Determination of Physicochemical properties and metal levels in soil, water, and plant

From Alice landfill site.

By

Maphuhla N.G (201214220)

**MSc Research Project** 



# University of Fort Hare Together in Excellence

A thesis submitted in partial fulfillment of the requirements for the award of the degree

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**Department of Chemistry** 

Faculty of the Science & Agriculture

**University of Fort Hare** 

Private bag X1314

Alice, 5700

South Africa

Supervisor: Prof. O. OYEDEJI

**Co-supervisor: Prof. F.B LEWU** 

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## **DECLARATION**

I, **Maphuhla Nontobeko Gloria**, declare that this dissertation is my original work. It is being submitted for the degree of Masters of Science (MSc) in Chemistry at University of Fort Hare. It has not been submitted for any degree or examination at this or any other university.

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Maphuhla Nontobeko Gloria (201214220)	Date
Prof. O. Oyedeji	Date
	••••••
Prof. F.B Lewu	Date

#### **DEDICATION**

I dedicate this project to God Almighty my creator, my strong pillar, my source of inspiration, wisdom, knowledge, and understanding. He has been the source of my strength throughout this program and on His wings only have I soared

I also dedicate this work to my dearest mother B.A Maphuhla who patiently nurtured me in all spheres of life, for her support and guidance in everything I do.

Finally to my late father J.N. Maphuhla, whom his memories have been a source of inspiration to me. Even though you were not educated but you wanted your children to have the best education and be better people in future. I hope you are happy and proud of me because I did your wishes.

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# **CONFERENCES AND PUBLICATIONS**

# Workshop output

1. 21<sup>st</sup> ACCESS Habitable Planet student workshop from 8<sup>th</sup> – 18<sup>th</sup> July 2016 (VUT)

Why the planet earth is more habitable, and effects of climate changes.

# Articles under preparation

1. Maphuhla N.G, Lewu F.B, Oyedeji A.O, and Oyedeji O. Determination of physicochemical properties and metal levels in soil, water, and plant from Alice landfill site. *In Press* 

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# LISTS OF ABBREVIATIONS

AASAtomic Absorption Spectrophotometer
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- ANOVA.....Analysis of Variance
- BOD .....Biochemical oxygen demand
- CS AAS.....Continuum Source Atomic Absorption Spectrophotometer
- DWAF.....Department of Water Affairs and Forestry
- EDTA.....Ethylenediaminetetraacetic acid
- EC.....Electrical Conductivity
- HNO<sub>3</sub>.....Nitric acid
- H<sub>2</sub>SO<sub>4</sub>.....Sulphuric acid
- LS AAS.....Line Source Atomic Absorption Spectrophotometer
- mL.....Millilitres
- OD.....Oxygen Demand
- SOC.....Soil Organic Carbon
- SOM.....Soil Organic Matter
- SPSS.....Statistical Package for Social Sciences
- ppm.....Parts per million
- TDS.....Total Dissolved Solids
- USEPA.....US Environmental Protection Agency
- WHO ......World Health Organisation
- µS/cm......Micro Siemens per centimeter
- mS/cm......Milli Siemens per centimeter

#### ABSTRACT

The state of soil is of great significance because it is a common medium for plant growth, which provides important nutrients to plants. Water pollution is the build-up of harmful substances in water bodies to the level that results in health problems for people and animals. Heavy metal pollution (of soil, water, and plants) and their health effects on people is a persistent social issue, and several types of research have recognized health risks of residents living close to open dumpsites. Dump sites are sources of heavy metal impurity and toxicity to the surrounding environment.

Analyses were done on water and soil samples for temperature, pH, Electrical conductivity (EC), Total dissolved solids (TDS), alkalinity, organic matter, organic carbon and total hardness. The pH results range from slightly acidic (6.79) to neutral soil pH (7.09), and have been recorded within the normal range from WHO. All the determined physicochemical properties in soil and water have been recorded within the normal range, except for EC in water which was found to be above the permissible limits by WHO. The heavy metals concentration was determined using the AAS technique. The results obtained shows that the dumpsite's soil consists of high metal concentration when compared to control site. The concentration in dumpsites ranges between  $1.2783 \pm 0.83$  mg/kg to  $26.3213 \pm 6.37$  mg/kg. The descending order for selected metal concentrations were in this following order Mn> Cu>Hg>Pb. The Pb and Hg mean concentration was recorded above permissible limits, while the Mn and Cu were within the normal range suggested by WHO. In both water and *Acacia karroo* samples the Cu was not detected. The trend of metal concentration in water sample was found to be in this order Hg> Mn > Pb> Cu, while in *Acacia karroo* metal concentration is Hg> Mn> Pb> Cu.

The one-way ANOVA test was used to compare the mean concentration of selected metals in each sampling site. The results show that there is a statistically significant difference between the mean concentrations of selected metals; this is supported by the value of F-static and p-value (p < 0.05)

#### **CHAPTER ONE**

#### **1.0 INTRODUCTION/ LITERATURE REVIEW**

#### 1.1 Soil

The soil is a weather-beaten and broken outer layer of earth's terrestrial surface [1]. It is also a thin layer that results from chemical, physical and biological weathering of different rocks types described as parent material [2]. It is one of the most valuable nation's assets and it is frequently the characteristic that determines the region's wealth. The soil is important for life because it directly or indirectly supports life [3]. It also provides nutrients and mechanical help to plants, building materials, hunting grounds for animals and is a large lake for water [1]. Chemical, physical and biological composition of each layer of the soil profile control the overall behavior of soil. Soil fertility is mostly affected by soil chemical properties and reactions, in terms of effects on nutrient availability [2]. During the decomposition of organic matter, the organic matter combines with the inorganic matter of rock and water to form soil [4]. Soil can act as a strainer to keep the quality of water, air, and other resources. It also provides a physical matrix, chemical environment and biological setting for water, nutrients, air and heat exchange for living organisms [5].

#### 1.1.1 Soil composition

The soil is made up of minerals, organic matter, water and air [3]. It consists of 95 % solid inorganic and 5 % organic components in several stages of decomposition. The inorganic material is a mixture of primary particles which are:

- ✓ Sand between 2 0.02 mm diameter
- ✓ Silt between 0.02 0.002 mm diameter
- ✓ And the clay which is less than 0.002 mm diameter [2, 3].

Soil minerals are inorganic matter containing approximately 64 elements and, 16 of those elements are important for plant growth. Most of the soil's top layers have a large quantity of nutrients which are rich in organic matter and nutrients such as Phosphorus (P), Potassium (K), Nitrogen (N), Magnesium (Mg), Iron (Fe), Silicon (Si), Calcium (Ca), Sulphur (S), and Aluminium (Al) [3].

#### **1.2 Soil chemical properties**

#### **1.2.1 Soil Organic Matter**

Organic matter is a short term product in a natural cycle of decomposition of plants and animal remains after a large group of microbes have consumed carbon and other easily usable components that ended up in ground soil [6]. The decomposed organic matter is called humus and it occurs naturally in soil depending on climatic conditions of the soil. [4].

The physical properties of soil are mainly influenced by the quantity of organic matter, the soil structure, and the parent materials of soil. Organic matter occurs naturally in soil or can be added through the use of additives such as manure and compost [3].

The organic matter contains carbon, which is the energy source for microorganisms (microbes) in the soil. Dry soil in warm climates has less organic matter than the wet soil in cool climates. Soil organic matter affects the chemical, physical and biological properties of the soil in ways that are almost always good for crop production [7.].

#### **1.2.2 Soil Minerals**

Normal soil usually contains approximately 45 % of minerals. The soil composition can change every day depending on many factors such as water supply, plowing processes, and the type of soil. Minerals play an important role in soil fertility because the surfaces of minerals act as future sites for nutrient storage [8]. Soil minerals are natural inorganic compounds with exact physical, chemical and crystalline properties. Minerals can be arranged into primary (chemically unchanged), secondary (chemically changed) minerals, silicates and non-silicates, crystalline and non-crystalline minerals [9]. In soil, minerals are important because they provide volume and mass to the soil, supply elements that are needed to grow plants, and offer materials to form other minerals [8].

Primarily, minerals are formed at a raised temperature, from the cooling of magma, during the solidification of the original rock. These primary minerals include K-feldspars (orthoclase, sanidine, and microcline), Micas (muscovite, biotite, and phlogopite) and clay – size micas (illite). Primary minerals are widely distributed in many soil types, including highly weathered and sandy soil [10]. Primary minerals are usually found in sand and coarse silt fractions, while secondary minerals are present in clay and fine silt fractions [11].

They act as essential storage for K, with over 90 % K in soil existing in the structures of these minerals. An important amount of Ca (calcium), Na (sodium) and Si (silicone) are present in the feldspars; this includes a small amount of Mn (manganese) and Cu (copper). In many types of soil, the most important sources of K are micas and illite. Micas and illite contain Mg (magnesium), Fe (iron), Ca (calcium), Na (sodium), Si (silicon) and many other micronutrients. Carbonate minerals especially those taken from soil parent material and those formed through pedogenic processes in soil act both as the source and the sink for Mg and Ca in the soil. Many nutrient elements in soil solution are released from the weathering of physical, chemical and biological primary minerals [9].

