# QUANTIFYING TOXIC CONTAMINANTS IN FOUR MAJOR DUMP SITES OF THABO MOFUTSANYANE DISTRICT, EASTERN FREE STATE

By

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## Declaration

I declare that the mini-dissertation is hereby submitted for the fulfilment of Masters of Science degree at the university of the Free State is an original work by S.Q.N. Lamula under the supervision of Dr. A.O.T. Ashafa and co-supervisor Dr. T.J. Tsilo. This mini-dissertation has not been submitted anywhere in any form to another University. I therefore cede copyright of this min-dissertation in favour of the University of the Free State.

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#### Abstract

The large number of cases of groundwater pollution at landfills and the substantial resources spent on remediation suggests that landfill leachate is a significant source of pollutants, especially when considering different kinds of contaminants in landfill leachates. The longterm effect of the geological barrier beneath municipal-waste landfills is a critical issue for soil and groundwater protection. Soil to plant transfer of trace metals is the major pathway of human exposure to metal contaminations. Therefore, the present study was conducted to determine trace metal levels such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), cobalt (Co) and zinc (Zn) in soil and plant samples collected from four major dumpsites in Thabo Mofutsanyane District, Eastern Free State in South Africa. Samples (soil and plants) were collected from Harrismith, Qwaqwa and Bethlehem from two different landfills. Soil samples were collected at a depth of 0-15 cm from each part and pooled to form a composite sample. Plant samples were pulled from the soil together with their roots using an ager. Four acid digest techniques (HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and HF) were used and inductively coupled plasma optical emission spectrometry (ICP-OES) determined the concentrations of heavy metals. During the four seasons (spring, summer, autumn and winter), the concentration of Zn was higher in summer with value of 3076.56±12.02 compared to winter 1733.51±39.33. The concentration of Pb was within the threshold except in Qwaqwa and Bethlehem site A with values of 315.79±30.26 and 230.82±35.24. Cd concentration fluctuates during the seasons but the highest value of 6.15±0.06 was recorded during winter. The level of Mn in all dumpsites was very unstable and above the standard permissible limit. The common plants identified in the dumpsites are Cosmos species, Eragrostis plana, Elusine indica, and were all found to contain high level of heavy metals. Principal Correlation Analysis (PCA) analysis showed that Qwaqwa and Harrismith had the highest load of heavy metals and the dendrogram confirmed the similarity in metal distributions in the dumpsites. This study highlights environmental implications of heavy and trace metals in all dumpsites studied. There was no significant difference in the concentration of metals within and outside the dumpsites which confirms metals can be distributed above 10 m range. All the trace metals analysed in this study had higher concentrations above the permitted limits set by USEPA and WHO. This study revealed the levels and impacts of heavy metal concentrations on the dumpsites, as well as the risks they may pose to near or far surroundings and its attendant health implications.

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#### **CHAPTER ONE**

#### INTRODUCTION AND LITERATURE REVIEW

The earth's crust consist of natural trace metals which are known to be essential for growth and development of humans, animals and plants (Cabral *et al.*, 2015). Recent studies have shown that prolong exposure to heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), cobalt (Co), manganese (Mn) and zinc (Zn) can have negative effects on both humans and plants, even at low concentrations (Gebrekidan *et al.*, 2013; Di Giuseppe *et al.*, 2014; Capra *et al.*, 2014; Eijsackers *et al.*, 2014; Wu *et al.*, 2015). Heavy metals are dangerous due to their persistence and toxic nature in the environment (Prechthai *et al.*, 2008b). Metal contaminations of land as a result of wastes generated from different industries may have deleterious effects on soil quality and anthropogenic activities thereby increasing the rate of accumulation of heavy metals in the soil (Desaules, 2012; Cabral *et al.*, 2015).

The term municipal solid waste (MSW) describes the stream of solid waste generated by households, commercial establishments, industries and institutions (Prechthai *et al.*, 2008a). As the final MSW disposal method, landfill is a widely accepted technology, especially in developing countries (Long *et al.*, 2011). Over many decades and to this present period, countries around the globe still use landfills to dispose majority of waste materials (Zhang *et al.*, 2014). For example, the United States Environmental Protection Agency (USEPA) reported that, approximately 50% or 128.3 million tons of the MSW generated is buried in landfills and in China, more than 90% of the MSW is disposed by landfill (USEPA, 2002). However, treatment of MSW by landfill has been and is still connected with risk of pollution (Long *et al.*, 2011). Due to industrialization and associated increase of solid waste generated

every year, developed countries have made a priority to develop strategies and policies that reduce land contamination and built landfills which minimize land pollution (Li *et al.*, 2014).

The large number of cases of groundwater pollution from landfills suggests that landfill leachates is a significant source of pollutants (He *et al.*, 2006). When considering different kinds of contaminants in landfill leachates, it makes it more dynamic and also challenging to assess and evaluate the danger it possess to surrounding environments (Kiddee *et al.*, 2014). Landfills are heterogeneous environments consisting of many waste materials which are made of or contains heavy metals. These include household dust, batteries, disposable household materials (e.g bottle tops), plastics, paints and inks, body care products, medicines and household pesticides (Ali *et al.*, 2014). Municipal solid waste (MSW) is an extremely heterogeneous material independent of its geometry, particle size or chemical composition (Flyhammar, 1997). At the time of deposition, the waste might contain substances such as organic matters or materials which are not stable near the surface environment. During stabilization of these chemical compounds, biological mediated substances are often released from the waste as either gas or dissolved compounds in contaminated water (leachates) (Flyhammar, 1997). Therefore, knowledge of degradation processes inside the landfills is key to the understanding and controlling environmental impacts (Zhang *et al.*, 2014).

The behaviour of open dumpsite can be quite challenging compared to a closed one and it is not easy to predict the degradation processes due to the heterogeneity nature (Ward *et al.*, 2005). The reactivity of open dumpsites will also be influenced by factors such as precipitation, temperature and light which affect aerobic and anaerobic processes that eventually affect the rate of solid waste degradation (Stutter *et al.*, 2015). Under anaerobic condition, the metals that are bound to carbonate, organic compound and sulphide are more stable and retained in the landfill itself, whereas the metals bound to Fe and Mn oxide are unstable (Flyhammar, 1997). This is in contrast with the case of an open dumpsite, which is exposed to the atmospheric condition and undergoes different biological and chemical reactions due to oxygen diffusion (Kiddee *et al.*, 2014).

In a high redox condition, the binding of metals to Mn and Fe oxide increases, whereas binding to carbonate, organic compound and sulphide tend to decrease. With more possibility of oxygen diffusion through the upper layer of dumpsite and with sufficient moisture content, the degradation rate and the acid buffer capacity of the dumpsite is highly influenced. Under this condition there is a drop in alkalinity, pH and sulphide oxidation, where heavy metals are easily available and released (Prechthai et al., 2008a). According to Masi et al. (2014), old open dumpsites without any sort of protection for reducing emissions, are a huge source of local pollution due to the leaching of hazardous substances. These sites, although no longer used, still represent an important source of environmental risk, mainly for the presence of micro-pollutants, such as heavy metals. These sites can cause pollution of groundwater and surface water due to leaching and runoff. The estimation of total concentration of an organic chemical in the soil is underestimated by the fact that MSW have a higher affinity to bind to heavy metals (Northcott and Jones, 2000). Recent studies have shown that many chemicals form persistent and permanently bound residues in soil (Smith, 2009; Long et al., 2011; Di Giuseppe et al., 2014; Li et al., 2014). This has an effect on the long-term partitioning behaviour, bioavailability and toxicity of organic compounds in the soil and sediments (Ward et al., 2005). The binding capacity of heavy metals (MBC) to the solid waste undermines the estimation of total concentration in soil, which is also influenced by adsorption and sorption of heavy and trace metals (Ward et al., 2005). The most significant process in heavy metal retardation in soil is the adsorption of these reactive substances. In other words, adsorptive bonding primarily controls the mobility and leaching danger in soils (Zupančič et al., 2009). Several studies have shown that the sorption of heavy metals varies strongly in soils, as a result of variation in soil pH, clay content, oxide content and soil organic carbon content (Yu et al., 2014; Barbieri et al., 2014; Li et al., 2015).

Prechthai et al. (2008b) reported that the effects of heavy metals were found to vary with the conditions prevailing in the dumpsites and its binding forms. In the case of close dumpsites, during anaerobic condition, the metals that are bound to carbonate, organic compound and sulphide are more stable and retained in the landfill itself, whereas the metals bound to iron (Fe) and manganese (Mn) oxide are unstable. This is in contrast with the case of an open dumpsite. The open dumpsite being exposed to the atmospheric condition undergoes different effects due to oxygen diffusion. With more possibility of oxygen diffusion through the upper layer of dumpsite and with sufficient moisture content, the degradation rate and the acid buffer capacity of the dumpsite is highly influenced (Kiddee et al., 2014). Under this condition, there is a drop in alkalinity, pH and sulphide oxidation, where heavy metals are easily available and released. These heavy metals from the surface layer of dumpsite, creeps into the bottom layer of the dumpsite where anaerobic condition prevails. Under this condition, the heavy metals are immobilize and retained in the solid waste again (Ward et al., 2005). This is confirmed from the observed high concentration of heavy metal at deeper layer of landfills (Li et al., 2015). While most literature studies, routinely report leachate concentrations of heavy metals in low mg/l range (Zbang et al., 2008; Barbieri et al., 2014; Eijsackers et al., 2014), these leached concentrations are only a fraction of the metal associated with the waste solids (Ward et al., 2005). According to Li et al. (2015), chemical and physical affinity of metal ions and the various waste materials may reduce their leachability under typical landfill conditions. The mobility of these metal species may be increased over time as the waste becomes more acidic and as oxidizing conditions dominates. An increase in pH also elevates the level of certain heavy metals and increases the level of leachates (Smith, 2009).

Chemical reactions such as photolysis, hydrolysis, oxidation, cations exchange capacity and reaction with mineral surfaces; biotic losses including bioaccumulation, transformation and mineralisation by soil and sediment microbial populations; and binding to environmental solids, all these make organic chemicals in dumpsites to be more unpredictable (Northcott and Jones, 2000). Total concentrations of heavy metals in solution have not been shown to correlate with their toxicity or bioavailability and no consensus exists among researchers for identifying or quantifying specific toxic species. Site-specific conditions are critical for the formation of metal complexes with inorganic or organic ligands (Ward et al., 2005). Bolan et al. (2014) reported that there is a possibility of overestimating and, or underestimating the total concentration of compounds in the soil and sediment when conducting environmental assessments. This includes the term 'bioavailability fractions' which is considered as the fraction of the total contaminant in the interstitial water and soil particles that is available to the receptor organism (Vig et al., 2003). In a related report, Remon et al. (2013) described 'bioavailability' as a complex term, in which both dynamic processes and species specific interactions are involved. It is strongly associated to the organism under evaluation, the type of exposure and the chemical speciation of the metals (Ben Salem et al., 2014). However, the term 'bioavailable' itself is vague and can be misleading. In the context of soil chemical fractionation, the term 'bioavailable fraction' deviates from the IUPAC recommended terminology, as 'fractionation' referring to the classification of an analyte or group of analytes accordingly to physical or chemical properties (Marigómez et al., 2004). Marigómez et al. (2004) pointed out that some authors differentiated between 'external bioavailability' or 'bioaccessibility', which largely depends on the ability of metals to be dissolved and released from media or food and 'internal bioavailability' which reflects the ability to be absorbed by the organism, reach target tissues and exert toxicological effects. The availability of heavy metals for plant uptake is often described as phytoavailability (Meers et al., 2007).

When determining the total content and bioavailability of heavy metals in soil, some of researchers use biological indicators such as plants and organisms to conduct experimental studies (Meers et al., 2007; Boshoff et al., 2014; Ben Salem et al., 2014; Sakho et al., 2015). The use of plants as accumulation indicators has been well explored. Several species are considered as good bio-indicators of soil contamination such as the White poplar Populusalba Linnaeus, Scots Pine Pinus sylvestris, the perennial rye grass Lolium perenneor the Red clover Trifolium pratense, which are considered as native plants to the environment (Boshoff et al., 2014). The advantage of using common and native growing plants such as nettle and grass to model and predict soil and plant metal concentrations is that they are known to survive and reproduce under environmental stress (Vystavna et al., 2015). They are exposed only for a specific period of time (i.e. plant growth season) to available pollutants and they are present in most ecosystems which makes comparisons among a broad range of sites (even across continents) possible (Boshoff et al., 2014). Field responses of plants are complex because of many factors: toxicity of metals is mediated by texture and soil status and by synergistic behaviour of different chemicals (Kulizhskiy et al., 2014). The absence/presence of certain plants to a particular polluted environment will give an indication of the state of contamination of the soil, even before the experiment (King et al., 2006). Plant characteristics relevant to field behaviour therefore encompass morphological and architectural responses to metal distributions where many issues play a role, including the distance of roots from the areas containing high metal concentrations. An important question is how to study these processes at a small scale using an easy, cheap, replicable and reliable technique (Bochicchio et al., 2015).

In view of the potential toxicity, persistent nature and cumulative behaviour as well as the consumption of vegetables and fruits, there is a need to test and analyse food items to ensure that the levels of these contaminants meet the agreed international requirements. Regular

survey and monitoring programmes of the concentration of heavy metals in food products have been carried out for decades in most developed countries (Gebrekidan *et al.*, 2013; Capra *et al.*, 2014). The heavy metals concentration in MSW compared to other solid fuels such as biomass and coal is relatively high and in addition to that, variations in heavy metal concentrations in MSW are large, also within each fraction of MSW (Sorum *et al.*, 2003). Hence, selective soil and plant extraction procedures are very crucial when quantifying heavy metal content and conducting risk assessments on the environment (Malandrino *et al.*, 2011). Water soluble metal ions can easily be mobilised and may be considered as highly 'bioavailable' and to assess the readily available metal fractions under field conditions, collection and analysis of pure water has therefore become an important aspect of man environmental monitoring programs (Remon *et al.*, 2013). In addition, Chapman *et al.* (2013) concluded that pore water testing and analyses can be effective tools provided their limitations are well understood by researchers and managers.

Currently, there exists a gap between legislation and practise of environmental protection in SA (Eijsackers *et al.*, 2014). The large amounts of heavy metals in municipal solid waste (MSW) totally dominate the outflow from cities (Backnäs *et al.*, 2012). Soil contamination is man-made and it is site-specific, local, regional and global environmental problem and its assessment (Desaules, 2012). The mobility and bioavailability of heavy metals in the environment depends not only on their total concentration but also on their association with the solid phase to which they are bound (Acosta *et al.*, 2011). The risks posed by mobilization of heavy metals strongly depend on the pathways that the toxic metals follow. These can be subdivided in soil–plant and soil–water pathways (Meers *et al.*, 2007). In the first case, an important risk is generated by the entrance of the metals into the trophic chain followed by subsequent dispersion associated with the local fauna. In the second case, metal mobilization through dissolution in runoff or lixiviation water poses a direct risk of

groundwater contamination (Meers *et al.*, 2007). In depth understanding of the contamination characteristics of heavy metals in soils and identifying the environmental exposure risks not only are the basic pre-conditions for soil pollution prevention and control, but also provide important information for making decisions for remediation of contaminated soils (Chen *et al.*, 2013).

Heavy elements such as Pb, Zn, Cd, Hg and Cr generally referred to as metals and metalloids have densities greater than 5 g/cm<sup>3</sup> (Bolan *et al.*, 2014). Metalloids such as arsenic (As) often fall into the heavy metal category due to similarities in chemical properties and environmental behaviour (Chen *et al.*, 2015). Organic chemicals are different in their nature and turn to react differently whenever they are either mixed with each other or come in contact with other solvents or solids (Bolan *et al.*, 2014). Once heavy metals are released from the soil, they persist for a long time and they are not easily removed (Wu *et al.*, 2015). This kind of pollution not only degrades the quality of the atmosphere, water bodies and food crops, but also threatens the health and well-being of animals and humans by way of the food chain (Ward *et al.*, 2005).

In developed countries, efforts have been made to evaluate the implication of trace and heavy metals as well as MSW management on humans, plants and the environment that comes from open landfills. There is a paucity of information on heavy metals bioavailability in soil and the impact open dumpsites in South Africa. Therefore, the present study was conducted to determine the various concentrations of trace and heavy metal (As, Cd, Cr, Cu, Mn, Pb, Hg, Ni, Se and Zn) in soil samples collected from four major dumpsites in Thabo Mofutsanyane District, Eastern Free State during different seasons of the year. Since soil to plant transfer of trace metals is the major pathway of human exposure to metal contamination.

#### **CHAPTER 2**

#### **OBJECTIVE OF THE STUDY**

#### 2.1. Statement of the problem

Recent industrialisation and increase in population have increased the accumulation of heavy metals in the soil environment (Nazeer *et al.*, 2014). As the final municipality solid waste (MSW) disposal method, landfill is a widely accepted technology, especially in developing countries. The large number of cases of groundwater pollution at landfills suggests that landfill leachate is a significant source of pollutants, especially when considering different kinds of contaminants in landfill leachates. Heavy metals are dangerous because of their persistence and toxic nature. Heavy metals can be transferred to the ecosystem components such as underground water or crops and ultimately affecting human health through water supply and food web (Marigómez *et al.*, 2004). Other heavy metals can persist in the air for a long time and that can lead to inhalation of these metals, thus leading to health problems (Net *et al.*, 2015).

South African (SA) soils, like those in the rest of the world, have become increasingly deteriorated due to anthropogenic activities (Lion and Olowoyo, 2013). South Africa being a developing country, many industries that produce different products need the space in the environments to discharge their wastes, therefore creating dump sites. In South Africa, the scenario is worse in urban soils due to the recent dramatic industrialization and urbanization activities to meet up the demands of increasing population. Elevated concentrations of potentially toxic elements in the urban soils indicate that the urban residents are exposed to contaminated soils (Wei *et al.*, 2010). Illegal dumping of waste is a major problem in South Africa, especially around the Free State province. This is followed by unauthorised landfills with the majority located within residential areas and poor protective structures of dumpsites.

Infants and toddlers are particularly vulnerable to trace metal exposure and poisoning due to the maximal brain growth and differentiation of children at early ages (Wu *et al.*, 2015). Moreover, trace element adsorptions from the digestion system and haemoglobin sensitivity to trace elements are much higher in children compared to adults (Bdour *et al.*, 2007). These problems are particularly worrisome in Free State province, due to large population in close proximity to industrial and other urbanized activities as well as open landfills. Over the last few decades, a significant number of studies have addressed the contamination of soils with trace elements in several countries (Adeniyi, 1996; Flyhammar, 1997; Ward *et al.*, 2005; Zhang *et al.*, 2008), to our knowledge, no such study has yet been conducted in the Free State province, South Africa. Therefore, this is the first study investigating the scenario of trace element contamination in soils of residential urbanized area in Free State province. The study determined the concentrations of trace elements in soils and plants from four major open dumpsites of Thabo Mofutsanyane District, South Africa and to evaluate possible ecological, environmental and health impact of trace metals from landfills.

#### 2.2 Objectives

#### 2.2.1. General objective

The overall objective of this study is to quantify toxic contaminants of four major dumpsites of Thabo Mofutsanyane district and Eastern Free State in South Africa using soil and plant as test samples.

