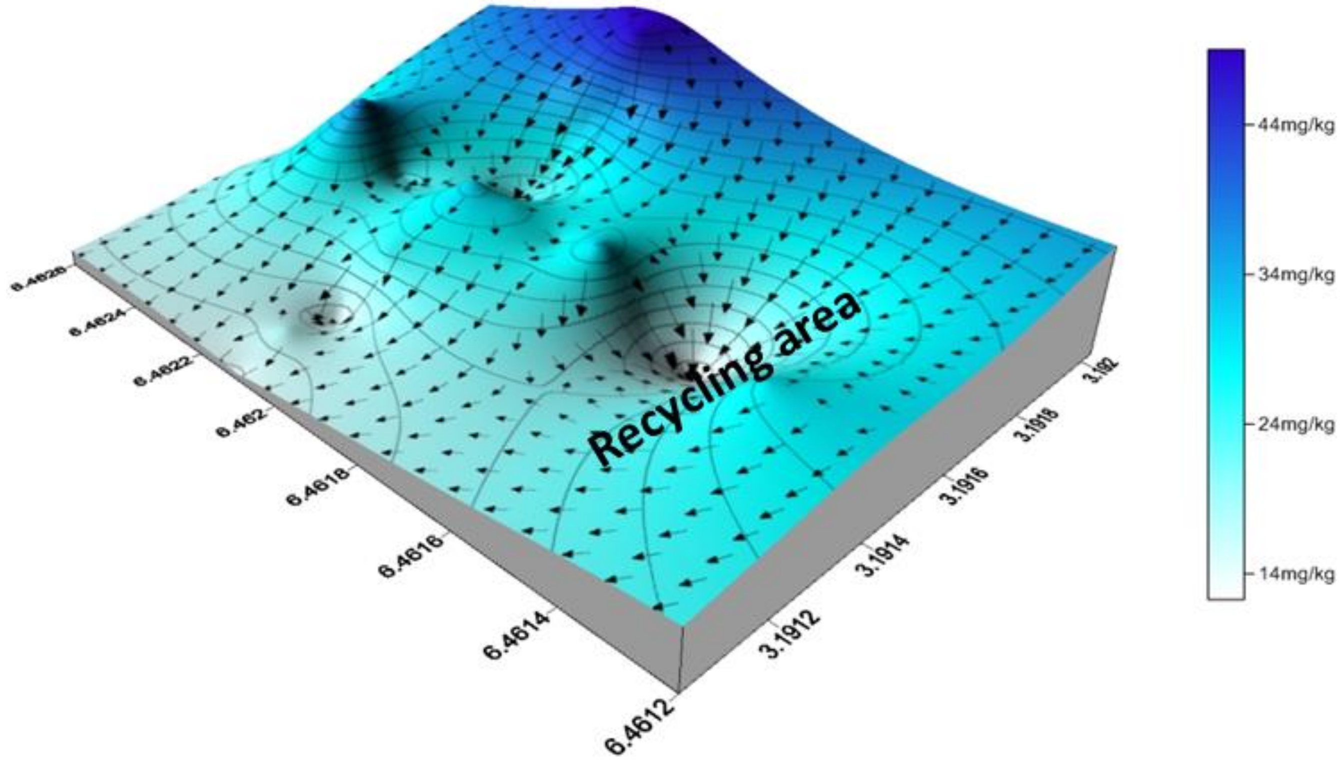


Cr distribution in the wet season.

7.5: Cr distribution in 10-20cm depth

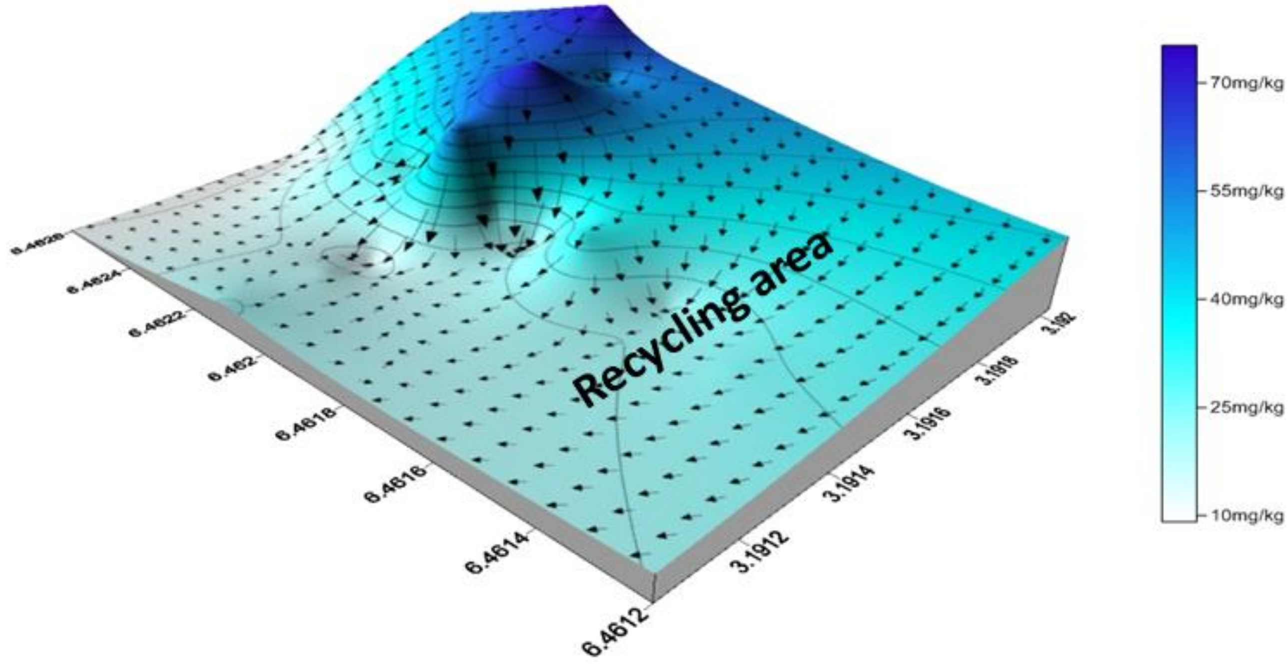


Cr distribution in the dry season.

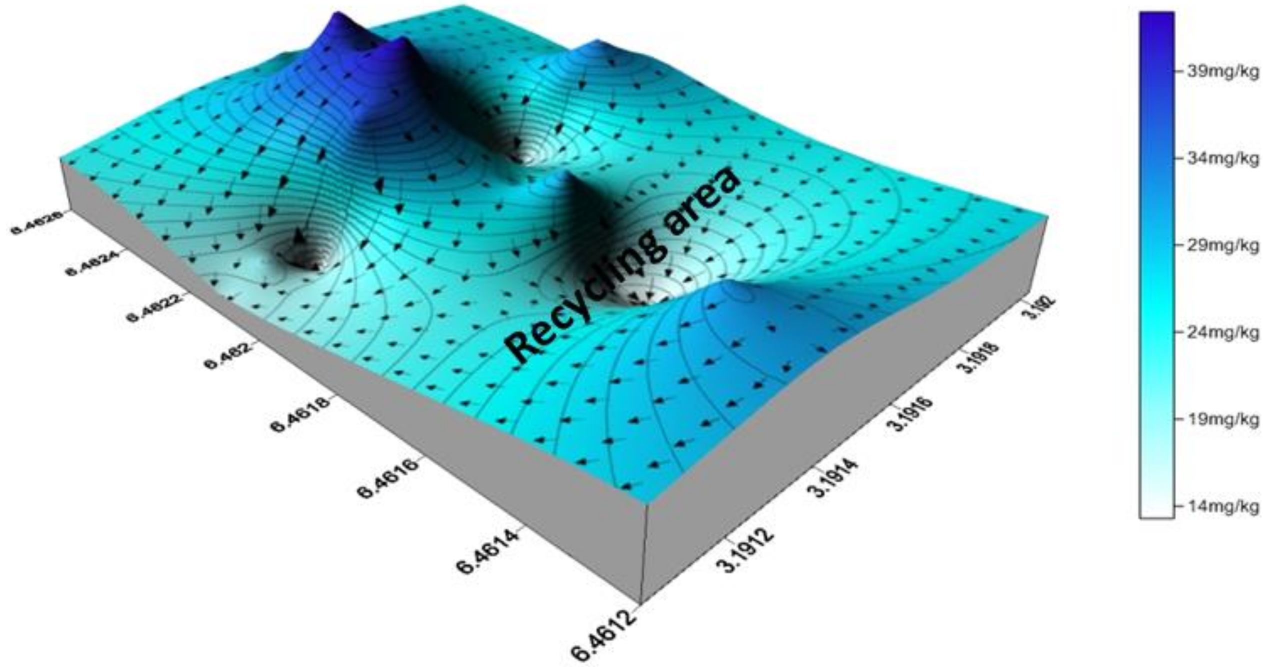


Cr distribution in the wet season.

7.6: Cr distribution in 20-30cm depth

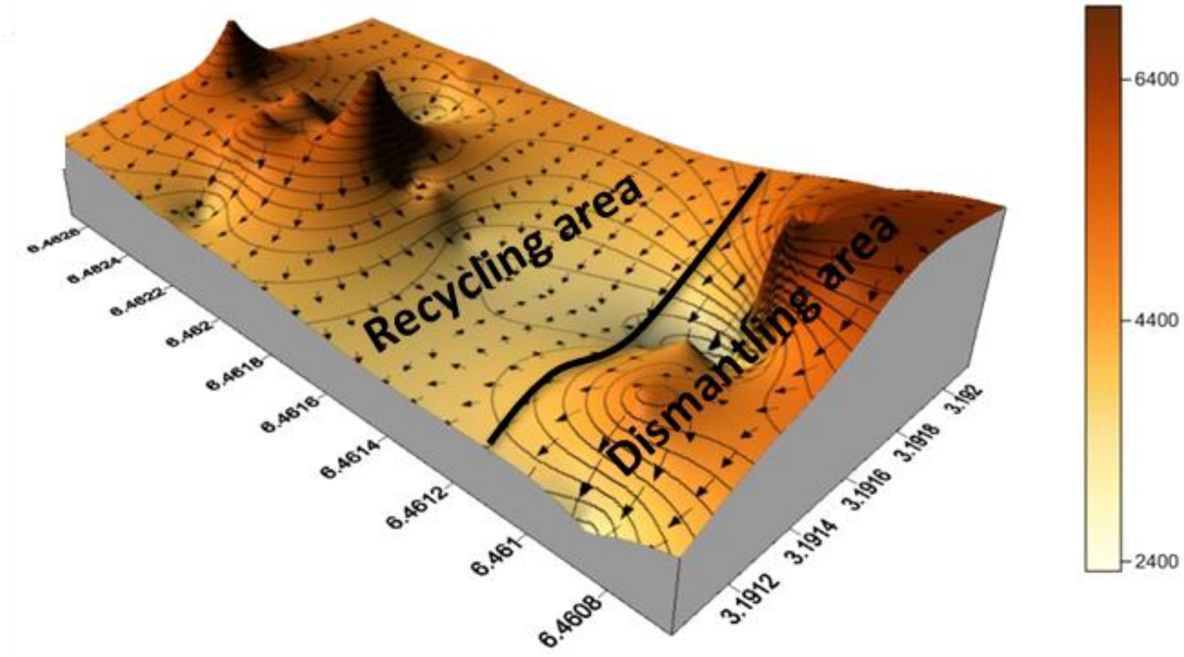


Cr distribution in the dry season.

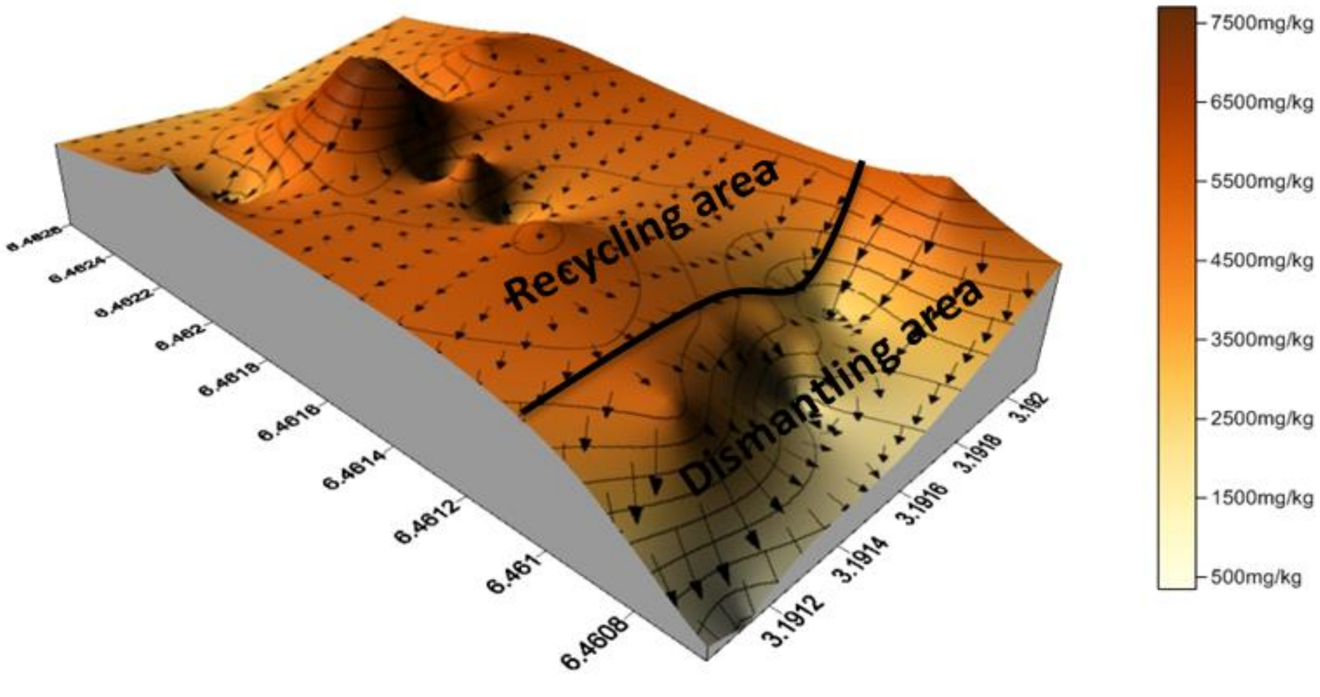


Cr distribution in the wet season.