Table 1: Average	mineralogical	and	nutrient	element	composition	of	common	rocks	on	the
Earth's land surface	e. [10]									

Mineral	Igneous rock	Shale (%0	Sandstone	Nutrient-element constituents	
constituent					
				Major	Minor
Feldspars	59.5	30	11.5	K, Ca, Na	Cu, Mn, Ni,
					Co, Zn, Mo
Micas	3.8	-	Sm	K, Ca, Na, Mg,	Ni, Mn, Co,
				Fe	Zn, Cu
Clay	-	25.0	6.6	K, Mg, Fe, Ca,	-
				Na	
Iron oxides	-	5.6	1.8	Fe	Mn, Zn, Ni,
					Со
Carbonates	-	5.7	11.1	Ca, Fe, Mg	_
Other minerals	-	11.4	2.2	-	_

In spite of the fact that, the weathering rates of primary minerals for some elements are not fast enough to meet the requirements of plant nutrients on a short-term basis, the mineral weathering is therefore an important and long-term source of some geochemically obtained nutrients. The capacity of nutrient supply in soil decreases through the weathering of primary minerals, while on the other hand soil weathering increases [9,10].

The secondary minerals occur in soil at low-temperature reactions during the weathering of primary minerals in an aqueous environment on the earth's surface. These secondary minerals control nutrients through adsorption-desorption, dissolution-precipitation, and oxidation-reduction reactions. Secondary minerals act as a source of nutrients, they precipitate and hold important nutrients. In many cases, the secondary minerals serve as storage, where nutrients are held strongly enough to prevent leaching and weakly enough to allow plants to attract them to reach their nutritional need [10].

The minerals that control most of the soils are silicates; these include other groups of soil minerals such as sulfides, oxides, carbonates, phosphate, and non-halides (non-silicates). They supply physical support for plants, provide for soil structure formation, and can serve as sorbents for some environmental pollutants [12]. Many mineral structures are linked by either ionic or covalent bonds to form coordinated polyhedrons with different composition and inter-atomic distance characteristics, which impact the overall physicochemical behavior. Negative and neutral charges which are found around soil minerals influence the solubility of soil to retain important nutrients such as cations, contributing to a soil cation exchange capacity (CEC). Due to the crystallization within igneous or metaphoric rocks, deposition in primary minerals of sedimentary rocks does not experience chemical or structural change [9].

#### 1.2.3 Soil pH

The negative logarithm of  $H^+$  activity is called pH, therefore the soil pH is a measure of the intensity of activity and not the amount of the acid present [13]. The scale of a pH ranges between 0 to 14, where the pH value that is below 7 indicates acidity while the pH value that is more than 7 is said to be alkaline and pH value of 7 is neutral. In soil when the amount hydrogen ion increases, the pH of the soil decreases, thus becoming more acidic. From 7 to 0 the soil is increasingly more acidic and from 7 to 14 the soil is increasingly more alkaline or basic [14].

The pH scale is based on the ionic product of pure water. Water dissociates slowly to form

 $H_2O \rightleftharpoons H^+ + OH^-$ ......(2)  $Kw = [H^+] \times [OH^-]$  .....(3)  $= 10^{-14} \text{ at } 23 \text{ }^{\circ}C$ 

Since  $[H^+] = [OH^-]$  in pure water, each is equal to  $10^{-7}$  [15].

Three soil pH ranges that are particularly informative, a pH <4 shows the presence of free acids generally from the oxidation of sulfides, a pH <5.5 suggest the likely occurrence of exchangeable Al ions, and pH from 7.8 to 8.2 show the presence of CaCO<sub>3</sub> [16].

In the soil, the pH is usually found to range from 3 to 9. Determination of pH in soil is an important aspect for characterizing the soil from the standard point of nutrient availability and physical condition, structure, and permeability. It provides information on the strength of poisonous materials present in the soil. The determination of pH in soil provides the most reasonable basis for managing soil in selected agricultural crops [13].

Most minerals and nutrients are more soluble and more available in the acidic soil than in neutral or slightly alkaline soils. The soil pH can also impact the growth of plants by its effects on the activity of advantageous microorganisms (bacteria) that decompose soil organic matter, in which the plant growth can be delayed or stopped in highly acidic soils. This stops the organic matter from being broken down, which results in the increase of organic matter and limits nutrients such as nitrogen which is held in the organic matter [14].

Soil pH controls most of the chemical processes that specifically affect the nutrient availability of the plant by controlling the chemical forms of nutrients. Acidity in soil is the result of  $H^+$  and  $Al^{3+}$ ions in soil solution that is absorbed to the soil surface. Several processes contribute to the formation of acidic soil; this includes the rainfall, the use of fertilizer, the root activity of plants and the weathering of primary and secondary minerals. Also, soil pollutants such as acid rain and mine- spoiling can increase the acidity in the soil [16].

Hydrogen ions in solution are in equilibrium with those held on the particle surface of the soil. The total acidity of soil includes both active and "reverse" (or exchangeable acidity), that means two soils with the same pH may have different amounts of reverse acidity.

Sources of  $H^+$  ions in soil solution include carbonic acid produced when CO<sub>2</sub> from decomposed organic matter, root respiration, and the soil atmosphere is dissolved in soil water, the reaction of aluminium ions (Al<sup>3+</sup>) with water, nitrification of ammonium from fertilisers and organic matter mineralisation, rainwater, and acid rain [15].

Most of the soil falls on pH range of 4 to 8 and many plants have a preference to grow and produce better on slightly acidic and neutral soil, while some crops like berries grow perfectly on strongly acidic soil [17].

#### **1.2.4 Soil acidity**

Acidification of soil is a natural process that occurs when the rock surfaces are first settled by algae and lichens. Acids usually come from the carbon and nitrogen cycles which are involved in the weathering of soil and rock minerals during the development processes of soil [18]. Acidity in the soil can result in a clear decrease of root growth and the uptake of nutrients while changing the cation or anion uptake ratio. The low pH generally reduces the uptake of cations, while stimulating anion uptake. Therefore the low pH decreases excess cation uptake and eliminates  $H^+$  [19].

The common sources of soil acidity come from the  $H^+$  ions that are released when high levels of  $Al^{3+}$  ions react with water molecules in soil [20]. In other places acidity in soil is caused by warm temperatures and high rainfall, these results in the formation of acidic soil with fewer nutrients. Anthropogenic activities can also contribute to soil acidity; processes such as the application of  $NH_4^+$  ions-producing fertilizers acidify the soil through a biological reaction where  $NH_4^+$  oxidizes to  $NO_3^-$  and  $H^+$ . Industrial activities basically release sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides which later react with water to form acid rain that acidifies soils, especially in forest soils with low buffering capacities [21].

In soil when pH decreases below 5.5 the availability of  $Al^{3+}$  and  $Mn^{2+}$  ions increases and may reach a point where they become poisonous to plants. Acidic soil is known as the soils that have pH value of less than 7. The acidity is caused by the concentration of hydrogen ions. When H<sup>+</sup> ion concentration increases, the soil pH becomes low [20]. Processes such as leaching, erosion, crop uptake of basic cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup>), the decomposition of plant residues and plant roots exudates cause an increase in soil acidity. Acidic soils are infertile due to aluminium and manganese ion toxicities, and lack of calcium and phosphorus ions [21]. When soil pH decreases, micronutrients in the soil become more available. Soil acidity has an impact on certain plant pathogens (disease-causing organisms) [20]. The soil acidity can increase the effects of poisonous elements, reduce the plant production, impact important soil biological functions like nitrification, and make the soil more prone to soil structure decrease and erosion. Soil acidity occurs naturally in high rainfall areas and differs according to the landscape geology, clay mineralogy, soil texture and buffering capacity [22]. Soil becomes slowly more acidic with time in the natural ecosystem. The newly formed soil is found to be less acidic when compared to the old and weathered soil [18].

#### **1.2.5 Soil alkalinity**

The alkalinity of soil is a state that results from the increase of soluble salts in the soil. The alkaline soil is mainly detected in the desert environment around the world. The level of alkalinity in soil is usually measured in terms of pH. The scale of pH is divided into 14 divisions. Soil pH with a value below 7 is acidic or sour soil, while soil pH with the value above 7 is called alkaline or basic or sweet soil [17]. A pH of 9 is found to be ten times more alkaline than pH of 8; therefore this implies that pH of 10 is 100 times more alkaline than pH of 8. High concentration of sodium carbonates (NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>) results in an increase of alkaline conditions [23]. Alkaline soils have a high capacity of base cations ( $K^+$ , Ca<sup>2+</sup>, Mg  $^{2+}$ , and Na<sup>+</sup>). This is due to the build-up of soluble salts which are classified as saline soil, sodic soil, saline-sodic soil or alkaline soil. All saline and sodic soils have high salt concentrations, with saline soils being dominated by calcium and magnesium salts and sodic soils being dominated by sodium [24]. The damage caused by alkaline environments are more striking than those resulted from the salinity; this includes the dangerous effects of sodium ion breaking down the soil structure, carbonate ions toxicity, less uptake of calcium ions and corrosive effect of high alkalinity – hence the name black alkali. In desert regions, alkalinity and salinity increase because of high evaporation rates, which pass precipitation so that the moisture in the soil is brought upwards to the surfaces rather than leaching downwards. The increase in moisture carries the salts upwards [17].

#### 1.3 Soil heavy metals

"Heavy metal" is a term used to describe common transition metals that have the ability to cause risk to the environment. Heavy metals such as hexavalent chrome are known to be carcinogenic, while other heavy metals are related to the environment. Extreme pH, redox, and geology can have a mobilizing or immobilizing effect on some dependent heavy metals, whether it is anionic or cationic [25].