#### 2.2.2. Specific objectives

- Determine the major toxic contaminants such as heavy and trace metals during different seasons.
- To determine the level of heavy metal contaminations in plant species and soil and to identify various plant species in the dumpsites.

- To compare the level of contaminants such as As, Cd, Co, Cu, Mn, Pb etc in the four dumpsites.
- To determine whether these plant species can be considered as biological indicators to monitor the changes in the environment.

#### **CHAPTER 3**

#### MATERIALS AND METHODS

#### 3.1. Study area

Maluti-A-Phofung (MAP) local municipality is situated in the Free State Province of South Africa. It is situated within the boundaries of the Thabo Mofutsanyana District Municipality in the Eastern Free State. It was established in terms of the provincial Gazette No. 14 of 28 February 2000 issued in terms of Section 21 of the Local Government Notice and Municipal Demarcation Act No.27 of 1998. MAP is a local municipality FS194 and was established on the 5<sup>th</sup> December 2001. MAP is made up of four former transitional local council (TLC) Local Authorities which are Qwaqwa Rural, Phuthaditjhaba, Harrismith and Kestell. Figure 1 below shows the locality of MAP. The municipality comprises of 35 wards and covers approximately 4,421 km<sup>2</sup> in extent. Phuthaditjhaba is the urban centre of Qwaqwa and serves as the administrative head office of MAP municipality. Surrounding Phuthaditjhaba are rural villages of Qwaqwa established on tribal land administered by Department of Land Affairs. Harrismith is a service centre for the surrounding rural areas and a trading belt serving the passing N3 highway which links the Gauteng and KwaZulu-Natal provinces. Harrismith is surrounded by Tshiame located 12 km to the west and Intabazwe, which is located 1.5 km to the north. The town is an economic hub for people living in Tshiame, Intabazwe and Qwaqwa. Kestell is a service centre for the surrounding agricultural oriented rural area with Tholong as the township. Kestell is situated along the N5 road that links Harrismith with Bethlehem. The rural areas of Maluti-A-Phofung comprise commercial farms and major nature conservation centres such as Qwaqwa National Park, Platberg, Sterkfontein Dam and Maluti Mountain Range.

The area is not only a tourist attraction destination, but also makes a big contribution in generating gross agricultural income for the whole of the Province and is also highly regarded

for its beef production. In comparison with the demographic composition of the rest of the Thabo Mofutsanyana District, MAP municipality has the highest population density with the 3rd highest population density in the Free State. Maluti-A-Phofung Local Municipality (MAP) is a Category B municipality located in the eastern part of the Free State Province. MAP forms part of a scenic tapestry, which changes dramatically with each season, the beauty and tranquillity of which is palpable and almost overwhelming, which has as its rockbed the famous Maluti Mountains, from which the Municipality is named. Majestic mountains with sandstone cliffs, fertile valleys of crops that stretch as far as the eye can see, fields of Cosmos and the golden yellow hues of Sunflowers, are just a few of the enchanting sights that make this region unique. Battle sites and memorials left over from bygone wars, ancient fossil footprints from a prehistoric era, a wealth of art and craft and renowned resorts make this part of the region a destination to explore. The municipality is made up of three major towns, namely: Harrismith, Kestell and Qwaqwa/Phuthaditjhaba. Dihlabeng Local Municipality is an administrative area in the Thabo Mofutsanyana District of the Free State in South. It was established under Section 12 of the Local Government Structures Act, 117 of 1998, after the first general local government elections of 5<sup>th</sup> December 2000 which heralded the final phase of local government reform as envisaged in 1994 at the onset of the process of democratisation. The Municipality is a category B as defined in the Local Government Structures Act and shares executive and legislative authority with the category C municipality within whose area it falls i.e. Thabo Mofutsanyane District Municipality. The type is that of a Collective Executive System combined with a Ward Participatory System.

The Dihlabeng Local Municipality is situated within the boundaries of the Thabo Mofutsanyana District Municipality in the Eastern Free State. The geographical area is 7550.4910 km<sup>2</sup>. The Municipality consists of the towns Bethlehem (including Bohlokong & Bakenpark), Clarence (incl. Kgubetswana), Fouriesburg (incl. Mashaeng), Paul Roux (incl. Fateng-Tse-Ntsho) and Rosendal (including Mautse).



Figure 1: Map of South Africa with the shaded areas indicating the locations of interest for the study. The star indicates the study sites (Source: Google Map)

#### 3.2. Description of dumpsites

Four major municipal solid waste dumpsites, two from Bethlehem, one each from Harrismith and Qwaqwa around the Eastern Free State, Thabo Mofutsanyane District, South Africa were considered for the two dumpsites in Bethlehem, one is located near the Bohlokong residential (township) areas (28° 53' 57" S and 28° 57" 66" E) and is currently being in operation for 2 years, while the other one is located in the suburbs area called Panorama (29° 43' 67" S and 28° 37' 43" E). The other two landfills are from Harrismith, Ntabazwe Township (28° 54' 57" S and 29° 46' 39" E) and Qwaqwa, Letsha Le-Maduke (28° 45' 67" S and 28° 34' 67" E) and they are both currently active.

#### 3.3. Soil, plant sampling and characterization

A random sampling technique for collection of soil samples was used. Soil samples were collected inside the dumpsite, not more than 15 m apart and outside the dumpsites, not more than 15 meters away from the dumpsites. Soil samples from four different locations inside and outside the dumpsites, ten meters apart, were collected and each mixed to be the representative of the inside and outside of the dumpsite. The soil was scooped at 0-25 cm depth using an auger. Collection of soil samples was repeated during four different seasons (spring, summer, autumn and winter) of the year (2014 and 2015) to represent the dry and wet seasons

plant samples of *Panicum maximum* (green panic), *Eragrostis plana* (South African lovegrass), *Cosmos* and *Eleusine indica* (Indian goose grass, wiregrass, crow foot grass) were collected inside the dumpsite, not more than 15 m apart and outside the dumpsites, not more than 15 meters away from the dumpsites. Plant samples were identified by Dr. Erwin Siebern from the University of the Free State (Qwaqwa campus) herbarium. Plant samples from four different locations inside and outside the dumpsites, ten meters apart, were collected and each mixed to be the representative of the inside and outside of the dumpsite. Plant samples were

also pulled from the soil together with their roots at the depth of 0-15cm with an auger. Plants were collected inside and outside the dumpsites ten meters apart. Collection of plant samples was repeated during four different seasons (spring, summer, autumn and winter) of the year (2014 and 2015) to represent the dry and wet seasons.

#### 3.4. Metal concentration of soil and plant samples

Soil samples were dried for four weeks at room temperature, ground and sieved with a 500 mm sieve element in order to achieve uniform sized particles. The ground soil samples were analysed for trace metal concentrations using the four acid digest techniques (HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and HF) as described by Pastor and Hernández, (2012) where the acids were added to 5.0 g of soil and the resulting solution made to volume. Complete digestion of the samples was performed at 200 °C for 6 h. After that, the samples were diluted to 10 mL with Milli-Q water. Digestion of samples was carried out in duplicates with six blanks for each series. Analyses of both the soil sample extracts were carried out using an inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent Technologies 7500c, Tokyo, Japan), according to the method of He *et al.*, (2006).

Plant samples were also collected from the same sites where soils were collected. At harvest, plants were mixed into shoots and roots properly washed with deionized water to remove all visible soil particles. Plant samples were first dried at 70 °C for 24 h. HNO<sub>3</sub>: HClO<sub>4</sub> = 7:1 (Trace Select, Fluka, Germany). Digestion of plant samples was performed to determine total metal concentration using a method of Ali *et al.*, (2014). Four millilitres of a 7:1 mixture of HNO<sub>3</sub>:HClO<sub>4</sub> was added to approximately 0.3 g of plant material and left in a closed PFA vial for 24 h (Savillex, 0275R, USA). Complete digestion of the samples was performed at 200 °C for 6 h. After that, the samples were diluted to 10 mL with Milli-Q water. Digestion of samples was carried out in duplicates with six blanks for each series. Analyses of both the plant sample extracts were carried out using an inductively coupled plasma optical emission

spectrometry (ICP-OES) (Agilent Technologies 7500c, Tokyo, Japan), according to the method of He *et al.*, (2006). Figure 2 shows acid digestion of soil samples after 24 h and filtration of the extracts using Whitman No. 1 filter paper. All extractions and analyses were carried out in the Agricultural Research Council, Institute for Soil, Climate and Water Analysis, Pretoria, SA.

In order to determine the pH, cation exchange capacity (CEC), clay percentage, traces minerals and trace elements. The soil pH was measured with a solid/liquid ratio of 1:20 (w/v) after the solutions had been allowed to equilibrate for 48 h. The metal elements in soil samples were analysed by digesting method using the HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> hot block digestion procedure (USEPA, 2002), followed by the metal determination in solution using inductively coupled plasma method (ICP-AES, ICAP 6000 Radial, Thermo, U.K.). The water-extractable cation and anion concentrations were determined by diluting the samples with distilled water. After agitation for 24 h at room temperature, the suspensions were filtered through 0.45-µm membrane filters. The water soluble cations in the filtrate were measured by ICP-AES and the water soluble anions were analysed using an ion chromatograph (HIC-SP/HIC-NS, Shimadzu, Japan). Figure 3 shows testing of the soil pH, clay percentage, total carbon and extract analysation using ICP-AES chemical analysis followed USEPA approved QA/QC plan with a blank, a duplicate and a spike every 20 sample. All extractions and analyses were carried out at the Agricultural Research Council, Small Grain Institute, Bethlehem, South Africa.

#### 3.5. Statistical analysis

The community analysis package; the Principal Component Analysis (PCA) technique was applied to determine the correlation between the heavy metals and the sites. Descriptive statistics of metals and soil properties were performed applying the Excel for Windows software package. Analysis of variances (ANOVA) tests to determine the statistical significance of the observed differences among various amounts of metal released for each dumpsite concentration. Correlation matrix and PCA were used to evaluate the effect of soil properties on the percentage of released metals. Varimax rotation was applied because it minimizes the number of variables with a high loading on each component and facilitates the interpretation of results. Using the cluster analysis, this technique clusters variables into groups such that variables belonging to one group are highly correlated with one another. Statistical analysis was carried out using SPSS 20.0 for Windows (Ravisankar *et al.*, 2015). Differences in the concentrations of trace metals from the sites were determined using either the Student t-test or the analysis of variance. A Mann-Whitney U-test was used to further test for the significant difference of contaminants concentrations between the inside and outside of each of the three dump sites.



Figure 2: Acid digestion of soil samples after 24 h and filtration of the extracts using Whitman No. 1 filter paper.



Figure 3: Testing of the soil pH, clay percentage ,total carbon and extract analsation

using ICP-AES

#### 4. RESULTS

#### 4.1. Heavy metals in soils

The variations in concentrations of heavy metals in soil from four dumpsites are as shown in Table 4.1. The active site (the site that is currently operational), while the inactive site (the site that is no longer operating). From the study, the values of Zinc (Zn) from the soil samples during the dry season (autumn) were observed to be fluctuating within and outside the dumpsites. The values of Zn content within the dump sites of Harrismith, Qwaqwa, Bethlehem active site (site A) and Bethlehem inactive site (site B) were 33.50±0.07, 105.03±24.41, 144.99±10.61 and 109.98±2.88 mg/kg, respectively. When compared with the outside of the dumpsites, the results of Zn concentration from Harrismith, Qwaqwa, Bethlehem active site and Bethlehem inactive site were 46.52±0.22, 81.40±28.05, 45.93±6.09 and 147.88±11.59 mg/kg, respectively (Table 4.1). The highest concentration of Zn from the dumpsites was between Bethlehem site B within and outside the dumpsite. The second collection of samples during the dry season (winter), the Zn content both within and outside the dumpsites under study changed drastically (Table 4.2). It was observed that during the winter period, Zn concentrations were elevated. Similar trends of fluctuations of Zn concentration was also observed during the wet season. During the wet season (spring), Zn concentration inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B was 53.11±3.99, 56.28±2.54, 171.35±4.17 and 36.89±2.73 mg/kg, respectively. The outside of the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B, the concentration of Zn was 34.39±1.79, 85.93±1.34, 52.81±2.93 and 49.66±1.85 mg/kg, respectively. During the second collection of samples in the wet season (summer), it was observed that Zn concentration was increasing. This increase was observed during the dry season. Most heavy metals slightly increased during the wet season. Zn concentration inside the dumpsites from

Harrismith, Qwaqwa, Bethlehem site A and site B was  $125.7\pm5.23$ ,  $52.87\pm3.91$ ,  $82.26\pm1.02$  and  $31.26\pm4.15$  mg/kg, respectively. The outside of the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B, the Zn content was  $56.23\pm17.12$ ,  $92.11\pm0.83$ ,  $88.8\pm41.02$  and  $3076.5\pm12.02$  mg/kg, respectively. Comparing the four seasons (autumn, winter, spring and summer), the Zn concentration was higher in winter than during dry season and wet season, except in Bethlehem site B outside the dumpsite, during the summer season where it had much elevated concentration of  $3076.56\pm12.02$  mg/kg (Table 4.4).

In addition, lead (Pb) and cadmium (Cd) had similar results with Zn in all the sites during different season. During the dry season (autumn), Pb concentration from Harrismith, Owaqwa, Bethlehem site A and site B within the dumpsites was  $13.49\pm0.37$ ,  $12.60\pm0.24$ , 20.82±3.94 and 16.01±0.14 mg/kg, respectively. The outside of the dumping sites from Harrismith, Owagwa, Bethlehem site A and site B, Pb concentration was 14.93±1.32, 15.45±5.62, 13.44±0.89 and 24.25±2.30 mg/kg, respectively. Similar to Zn concentration, during the second collection of samples in the dry season (winter), Pb concentration changed drastically with elevated concentrations values from Qwaqwa dumpsite both inside and outside and Bethlehem site A (inside) dumpsite of 118.44±4.51, 315.79±30.26 and 230.82±35.24 mg/kg, respectively (Table 4.2). It was observed that in Harrismith dumpsite (inside), there was a significant decrease in Pb concentration with the value of  $0.17\pm0.02$ mg/kg (Table 4.2). During the wet season (14 November 2014), Pb concentration from Harrismith, Owaqwa, Bethlehem site A and site B within the dumpsites was  $14.44\pm0.43$ ,  $12.04\pm0.23$ ,  $22.21\pm0.50$  and  $9.5\pm10.72$  mg/kg, respectively. In comparison with Pb concentration outside of the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B was 11.86±0.61, 12.06±0.13, 18.35±0.30 and 9.15±0.32 mg/kg, respectively (Table 4.3). During the spring and summer seasons, it was observed that the values of Pb concentration from the dumpsites, both inside and outside were not significantly different, except in Bethlehem site B which was 76.13±4.57 mg/kg.

Cadmium (Cd) fluctuation in soil from the dumpsites in Harrismith, Qwaqwa, Bethlehem site A and site B was also similar to Zn and Pb fluctuation. During the dry season (autumn), Cd concentration was found to be in the range of  $0.04\pm0.004$ - $0.28\pm0.29$  mg/kg. This is below the maximum permissible limit set by the SEPA and WHO, including the regional guidelines from SA agricultural soils (Table 4.1 and Appendix 3). On the second collection of samples, during the dry season (winter), the Cd concentration changed drastically from the same dumpsites now ranging from  $2.82\pm0.56$ - $6.15\pm0.06$  mg/kg (Table 4.2). The drastic increase was similar to the concentrations observed for Zn and Pb during winter season. It is noteworthy that during the spring and summer season, Cd concentration showed values below the threshold ranging from  $0.05\pm0.008$ - $0.43\pm0.06$  mg/kg (Table 4.3 and 4.4). This was also similar to Zn and Pb (Table 4.3 and 4.4).

High values of Manganese (Mn) were observed from all the dumpsites during the autumn and winter seasons. Mn concentration during the autumn from Harrismith, Qwaqwa, Bethlehem site A and site B inside the dumpsites was  $319.89\pm31.48$ ,  $405.01\pm405.7$ ,  $494.68\pm35.92$  and  $256.73\pm32.81$  mg/kg, respectively. On the outside of the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B, Mn concentration was  $298.69\pm32.10$ ,  $1181.76\pm1.87$ ,  $598.74\pm97.90$  and  $581.42\pm49.51$  mg/kg, respectively. During the second collection of sample in the dry season (winter), the Mn values remained higher during winter season, Mn concentration inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B marked higher during winter season, Mn concentration inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B marked higher during winter season, Mn concentration inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B marked higher during winter season, Mn concentration inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B marked higher during winter season, Mn concentration inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B marked higher during winter season, Mn concentration inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B marked higher during winter season was  $669.20\pm115.18$ ,  $511.24\pm32.23$ ,  $470.49\pm5.17$  and  $525.46\pm28.91$  mg/kg, respectively. On the outside of the dumping sites form Harrismith, Qwaqwa, Bethlehem site A and site B, Mn

concentration was  $592.01\pm7.18$ ,  $696.13\pm44.46$ ,  $799.46\pm84.50$  and  $420.49\pm313.32$  mg/kg, respectively. When the dry season was compared to the wet season, a drastical decrease in concentration of Mn was observed (Table 4.3). During the spring season, Mn concentration inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B was  $57.69\pm3.00$ ,  $78.94\pm4.10$ ,  $56.51\pm2.10$  and  $318.75\pm13.22$  mg/kg, respectively. On the outside of the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B during the spring season, Mn concentration in soil was  $64.25\pm4.18$ ,  $102.1\pm0.57$ ,  $85.57\pm36$  and  $238.95\pm0.64$  mg/kg, respectively. The concentration remained relatively low during the second collection of samples in wet season. During the summer season, Mn concentration inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B was  $59.78\pm4.55$ ,  $100.12\pm1.53$ ,  $78.15\pm10.95$  and  $116.0\pm1.70$  mg/kg, respectively. On the outside of the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B was  $59.78\pm4.55$ ,  $100.12\pm1.53$ ,  $78.15\pm10.95$  and  $116.0\pm1.70$  mg/kg, respectively. On the outside of the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B, Mn concentration was  $62.48\pm4.84$ ,  $82.56\pm0.46$ ,  $78.78\pm0.15$  and  $197.79\pm191.64$  mg/kg, respectively.

