ASSESSMENT OF SOIL AND LEACHATE HEAVY METAL CONTAMINATION AT THE WELTEVREDEN LANDFILL, POLOKWANE

by

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DECLARATION

I, Vutlhari Makhaokane Manyike declare that the mini-dissertation hereby submitted to the University of Limpopo, for the degree of Master of Science in Agriculture (Soil Science) has not been submitted previously by me for a degree at this or any other university; that it is my work in design and execution, and that all materials contained herein have been duly acknowledged.

_____ _____

Manyike VM (Miss) Date

DEDICATION

This study is dedicated to my family

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ABSTRACT

In recent times, there has been increasing environmental concern that municipal solid waste (MSW) landfills are potentially a sink of persistent heavy metal contaminants. The contamination of landfill soil by heavy metals seems to be widespread in MSW landfills. Overtime, the accumulation of heavy metals in landfill soils resulting from the disposal of municipal waste represents a threat to the environment. Despite this, the provenance of heavy metals in landfill soils, leachates and groundwater quality is rarely known with certainty and whether concentrations of the heavy metals exceed the statutory recommended thresholds for safety. Therefore, the present study was conducted to (1) assess heavy metal contamination of soil and leachates from the Weltevreden landfill site and (2) examine the spatial variability and distribution patterns of heavy metals across the landfill site using geostatistical techniques. Soil samples were collected from the landfill site and an area located 100 m away from the landfill site (reference site). Soil samples were collected at a depth of 0-30 cm using a 50 m x 50 m grid. At the nodes of the grid, landfill characteristics, including the landscape position, elevation, latitude and longitude of each sample location were recorded to analyse and map the spatial distribution of the heavy metal concentrations across the site. Collected soil samples were analysed for total concentration of arsenic (As), cadmium (Cd), lead (Pb), nickel (Ni), manganese (Mn), zinc (Zn), cobalt (Co), copper (Cu) and iron (Fe) and physicochemical properties such as soil pH, soil organic carbon (SOC) and soil texture were analysed. Leachable heavy metals in the collected soil samples at the landfill site were determined using the toxicity characteristics leaching procedure (TCLP). The extent of pollution in the landfill soil was determined using the contamination factor (CF), enrichment factor (EF), pollution load index (PLI), ecological risk factor (E_r) and ecological risk index (RI). The study also characterised the spatial structure of the soil heavy metals in the landfill site by computing semivariograms and determining their spatial distribution using the ordinary kriging (OK) geostatistical technique.

The results obtained in this study revealed that the concentration of all heavy metals in the soil was higher in the landfill site compared to the reference site. The only heavy metal which was an exception to this pattern was Fe. The results also showed that the mean concentration of As and Cd in the landfill soil was above the acceptable limits of the South African National Norms and Standards for Remediation of Contaminated

Land and Soil Quality. The correlation analysis revealed that most of the heavy metals were strongly positively correlated with each other (As, Cd, Pb, Ni, Zn and Co). The results of the different indices show moderate contamination of the landfill soil by As, Cd, Cr, Pb, Ni, Mn, Zn, Co and Cu. The PLI index shows that the landfill site is highly polluted with heavy metals (PLI>1). The calculated enrichment factors suggest an anthropogenic origin for Cd and Pb, and natural origins for As, Cr, Mn, Co and Cu. Among the analysed heavy metals, a moderate ecological risk was observed only in the case of Cd concentration in the landfill soil. Meanwhile, the other investigated heavy metals had a low ecological risk. The overall ecological risk status of the heavy metals in the landfill soils was found to be low.

Geostatistical analysis of the data revealed that Cu was characterised by a strong spatial dependence while Cd, Pb and Fe showed moderate spatial dependence and As, Cr, Ni Mn, Zn and Co were characterised by a weak spatial dependence. Copper accumulation in the soil was linked to natural factors such as soil mineralogy while As, Cr, Co, Ni, Mn and Zn accrual were linked to anthropogenic activities such as waste disposal. Iron, Pb and Cd were driven by both natural and anthropogenic factors. Based on the interpolated maps, similar spatial patterns were observed for Cd and Pb kriged maps, whereby hotspots were in the northwestern parts of the landfill site. Meanwhile, Mn, Zn and Fe were also found to exhibit similar concentration hotspots in the southwest part of the landfill. The distribution of Cr displayed high concentrations in the central part of the landfill. Similarly, As, Ni and Co showed similar distribution with the southwest parts also having high concentrations. Results from TCLP confirmed concentrations of Cd, Ni and Mn that were found to be above the South African National Norms and Standards for Remediation of Contaminated Land and Soil Quality while Zn, Co and Cu were within acceptable levels. Overall, the results show that the disposal of waste at the Weltevreden landfill site led to differences in the concentration of heavy metals. The current study has offered a better understanding of the current state and potential pollution risks as well as the spatial distribution of heavy metals in the landfill soil. It is envisaged that these findings will help landfill managers to properly manage the municipal solid waste at the Weltevreden landfill site to minimise heavy metal contamination.

Keywords: Contamination, ecological risk index, heavy metals, kriging, landfill, pollution, soil spatial variability

CHAPTER 1
GENERAL INTRODUCTION

1.1 Background

Heavy metals are introduced into the environment through natural (geogenic) as well as anthropogenic sources. Despite heavy metals being naturally occurring elements throughout the earth's crust, most environmental contamination occurs as a result of anthropogenic activities, such as the disposal of municipal solid waste (Tchounwou *et al*., 2012). Several heavy metals may be found in landfill sites due to the presence of alloys, paints, dyes, inks on paper, lamp filaments, electrical wiring batteries and reclaimed metal (Abd El-Salam and Abu-Zuid, 2015).

Municipal solid waste (MSW) refers to the complex combination of chemicals, hospital wastes, organic and inorganic materials (Muhammad *et al*., 2014). MSW mainly comprises general and hazardous waste in the form of biodegradable waste, paper, plastic, glass, metal, textile and leather (Cheng and Hu, 2010). The characteristics and composition of MSW vary significantly from one municipality to another and from country to country. The variation depends mainly on the socio-economic conditions, location, season, waste collection and disposal methods, sampling and sorting procedures (Fereja, 2021).

As a result of anthropogenic activities throughout the world, MSW is increasing daily despite much awareness (Ahmad *et al*., 2021). The burgeoning population and urbanization in municipal areas have led to a continuous increase in the generation of MSW (Zhang *et al*., 2010; Ayuba *et al*., 2013). One of the major environmental and public health problems in developing countries is the effective management of municipal solid waste (MSW) (Renou *et al*., 2008; Kassim, 2012). Among the various waste management methods (landfilling, incineration, composting, etc.), landfilling is the cheapest, easiest, and most cost-effective method. Most developing countries, such as South Africa, dispose of innocuous solid waste in landfills, with 90% of waste being disposed of there (Gonzalez-Valencia *et al*., 2016; Rasmeni and Madriya, 2019). This is because landfills are an inexpensive, simple, and economical way of managing solid waste (Boateng *et al*., 2019). In several landfills, however, the wastes are not sorted, and leachate and toxic gases are released into the environment by accident (Oyeku and Eludoyin, 2010). Consequently, unhygienic landfills are common in developing countries (i.e., close to residential buildings) and seasonal high-water table areas (Alimba *et al*., 2006).

The characteristics of the soils where landfills are located have been reported to reflect the quality of underground water through lateral movement (Aziz and Othman, 2017). Soils are imperative environmental components that support food production, crucial ecosystem services, recycling of essential nutrients and influence human well-being. Soil quality is thus considered a key element of ecosystem function and hence plays an important role when deciding the method of solid waste disposal (Alghamdi *et al*., 2019). Soil quality refers to the capacity of a special kind of soil to function, within natural or managed ecosystems to maintain or enhance water and air quality and support human health and habitation (Doran and Zeiss, 2000).

1.2 Problem statement

In South Africa, municipal solid waste (MSW) landfills are characterised by large ground excavations of copious amounts of waste buried and covered with soil (Sekhohola-Dlamini *et al*., 2021). In recent times, there has been increasing environmental concern that MSW landfills are potentially a sink for persistent heavy metal contaminants (Nyika *et al*., 2020; Osibote and Oputu, 2020; Oruko *et al*., 2021). This is potentiated by the continuous disposal of solid waste material in landfills which may result in heavy metal concentrations exceeding natural background levels (Kabir *et al*., 2012). Soil contamination by heavy metals is further worsened by a number of MSW landfills in South Africa operating without proper leachate collection and treatment facilities (Ololade *et al*., 2019). This is particularly true for the Weltevreden MSW landfill in Polokwane, which is the focus of this proposed study. In MSW landfills, the disposal of waste takes place directly on the soil surface, with by-products of decomposed waste subject to leaching by rainwater (Mavimbela *et al*., 2019). In the presence of infiltrating water, the leachate permeates the landfill and migrates down the landfill profile into the groundwater (Mepaiyeda *et al*., 2020). The leachate, which contains various types of toxic chemicals, including organic and inorganic substances (heavy metals) released during the biodegradation of waste contaminates the surrounding natural ecosystems. Heavy metal contamination poses a severe threat to environmental quality as it affects adjacent receptors to the landfill including surrounding vegetation, and soil and also impairs receiving surface and groundwater resources (Parth *et al*., 2011; Nyika and Onyari, 2019). Heavy metal pollution generated by landfill leachate has become increasingly concerning because of the serious implications for human health (Boateng *et al*., 2019).

1.3 Rationale

Contaminated sites contain a complex mixture of metals, which creates a myriad of interactions that influence metal bioavailability (Gadd, 2005). Knowledge gaps exist in our understanding of the site conditions that govern the possible landscape pathways that lead to heavy metal contamination in landfills. The most important physicochemical soil properties controlling heavy metal contamination in landfills are less known. Ultimately, any form of contaminated landfill management will be practicable only if the threshold concentrations of heavy metals in landfills are thoroughly understood. The soil is the interface for precipitation incidents, generates surface runoff and infiltration and acts as a media for leachate interflow into groundwater (Amadi, 2011; Ravindra and Mor, 2019). Understanding the quality of groundwater collected from boreholes in the vicinity of landfills is not only important for general geochemical knowledge but also vital for the management of water resources used by communities residing near the landfills (Vaverková and Adamcová, 2015; Mepaiyeda *et al*., 2020).

1.4 Purpose of the study

1.4.1 Aim

The aim of the study was to investigate heavy metal concentrations and potential contamination in soil at the Weltevreden landfill site.

1.4.2 Objectives

The objectives of the study were:

i. To assess heavy metal contamination in soils and leachates from the Weltevreden MSW landfill site.
ii. To examine the spatial variability and distribution patterns of heavy metals across the landfill site using geostatistical techniques.

1.4.3 Research questions

The project seeks to address the following research questions:

i. What are the heavy metal concentrations of soils and leachates collected from the Weltevreden MSW landfill site?
ii. How do heavy metals in the soil vary spatially across the landfill site?

CHAPTER 2

LITERATURE REVIEW

2.1 Factors to be considered when selecting a landfill site

Siting a landfill requires an extensive evaluation process to identify the best disposal location (Soltani *et al*., 2015). The landfill site selection process aims to find the most appropriate location with a minimal impact on the environment and the local population (Kharlamova *et al*., 2016). Selecting an appropriate landfill site reduces potential environmental impacts and provides a sound basis for effective management of the environment. However, the site selection process for landfills is also regarded as one of the most complex aspects of solid waste management systems since it depends on various factors. This includes environmental, financial, social and technical factors (Şener *et al*., 2010).

Environmental factors are extremely crucial since landfills may influence the bio-physicochemical characteristics of the environment and the ecology of the landfill area (Al-Anbari *et al*., 2018). Morphological characteristics such as soil texture, soil permeability and the slope of an area are considered the most widely used environmental factors (Alavi *et al*., 2013). Soil texture has a substantial effect on the amount of water that can penetrate the ground and hence it influences the ability of pollutants to move vertically into the unsaturated zone. Fine soil particles including silt and clay can decrease the relative soil permeability and can confine the movement of landfill pollutants (Lee *et al*., 2003). Highly permeable soil, such as sandy and sandy loam textures soils, are unsuitable for landfilling, while low permeability soils, including clayey and clay loam textured soils are considered suitable. Relatively low to medium permeability soil such as sandy clay is fairly suitable for landfills (Aydi *et al*., 2013; Bahrani *et al*., 2016). Demesouka *et al*. (2014) reported that clay-rich soil (possibly, more than 50% clay), high soil thickness and very low permeability soil (preferably 0.05 m/ day or less) should be considered for landfill site construction. Sandy soil should not be selected for landfill sites because of the very high porosity and high water permeability rate, which can allow landfills to contribute towards the deterioration of the quality of the water in neighbouring areas (Motlagh and Sayadi, 2015).

The slope is the measure of the rate of change of elevation of surface location and is normally expressed in percent or degree slope (Chang, 2018). Elevation and slope

are also considered the basic criteria for landfill site selection. These land attributes have an inverse relation with landfill suitability. For instance, as the degree of slope and height of elevation increases, the suitability of an area for a landfill site will decrease (Şener *et al*., 2011). Some studies have reported that areas with steep slopes will have a high risk of pollution and greater leachate migration and are potentially not suitable for dumping sites (Ebistu and Minale, 2013). The Department of Water Affairs and Forestry stipulates that steeply sloped ridges and high mountain tops should not be considered for waste disposal (DWAF, 1994). Valleys and low-lying areas which are subject to flooding should also not be considered for landfilling. Land surfaces characterized by a slope gradient that is more than 25° are not considered suitable (Güler and Yomralıoğlu, 2017), while land with a slope of less than 10° is highly suitable for landfill sites (Nas *et al*., 2010).

2.2 Types of landfills

2.2.1 Semi-controlled landfills

Semi-controlled landfills are operated landfills that are located in designated dumpsites where municipal solid waste refuse is sorted, shredded and compacted before disposal (Nanda and Berruti, 2021). The waste is then covered with a layer of soil to reduce the potential for environmental disturbances that may arise (Ambat, 2020). Semi-controlled landfills are subject to basic control mechanisms. These include the presence of an authority figure on site, control of vehicular movement and access to landfill, and basic waste handling techniques to ensure control and consolidation of the total body of wastes (Ozbay *et al*., 2021). Although semi-controlled landfills are relatively less malodorous due to topsoil cover, they are not engineered to manage leachate discharge (Narayana, 2009).