The uptake of heavy metals in soil by plants depends on the plant species and bioavailability of metals in the soil. In urban and agricultural soil, heavy metals contamination occurs as a result of mining, and the use of synthetic products such as batteries, pesticides, paints and industrial wastes [26].

Heavy metal and metalloids occur in soil not only from natural sources, which are soil erosion and weathering of rocks, but also from human activities such as industrial activities, agricultural production and household wastewater [27] which results in the increase of their concentration in soil, and they become dangerous to both plants and animals. Metals exist as separate entities or in combination with other soil components. These components include the absorbed exchangeable ions on inorganic metal compounds such as carbonates and phosphates, soluble metal compounds or free ions in the soil solution, and metals attached to silicate minerals [28]. Properties of soil affect metal availability in different ways. The major factor is soil pH; availability of some metals such as Cd and Zn decreases with the increase in soil pH. Organic matter and hydrous ferric oxide have been shown to decrease heavy metals availability through immobilization. Heavy metals can modify some soil properties specifically soil biological properties and affect the diversity and activities of soil microorganisms. The toxicity of these metals on soil microorganisms depends on the number of factors such as temperature, pH, clay materials, organic matter and chemical forms of metals [29].

The top layer of soil retains heavy metals present in irrigation water through adsorption by soil particles. After the accumulation of heavy metals in soil, they can be released into the soil pore water and taken up by plants [11].

The soil is a very composite heterogeneous medium, which is made up of solid phases (the soil matrix) containing organic matter and minerals and fluid phases (the soil water and soil air), that are directly involved with each other and ions entering the soil system.

Adsorption is an important process that is responsible for the building up of heavy metals. An essential interaction involved in heavy metal adsorption in soils is mainly inorganic colloids such as clays, metal oxides, and hydroxides, metal carbonates and phosphates. Adsorption of heavy metals onto these surfaces regulates their solution concentration, which is also impacted by inorganic and organic ligands [30].

In other cases an increase in pH of the soil may certainly result in a decrease in metal availability; an example is molybdenum in the soil which is found in the form of  $MoO_4$  and is more soluble in high soil pH [31]. The soil is the main sink for heavy metals released into the environment by through anthropogenic activities, unlike organic contaminants which oxidize to carbon (IV) oxide by microbial action [32].

In soil, heavy metal pollution changes the composition and the activity of microbial soil communities. The bioactivity, richness and microbial diversity decrease with the increase in the concentration of heavy metals [33]. Indirectly, these heavy metals take part in the ecosystem and through leaching, they infiltrate the ground [34].

#### 1.4 Water

Water is a colorless, tasteless and odorless liquid that is important to all forms of life. Chemically, water is a compound of two hydrogens and single oxygen atom. It is chemically active reacting with many substances which include certain metals and metal oxides to form bases and other oxides of nonmetals to form acids [35]. It appears in three forms of matter in nature (which includes solid, liquid and gas) and may take different forms on earth [36].

Water is a major constituent of an organism's fluid and covers up to 71 % of the earth's surface [37]. Most of the living tissue of the human body is made up of water; it constitutes 92 % of blood plasma, about 80 % of muscle tissue and 60 % of red blood cells [38]. It circulates through the land to transport, dissolve substances, and replenish nutrients and organic matter and to remove waste [39]. Apart from drinking purposes, water is used for many reasons by humans. They use water for cooking, washing clothes, washing their bodies and also irrigation for the growth of farm crops and stock as well as in the manufacturing of many products used by humans [40].

South Africa is a water scarce country, where the demand for water is in excess of natural water availability in several river basins [41]. The South African Constitution accepted that water is a basic human right, the origin of all things and the giver of life [42]. The Constitution of South Africa asserts that everyone has a right to access quality water and sanitation. Eastern Cape Province remains one of the provinces that falls behind in terms of rural and industrial development. Water continues to be observed as a scarce resource in many places around Eastern Cape [43]. The changing of water's physicochemical properties such as acidity (pH), Electrical conductivity and temperature, are mainly affected by an increase in chemical nutrient concentration in such a way that it becomes a major yield of the ecosystem. Water population in this form can result in a critical decrease of water quality which has negative impacts on humans and animal health [44].

Water plays a major role in the world's economy as it functions as a solvent for a wide variety of chemical substances and facilitates industrial cooling and transportation [45]. Water is a good polar solvent and is often denoted as the universal solvent. Pure water has a low electrical conductivity, but it rises with the dissolution of a small quantity of ionic material such as sodium chloride (NaCl) [46].

#### 1.4.1 Water pollution

Worldwide the most challenging problem the world is facing is pollution of water. Water pollution is the building up of harmful substances in water bodies to the level that results in health problems for people and animals [47]. It is also a change in any chemical, biological, and physical quality of water. Water pollution occurs as a result of human activities such as releases of effluents on water [48]. Water pollution is accountable for the deaths of more than 14000 people daily [35].

When water is polluted, both the physical and social health of a society is in danger and it's an affront to human dignity [26]. A previous investigation demonstrated that many of small water works in South Africa have struggled in providing suitable treatment and disinfection which resulted in water users being in danger of waterborne disease even from treated water supplies. In Eastern Cape, water quality is a major problem in many of the rural areas.

Eastern Cape is the second largest province in South Africa and it consists of many rural areas. Due to lack of resources many rural communities are currently suffering to get a supply of healthy water and sanitation facilities. Rural communities have access to the drinkable water supply that falls below the minimum quality standards set by DWAF or WHO [41]. Most of these areas are characterized by low-grade infrastructure, low wages, poor site circumstances, and unreliable water availability and poor right to use health services [42].

The major pollutants resulting in poor water quality include a wide spectrum of chemicals, pathogens, and physical or sensory changes such as raised temperature and discoloration [44]. Other natural and anthropogenic materials may cause turbidity (cloudiness) which blocks light and disturbs the growth of a plant, and blocks the gills of some aquatic animals.

#### **1.5 Medicinal Plants**

Medicinal plants are plants that contain properties or compounds which can be used for healing purposes and for the synthesis of metabolites to produce useful drugs [42]. In plants, other chemical components have responsibility for healing and possess nutrients properties as well as anti-toxicity [43]. Medicinal plants can carry different phytochemicals as well as minerals, vitamins and trace elements. Many plants appear like weed but each plant carries therapeutic secrets [44]. Many studies have been conducted to discover the safety, quality and energetic principles in many plants [50].

# 1.5.1 Acacia karroo



Figure 1: The picture of Acacia karroo

*Acacia Karroo* is an average to a large, single-stemmed and deciduous tree with a rounded crown often broader than tall and it grows up to 12M high [46]. It is one of the fastest developing Acacias and produces high-density wood (800-890 kg/m<sup>3</sup>) [51].

The species consists of paired, grayish to white thorns, finely textured dark green leaves, and produces yellow pompom flowers which are sweet smelling. The seed pods are narrow, flat and sickle-cell shaped [46].

Unlike other pioneer plants, *Acacia Karroo* has nitrogen-fixing microorganisms which are attached to its roots that make the soil around every tree increase its fertility [45]. *Acacia karroo* belongs to the *Fabaceae* family and subfamily *Mimosoideae*. It is commonly known in many cultures; common names are Sweet thorn (English); Soetdoring (Afrikaans); Mookana (North Sotho); Mooka (Tswana); umuNga (Zulu or Xhosa) [51].

*Acacia karroo* got its name after the Karroo region of former Cape Province of South Africa, where it is commonly found [47].

Home-grown in large parts of southern African countries that include South Africa, Botswana, Lesotho, Zimbabwe, Swaziland, Zambia, it is probably South Africa's most common tree. Sweet thorn was given this name because of the gum which is exuded from wounds in the bark of the tree [48].

#### 1.6 Heavy metals

Heavy metals are natural components of the Earth's crust. They are outlined as those metals with the determined gravity of more than 5g/cm3 high. Most common heavy metals are Cd, Pb, Hg, Cu, Ni, Cr, and Fe. Ni and Fe are the most important elements for the survival of all living organisms if they are present in small required levels, while other elements such as Pb, Hg and Cd are dangerous in living organisms even if they are present in small amounts and can generate abnormal functioning of organs in some living organisms [52].

Heavy metals are non-biodegradable hence they are not readily purified and are removed by metabolic activities once present in the environment; this is responsible for their growth in the environment [53]. In humans, heavy metals become more dangerous when they are not mobilized by the body and tend to build up in soft tissues [54]. They are risky because they have a tendency to bio-accumulate and have long time persistance through contact with soil components and as a result, they enter the food chain via plants and animals [55].

In some cases, wastes are discarded recklessly regardless of their environmental consequences, while in some dumpsites wastes are burnt in the open and ashes abandoned at the sites [47].

The burning of wastes gets rid of organic materials and oxidized the metals, leaving the ash richer in metal substances. Some farmers fetch the decomposed parts of the dumpsites and use it on their farmlands as fertilizer (manure) for cultivating fruits and vegetables [55]. It has been reported that concentrations of heavy metals in the soil around waste dumpsites are influenced by types of wastes, topography, runoffs and level of scavenging [47].

The pollution of heavy metals can disturb the water and soil ecosystem and may result in an important loss of soil quality through their poisonous processes catalyzed by soil microorganisms and poor quality of water [52].