Table 4.1: Concentration (mg/kg) of heavy metals in soils found in four major dumpsites in Thabo Mofutsanyane District, Eastern Free State, collected during the autumn season (15 April 2014)

No. of sites	Sample site	Cr	Mn	Со	Ni	Cu	Zn	As	Cđ	Hg	РЬ	Al %
1: A	H; W	9.76±0.16	319.89±31.48	7.27±0.31	11.88±0.62	8.01±0.13	33.50±0.07	4.20±0.15	0.10±0.01	0.05±0.005	13.49±0.37	0.007
В	H: O	12.77±0.79	298.69±32.10	6.77±0.95	$15.95 \pm 0.52$	8.79±0.25	46.52±0.22	3.38±0.43	$0.23 \pm 0.11$	$0.05 \pm 0.007$	14.93±1.32	0.025
2: A	Q: W	44.87±20.68	405.01±405.7	7.54±0.06	19.46±16.34	42.72±27.54	105.03±24.41	2.12±0.13	$0.17 \pm 0.04$	0.05±0.01	12.60±0.24	0.019
В	Q: O	119.06±1.24	1181.76±1.87	31.20±0.34	35.14±1.49	62.27±0.33	81.40±28.05	4.45±1.52	$0.14{\pm}0.01$	0.05±0.19	15.45±5.62	0.236
3: A	B: A: W	22.72±7.68	494.68±35.92	5.95±0.06	13.70±0.34	14.41±0.51	$144.99 \pm 10.61$	4.04±0.12	0.28±0.29	0.12±0.13	20.82±3.94	0.028
В	B: A: O	16.12±0.50	598.74±97.9	7.97±1.10	21.12±0.56	11.07±0.18	45.93±6.09	3.05±0.26	$0.04 \pm 0.004$	$0.05 \pm 0.01$	13.44±0.89	0.009
4: A	B: I: W	28.27±0.91	256.73±32.81	3.82±0.12	8.94±1.12	17.58±0.71	$109.98 \pm 2.88$	2.51±0.13	0.27±0.01	$0.08 \pm 0.02$	$16.01 \pm 0.14$	0.036
В	B: I: O	60.16±4.73	581.42±49.51	8.69±0.19	20.25±1.13	16.97±0.89	$147.88 \pm 11.59$	5.35±0.37	$0.20{\pm}0.009$	$0.09 \pm 0.06$	24.25±2.30	0.039

H: W; Harrismith: Within, H: O; Harrismith: Outer, Q: W; Qwaqwa: within, Q: O; Qwaqwa: outer, B: A: W; Bethlehem: Active: Within, B: A: O; Bethlehem: Active: outer, B: I: W; Bethlehem: Inactive: Within, B: I: O; Bethlehem: Inactive: Within
Table 4.2: Concentration (mg/kg) of heavy metals in soils found in four major dumpsites in Thabo Mofutsanyane District, Eastern Free State, collected during the winter season (15 July 2014)

No. of	Sample sites	Cr	Mn	Со	Ni	Cu	Zn	As	Cd	Hg	Рb	Al %
1: A	H; W	46.964±6.55	669.20±115.18	6.38±1.15	18.82±2.04	37.03±17.31	657.85±84.47	6.81±0.84	1.28±0.13	0.09±0.007	0.17±0.02	0.023
В	H: O	56.87±1.96	592.01±7.18	9.53±0.51	33.83±0.15	17.72±0.59	57.44±0.90	5.24±0.47	0.37±0.20	0.06±0.04	15.68±0.68	0.009
2: A	Q: W	84.13±1.56	511.24±32.23	13.73±0.30	37.28±0.33	61.42±3.09	1055.82±130.79	2.78±0.16	1.62±0.12	$0.07 \pm 0.05$	118.44±4.51	0.029
В	Q: 0	113.46±10.37	696.13±44.46	13.39±0.08	35.14±0.62	75.04±0.12	1733.51±39.33	2.74±0.02	6.15±0.06	0.03±0.006	315.79±30.26	0.032
3: A	B: A: W	71.49±0.93	470.49±5.17	7.08±0.06	37.25±8.54	218.89±1.33	777.51±62.79	5.24±1.20	2.82±0.56	0.06±0.004	230.82±35.24	0.011
В	B:A: O	20.65±5.65	799.46±84.50	7.74±0.35	27.42±1.28	11.68±0.03	57.31±1.50	6.09±0.23	0.17±0.02	0.03±0.03	19.51±0.11	0.015
4: A	B: I: W	51.48±9.41	525.46±28.91	23.58±9.18	17.07±0.28	15.09±0.88	301.29±27.37	2.71±0.23	0.34±0.07	$0.08 \pm 0.03$	26.67±0.34	0.013
В	B: I: O	38.20±9.33	420.49±313.32	20.73±16.94	14.02±7.45	35.2±27.25	181.58±74.51	2.35±0.45	0.21±0.06	0.32±0.40	19.47±6.45	0.012

No. of sites	Sample site	Cr	Mn	Со	Ni	Cu	Zn	As	Cd	Hg	Pb
1: A	H: W	63.69±5.40	57.69±3.00	<0.0001±0	36.37±0.27	29.6±0.10	53.11±3.99	4.87±0.29	$0.07 \pm 0.0007$	$0.02 \pm 0.008$	14.44±0.43
В	H: O	20.52±0.27	64.25±4.18	1.13±1.60	14.76±0.82	14.92±0.10	34.39±1.78	3.44±0.2	$0.05 \pm 0.008$	<0.0001±0	11.86±0.61
2: A	Q: W	86.42±3.10	78.94±4.10	22.48±0.65	41.47±0.89	46.25±1.26	56.28±2.54	1.98±0.12	$0.11 \pm 0.002$	<0.0001±0	12.04±0.23
В	Q: O	151.1±1.70	102.1±0.57	5.96±6.52	56.99±0.96	61.46±1.96	85.93±1.34	2.08±0.23	0.13±0.001	0.02±0.002	12.06±0.13
3: A	BA: W	47.1±6.62	56.51±2.10	1.58±2.32	20.03±0.59	37.92±2.76	171.35±4.17	4.07±0.20	0.43±0.06	0.62±0.88	22.21±0.50
В	B: A: O	58.01±2.08	85.47±5.36	16.66±0.81	26.46±2.05	30.91±1.22	52.81±2.93	5.76±0.03	0.06±0.002	<0.0001±0	18.35±0.30
4: A	B: I: W	39.74±1.13	318.75±13.22	6.86±0.38	12.87±0.77	13.8±0.77	36.89±2.73	1.63±0.17	0.07±0.001	<0.0001±0	9.5±10.72
В	B: I: O	45.14±20.07	238.95±0.64	6.37±0.26	8.04±0.30	13.75±0.64	49.66±1.85	1.8±0.87	0.08±0.0007	<0.0001±0	9.15±0.32

Table 4.3: Concentration (mg/kg) of heavy metals in soils found in four major dumpsites in Thabo Mofutsanyane District, Eastern Free State, collected during the spring season (15 November 2014)

No. of sites	Sample site	Cr	Mn	Со	Ni	Cu	Zn	As	Cd	Hg	Рb
1: A	H:W	34.94±1.60	59.78±4.55	<0.0001±0	22.12±1.20	54.89±38.11	125.7±5.23	3.77±0.36	0.36±0.02	0.97±1.37	17.83±0.16
В	H: O	28.32±1.46	62.48±4.84	0.09±0.08	16.03±1.37	175.61±22.12	56.23±17.12	1.75±0.01	$0.08 \pm 0.007$	0.03±0.04	30.23±13.97
2: A	Q: W	147.8±18.95	100.12±1.53	10.52±0.34	40.49±3.13	48±1.50	52.87±3.91	1.42±0.05	$0.09 \pm 0.005$	2.42±0.06	11.16±1.00
В	Q: 0	83.07±0.67	82.56±0.46	20.93±0.23	31.69±1.36	51.45±0.80	92.11±0.83	1.78±0.13	0.3±0.005	0.04±0.04	11.53±0.42
3: A	B: A: W	62.28±2.38	78.15±10.95	8.03±11.35	24.15±12.04	33.95±0.32	82.26±1.02	2.49±0.20	0.18±0.002	0.08±0	13.93±0.18
В	B: A: O	41.84±5.81	78.78±0.15	7.1±3.27	26.68±3.30	39.5±0.74	88.8±41.02	3.56±0.69	0.12±0.01	<0.0001±0	15.06±0.46
4: A	B: I: W	88.07±7.22	116±1.70	16.06±18.84	26.81±2.22	37.86±2.33	31.26±4.15	1.44±0.41	$0.07 \pm 0.008$	<0.0001±0	13.3±0.58
В	B: I: O	50.78±1.03	197.79±191.64	18.75±4.86	17.81±0.33	76.9±3.25	3076.5±12.02	2.54±0.15	2.54±0.04	0.03±0.02	76.13±4.57

Table 4.4: Concentration (mg/kg) of heavy metals in soils found in four major dumpsites in Thabo Mofutsanyane District, Eastern Free State, collected during the summer season (15 February 2015)

#### 4.2. Heavy metals in plants

During the dry season, plant samples were analysed for Zn, Mg, Mn and Cu (Table 4.5 and Table 4.6). From the study, Zn values varied across different dumpsites. During the autumn season, from Harrismith, Owaqwa, Bethlehem site A and site B inside the dumpsite, Zn concentration in plant samples was  $46.2\pm 1.98$ ,  $112.0\pm 2.12$ ,  $86.2\pm 5.94$  and  $127.0\pm 0.71$  mg/kg, respectively. When determining the level outside of the same dumpsites from Qwaqwa, Bethlehem site A and site B, Zn concentration was 62.2±5.52, 57.7±2.47 and 95.7±7.64 mg/kg, respectively. Harrismith outside the dumpsite had no plants due to the small swamp and overgrazing (Table 4.5). During the winter season, only Bethlehem site A and site B were sampled. Zn concentration from Bethlehem site A and site B was 71.6±3.28 and 73.0±1.88 mg/kg, respectively. When determining the level outside of the dumpsites from Bethlehem site A and site B, Zn concentration was 40.4±0.57 and 26.9±1.06 mg/kg, respectively. Harrismith and Qwaqwa were not sampled due to the fires around the landfills and unavailability of plant samples (Table 4.6). During the spring and summer seasons, plant sampled were analysed for Mg, Al, Mn, Zn, Cu, Cr, Pb, Co, Cd and Se. During the spring season, Zn concentrations from Harrismith, Qwaqwa, Bethlehem site A and site B inside the dumping sites was 89±6.33, 129.7±10.3, 131.2±1.63 and 134.6±4.36 mg/kg, respectively. To the outside of the dumpsites from Harrismith, Qwaqwa and Bethlehem site A and site B, Zn concentration in plants was 71.2±1.85, 57.8±0.03, 36.9±2.41 and 62.1±4.25 mg/kg, respectively (Table 4.7). Zn concentration during autumn, winter and spring from randomly sampled sites and unidentified plant samples from the dumpsites under the study showed no significant differences of heavy metal concentrations in tissues.

The plant samples were tested for lead (Pb) concentration during the spring season. Plant samples inside the dumpsites from Harrismith, Qwaqwa, and Bethlehem site A and site B

was  $3.1\pm0.30$ ,  $2.4\pm0.00$ ,  $8.1\pm0.30$  and  $2.6\pm0.30$  mg/kg, respectively. On the outside of the dumpsites from Harrismith, Bethlehem site A and site B, Pb concentration in plants was  $3.3\pm0.70$ ,  $0.4\pm0.10$  and  $1.8\pm0.50$  mg/kg, respectively. The concentration for Pb outside the Qwaqwa dumpsite was not detected. It is interesting to note that the concentrate on of Cd was relatively low during the spring season. Cd concentrations during the spring period inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B was  $0.2\pm0.003$ ,  $0.2\pm0.002$ ,  $0.2\pm0.001$  and  $0.1\pm0.00$  mg/kg, respectively. The outside of the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B, Cd concentration was  $0.5\pm0.60$ ,  $0.1\pm0.003$ ,  $0.8\pm0.10$  and  $0.3\pm0.002$  mg/kg, respectively (Table 4.7). During the spring season, Mn concentrations in plant samples were elevated from most dumpsites, except in Harrismith outside the dumpsite, where it decreased when compared with winter season. The concentration of Mn inside the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B was  $114.6\pm7.82$ ,  $98.8\pm10.13$ ,  $379.7\pm13.39$  and  $156.4\pm7.47$  mg/kg, respectively. On the inside of the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B, Mn content was  $137\pm11.88$ ,  $53.4\pm0.61$ ,  $36.9\pm5.54$  and  $187.2\pm20.29$  mg/kg, respectively.

Table 4.8 shows the plant samples identified from various dumpsites. Similar to the soil samples, Zn, Pb and Cd showed a similar trend across all the dumpsites. There was a dramatic change in the concentration of these metals during the summer season. From Harrismith inside the dumpsite, *Cosmos* species, showed values for Zn, Pb and Cd to be 122.4 $\pm$ 5.0, 5.6 $\pm$ 0.33 and 0.2 $\pm$ 0.12 mg/kg, respectively. The outside of the Harrismith dumpsite, the concentration of Zn, Pb and Cd to the *Cosmos* species was 52.8 $\pm$ 2.0, 4.8 $\pm$ 0.10 and 0.04 $\pm$ 0.00 mg/kg, respectively. From Qwaqwa dumpsite (inside), the concentration of Zn, Pb and Cd in *Eleusine indica* was 50.8 $\pm$ 3.0, 1.3 $\pm$ 0.23 and 0.1 $\pm$ 0.00 mg/kg, respectively. The outside the dumpsite, spectively. The concentration of Zn, Pb and Cd in *Eleusine indica* was 50.8 $\pm$ 3.0, 1.3 $\pm$ 0.23 and 0.1 $\pm$ 0.00 mg/kg, respectively. The concentration of Zn, Pb and Cd in *Eleusine indica* was 50.8 $\pm$ 3.0, 1.3 $\pm$ 0.23 and 0.1 $\pm$ 0.00 mg/kg, respectively.

*plana* showed Zn, Pb and Cd concentration to be  $104\pm11.7$ ,  $10.6\pm0.81$  and  $0.2\pm0.00$  mg/kg, respectively. The *Cosmos* outside the dumpsite from Bethlehem site A, concentration of 75.0±2.3, 3.8±0.12 and 0.4±0.00 mg/kg was observed for Zn, Pb and Cd, respectively. The *Cosmos* species in Bethlehem site B inside the dumpsite, showed the concentration of Zn, Pb and Cd to be  $123.0\pm6.5$ ,  $4.5\pm0.01$  and  $0.6\pm0.00$  mg/kg,

On the outside of the dumpsites Bethlehem site B, the content of Zn, Pb and Cd in *Cosmos* species was  $66.0\pm26.6$ ,  $3.0\pm0.01$  and  $0.1\pm0.00$  mg/kg, respectively. This was the trend observed from different dumpsites. High Mn values were also observed in plants across all the dumpsites. Fluctuation of concentrations of heavy metals in plant samples between the seasons showed some similarities with fluctuation of soil concentration between seasons. Another interesting observation between the uptake of heavy metals by plants and the concentration of heavy metals in soil was that both soil and plant had high Mn values during winter season.

No. o sites	f Sample sites	Tot. C %	Mg (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Cu (mg/kg)
1: A	H: B	32.2	352±0.08	197±0.19	46.2±1.98	14.6±0.49
2: A	Q: O	32.2	548±0.07	416±21.21	62.2±5.52	33.1±0.99
В	Q: W	39.5	477±0.06	171±4.95	112±2.12	16.1±0.57
3: A	B: A: W	34.4	167±0.02	116±10.61	86.2±5.94	19.2±0.64
В	B: A: O	42.1	173±0.02	77.4±4.95	57.7±2.47	6.46±0.69
4: A	B: I: W	34.0	238±0.02	190±7.78	127±0.71	29.0±0.14
В	B: I: O	29.8	388±0.09	219±17.68	95.7±7.64	23.3±0.28

Table 4.5: Concentration of heavy metals in plants found in four major dumpsites in Thabo Mofutsanyane District, Eastern Free State (mg/kg), collected during the autumn season (15 April 2014)

No. of site	Sample sites	Tot. C %	Mg (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Cu (mg/kg)
1: A	B: A: W	19.6	327±4.95	280±1.41	71.6±0.50	42.8±0.85
В	B: A: O	42.2	113±2.83	68.3±1.70	40.4±0.57	6.08±0.70
2: A	B: I: W	26.1	283±2.83	48.0±2.12	73.0±1.41	16.5±0.36
В	B: I: O	8.34	137±4.49	104±2.12	26.9±1.06	22.6±0.29

Table 4.6: Concentrations (mg/kg) of heavy metals in plants found in four major dumpsites in Thabo Mofutsanyane District, Eastern Free State, collected during the winter season (15 July 2014)

B: A: W; Bethlehem: Active: Within, B: A: O; Bethlehem: Active: outer, B: I: W; Bethlehem: Inactive: Within, B: I: O; Bethlehem: Inactive: Within

No. of sites	Sample site	Mg	Al	Mn	Zn	Cu	Cr	Pb	Со	Cd	Se
1: A	H; W	4666±0.007	3921±28.28	114.6±7.82	89±6.33	26.5±2.83	7.1±0.20	3.1±0.30	2.2±0.10	0.2±0.0037	2.9±0.10
В	H: O	1398±0.005	4958±1039.50	137±11.88	71.2±1.85	19.8±1.36	4.9±0.10	3.3±0.70	1.6±0.10	0.5±0.60	ND
2: A	Q: W	7730±0.020	3543±547.34	98.8±10.13	129.7±10.3	24.2±1.72	ND	2.4±0.0008	2.8±0.10	0.2±0.0028	ND
В	Q: 0	1536±0.002	1388±93.79	53.4±0.61	57.8±0.93	11.3±0.28	4±0.10	ND	1.9±0.009	0.1±0.0031	ND
3: A	B: A : W	3388±0.004	1357±743.57	379.7±13.39	131.2±1.63	34±1.26	4.5±0.70	8.1±0.30	5.3±0.50	0.2±0.0014	ND
в	B: A : O	1419±0.012	1029±131.20	36.9±5.54	36.9±2.41	9.6±1.14	6±0.20	0.4±0.10	0.4±0.10	0.8±0.10	1.9±0.10
4: A	B: I: W	3202±0.017	4935±216.37	156.4±7.47	134.6±4.36	22.8±1.40	34.7±0.60	2.6±0.30	2±0.0045	0.1±0.0007	1.6±.0.20
В	B: I: O	3534±0.034	2945±241.12	187.2±20.29	62.1±4.25	13±0.99	13.6±0.40	1.8±0.50	1.1±0.00	0.3±0.0019	3.1±0.20

Table 4.7: Concentration (mg/kg) of heavy metals in plants found in four major dumpsites in Thabo Mofutsanyane District, Eastern Free State, collected during the spring season (15 November 2015)

A: O; Bethlehem: Active: outer, B: I: W; Bethlehem: Inactive: Within, B: I: O; Bethlehem: Inactive: Within, ND: not detected