7.7: Cu distribution in 0-10cm depth

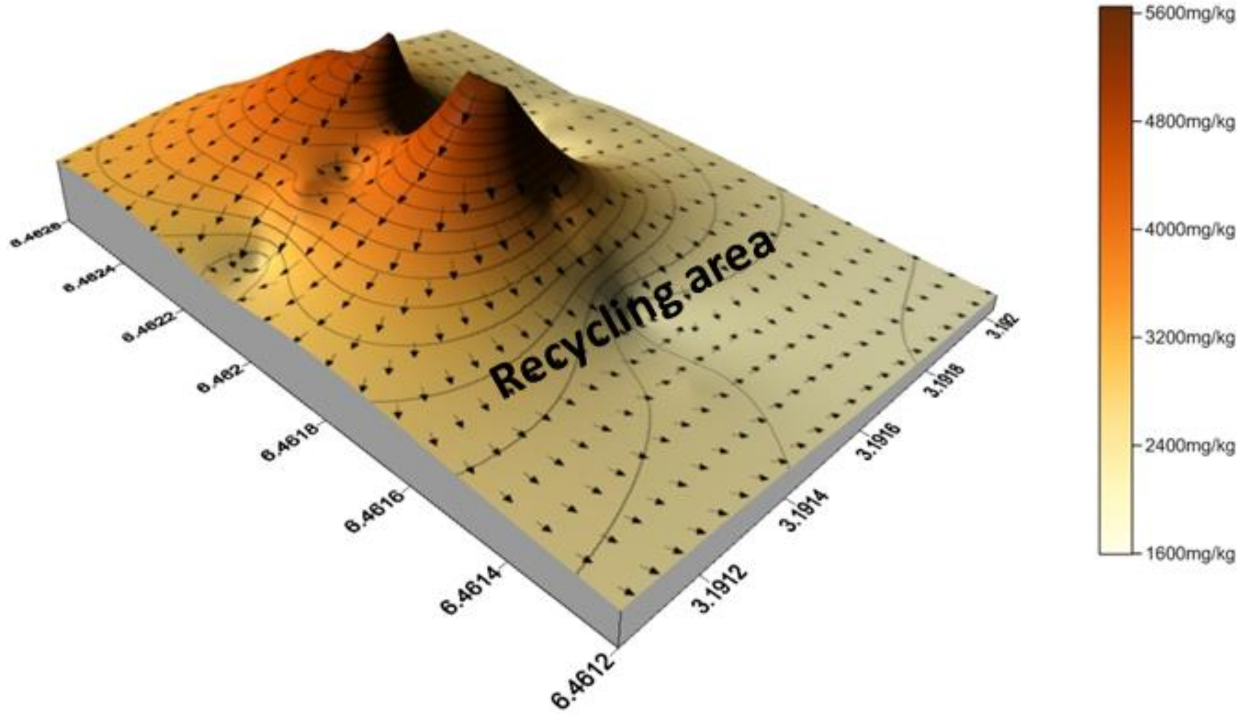


Cu distribution in the dry season.

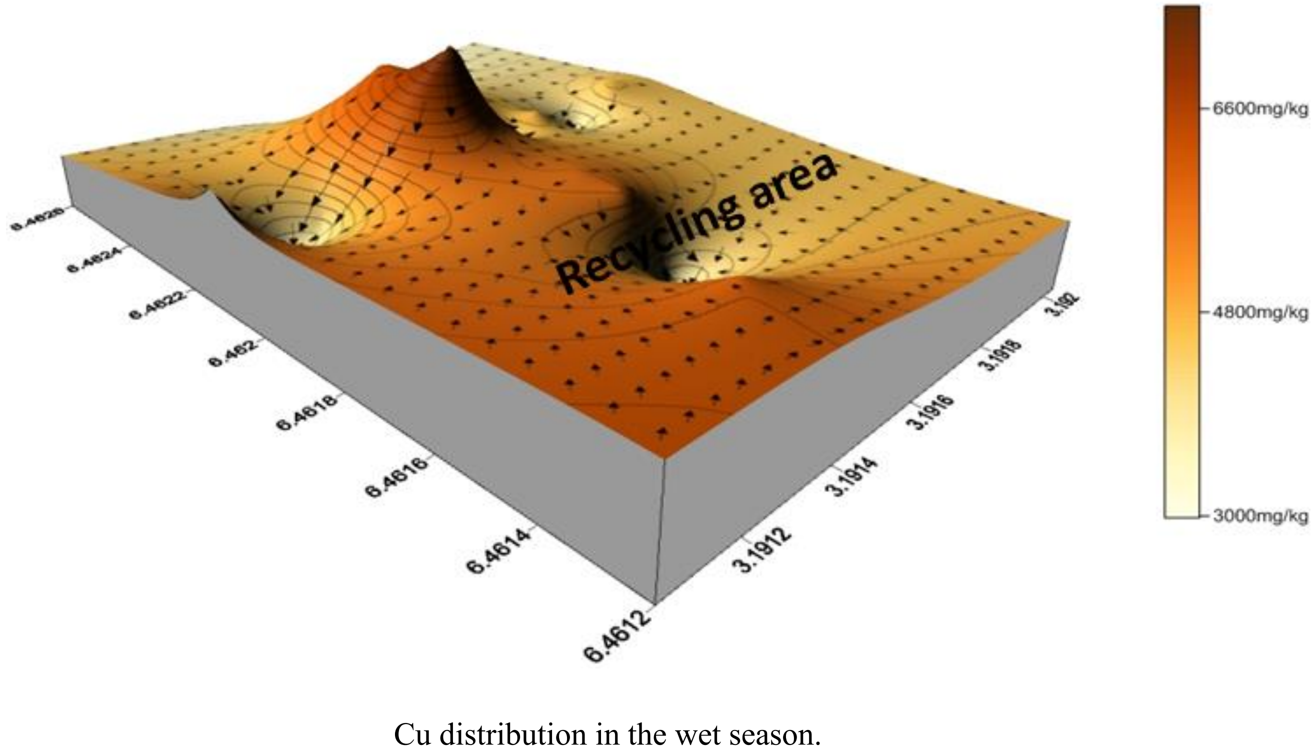


Cu distribution in the wet season.

7.8: Cu distribution in 10-20cm depth

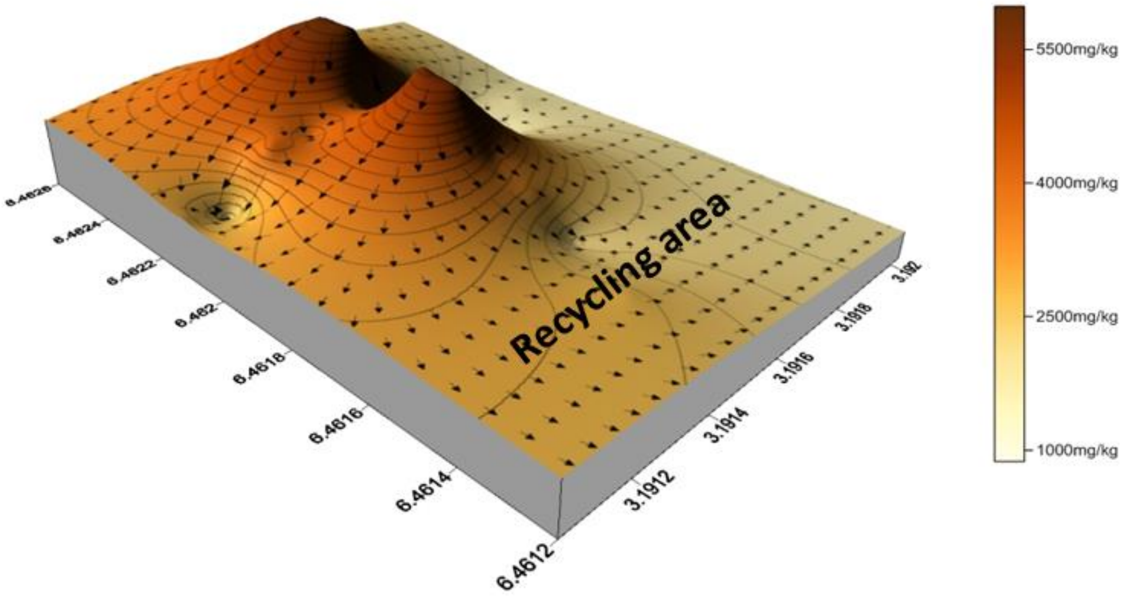


Cu distribution in the dry season.

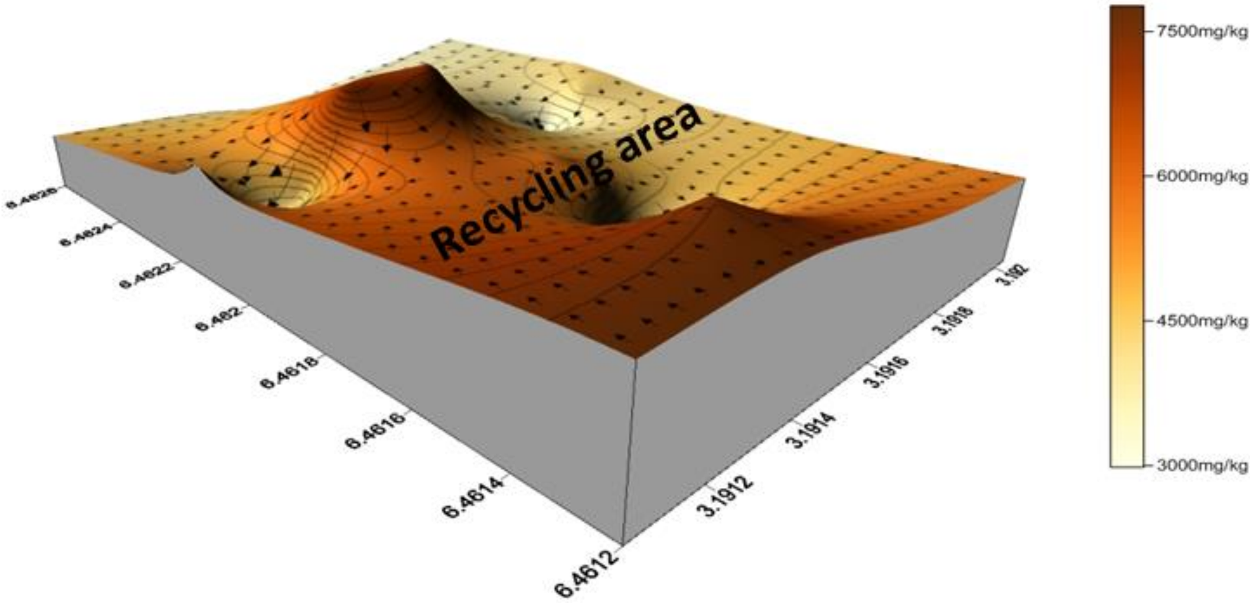


Cu distribution in the wet season.

7.9: Cu distribution in 20-30cm depth

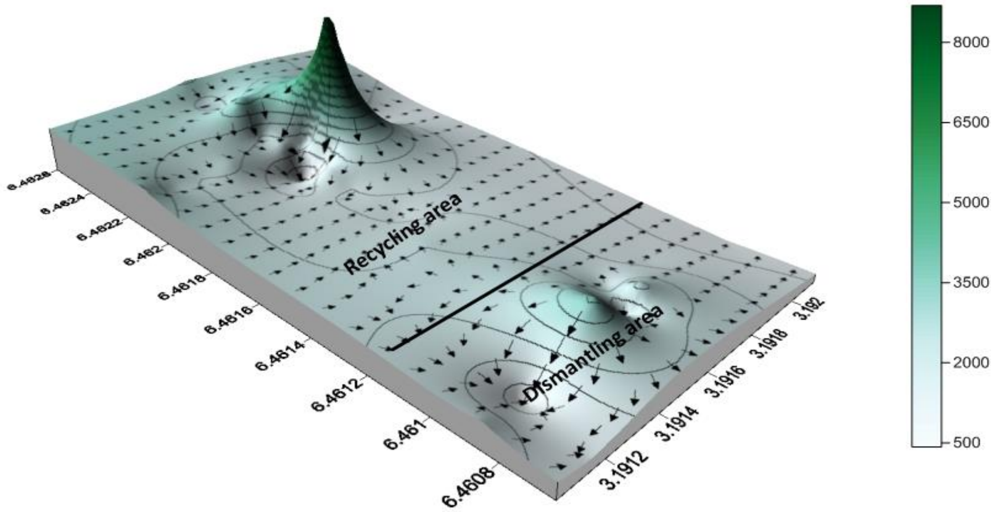


Cu distribution in the dry season.