In many places in developing countries dumpsites exist and most of them are still uncontrolled and unmanaged. This causes risk on human health for the next several years because most of them are open dumpsites. Due to certain physical and chemical properties, some metals such as Hg, Cd, and Pb are used in some industrial products including batteries, circuit, and certain pigments [56].

Dumpsites produce health hazards even to the people passing or staying close to the dumps. This is due to the unpleasant smell coming from the activities of micro-organisms on the organic waste. The unrestricted burning of municipal solid waste results in serious environmental pollution, which later affect the solid-waste workers and pickers. Human scavengers may also result in unintentional fires since metals are easier to see and recover among ashes after the fires than among piles of mixed garbage [57].

Inappropriate management strategies of waste are dangerous to humans staying in cities, especially those living near the dumpsites due to contamination occurring in soil, water and air from the garbage. The increase of living organisms even at low levels they can result in long-term cumulative health effects which are among the leading health concerns all over the world [58].

#### 1.7 Atomic Absorption Spectrophotometry (AAS)

It is one of the most common instrumental approaches for investigating metals and some metalloids. It is also a spectroanalytical method for the quantitative determination of chemical elements using absorption of light by free atoms in the gaseous state. In analytical chemistry, this technique is used to determine the concentration of an exact element in an analyzed sample [59].

#### 1.7.1 Principles

Basically, this technique uses the principle that free atoms (gas) formed in an atomizer which can absorb light at a specific frequency. AAS quantifies the absorption of the ground state in the gaseous phase. Atoms absorb ultraviolet visible light and move to higher electronic energy levels. The analyte concentration is determined from the amounts of absorption and that relies on the Beer-Lambert law [60].

$$A = \varepsilon. b.C$$

In general, each wavelength matches to only particular elements, and the thickness of the absorption line is only of the order of less flux without sample and with a sample in an atomizer, this measured using a detector and then the proportion between two values (absorbance) is converted to analyte concentration or mass [61].

#### 1.7.2 Quantitative laws (Beer's Law)

The concentration of the absorbing species in the sample is determined by applying Beer-Lambert law. This law states that the absorption of light by a solution changes exponentially with the concentration, all else remaining the same.

$$A = \varepsilon. b. C$$

Where A= is the absorbance,  $\varepsilon$  = is the wavelength dependent molar absorptivity coefficient, C = is the analyte concentration and b = is the path length.

Applying the Beers – Lambert law in AAS is hard because of variations in the atomization from sample matrix and non-uniformity of concentration and the part length of analyte atoms. The relationship between A and two intensities is given by the following formula:

$$A = log10 \ (\frac{I^{\circ}}{I})$$

A zero absorbance at some wavelength indicates that no light of specific wavelength has been absorbed; the intensities of the sample and the reference beam are both the same so the ratio is 1.

$$\left(\frac{l^{\circ}}{l}\right) = 1$$
, Because of  $\log_{10}$  of  $1 = 0$ 

When the electromagnetic radiation of monochromator passes through an infinitesimally thin layer of the sample, of thickness  $d_x$ , it experiences a decrease in power of dP. The fractional decrease in power is proportional to the sample's thickness and analyte concentration C, thus

$$-\frac{dP}{P} = a.C.dx$$
(1)

Where P = is the power incident on a thin layer of the sample, and a = is a proportionality constant. The integrating of the left side of the above equation (1) from P = P<sub>0</sub> to P=P<sub>T</sub> and the right side from x =0 to x = b where b is the sample's overall thickness [59].

$$-\int_{P=Po}^{P=Px} \left(\frac{dP}{P}\right) = AC \int_{x=0}^{x=b} dx$$
  
Gives : 
$$\ln\left[\frac{Po}{Pt}\right] = a.b.c$$

Converting from ln to log and substituting equation:

$$A = a.b.C$$

#### **1.7.3 Instrumentation**

AAS are made up using a single beam or double beam. The requirements for AAS are a light source, a cell which is also known as a flame, monochromator and a detector. In nowadays the commonly used atomizers are flames and electrochemical atomizers (graphite tubes).

The flame is set between the source and monochromator. The light passes through a monochromator in order to isolate the particular element radiation from any other particle emission released by the light source, which is finally measured by a detector. The detector amplifier is tuned to receive only radiation controlled at a frequency of the chopper [52].



Figure 2: The schematic diagram of an Atomic Absorption Spectroscopy [61].

#### 1.7.4 Sources

Radiation sources can be differentiated between line sources (LS AAS) and continuum sources (CS-AAS). Absorption lines are very small, usually only ranging between 0.002 - 0.005 nm. Line sources release a small band of radiation which is essential because they are highly selective, providing high sensitivity and decrease in the spectral interference of other elements, ions, and molecules that have comparable spectral lines [61].

In LS AAS, the high determination that is required for the measurement of atomic absorption is provided by the narrow line emission of the radiation source and the monochromator simply has to resolve the analytical line from other radiation emitted by the lamp. Continuum sources are usually used for background correction to exclude the matrix so only the signal of the analyte is experiential. When a continuum radiation source is used for AAS measurement it is essential to work with a high-resolution monochromator. The resolution has to be equal to or better than half the width of an atomic absorption line (about 2 pm) in order to avoid losses of sensitivity and linearity of the calibration graph [61].

There are many examples of line sources but the most commonly used is the Hollow Cathode Lamp (HCL) and the Electrodeless Discharge Lamp (EDL). HCL is an airtight lamp filled with argon gas or neon gas and kept around 1-5 torr. The inactive gas is ionized as a high voltage potential difference between the tungsten anode and uses specific cylindrical cathode [48].



Figure 3: The design of a Hollow Cathode Lamp [59].

#### 1.7.5 Burners

In most commercial instruments the burner that is used is called premix chamber burner, sometimes called laminar –flow burner. Premix burners are generally limited to relatively slow-burning velocity flames.

✓ <u>A premix burner system actually involves two key components, the burner head or nozzle, and the gas-air mixing device that feeds it. The fuel and support gasses are mixed in a chamber before they come in the burner head (through a slot) where they combust. The sample solution is again aspirated through a capillary by the 'Venturi effect' using the support gas for the aspiration. Large droplets of the sample reduce and drain out of the chamber. The remaining fine droplets mix with the gases and enter the flame. As much as 90 % of the droplets condense out, leaving only 10 % to enter the flame. The 90 % of the sample that does not reach the flame will move back through the mixing chamber and out as waste drain.</u>

The premix burners are generally limited to moderately low-burning velocity flames. The most unresolved disadvantage of the premix burner is that only low burning-velocity flames can be used.

A burning velocity which is higher than the rate of flow gasses leaving the burner will cause the flame to move down into the burner causing a bang commonly known as a flashback. Because of this limitation, it is somewhat hard to use high burning velocity gasses, which include oxygen-based flames.

A popular version of premix burner is boiling burner. Boiling is a three-slot burner head that results in a bigger flame and less distortion of the radiation passing through at the edges of the flame. This burner warps more easily than others, though care must be taken not to become excessively hot.

#### ✓ <u>Total Consumption Burner</u>

The fuel and support gasses are mixed in a chamber before they go in the burner head where they combust. The sample solution is aspirated through a capillary by Venturi effect, using the support gas for aspiration.

The air produces an incomplete vacuum at the end of the capillary, drawing the sample through the capillary and is broken into the fine spray at the tip. This is the usual process and is called nebulization [62].

Although a large portion of the aspirated sample is lost in a chamber, the efficiency is finer and has a long path in producing an atomic vapour that enters the flame at a high speed. The burner is called total consumption because the whole aspirated sample goes in the flame. All desolvation, atomization and excitation occur in the flame [62].

However, the total consumption burner can be used to aspirate viscous and 'high solids' samples with more ease, such as pure serum and urine. Also, this burner can be used for most types of flames, both low- and high burning velocity flames. The Venturi Effect is the reduction in fluid pressure that results when a fluid flows through a constricted section of pipe [62].

#### 1.7.6 Flames

The most widely used flames for AAS are the air-acetylene flame and the nitrous oxideacetylene flame with premix burners. The final high-temperature flame is not required and may even be detrimental for many cases in the atomic absorption because it will result in ionization of gaseous atoms. The air-acetylene flame is very useful to those elements that tend to form heat – stable oxides. The air-acetylene and other hydrocarbon flames absorb a large fraction of the radiation at wavelengths below 200nm and an argon-hydrogen entrained air flame is preferred for this region of the spectrum for maximum detectability. This is a colorless flame entrained air is the actual oxidant gas. It is used for elements such as arsenic (193.5nm) and selenium (197.0) when they are separated from the sample solution by volatilization as their hydrides (AsH<sub>3</sub>, H<sub>2</sub>Se) and passage of these gasses into the flame.

This is necessary because this cool flame is more subject to chemical interference than other flames. A nitrous oxide-acetylene flame offers an advantage in this region of the spectrum when the threats of molecular implications exist: the flame's absorption is fairly small at short wavelengths [63].