Sample		Mg	Al	Mn	Zn	Cu	Cr	Pb	Со	Cd	Se
site H· W	Panicum maximum	3222+0.012	8459+937 8	153 7+12 5	117 1+96	19 1+2 7	$10.9\pm0.7$	5.7+0.32	1.9±0.11	0.2±0.00	4.6±0.30
11. **	Cosmos	2859±0.007	12503±715.9	405.9±12.4	122.4±5.0	20.5±1.5	12.8±0.3	5.6±0.33	3.6±0.00	0.2±0.12	3.7±0.44
H: O	Cosmos	9310±0.001	4544±458.6	122.0±0.50	52.8±2.0	8.5±0.5	10.0±0.6	4.8±0.10	2.3±0.00	0.04±0.00	4.0±0.72
	Eleusine indica	2349±0.011	2757±422.4	110.0±16.2	67.4±5.4	10.0±0.8	4.4±0.7	2.2±0.00	0.9±0.10	$0.2 \pm 0.00$	2.9±0.20
O: W	Unidentified (daisy)	4043±0.036	14410±4130.5	307.3±67.0	73.6±5.2	$23.9 \pm 4.4$	31.5±16.3	3.7±1.61	6.0±0.10	0.1±0.00	6.4±2.36
	Eleusine indica	3205±0.013	3134±435.8	109.2±9.5	50.8±3.0	12.0±1.3	7.7±0.1	1.3±0.23	1.8±0.11	0.1±0.00	$2.8 \pm 0.10$
Q: 0	Eragrostis plana	4001±0.011	4230±95.5	108.8±5.7	41.7±0.5	14.3±0.4	11.1±0.2	1.4±0.14	2.8±0.00	0.1±0.00	$4.0 \pm 0.00$
	Cosmos	6428±0.025	8238±874.7	234.7±35.2	83.5±10.2	22.4±3.1	22.9±0.7	3.2±0.23	5.6±0.20	0.4±0.20	4.8±0.26
BA: W	Eragrostis plana	2584±0.023	15020±2600.8	327.2±42.3	104.8±11.7	18.2±1.9	17.2±0.0	10.6±0.81	5.1±0.22	0.2±0.00	$4.4 \pm 0.00$
	Unidentified (daisy)	4861±0.017	14233±505.6	221.5±14.8	132.8±2.2	21.2±1.5	17.9±0.3	5.1±0.34	3.0±0.10	0.7±0.00	5.0±0.13
B: A: O	Cosmos	4452±0.120	3689±361.0	97.5±3.4	75.0±2.3	15.7±0.1	10.9±0.4	3.8±0.12	1.8±0.10	$0.4 \pm 0.00$	4.4±0.56
	Hericrusium	4422±0.007	5709±515.3	101.8±9.5	90.5±4.5	15.3±0.4	13.5±0.2	3.7±1.30	2.4±0.11	0.2±0.10	2.6±0.50
B: I: W	Unidentified (daisy)	3614±0.006	1932±213.9	70.6±4.6	135.5±5.4	26.9±0.3	4.4±0.0	0.7±0.30	1.0±0.10	0.5±0.10	2.8±0.29
	Cosmos	3975±0.032	1054±154.6	54.9±3.7	123.0±6.5	15.8±1.0	2.3±0.1	4.5±0.01	0.7±0.00	0.6±0.00	2.8±0.42
B: I: O	Unidentified (daisy)	5238±0.009	10464±1306.5	344.3±21.4	97.5±21.4	21.5±1.8	15.9±0.4	4.5±0.12	4.0±0.00	0.1±0.00	4.5±0.30
	Cosmos	6130±0.030	6380±540.8	170.0±14.5	66.0±26.6	19.0±1.0	12.7±0.2	3.0±0.01	2.3±0.10	0.1±0.00	4.7±0.20

Table 4.8: Concentration (mg/kg) of heavy metals in plants found in four major dumpsites in Thabo Mofutsanyane District, Eastern Free State, collected during the summer season (15 February 2015)

#### 4.3. Trace metal and physiochemical analysis of the four major dump site

Table 4.9 shows the clay percentage (clay %) and the organic carbon percentage for soil samples collected from four major dumpsites in Thabo Mofutsanyane District, Eastern Free State, during the dry and wet season. During the dry season, the percentage of clay from Harrismith, Owaqwa, Bethlehem site A and site B dumpsites ranged from 16-66, 28-46, 22-56 and 22-24%, respectively. During the wet season, the percentage of clay from Harrismith, Qwaqwa, Bethlehem site A and site B dumpsites ranged from 22-46, 30-54, 24-36 and 18-32%, respectively. The organic carbon during the dry season from Harrismith, Qwaqwa, Bethlehem site A and site B dumpsite was 0.30-3.30, 0.91-3.13, 0.49-6.74 and 1.68-2.66%, respectively. During the wet season, the organic carbon percentage from Harrismith, Qwaqwa, Bethlehem site A and site B range from 0.11-1.73, 0.73-2.04, 0.60-2.56 and 0.90-3.01%, respectively. The hydrogen ion concentration (pH) inside the dumpsites from Harrismith, Bethlehem site A and site B and Qwaqwa was 7.4, 7.2, 6.3 and 6.6, respectively. On the outside of the same dumpsites, the pH was 8.1, 7.4, 7.2 and 4.6, respectively (Table 4.10). All the dumpsites under study showed no acid saturation, except in Qwaqwa outside the dumping site with 3.70%. The cation exchangeable capacity (CEC) inside the dumpsites form Harrismith, Bethlehem site A and site B and Qwaqwa ranged to 20.87, 19.61, 10.20 and 28.95 cmol,kg<sup>-1</sup>, respectively. The outside of the dumpsites from Harrismith, Bethlehem site and site B and Qwaqwa, the CEC was 13.69, 18.33, 27.81 and 26.93 cmol,kg<sup>-1</sup>, respectively. High values of potassium (K), calcium (Ca) and Magnesium (Mg) were observed across all the dumpsites which ranged from 194.4-1130.3, 1138-4516 and 279.9-1033.1 mg/kg, respectively. Sodium (Na) showed fluctuations of concentration across the dumpsites. Harrismith, Bethlehem site A and site B and Qwaqwa dumpsites (inside), Na concentration was 163.7, 145.3, 54.4 and 485.8 mg/kg, respectively. On the outside of the same dumpsites, Na concentration was 405.3, 109.5, 47.9 and 115.2 mg/kg, respectively (Table 4.6). Phosphorus (P) and Zinc (Zn) concentrations were not abundant in soil across all the dumpsites under study (Table 4.10).

		Dry seasor	n (15 M	lay & 15 July 2014)		Wet season (15 No	vember & 15 February	2015)
Sample sites		Clay Hydrome %		Organic Carbon %		Clay Hydrome %	Organic Carbon %	
H; W	16	12	3.30	2.26	46	32	0.59	1.73
H: O	24	66	0.78	0.30	32	22	0.11	0.64
Q: W	28	46	0.91	1.04	30	54	0.73	1.63
Q: O	46	16	1.48	3.13	46	32	1.96	2.04
B:A:W	22	NT	2.77	6.74	24	36	2.56	2.30
B:A: O	44	56	0.49	0.50	36	30	0.60	0.68
B: I: W	22	NT	1.97	1.68	22	32	0.90	1.11
B: I: O	24	14	2.66	1.95	18	18	1.60	3.01

Table 4.9: Physiochemical analysis of soil samples collected from four major dumpsites in Thabo Mofutsanyane district, Eastern Free State, Sampled during the dry and wet season

No. of	Sample	PH	Р	K	Ca	Mg	Na	EA	As	Ca/Mg	(Ca+Mg)/k	CEC	Zn
sites	Sites	(KCl)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)		%			cmol,kg <sup>-1</sup>	(HCl)
1	H: W	7.4	51.2	446.0	3345	279.9	163.7	0.00	0.00	7.29	16.67	20.87	13.86
2	H: O	8.1	17.1	1130.3	1138	408.0	405.3	0.00	0.00	1.70	3.12	13.69	3.34
3	B: A: W	7.2	30.3	495.6	2945	364.4	145.3	0.00	0.00	4.93	13.97	19.61	13.47
4	B: A: O	7.4	2.4	349.1	2619	472.3	109.5	0.00	0.00	3.38	19.00	18.33	0.91
5	B: I: W	6.3	78.0	360.2	1525	172.9	54.4	0.00	0.00	5.38	9.81	10.20	10.75
6	B: I: O	7.2	13.5	435.4	4516	477.1	47.9	0.00	0.00	5.77	23.79	27.81	10.01
7	Q: W	6.6	13.8	459.2	3547	967.4	485.8	0.00	0.00	2.24	21.85	28.95	0.67
8	Q: O	4.6	1.7	194.4	3294	1033.1	115.2	1.00	3.70	1.95	50.14	26.93	3.43

Table 4.10: Mineral contents of the four major dump sites within the Thabo Mofutsanyane District, Eastern Free State

AS: Acid saturation, CEC: Cation exchangeable capacity (calculated), (): Results as a % of CEC

# **Extraction methods**

P-bray 1

Cations- NH<sub>4</sub>OAc



**Figure 4:** Multivariate statistical analysis of heavy metal concentration in soils using the PCA during the dry season (15 April 2014). The graph shows the sample sites and the heavy metals. The arrows represent the strength of correlation between the heavy metals and sample sites.



**Figure 5:** Multivariate statistical analysis of heavy metal concentration in soils using the PCA during the dry season (15 July 2014). The graph shows the sample sites and the heavy metals. The arrows represent the strength of correlation between the heavy metals and sample sites.



**Figure 6:** Multivariate statistical analysis of heavy metal concentration in soils using the PCA during the wet season (15 November 2014). The graph shows the sample sites and the heavy metals. The arrows represent the strength of correlation between the heavy metals and sample sites.



**Figure 7:** Multivariate statistical analysis of heavy metal concentration in soils using the PCA during the wet season (15 February 2015). The graph shows the sample sites and the heavy metals. The arrows represent the strength of correlation between the heavy metals and sample sites.



**Figure 8:** Multivariate statistical analysis of heavy metal concentration in plants using the PCA during the dry season (15 April 2014). The graph shows the sample sites and the heavy metals. The arrows represent the strength of correlation between the heavy metals and sample sites.



**Figure 9:** Multivariate statistical analysis of heavy metal concentration in plants using the PCA during the wet season (15 July 2014). The graph shows the sample sites and the heavy metals. The arrows represent the strength of correlation between the heavy metals and sample sites.



**Figure 10:** Multivariate statistical analysis of heavy metal concentration in plants using the PCA during the wet season (15 November 2014). The graph shows the sample sites and the heavy metals. The arrows represent the strength of correlation between the heavy metals and sample sites.

### Rescaled distance cluster combine



Figure 11: Dendrogram obtained by hierarchical clustering analysis of soils sampled sites during the autumn season (15 April 2014).

Harr: W; Harrismith: Within, Harr: O; Harrismith: Outer, QWA: W; Qwaqwa: within, QWA: O; Qwaqwa: outer, BTLM: A: W; Bethlehem: Active: Within, BTLM: A: O; Bethlehem: Active: outer, BTLM: IN: W; Bethlehem: Inactive: Within, BTLM: IN: O; Bethlehem: Inactive: Within

## Rescaled distance cluster combine



Figure 12: Dendrogram obtained by hierarchical clustering analysis of soil sampled sites during the winter season (15 July 2014).

### Rescaled distance cluster combine



Figure 13: Dendrogram obtained by hierarchical clustering analysis of soils sampled sites during the spring season (15 November 2014).

Harr: W; Harrismith: Within, Harr: O; Harrismith: Outer, QWA: W; Qwaqwa: within, QWA: O; Qwaqwa: outer, BTLM: A: W; Bethlehem: Active: Within, BTLM: A: O; Bethlehem: Active: outer, BTLM: IN: W; Bethlehem: Inactive: Within, BTLM: IN: O; Bethlehem: Inactive: Within

# **Rescaled distance cluster combine**

3.05E3	1144202.4
-	Harr:W - QWA:O - BTLM:A:W - BTLM:A:O - QWA:W
	BTLM:IN:W Harr:O BTLM:IN:O

14: Dendrogram obtained by hierarchical clustering analysis of soils sampled sites during the summer season (15 February 2015)

Rescaled distance cluster combine for plant samples



Figure 15: Dendrogram obtained by hierarchical clustering analysis of plants sampled sites during the autunm season (15 April 2014)

Harr: W; Harrismith: Within, Harr: O; Harrismith: Outer, QWA: W; Qwaqwa: within, QWA: O; Qwaqwa: outer, BTLM: A: W; Bethlehem: Active: Within, BTLM: A: O; Bethlehem: Active: outer, BTLM: IN: W; Bethlehem: Inactive: Within, BTLM: IN: O; Bethlehem: Inactive: Within

Rescaled distance cluster combine for plant samples



Figure 16: Dendrogram obtained by hierarchical clustering analysis of plants sampled sites during the winter season (15 July 2014)

BTLM: A: W; Bethlehem: Active: Within, BTLM: A: O; Bethlehem: Active: outer, BTLM: IN: W; Bethlehem: Inactive: Within, BTLM: IN: O; Bethlehem: Inactive: Within

Rescaled distance cluster combine for plant samples



Figure 17: Dendrogram obtained by hierarchical clustering analysis of plants sampled sites during the spring season (15 November 2014)

Rescaled distance cluster combine for soil samples



Figure 18: Dendrogram obtained by hierarchical clustering analysis of asociation of heavy metals durring elevated concentration.

### 4.4. Heavy metal identification in soil and plants based on PCA

Principal component analysis (PCA) technique was applied to infer the hypothetical source of heavy metals (natural or anthropogenic). PCA was performed by varimax rotation. Varimax rotation was employed because orthogonal rotation minimizes the number of variables with a high loading on each component and therefore facilitates the interpretation of PCA results. This technique clusters variables into groups such that variables belonging to one group are highly correlated with one another. The results of the PCA of heavy metal contents in soil for dry and wet season are shown in Figure 4 to Figure 7. Qwaqwa dumpsite had a significant correlation with loading of heavy metals during autumn and winter collection followed by Harrismith which had a selected number of heavy metal (Mn, As and Cu) loading from its dumpsite (Figure 4 and Figure 5). During the spring season, the PCA showed more heavy metal loading in Bethlehem site A inside the dumpsite, followed by Qwaqwa outside the dumpsite. During the summer season, the PCA plot showed more heavy metal loading in Qwaqwa (inside) the dumping site followed by the Bethlehem site B both inside and outside the dumpsite (Figure 7).

The study revealed heavy metal loading in plant samples during autumn and this was more pronounced in Qwaqwa (inside) dumpsite, followed by Bethlehem site B inside the dumpsite. During the winter season, heavy metals loading were more pronounced in Bethlehem site A inside the dumpsite. Heavy metals distribution or loading in the dumpsites changed drastically during the spring season. The high levels of heavy metal distributions observed in this study showed thatBethlehem site A (inside) had the highest metal concentrations in plants, followed by Qwaqwa (inside), Harrismith (inside) and Bethlehem site B (inside), respectively (Figure 10).

### 4.5. Correlation matrix

The inter-element relationship in soil matrix provides information on heavy metal sources and pathways in the geo-environment (Chandrasekaran et al., 2015). Correlation between the heavy metals and dumpsites agreed with results obtained by PCA and correlation matrix from this study. Correlation matrix was useful in confirming the correlation between heavy metals loading and dumpsites. The positive correlation confirmed that heavy metal loading is associated with the dumpsites, while the negative correlation means that metal loading is not associated with various dumpsites. To all the sites, recorded values were more than p= 0.05 and that leads to the conclusion that a test failed to reveal a statistical difference. During autumn season, a paired samples t-test failed to reveal a statistical difference between the inside and outside of the Harrismith, Qwaqwa, Bethlehem site A and site B dumpsites, with (t (10) = 0.002, p = .998,  $\alpha = .05$ ), (t (10) = 1.159, p = .2.74,  $\alpha = .05$ ), (t (10) = 0.028, p = .978,  $\alpha = .05$ ) and (t (10) = 1.324, p = .215,  $\alpha = .05$ ), respectively (Appendix 7). This suggests that heavy metal concentrations or levels might be due to same sources. When the heavy metal concentrations were elevated, there was no statistical difference between the inside and outside of the dumpsites from Harrismith, Qwaqwa, Bethlehem site A and site B dumpsites, with (t (10) = 1.091, p = .301,  $\alpha$  = .05), (t (10) = 1.621, p = .136,  $\alpha$  = .05), (t (10) = 1.032, p = .326,  $\alpha = .05$ ) and (t (10) = 1.516, p = .1.60,  $\alpha = .05$ ), respectively (appendix 8). When compared with the wet season, no noticeable changes in differences between the inside and outside were seen. During the spring season, a paired samples t-test failed to reveal a statistical difference hetween the inside and outside of the Harrismith, Qwaqwa, Bethlehem site A and site B dumpsites, with (t (9) = 1.978, p = .079,  $\alpha$  = .05), (t (10) = 1.843, p = .098,  $\alpha$ = .05), (t (9) = .523, p = .613,  $\alpha$  = .05) and (t (9) = .814, p = .437,  $\alpha$  = .05), respectively (Appendix 9). The same trend continued to the summer season, where a paired samples t-test failed to reveal a statistical difference between the inside and outside of the Harrismith, Qwaqwa, Bethlehem site A and site B dumpsites, with (t (9) = .344, p = .739,  $\alpha$  = .05), (t (9) = .479, p = .643,  $\alpha$  = .05), (t (9) = .172, p = .867,  $\alpha$  = .05) and (t (9) = 1.052, p = .320,  $\alpha$  = .05), respectively (appendix 10).

The plants followed the same trend during the autumn, winter and spring season. Autumn plant samples varied among the dumpsites but a paired samples t-test failed to reveal a statistically reliable difference between the inside and outside of the Harrismith, Qwaqwa, Bethlehem site A and site B dumpsites, with (t (9) = 1.978, p = .079,  $\alpha$  = .05), (t (9) = 1.843, p = .098,  $\alpha$  = .05), (t (9) = .523, p = .613,  $\alpha$  = .05) and (t (9) = .814, p = .437,  $\alpha$  = .05), respectively (Appendix not shown). During the winter season, a paired samples t-test also failed with confident to reveal a statistical difference between the inside and outside Bethlehem site A and site B dumpsites, with (t (4) = .1.240, p = .283,  $\alpha$  = .05) and (t (4) = .023, p = .983,  $\alpha$  = .05), respectively, (Appendix 12). This was also observe during the spring season, a paired samples t-test failed to reveal a statistical difference between the inside and outside of the Harrismith, Qwaqwa, Bethlehem site A and site B dumpsites, with (t (9) = .633, p = .543,  $\alpha$  = .05), (t (9) = .1.344, p = .212,  $\alpha$  = .05), (t (9) = .1.435, p = .1.85,  $\alpha$  = .05) and (t (9) = .845, p = .420,  $\alpha$  = .05), respectively (appendix 13).

#### 4.6. Cluster analysis

Cluster analysis (CA), clusters variables into groups such that highly related variables belong to one group. Based on information assessed from principal component analysis, hierarchical cluster analysis was performed. Four main clusters were distinguished in the dendrogram obtained from the CA performed on the analysed parameters with Ward's method and the squared Euclidean distance as a similarity measure. The summary of the cluster analysis for soil samples during the dry and wet season is shown in figures 11 to 15. During the dry season, two distinct clusters can be observed from the CA. Harrismith dumpsite showed similarity from the inside to the outside of the dumpsite. This suggested that concentration level of metals were similar inside and outside during this period. Bethlehem site A inside the dumpsite and Bethlehem site B outside the dumpsites were also similar during this period. Owaqwa outside the dumpsite showed to be the divergent site observed from the clusters. This suggests that levels were much different from the other dumpsites. This is confirmed by PCA that shows strong heavy metal loading in Qwaqwa outside the dumpsite during the autumn season (Figure 4). In winter during an increase of metal concentration in soils, Qwaqwa and Bethlehem site A inside both sites was similar. The other cluster was between Harrismith and Bethlehem site A inside both sites. During the winter period, Bethlehem site B was similar both inside and outside the dumpsite. Qwaqwa outside the dumpsite was the only divergent followed by Harrismith inside the dumpsite. During the spring only two clusters were closely similar. Harrismith inside and Bethlehem site A outside the dumpsite were similar and Bethlehem site B both inside and outside were similar. Also in summer Bethlehem site A was similar both inside and outside the dumpsite and Qwaqwa inside and Bethlehem site B inside were also similar during this period. Bethlehem site B outside the dumpsite was the more divergent site.