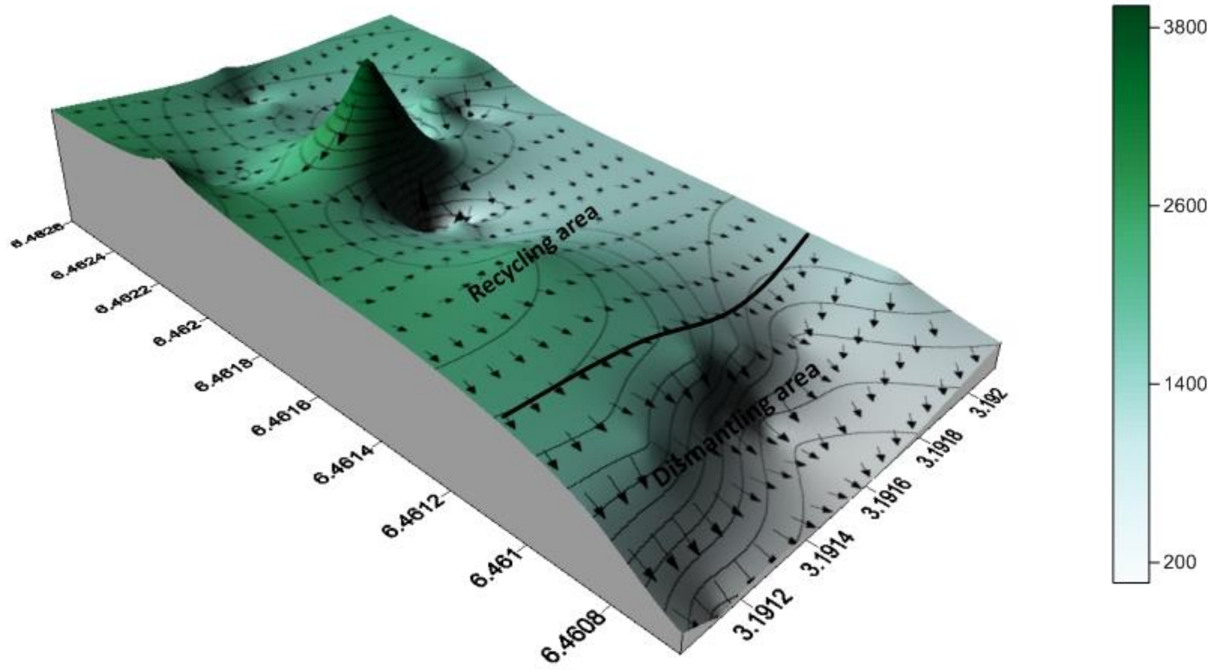


Cu distribution in the wet season.

7.10: Pb distribution in 0-10cm depth

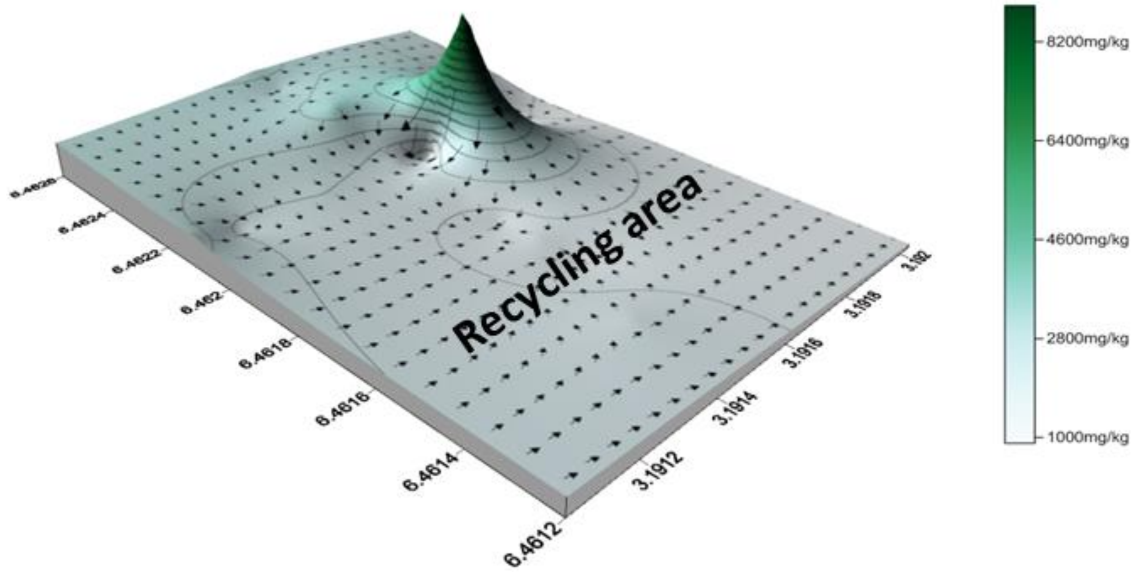


Pb distribution in the dry season.

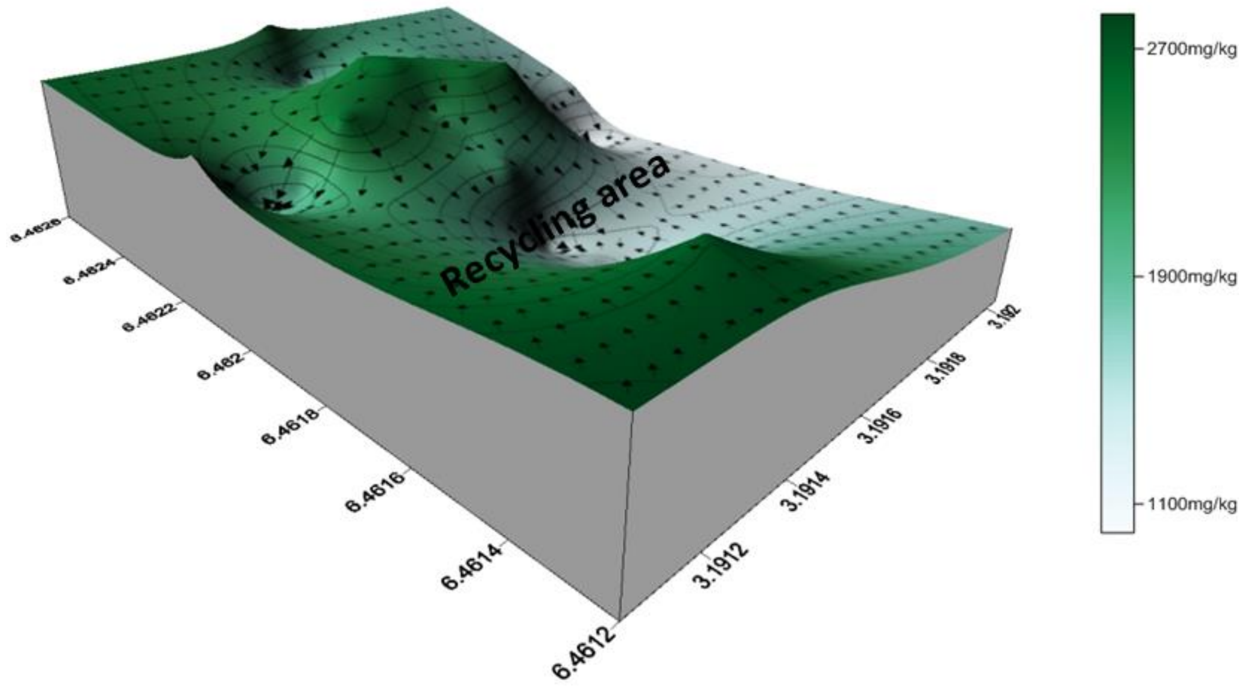


Pb distribution in the wet season.

7.11: Pb distribution in 10-20cm depth

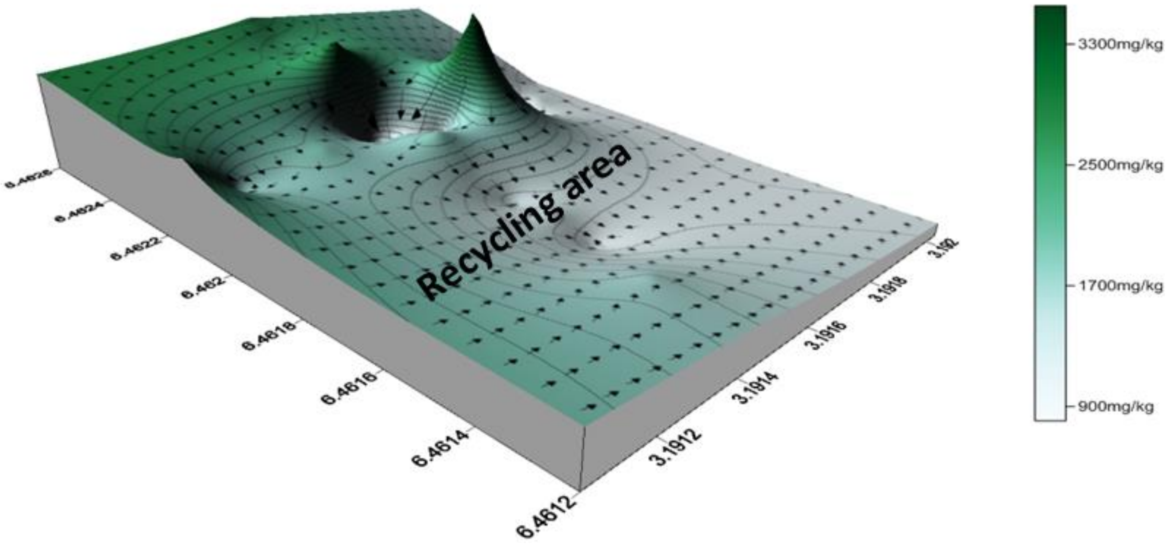


Pb distribution in the dry season.

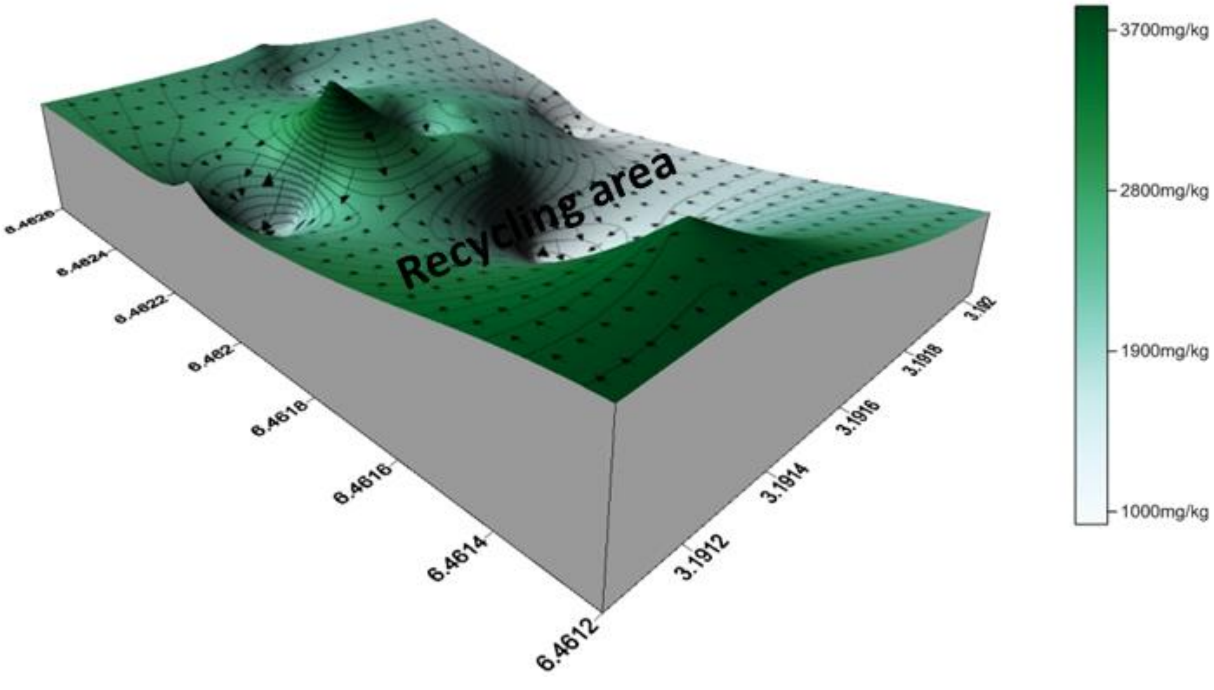


Pb distribution in the wet season.