Oxidant fuel	Temperature ( <sup>0</sup> C)	Burning velocity (cm/s)
	1700 1000	
Air-natural gas	1700-1900	55
Air-acetylene	2125-2400	160
Air- hydrogen	2000-2050	320-440
Oxygen-natural gas	2740	-
Oxygen-acetylene	3063-3135	1100
Oxygen-hydrogen	2550-2700	2000
N <sub>2</sub> O- acetylene	2700-2800	350-450
N <sub>2</sub> O- Hydrogen	2607	380

Table 2: Temperature and Burning velocity of oxidant gasses used in AAS

## **1.7.7 Sample preparation**

Normally the sample in atomic spectroscopy is found in two forms which are solid or liquid. The liquid phase looks to be the coolest form in which to handle the sample, but some requirement for filtration is essential. However, the characteristic lack of sensitivity of many spectroscopic techniques and the need to carry out determinations at very low levels means that some form of pre-concentration is always required. If the sample is in a solid form, the best requirement is to change it to liquid form even though it is possible for the sample in solid form to be analyzed directly using atomic spectroscopy but it's not a chosen approach [62].

The principal purposes of sample preparation for residue analysis are; dissolution of the analytes in a suitable solvent, isolation of the analytes of interest from as many meddling compounds as possible, and pre-concentration. The selection of a sample preparation method is dependent upon these:

- $\checkmark$  The analyte,
- $\checkmark$  The analyte concentration levels,
- $\checkmark$  The sample matrix
- ✓ The instrumental measurement technique
- $\checkmark$  And the required sample size.

For the simplest analyses of metals and alloys, the electrodes made of the sample material itself may be used as a disc or cylinder being cut or cast from the powder. Homogeneity of the electrode is of prime importance. A pointed graphite rod or tungsten is used as a counter electrode. A laser is focused directly on the sample and will provide a signal from a very small part of it. Mostly valued is the potential of the laser for the analysis of very small species [63].

#### **1.8 Problem statement**

Most developing countries including South Africa use dumping to remove waste because it remains the affordable option [64]. In South Africa, most municipalities are said to have arranged landfills with detailed strategies and procedures to manage them. Though there are principles, studies have shown that local and district municipalities in Eastern Cape and South Africa as a whole are facing several challenges, including the illegal dumping and inappropriate management of dumping sites [65].

In some places, landfills work as open dump sites where garbage from town and surrounding environments are dumped and often burned to ashes leaving soil rich with metals [66]. These studies show that 60 % of disposal waste in the landfill contains recyclable waste. The uncontrolled sites pose a high risk to human health and animals around the site [67].

Communities in South Africa are simultaneously faced with poverty, degraded environment, unavailability of jobs, and restricted access to safe drinking water and sanitation [68]. Alice landfill site under Nkonkobe municipality is poorly managed. Waste pickers and animals around the site access the site at any time of the day [65].

To them, a truck with garbage is just like the source of food and cash in vans filled with money. Needy people from close villages such as Sheshegu collect food at dumpsites to feed their families as well as to recover any material that they could reuse in their houses [68]. These people are in danger of being affected by contagious diseases since they use their hands to dig in those plastic wastes and they can be injured as there are several sharp materials in the rubbish [65].

## 1.9 Aim and objectives

The aims of this study are to evaluate the physicochemical parameters and metals in the soil, water and plant from Alice landfill site, to find how the anthropogenic activities occurring in and outside of Alice landfill site can affect the concentration of the present metals, and how human health, animals, and environment at large can potentially be affected by heavy metal pollution.

**Objectives:** 

- $\checkmark$  To determine the chemical properties of soil and plant samples
- $\checkmark$  To determine physicochemical parameters of water samples.
- $\checkmark$  To quantify metals availability in soil and plant
- $\checkmark$  To determine metal presence in water.

#### 2.0 LITERATURE REVIEW

#### 2.1 Heavy metal pollution of water

South Africa is one of the 30 driest countries in the world. Water quality is poor due to natural and anthropogenic activities such as the release of impure substances into the environment which end up accumulating in water through the runoffs and soil erosion, resulting in contamination of water. Metals are classified as one of those pollutants of concern because of their ability to harm the environment and their ability to bioaccumulate i.e stay for a long period of time before being decomposed.

Öztürk *et al* (2009) conducted a study to determine the availability of heavy metals and their concentration in fish, water and sediments from Avsar dam Lake of Turkey. It is because the fish was the source of food in that area. In their findings, the results showed that metal concentration in the Avsar dam lake was at a low concentration compared to another sample site, this is due to the domestic activities that occur inside and outside the dam. Also, the metal concentration in water was found to be lower than the concentration of metals in sediments. This suggests that concentration of other metals is more at the lowest part of liquid water. However, the fish samples were found to contain high levels of metals which are more than the levels required by humans, and that can result in health problems to those eat such fish [69].

In 2013 Mohod and Dhote investigated the presence of heavy metals in drinking water and their effect on human health. The study was conducted because of the link showing human poisoning due to heavy metals such as Cd from the drinking water. The obtained results revealed the samples of drinking water contained a high amount of heavy metals and were found to be more than the permissible limits from WHO or USEPA. These results show that most of the water samples were inappropriate for drinking purposes. They also showed that a great part of the population had a notable chance of being affected by these heavy metals. This tells us that water for drinking purpose needs special treatment before use so as to prevent people from being affected by various diseases such as organ dysfunction like kidneys that may be caused by the presence of heavy metals in their drinking water [70].

Similarly, a study determining the metal level in different dams around Eastern Cape has been done by Fatoki (2013). The obtained results show that the Cd concentration in dams and rivers of Tyhume, Buffalo, Sandile, and Keiskamma is exceptionally high except in those dams from Umtata. Zn and Hg levels were within the normal accepted standard limits in all surface water. They found out that high levels of Cd in water could be caused by runoffs from agricultural soil that use phosphate fertilizers and from natural sources due to the geology of the catchment of soil [71].

The findings of the study conducted by Bala (2008) on determining the heavy metal level in water collected from two pollution areas show that the levels of metal concentration in water from polluted sites are significantly higher than the levels of heavy metal concentration in water from the control site. It was found again that the mean values of these metals exceeded the maximum allowed concentration of metals in water [72].

Onwughara *et al*, (2013) conducted a study on analysis of water samples for physiochemical properties on water using standard methods and evaluated with WHO standards. The results achieved show that all analyzed physiochemical parameters in water samples are within the permissible limits of WHO except total dissolved solids (TDS), biochemical oxygen demand (BOD), dissolved oxygen (DO) and phosphates that were found to exhibit maximum allowed concentration. The results indicate that the water source is polluted and is not good for human consumption [73].

#### 2.2 Soil pollution due to dump site activities

Many places such as Nigeria are faced with environmental challenges which are caused by unacceptable disposal of waste near the community and public places around town and dumpsites especially those soils situated on undeveloped plots of land are used as fertilizers. Benjamin *et al*, (2012) conducted a research to determine the concentration of heavy metals in some selected waste dumpsites around Nigeria (in Gboko, Metropolis and Benue state). The study showed that collected soil samples have a mean pH value that varies from 7.15 - 7.70 for north and south Gboko. They used aqua regia extraction for determining the presence of heavy metals and followed by Atomic Absorption Spectrophotometry (AAS) for metal analyses. They found that the samples of soil contain the following metals: Pb, Ni, Cd, Al, Cr, and As. The concentration of these heavy metals is different, at North Gboko the concentration was high compared to south Gboko.
The concentration of the heavy metals in all these dump sites were found to lie within the limits of WHO except the Cd and Cr which were moderately above limits [74].

A study on the concentration of heavy metals in soil, plant leaves and crops are grown around dump sites in the land of Lafia Metropolis and Nasarawa state in Nigeria was done in 2012 (Opaluwa *et.al*, 2012). They wanted to estimate levels of pollution of the farm lands around the dumpsite in Lafia, the area where plants crops are grown and unprotected to heavy metals. Hence they estimated the safety levels in crops and plant leaves which were being cultivated for consumption by humans. The metal concentration of soil samples was found to be less than the concentration of metals in plant samples and this concentration was measured in mg/kg. In soil, Pb concentration was lower than EU upper limits (300 mg/kg) and lower than the maximum tolerable levels proposed for agricultural soil. However, they also found that the Pb concentration could be as a result of its sources from car exhaust gas, dry cell battery run-off waste and atmospheric deposition which could result in its bioaccumulation in plants through their uptake from the soil that finally enters the food chain. Pb was found to have higher levels that are above WHO standard. In plant leaves (Roselle and spinach leaves) the heavy metal concentration from both sites was lower than the concentration of heavy metals found in control site plants.

This was proof that the soil could be attributed to the free movement of metals from dumpsites to farmlands through leaching and overflows; heavy metals in a very high concentration in plants may create a risk to consumers of these plants around this place [55].

Soil contamination around mining areas has not yet been taken into consideration. Mining is one of the biggest sectors of the South African economy which also helps different developmental projects. This was proved by a study conducted by Olowoyo *et al*, (2013) on investigating the concentration of different elements in soil and plants composition from a mining area. The results indicated that all the selected elements had a concentration which is more than the allowed permissible values from environmental agencies. The concentration from soil samples was in this following order Al > Fe> Ca > Mg > Cr > Na > Mn > Ni > Zn > V > Cu > Pb > As > Cd and the difference in concentration was found to be significant (p> 0.05). The results also show that the soil around the mining area was strictly contaminated by Ni and Cr; this was proved by the pollution index and geoaccumulation index. The concentration of three elements (Fe, Ni, and Cr) was shown to be high enough to harm the environment. In the same study the concentration of elements found on *Cymbopogon excavatus* grass were in this order Mn > Fe > Cr > Zn > Cu > Pb > As. The difference in concentration of these metals was significant (p> 0.05). The concentration of Cr and Pb were reported to be more in roots compared to leaves [75].