2.2.2 Sanitary landfills

A sanitary landfill is a modern engineered landfill where waste is allowed to decompose into biologically and chemically inert materials in a setting isolated from the environment (Hossain *et al*., 2011). Sanitary landfills emphasise technical aspects like siting, design, operation and long-term environmental impacts (Kamaruddin *et al*., 2017). It is constructed to ensure control of waste and avoidance of surface water through the installation of well-designed and well-constructed surface drainage. A typical sanitary landfill is composed of a baseliner, daily cover liner, leachate collection and monitoring system; landfill gas monitoring facilities and other pollution treatment

processes (Al-Fatlawi, 2015). Sanitary landfills provide the most commonly used waste disposal solution that is desired to eliminate or reduce the risk of environmental or public health hazards due to waste disposal (Gunarathne *et al*., 2020).

2.3 Production and composition of leachates

Landfill leachate is one of the major pollution problems caused by MSW landfill, which is generated by the biochemical disintegration of organic waste, surface runoff infiltration of rainfall and groundwater percolation (Białowiec, 2011; Adhikari *et al*., 2014; Keyikoglu *et al*., 2021). Generally, leachates may contain large amounts of organic matter (biodegradable, but also refractory to biodegradation), as well as ammonia-nitrogen, heavy metals, chlorinated organic and inorganic salts (He *et al*., 2019; Keyikoglu *et al*., 2021). Several complex events occur sequentially within landfills that can be categorized as physical, chemical and biological processes (Aderemi *et al*., 2011). These processes are responsible for disintegrating or transforming waste. The flow of water through the transformed waste results in pollutants from the waste material being drawn out and leached with the percolating water (Aderemi *et al*., 2011). As landfilling proceeds, leachate is formed shortly after the beginning of the process and may continue for hundreds or possibly even thousands of years (Brennan *et al*., 2016). The composition of leachates varies depending on the landfill age, climate and waste composition (Vidhya *et al*., 2010).

2.4 Factors affecting the composition of leachates in landfills

2.4.1 Landfill age

Landfill leachate is largely determined by the age of the landfill and in particular, by the phases of the landfill (Table 1). The phases include aerobic, anaerobic acid, methane fermentation and maturation phase (Kjeldsen *et al*., 2002). Young leachate is classified as less than 5 years old, while intermediate leachate is between 5-10 years old and old leachate is generated for more than ten years (Miao *et al*., 2019). During the first phase, which is usually brief, organic matter is degraded aerobically. The degradation continues anaerobically in the absence of oxygen (Bhalla *et al*., 2013). Anaerobic degradation occurs in two major fermentation phases, the acidogenic phase, which produces young, biodegradable leachate and the methanogenic phase, which produces old, stabilized leachate (Jayawardhana *et al*., 2016). Young leachate from the early acidogenic phase contains high levels of chemical oxygen demand (COD) and biological oxygen demand (BOD) (Naveen *et*

al., 2016). COD is the required amount of dissolved oxygen to complete the chemical decomposition process of the organic materials in leachate, whereas BOD is the amount of dissolved oxygen consumed by bacteria and other microorganisms while they decompose organic matter under aerobic conditions (Najafzadeh and Ghaemi, 2019). These complex organic compounds are fermented anaerobically, producing mainly soluble organic acids such as free volatile fatty acids (VFAs), amino acids and gases like hydrogen (H_2) and carbon dioxide (CO_2) (Renou *et al*., 2008). It is during this phase that the metals are more soluble due to the lower pH and the bonding with the VFAs, resulting in relatively high concentrations of Fe, Mn, Ni and Zn (Renou *et al*., 2008). Old leachate from the methanogenic phase has a lower concentration of VFAs (Naveen *et al*., 2017). This is due to their conversion into methane (CH_4) and CO_2 as gaseous end products during this second fermentation period. The decrease in VFAs results in an increase in leachate pH. A characteristic pH value for stabilised leachates is around 8 (Bhalla *et al*., 2013). Generally, metal ions are present at low concentrations due to their decreasing solubility with increasing pH, but lead (Pb) is an exception as it forms very stable complexes with humic acids (Renou *et al*., 2008).

Table 1: Composition of leachate at different ages of landfill.

Parameter	Young	Intermediate	Old
Age (years)	<5	5-10	>10
pH	<6.5	6.5-7.5	>7.5
BOD_5 (mgO_2/L)	>4000	1000-4000	<400
COD (mgO_2/L)	>10 000	4 000-10 000	<4 000
BOD_5/COD	0.5-1.0	0.1-0.5	<0.1
Organic compounds	80% volatile fatty acids	5-30% volatile fatty acids + humic and fluvic acids	Humic and fulvic acids
Heavy metals	Low-medium	Low	Low
Biodegradability	Medium	Medium	Low

Source: Adhikari and Khanal (2015)

2.4.2 Climate

The amount of rainfall and temperature in an area also affects the amount of leachate produced at landfill sites (Aziz *et al*., 2014). Precipitation increases potential infiltration in the landfill, and this leads to leachate generation. Precipitation percolates through

the waste and extracts dissolved and suspended components from the biodegrading waste through several physical and chemical reactions (Abbas *et al*., 2009). Through its influence on microbial activities, temperature affects the quality and quantity of leachate (Adhikari *et al*., 2014). Landfill temperature, a largely uncontrollable factor influencing leachate quality has been shown to fluctuate with seasonal ambient temperature variations (Dasgupta, 2013). Temperature affects bacterial growth and chemical reactions within the landfill. Each microorganism possesses an optimum growth temperature, and any deviation from that temperature will decrease growth due to enzyme deactivation and cell wall rupture. During wet and hot temperatures, bacterial growth and chemical reactions increase due to enzyme activation caused by an increase in moisture content in the landfill (Adhikari *et al*., 2014). Due to moisture availability, organic matter ferments faster during hot, wet temperatures as compared to cool, dry temperatures (Moreno, 2011). As a result, there will be large volumes of wastewater containing various contaminants. In dry cool and dry hot temperatures, landfill leachate production may be reduced due to high rates of evaporation, which lowers moisture content in the landfill. The leachate produced under these conditions is, however, highly concentrated, and therefore more toxic. The rate of biodegradation and stabilisation is slow in landfills with low moisture contents that contain more than 20% but less than 40% of water, as reported by Adhikari *et al*. (2014).

2.4.3 Waste composition

The type of waste disposed of in the landfill affects the composition of leachate generated in the landfill. In general, the composition of waste determines the extent of biological activity within landfill sites (Wimalasuriya *et al*., 2011). Various types of wastes from household, commercial, industrial, institutional, municipal services and construction debris have different types of organic and inorganic materials available in different amounts as shown in Figure 1 (Moreno, 2011). Organic materials are degradable, especially materials like those found in kitchen waste, garden waste, and crop and animal residues, whereas inorganic materials are not degradable, and these include materials like plastics, glass, and metals (Jain *et al*., 2015). The higher the content of organic materials in the landfill, the more important the biological process (Adhikari and Khanal, 2015). In a study by Moreno (2011), large amounts of paper disposed of at the landfill led to a decrease in the waste decomposition process, decreasing the amount of leachate generated since the paper is resistant to microbial

decomposition. Hazardous wastes from residential, industrial, commercial, and institutional sources contribute to toxic landfill leachates (Jang and Townsend, 2003).

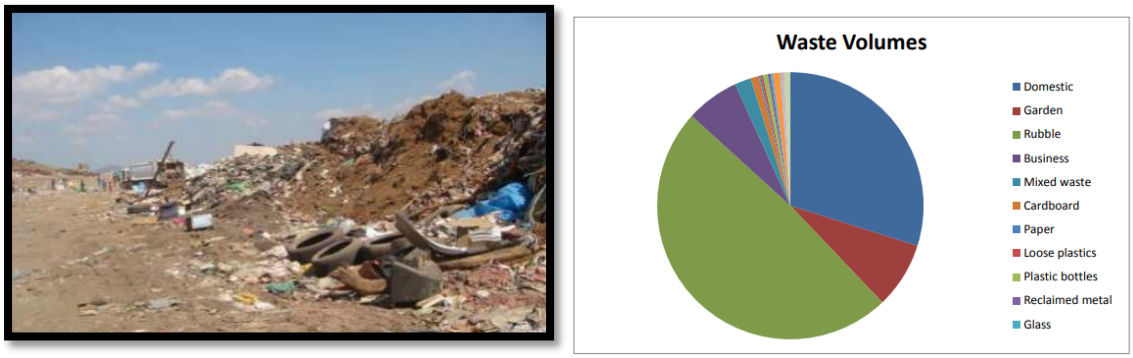


Figure 1: Composition and proportion of the different types of wastes disposed of at the Weltevreden landfill site.
Source: PLM (2016)

2.5 Availability of heavy metals in landfills

Heavy metals entering the soil may end up in forms that are phytoavailable and immobile, sometimes becoming mobile and phytoavailable with time (Mitra *et al*., 2003; Kirpchtchikova *et al*., 2006). The definition of metal availability varies both amongst scientists and the origin of the discipline. Here, availability is defined as the rate and extent to which heavy metals are released from the soil into the environment by leaching into groundwater. Violante *et al.* (2020) reported that the availability of heavy metals is controlled by the processes of oxidation, reduction, adsorption, precipitation and desorption. Heavy metal availability and mobility in landfill soils depend on their chemical properties and speciation as affected by soil factors such as soil pH, redox reactions, organic matter content, texture and aggregate stability (Zhong *et al*., 2020; Ediagbonya and Ajayi, 2021).

2.6 Factors affecting the availability of heavy metals in landfills

2.6.1 Soil pH

Soil pH is considered the master variable that influences metal behaviour in soil ecosystems (Uchimiya *et al*., 2020). It is a crucial factor that affects metal speciation in soils (Zhong *et al*., 2020). Soil pH is very important for most heavy metals since metal availability is relatively low when the pH is around 6.5 to 7. Soil pH is the most important factor since it controls virtually all aspects of the physical, chemical and biological processes. These processes can change the availability of metals, including

dissolution and precipitation of metal solid phases, and complexation and acid-base reactions of metal species (Fairbrother *et al*., 2007).

The soil's ability to immobilize heavy metals increases with rising pH and peaks under mildly alkaline conditions. At high pH, metals tend to form insoluble metal mineral phosphates and carbonates, whereas at low pH they tend to be found as free ionic species or as soluble organometals and are more bioavailable (Olaniran *et al*., 2013). The pH of the soil solution maintained at neutral and alkaline levels decreases the mobility of heavy metals (Munoz-Melendez *et al*., 2020) due to the precipitation of hydroxides, carbonates, or the formation of insoluble organic complexes (Agyarko *et al*., 2010). In some cases, the hydroxo-metal complexes, such as those formed with cadmium, nickel, and zinc are soluble, while those formed with chromium and iron are insoluble. The effect of pH on the mobility of metallic elements is, however, highly variable in the soil and it depends on the content and type of organic matter (Vamerali *et al*., 2010; Ali *et al*., 2013). At acidic pH, more protons (H^+) are available to saturate metal-binding sites; therefore, metals are less likely to form insoluble precipitates with phosphates when the pH of the system is lowered because much of the phosphate has been protonated (Chibuike and Obiora, 2014).

2.6.2 Redox potential

Redox potential is a measure of the propensity of a chemical or biological species to either acquire or lose electrons through ionization (Lu and Marshall, 2013). A species with a higher reduction potential possesses a higher tendency to acquire electrons and be reduced. Conversely, a species with a higher oxidation potential possesses a higher tendency to lose electrons and be oxidized (Zanello, 2003). Redox reactions strongly affect the behaviour of heavy metals leached from landfills (Lyngklide and Christensen, 1992; Christensen *et al*., 2001). This effect comes in two ways: firstly, redox reactions can affect the forms, mobility and toxicity of multivalent metals by involving these metals directly in the redox reactions; and secondly, redox reactions can change the environmental conditions, such as redox potential (Eh) and pH, during redox processes, which indirectly affects the behaviour and toxicity of some other metals with mono-valence (Kamon *et al*., 2002). Acidogenic fermentation of organic MSW brings about a decrease in leachate pH, high concentrations of volatile acids and considerable concentrations of inorganic ions e.g., chloride (Cl^-), sulphate (SO_4^{2-}), calcium (Ca^{2+}), magnesium (Mg^{2+}) and sodium (Na^+). The decrease in pH is due to

the production of VFAs and high partial pressures of CO_2, whilst the increased concentrations of anions and cations result from leaching (lixiviation) of easily soluble organic material present in the waste mass (Emereibeole *et al*., 2021).

When soil moisture content increases Eh decreases, leading to anaerobic soil conditions because of the rapid consumption of oxygen by microbes and the resulting partial or total loss of oxygen (Bohrerova *et al*., 2004). As the redox potential decreases, sulphate is slowly reduced, generating sulphides, which may precipitate iron, manganese and heavy metals that are dissolved by the acid fermentation.

2.7 Effect of heavy metal contamination on landfill soil properties

When waste is disposed of in landfills, heavy metals are transferred into the soil where they alter the physical, chemical and biological properties of the soil (Su *et al*., 2014). Soil characteristics are negatively influenced by heavy metal contamination. Heavy metal contamination refers to the excess accumulation of heavy metals in the soil as a result of anthropogenic activities, including landfilling (Su *et al*., 2014; Bansal, 2018).

2.7.1 Soil biological properties

The soil microbial community has a fundamental role in the process of organic matter degradation and mineralization, which allows the recycling of nutrients (Margesin *et al*., 2011). Although metals are essential, at higher concentrations they become toxic and present different problems to soil microorganisms. Soils contaminated with heavy metals reduce the diversity of the microbial community structure (Renella *et al*., 2004; Imfeld and Vuilleumier, 2012). Heavy metal contamination has been found to indirectly affect soil enzymatic activities by shifting the microbial composition and community (Huang *et al*., 2017). The degree of tolerance to heavy metal contamination varies among microbial communities (Rajapaksha *et al*., 2004). Soils contaminated with heavy metals select the microbial community that can utilize more C for biosynthesis and reduce microbial metabolic processes. As a result, fungi become dominant over bacteria at an increasing gradient of metal contamination (Lu *et al*., 2013). These dominant microorganisms are characterised by lower diversity and higher resistance to heavy metals but decreased biological activity (Zhao *et al*., 2019).