7.12: Pb distribution in 20-30cm depth

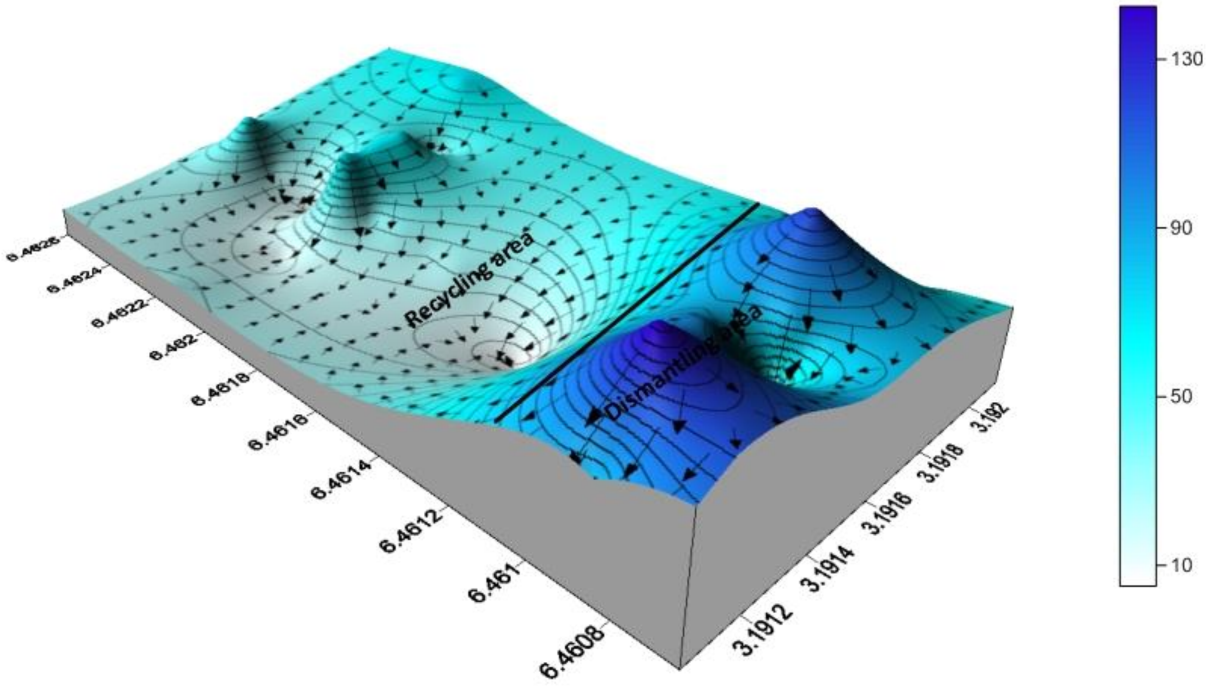


Pb distribution in the dry season.

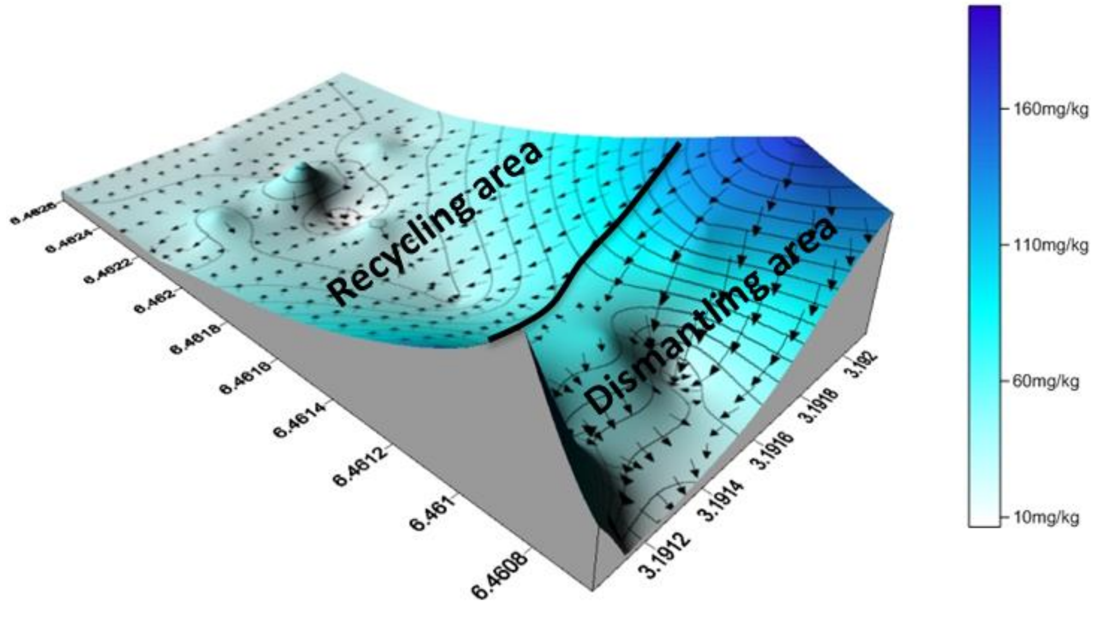


Pb distribution in the wet season.

7.13: Ni distribution in 0-10cm depth

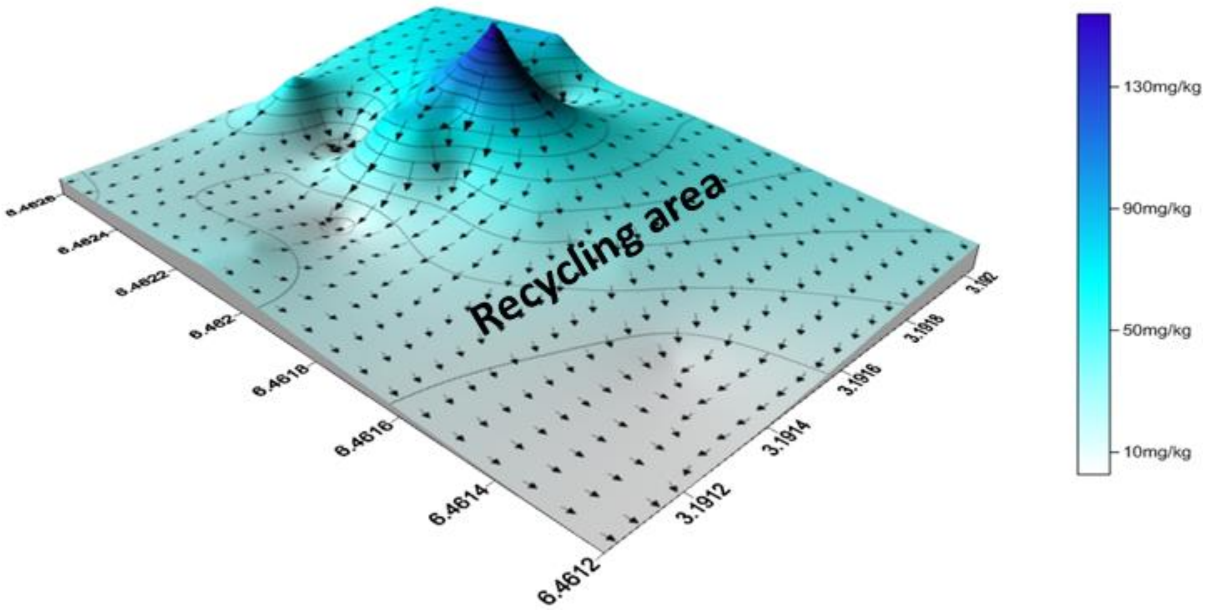


Ni distribution in the dry season.

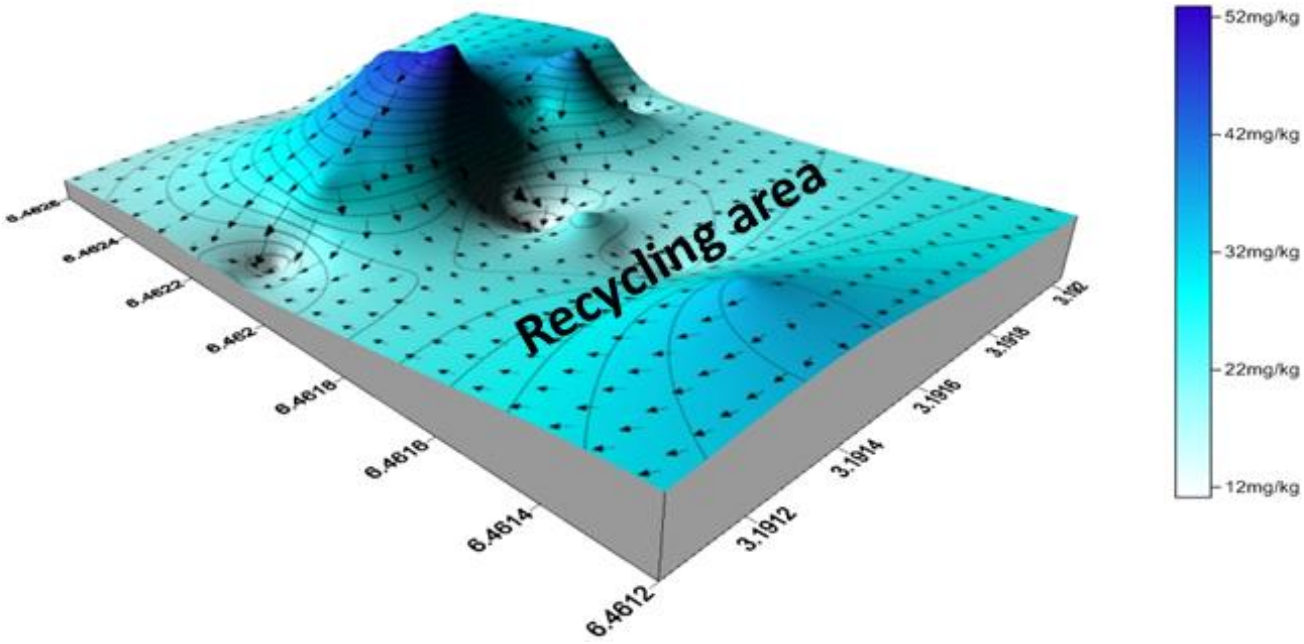


Ni distribution in the wet season.

7.14: Ni distribution in 10-20cm depth

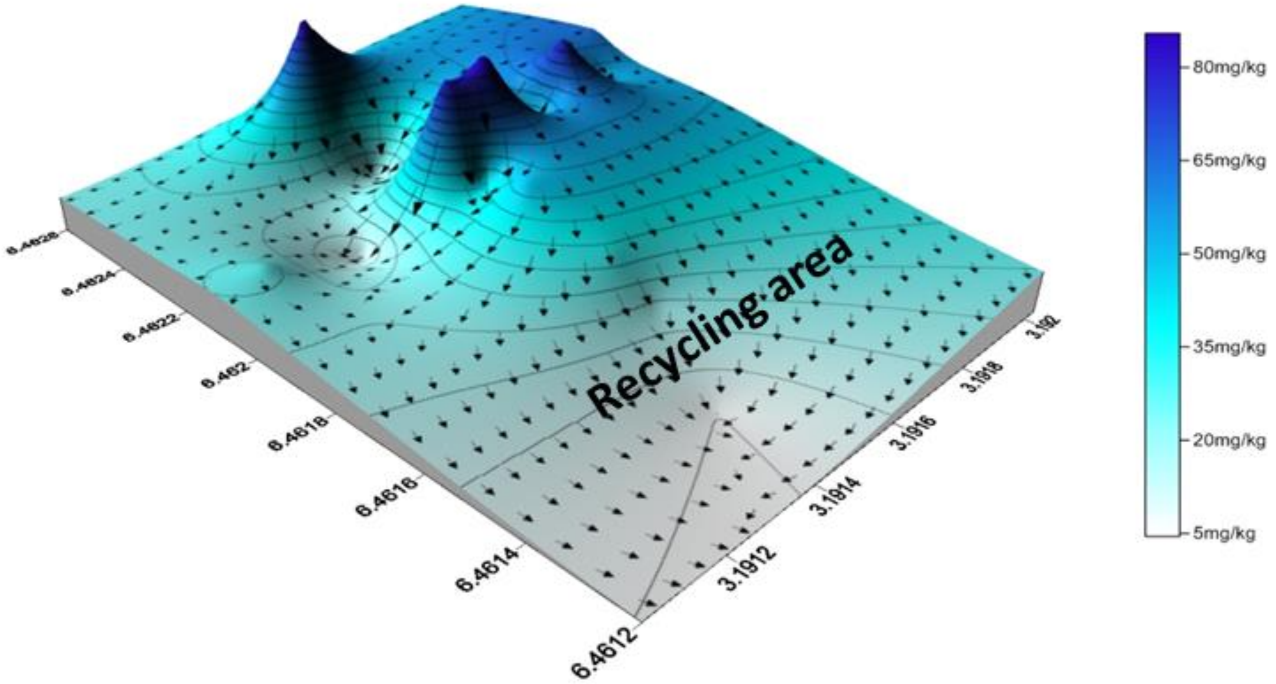


Ni distribution in the dry season.