The analysis was done to determine heavy metal concentration in soil and plants from Okeogi municipal area, Iree in Nigeria by Olufunmilayo *et al*, (2014). The results indicate that only Pb concentration from dumpsite soil was more than the permissible limits, while other metals such as Zn were within allowable limits. The concentrations of all selected heavy metals in the dumpsite were found to carry higher values than those from the control site. The heavy metal concentration for both dumpsite and control site followed this order Pb > Zn > Mn > Cu > Cd > Co, and most of them fell below the permissible limits, while for plant sample the concentration differs from one element to the other. The higher concentration of heavy metals in plants occurs mostly as a result of waste composition from dumpsites. The reported results from the plant sample suggest that the consumption of vegetables that are grown in such places can be dangerous to human health [76].

### 2.3 Acacia Karroo

Studies have shown that there is no much work done on *Acacia karroo* in South Africa and in other countries. The Acacia species are a major source of food for certain animals such as goats especially when feed production is limited. The study on the potential of *Acacia Karroo* leaf meals as a protein supplement for fattening goats was done by Masuku (2013). The results indicated that the supplement from *Acacia Karroo* had a positive effect on weight gain as food supply and body shape of Boer goats with the best addition rate of 25%. Since *Acacia Karroo* is a plant species that is readily available and liked by goats over the years, it can be used as an available source of food for their survival [77]. Ngambu (2011) also investigated the effect of *Acacia Karroo* supplementation on the quality of meat from Xhosa lop-eared goats. The results obtained indicated that the supplement from *Acacia Karroo* supplement for a supplement for *Acacia Karroo* has a vital response to the color of meat, the pH, and on cooking processes. *Acacia Karroo* supplement has an advantage of increasing physiochemical meat value and physical characteristics, such as moistness and gentleness. The boiled meat had higher sensory scores than the roasted meat [78].

Most natural plants worldwide have the possibility of being used for healing or health purposes and sometimes as a source of food and medicine for different kinds of diseases. Siddique *et.al* (2013), reported on the determination of heavy metals in medicinal plants using AAS. The aim was to find the available metals and their quantity in the plants used for medicinal purpose in the community. The results showed that there are no resultant spectral peaks revealed in AAS for metal Cd, Pb, As and Hg. But in some plants, these metals were found to be present [12]. This was caused by the primary source of impurity that was found in both soil and environment i.e heavy metals (HMs). This may explain the greater incidence and concentrations of Cd, Pb, As and Hg against other HMs in plants. They suggested that plants rich with nutrients in the root, rhizome, and seeds have to be examined wisely before usage [79].

### 2.4 Manganese (Mn)

Manganese (Mn) constitutes 0.1% of the earth's crust which results in it being one of the 12 largest elements. Mn mostly occurs as pyrolusite (MnO<sub>2</sub>), Psilomelane (BaH<sub>2</sub>O)<sub>2</sub>Mn<sub>5</sub>O<sub>10</sub> and as a smaller size as rhodochrosite (MnCO<sub>3</sub>). Mn compounds are powerful oxidizing agents; they occur in different oxidation states (+4 and +7). Mn ions contain different colors depending on their oxidation states, and in industries, they are used as pigments while MnO<sub>2</sub> is used as cathode material in standard and alkaline disposable dry cells and batteries. The "+2" oxidation state of Mn is the most stable state among other oxidation states and is the one used in living organisms for important functions because other states are poisonous to the human body. When Mn concentration rise in the human body or in the environment people, can suffer from cerebellum dysfunction and neurological damage [80].

Mn is an important micronutrient in most organisms and plants. In plants, it plays a major role in the metabolic process, mainly in photosynthesis and as an enzyme antioxidant cofactor. The shortage of Mn in plants becomes dangerous to chloroplasts because it has an effect on the water-splitting system, photosystem ii (PS ii) which produces needed electrons for photosynthesis [81]. High levels of Mn concentration in plant parts (tissues) can change different processes including enzyme activity, absorption, translocation and usage of other mineral elements (Ca, Mg, Fe and P) as well as causing oxidative stress. Mn poisoning is a global problem in places with acidic soils because it changes physiological, biochemical and molecular processes at the cell level [82].

### 2.5 Copper (Cu)

Copper (Cu) is a reddish cubic crystal and d-block element. It occurs in rocks, soil, water, plants, and animals. It is an important chemical element needed for the growth of both plants and animals. It is also used as a component in metal alloys, electrical wiring, and preservatives for wood, leather, and fabrics [83]. It is malleable, ductile and a very good conductor of both electricity and heat. Cu has low chemical reactivity and is a very common matter that occurs naturally in the environment which does not break down due to the fact that it arises in plants and animals when it is present in soils [84].

In humans, Cu helps in the building up of hemoglobin while in plants it functions in seed production, disease resistance, and water regulation. A high amount of Cu in the human body results in anemia, liver and kidney failure as well as stomach and intestinal irritation. In water, Cu increases through Cu pipes and from additives made for control of algae growth [85]. When Cu ions combine with organic matter it forms strong coordination complexes, hence Cu is generally found to bind organic matter in soil. Soil organic matter can be an essential factor in determining the bioavailability of Cu [86].

### 2.6 Lead (Pb)

It is a soft silver blue-white cubic crystal with a p-block element. It is used in storage batteries, vibration absorbers and plumbing pigments [83]. Pb has an 11.3 g/cm3 density and is found in sulfide mineral galena, carbonate cerussite, and sulfate anglesite. It exists in different oxidation states (0, 1, 2 and 4) that are of ecological importance. Oxidation state +2 is the form in which most Pb is bioaccumulated by aquatic organisms. Pb is one the metals of great concern because of its toxicity, persistance and its ability to accumulate in the aquatic system [80]. Lead is the most common industrial element that has been found in large areas of soil, water, air, and food. In early civilization, societies used lead to manufacture materials such as kitchen utensils, trays, jugs, and decorative articles that are present in homes. Its increase in the industrial application has resulted in it being broadly distributed in the environment [87].

Pb is a common and very dangerous heavy metal even when present in small amounts. It enters water through corrosion of plumbing materials. Other sources of Pb include the paint, mining waste, burning ash, car emission, water from Pb pipes, and solders that are used to join Cu pipes.

Consumption of substances containing Pb can result in delayed physical and mental development of new born babies and children. To old people, it can cause kidney failure, damage to the brain, nervous system and red blood cell ability, cancer and hypertension [88].

Lead complexes such as lead oxides and hydroxides, lead-metal oxyanion, ionic Pb and Pb (ii) are common forms of Pb that are released into the soil, ground water, and water surfaces.  $Pb^{2+}$  is the most reactive and general form of lead compound that produces mononuclear and polynuclear oxides and hydroxides.

The most stable solid form within the soil matrix is lead sulfide (PbS) which is formed under low conditions when the concentration of sulfide has increased. White paint usually contains the basic salts formed from Pb, salts such as  $Pb(OH)_2 \cdot 2PbCO_3$ . This salt is a considerable source of chronic Pb poisoning to kids who eat peeling white paint [85].

#### 2.7 Mercury (Hg)

In the environment, mercury can be found in three forms; it can exist in its elemental form, as organic mercury, and inorganic mercury. Mercury in element form is a shiny silver-white liquid metal, which in spite of its low vapour pressure can be converted to a vapour at room temperature because of its low invisible heat of evaporation [89]. Inorganic mercury is found in two forms in nature which is mercurous and mercuric form. Mercuric salts have high water solubility and toxicity than elemental mercury and are highly absorbable by the gastrointestinal tract [90]. The most common form and major source of organic mercury found in the ecosystem is methylmercury (MeHg). MeHg is less soluble in water; therefore it is regarded as relatively lipid-soluble [20]. Possible sources of organic mercury include exposure to fossil fuel emissions, the burning of medicinal waste, dental amalgam, and different commercial products which include skin creams, germicidal, soaps, analgesic, thermometer, and vaccinations, includes the phenylmercury and ethyl mercury compounds [89, 91].

Accumulation of Hg in humans can cause damage to the nervous system, kidney, and vision. Mercury pollution can result in chest pain or angina especially in people who are under the age of 45. There is also good evidence linking mercury with hemolytic and aplastic anemia as mercury is thought to compete with iron for finding hemoglobin [92].

Poisonous moisture formed from Hg evaporation or incineration of material containing mercury and medicinal waste can enter the respiratory system and pass immediately into the circulation system [93].

The most known natural source of Hg is degassing of the earth's crust, emissions from volcanoes and evaporation from natural bodies of water which can also occur as a result of leaching of soil due to acid rain [88]. Around the world, mercury is used in industrial processes for the manufacturing of different products such as batteries, lamps, and thermometers. It is also used in dentistry as amalgam fillings and in the pharmaceutical industry. The main pathway for Hg to humans is through the food chain and not by inhalation [84].

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## **CHAPTER TWO**

### **2.0 METHODOLOGY**

## 2.1 Sampling site

The investigation was carried out in Alice Township under Raymond Mhlaba Municipality, using two areas the Alice landfill site and the East campus inside the University of Fort Hare. The East campus was used as a control site and is  $\pm 4$  km from the dumping site. The landfill site is located about 2 kms from the Happy Rest residential area. The site is about two hectares. The landfill is registered with the Department of Water Affairs (DWAF) as G: C: B- and is expected to be managed according to their minimum requirements. The whole dumping site is covered by the very large amount of different natural plants. It was divided into three portions: portion A (east side) where the ground is covered by broken glass, portion B (south side) is full of rusted tins and broken glass after burning of disposal waste and portion C is outside the fencing and is covered with natural plants. The dam is located outside the dumpsite at about 200 meters away and is close to the cow's kraal.