For plant samples, the cluster analysis for dry season is shown in figure 15 and figure 16 and only the spring season is shown in figure 17 for the wet season. Cluster analysis was conducted to identify heavy metals associated with each other and possible the sources during the elevated season and are illustrated with the dendrogram of Figure 18. During autumn season, two clusters we observed. Cluster I have Qwaqwa outside the dumpsite and Bethlehem site B inside the dumpsite, while cluster II Bethlehem site A inside and outside the dumpsite (Figure 15). In winter season, Bethlehem site A outside the dumpsite and Bethlehem site B inside the dumpsite formed a cluster. During the spring season, three clusters were observed. Clusters I, Harrismith inside the dumpsite and Bethlehem site B outside the dumpsite. Cluster II, Harrismith outside the dumpsite and Bethlehem site B inside the dumpsite. Cluster III, Qwaqwa outside the dumpsite and Bethlehem site A inside the dumpsite.

## **CHAPTER 5**

#### DISCUSSION

From the study, the concentrations of heavy metals such as ,arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), cobalt (Co) and zinc (Zn) of the soil samples from four major dumpsites in Thabo Mofutsanyane district and Eastern Free State province in South Africa were in the order, Mn> Zn> Cr> Cu> Ni> Pb> Co> As> Cd> Hg, with the ranges of 298.69-1181, 32.50-1055.82, 20.65-151.65, 11.07-61.46, 8.04.-56.99, 0.17-315, <0.001-16.66, 2.12-6.09, 0.05-6.15 and <0.001-0.32 mg/kg, respectively. Similar values from dumpsites with MSW have been extensively documented by (Ward et al., 2005; Pastor and Hernández, 2012; Wu et al., 2015). From the study, it was observed that the hydrogen in concentration (pH) of all the landfills ranged from 6.3-8.1, except in Qwaqwa ten metres outside the landfill which was 4.6. Soil pH is the foundation of understanding soil chemistry and nutrient reaction. It should be the first consideration when evaluating a soil test (Xu et al., 2016) (Table 4.6). Ali et al. (2014) conducted similar study on open dumping of municipal solid waste and its hazardous impacts on soil and vegetation diversity at waste dumping sites of Islamabad city and obtained pH ranges of 8.3-9.1 at disposal sites. This is higher than the range obtained on the current study and the difference in pH may be due to different environmental conditions and the materials at the dumpsite.

Soil organic matter is also an important soil property affecting trace metal availability, as it can either decrease or increase soil metal mobility (Yu *et al.*, 2014). The moisture and organic carbon contents are considered as the essential factor influencing the metal stability in landfill. Therefore, determination of moisture content and organic carbon in the waste from dumpsite is necessary (Xu *et al.*, 2016). From this study, the organic carbon percentage ranged from 0.30-6.74 % during the dry season. There was a decrease in the percentage of the

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organic carbon during the wet season, with the range of 0.11-3.01%. These values were below the range reported by Prechthai *et al.* (2008a) of 8.9-28.1%, during the study on quality assessment of mined MSW from an open dumpsite for recycling. The low availability of organic carbon can be explained by the high clay content (mostly >50%) of these soils and soil acidification during the oxidation period prior to the collection of these soil (Yuan *et al.*, 2015).

The presence of certain heavy metals such as Mn and iron (Fe) may also influence the mobility and bioavailability of other metals like Zn, Pb and Cd (Mukwaturi and Lin, 2015). Heavy metals in municipal solid waste (MSW) fluctuate in different seasons. For example, during the rainy season, heavy metals might become immobile as a result of hydrolysis processes (Mukwaturi and Lin, 2015). The mobility and bioavailability of heavy metals in the environment depends not only on their total concentration but also on their association with the solid phase to which they are bound (Prechthai *et al.*, 2008b). These associations are governed by a range of different physical and chemical processes such as: sorption/ desorption and precipitation/dissolution conditions (Ward *et al.*, 2005).

In relation to Zn, it was observed that there was a fluctuation in concentration values in the soil samples in respect of seasons (Table 4.1, 4.2, 4.3 and 4.4). Zinc is an essential trace element for humans, animals and higher plants (Ben Salem *et al.*, 2014). Zinc is easily adsorbed by clay and organic components and accumulates in most soils in the top horizon. Soils with a high adsorption capacity render the Zn less available for plant uptake. The mobility of Zn increases when the soil pH decreases (Chapman *et al.*, 2013). Most Zn is added during industrial activities, such as mining, coal, waste combustion and steel processing. During the dry season (autumn), Zn concentration in all dumpsites was found to be within the range of  $33.50\pm0.07-147.88\pm11.59$  mg/kg. The results of the study is comparable to 86-120 mg/kg reported by Achiba *et al.* (2010), during the study of

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accumulation and fractionation of trace metals in a Tunisian calcareous soil amended with farmyard manure and municipal solid waste compost. However, it was observed that the concentration of Zn fluctuated from one site to another especially during the spring season. Interestingly, the maximum permissible limit set by SEPA and WHO for Zn is 150 and 300 mg/kg (Thibier and Vallat, 2014) (Appendix 6). Surprisingly, it was only Qwaqwa outside the dumpsite which had values above the permissible levels of  $1733.51\pm 39.33$  mg/kg. The high levels of Zn concentration in this dumpsite might be due to the low pH level which was 4.6. Zn availability often increases under acidic soil conditions and decrease as pH increases; however this effect is not universal (Prechthai et al., 2008b). During the winter season, all the dumpsites (inside), Zn was found to be within the range of  $301.29\pm27.37-1055.82\pm130.79$ mg/kg. At the pH of 7.0, Pastor and Hernández, (2012), reported low values which ranged from 25-68 mg/kg when determining heavy metals, salts and organic residues in old solid urban waste landfills and surface waters in their discharge areas. Similar values of 1040 mg/kg were reported by He et al. (2006), when assessing in situ distributions and characteristics of heavy metals in full-scale landfill layers. The values are above the acceptable limit set by SEPA and WHO. It was also noticed that during the spring and summer season, the concentration of Zn decreased. This fluctuation in values of Zn from this study might also be influenced by the different of seasons and temperatures in soil. During the dry season (Table 4.1 & 4.2), Zn concentration was elevated, while in the wet season there was a decrease in the total concentration (Table 4.3 & 4.4). It is possible that processes such as hydrolysis may reduce the mobility of Zn under wet conditions (Mukwaturi and Lin, 2015).

The decrease continued during the summer season, Zn concentration was found to be in the range of  $31.26\pm4.15-171.35\pm4.17$  mg/kg in all the landfills, except in Bethlehem site B outside the dumpsite, which was  $3076.5\pm12.02$  mg/kg; way above the threshold. This highest

concentration might be due to organic matter or cation exchange capacity (CEC). Organic matter is a source of Zn and the organic compounds in organic matter can chelate inorganic sources of Zn and increase their availability (Xu *et al.*, 2016).

In plants, Zn is one of the essential micronutrients required for optimum crop growth. Plants take up zinc in its divalent form (Shahbazi *et al.*, 2016). At this time it still remains unclear whether this uptake is facilitated as diffusion through membranes specific for Zn ion or whether it is mediated by specific transporters (Ali *et al.*, 2014).

From the present study, Zn concentration varies from plant to plant rather than season to season. During the dry season (autumn and winter), Zn concentration to all dumpsites ranged from 40.4-127 mg/kg, while in wet season (spring and summer), Zn concentration in all dumpsites ranged from 41.1-135.5 mg/kg. These ranges are lower than those documented by (Del Río-Celestino et al., 2006; Ali et al., 2014 ) which ranged from 153.2-1253.2 mg/kg and 196.99-632.48 mg/kg, respectively. Del Río-Celestinoet al. (2006), discovered that Chenopodium album, which is a fast-growing weedy annual plant in the genus Chenopodium, accumulate Zn up to >1000 mg/kg, which was referred to as a hyperaccumulator. It is difficult to determine the uptake of Zn by plants because the process can be facilitated or interfered by other heavy metals (Kisko et al., 2015). Presence of calcium carbonate decreases the availability of Zn due to higher soil pH. The poor Zn availability in alkaline calcareous soils is precisely due to the formation of Zn carbonate (Liu et al., 2001). High levels of soil phosphorus are also commonly responsible for Zn deficiency (Kisko et al., 2015). Presence of excess amount of copper can also reduce zinc availability because the absorption of both cations is through the same mechanism, which causes interference in the uptake (Adeniyi, 1996).

Manganese (Mn) is one of the most abundant metals in soils, where it occurs as oxides and hydroxides, and it cycles through its various oxidation states (Cabral *et al.*, 2015). Manganese occurs principally as pyrolusite (MnO<sub>2</sub>) and to a lesser extent as rhodochrosite (MnCO<sub>3</sub>). From the study, Mn in all the sample sites during autumn and winter was found to be within the range of 256.73-1181.76 mg/kg (Table 4.1, 4.2 and Appendix 6). The value of Mn during winter was above maximum permissible limit set by WHO, which is 320 mg/kg. In Qwawqa outside the dumpsite, the value of Mn was 1181.76 mg/kg above the permissible limit (Table 4.1). The value of Mn from Qwaqwa dumpsite was found to be lower than that in a similar study by Ben Salem *et al.* (2014), where values of 2877 and 2040 mg/kg were obtained during summer and winter seasons. It clearly shows that the concentration of Mn varies with the seasons, especially during spring and summer. The values obtained during these seasons were found to be below the standard permissible limit (Table 4.3 & 4.4). Perhaps, the high values observed during the winter season might probably be as a result of high oxidation or the waste materials consisting of mainly ores and disinfectants (Ben Salem *et al.*, 2014).

Moreover, the maximum permissible limit of Mn in plants according to WHO is 200 mg/kg (Appendix 6). The concentration of Mn in plants during the dry season was between 48.0-197 mg/kg which was far below the permissible level. Surprisingly, in Qwaqwa within and Bethlehem site A within and Bethlehem site B outside the dumpsites, the values obtained were 416, 215 and 280 mg/kg, which are above the permissible levels. The high level of Mn obtained from these dumpsites could be attributed to the high ion concentration of 4.6. At pH below 5.0, Mn can become available to plants and may results in accumulation and become toxic to plants and possible humans (Masi *et al.*, 2014). Similar values of 46.3-442 mg/kg were also reported by Dziubanek *et al.* (2015), when they determined the contamination of food crops grown on soils with elevated heavy metals content in Silesia, Poland. During the spring season, Mn concentrations in plants from all the sample sites ranged from 36.9-187

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mg/kg, except in Bethlehem site A inside the dumpsite which was 379 mg/kg (Table 4.7). In Harrismith inside the dumpsite during summer, the *Cosmos* spp. showed Mn concentration of 405.9 mg/kg. This was the highest concentration of Mn in all the plants investigated from the dumpsites under study (Table 4.8). The high values of Mn concentrations in different medicinal plants using five medicinal species (*Bidens tripartite L., Leonurus cardiac L., Marrubium vulgare L., Melissa officinali., L.* and *Origanum heracleoticum L.*) from contaminated dumpsites were reported by Zheljazkov *et al.* (2008). The values ranged from 690.8-841.4 mg/kg, which was above the concentrations obtained in this study. High amounts of other nutrients and heavy metals such as copper (Cu), iron (Fe), nickel (Ni), and zinc (Zn) in soils may inhibit Mn uptake by plants and induce Mn deficiency (Zheljazkov *et al.*, 2008).

Lead (Pb) is a toxic metal and high doses of Pb can damage the nervous system, kidneys, and bones and can even be lethal (Li *et al.*, 2015). Continuous low level exposure to Pb can accumulate in the body and cause damages to vital organs (Chapman *et al.*, 2013). Individuals may be exposed to lead through several sources, such as the use of lead-glazed pottery, stained glass working, and target practice in poorly ventilated indoor firing ranges (Xu *et al.*, 2013). During the dry season, Pb in most sites was found to be within the range of 12.49-26.67 mg/kg which is below the permissible limits set by SEPA (85mg/kg) and WHO (35 mg/kg), except in Qwaqwa (inside and outside the dumpsite) and Bethlehem site A (inside the dumpsite) with values of 118.44, 315.79 and 230.82 mg/kg, respectively which are above the permissible limit (Table 4.1& 4.2). Masi *et al.* (2014), reported similar values of 261.0-36 mg/kg when assessing the possible reuse of MSW coming from landfill mining of old open dumpsites. The study was conducted during summer period (June and July 2009) in old closed dumpsite of Lavello (Basilicata Region-Southern Italy). Pb is pH dependent and its mobility is increased by lower pH (Di Giuseppe *et al.*, 2014). Lead can also mobilize from soil when lead-bearing soil particles run off due to surface waters during heavy rains. This

might explain higher values in Qwaqwa outside the dumpsite (Table 4.2). Subsequently, the concentration of Pb during the wet season was found to be within the acceptable limit and the range was between 9.15-76.13 mg/kg. The decrease might be due to immobilization under wet conditions (Mukwaturi and Lin, 2015).

Plants growing from four dumpsites accumulated unequal amounts of Pb (Table 4.7 and 4.8). The highest Pb concentrations were found in plants from Bethlehem site A inside the dumpsite during the spring and summer season which was 8.1 and 10.6 mg/kg, respectively. These two values are considered as being above the maximum permissible limit in plant set by WHO, which is 5.5 mg/kg (Table 4.7, 4.8 and Appendix 6). Results from this study demonstrated that although all five species accumulated lead, they exhibited differential ability to take up lead from solid media (e.g., perlite/vermiculite) and to transport and concentrate lead in their shoots. Similar results were reported by Nabulo *et al.* (2006). Using *Brassica oleraceae* (wild cabbage), observed that plants can take up to 30 mg/kg of Pb from the soil.

Cadmium (Cd) is highly toxic metal not known to have any beneficial effects for plants and animals (Smith, 2009). Cadmium is a naturally occurring metallic element found in soil, water and plants and it is more mobile in aquatic environment than other heavy metals (Vig *et al.*, 2003). Many Cadmium compounds are also believed to be carcinogenic (Li *et al.*, 2015). Cadmium enters the body via the gastrointestinal tract when eating food products grown on contaminated soils. Smokers may receive a considerable part of their cadmium intake by inhaling cigarette smoke. The adverse physiological effects commonly encountered due to high cadmium exposure include depressed growth rate, anaemia, hypertension, damage to renal tubules and poor mineralization of bones (Di Giuseppe *et al.*, 2014). The result of the study during the dry season shows that Cd was found in all the sites and the concentration values ranged between 0.04-0.28 mg/kg. Thesevalues are below the maximum permissible limit set by the SEPA and WHO, including the regional guidelines from SA agricultural soil, which is 0.8, 1.5 and 2 mg/kg, respectively (Table 4.2 and Appendix 3). It was only in Qwaqwa outside the landfill and in Bethlehem site B inside the dumpsite that Cd concentration was 6.15 and 2.82 mg/kg, respectively. These concentrations are above the permissible limit set by WHO and USEPA (Appendix 6). Similar results are also reported by (Masi *et al.*, 2014; Ben Salem *et al.*, 2014 and Ravisankar *et al.*, 2015). The increase of Cd concentration from Qwaqwa outside the dumpsite and Bethlehem site B inside the dumpsite might be the result of the pH level, which was 4.6 and 6.3 (Table 4.10), respectively. Cd becomes readily available under acidic soil conditions (Nabulo *et al.*, 2006). During the wet season, Cd shows values below the threshold ranging from 0.05-0.43 mg/kg, expect Bethlehem abandon sites outside the landfill with 2.54 mg/kg. Under wet conditions most heavy metals tends to immobilize (Mukwaturi and Lin, 2015).

Cadmium (Cd) is a trace element with unknown essential functions for plants. Cd is, however, readily absorbed by plant roots and translocated to above-ground parts (Nabulo *et al.*, 2006). Cadmium concentrations (dry weight-based) are typically higher in the plant leaves than in fruits or storage organs (Ali *et al.*, 2014). Plants showed different concentrations of Cd in their tissues, this might be due the immobilization of Cd under wet conditions or as the results of Zn and Pb which can interfere with the uptake of Cd by plants (Mukwaturi and Lin, 2015). In all the dumpsites under study, Cd concentration in plants during the wet season ranged from 0.1-0.8 mg/kg.

The highest concentrations of Cd to all the sites under study in plants were 24, 25 and 36 mg/kg. The values are lower than those reported in the review study of Ullah *et al.* (2015).

The uptake of Cd by plant increases proportionally to increasing soil Cd, when soil contains substantial concentration of  $Cd^2$ + salts (Masi *et al.*, 2014).

Chromium (Cr) is naturally abundant in the environment and found in varying concentrations in air, soil, water and biological matter (Kumpiene et al., 2008). It is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, FeCr<sub>2</sub>O<sub>4</sub>. The result of Cr concentration during the dry season (autumn) in all the sample sites was found to be in the ranged of 9.76-60.16 mg/kg. The regional permissible limit for Cr in South Africa and the United State of America is 80 and 1500 mg/kg, respectively (Appendix 3). In Qwaqwa outside the dumping site, Cr was 119.06 mg/kg. The value exceeds the maximum permissible limit set by SEPA and WHO which is 50 mg/kg. In table 4.2, the concentrations of chromium in the soil were in the range of 20.65-84.13 mg/kg. According to the regional maximum guidelines of SA and USA the standard limit is (80 mg/kg), while the SEPA and WHO limit is 100 mg/kg (Appendix 6). The only site where the concentration of Cr was found to be above the permissible limit with a concentration value of 113.46 mg/kg was in Qwaqwa outside the dumpsite. Similar findings were observed on the work of Ali et al. (2014). There were no major changes in concentration levels of Cr during the spring season. Cr concentrations ranged from 20.52-86.42 mg/kg below the maximum permissible limits. Interestingly, in Qwaqwa outside the dumpsite, similar to autumn and winter, Cr was 151.1 mg/kg. The same trend was seen during the summer season, where all the dumpsites, Cr concentrations ranged from 28.32-88.07 mg/kg. The values are within the acceptable maximum permissible limits. Notably, in Qwaqwa inside the dumpsite, Cr was 147.8 mg/kg. The value is above the permissible limit. The higher values of Cr observed in Qwaqwa may be as a result of lower pH. Chromium mobility is decreased by adsorption to clays and oxide

minerals below pH 5 and low solubility above pH 5 due to the formation of  $Cr(OH)_3(s)$  (Esmaeili *et al.*, 2014).

Chromium compounds are highly toxic to plants and are detrimental to their growth and development. Although some crops are not affected by low Cr concentration (Hajar *et al.*, 2014). Cr is toxic to most higher plants at 100  $\mu$ Mkg<sup>-1</sup>/ dry weight (Dube *et al.*, 2003). During the spring season, Cr concentration in plants ranged from 4.0-34.7 mg/kg, while in summer it ranged from 2.3-31.5 mg/kg. The highest concentration of Cr was obtained in Qwaqwa inside the dumpsite. Recent studies (Dube *et al.*, 2003; Zupančič *et al.*, 2009; UdDin *et al.*, 2015) also reported similar findings. All the concentrations observed in plants were above the maximum permissible limit set by USEPA and WHO, which is 1.30 and 1.5 mg/kg, respectively. The pathway of Cr(VI) transport is an active mechanism involving carriers of essential anions such as sulphate (Harborne, 1977). Fe, S and P are known also to compete with Cr for carrier binding (Dube *et al.*, 2003).