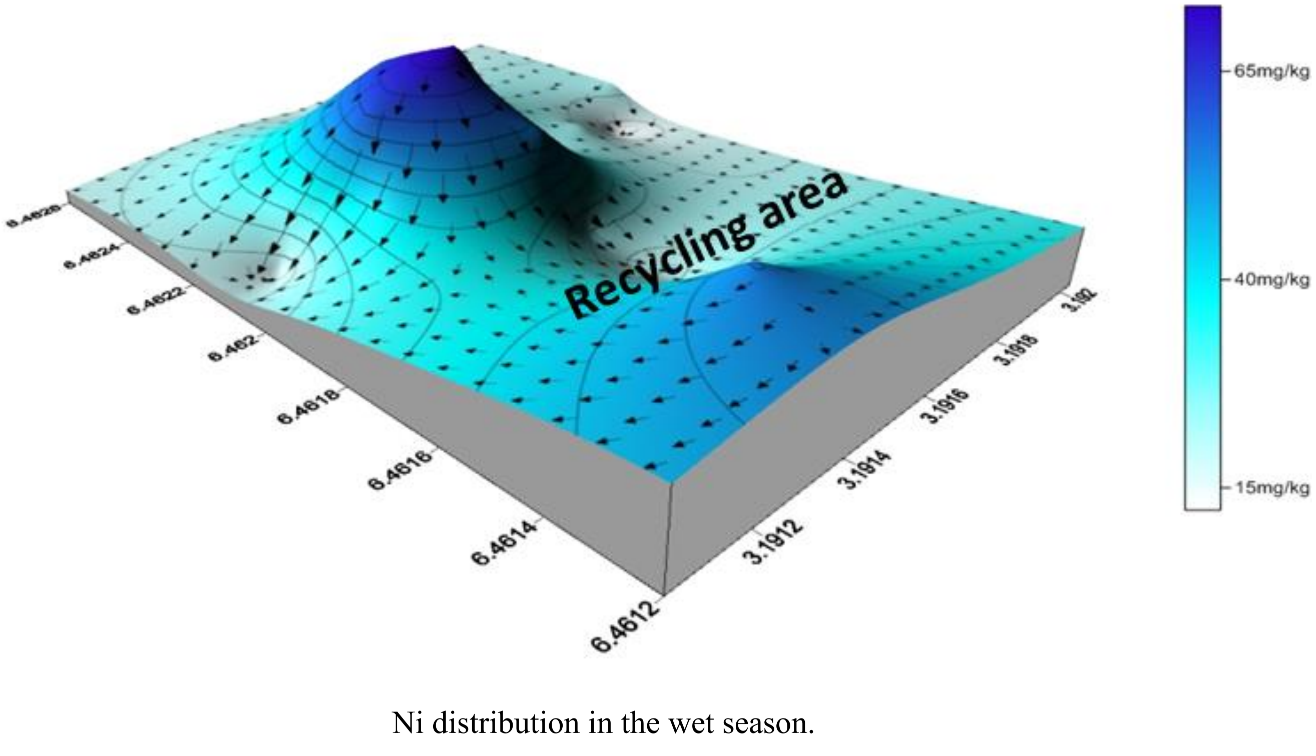


Ni distribution in the wet season.

7.15: Ni distribution in 20-30cm depth

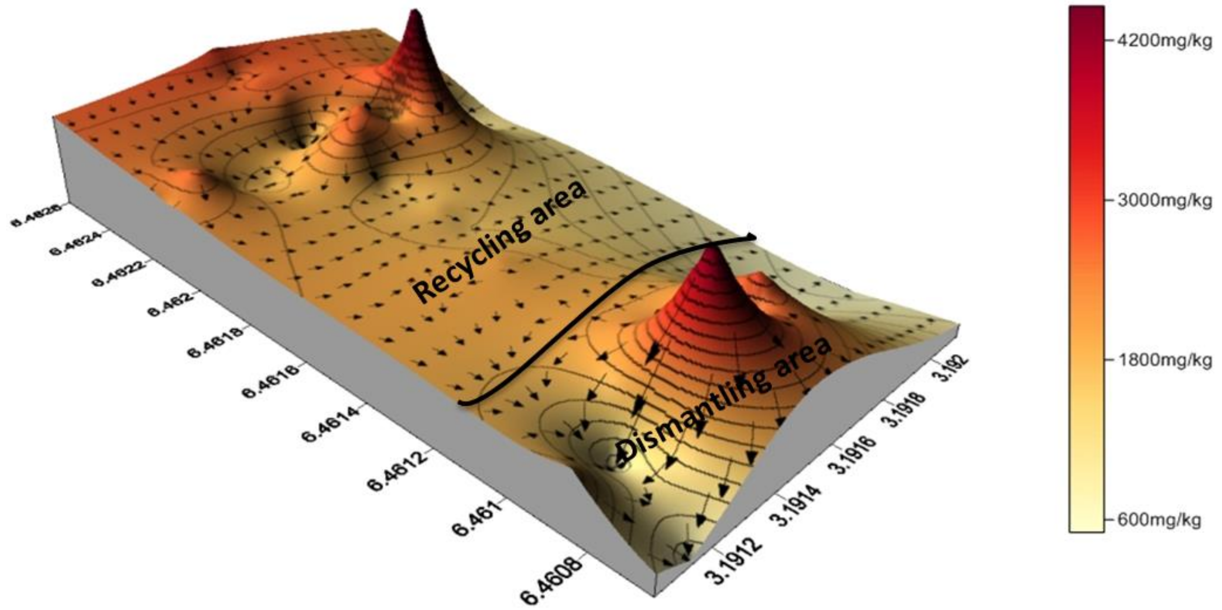


Ni distribution in the dry season.

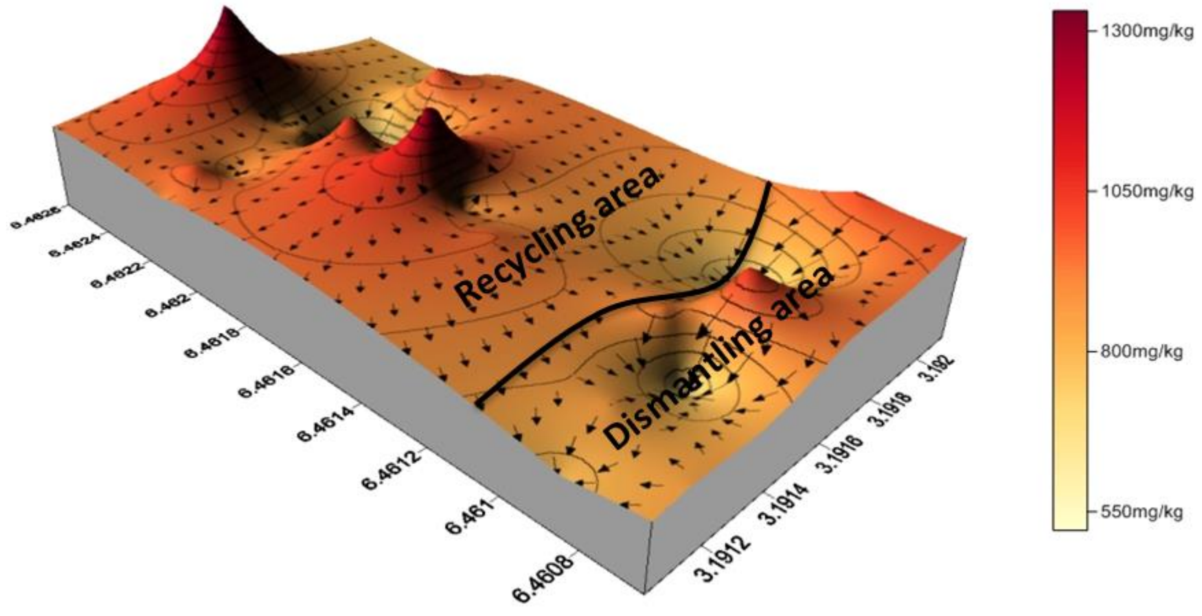


Ni distribution in the wet season.

7.16: Zn distribution in 0-10cm depth

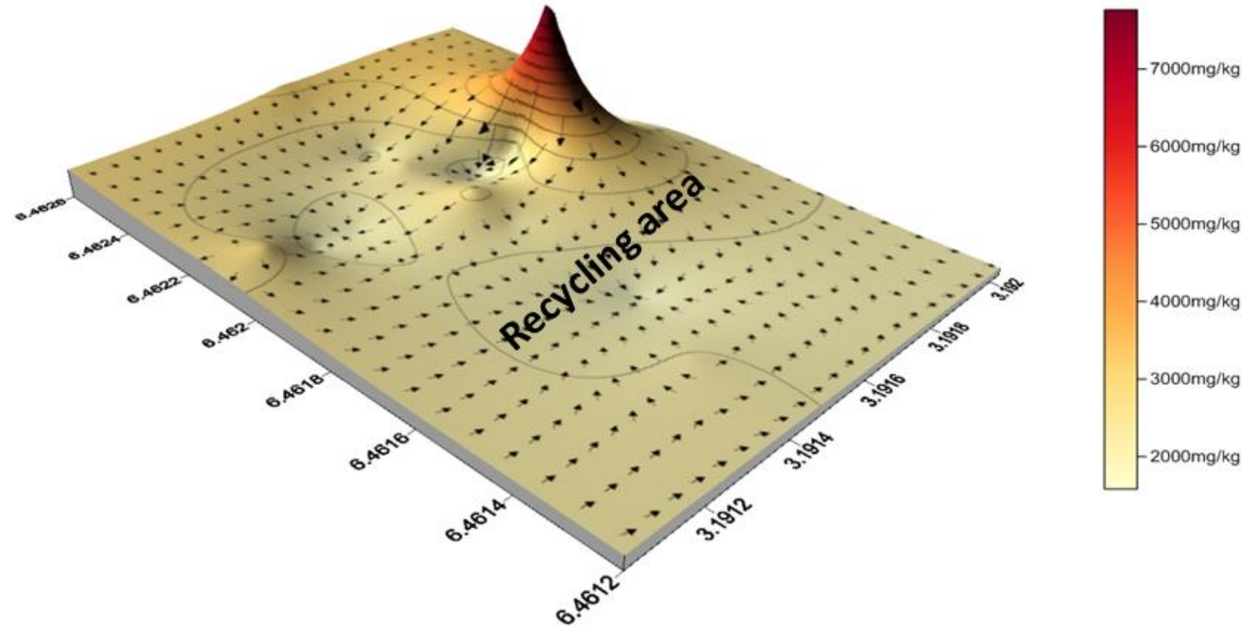


Zn distribution in the dry season.

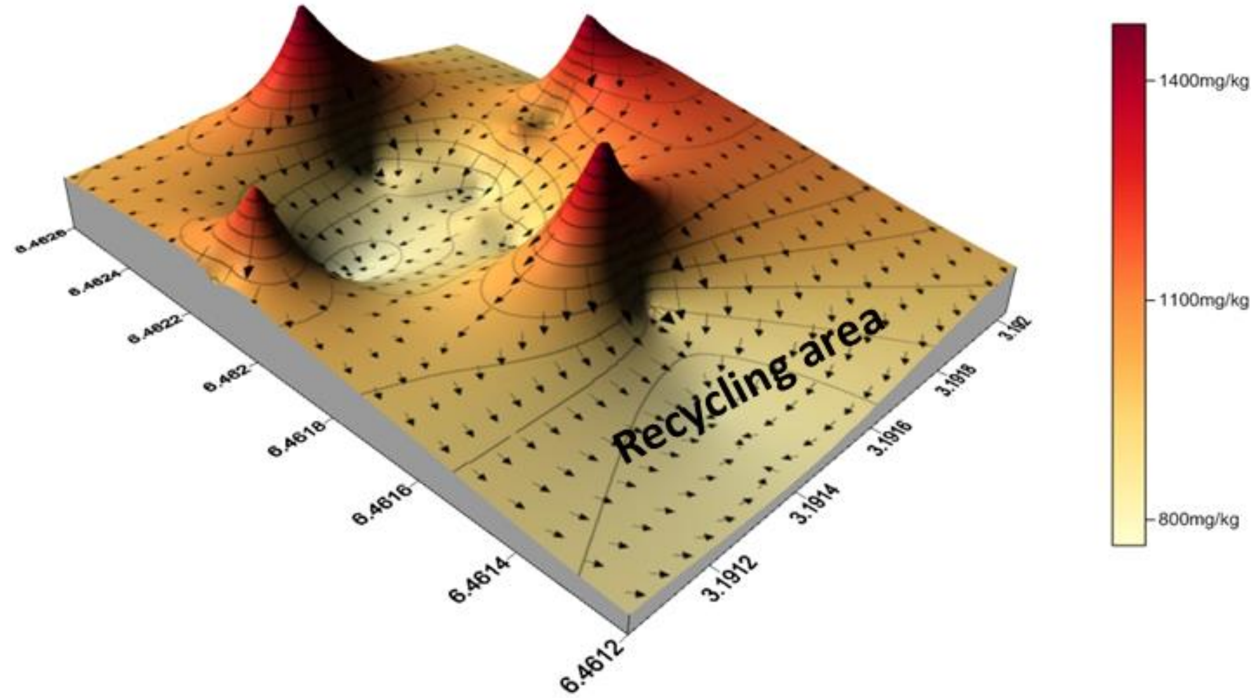


Zn distribution in the wet season.