2.7.2 Soil chemical properties

The presence of toxic metals in landfills also alters soil physicochemical properties. Toxic metals alter pH, available organic matter, water-holding capacity, infiltration and

porosity (Li *et al*., 2018). A study conducted by Ali *et al*. (2014) established that soil quality at disposal sites in Islamabad city, Pakistan deteriorated due to high pH levels, electrical conductivity, total dissolved solids (TDS) and heavy metals concentrations such as Pb, Ni, Zn and Cr. Furthermore, it has been stated that long-term dumping of municipal solid waste in open disposal sites impacts the soil. This further translates into the contamination of surface and groundwater as well as influences land productivity in areas close to the landfill (Ali *et al*., 2014). The heavy metals in soil tend to interact with each other and with other soil properties. These interactions are highly influenced by soil chemical properties (Tripathi and Misra, 2012). Cation exchange capacity, total nitrogen, phosphorus, calcium, potassium, sodium and organic carbon have been positively linked with chromium, zinc and lead, but not with copper or nickel (Dawaki *et al*., 2013). A negative relationship was shown by the heavy metals with clay content, which was significant with total Zn, Pb and Cd, and with all exchangeable forms except Cu. Similarly, Tripathi and Misra (2012) found a positive association between chromium, nickel and lead while copper was strongly correlated with nickel and zinc. Moreover, lead and zinc also were significantly positively correlated, an indication that the heavy metals originated from the same source.

2.8 Effect of landfills on groundwater pollution

One of the major causes of groundwater resource contamination is landfills (Han *et al*., 2016). Landfills are most identified with the gradual pollution of groundwater resources by contaminants in waste-derived liquids (Abd El-Salam, 2015). Waste placed in landfills is subjected to either groundwater underflow or infiltration from precipitation. Precipitation passes through the waste resulting in the occurrence of chemical and physical reactions that carry dissolved constituents that accumulate at the bottom of the landfill and percolate through the soil to the groundwater (Mor *et al*., 2006; Vaverková, 2019). The main factors influencing the pollution from leachate are the concentration and flux, the landfill siting, that is, the hydrogeological setting and the basic quality volume and sensitivity of the receiving groundwater and surface water (Chandrappa and Das, 2012). The leachate often has significant potential to pollute groundwater as shown in Figure 2.

Several studies have consistently revealed that there are clear associations between the percolation of leachates (heavy metals) from landfills and the pollution of adjacent monitoring boreholes (Adamcová *et al*., 2016; Naveen *et al*., 2018; Ololade *et al*.,

2019). A recent study by Mepaiyeda *et al*. (2020) conducted in a semi-arid area showed a decrease in groundwater quality and migration of contaminants, northwards, in the direction of the groundwater flow. Their work found the concentration of heavy metals in water samples to be above the generally acceptable limits, possibly, due to the dumping of toxic and hazardous waste in the landfill. Furthermore, a study by Vahabian *et al*., (2019) showed that organic and inorganic constituents in leachate negatively affect the groundwater quality, making it unsuitable for domestic water supply. In contrast to this, Aderemi *et al*. (2011) have reported on the minimal impact that landfill leachate has on groundwater quality. This was attributed to the existing soil stratigraphy at the site consisting of clay which is deduced to have a significant influence on the natural attenuation of leachate into groundwater. This is supported by prior research that suggests that the type and extent of chemical contamination of the groundwater are largely dependent on the geochemistry of the soil through which the water flows before reaching the aquifers (Saddique *et al*., 2012).

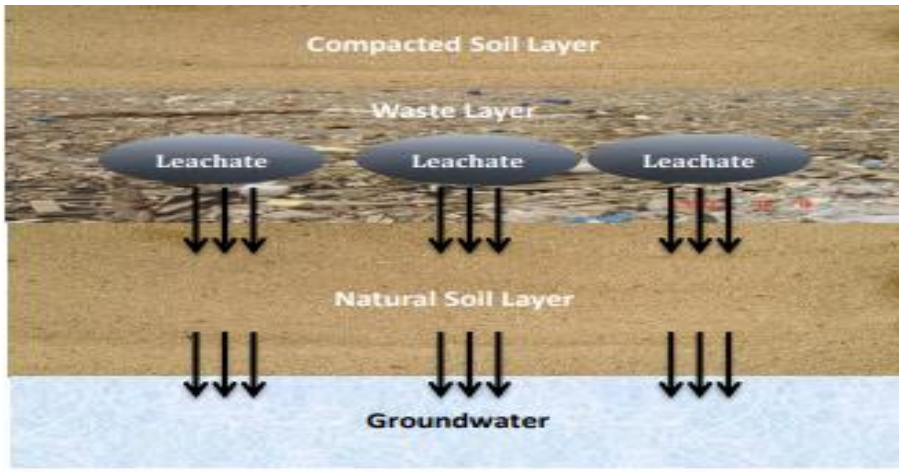


Figure 2: Leachate migration to the aquatic environment by moving from the bottom of unlined landfills through unsaturated soil layers to the groundwater.
Source: Fadhullah *et al*. (2019); Mishra *et al*. (2019)

CHAPTER 3

METHODOLOGY AND ANALYTICAL PROCEDURES

3.1 Description and history of the landfill site

The study site is located at Weltevreden landfill site (23° 56' S; 29° 29' E), in the Limpopo Province of South Africa in Capricorn District Municipality (Figure 3). It receives an average mean annual precipitation of about 478 mm and the climate is semi-arid with rainfall occurring mostly in the summer months of October and March as well as maximum temperatures ranging from 28.1°C to 36.8°C (PLM, 2010). The landfill site lies between 1335 and 1364 m above sea level, with a flat gradient of 0-3%. The site is characterised by shallow soils, with an orthic A horizon (topsoil) underlain by a lithocutanic B horizon (subsoil), classified as a Glenrosa soil form (Soil Classification Working Group, 1991) or Leptsol (IUSS Working Group WRB, 2022). As shown in Table 2, the reference site is characterised by a sandy loam texture with average sand, silt and clay percentages of 74, 18 and 8, respectively. On the other hand, the landfill site was loamy sand textured with average percentages of 80, 12 and 8 for sand, silt and clay, respectively.

The Weltevreden landfill site has operated since 1998 after being licensed by the Department of Water Affairs and Forestry in terms of the Environment Conservation Act of 1973. It has a fenced surface area of approximately 40 ha. The site is classified as a general waste, medium-sized landfill with sporadic leachate generation (G: M: B^-) (DWAF, 1998; PLM, 2016). As a semi-controlled landfill site, waste at the site is sorted and compacted and no leachate collection system is available to store leachate generated from the landfill. The landfill site receives various forms of solid waste material (e.g., metals, paper, glass, plastic, organic, rubble, etc.) from different transfer stations in the Polokwane Local Municipality (PLM, 2016).

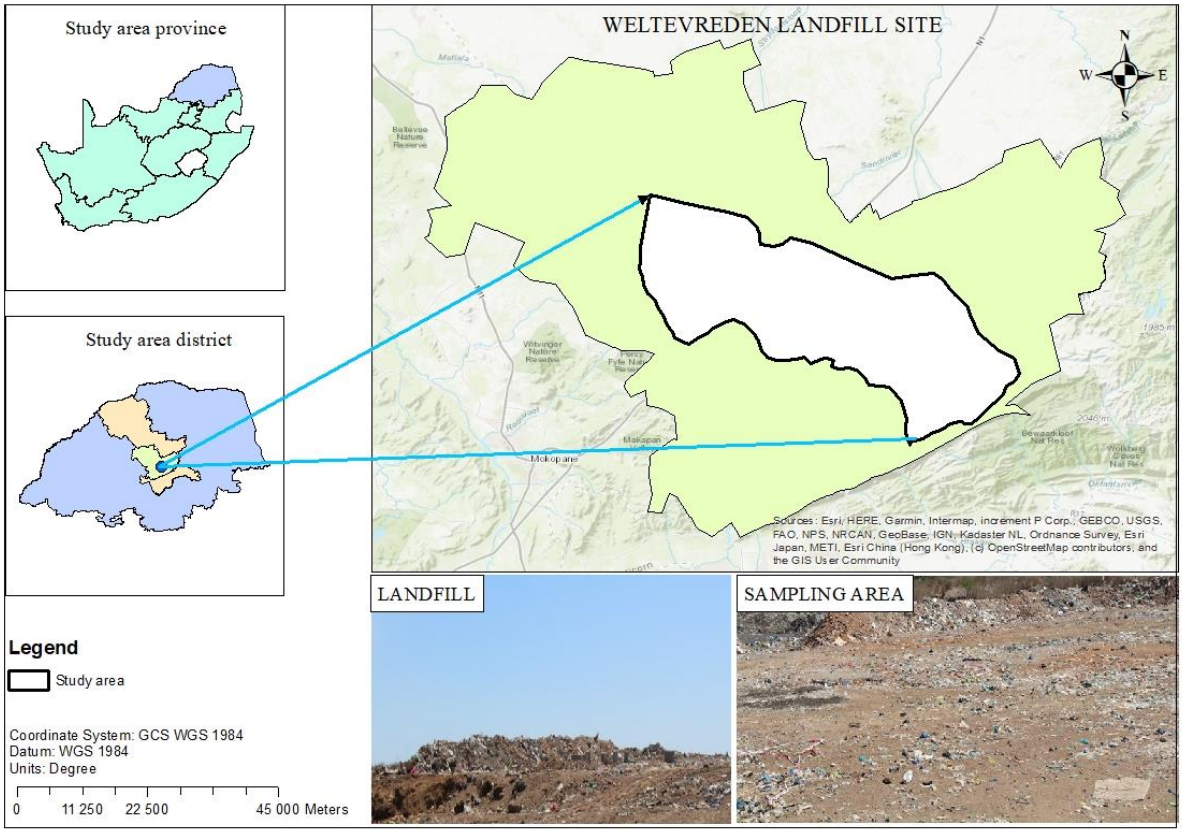


Figure 3: Study map of Weltevreden landfill site in the Limpopo province, South Africa

3.2 Soil sampling strategy

In October 2021, two areas were distinguished within the landfill, namely the landfill itself and an open area located 100 m away from the landfill site (reference site). The reference site served to compare soil heavy metal concentration to the landfill site. A handheld GARMIN GPS-60 receiver was used to record the elevation and locate the sampling points whose coordinates were georeferenced and documented. This GPS technology enhanced the precision of data obtained and integrated it into the geographic information system (GIS). For soil characterization, soil pits were opened and described on the reference site following the Soil Classification Working Group (1991). Sampling locations of the soil pits were identified according to changes in topography on the reference site. A total of 28 soil samples were collected with an auger at the landfill site at a depth of 0-30 cm using a 50 m × 50 m grid.

3.3 Soil chemical and physical analysis

The soil samples collected from both the landfill site and the reference site were air-dried, crushed and passed through a 2 mm sieve for analysis. Soil pH was determined

in a 1:2.5 solution ratio in both deionised water and 1 M KCl suspension using a standard glass electrode (MetrohmHersiau E396B) (Rhoades, 1982). Particle size distribution was determined by the hydrometer method (Bouyoucos, 1962) using sodium hexametaphosphate as a dispersant. Soil organic carbon (SOC) was determined from each soil sample using the Walkley-Black method (Walkley and Black, 1934).

Table 2: Basic morphological characteristics of soil at the landfill and reference site.

Location	Depth	pH (H_2O)	Sand %	Silt %	Clay %	Textural class
Reference site	0-30	6.98	74.58	11.86	7.83	Sandy loam
Landfill site	0-30	8.13	79.82	17.58	8.32	Loamy sand

3.4 Soil heavy metal analysis

To determine the concentrations of arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), manganese (Mn), zinc (Zn), cobalt (Co), copper (Cu) and iron (Fe) in the landfill and reference site soil, soil samples were digested according to the EPA Method 3050B (USEPA, 1996). For each soil sample, 0.4 g was measured into centrifuge tubes and added to a solution of 5 ml of 65% nitric acid (HNO_3) and 30% of 3 ml of hydrogen peroxide (H_2O_2) and boiled in a water bath for 3 hours. The obtained clear solutions were made up to a volume of 50 ml with deionised water. A Shimadzu-9000 inductively coupled atomic emission spectroscopy (ICP-AES) was used to measure the concentration of As, Cd, Cr, Pb, Ni, Mn, Zn, Co, Cu and Fe in the digested samples.

3.5 Leachate analysis

The toxicity characteristics leaching procedure (TCLP) was conducted following the United States Environmental Protection Agency (USEPA) Method 1311 (USEPA, 1992). The TCLP method was used to simulate landfill conditions to estimate the mobility of heavy metals present. Due to its ability to absorb contaminants, the percolating liquid often reacts with solid waste in landfills, posing environmental and public health risks. The TCLP analysis determines which contaminants identified by the USEPA are present in the leachate and their concentrations.

To determine the proper extraction fluid, a preliminary evaluation of the soil pH was performed. This was done by adding 5 g of soil and 96.5 ml of distilled water to a 500 ml beaker and stirring vigorously before measuring the soil pH. Since the pH was found

to be less than 5, extraction fluid 1 (pH 4.93 ± 0.05) was chosen for the TCLP analysis. The solution was prepared by diluting 5.7 ml of glacial acetic acid and 64.3 ml of NaOH with distilled water in a 1L volumetric flask. Into extracting bottles, 2 g of soil and 40 ml of TCLP fluid 1 were added and the mixture was rotated at 30 revolutions per minute for 18±2 hours before being passed through a filter paper. To reduce the pH below 2, nitric acid (HNO_3) was added to each aliquot. The detection of extracted heavy metals was done by inductively coupled plasma optical emission spectrometry (ICP-OES) using an optima 3000DV spectrometer (PerkinElmer, Inc., Shelton, CT, USA).