Copper (Cu) is the third most used metal in the world (Karim *et al.*, 2014). Copper is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin (Bou Kheir *et al.*, 2014). In plants, Cu is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage and stomach and intestinal irritation (Gebrekidan *et al.*, 2013). Cu's interaction with the environment is complex, research shows that most Cu introduced into the environment rapidly becomes stable and results in a form which does not pose a risk to the environment. In fact, unlike some man-made materials, Cu is not magnified in the body or bio-accumulated in the food chain. In the soil, Cu strongly complexes to the organic implying that only a small fraction of copper will be found in solution as ionic copper, Cu(II). The result of Cu during the dry

season in all sites was found to be in the range of 8.01-37.03 mg/kg. The permissible limit of Cu is not yet clear. Environmental protection agencies have not established a safe limit for Cu in the environment. According to the current information this falls within the maximum permissible limit set by SEPA and WHO, which is 50 and 40 mg/kg (Wenclawiak, 2009). In Qwaqwa outside the dumpsite, value of Cu was 62.27 mg/kg (Table 4.1). It is noteworthy that this value is still within the tolerance range. Table 4.2 shows similar results, Cu being above the permissible limits in Qwaqwa dumpsite (inside and outside) and Bethlehem site B inside the dumpsite, having values ranging from 61.42, 75.04 and 218.89 mg/kg, respectively. Higher concentrations in these dumpsites may be attributed to lower pH level. The solubility of Cu is drastically increased at pH 5.5, which is rather close to the ideal farmland pH of 6.0–6.5 (Kumpiene et al., 2008). The mobility of Cu is related to the pH of the soil; the lower the pH, the more mobile the Cu will be (Di Giuseppe et al., 2014). The values from this study are higher than 9.46 µgg<sup>-1</sup> reported by Ali et al. (2014). High levels of Cu in Bethlehem site A within might be the result of the pH which is 7.2. The mobility and bioavailability of Cu depends largely on the pH level and less on the organic matter and soil texture (Glatstein and Francisca, 2015). Similar trends are seen during the wet season. Cu is only higher from the sites that have the acidic or slightly acidic conditions (Table 4.3 & 4.4). The abundance of Cu observed in this study revealed that the dumpsites under study were acidic and that the binding capacity of Cu to solid waste (SW) is weak, leading to easy leaching.

In plants, Cu concentration to all the plants ranged from 6.46-34.0 mg/kg. Metal concentrations in plants vary with plant species (Anjos *et al.*, 2012). Under normal growing conditions, plants can potentially accumulate certain metal ions at an higher magnitude greater than the surrounding medium (UdDin *et al.*, 2015). Cu in plants from the dumpsites during the dry and wet season ranged from 6.46-34.0 mg/kg. All the dumpsites had Cu 67

concentration above 10 mg/kg, except in Bethlehem site A which was 6.46 and 6.08 mg/kg during the dry season. During the spring season, Cu concentration in Bethlehem site A outside the dumpsite was 9.60 mg/kg. The *Cosmos* species during the summer season, Harrismith dumpsite (outside) also accumulated low amounts of Cu, which was 8.5 mg/kg. The permissible limit set by USEPA and WHO in plants is 10 mg/kg. The combination of elevated soil pH and high organic matter in the study site may have played a role in the limited plant availability of heavy metals in the soil, resulting in low plant uptake of these metals (Yoon *et al.*, 2006). The lower uptake of Cu by plants both inside and outside the dumpsites in this study gave an indication that ten meters away from the dumpsite soil conditions are not different from the inside. However, no significant correlations were found between metal concentrations and soil pH. Plant roots appear to absorb Zn and Cu by the same mechanism. This causes interference in the uptake of one when the other is in excess in the root zone (Prechthai *et al.*, 2008a).

Mercury (Hg) belongs to same group of the periodic table with Zn and Cd. Hg is usually recovered as a by-product of ore processing (Smith, 2009). Coal combustion is a major source of Hg contamination. Releases from manometers at pressure measuring stations along gas/oil pipelines also contribute to Hg contamination. After release to the environment, Hg usually exists in mercuric (Hg<sup>2+</sup>), mercurous (Hg2<sup>2+</sup>), elemental (Hg<sup>o</sup>), or alkylated form (methyl/ethyl mercury) (Sultana *et al.*, 2015). Mercury is most toxic in its alkylated forms which are soluble in water and volatile in air (Sultana *et al.*, 2015). Mercury is associated with kidney damage (Chen *et al.*, 2015). During the dry season, Hg in all the sites was found to be in the range of 0.08-0.32 mg/kg. These values are below the maximum permissible limit set by WHO, which is 0.8 mg/kg. The concentration level of Hg during the wet season did not change. It was only in Qwaqwa inside the dumpsite where Hg was 2.54 mg/kg. This study has a solution is a low of the season of the during the tet al. (2011) of 31.78-129.8 mg/kg. This study has a solution is a major source of the season did not change. It was only in Qwaqwa inside tet al. (2011) of 31.78-129.8 mg/kg. This study has a solution of the during the tet al. (2011) of 31.78-129.8 mg/kg.

shown that many industrial companies around the Eastern Free State don't process or dispose things from the dumpsites associated with Hg.

Arsenate (As) and other anionic forms of arsenic behave as chelates and can precipitate when metal cations are present (Martin *et al.*, 2015). Metal arsenate complexes are stable only under certain conditions. Arsenic mobility increases as pH increases (Kumpiene *et al.*, 2008). Many As compounds adsorb strongly to soils, therefore, they are transported only over short distances in groundwater and surface water (Ahemad *et al.*, 2014). Arsenic is associated with skin damage, increased risk of cancer, and problems with circulatory system (Higashidani *et al.*, 2014). The results from this study during the dry season (autumn and winter), showed that As range between 2.12-6.81 mg/kg (Table 4.1 & 4.2). In spring and summer, As was even lower ranging between 1.42-5.76 mg/kg. There were no notable differences of concentrations of As between the inside and the outside of the dumpsites. However, during the wet season As values was observed to be lower both inside and outside the dumpsites indicating possible leaching of As into dipper layers and thus affecting the ground water. There is not much information on the health and environmental effects of As in the literature. Prolonged exposure to As may however have negative effects on health of humans and animals (Martin *et al.*, 2015).

Cobalt is essential for the proper functioning of all body cells, particularly those involved in the bone marrow, the nervous system, and the gastro-intestinal system. It is also essential for the formation of red blood cells as well as for a normal growth rate in children (Pourret *et al.*, 2015). Although it is essential, the body requires only a minute quantity of this element and therefore true dietary deficiency in humans is rare and mainly associated with strict vegetarian diets (Pourret *et al.*, 2015). Toxicity is not common but may lead to cardiovascular effects, bronchial symptoms, emphysema and fibrosis. Cobalt is mainly present in horizons rich in organic matter and clays and it is immobile in alkaline conditions, but leaches through the soil profile under acid conditions (Smith, 2009). Cobalt concentrations in soils are also related to the clay content and organic material. The maximum permissible limit of Co is still not clear. According to the SA (1991 and 1997) regional guidelines for maximum permissible trace element concentrations in agricultural soil, the permissible maximum limit of Co is 20 mg/kg (Appendix3). In all the sites during the dry season Co had values below the permissible limit. Interestingly, Qwaqwa outside the dumpsite and Bethlehem site B inside the dumpsite, Co was 31.20 and 23.58 mg/kg. Statistical assessment of heavy metal pollution in sediments of east coast of Tamilnadu using Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF) by Ravisankar et al. (2015) reported similar values which ranged between 23.9-44.0 mg/kg. During the wet season, Co in all the dumpsite was within the threshold set by different environmental protection agencies. Co is considered as being highly immobile especially under alkaline and water conditions (Martin et al., 2015). Observable enough, during the four different seasons, Co is higher in Qwaqwa dumpsite which is having a pH 4.6 and lesser to the other sites which are more or less alkaline. Plant uptake of Co is a function of the Co concentration in the soil solution and it is readily taken up. Although only a few plant species accumulate significant cobalt levels to cause severe phytotoxicity. Iron and manganese oxides are known to have an affinity for selective Co adsorption (Grzybek et al., 2015). Tested during the wet season, Co in plants ranged from 0.4-6.0 mg/kg (Table 4.7 and 4.8).

Nickel (Ni) is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. It is highest in soils with high clay content (Cabral *et al.*, 2015). It is a phytotoxic element with no essential role in plant metabolism and when present in soluble form, it is readily absorbed by plant roots (Gebrekidan *et al.*, 2013). Nickel is not known to accumulate

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in plants or animals and as a result Ni has not been found to bio-magnify in the food chain (Eijsackers et al., 2014). The most common adverse health effect of nickel in humans is an allergic reaction when articles containing it are in direct contact with the skin, when it is ingested with food and water, or inhaled in dust. Further contact with it will produce a negative reaction to human sensitive to nickel. The most common reaction is a skin rash at the site of contact. Less frequently, allergic people have asthma attacks following exposure to nickel (Gebrekidan et al., 2013). From the current study, Ni during the dry season in all the sample sites was found to be in the range of 8.94-37.28 mg/kg. The values were below the maximum permissible limit set by SEPA, WHO and SA regional maximum guidelines, which are 40, 50 and 50 mg/kg, respectively. Similar trends were observed during the dry season. Ni was in the range of 8.04-56.99 mg/kg, which is considered as being in the acceptable limits according to most environmental protection agencies. Like the Co, Ni is also influenced by the pH and alkaline conditions. In acidic conditions Ni becomes mobile and readily available and in alkaline conditions it becomes immobile (Ben Salem et al., 2014). Qwaqwa dumpsite had high Ni values than all the dumpsites under the current study. There was no constant pattern of Mn values across the dumpsites under study. Masi et al. (2014), assessed the possible reuse of MSW coming from landfill mining of old open dumpsites reported values of up to 205.5 mg/kg. The high values were expected due to the mining waste. Ben Salem et al. (2014) on seasonal variation of heavy metals in water, sediment and roach tissues in a landfill draining system pond (Etueffont, France) reported 45.61 mg/kg for summer and 38.73 mg/kg for autumn. The data for Ni concentration in plants was not available.

The concentrations of trace metals, such as calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P) and zinc (Zn) in soil of four major dumpsites in Thabo Mofutsanyane District, Eastern Free State, South Africa decreased in the following order, Ca> Mg> K> Na> P> Zn, respectively (Table 4.6). In the case of Mg in table 4.6, higher values might be the

results of organic matter or cation exchange capacity rather than the pH. According to Xu et al. (2016), low soil pH decreases Mg availability and high soil pH increases availability. This statement contradicts the findings from Qwaqwa outside the dumpsite, where the pH was 4.6 and the value for Mg is 1033.1 mg/kg, higher than all the sites (Table 4.6). This observation is also in contrast with other works done by (Ravisankar et al., 2015; Chai et al., 2015). Pan et al. (2015), discovered that most of Mg concentrations are the results of withered bed rock materials and suspended soil sediment. Mg concentrations due to withering and other sources is also documented by Ma et al. (2015). Unlike sulphide mine sites where heavy metals are easily mobilized under acidic conditions. The pH of heavy metal contaminated sites resulting from other industrial processes is predominantly circumneutral, or less acidic, under which most of heavy metals tend to be retained in soils. Mobilization of heavy metals from such contaminated sites may or may not take place, depending on specific environmental conditions, and it is likely that release of heavy metals from contaminated soils, if any, is limited to certain periods of time when environmental conditions become favourable. This complexity makes it difficult to predict environmental risks from heavy metals based on their total amounts contained in the contaminated soils (Pastor and Hernández, 2012). Carbon exchange capacity (CEC) is also another important factor in the heavy metal adsorption. As reported by most soil testing laboratories, the CEC is a calculated value that is an estimate of the soils ability to attract, retain, and exchange cation elements. It is reported in mill equivalents per 100 grams of soil (meq/100g) (Yu et al., 2014). The soil is made up of many important components such as clay being the most significant and organic matter, while a small percentage of most soil is also important for several other reasons. Soils that have a large number of negative charges on their surface, thus they attract cation elements and contribute to a higher CEC. At the same time, they also repel anion nutrients ("like" charges) (Sakho et al., 2015). Larger CEC values indicate that a soil has a greater capacity to hold

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cations while low CEC values show that the soils hold fewer nutrients, and will likely be subject to leaching of mobile "anion" nutrients (Halvorson *et al.*, 2011). In case of Mg in this study, low CEC soils hold less Mg, while high CEC soils can hold abundant Mg. High values of Mg recorded in this study correlate with those documented by Li *et al.* (2013). The latter study indicated that as time goes on, changes in hydraulic characteristics can directly affect the barrier performance of compacted clay and an increase in the hydraulic conductivity of the impermeable layer can lead to leachate leakage in landfills. From the study, CEC values ranged from 10.20-28.95 cmol,kg<sup>-1</sup>. These values are relatively high and this might be the reason for the fluctuation of other trace metals. The other possibility may be the results of trace metals which affect the mobility and bioavailability of other trace metals. For example, high values of Ca and K may directly decrease the mobility and bioavailability of Mg in soil (Liu *et al.*, 2001). The results for Ca, Mg, K, P and Zn are summarized in Table 4.6.

Cluster analysis of four dumpsites was conducted to identify heavy metals associated with dumpsites and are illustrated with the dendrogram of Figure 11-17. The clusters are grouped and changed according to the similarity in levels of heavy metal concentrations and changes as the seasons change. This might be due to seasonal variations which affect the mobility of other heavy metals (Ben Salem *et al.*, 2014). The changes observed in the group are summarized in (Figure 11-17). Cluster analysis was conducted to identify heavy metals associated with each other and possible the sources during the elevated season and are illustrated with the dendrogram of Figure 18. The elements were hierarchically clustered based on the total metal concentrations in the sediments and two distinct clusters were identified. Group I contained Mn and Zn which may be geochemically associated in nature due to a heterogeneous source or they were extremely mobile during this period. Group II contained Co, As, Cd, Hg, Al and Ni, these elements probably came from a common anthropogenic source or elevation of concentrations was due to chemical or physical

processes in soil. The heterogeneity nature of the MSW might be the source of association illustrated by the cluster analysis. Pb and Cu were closely clustered, that meant their elevated concentrations may be the results of anthropogenic processes. The results of cluster analysis (CA) were consistent with those of principal component analysis, which indicated that the trace elements were derived from the same source of origin.

In addition, dumpsites may contain used electronic units which consist of unprocessed heavy metals that will eventually go into the soil as solution with time. Nevertheless, the accurateness of the lifetime distribution and product sales data are crucial to forecasting the velocity of the changes in material composition and plastic waste volumes. Furthermore, changes in the material utilized by Original Equipment Manufacturer Services (OEMS) have a significant influence on waste composition, whereas the point in time when these changes will influence the waste composition depends on the product lifetime distribution. Therefore, the reliability of forecasting waste composition should always be based on function of the lifetime distribution of the products (Peeters *et al.*, 2015).

High concentrations of heavy metals observed in Qwaqwa dumpsites may be the result of many industries around the area dumping waste into the environment. In contrast to others dumpsites, they have relatively few number of companies and it can be assumed that deposition of household solid wastes are associated with high population in Qwaqwa. The age of the dumpsites may probably be another reason for high concentration of heavy metals, since it is the oldest dumpsites amongst the four dumpsites. It was also observed from the survey that in Qwaqwa waste materials were not categorically dumped, waste materials such as plastics, gasoline containers are dumped at the site and there is no alternate place for disposal of such waste. The soils are often dry around Qwaqwa with nutrients deficient and fast-draining. Without any precipitation for a long time, the soil can remain acidic under the

elevated pH, thus leading to mobility of certain heavy metals in the soil (Pan *et al.*, 2015). This was evident in this study at QwaQwa during winter season.

The low values of certain heavy metals such as Hg observed from different dumpsites might be due to the absence of waste from companies that have been noted to produce Hg as byproducts. These include the absence of mining companies and heavy food processing production companies. Dumpsites from the areas under study were found to dispose about 75 percent of plastic wastes materials, followed by 15 percent of beverages containers. For instance, where high amounts of heavy metals were noticed in Bethlehem, this was attributed to companies discharging untreated waste into the dumpsites. The close association observed between Harrismith and Qwaqwa dumpsites might be due to similar waste materials discharged into the environment. The slight differences in Bethlehem dumpsites might be as a result of improved recycling of waste and proper monitoring of waste to be dumped at the site by various companies.

# **CHAPTER 6**

## CONCLUSION AND RECOMMENDATIONS

Pollution of the environment is becoming a challenge to most developing countries such as South Africa. The uncontrolled disposal of waste (solid and liquid) into the environment has serious implication to the health of humans, animals and plants. Evaluating the level of heavy and trace metals concentration from different dumpsites has provided adequate information on the level of contamination in our environment. The study showed that As, Co, Cr, Cu, Mn, Ni, Pb and Zn are abundant in municipal waste sites. High concentrations of heavy metals from the dumpsites indicated high levels of soil contaminations. Heavy metals in plants collected from the dumpsites varied from plant to plant and also from site to site under different environmental conditions. From the current study, heavy metal concentrations in soil and plants from the dumpsites were not significantly different from that in the soil and plants ten meters away from it. The study has also shown that the heavy metal concentrations from the dumpsites may become evenly distributed in the soil within the dumpsites and surrounding soils. The question is how far can heavy metal leachates travel from the soil? The Qwaqwa dumpsite had the highest concentrations of heavy metals both within and outside the dumpsites. Cr, Mn, Cd and Pb concentrations in Qwaqwa dumpsite were much higher than those of other dumpsites, especially Pb concentration outside the dumpsite. Free State is a dry area, making it easy for heavy metals suspended on soil sediments to travel a long distance and in some cases of higher values outside the dumpsites than the inside may be due to erosion of such sediments from the dumpsites. The study has also shown that seasonal variation plays a big role in metal concentrations in soils. Municipal solid waste management services in most of the countries come as a third priority in municipal commitments, after water supply and sanitation. This is the case in South Africa. Open waste dumpsites under study are located in the residential area and they are extremely under scrutiny due to the latest health incidents and communities protesting against such disposal sites. However they are under pressure from their own legislation to move away from the current disposal practices of open dumping to sanitary land filling. Such a change is unlikely to occur in the nearest future due to limitations on finance, shortage of technical resources and lack of institutional arrangements. The main environmental problem associated with the disposal sites is the potential risk posed to the soil. Since the waste was disposed directly onto surface of soil, a number of contaminants including heavy metals readily penetrate and eventually they contaminate the soil and affect vegetation diversity of the area.

## Recommendations

- Most studies have documented the estimated rate of degradation of municipal solid waste in sanitary closed dumpsites; no studies have documented it on open dumpsites. Hence, there is a need for the long term studies to understand the dynamics of MSW in open dumpsites if the land has to be rehabilitated in the near future.
- In this study, heavy metal concentrations or leachates were quantified up to ten meters away from the dumpsite, where there was a positive correlation between heavy metal concentrations in the dumpsites and soil outside the dumpsites, which suggested that they were from the same source. The study has revealed the possibilities of heavy metals traveling a long distance via underground water. This necessitates the need to increase the distance in order to find out the traveling distance of leachates from the soil.