7.17: Zn distribution in 10-20cm depth

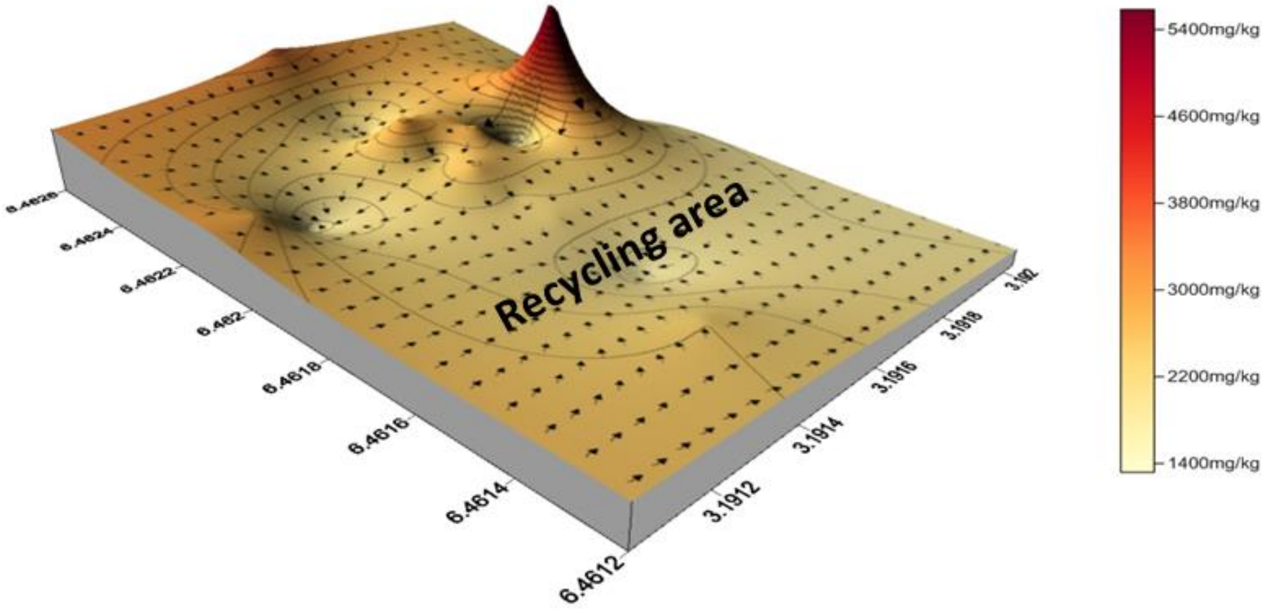


Zn distribution in the dry season

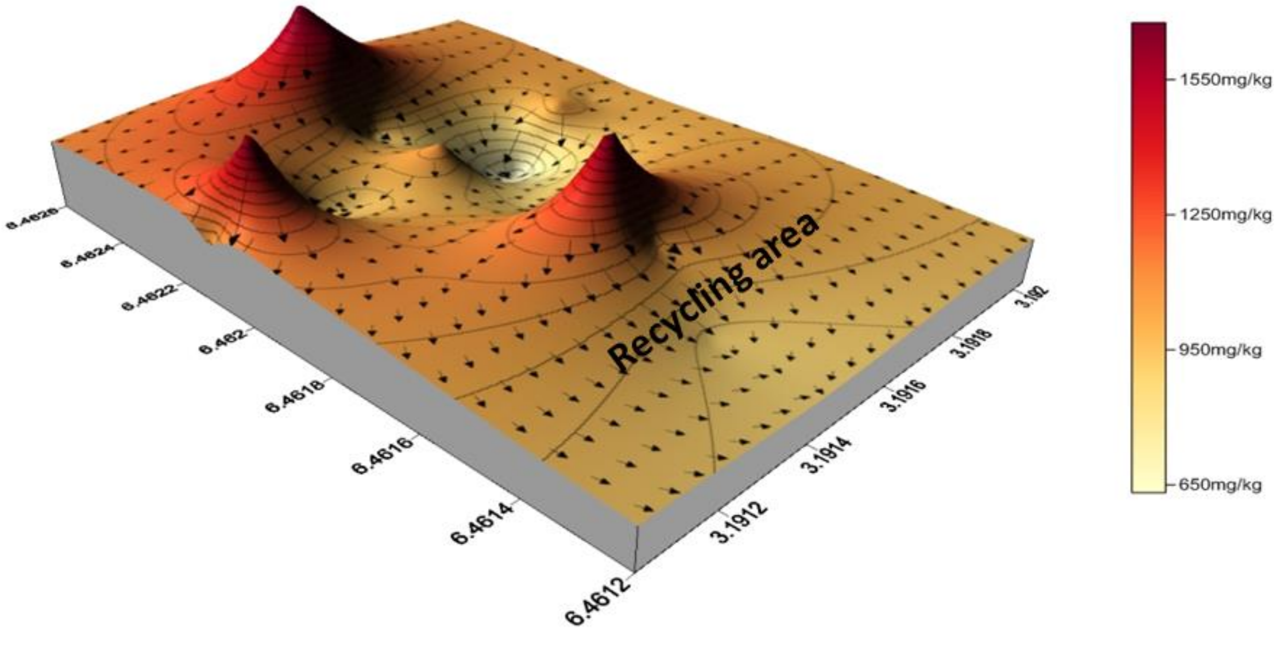


Zn distribution in the wet season

7.18: Zn distribution in 20-30cm depth

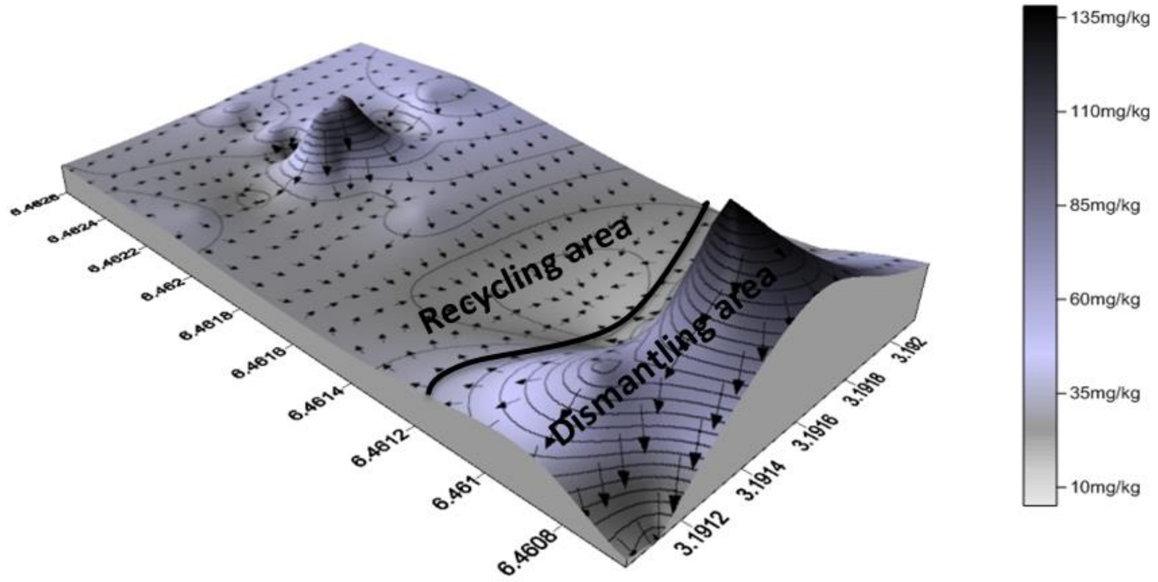


Zn distribution in the dry season

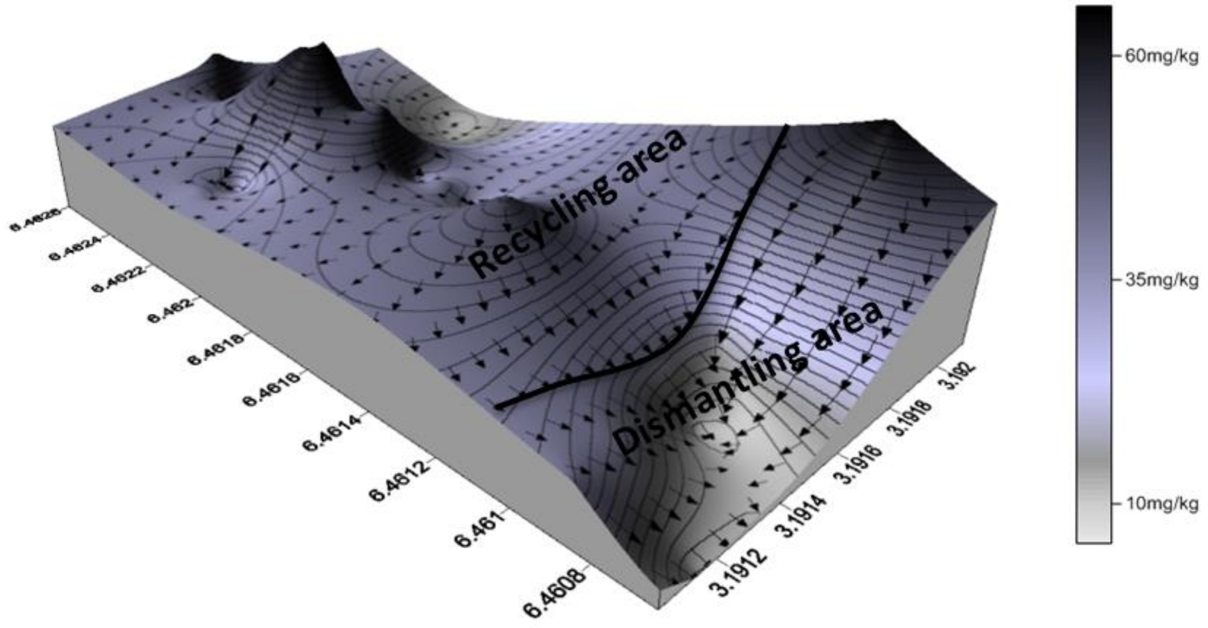


Zn distribution in the wet season

7.19: Sb distribution in 0-10cm depth

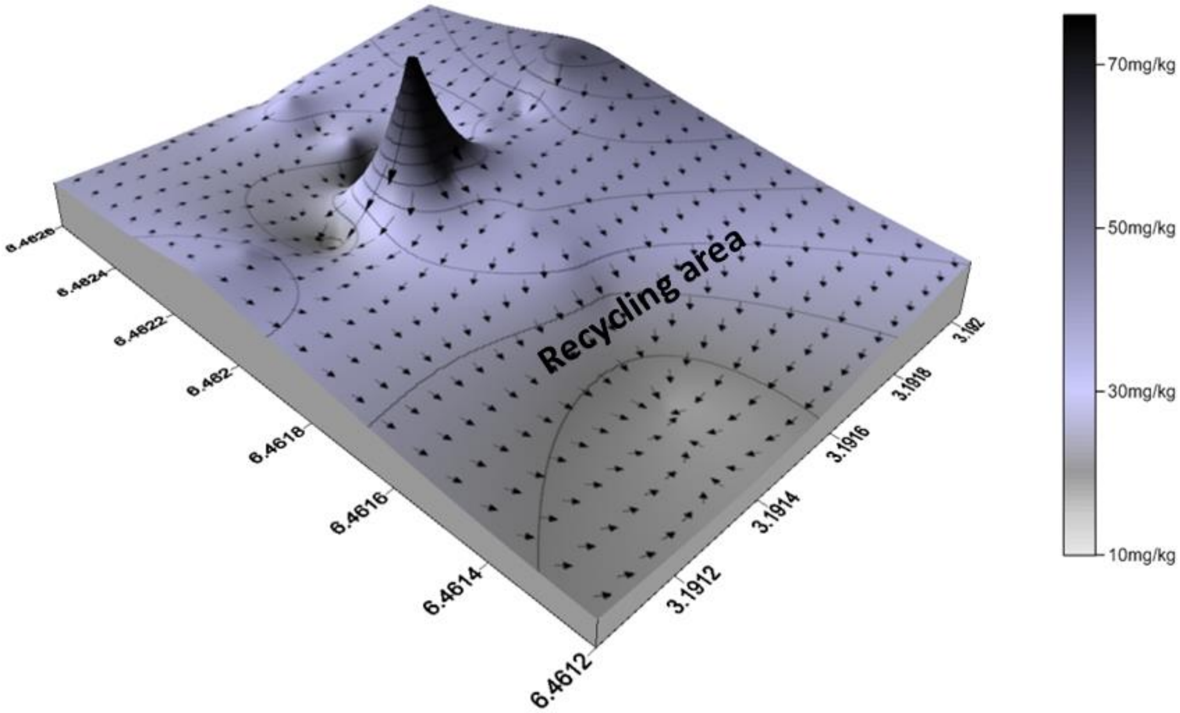


Sb distribution in the dry season

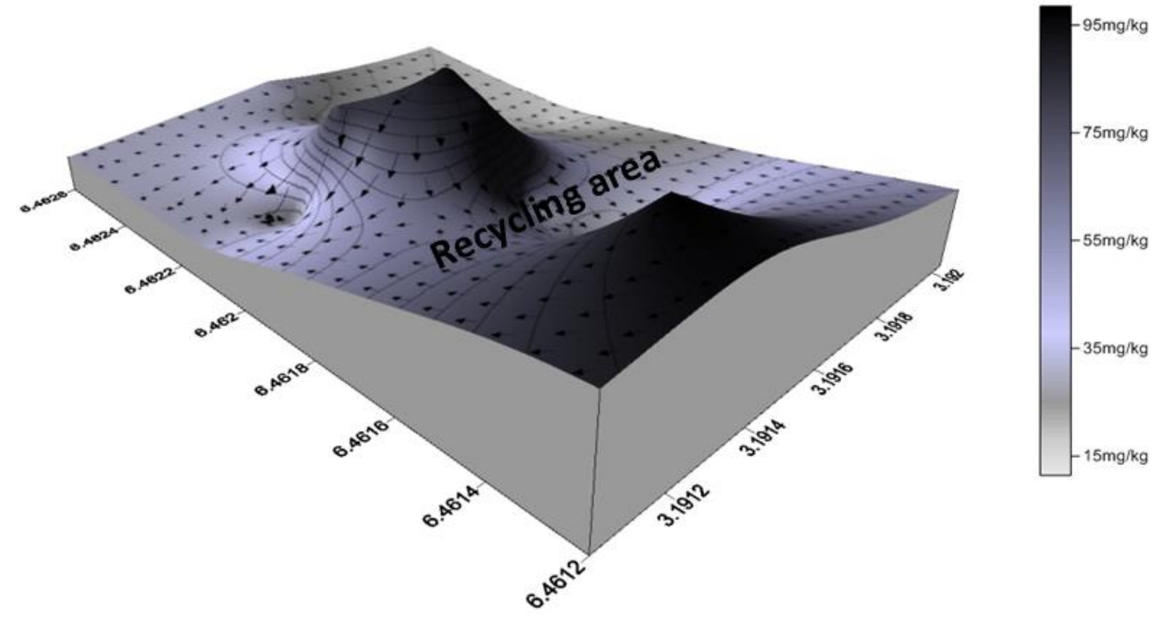


Sb distribution in the wet season

7.20: Sb distribution in 10-20cm depth

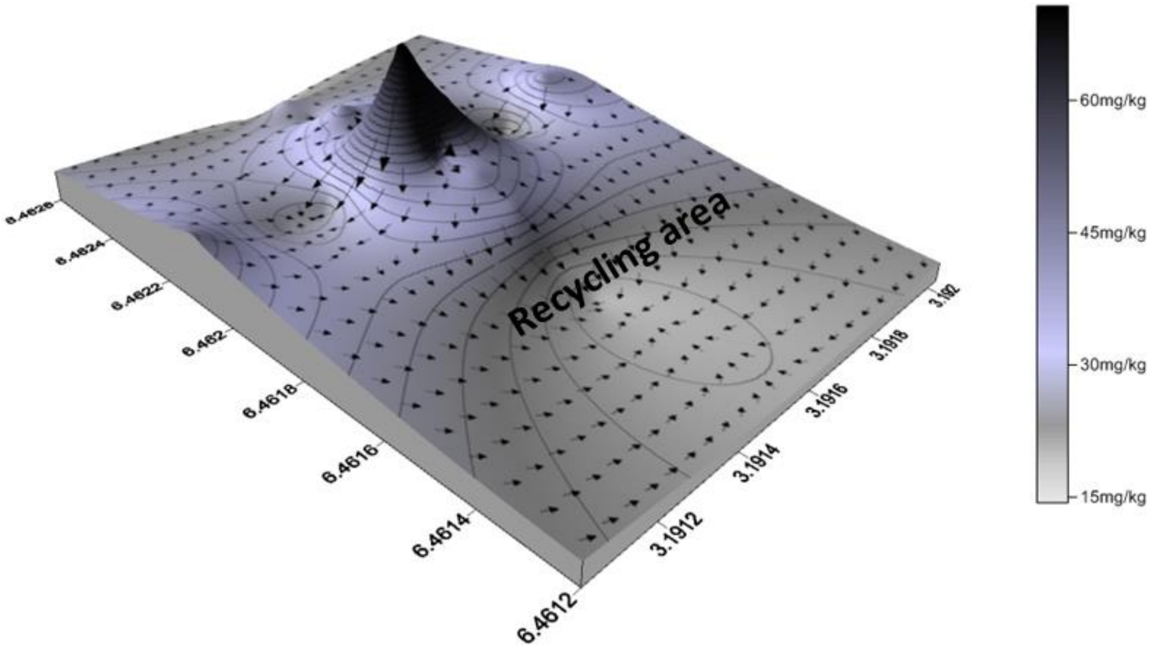


Sb distribution in the dry season

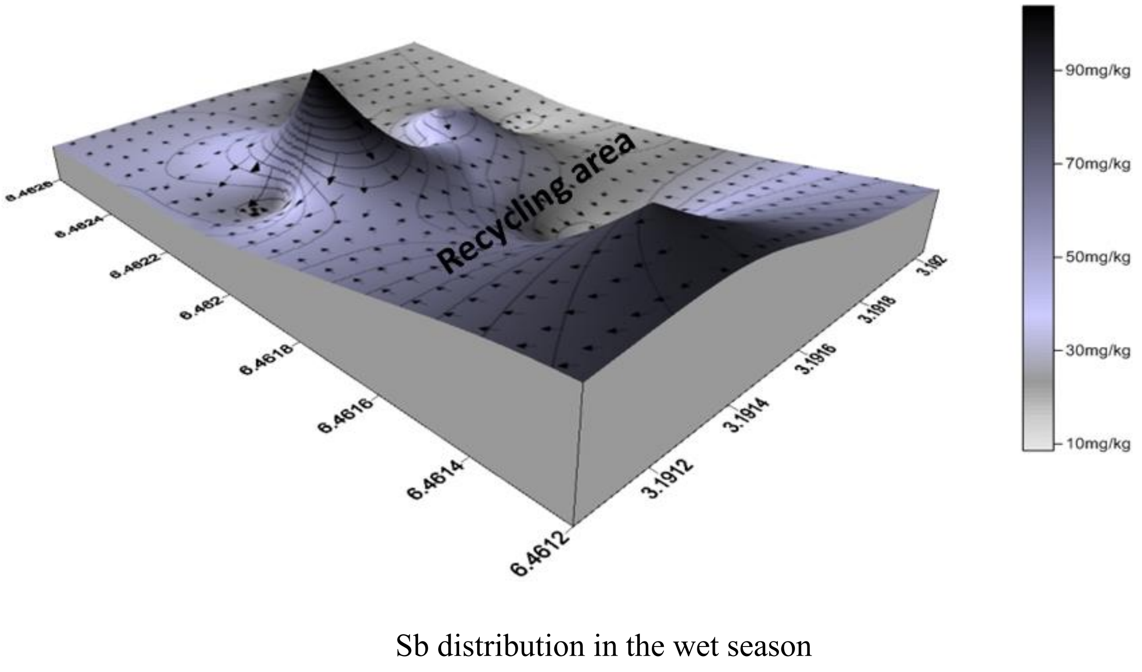


Sb distribution in the wet season

7.21: Sb distribution in 20-30cm depth

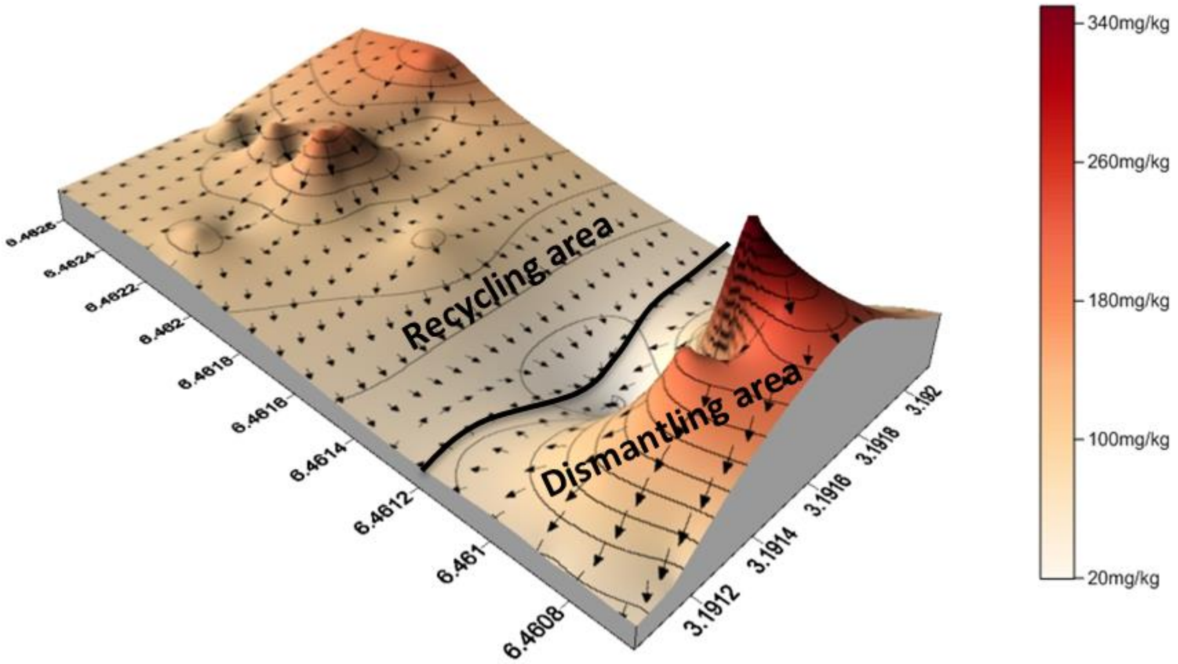


Sb distribution in the dry season

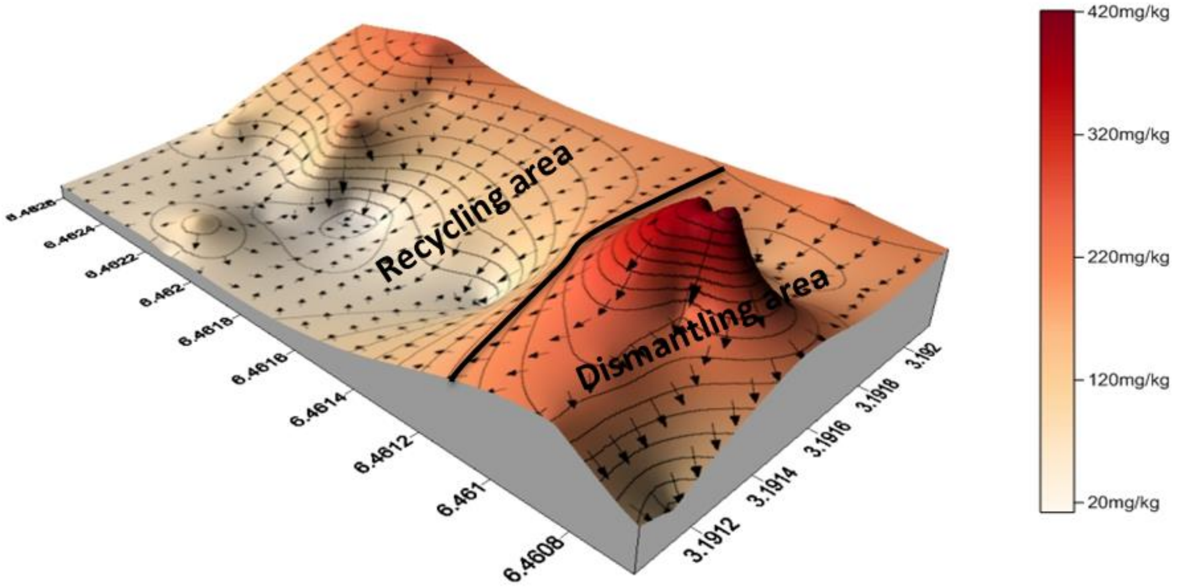


Sb distribution in the wet season

7.22: Mn distribution in 0-10cm depth

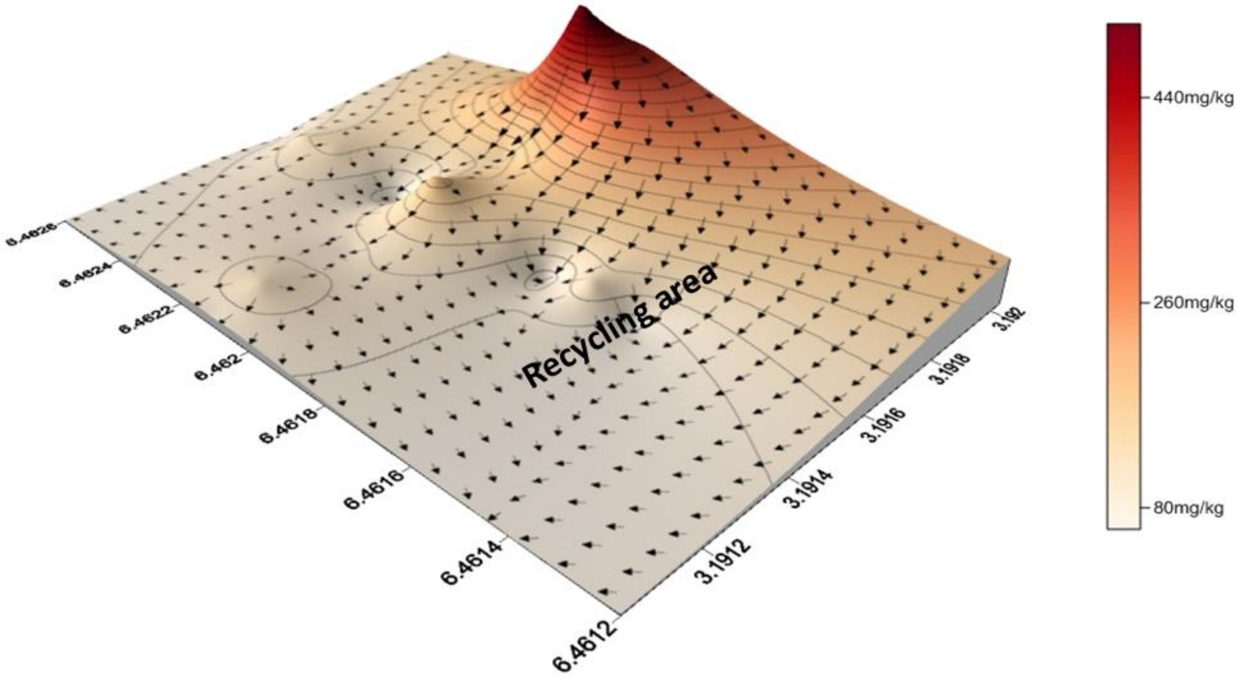


Mn distribution in the dry season

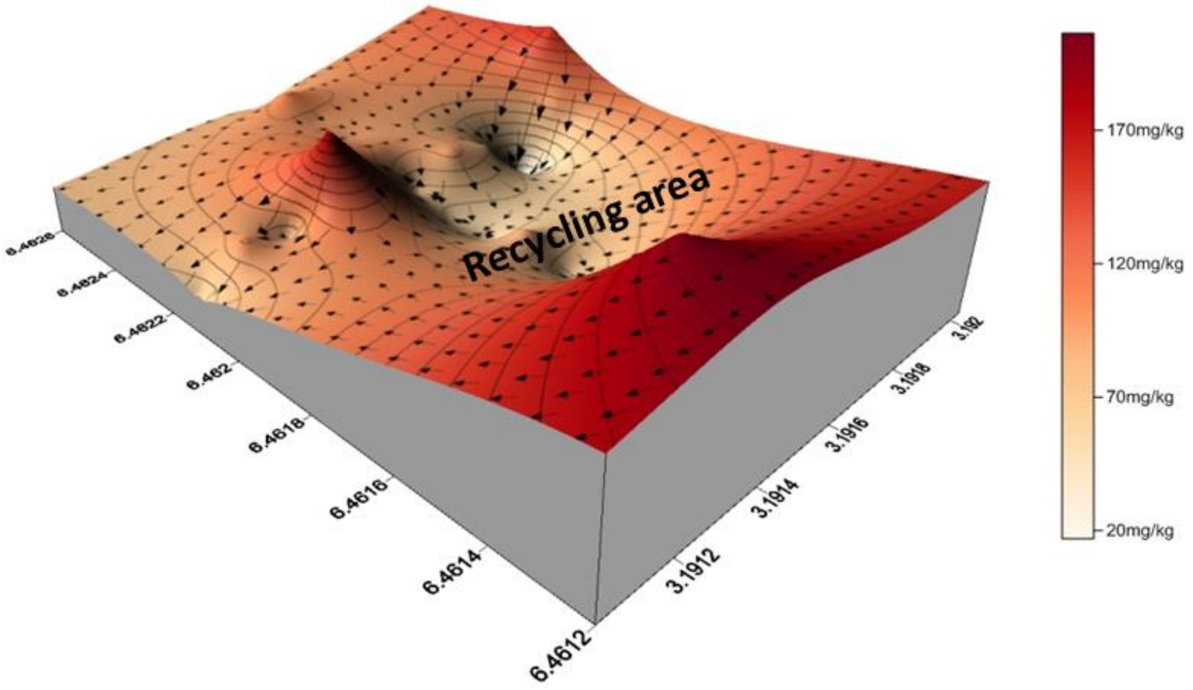


Mn distribution in the wet season

7.23: Mn distribution in 10-20cm depth

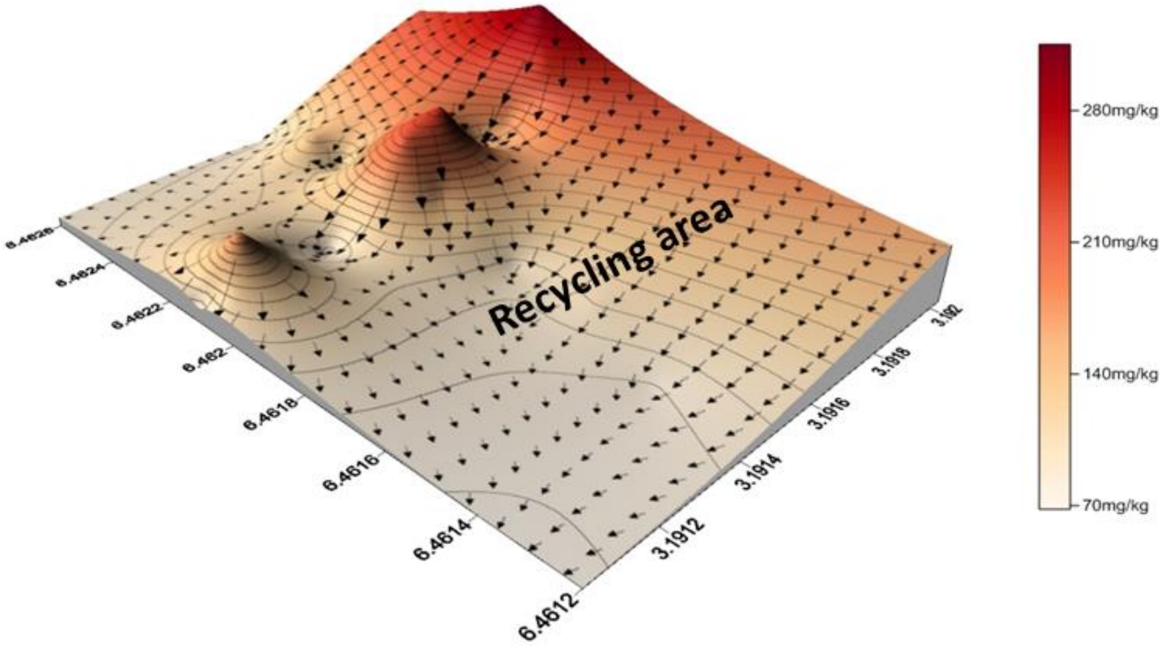


Mn distribution in the dry season

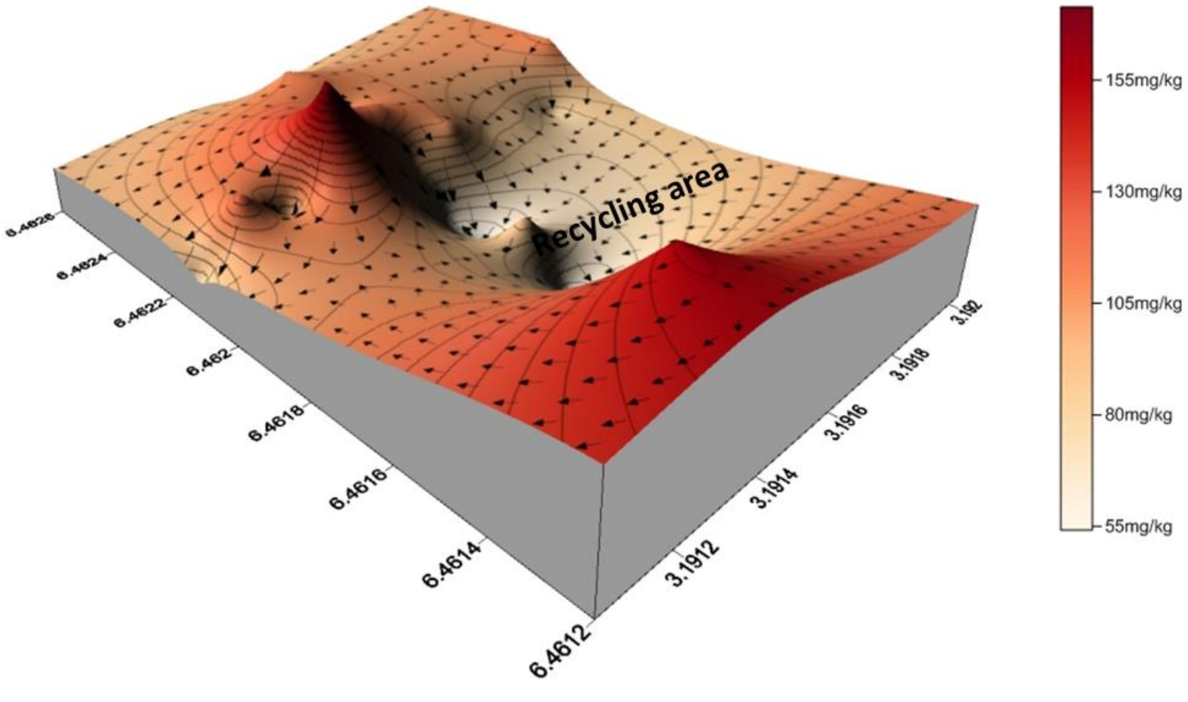


Mn distribution in the wet season

7.24: Mn distribution in 20-30cm depth



Mn distribution in the dry season



Mn distribution in the wet season

Appendix 8: Oral bioaccessibility

Oral bioaccessibility of metals in study site

			Cd	Cr	Cu	Mn	Ni	Pb	Sb	Zn
					Dry season					
Recycling area	0-10cm	GE	6.35	9.1	2139	27.21	18.4	606.7	42.22	312
		GI	3.72	7.28	1801	21.22	12.45	195.52	26.46	283
		TMC	10.61	22.86	5297	82.42	56.6	1504	88.2	976.8
		%BF	35%	32%	34%	26%	22%	13%	30%	29%
	10-20cm	GE	5.94	8.78	2190	31.76	8.96	1028	30.88	398
		GI	3.38	6.64	1664	21.1	7.84	427.2	18.41	305
		TMC	11.21	23.12	5676	95.92	37.34	2688.9	68.19	1178
		%BF	30%	29%	29%	22%	21%	16%	27%	26%
	20-30cm	GE	6.23	10.5	2204	25.94	21.67	983.7	25.23	400