Figure 4: The picture showing the map of the landfill site [1].

## 2.2.0 Sample collection

The samples were collected two times a week for six weeks. The soil samples were collected at Site A using clean stainless steel soil Auger by twisting it from 0-50 cm depths at each portion of sampling site while the uncontaminated soil was collected from Site B.

The collected dry soil samples from each site of each portion were placed in clean and labelled polyethylene bags and then transported to the laboratory for further analysis.



Figure 5: The collection of soil samples in three portions of site A

The samples of *Acacia Karroo* inside the dumpsite were collected randomly with a stainless steel knife which was first sterilised with HNO<sub>3</sub>. For plant identification, the plant sample was deposited in the herbarium of the Botany department at the University of Fort Hare. The plant was then identified by Professor A. Maroyi and a voucher specimen number issued (NG/01) [2].

Pre-cleaned plastic bottles were rinsed with distilled water and the sample to be collected. Bottles were used to collect water sample below the surface. The samples were acidified using nitric acid and kept in ice bags at  $4 \, {}^{\circ}C$  [3].

# 2.2.1 Physicochemical properties

Analytical methods for the physicochemical properties of water which are temperature, pH, and electrical conductivity, were measured at the collection site by the use of multi-parameter water quality instruments [4].

Table 3.	Methods	used for	determination	of differen	t physicoc	hemical	nronerties in	water
<u>1 abic 5</u> .	Methous	uscu 101	ucicilimation	of unficient	i pilysicoc	nennear	properties in	water.

Determined parameter	Method used
Temperature	Thermometer
рН	pH meter
Electrical conductivity	Electrical conductivity meter

# 2.2.2 Determination of alkalinity

Two or three drops of phenolphthalein were dropped into 100 mL of the water sample. The appearance of pink color in the water indicates the alkalinity. The solution was titrated with  $0.02 \text{ N H}_2\text{SO}_4$  until the color disappeared [5].

## 2.2.3 Total hardness

50 mL of water sample was mixed with 1-2 mL buffer of pH10 and few drops of Eriochrome black-T indicator; the contents were then titrated with 0.01M EDTA till the wine-red solution changed to blue [5].

<u>Calculation</u>: Hardness (mg/L) =  $\frac{C \times D \times 1000}{mL \text{ of sample}}$ 

Where C = mL of EDTA for titration, D = mg of CaCO<sub>3</sub> equivalent to 1 mL of EDTA

# 2.2.4 Total dissolved solids

An evaporating dish and filter paper were washed, dried and weighed. 50 mL of well-mixed water sample was pipetted and filtered using Whatman filter paper. The filtered sample was transferred into an evaporating dish and dried at 180 °C. When the sample was dry, the evaporating dish was then cooled in a desiccator and the mass was measured[6].

Calculation:

mg/L Dissolved solids = 
$$\frac{(A-B) \times 1000}{mL \text{ of sample}}$$

Where A = mass of dried residue + dish (mg), B = is the mass of dish.

## 2.2.5 Moisture content determination

In a beaker of known mass, the soil samples were added and the mass measured. The samples were oven dried at 105 °C for 24 hours until constant mass was obtained. After heating, the samples were cooled to room temperature and placed in a clean plastic bag for further analysis [7].

Calculation:

% Mass = 
$$\left(\frac{\text{Air dried-Oven dried}}{\text{Oven dried}}\right) \times 100 \%$$

Using a mortar and pestle, soil samples were crushed and sieved in a 2 mm mesh to remove coarse debris and to obtain representative samples [7].

For the plant: Plant parts were separated, pre-cleaned with distilled water and dried to a constant mass at 80 °C in an oven. Dried samples were crushed into a fine powder using mortar and pestle. The sample was sieved using 2mm mesh to obtain fine powder and was placed in a plastic bag [8].

### 2.2.6 Determination of soil pH

In a 100 mL beaker of known mass, 20 g of sieved soil sample and 20 mL of 0.01 M calcium chloride solution was added; the formed mixture was stirred and allowed to stand for 30 minutes with occasional stirring. The determination of pH was done by immersing a glass electrode into the partially settled solution, making sure the electrode didn't touch the walls of the beaker [9].

### 2.2.7 Organic carbon

1.0 g of soil sample was weighed into a 250 mL conical flask, 10 mL of  $K_2Cr_2O_7$  was added and the flask was gently swirled to dissolve the soil. 20 mL of conc.  $H_2SO_4$  was quickly added, then mixed thoroughly and allowed to stand in a fume hood for 30 minutes to cool down. 200 mL of water was added and the formed suspension was filtered through filter paper. 3-5 drops of ferroin indicator were added and the solution was titrated with FeSO<sub>4</sub>.

The end point was approached when the solution changed from dark green to blue to reddish brown [10].

### Calculation:

Organic carbon (%) = M x (
$$\frac{V_1 - V_2}{Mass of soil}$$
) x 0.39

Organic matter (%) = organic carbon (%) x 1.724

Where M= concentration of FeSO<sub>4</sub>, V1 = Volume of blank, V2 = Volume of FeSO<sub>4</sub>, 0.39 = constant and 1.724 = constant.

#### **2.2.8 Soil Electrical conductivity (salinity)**

10 mL of well-mixed water sample was added in a measuring cylinder. Small soil particles were also added to the water until the contents of the container increased by 5 mL to bring the volume up to 15 mL. Extra water was then added to bring the total volume up to 30 mL. The contents were shaken intermittently for five minutes and allowed to settle for five minutes. An EC probe was dipped into the solution to take a reading [11].

## 2.3 Heavy metal analysis

## 2.3.1 Sample treatment

20 mL HNO<sub>3</sub> was weighed out and added to 10 g of the soil sample in a 250 mL conical flask. The contents in the flask were placed on a hotplate until the solution reduced to 5 mL, after which 20 mL of distilled water was added until the suspension was reduced to 10 mL. When digestion finished, the residue was allowed to cool at room temperature and was filtered using Whatman filter paper and made up to 50 mL in a volumetric flask with distilled water [12].

For *Acacia Karroo* samples, 2g was weighed into a clean crucible, burnt to ashes at 450  $^{0}$ C and then cooled in a desiccator. The ash was dissolved in 5 mL of 20% HCl, placed in a 100 mL volumetric flask and made up to the mark using deionized water [13].

For water samples, 100 mL were added to 10 mL concentrated  $HNO_3$ . The sample was heated gently and then evaporated on a hot plate a 20 mL volume. The beaker was allowed to cool and 5 mL of concentrated  $HNO_3$  was added. The heating was continued with the addition of  $HNO_3$  until digestion was complete.

The samples were evaporated again to dryness and beakers were cooled. 5 mL of HCl solution (1:1 v/v) was added and the solution was warmed. 5 mL of 5M NaOH was added and then filtered into a 100 mL volumetric flask and filled up to the mark with distilled water [3].

## 2.3.2 Metal analysis

An Atomic Absorption Spectrophotometer (AAS) was used to analyze metals from digested samples [2]. The statistical analysis of data was performed using Statistical Package for Social Science (SPSS), which is a Microsoft office excel and computing package.

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### **CHAPTER THREE**

## 3.0 RESULTS AND DISCUSSION

#### **3.1 Soil results analysis**

44 soil samples were collected from both sites (three portions from site A and Site B), and 12 water bottles of water samples were also collected. The *Acacia karroo* samples were collected only on portion C of site A because it was the only portion having this plant.

## 3.1.1 Physico-chemical properties of soil

	Site A-Portion A	Site A-Portion B	Site A-Portion C	<u>Site B</u>
Soil pH	7.06 ±0.22	$7.09 \pm 0.37$	6.79±0.25	6.67±0.28
Moisture content (%)	12.30±1.89	13.48±3.43	11.07±3.39	10.16±2.30
Organic carbon (%)	1.10±0.36	1.33±0.64	1.19±0.48	2.01±0.83
Organic matter (%)	1.87±0.62	2.30±1.10	2.05±0.84	2.16±2.24
Electrical conductivity (µs/cm)	536.67±237.75	421.98±202.88	470.58±277.73	127.69±74.65

<u>**Table 4**</u>: The physicochemical properties of soils (mean and standard deviation)

Table 1 above indicates the results obtained for the physicochemical properties of soil samples on the undeveloped waste dump site and the control site which includes the soil pH, moisture content, Organic Carbon, Organic matter and Electrical conductivity which were used to identify the salinity of the soil.

**Soil pH**: Soil pH is a measure of hydronium ion  $(H_3O^+, or more commonly the H^+)$  activity in soil solution. It is also an indicator of soil acidity or alkalinity, which is a primary factor in controlling the availability of nutrients, microbial processes and plant growth [1].

The soil pH differed among the portions of dump sites. The difference in pH may be caused by the wet climate which has great potential for acidic soil, organic matter decomposition which produces  $H^+$  (hydrogen ions) and the type of sampling which occurred in diverse parts around each portion [2]. The mean hydrogen ion concentration (pH) in the dump site ranges from 6.79 to 7.09 with the standard deviation of 0.22 - 0.37, while in the control site the mean pH is 6.67 with a standard deviation of 0.28.