3.6 Assessment of soil heavy metal contamination

The enrichment factor (EF), contamination factor (CF), pollution load index (PLI) and potential ecological risk (RI) were calculated to estimate the intensity of soil contamination and pollution in heavy metals. These indices allow knowing the respective contribution of anthropic and natural sources possibly present in the soils of the Weltevreden landfill site.

3.6.1 Contamination factor (CF)

The CF for each of the samples analysed was used to determine the extent of heavy metal contamination in the landfill soils. It was calculated as the ratio between the metal content in the soil sample to the background or normal concentration of the metal (Liu *et al*., 2005), as shown in equation 1.

$$CF = \frac{C_m \text{ sample}}{C_m \text{ background}} \quad (1)$$

Where C_m sample is the concentration of heavy metal in soils from the landfill and C_m background is the concentration of the same heavy metal in background samples. In this case, samples from the reference site were used as background samples. An interpretation of CF values is given in Appendix 1.

3.6.2 Enrichment factor (EF)

The EF is used to calculate the amount of pollution due to heavy metals in soils. The methodology is effective in comparing the content of metals in soils and evaluating their origin. Using this factor, anthropogenic inputs can be differentiated from natural sources, thereby defining the intensity of contamination (Dung *et al*., 2013). A reference metal like iron (Fe) or manganese (Mn) is usually used to normalize the metal concentration to account for lithogenic input. Due to its natural occurrence at the

landfill site, iron was chosen as the immobile reference element for this calculation (Fang *et al*., 2006). The EF was calculated as follows:

$$EF = \frac{[C]_{Sample}/[Fe]_{Sample}}{[C]_{Ref}/[Fe]_{Ref}} \quad (2)$$

Where $[C]_{sample}$ is the metal concentration M in the sample; $[Fe]_{sample}$ is the concentration of iron in the sample; $[C]_{ref}$ is the concentration of metal M in the reference material and $[Fe]_{ref}$ is the concentration of iron in the reference material (Okuo and Ndiokwere, 2006). An interpretation of EF values is given in Appendix 2.

3.6.3 Pollution Load Index (PLI)

The PLI, proposed by Tomlinson *et al*. (1980) was used to determine the level of pollution caused by the heavy metals at the landfill site (Appendix 3). It provides an easy way to prove the deterioration of the soil conditions as a result of the accumulation of heavy metals (Varol, 2011).

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots CF_n} \quad (3)$$

Where CF = contamination factor and n = number of metals

3.6.4 Potential Ecological Risk Index (RI)

In this study, the Hakanson (1980) potential ecological risk index method was adopted to evaluate the risk degrees of heavy metals in the landfill soil. The RI provides information about the risk or effects associated with the overall contamination of soil by heavy metals. The potential ecological risk index was calculated by the following equations:

$$E^i_r = T^i_r \times C^i_f \quad (4)$$

$$RI = \sum_{i=1}^{n} E^i_r \quad (5)$$

Where C^i_f is the pollution coefficient of a single heavy metal, T^i_r was the corresponding toxic response factor of pollutant, and the response factors of each heavy metal were Cd=30, As=10, Cr=2, Pb=Ni=Co=Cu=5, Mn=Zn=1. E^i_r is the potential ecological risk index of a single heavy metal element i. The classifications of ecological risks according to E_r and RI ranges are indicated in Appendix 4 and 5, respectively.

3.7 Statistical analysis

Basic statistics of the data including minimum, maximum, mean, median and coefficient of variation were computed following Webster (2001). Box plots which visually display the distribution of heavy metals in the landfill site and the reference site were generated using SigmaPlot 14.0 (Systat Software Inc., California, USA). A two-sample t-test was used to investigate whether there are differences in the heavy metal concentrations between the reference site and the landfill site using GraphPad Prism 9.4.1 (GraphPad Software, California, USA). Pearson correlation coefficient was determined to explore the relationship between heavy metal concentrations and physicochemical properties (soil pH, SOC, soil texture) and landfill site attributes (elevation).

3.8 Geostatistical analysis

Our study used the kriging interpolation method in ArcGIS 10.6 (ESRI, Redlands, CA, USA) to analyse the spatial distribution of heavy metals. Kriging is based on Matheron's theory which states that samples distributed close together in space are more likely to be similar, compared to those that are further apart (Matheron, 1963). Kriging assumes that the distance or direction between sample points reflects a spatial correlation that can be used to explain variation on the surface (Tan and Xu, 2014). This interpolation method employs a semivariogram to describe the spatial relationship between samples with regard to the distance between them (Webster and Oliver, 2001; McGrath *et al*., 2004). Kriging is more advanced than some other interpolation methods because the method considers two sets of distances. One set is the distance between a location of interest and the sample locations, and the second is the distance between sample locations (Ha *et al*., 2014). Depending on the stochastic properties of random fields, different types of kriging methods apply. The type of kriging determines the linear constraint on weights implied by the unbiased condition (Xie *et al*., 2011). There are several types of kriging including simple kriging (SK), ordinary kriging (OK), universal kriging (UK), etc. The OK method was applied in this study. The weights of OK are derived from the kriging equations using a variogram-variance function. Ordinary kriging assumes that the mean and variance of the values are constant across the spatial field. There are three important steps in the application of the OK method. First is the establishment of spatial continuity through the semi-variogram which is a function of the variations in values over distance, the

second is fitting a model to the generated semi-variogram and the final step is the actual estimation through the fitted model (Pyrcz and Deutsch, 2014).

A semi-variogram measures the average variance between sample points at specific distances (lags). The semivariogram depicts the structure of spatial variability of the measured sample points (Li and Heap, 2011). Once each pair of locations is plotted, a model is fit through them. Standard variogram models are generally used in traditional OK (Adhikary *et al*., 2016). In this study, the most commonly used standard variogram models were considered (spherical, exponential, linear, and Gaussian models). Initially, an experimental variogram $\gamma(d)$ is derived from the observed data by:

$$\gamma(d) = \frac{1}{2N(d)} \sum_{i=1}^{N(d)} [\theta(x_i + d) - \theta(x_i)^2 \qquad (6)$$

Where $\Theta(x_i)$ and $\Theta (x_i + d)$ are the soil property values at corresponding sampling locations x_i and $(x_i + d)$, respectively, for a separation distance d, and N (d) is the number of data pairs. The standard variogram models $\gamma_{std}(d)$ were then fitted to the experimental variogram $\gamma_{(d)}$. The linear and the Gaussian models were identified as the best-fitted model based on visualising how well the estimated curves fit the data and how much the estimated total variance deviates from the sample variance (Reza *et al*., 2015).

These models, like the other standard semi-variance models, are parameterised by the nugget, sill and range. These parameters provide information about the structure as well as the input parameters for the kriging interpolation. Sill is the lag distance between measurements at which one value for a variable does not influence neighbouring values (Vasu *et al*., 2017). The range (distance of spatial dependence) expressed as distance could be interpreted as the diameter of the zone of influence that represented the average maximum distance over which a heavy metal of two samples was related. The ratio of nugget and sill is commonly used to express the spatial autocorrelation of regional variables, which also indicates the predominant factors among all natural and anthropogenic factors (Robertson *et al*., 1997). A ratio of less than 0.25 represents a strong spatial correlation between data while a ratio of 0.25 to 0.75 represents a moderate spatial correlation. Lastly, a ratio of more than 0.75 represents a low spatial correlation between the data, or no correlation at all (Tuominen *et al*., 2003).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results

4.1.1 The concentration of heavy metals in soil

Descriptive statistics for the concentration of heavy metals in the reference soil and the landfill soil are summarised in Table 3. The mean concentration of heavy metals in the reference site ranged between 0.39 and 111 mg/kg and in the landfill site ranged between 0.32 and 104 mg/kg. The coefficient of variation (CV) values in the study area ranged from 21% to 754%, indicating moderate to high variations (Appendix 6). Arsenic, Cd, Pb, Ni, Zn and Co were significantly higher ($P \leq 0.05$) in the landfill site compared to the reference site as shown in Figure 4 and Figure 5a (Appendix 7). As evident in Figure 5(b-d), the mean concentrations of Cr, Mn and Cu were higher in the landfill site than in the reference site. Conversely, the concentration of Fe in the landfill site was 36% lower compared to the reference site as observed in Figure 5e. According to the South African National Norms and Standards for Remediation of Contaminated Land and Soil Quality (DEA, 2013), Only As and Cd were above the permissible limits while the other heavy metals were below the limits. When the concentration of a pollutant exceeds some standard threshold value, remedial action is necessary (Atteia *et al*., 1994). In this context, the South African National Norms and Standards for Remediation of Contaminated Land and Soil Quality (DEA, 2013) declares that a remediation order should be issued under section 38(2), detailing the measures to be taken to monitor or manage the risk.

Table 3: Descriptive statistics of soil heavy metal concentrations in soils collected from the landfill site and the reference site.

N	Reference site					Landfill site				
	Heavy metals (mg/kg)	Mean ± SE	Min	Max	CV (%)	Mean ± SE	Min	Max	CV (%)	DEA (mg/kg)
28	As	6.93 ± 1.13	2.85	11	40	13.01 ± 0.58	6.41	19.9	30	5.8
28	Cd	3.16 ± 0.43	1.98	5.03	34	6.67 ± 0.37	2.59	11.4	20	7.5
28	Cr	2.10 ± 0.34	1.17	3.62	39	2.90 ± 0.11	1.49	4.72	32	6.5
28	Pb	1.65 ± 0.22	1.07	2.58	32	3.71 ± 0.23	1.28	6.98	24	50
28	Ni	1.78 ± 0.33	1.00	3.29	45	2.89 ± 0.13	1.27	4.98	35	16
28	Mn	2.37 ± 1.05	0.89	1.05	109	3.23 ± 0.21	1.05	5.04	21	20
28	Zn	1.91 ± 0.18	1.32	2.67	23	2.44 ± 0.10	1.2	3.7	30	1000
28	Co	1.40 ± 0.21	0.80	2.26	37	2.29 ± 0.13	1.02	4.96	25	91
28	Cu	0.55 ± 0.08	0.39	0.93	37	0.66 ± 0.03	0.32	1.18	36	240
28	Fe	79.77 ± 11.21	44.8	111	754	51.15 ± 3.45	24.8	104	123	ND

N, number of samples; SE, standard error; Min., minimum; Max., maximum; CV, coefficient of variation; DEA, Department of Environmental Affairs (2013) maximum permissible levels; ND, not documented

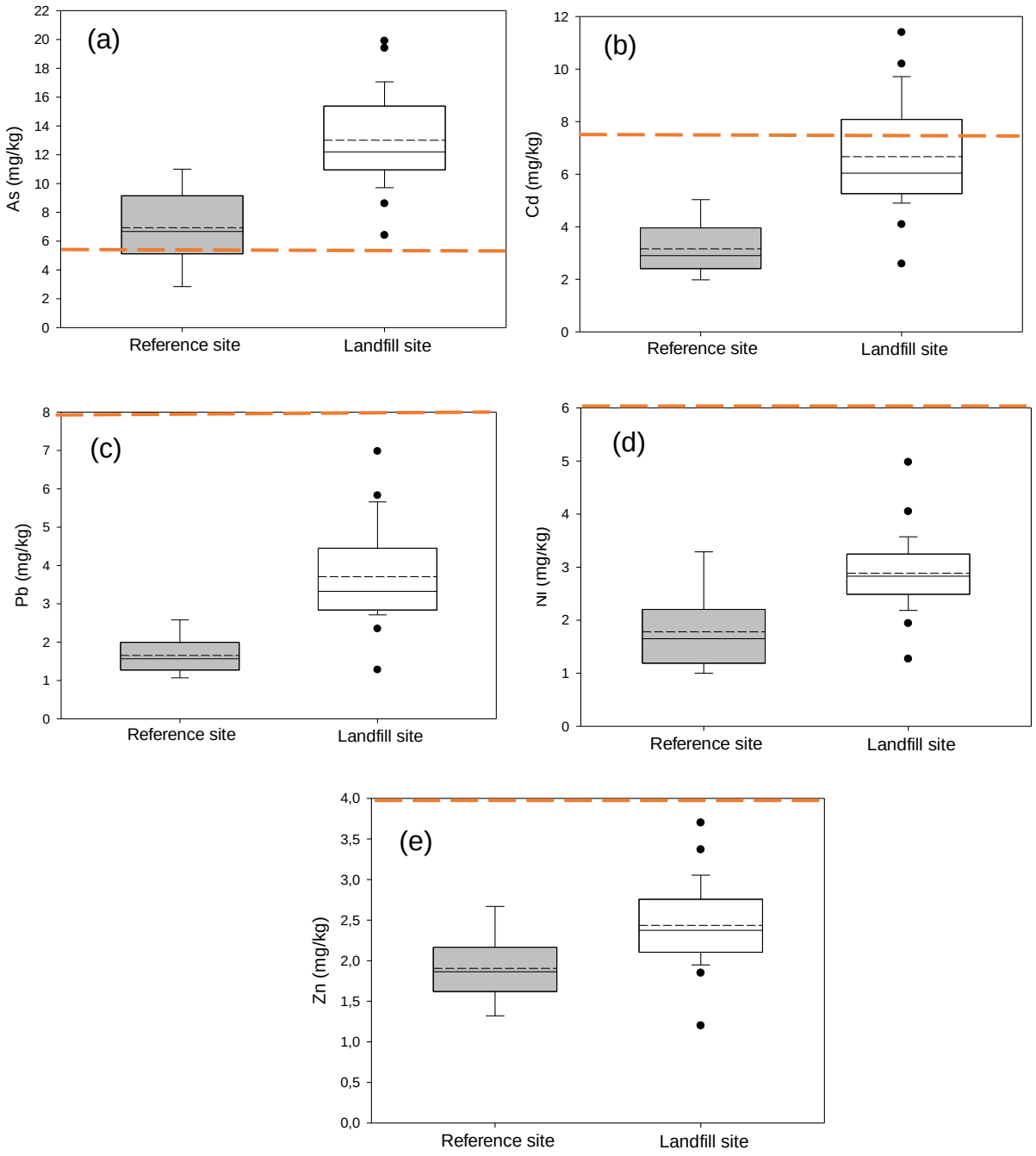


Figure 4: Concentration of (a) arsenic (As), (b) cadmium (Cd), (c) lead (Pb), (d) nickel (Ni) and (e) zinc (Zn) in the reference site and landfill site. Boxes represent the 25th, 50th and 75th percentiles; whiskers represent the 5th to 95th percentiles. The dashed line is the mean value, the solid line is the median and the box represents the upper and lower quartile. The dotted orange line represents DEA's permissible limits.