- The outside of Qwaqwa dumpsite had higher heavy metals concentrations than the inside. The author suggested that it might have been the result of the slope of which was nearly steep, thus contributing to fast travel of leachates in soil sediments. How big is the role of the slope on the metal traveling distance, which needs more investigation.
- > And to assess the vegetation cover change, following environmental rehabilitation

# **CHAPTER 7**

#### REFERENCES

- Achiba, W.B., Lakhdar, A., Gabteni, N., Laing, G.D., Verloo, M., Boeckx, P., Van Cleemput, O., Jedidi, N. & Gallali, T. 2010. Accumulation and fractionation of trace metals in a Tunisian calcareous soil amended with farmyard manure and municipal solid waste compost. J. Hazard. Mater. 176, 99–108. doi:10.1016/j.jhazmat.2009.11.004
- Acosta, J.A., Jansen, B., Kalbitz, K., Faz, A. & Martínez-Martínez, S. 2011. Salinity increases mobility of heavy metals in soils. Chemosphere 85, 1318–1324. doi:10.1016/j.chemosphere.2011.07.046
- Adeniyi, A.A. 1996. Determination of cadmium, copper, iron, lead, manganese, and zinc in water leaf (Talinum triangulare) in dumpsites. Environ. Int. 22, 259–262. doi:10.1016/0160-4120(96)00011-6
- Ahemad, M. 2014. Remediation of metalliferous soils through the heavy metal resistant plant growth promoting bacteria: Paradigms and prospects. Arab. J. Chem. doi:10.1016/j.arabjc.2014.11.020
- Ali, S.M., Pervaiz, A., Afzal, B., Hamid, N. & Yasmin, A. 2014. Open dumping of municipal solid waste and its hazardous impacts on soil and vegetation diversity at waste dumping sites of Islamabad city. J. King Saud Univ. - Sci. 26, 59–65. doi:10.1016/j.jksus.2013.08.003
- Anjos, C., Magalhães, M.C.F. & Abreu, M.M. 2012. Metal (Al, Mn, Pb and Zn) soils extractable reagents for available fraction assessment: Comparison using plants, and dry and moist soils from the Braçal abandoned lead mine area, Portugal. J. Geochem. Explor., reclamation of mining site soils 113, 45–55. doi:10.1016/j.gexplo.2011.07.004
- Backnäs, S., Laine-Kaulio, H. & Kløve, B. 2012. Phosphorus forms and related soil chemistry in preferential flowpaths and the soil matrix of a forested podzolic till soil profile. Geoderma 189–190, 50–64. doi:10.1016/j.geoderma.2012.04.016
- Barbieri, M., Sappa, G., Vitale, S., Parisse, B. & Battistel, M. 2014. Soil control of trace metals concentrations in landfills: A case study of the largest landfill in Europe, Malagrotta, Rome. J. Geochem. Explor. 143, 146–154. doi:10.1016/j.gexplo.2014.04.001
- Bdour, A., Altrabsheh, B., Hadadin, N. & Al-Shareif, M. 2007. Assessment of medical wastes management practice: A case study of the northern part of Jordan. Waste Manag. 27, 746–759. doi:10.1016/j.wasman.2006.03.004
- Ben Salem, Z., Capelli, N., Laffray, X., Elise, G., Ayadi, H. & Aleya, L. 2014. Seasonal variation of heavy metals in water, sediment and roach tissues in a landfill draining system pond (Etueffont, France). Ecol. Eng. 69, 25–37. doi:10.1016/j.ecoleng.2014.03.072

- Bochicchio, R., Sofo, A., Terzano, R., Gattullo, C.E., Amato, M. & Scopa, A. 2015. Root architecture and morphometric analysis of Arabidopsis thaliana grown in Cd/Cu/Zngradient agar dishes: A new screening technique for studying plant response to metals. Plant Physiol. Biochem. 91, 20–27. doi:10.1016/j.plaphy.2015.03.010
- Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., Kirkham, M.B. & Scheckel, K. 2014. Remediation of heavy metal (loid)s contaminated soils To mobilize or to immobilize? J. Hazard. Mater. 266, 141–166. doi:10.1016/j.jhazmat.2013.12.018
- Boshoff, M., De Jonge, M., Scheifler, R. & Bervoets, L. 2014. Predicting As, Cd, Cu, Pb and Zn levels in grasses (Agrostis sp. and Poa sp.) and stinging nettle (Urtica dioica) applying soil-plant transfer models. Sci. Total Environ. 493, 862-871. doi:10.1016/j.scitotenv.2014.06.076
- Bou Kheir, R., Shomar, B., Greve, M.B. & Greve, M.H. 2014. On the quantitative relationships between environmental parameters and heavy metals pollution in Mediterranean soils using GIS regression-trees: The case study of Lebanon. J. Geochem. Explor., Soil Pollution and Reclamation: Advances in Data, Experiments and Application 147, Part B, 250–259. doi:10.1016/j.gexplo.2014.05.015
- Cabral Pinto, M.M.S., Ferreira da Silva, E., Silva, M.M.V.G. & Melo-Gonçalves, P. 2015. Heavy metals of Santiago Island (Cape Verde) top soils: Estimated Background Value maps and environmental risk assessment. J. Afr. Earth Sci. 101, 162–176. doi:10.1016/j.jafrearsci.2014.09.011
- Capra, G.F., Coppola, E., Odierna, P., Grilli, E., Vacca, S. & Buondonno, A. 2014. Occurrence and distribution of key potentially toxic elements (PTEs) in agricultural soils: a paradigmatic case study in an area affected by illegal landfills. J. Geochem. Explor. 145, 169–180. doi:10.1016/j.gexplo.2014.06.007
- Chai, Y., Guo, J., Chai, S., Cai, J., Xue, L. & Zhang, Q. 2015. Source identification of eight heavy metals in grassland soils by multivariate analysis from the Baicheng–Songyuan area, Jilin Province, Northeast China. Chemosphere 134, 67–75. doi:10.1016/j.chemosphere.2015.04.008
- Chandrasekaran, A., Ravisankar, R., Harikrishnan, N., Satapathy, K.K., Prasad, M.V.R.& Kanagasabapathy, K.V. 2015. Multivariate statistical analysis of heavy metal concentration in soils of Yelagiri Hills, Tamilnadu, India – Spectroscopical approach. Spectrochim. Acta. A. Mol. Biomol. Spectrosc. 137, 589–600. doi:10.1016/j.saa.2014.08.093
- Chapman, E.E.V., Dave, G.& Murimboh, J.D. 2013. A review of metal (Pb and Zn) sensitive and pH tolerant bioassay organisms for risk screening of metal-contaminated acidic soils. Environ. Pollut. 179, 326–342. doi:10.1016/j.envpol.2013.04.027
- Chen, H., Teng, Y., Lu, S., Wang, Y. & Wang, J. 2015. Contamination features and health risk of soil heavy metals in China. Sci. Total Environ. 512–513, 143–153. doi:10.1016/j.scitotenv.2015.01.025

- Chen, Z., D'Alfonso, A.J., Weyland, M., Taplin, D.J., Allen, L.J. & Findlay, S.D. 2013. Energy dispersive X-ray analysis on an absolute scale in scanning transmission electron microscopy. Ultramicroscopy. doi:10.1016/j.ultramic.2015.05.010
- Del Río-Celestino, M., Font, R., Moreno-Rojas, R. & De Haro-Bailón, A. 2006. Uptake of lead and zinc by wild plants growing on contaminated soils. Ind. Crops Prod., 2005 Annual Meeting of the Association for the Advancement of Industrial Crops: The International Conference on Industrial Crops and Rural Development 24, 230–237. doi:10.1016/j.indcrop.2006.06.013
- Desaules, A. 2012. Critical evaluation of soil contamination assessment methods for trace metals. Sci. Total Environ. 426, 120–131. doi:10.1016/j.scitotenv.2012.03.035
- Di Giuseppe, D., Vittori Antisari, L., Ferronato, C. & Bianchini, G. 2014. New insights on mobility and bioavailability of heavy metals in soils of the Padanian alluvial plain (Ferrara Province, northern Italy). Chem. Erde - Geochem. 74, 615–623. doi:10.1016/j.chemer.2014.02.004
- Dube, B.K., Tewari, K., Chatterjee, J. & Chatterjee, C. 2003. Excess chromium alters uptake and translocation of certain nutrients in citrullus. Chemosphere 53, 1147–1153. doi:10.1016/S0045-6535(03)00570-8
- Dziubanek, G., Piekut, A., Rusin, M., Baranowska, R. & Hajok, I. 2015. Contamination of food crops grown on soils with elevated heavy metals content. Ecotoxicol. Environ. Saf. 118, 183–189. doi:10.1016/j.ecoenv.2015.04.032
- Eijsackers, H., Swartjes, F.A., van Rensburg, L. & Maboeta, M.S. 2014. The need for attuned soil quality risk assessment for non-Western humans and ecosystems, exemplified by mining areas in South Africa. Environ. Sci. Policy 44, 174–180. doi:10.1016/j.envsci.2014.07.017
- Esmaeili, A., Moore, F., Keshavarzi, B., Jaafarzadeh, N. & Kermani, M. 2014. A geochemical survey of heavy metals in agricultural and background soils of the Isfahan industrial zone, Iran. CATENA 121, 88–98. doi:10.1016/j.catena.2014.05.003
- Flyhammar, P. 1997. Estimation of heavy metal transformations in municipal solid waste. Sci. Total Environ. 198, 123–133. doi:10.1016/S0048-9697(97)05439-9
- Gebrekidan, A., Weldegebriel, Y., Hadera, A. & Van der Bruggen, B. 2013. Toxicological assessment of heavy metals accumulated in vegetables and fruits grown in Ginfel river near Sheba Tannery, Tigray, Northern Ethiopia. Ecotoxicol. Environ. Saf. 95, 171–178. doi:10.1016/j.ecoenv.2013.05.035
- Glatstein, D.A. & Francisca, F.M. 2015. Influence of pH and ionic strength on Cd, Cu and Pb removal from water by adsorption in Na-bentonite. Appl. Clay Sci. 118, 61–67. doi:10.1016/j.clay.2015.09.003
- Grzybek, G., Stelmachowski, P., Indyka, P., Inger, M., Wilk, M., Kotarba, A. &Sojka, Z. 2015. Cobalt-zinc spinel dispersed over cordierite monoliths for catalytic N2O abatement from nitric acid plants. Catal. Today, Air and Water Pollution Abatement Catalysis (AWPAC 2014) 257, Part 1, 93–97. doi:10.1016/j.cattod.2015.02.022

- Hajar, E.W.I., Sulaiman, A.Z.B. & Sakinah, A.M.M. 2014. Assessment of Heavy Metals Tolerance in Leaves, Stems and Flowers of Stevia Rebaudiana Plant. Procedia Environ. Sci., The 4th International Conference on Sustainable Future for Human Security SUSTAIN 2013 20, 386–393. doi:10.1016/j.proenv.2014.03.049
- Halvorson, J.J., Gonzalez, J.M. & Hagerman, A.E. 2011. Repeated applications of tannins and related phenolic compounds are retained by soil and affect cation exchange capacity. Soil Biol. Biochem. 43, 1139–1147. doi:10.1016/j.soilbio.2011.01.023
- Harborne, J.B. 1977. Biochemical Interaction Between Plants and Insects: Edited by J. W. Wallace and R. L. Mansell. Volume 10 in the Recent Advances in Phytochemistry series. Plenum Press New York, 1976. 425 pp. Price no. Phytochemistry 16, 1465– 1466. doi:10.1016/S0031-9422(00)88819-6
- He, P.J., Xiao, Z., Shao, L.M., Yu, J.Y. & Lee, D.J. 2006. In situ distributions and characteristics of heavy metals in full-scale landfill layers. J. Hazard. Mater. 137, 1385–1394. doi:10.1016/j.jhazmat.2006.04.033
- Karim, Z., Qureshi, B.A., Mumtaz, M. & Qureshi, S. 2014. Heavy metal content in urban soils as an indicator of anthropogenic and natural influences on landscape of Karachi—A multivariate spatio-temporal analysis. Ecol. Indic., Contemporary concepts and novel methods fostering indicator-based approach to urban complexities 42, 20–31. doi:10.1016/j.ecolind.2013.07.020
- Kiddee, P., Naidu, R., Wong, M.H., Hearn, L. & Muller, J.F. 2014. Field investigation of the quality of fresh and aged leachates from selected landfills receiving e-waste in an arid climate. Waste Manag. 34, 2292–2304. doi:10.1016/j.wasman.2014.06.018
- King, R.F., Royle, A., Putwain, P.D. & Dickinson, N.M. 2006. Changing contaminant mobility in a dredged canal sediment during a three-year phytoremediation trial. Environ. Pollut. 143, 318–326. doi:10.1016/j.envpol.2005.11.024
- Kisko, M., Bouain, N., Rouached, A., Choudhary, S.P. & Rouached, H. 2015. Molecular mechanisms of phosphate and zinc signalling crosstalk in plants: Phosphate and zinc loading into root xylem in Arabidopsis. Environ. Exp. Bot., Plant signalling mechanisms in response to the environment 114, 57–64. doi:10.1016/j.envexpbot.2014.05.013
- Kulizhskiy, S., Rodikova, A., Evseeva, N., Kvasnikova, Z. & Kashiro, M. 2014. The Components of Critical Zone (Soil and Vegetation) as Indicators of Atmospheric Pollution with Heavy Metals of the Tomsk District (Western Siberia) in the Natural Ecosystems. Procedia Earth Planet. Sci., Geochemistry of the Earth's surface GES-10 Paris France, 18-23 August, 2014. 10, 399–404. doi:10.1016/j.proeps.2014.08.071
- Kumpiene, J., Lagerkvist, A. & Maurice, C. 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. Waste Manag. 28, 215–225. doi:10.1016/j.wasman.2006.12.012

- Li, J., Jia, C., Lu, Y., Tang, S. & Shim, H. 2015. Multivariate analysis of heavy metal leaching from urban soils following simulated acid rain. Microchem. J. 122, 89–95. doi:10.1016/j.microc.2015.04.015
- Li, J., Xue, Q., Wang, P. & Liu, L. 2013. Influence of leachate pollution on mechanical properties of compacted clay: A case study on behaviors and mechanisms. Eng. Geol. 167, 128–133. doi:10.1016/j.enggeo.2013.10.013
- Li, N., Kang, Y., Pan, W., Zeng, L., Zhang, Q. & Luo, J. 2015. Concentration and transportation of heavy metals in vegetables and risk assessment of human exposure to bioaccessible heavy metals in soil near a waste-incinerator site, South China. Sci. Total Environ. 521–522, 144–151. doi:10.1016/j.scitotenv.2015.03.081
- Li, P., Lin, C., Cheng, H., Duan, X. & Lei, K. 2015. Contamination and health risks of soil heavy metals around a lead/zinc smelter in southwestern China. Ecotoxicol. Environ. Saf. 113, 391–399. doi:10.1016/j.ecoenv.2014.12.025
- Li, Z., Ma, Z., van der Kuijp, T.J., Yuan, Z. & Huang, L. 2014. A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment. Sci. Total Environ. 468–469, 843–853. doi:10.1016/j.scitotenv.2013.08.090
- Lion, G.N. & Olowoyo, J.O. 2013. Population health risk due to dietary intake of toxic heavy metals from Spinacia oleracea harvested from soils collected in and around Tshwane, South Africa. South Afr. J. Bot. 88, 178–182. doi:10.1016/j.sajb.2013.07.014
- Liu, Z.Q., Yang, J., Mu, J.J., Liang, Y.M., Wang, Y.X., Zhu, D.J., Sun, C.F. & Ye, T. 2001. Adding potasium and calcium to the dietary salt as a hypertension- preventive approach in adolescents with higher blood pressure and their family members: a single blind random-controllized trial. Am. J. Hypertens. 14, A145. doi:10.1016/S0895-7061(01)01941-0
- Long, Y.Y., Shen, D.S., Wang, H.T., Lu, W.J. & Zhao, Y. 2011. Heavy metal source analysis in municipal solid waste (MSW): Case study on Cu and Zn. J. Hazard. Mater. 186, 1082–1087. doi:10.1016/j.jhazmat.2010.11.106
- Malandrino, M., Abollino, O., Buoso, S., Giacomino, A., La Gioia, C. & Mentasti, E. 2011. Accumulation of heavy metals from contaminated soil to plants and evaluation of soil remediation by vermiculite. Chemosphere 82, 169–178. doi:10.1016/j.chemosphere.2010.10.028
- Ma, L., Teng, F.Z., Jin, L., Ke, S., Yang, W., Gu, H.O. & Brantley, S.L. 2015. Magnesium isotope fractionation during shale weathering in the Shale Hills Critical Zone Observatory: Accumulation of light Mg isotopes in soils by clay mineral transformation. Chem. Geol. 397, 37–50. doi:10.1016/j.chemgeo.2015.01.010
- Marigómez, I., Soto, M., Orbea, A., Caneio, I. & Cajaraville, M.P. 2004. Chapter 14 -Biomonitoring of environmental pollution along the Basque coast, using molecular, cellular and tissue-level biomarkers: an integrative approach, in: Collins, Á.B. and M.

(Ed.), Elsevier Oceanography Series, Oceanography and Marine Environment of the Basque Country. Elsevier, pp. 335–364.