		GI	3.85	8.59	1743	19.46	15.2	556	16.7	310
		TMC	12.71	31.81	5801	81.07	72.24	2981	58.67	1290
		%BF	30%	27%	30%	24%	21%	19%	28%	24%
Dismantling area	0-5cm	GE	3.3	7.34	1226.38	52.87	7.16	527.06	32.28	623.22
		GI	1.48	4.29	898.92	33.55	6.15	411.33	17.89	432.66
		TMC	6.3	27.6	4167	149.39	31.53	1977	81.43	1874
		%BF	23%	16%	22%	22%	20%	21%	22%	23%
					Wet season					
Recycling area	0-10cm	GE	5.2	8.94	2006	16.23	12.7	785	26.28	223
		GI	3.04	7.11	1652	10.39	9.18	310	17.2	154
		TMC	9.98	26.22	5140	49.98	43.98	2230	62.54	688.3
		%BF	30%	27%	32%	21%	21%	14%	28%	22%

	10-20cm	GE	6.96	20.86	1992	33.04	10.49	684	21.62	246
		GI	4.08	15.24	1658	23.42	7.82	324	13.92	188
		TMC	15.19	54.97	4995	102.88	39.28	2145	50.61	751
		%BF	27%	28%	33%	23%	20%	15%	28%	25%
	20-30cm	GE	4.56	10.38	1862	23.88	15.79	628	27.86	244.6
		GI	2.65	7.55	1444	14.92	9.77	240.8	17.88	170.24
		TMC	9.7	32.62	5026	68.6	50.9	1984	71.68	804
		%BF	27%	23%	29%	22%	19%	12%	25%	21%
Dismantling area	0-5cm	GE	2.37	7.81	1152.26	50.67	11.72	482.1	23.42	547.95
		GI	1.49	4.67	857.73	35.55	7.18	408	17.7	482.26
		TMC	5.21	24.89	3948.67	145	42.39	1908	65.41	1810
		%BF	29%	19%	22%	25%	17%	21%	27%	27%

Where GE is gastric phase, GI is gastrointestinal phase, TMC is total metal concentration %BF is percentage bioaccessibility factor.

Appendix 9:

Participant information sheet

Title of project: Environmental risk assessment for an informal e-waste recycling site in Lagos State, Nigeria

You are being invited to take part in this research study. Before you decide, it is important for you to understand why the research is being done and what it entails. Please listen carefully as I read the following information. If you wish to ask for more information please feel free to interrupt me. Take time to decide whether or not you wish to take part in the research.

What is the purpose of this study?

The purpose of the study is to explore the knowledge of my target audience (informal e-waste recyclers) on environmental and health impact of informal e-waste recycling. The information obtained will be used in the risk evaluation of the study.