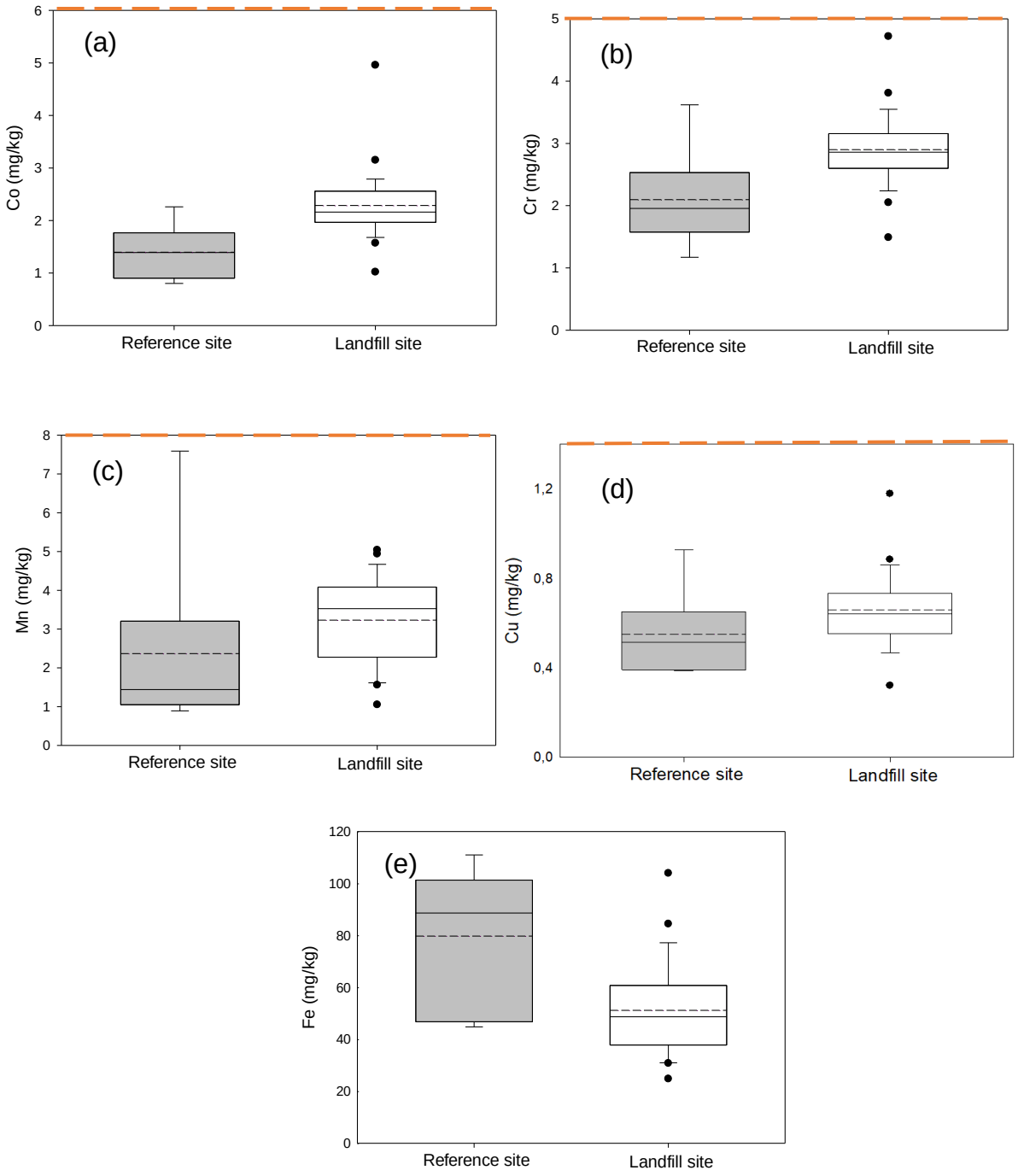
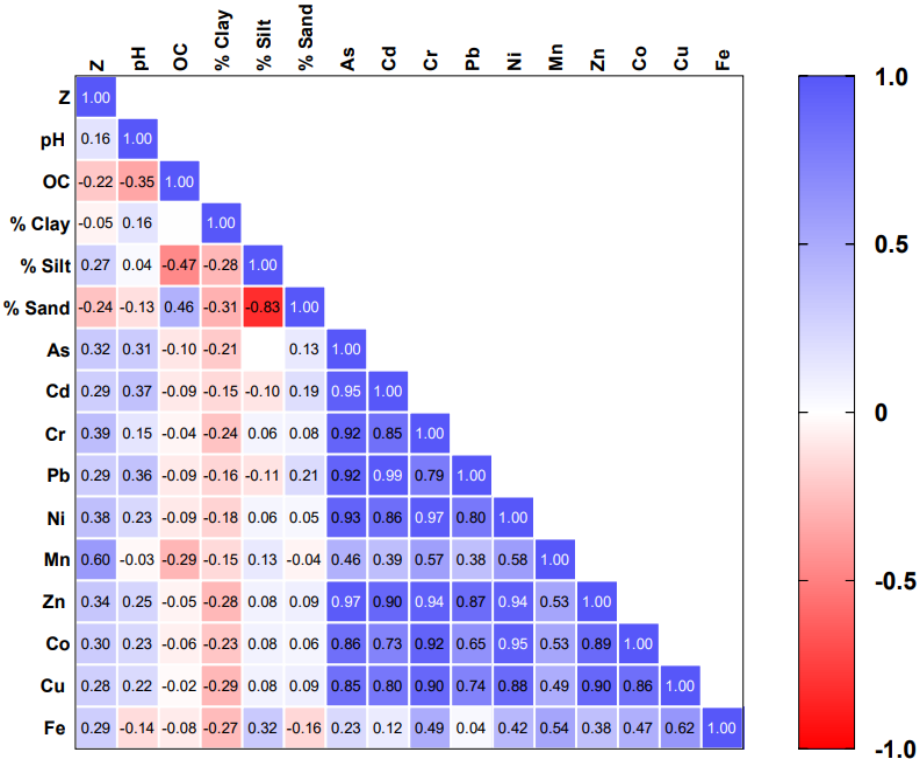


Figure 5: Concentration of (a) cobalt (Co), (b) chromium (Cr), (c) manganese (Mn), (d) copper (Cu) and (c) iron (Fe) in the reference site and landfill site. Boxes represent the 25th, 50th and 75th percentiles; whiskers represent the 5th to 95th percentiles. The dashed line is the mean value, the solid line is the median and the box represents the upper and lower quartile. The dotted orange line represents DEA's permissible limits.

4.1.2 Correlation analysis between heavy metals and inherent soil properties

Pearson's correlation coefficients (r) were determined to characterise the relationship between heavy metals and edaphic factors (elevation, pH, SOC, clay %, silt % and sand %) in the reference site and the landfill site, with the results displayed in Figure 6. The correlation analysis for the landfill site (Figure 6a) revealed positive correlations between the heavy metals that exceeded the threshold limits; As and Cd ($r = 0.95$; $P < 0.05$), as well as As with Pb ($r = 0.92$), Ni ($r = 0.93$), Zn ($r = 0.97$) and Co ($r = 0.86$). Cadmium (Cd) was positively correlated with Pb ($r = 0.99$), Ni ($r = 0.86$), Zn ($r = 0.97$) and Co ($r = 0.86$). There was a positive correlation between Pb and Ni ($r = 0.80$), Zn ($r = 0.87$) and Co ($r = 0.65$). The correlation analysis also showed that Ni was positively correlated with Mn ($r = 0.58$), Zn ($r = 0.94$) and Co ($r = 0.95$). In the case of the reference site (Figure 6b), the correlation analysis showed a positive correlation between clay % and Fe ($r = 0.69$) and a negative correlation between As and elevation ($r = -0.70$).

(a)



(b)

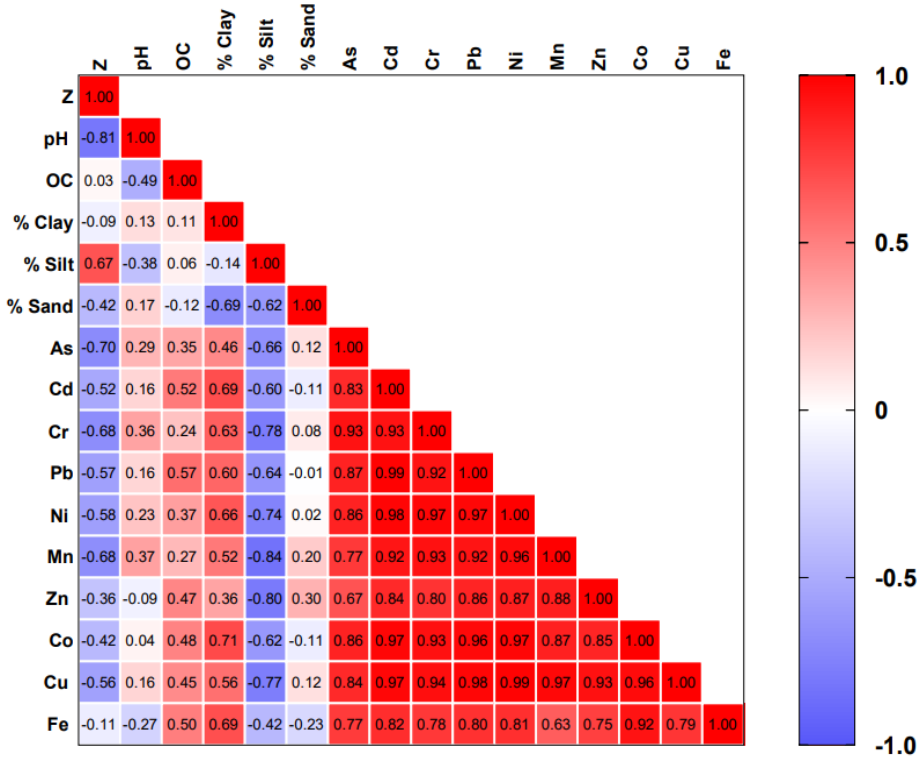


Figure 6: Correlation analysis between heavy metals and edaphic factors in the (a) landfill site and (b) reference site. Z, elevation; OC, organic carbon; As, arsenic; Cd, cadmium; Cr, chromium; Pb, lead; Ni, nickel; Mn, manganese; Zn, zinc; Co, cobalt; Cu, copper; Fe, iron.

4.1.3 Assessment of heavy metal contamination and pollution at the landfill site

Heavy metal pollution was evaluated according to contamination factor CF, enrichment factor (ER), pollution load index (PLI), ecological risk factor (E_r) and the potential ecological risk index (RI). The mean CF, EF and PLI values for the studied soils are shown in Table 4. The mean concentrations of heavy metals (Cd, As, Cr, Pb, Ni, Mn, Zn, Cu and Co) were found to indicate moderate contamination ($1 \leq CF < 3$), whereas the CF of Fe was less than 1 (0.64), presenting low contamination in the study area. The average EF values of the heavy metal contents ranged from 0.73 to 3.29, which indicated that the landfill soil pollution levels were low to moderate. The mean enrichment factors of As, Cr, Ni, Mn, Zn, Cu and Co were less than 2, indicating that the heavy metals in the soil have deficient to minimum enrichment ($EF < 2$). The mean enrichment factor values of Cd and Pb estimated, on the other hand, indicated moderate soil enrichment (EF= 2-5). The PLI value was found to be greater than 1 (1.44). The E_r for each heavy metal was calculated and found to differ (Table 5). The order of E_r values for the heavy metals in the soil was Cd > As > Pb > Co > Ni > Cu > Cr > Mn > Zn, with values of 63.32, 18.78, 11.24, 8.16, 8.11, 5.99, 2.76, 1.36 and 1.28, respectively. Cadmium was found to have an E_r value of more than 40, presenting a moderate ecological risk; while the average E_r values of the other heavy metals were less than 40, indicating a low risk. Lastly, the RI (multi-ecological) of heavy metals in soils was used to assess the ecological risk status of this study area, the RI of the whole area was 121, indicating that the ecological risk status of the heavy metals in soils of this whole area was low.

Table 4: Average CF, EF and PLI values in the Weltevreden landfill site.

Heavy metal	CF	EF	PLI
As	1.88	2.93	
Cd	2.11	3.29	
Cr	1.38	2.15	
Pb	2.25	3.51	
Ni	1.62	2.53	1.44
Mn	1.36	2.13	
Zn	1.28	1.99	
Cu	1.20	1.97	
Co	1.63	0.73	
Fe	0.64		

CF, contamination factor; EF, enrichment factor; PLI, pollution load index

Table 5: Results of potential ecological risk assessment.

Heavy metal	ER	RI
As	18.78	
Cd	63.32	
Cr	2.76	
Co	8.16	
Cu	5.99	121
Pb	11.24	
Mn	1.36	
Ni	8.11	
Zn	1.28	

ER, potential risk factors; RI potential ecological risk index.

4.1.4 Spatial variability and structure of soil heavy metals across the landfill site

The possible spatial structure of the various heavy metals was identified by calculating the semivariograms and the best model that describes these spatial structures was identified. In the study, heavy metals such as As, Cd, Cr, Pb, Ni, Mn, Zn and Co presented medium variability while Cu and Fe were characterised by high variability (Appendix 6). Model parameters for the best fit semivariogram models are presented in Table 6 and Figures (7-9). Analysis of the isotropic variogram indicated that As, Cr,

Ni, Mn, Zn and Co were well described with the linear model. The distance of spatial dependence for the abovementioned heavy metals was found to be 2.44 m (Table 6). The nugget-to-sill ratio was found to be 100% which indicates a weak spatial dependence. On the other hand, the semivariograms for Cd, Pb, Cu and Fe were well described with the gaussian model, and the distance of spatial dependence was 16.11 m, 23.21 m, 32.56 m and 11.60 m, respectively. The nugget-to-sill ratio of Cd, Pb and Fe was found to be 39%, 29% and 37%, respectively, indicating moderate spatially dependent structure. Lastly, the nugget-to-sill ratio of Cu was 12% which indicates a strong spatially dependent structure.