- Martin, M., Stanchi, S., Jakeer Hossain, K.M., Imamul Huq, S.M. & Barberis, E. 2015. Potential phosphorus and arsenic mobilization from Bangladesh soils by particle dispersion. Sci. Total Environ. 536, 973–980. doi:10.1016/j.scitotenv.2015.06.008
- Masi, S., Caniani, D., Grieco, E., Lioi, D.S. & Mancini, I.M. 2014. Assessment of the possible reuse of MSW coming from landfill mining of old open dumpsites. Waste Manag. 34, 702–710. doi:10.1016/j.wasman.2013.12.013
- Meers, E., Samson, R., Tack, F.M.G., Ruttens, A., Vandegehuchte, M., Vangronsveld, J. & Verloo, M.G. 2007. Phytoavailability assessment of heavy metals in soils by single extractions and accumulation by Phaseolus vulgaris. Environ. Exp. Bot. 60, 385–396. doi:10.1016/j.envexpbot.2006.12.010
- Mukwaturi, M. & Lin, C. 2015. Mobilization of heavy metals from urban contaminated soils under water inundation conditions. J. Hazard. Mater. 285, 445–452. doi:10.1016/j.jhazmat.2014.10.020
- Nabulo, G., Oryem-Origa, H. & Diamond, M. 2006. Assessment of lead, cadmium, and zinc contamination of roadside soils, surface films, and vegetables in Kampala City, Uganda. Environ. Res. 101, 42–52. doi:10.1016/j.envres.2005.12.016
- Nazeer, S., Hashmi, M.Z. & Malik, R.N. 2014. Heavy metals distribution, risk assessment and water quality characterization by water quality index of the River Soan, Pakistan. Ecol. Indic. 43, 262–270. doi:10.1016/j.ecolind.2014.03.010
- Net, S., Delmont, A., Sempéré, R., Paluselli, A. & Ouddane, B. 2015. Reliable quantification of phthalates in environmental matrices (air, water, sludge, sediment and soil): A review. Sci. Total Environ. 515–516, 162–180. doi:10.1016/j.scitotenv.2015.02.013
- Northcott, G.L. & Jones, K.C. 2000. Experimental approaches and analytical techniques for determining organic compound bound residues in soil and sediment. Environ. Pollut. 108, 19–43. doi:10.1016/S0269-7491(99)00199-2
- Pant, P., Allen, M. & Tansel, B. 2011. Mercury contamination in the riparian zones along the East Fork Poplar Creek at Oak Ridge. Ecotoxicol. Environ. Saf. 74, 467–472. doi:10.1016/j.ecoenv.2010.10.009
- Pan, Y., Tian, S., Li, X., Sun, Y., Li, Y., Wentworth, G.R. & Wang, Y. 2015. Trace elements in particulate matter from metropolitan regions of Northern China: Sources, concentrations and size distributions. Sci. Total Environ. 537, 9–22. doi:10.1016/j.scitotenv.2015.07.060
- Pastor, J. & Hernández, A.J. 2012. Heavy metals, salts and organic residues in old solid urban waste landfills and surface waters in their discharge areas: Determinants for restoring their impact. J. Environ. Manage., Environmental Risks and Problems, Strategies to reduce them through Biotechnology and Engineering 95, Supplement, S42–S49. doi:10.1016/j.jenvman.2011.06.048

- Peeters, J.R., Vanegas, P., Kellens, K., Wang, F., Huisman, J., Dewulf, W. & Duflou, J.R. 2015. Forecasting waste compositions: A case study on plastic waste of electronic display housings. *Waste management*. Volume 46. Pages 28-39.
- Pourret, O., Lange, B., Houben, D., Colinet, G., Shutcha, M. & Faucon, M.P. 2015. Modeling of cobalt and copper speciation in metalliferous soils from Katanga (Democratic Republic of Congo). J. Geochem. Explor. 149, 87–96. doi:10.1016/j.gexplo.2014.11.011
- Prechthai, T., Parkpian, P. & Visvanathan, C. 2008a. Assessment of heavy metal contamination and its mobilization from municipal solid waste open dumping site. J. Hazard. Mater. 156, 86–94. doi:10.1016/j.jhazmat.2007.11.119
- Prechthai, T., Padmasri, M. & Visvanathan, C. 2008b. Quality assessment of mined MSW from an open dumpsite for recycling potential. Resour. Conserv. Recycl. 53, 70–78. doi:10.1016/j.resconrec.2008.09.002
- Ravisankar, R., Sivakumar, S., Chandrasekaran, A., Kanagasabapathy, K.V., Prasad, M.V.R. & Satapathy, K.K. 2015. Statistical assessment of heavy metal pollution in sediments of east coast of Tamilnadu using Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF). Appl. Radiat. Isot. 102, 42–47. doi:10.1016/j.apradiso.2015.03.018
- Remon, E., Bouchardon, J.L., Le Guédard, M., Bessoule, J.J., Conord, C. & Faure, O. 2013. Are plants useful as accumulation indicators of metal bioavailability? Environ. Pollut. 175, 1–7. doi:10.1016/j.envpol.2012.12.015
- Sakho, I., Mesnage, V., Copard, Y., Deloffre, J., Faye, G., Lafite, R. & Niang, I. 2015. A cross-section analysis of sedimentary organic matter in a mangrove ecosystem under dry climate conditions: The Somone estuary, Senegal. J. Afr. Earth Sci. 101, 220–231. doi:10.1016/j.jafrearsci.2014.09.010
- Shahbazi, Y., Ahmadi, F. & Fakhari, F. 2016. Voltammetric determination of Pb, Cd, Zn, Cu and Se in milk and dairy products collected from Iran: An emphasis on permissible limits and risk assessment of exposure to heavy metals. Food Chem. 192, 1060–1067. doi:10.1016/j.foodchem.2015.07.123
- Smith, S.R. 2009. A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge. Environ. Int. 35, 142– 156. doi:10.1016/j.envint.2008.06.009
- Sørum, L., Frandsen, F.J. & Hustad, J.E. 2003. On the fate of heavy metals in municipal solid waste combustion Part I: devolatilisation of heavy metals on the grate. Fuel 82, 2273– 2283. doi:10.1016/S0016-2361(03)00178-9
- Stutter, M.I., Shand, C.A., George, T.S., Blackwell, M.S.A., Dixon, L., Bol, R., MacKay, R.L., Richardson, A.E., Condron, L.M. & Haygarth, P.M. 2015. Land use and soil factors affecting accumulation of phosphorus species in temperate soils. Geoderma, Special issue on developments in soil organic phosphorus cycling in natural and agricultural ecosystems 257–258, 29–39. doi:10.1016/j.geoderma.2015.03.020

- Sultana, M.S., Jolly, Y.N., Yeasmin, S., Islam, A., Satter, S., Tareq, S.M., 2015. Chapter 12 -Transfer of Heavy Metals and Radionuclides from Soil to Vegetables and Plants in Bangladesh, in: Mermut, K.R.H.S.Ö.R. (Ed.), Soil Remediation and Plants. Academic Press, San Diego, pp. 331–366.
- Thibier, M. & Vallat, B. 2014. Institutions Involved in Food Safety: World Organisation for Animal Health (OIE), in: Motarjemi, Y. (Ed.), Encyclopedia of Food Safety. Academic Press, Waltham, pp. 365–368.
- USEPA. 2002. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms: Fifth Edition ; October 2002; U.S. Environmental Protection Agency Office of Water (4303T) 1200 Pennsylvania Avenue, NW Washington, DC 20460; EPA-821-R-02-012
- UdDin, I., Bano, A. & Masood, S. 2015. Chromium toxicity tolerance of *Solanum nigrum L.* and *Parthenium hysterophorus L.* plants with reference to ion pattern, antioxidation activity and root exudation. Ecotoxicol. Environ. Saf. 113, 271–278. doi:10.1016/j.ecoenv.2014.12.014
- Ullah, A., Heng, S., Munis, M.F.H., Fahad, S. & Yang, X. 2015. Phytoremediation of heavy metals assisted by plant growth promoting (PGP) bacteria: A review. Environ. Exp. Bot. 117, 28–40. doi:10.1016/j.envexpbot.2015.05.001
- Vig, K., Megharaj, M., Sethunathan, N. & Naidu1, R. 2003. Bioavailability and toxicity of cadmium to microorganisms and their activities in soil: a review. Adv. Environ. Res., Heavy Metals in Soils 8, 121–135. doi:10.1016/S1093-0191(02)00135-1
- Vystavna, Y., Rätsep, R., Klymenko, N., Drozd, O., Pidlisnyuk, V. & Klymenko, M. 2015. Comparison of soil-to-root transfer and translocation coefficients of trace elements in vines of Chardonnay and Muscat white grown in the same vineyard. Sci. Hortic. 192, 89–96. doi:10.1016/j.scienta.2015.05.019
- Ward, M.L., Bitton, G. & Townsend, T. 2005. Heavy metal binding capacity (HMBC) of municipal solid waste landfill leachates. Chemosphere 60, 206–215. doi:10.1016/j.chemosphere.2004.12.054
- Wei, B. & Yang, L. 2010. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchem. J. 94, 99–107. doi:10.1016/j.microc.2009.09.014
- Wenclawiak, M. 2009. New USEPA regulations stand to impact metal fabrication and finishing operations. Met. Finish. 107, 51–57. doi:10.1016/S0026-0576(09)80076-7
- Wu, Q., Leung, J.Y.S., Geng, X., Chen, S., Huang, X., Li, H., Huang, Z., Zhu, L., Chen, J. & Lu, Y. 2015. Heavy metal contamination of soil and water in the vicinity of an abandoned e-waste recycling site: Implications for dissemination of heavy metals. Sci. Total Environ. 506–507, 217–225. doi:10.1016/j.scitotenv.2014.10.121
- Xu, D., Zhou, P., Zhan, J., Gao, Y., Dou, C. & Sun, Q. 2013. Assessment of trace metal bioavailability in garden soils and health risks via consumption of vegetables in the

vicinity of Tongling mining area, China. Ecotoxicol. Environ. Saf. 90, 103–111. doi:10.1016/j.ecoenv.2012.12.018

- Xu, X., Shi, Z., Li, D., Rey, A., Ruan, H., Craine, J.M., Liang, J., Zhou, J. & Luo, Y. 2016. Soil properties control decomposition of soil organic carbon: Results from dataassimilation analysis. Geoderma 262, 235–242. doi:10.1016/j.geoderma.2015.08.038
- Yoon, J., Cao, X., Zhou, Q. & Ma, L.Q. 2006. Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. Sci. Total Environ. 368, 456–464. doi:10.1016/j.scitotenv.2006.01.016
- Yuan, C., Fitzpatrick, R., Mosley, L.M. & Marschner, P. 2015. Sulfate reduction in sulfuric material after re-flooding: Effectiveness of organic carbon addition and pH increase depends on soil properties. J. Hazard. Mater. 298, 138–145. doi:10.1016/j.jhazmat.2015.05.013
- Yu, H., Huang, X., Ning, J., Zhu, B. & Cheng, Y. 2014. Effect of cation exchange capacity of soil on stabilized soil strength. Soils Found. 54, 1236–1240. doi:10.1016/j.sandf.2014.11.016
- Zhang, H., He, P.J. & Shao, L.M., 2008. Implication of heavy metals distribution for a municipal solid waste management system — a case study in Shanghai. Sci. Total Environ. 402, 257–267. doi:10.1016/j.scitotenv.2008.04.047
- Zhang, Y., Mason, S., McNeill, A. & McLaughlin, M.J. 2014. Application of the diffusive gradients in thin films technique for available potassium measurement in agricultural soils: Effects of competing cations on potassium uptake by the resin gel. Anal. Chim. Acta 842, 27–34. doi:10.1016/j.aca.2014.07.023
- Zheljazkov, V.D., Jeliazkova, E.A., Kovacheva, N. & Dzhurmanski, A. 2008. Metal uptake by medicinal plant species grown in soils contaminated by a smelter. Environ. Exp. Bot. 64, 207–216. doi:10.1016/j.envexpbot.2008.07.003
- Zupančič, M., Justin, M.Z., Bukovec, P. & Šelih, V.S. 2009. Chromium in soil layers and plants on closed landfill site after landfill leachate application. Waste Manag. 29, 1860–1869. doi:10.1016/j.wasman.2008.11.013

US EPA		NYS DEC				
Soil level requiring	g clean-up	Unrestricted use* Residential us				
Copper (Cu)		270	270			
Cadmium (Cd)	70	0.43	0.86			
Chromium (Cr)	230	11	22			
Nickel (Ni)	1600	72	140			
Lead (Pb)	400	200	400			
Zinc (Zn)	23,600	1100	2200			

Appendix 1: Levels of heavy metals in soil used to guide clean-up and land use decisions (mg/kg)

\*Includes agricultural use.

Appendix 2: Ranges of concentration (mg/kg<sup>-1</sup>) of trace elements in selected regions and in South Africa (Case study)

Concent	ration ranges					
	USA	Australia and New Zeal <sup>2</sup>	Florida <sup>3</sup>	Belgium <sup>4</sup>	South Africa Total (EPA 3050)	South Africa Available (EDTA)
Cd	0.04-0.8	0.04-2	0-0.33	0.02-5.3	0.62-2.74	0.89-117
Cr	-	05-110	0.89-80.7	1.17-119	5.82-353	0.87-4.52
Ni	4.1-56.8	2-400	1.7-48.5	0.3-23	3.43-159	0.57-9.78
Pb	4-23	<2-200	0.69-42.0	0.0-132	2.99-65.8	0.93-11.9
Zn	8-126	2-180	0.89-29.6	6.1-2.08	12.0-115	0.62-6.03
Cu	38-94.9	1-190	0.22-21.9	1.7-39	2.98-117	0.84-10.6
Со	-	2-170	-	0.03-7.7	1.51-68.5	0.64-16.1

1. Holmgren *et al.* (1993) – nitric acid digestion, agricultural soils without anthropogenic contamination, 5th and 95th %tile

2. Summers & Pech (1997) - nitric acid digestion of topsoil samples

3. Ma et al. (1997) - EPA3052 microwave digestion method

4. Tack et al. (1997) - aqua regia digestion method

Appendix 3: Regional guidelines for maximum permissible trace element concentrations in agricultural soil  $(mg/kg^{-1})$ 

	South Africa 1991 <sup>1</sup>	South Africa 1997 <sup>2</sup>	Europe <sup>3</sup>	USA <sup>4</sup>	Australia & New Zealand 1 <sup>3</sup>
Cd	2	2	1-3	20	3
Cr	80	80	-	1500	50
Ni	15	50	30-75	210	60
Pb	56	6.6	50-300	150	300
Zn	185	46.5	150-300	1400	200
Cu	100	6.6	50-140	750	60
Со	20	20	-	-	-

1 Dept. Nat. Health & Pop. Dev. (1991)

2 WRC (1997)

3 McLaughlin et al. (2000)

## 4 US EPA, 1995

Appendix 4: Derived statistics and recommended limits for total element concentrations (EPA 3050 method).

	97.5th %tile concentration (mg kg <sup>-1</sup> )	Samples > Permissible 1991	Maximum Limit (%) 1997	Total Investigation level (TIL) (mg kg <sup>-1</sup> )	Total maximum threshold level (TMT) (mg kg <sup>-1</sup> )
Cd	2.7	1	1	2	3
Cr	353	26	26	80	350
Ni	159	62	20	50	150
Pb	66	5	81	56	100
Zn	115	<1	32	185	200
Cu	117	3	85	100	120
Co	69	18	18	-	-

Appendix 5: Mobility potential of heavy metals in dumpsite

Step	Condition	Mobility	
1	Ion exchange	Cd > Mn > Zn > Cu > Cr > Pb > Ni	
2	Acid dissolution	Mn>Cd>Zn>Pb>Ni>Cu>Cr	
3	Reduction reaction	Mn > Zn > Pb > Cd > Cr > Ni > Cu	
4	Oxidation reaction	Cu > Cr > Ni > Pb > Zn > Cd > Mn	
5	Insolubility	Pb > Ni > Cr > Cd > Cu > Mn > Zn	

Appendix 6: State environmental protection polices (SEPA) and world health organisation (WHO) recommended guidelines for maximum permissible limits for total element concentrations in soils and plants ( $mg/kg^{-1}$ ).

	SEPA	(soils)	WHO	(soils)	SEPA (plants)	WHO (plants)
	2008		2008			
Cd	0.8		1.50		0.02	0.3
Cr	100		100		1.30	1.5
Cu	50		40		10	10
Ni	40		50		10	20
Pb	85		32		2	5.0
Zn	300		150		-	50
Mn	-		320		-	200
As	-		-		-	1.0
Hg	-		0.8		-	-
Co	-				-	-

Where target values are specified to indicate desirable maximum levels of elements in unpolluted soils.

Intervention when remedial action is necessary.

SOURCE: Denneman and Robberse 1990 15 and Ministry of Housing, Netherland 1994 16.

\*\*\*Source: WHO (1996) 17

SOURCE: Ayers and Wetcot (1976) irrigation Water Quality Criteria 18.

Appendix 7: Summary paired-sample Test: for heavy metals to the soil samples collected during the dry season (15 April 2014)

#### **Paired Sample Test**

Paired Differences										
		95% Confidence Interval of the Difference								
Sample sites		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)	Correlation
Pair 1	Harrssmith: Within- Outer	.00473	8.05113	2.42751	-5.40409	5.41355	.002	10	.998	.999
Pair 2	Qwaqwa: Within-Outer	81.05155	232.02191	69.95724	-74.82290	236.92599	1.159	10	.274	.981
Pair 3	Bethlehem: Active: Within-Outer	.38173	45.61702	13.75405	-30.26420	31.02766	.028	10	.978	.977
Pair 4	Bethlehem: Inactive: Within-Outer	38.27936	95.90962	28.91784	-26.15359	102.71232	1.324	10	.215	.986

Appendix 8: Summary of the paired-sample Test: for heavy metals to the soil samples collected during the dry season (15 July 2014)

## Paired Sample Test

		Paired Differences								
					95% Confiden	ice Interval of the Difference				· · · · ·
Sample sites		Mean	Std. Deviatio	nStd. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)	Correlation
Pair 1	Harrssmith: Within- Outer	59.62345	181.18941	54.63066	-62.10125	181.34816	1.091	10	.301	.011
Pair 2	Qwaqwa: Within-Outer	100.44118	205.54642	61.97458	-37.64678	238.52914	1.621	10	.136	.000
Pair 3	Bethlehem: Active: Within-Outer	79.23509	254.58329	76.75975	-91.79629	250.26647	1.032	10	.326	.157
Pair 4	Bethlehem: Inactive: Within-Outer	21.01827	45.97823	13.86296	-9.87032	51.90687	1.516	10	.160	.000

Appendix 9: Summary of the paired-sample Test: for heavy metals to the soils sample collected during the wet season (15 November 2014)

	Paired Differences									
					95% Con	fidence Interval of the Difference				
Sample	sites	Mean	Std. Deviation	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)	correlation
Pair 1	Harrssmith: Within-Outer	9.45400	15.11369	4.77937	-1.35768	20.26568	1.978	9	.079	.807
Pair 2	Qwaqwa: Within-Outer	13.18600	22.62113	7.15343	-2.99618	29.36818	1.843	9	.098	.972
Pair 3	Bethlehem:Active:Within Outer	6.73300	40.67797	12.86350	-22.36627	35.83227	.523	9	.613	.622
Pair 4	Bethlehem: Inactive: Within-Outer	6.71700	26.10410	8.25484	-11.95675	25.39075	.814	9	.437	.994

## Paired Samples Test

Appendix 10: Summary of the paired-sample Test: for heavy metals to the soil samples collected during the wet season (15 February 2015)

_			Paired	Samples Test			_			
		Paired Differences								
-					95% Confidence Interval	of the Difference				
Sample	sites	Mean	Std. Deviation	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)	correlation
Pair 1	Harrssmith: Within-Outer	5.04900	56.41777	20.67859	-30.15628	38.37328	.421	9	.854	.582
Pair 2	Qwaqwa: Within-Outer	3.94300	46.00495	11.22349	-16.65982	24.24592	.543	9	.712	.823
Pair 3	Bethlehem: Active: Within Outer	.40600	2.45217	4.35658	-6.92496	5.23496	.234	9	.934	.969
Pair 4	Bethlehem: Inactive: Within-Outer	318.89000	758.60001	302.13594	-388.85114	12236.58926	1.064	9	.273	.042

Appendix 11: Summary of the paired-sample Test: for heavy metals to the plant samples collected during the dry season (15July 2014)

## Paired Samples Test

		Paired Differences								
					95% Confidence Interval of the	Difference				
Sample sites		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)	Correlation
Pair 1	Bethlehem:Active:Within Outer	51.44680	92.75725	41.48230	-63.72654	166.62014	1.240	4	.283	.789
Pair 2	Bethlehem: Inactive: Within-Outer	.38120	37.46042	16.75281	-46.13206	46.89446	.023	4	.983	.476

Appendix 12: Summary of the paired-sample Test: for heavy metals to the plant samples collected during the wet season (15 November 2014)

_				a sampies rest				_		
		Paired Differences								
					95% Confidence Interval of	he Difference				
Sample sites		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)	Correlation
Pair 1	Harrssmith: Within-Outer	223.83000	1118.28597	353.63307	-576.14359	1023.80359	.633	9	.543	.789
Pair 2	Qwaqwa: Within-Outer	847.86000	1995.22806	630.94651	-579.44017	2275.16017	1.344	9	.212	.943
Pair 3	Bethlehem: Active: Within- Outer	276.71000	609.73127	192.81396	-159.46547	712.88547	1.435	9	.185	.958
Pair 4	Bethlehem: Inactive: Within-Outer	173.06000	647.86626	204.87330	-290.39560	636.51560	.845	9	.420	.943

#### Paired Samples Test