Why were you chosen?

You have been chosen in order to gain an understanding from your own perspective on the impact of informal e-waste recycling.

Do I have to participate?

No you don’t have to participate, however it is going to be beneficial to the outcome of this research for you to participate.

What will happen to me if I take part in the research?

Absolutely nothing of negative impact will happen to you. I will be very glad you participated.

What are the possible risks to me of taking part in the research?

There are no risks involved. Your views will be respected and your interviews will be held confidential if published. You are not compelled to answer any questions you do not want to answer and the interview can be stopped at any point if you do not wish to continue.

What are the possible benefits of taking part?

I cannot promise anything as this is an academic work but the information generated could be used in creating a proper work environment.

What if there is a problem?

If you have any concern about any aspect of this study, you should ask to speak with me and i will address any questions you have.

What will happen to the results of the research?

Your interviews and answers will be used to develop the final thesis of this research and the outcome of the research will provide useful information on the informal recycling sector in Lagos State. It can also be used as a form of baseline data for subsequent research on informal e-waste recycling in Nigeria.

Appendix 10

Some basic prompts used in the open-ended interviews

i. Can you tell me about yourself? Your age, marital status, where you are from, what you do, how long you have been doing your job.

ii. Can you tell me more?

iii. What can you tell me about your job? Health or environmental impact

iv. Anything else?

v. Don’t think too much about what you say to me; just tell me what comes to your mind and exactly how it is.

vi. Can you explain why?

vii. Do you think this is good or not?