Table 6: Semivariogram parameters and models of reference landfill site soil samples.

Heavy	N	Model	Nugget	Sill (Co + Cs)	Range	Nugget/sill	r^2
As	28	Linear	8.78	8.78	2.44	100 (W)	0.712
Cd	28	Gaussian	3.78	9.67	16.11	39 (M)	0.096
Cr	28	Linear	0.31	0.31	2.44	100 (W)	0.895
Pb	28	Gaussian	1.42	4.85	23.21	29 (M)	0.061
Ni	28	Linear	0.43	0.43	2.44	100 (W)	0.925
Mn	28	Linear	1.15	1.15	2.44	100 (W)	0.525
Zn	28	Linear	0.25	0.25	2.44	100 (W)	0.485
Co	28	Linear	0.43	0.43	2.44	100 (W)	0.995
Cu	28	Gaussian	0.03	0.26	32.56	12 (S)	0.191
Fe	28	Gaussian	315	840.9	11.60	37 (M)	0.98

W, weak spatial dependence (>75%); M, moderate spatial dependence (25-75%); S, strong spatial dependence (>25%); r^2, determination coefficient

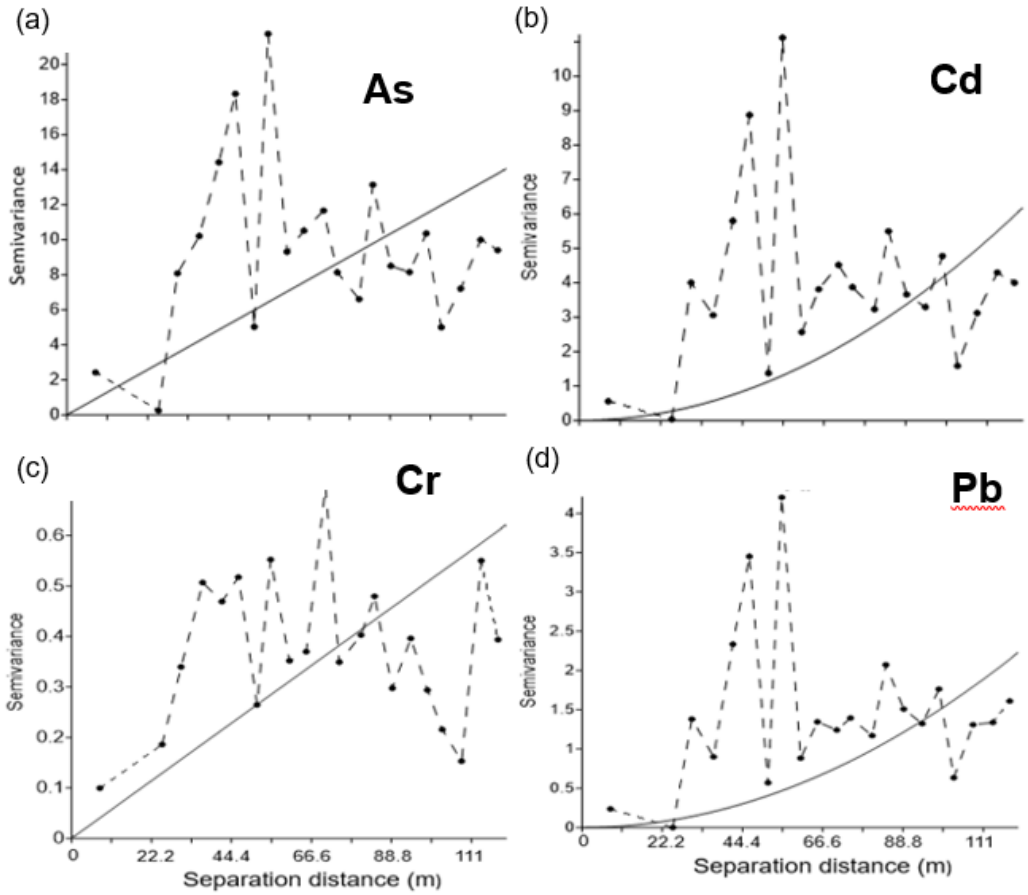


Figure 7: The best-fitted semivariogram models for (a) arsenic (As), (b) cadmium (Cd), (c) chromium (Cr) and (d) lead (Pb).

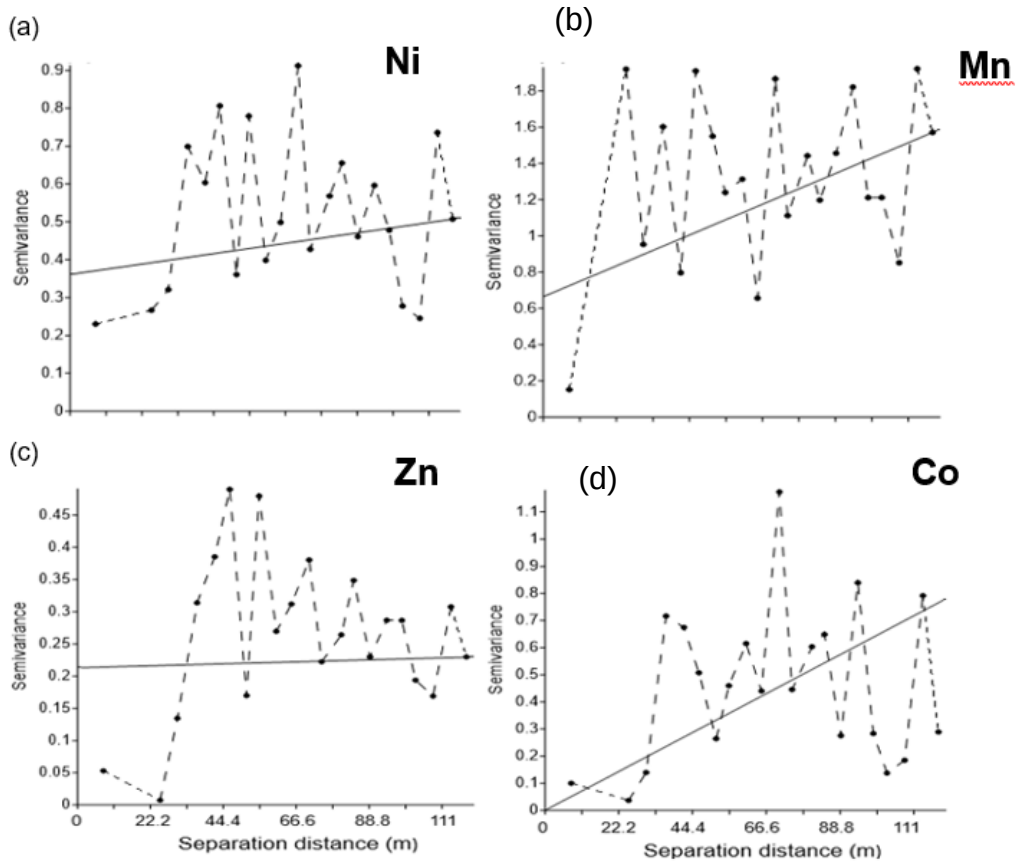


Figure 8: The best-fitted semivariogram model for (a) nickel (Ni), (b) manganese (Mn), (c) zinc (Zn), and (d) cobalt (Co).

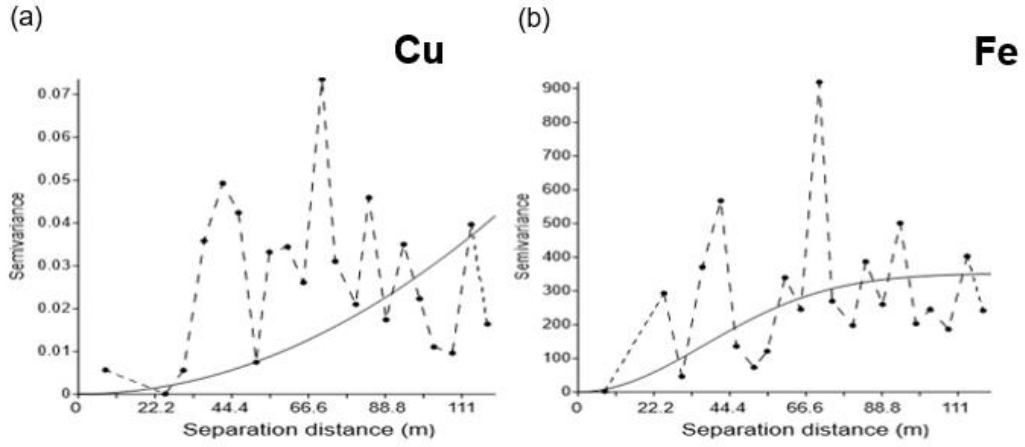


Figure 9: The best-fitted semivariogram model for (a) copper (Cu) and (b) iron (Fe).

4.1.5 Spatial distribution of heavy metals in soil

Implementing the best fit theoretical models and corresponding semivariogram parameters, spatial variability maps of heavy metals were computed and shown for heavy metals (Figures 10, 11 and 12). Lower degrees of pollution were observed in the southwest, northwest, and northeast parts of the landfill, while higher degrees were in the southwest, northwest and central parts of the landfill. The spatial maps for Cd, Pb and Zn displayed high concentrations (hotspots) in the northwestern parts of the landfill site (Figures 10b, 10d and 11c). Meanwhile, Mn and Fe were also found to exhibit hotspots in the southwest part of the landfill (Figures 11b and 12b). Iron also showed high concentrations in the northeastern parts of the landfill. The distribution of Cr at the landfill displayed high concentration in the central part of the landfill than in the surrounding regions. Similarly, As, Ni and Co showed high concentrations in the centre with the southwest parts also having high concentrations (Figures 10a, 11a and 11d). High concentrations of Cu were not observed at the landfill site (Figure 12a).

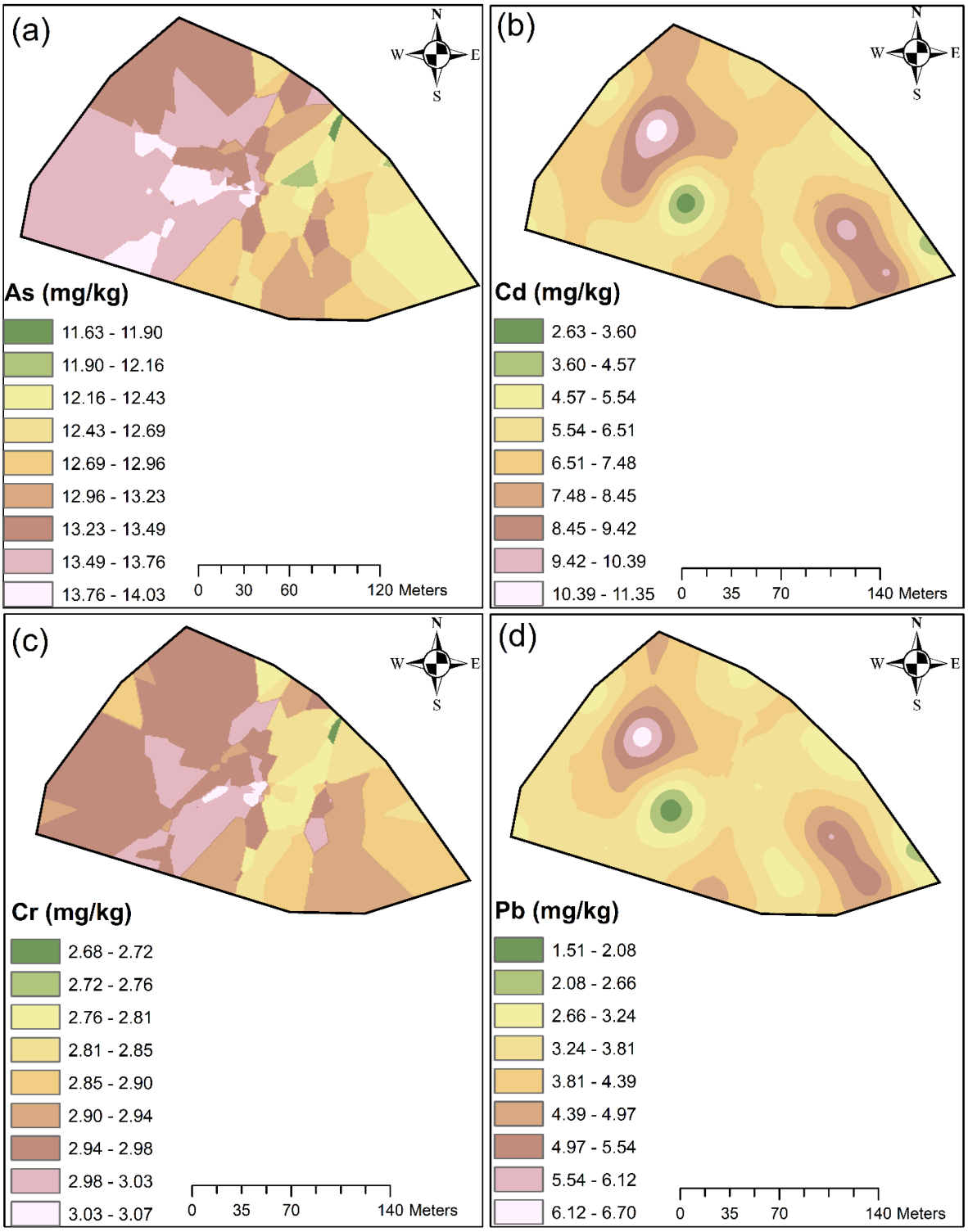


Figure 10: Kriged maps showing the spatial distribution of (a) arsenic (As), (b) cadmium (Cd), (c) chromium (Cr) and (d) lead (Pb) at the landfill site generated using ordinary kriging.

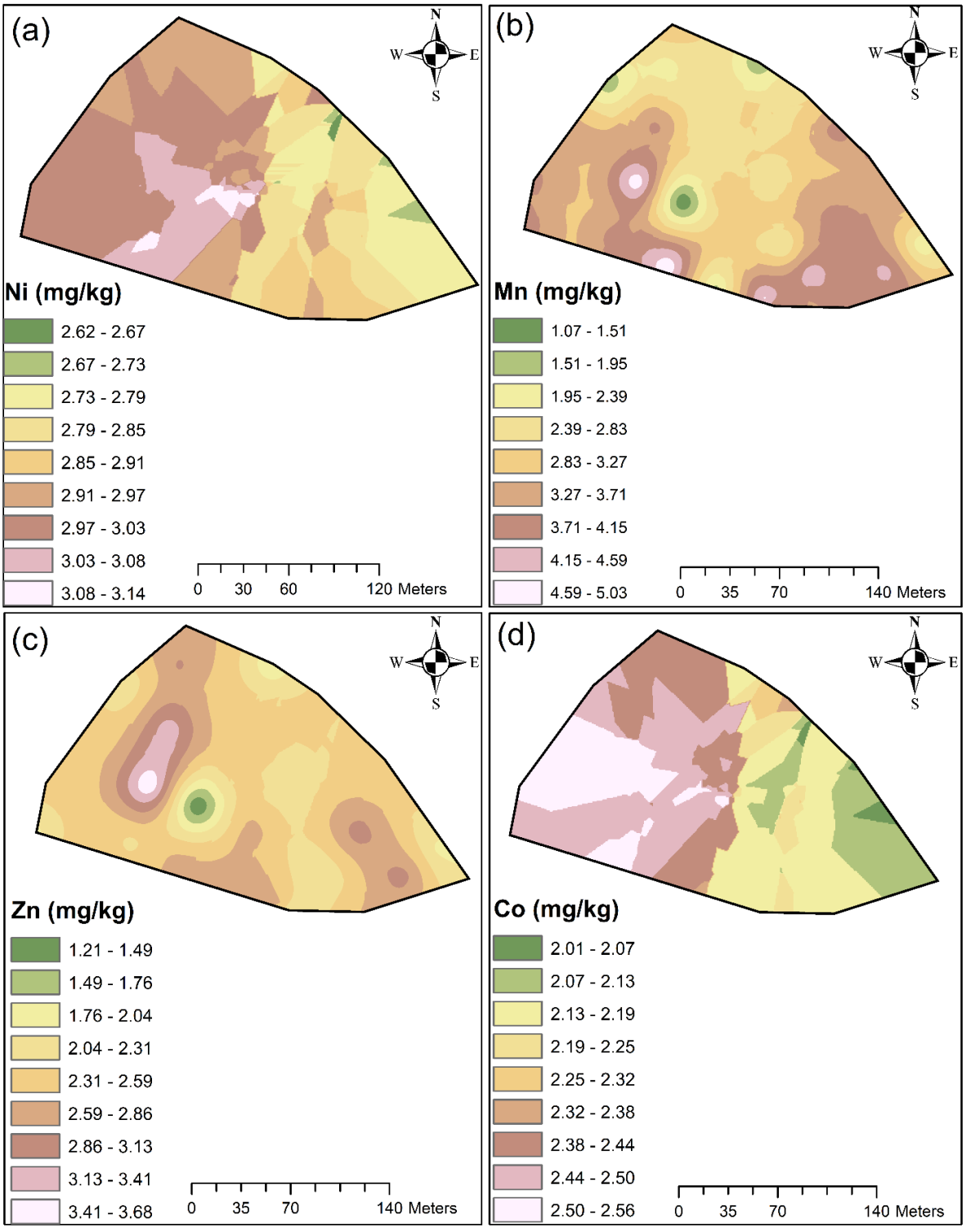


Figure 11: Kriged maps showing the spatial distribution of (a) nickel (Ni), (b) manganese (Mn), (c) zinc (Zn) and (d) cobalt (Co) at the landfill site generated using ordinary kriging.

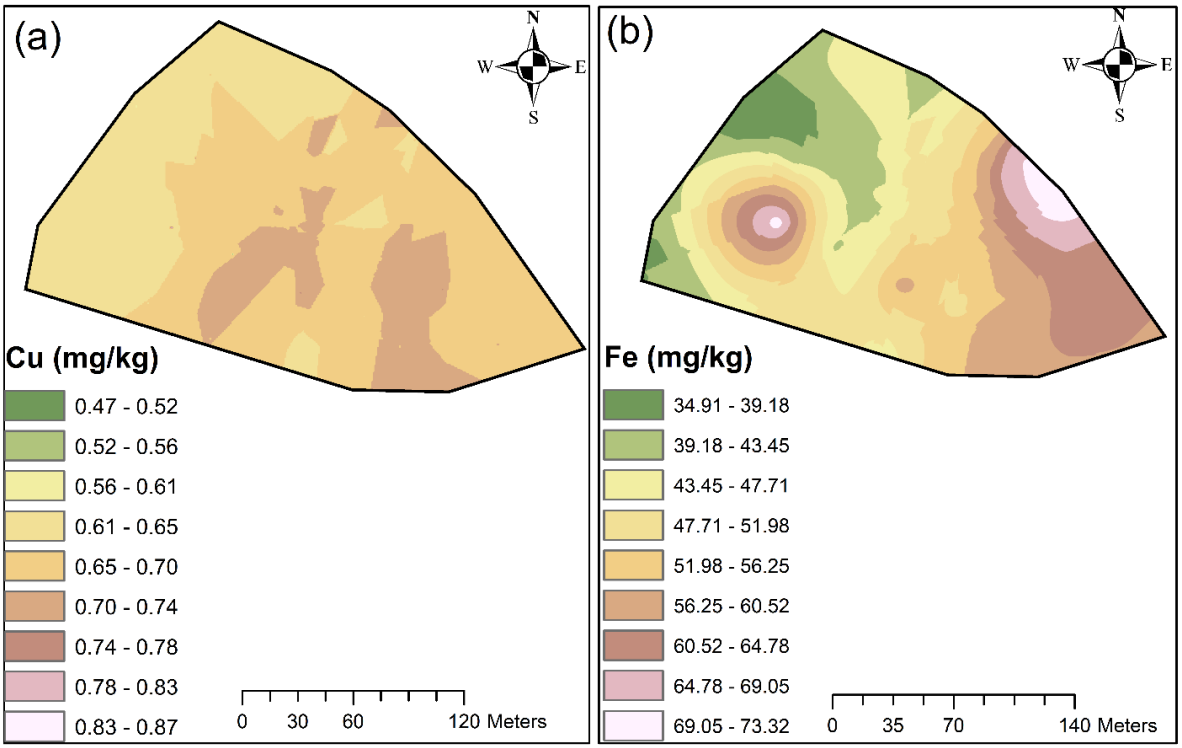


Figure 12: Kriged maps showing the spatial distribution of (a) copper (Cu) and (b) iron (Fe) at the landfill site generated using ordinary kriging.

4.1.6 Concentration of heavy metals in leachate

The observed heavy metal concentrations in leachate samples at different locations at the landfill site are presented in Table 7. Maximum concentration values of Cd, Ni, Mn, Zn, Co, C and Fe were found to be 0.06 mg/L, 0.41 mg/L, 4.47 mg/L, 0.29 mg/L, 0.37 mg/L, 0.04 mg/L, and 11.54 mg/L, respectively. The average concentration of heavy metals in leachate was Mn > Fe > Ni > Co > Zn > Cd > Cu. The CV ranged from 25 - 399%. Heavy metals Cd, Ni and Co showed medium variability while Mn, Zn, Cu and Fe showed high variability. When compared to the DEA guideline, the concentrations of Cd, Ni and Mn revealed levels above permissible limits, whereas Zn, Co and C were below the permissible limits (DEA, 2013).

The correlation analysis results of heavy metals in the soil and leachate are observed in Figure 13. The results show the relationship between heavy metals in soil and leachates. Copper (Cu) in the leachate was found to positively correlate with As and Cd ($r = 0.50$; $P < 0.05$) in the soil. There was a negative correlation between Fe in the soil and Co ($r=-0.54$) and Ni ($r = -0.51$) in the leachate with Fe.

Table 7: Heavy metal concentration of leachate in the landfill site.

Heavy metals (mg/L)	Mean ± SE	Min	Max	CV (%)	DEA (mg/L)
Cd	0.04 ± 0.00	0.03	0.06	26	0.003
Ni	0.29 ± 0.01	0.13	0.41	25	0.07
Mn	1.32 ± 0.17	0.12	4.47	66	0.5
Zn	0.05 ± 0.01	0.00	0.29	117	5.0
Co	0.26 ± 0.01	0.16	0.37	20	0.5
Cu	0.01 ± 0.00	0.00	0.04	127	2.0
Fe	0.54 ± 0.41	0.06	11.54	399	ND

SE, standard error; Min, minimum; Max, maximum; CV, coefficient of variation; DEA, Department of Environmental Affairs; ND, not documented

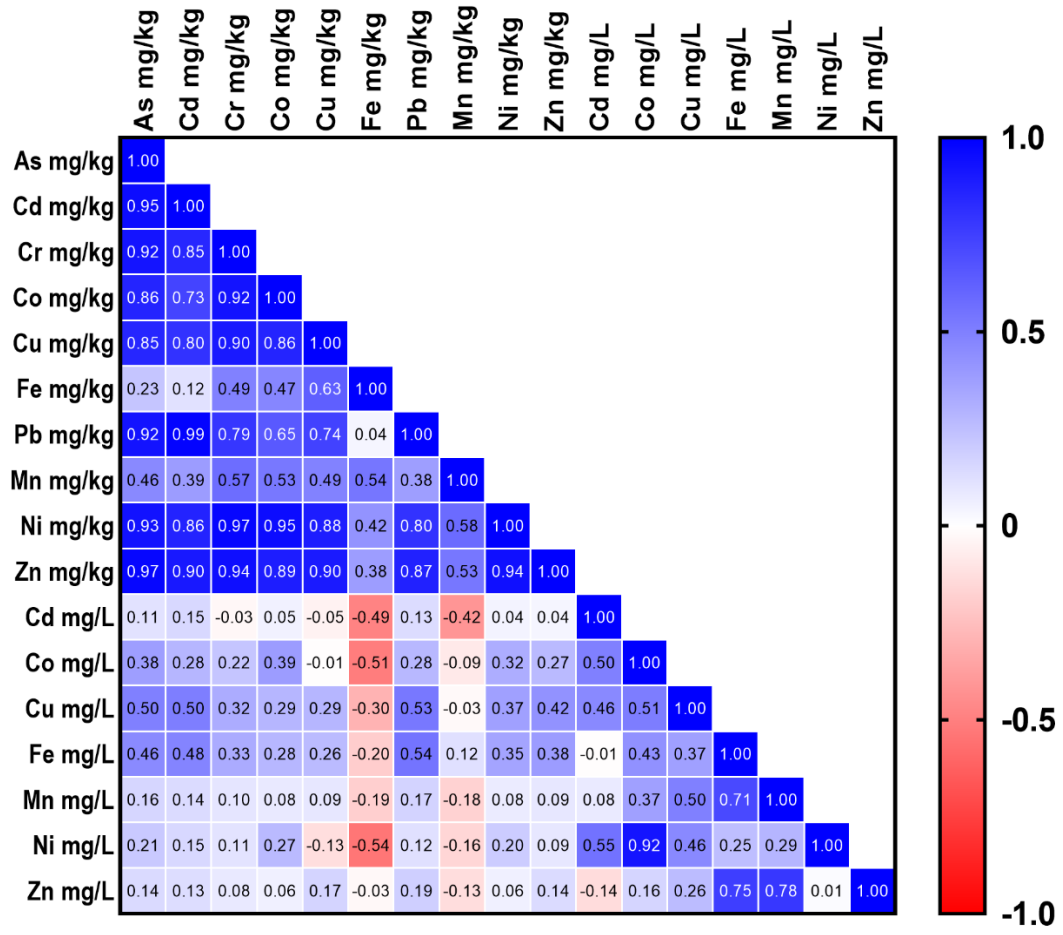


Figure 13: Correlation analysis between heavy metals in the soil and leachate

As, arsenic; Cd, cadmium; Cr, chromium; Pb, lead; Ni, nickel; Mn, manganese; Zn, zinc; Co, cobalt; Cu, copper; Fe, iron.

4.2 Discussion

4.2.1 Heavy metal concentrations in the soil

Solid wastes contain a significant amount of potentially toxic elements like heavy metals (Wang *et al*., 2017), which under suitable conditions may be released into the environment and subsequently change the geochemical characteristics of the exposed soil (Cobbina *et al*., 2013). In this study, the disposal of MSW led to significantly higher concentrations of As, Cd, Pb, Ni, Zn and Co in the landfill soil compared to the reference soil. This indicates that the successive inputs of metal-containing wastes in landfill lead to an accumulation of heavy metals due to their natural biogeochemical degradation (Armel *et al*., 2022).

Although heavy metals occur naturally and at low bearable quantities in the soil, disposal of waste has led to an increase in the amounts beyond tolerable limits (Ideriah *et al*., 2010; Tchounwou *et al*., 2012). In this study, concentrations of As and Cd recorded values above the South African permissible limits (DEA, 2013). These high concentrations could be attributed to the disposal of chromated copper arsenate (CCA)-treated wood, alloys, medicines, glass, Ni-Cd batteries, pigments, coatings and platings (Khan *et al*., 2017). The findings of the current study are consistent with those of Vongdala *et al*. (2019) who found Cd in the landfill soils to have exceeded the levels of Dutch Pollutant Standards. This was speculated to have been related to the high quantities of Cd in waste compositions that are disposed of in landfills (Calace *et al*., 2001). While Cr, Pb, Ni, Mn, Zn, Co and Cu were found to be within the permissible limits in this study, their presence in the soil cannot be overlooked since their quantities may be elevated by long-term accumulation (Kjeldsen *et al*., 2002).

Surprisingly, the concentration of As was also found to be above permissible limits in the reference site, unlike Cd. Although the concentration of As in the reference soil was above permissible limits, it was still much lower than the content of As in the landfill soil. Such a case might have been triggered by anaerobic bio-disintegration since it is unlikely that the metals dissolved, leached, and mobilised into the environments under normal conditions (Keshta, 2009). The transition from the aerobic phase to the anaerobic phase of landfill leachate may liberate As from dominant solid minerals such as alluvial soil and pyrite (Hussein *et al*., 2021). Due to the continuous discharge of arsenic compounds from solid wastes in these landfills and the anaerobic conditions within the waste pile, more As^{3+} would be formed. This anaerobic condition

in waste piles may also be triggered by competing biogeochemical processes in the leachate, resulting in the rise of more toxic As^{3+} species (Yusof *et al*., 1999).

According to Yang *et al*. (2020), correlation analysis has been described as an effective tool for identifying the common association soil heavy metals that may suggest a common source. Furthermore, the correlation analysis of the landfill soil in this study revealed significant positive correlations between As and Cd indicating that they possibly emanate from a common source (Nava- Martínez *et al*., 2012). The same source could be anthropogenic such as the effect of the leachate emanating from the landfill site (Sheijang *et al*., 2020).

A possible explanation for the observed higher Fe concentration in the reference site might be that the Weltevreden landfill site is characterized by biotite, a form of mica that releases considerable amounts of Fe into the soil during weathering (PLM, 2021). This was supported by the positive correlation between Fe and clay fraction shown in Figure 6b (r = 0.69). Fine-grained fraction (clay) is known to exhibit a higher tendency for Fe adsorption than course-grained soils since it contains soil particles with large surface areas such as clay minerals (Barker and Pilbeam, 2015). Another possible explanation for this is that smaller grain-size particles are known to retain more metals with high concentration due to several factors such as large surface area, sorption, coprecipitation and complex formation (Dung *et al*., 2002).

4.2.2 Pollution assessment of the landfill site

The individual contamination factor (CF) of heavy metals may be used to estimate the degree of contamination and relative retention time of heavy metals in soils. A high CF of heavy metals shows low retention time and high risk to the environment (Nemati *et al*., 2011). In our study, the moderate CF values of As, Cd, Cr, Pb, Ni, Mn, Zn, Cu and Co indicated that the soil at the Weltevreden landfill site was not heavily contaminated, and it would not pose an immediate threat to the environment (Nwankwo *et al*., 2019). The EF has been proposed as a useful method for measuring heavy metal sources (Bai *et al*., 2015). Generally, EF values lower than 2 are assumed to indicate a natural source metal source, while EF values greater than 2 indicate an anthropogenic pollution source (Adelopo *et al*., 2018). In this study, the EF values for Cd and Pb were much higher than the other heavy metals, indicating that the landfill had moderate enrichment for these heavy metals. Therefore, the high EF values for Cd and Pb

showed that the metals were concentrated from waste disposed of in the landfill (Karimian *et al*., 2021).

The observed PLI value of 1.44 suggests that waste disposal and bedrock weather contributed to the moderate CF and high PLI of the study area (Wiafe *et al*., 2022). Another possible reason for the observed high PLI value is the composition of the waste discarded at the landfill site. Similarly, high PLI values could be linked to the decomposed municipal solid waste and the accumulation of non-degradable heavy metals in the dumpsite over a long period (Ogundele *et al*., 2020).

According to the potential ecological risk assessment results, the dominant potential ecological risk source in the soil was found to be Cd. This could be related to its high toxicity coefficient of up to 30 since it can easily enter the groundwater via the leachate of landfill waste causing harm to the environment. This was consistent with the recent findings of Zhou *et al*. (2022) who related the E_r value of Cd to electronic wastes such as fluorescent lamps and batteries contained in domestic waste. Furthermore, the RI was found to be lower than 150, and therefore the ecological risk potential of the studied metals is categorized as being low risk.

4.2.3 Spatial variability and structure of heavy metals

Several soil intrinsic properties, such as soil parent material, soil texture, topography, and vegetation, contribute to the strong spatial dependence of heavy metals. According to Fu *et al*. (2014), weak spatial dependence results from extrinsic factors, while moderate spatial dependence is a result of both intrinsic and extrinsic factors. In this study, Cu exhibited high spatial variability and strong spatial dependence. The high spatial variability and strong spatial dependence of Cu may be related to that this metal occurs in the soil almost exclusively in a divalent form (Mishra *et al*., 2019). The largest fraction of Cu is generally present in the crystal lattices of primary and secondary minerals. The Cu ion can then be adsorbed to inorganic and organic negatively charged groups, and dissolved in the soil solution as Cu^{2+} and organic Cu complexes. It is specifically adsorbed to carbonates, soil organic matter, phyllosilicates, and hydrous oxides of Al, Fe, and Mn (Barker and Pilbeam, 2015). In support of this inference, we found a positive correlation between Cu with Fe and Mn. Numerous heavy metals such as As, Cr, Ni, Mn, Zn and Co were found to show low spatial variability and weak spatial dependence. In this study, the low spatial variability and weak spatial dependence were a result of extrinsic factors (disposal of municipal

solid waste at the landfill). Heavy metals in the soil from anthropogenic sources have been known to be more mobile, hence bioavailable than pedogenic, or lithogenic ones (Wuana and Okieimen, 2011). The common sources of As, Cr, Ni, Mn, Zn and Co include glass, wood preservatives, pigments, paints, batteries, alloys, waste wires, ink, etc., (Smiljanic *et al*., 2019).

Iron was found to have high spatial variability and a moderate spatial dependency, while Cd and Pb showed medium spatial variability with moderate spatial dependence. The moderate spatial dependence of Cd, Pb and Fe was determined by both intrinsic and extrinsic factors, and the intrinsic factors played a more important role. An explanation could be that under anoxic conditions, Fe^{3+} is readily reduced either by inorganic chemical reactions or by microbial processes. The weathering of soil mineral sources with a subsequent release of Fe could be affected by soil microbes through their involvement in redox, complexation, and acidification processes (Colombo *et al*., 2014).

4.2.4 Spatial distribution of heavy metals

Previous studies have justified that the distribution of heavy metals in soils is strongly influenced by various human activities such as landfilling (Cai *et al*., 2012; Guo *et al*., 2012; Qu *et al*., 2013). Generally, the spatial trends of heavy metals within the study area were as follows: The degree of heavy metal pollution was the highest in areas located in the southeast, central, and northeast parts of the landfill, and the degree of pollution was the lowest in the southwest, northwest, and northeast parts of the landfill. The similar spatial distribution patterns of As, Cr, Ni and Co and that of Cd, Pb and Zn indicate that these pollutants were strongly affected by the disposal of MSW. The distribution of Fe was different from the other heavy metals in such a way that the highest concentrations were found to be in both the southwest and the northeast direction, which was close to the reference site. This observation may indicate that other factors besides the disposal of MSW resulted in this, and this factor could be the mineralogy of the soil which had a greater effect at the reference site. This was confirmed by the positive correlation between Fe and clay content.

4.2.5 Concentration of heavy metals in leachate

The concentration of heavy metals in landfill leachate is an important parameter in selecting a leachate treatment method (Boateng *et al*., 2019). Heavy metals are usually found at moderate concentration levels in municipal landfill leachates (Abiriga

et al., 2020). The current study found that the concentration of Cd, Ni and Mn were above the stipulated standard for leachate discharge, while Zn, Co and Cu were within the standards (DEA, 2013). This high concentration can be ascribed to the disposal of toxic and hazardous waste substances in the landfill, contrary to the landfill design and classification (Mepaiyeda *et al*., 2020). This is because, in our study, the landfill site lacks proper lines and collection systems where raw leachate will laterally seep into and contaminate the soil and also groundwater (Hussein *et al*., 2021). Although within limits, the concentration of Cu in the leachate could have resulted in elevated levels of As observed in the soil. This is supported by the positive correlation (r=0.50) observed in Figure 13. In the event of rainfall coming into contact with CCA-treated wood structures above or in the landfill soil, some As, Cr, and Cu will dissolve and travel to the understory or adjacent soil. Consequently, soil metal concentrations may increase as a result of metals leaching (Townsend *et al*., 2003).

Generally, Mn exists naturally in soils, rocks and minerals hence its relative abundance on earth (Edokpayi *et al*., 2016). The presence of high Mn may have influenced the mobility of other metals like Cd and Ni through the reductive dissolution of manganese oxides (Mukwaturi and Lin, 2015). Manganese oxides present in soils are frequently nanometer-sized materials, which have a large surface area to volume ratio and thus are capable of binding Cd and Ni (Kumpiene *et al*., 2008). Ultimately, the mobility of heavy metals in the landfill site depends not only on their total concentration but also on their association with the solid phase to which they are bound (Prechthai *et al*., 2008).

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CHAPTER 5

SUMMARY, CONCLUSION AND RECOMMENDATIONS

The purpose of the study was to assess heavy metal contamination in soils and leachates from the Weltevreden MSW landfill site and to examine the spatial variability and distribution patterns of heavy metals across the landfill site using geostatistical techniques. In chapter 3, a landfill survey was conducted to quantify and compare heavy metal concentrations in leachate, to determine the edaphic factors controlling the availability of heavy metals in both sites, and to map their spatial distribution and variation of heavy metals on the soil at the landfill site. In chapter 4, the analysed heavy metal contents were used to calculate the contamination factor (CF), enrichment factor (EF), pollution load index (PLI), ecological risk factor (E_r) and ecological risk index (RI).

Differences in heavy metal contents were determined by comparing the heavy metal concentration of heavy metals in the landfill site to the neighbouring reference site. A correlation matrix was run to determine the relationship between the edaphic factors and the heavy metals in the soil. Spatial variability, dependence, and distribution of heavy metals across the landfill were evaluated using semivariograms and geostatistical techniques to determine whether the heavy metals had a good or poor structure and to also map their distribution across the landfill.

The results of this study showed heavy metal content was much higher in soil than in leachate since the metals are generally less mobile and adsorb onto soils. Based on the metals that were found in landfill soil samples, we can conclude that landfill soils are contaminated with As and Cd. The only significant correlations found to exist were between the heavy metals, and no edaphic factor explored in the study correlated with the heavy metals. The use of the CF indicator resulted in the soil being classified as moderately contaminated with Pb, Cd, As, Co, Ni, Mn, Zn, Mn and Cu in the study area. The landfill site presented moderate enrichment for Pb, Cd, As, Ni, Cr and Mn and low enrichment for Zn, Cu and Co. The ER value for Cd was classified into the moderate ecological risk level. However, the overall ecological risk index of heavy metals analysed was low (121), indicating very low potential ecological risks to soil ecosystems in the study area. Although the potential hazard was found to be low, the

presence of heavy metals especially As, Pb, Ni and Zn cannot be overlooked since their quantities may accumulate overtime.

Geostatistical and interpolation techniques were used to visualize the spatial structure and spatial distribution of soil heavy metals at the landfill site. For geostatistical analysis of heavy metals in the soil, the value of nugget: sill ranged from 12% to 100%, which indicates that internal (e.g., the soil forming processes) factors were dominant over external (e.g., human activities) factors. The spatial dependence of the majority of the heavy metals (As, Cr, Ni, Mn, Zn and Co) was weak, indicating that extrinsic factors played a vital role in spatial heterogeneity. Similar spatial distribution patterns in various heavy metals were observed across the landfill site. Heavy metals such as As, Cr, Ni and Co showed similar high concentrations in the central and southwestern parts of the landfill while low concentrations were observed in the northeastern parts. Similar spatial patterns showing the distribution of Cd, Pb, and Zn were observed in the northeastern (high concentration) and southwestern (low concentration) parts of the landfill.

Comparing the concentration of heavy metals at the Weltevreden landfill site to the South African permissible levels will help in the development of a baseline for soil characterisation of the landfill site. Furthermore, the background information on the landfill characteristics would be crucial to match the characteristics with the requirements for landfill selection to determine the suitability of the Weltevreden landfill site for waste disposal. The most effective way that landfill managers can reduce the impact of these heavy metals on the environment is to develop and implement an effective waste management plan such as designing a proper confinement and treatment facility. If left untreated, heavy metals such as Cd and Ni which were found to be high in the leachate will find their way into the groundwater and surrounding environment of the landfill site.

Future work will look into collecting deeper soil samples and testing water samples from boreholes at the landfill site to determine whether the disposal of MSW subsequently resulted in the contamination of groundwater and to also see if there is a need to design treatment and leachate collection facilities.

APPENDICES

Appendix 1: Classification of contamination factor (CF)

Index	Contamination	Classific	Reference
CF	Low	<1	Hakanson (1980)
	Moderate	1-3	
	Considerable	3-6	
	High	>6	

Appendix 2: Classification of enrichment factor (EF)

Index	Contamination	Classifi	Reference
EF	Low	≤2	Diop *et al*. (2015)
	Moderate	2-5	
	High	5-20	
	Very high	20-40	
	Extremely	>40	

Appendix 3: Classification of pollution load index (PLI)

Index	Pollution status	Classification	Reference
PLI	No pollution	<1	Tomlinson *et al*. (1980)
	Normal	1	
	Pollution	>1	

Appendix 4: Classification of ecological risk factor E_r

Index	Contamination	Classificatio	Reference
E_r	Low	<40	Hakanson (1980)
	Moderate	40-80	
	Considerable	80-160	
	High	160-320	
	Very high	>320	

Appendix 5: Classification of potential ecological risk index (RI)

Index	Contamination	Classificatio	Reference
RI	Low	<150	Kowalska *et al*. (2016)
	Moderate	150-300	
	Considerable	300-600	
	High	>600	

Appendix 6: Classification of coefficient of variation

Coefficient of variation, CV	Classes
<15%	Low
15-35%	Medium
>35%	High

Appendix 7: T-test results for heavy metal concentrations in the reference and the landfill site

Heavy metals	Reference site (mean)	Landfill site (mean)	P value
As	6.93	13.01	0.0014
Cd	3.16	1.13	<0.0001
Cr	2.10	2.90	0.0625
Pb	1.65	3.71	<0.0001
Ni	1.78	2.89	0.0173
Mn	2.27	3.23	0.4558
Zn	1.91	0.20	0.0243
Co	1.40	2.86	0.0058
Cu	0.55	0.66	0.2547
Fe	79.77	51.15	0.0506