The results revealed that the mean pH of the soil in dump sites stretched from slightly acidic to a neutral soil pH, while in the control site, the pH is slightly acidic. The normal ranges from WHO for soil are between 6.5 and 8.5 [3].

Therefore, according to the obtained results all collected soil samples from both sampling sites the pH was recorded within the normal range set by WHO. The movement and the availability of macronutrients and micronutrients in soil are affected by pH and other soil components. It has been found that as the pH decreases the solubility of metallic components in soil rises and becomes more available in different fractions because of the rise in solubility of ions in acidic surroundings.

According to the tabulated results we can conclude by saying both micro and macro nutrients availability were increased, their solubility and mobility were also enhanced, and beneficial soil organisms were most active [1].

**Moisture content:** Moisture content is known to be the amount of water present in the soil. In the results obtained it was found that the mean percentage of samples collected in the dumpsite range from 11.07% to 13.48% with a standard deviation of 3.39 to 3.43, while the mean value in control site was determined to be  $10.16 \pm 2.30$  respectively. The low levels of moisture content in both sites might be caused by the vertical slope of the land and the surface is slightly horizontal in the dumpsite. At the control site, the slope slants downwards since the site is situated near the mountain, therefore during rainy days water travels faster before the soil absorbs enough water. These results may also have been an indication of climate change, i.e during the sampling those days might have been too hot resulting in evaporation of ground water and causing the soil to be dry thus supplying less water to the plants. This can also demonstrate the type of soil and soil texture, which we can say was loamy soil. Loamy soil is a mixture of small and large soil particles, containing different sized air space, and thus possesing medium water permeability to plants [4].

**Soil Organic Carbon (SOC)**: Organic carbon is the most important indicator for evaluation of organic pollution on both soil and water. It acts as a storage house for plant nutrients and plays a major role in nutrient cycles. The average results of organic carbon showed different variations between sampling portions and ranged from low 1.10% too high 2.01%.

The descending order of this OC content in the landfill site (site A) is in this order  $1.33 \pm 0.64$  % >1.19 $\pm 0.48\%$  > 1.10  $\pm 0.36\%$ , where the highest amount is found in portion B followed by portion C and portion A, while in the control site OC ( $2.01\pm0.83\%$ ) was higher than the mean percentage for the dumpsite. In overall the percentages of OC in both sites was low, this may be due to warm temperatures which decreased SOC content by increasing decomposition [5].

**Soil Organic matter (SOM)**: Organic matter is a temporary product in the natural cycle of decomposition of the remains of plants and animal after a large group of microbes have consumed carbon and other easily usable components that end up in soil. The average mean concentration of soil organic matter (SOM) from the study sites was determined and ranged from  $1.87\pm0.62$  % to  $2.30\pm1.10$ %, with the highest SOM occurring at the portion B of site A. In the control site, SOM was found to be  $2.16\pm2.24$  %. The increase in % OM increases the rate of metal ion absorption. The decomposition of the organic components of waste by the action of microorganisms increases the level of organic matter in the dumped soil. This indicates that waste contaminated soils have relatively high organic matter content compared to that of non-waste contaminated soil [6].

**Electrical conductivity**: Electrical conductivity is the ability of a solution to conduct an electrical current. It is an essential indicator of soil health because it affects yields, sustainability, and availability of plants and also affects the activity of microorganisms which influences key soil processes such as the emission of greenhouse gasses such as NO<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>. The normal limits of EC in soil drafted by WHO ranges from 400 $\mu$ s/cm - 600 $\mu$ s/cm [7].

In the results obtained, the EC for soil samples collected in the dumpsites were recorded within the permissible limits for electrical conductivity set by WHO, while the soil samples from the control site were below the normal range from WHO with a mean average of 127.69  $\pm$  74.65µ/cm. The EC for dumpsite soils was high in portion A followed by portion C, and portion B was lower than the other two portions. The descending order of EC in landfill site was in this order 536±237.75 > 470.58  $\pm$  277.73 > 421  $\pm$  202.88.

# 3.1.2 Selected heavy metals in soil

# Lead (Pb)

Number of weeks	Site A-Portion A (ppm)	Site A-Portion B (ppm)	Site A-Portion C (ppm)	Site-B (ppm)
Week -1	1.7061	3.4796	1.6368	0.4982
Week -2	1.4075	2.4678	0.667	0.922
Week-3	0.6224	1.516	0.4091	0.2762
Week -4	0.9406	2.1156	0.1878	0.2408
Week -5	3.008	1.6857	1.1664	0.3298
Week -6	1.7648	2.5196	0.7673	0.3438
Mean	1.5749	2.2974	0.8057	0.4351
Standard deviation	±0.83	±0.71	±0.53	±0.25



Figure 6: Pb (lead) concentration (ppm) in soil sampled over a period of six weeks

The Pb was determined in all collected soil samples. The recommended standard limits of Pb in soil by WHO ranges from 0.05 to 0.1 mg/kg [8].

In this study, the obtained results show the presence of Pb concentration in the soil which was found to be above the normal range suggested by WHO.

The mean concentration of soil samples for both sites ranges from  $0.4351 \pm 0.25$  mg/kg to  $2.2974 \pm 0.71$  mg/kg. In the results, it was found that portion-B of site A contains high levels of Pb concentration of about  $2.2974 \pm 0.71$  mg/kg, while the control site (site-B) has low levels with a mean concentration of  $0.4351 \pm 0.25$  mg/kg. The mean concentration of Pb was found to be higher at the dumpsite (site A) compared to the low levels at the control site.

The sequence of occurrence in Pb concentration is as follows; portion-B > portion-A > portion-C > Site B. A pH greater than 5 and high levels of organic matter at least by 5% favours the accumulation of Pb. High Pb concentration in the dumpsite soil was due to large deposits of used batteries, used plastics materials, lubrication oils and automobile exhaust fumes. Lead is known for its harmful effects on humans as well as causing chronic neurological disorders, especially in foetus and children [9].

The ANOVA results show that there is a statistically significant difference in mean concentration of the two sites (site A and B). This is proved by the F-statistic value which is greater than the F-critical with the value of 10.7856 > 3.0984, p-value  $< \alpha$  (0.000198 < 0.05. The nondirectional null hypothesis is rejected.

# Mercury (Hg)

Number of weeks	Site A-Portion A (ppm)	Site A-Portion B (ppm)	Site A-Portion C (ppm)	Site-B (ppm)
Week -1	23.8959	18.9175	12.1865	2.5237
Week -2	6.9639	4.272	0.8661	*
Week -3	1.0302	6.285	4.2134	*
Week -4	11.1219	5.7388	5.8501	*
Week -5	3.5268	2.9481	2.7307	2.3194
Week -6	4.1844	1.9165	1.6452	1.6599
Mean	8.4539	6.6797	4.582	1.0838
Standard deviation	±8.31	±6.22	±4.13	±1.22

*Note:* \* = *not detected* 



**Figure 7**: Hg concentration in soil sampled over a period of six weeks.

The normal standard limit for Hg concentration in soil is recommended as 1.0 mg/kg by WHO. For this study, the mean concentration of Hg for all collected soil samples was recorded extremely above the suggested limit from WHO [10].

The high levels of Hg were recorded at portion-A of site A with a mean value of 8.4539  $\pm$ 8.31 mg/kg, followed by portion-B (6.6780  $\pm$ 6.22 mg/kg) and the lowest mean concentration was recorded at the control site with a mean concentration of 1.0838  $\pm$ 1.22 mg/kg.

This implies that the Hg concentration was found to be more at the landfill site compared to the control site. Incineration of municipal waste and waste from hospitals and clinics and emission coal-using power plants contributed to the high levels of Hg [11].

The results of the ANOVA test indicate that the F-critical > F-statistic, with a value of 3.0984 > 1.9066. This means that there was no statistical significant difference in the mean concentrations between the two sites. Therefore the mean concentration between portions of site-A and the control site is statistically equal. The p-value was found to be above 0.05 (p-value > 0.05) by the value of 0.1610 > 0.05. This means that we accept the nondirectional null hypothesis since the difference in the means is statistically significant.

# Manganese (Mn)

Number of weeks	Site A-Portion A	SiteA-Portion B	SiteA-Portion C	Site B (ppm)
	<u>(ppm)</u>	<u>(ppm)</u>	<u>(ppm)</u>	
Week -1	30.449	30.5225	30.3026	15.617
Week -2	30.1938	30.3489	30.3823	15.715
Week -3	30.3764	29.9415	30.0072	15.2485
Week -4	30.3606	29.358	29.3318	14.6544
Week -5	29.5795	29.8484	28.8874	15.2282
Week -6	29.7726	26.132	25.1243	24.3242
Mean	30.1220	29.3586	29.0059	16.7979
Standard deviation	±0.36	±1.63	±1.99	±3.71



Figure 8: Concentration of Mn in soil sampled over a period of six weeks

The permissible limits for Mn recommended by WHO in soil samples range between 1.00 - 45.0 mg/kg [12]. For all collected soil samples in both site-A and site-B, the mean concentration of Mn was recorded within the normal range. Even though the Mn mean concentration of soil samples was within the normal range, the mean concentration was higher in other portions which are portion A, portion B and portion C.

The high levels were recorded at portion-A of site A, followed by portion-B and portion-C, while site-B (control site) had lower levels compared to the portions of site-A. The mean concentration for site-A ranges from  $29.0053 \pm 1.99$  mg/kg to  $30.1220 \pm 0.36$  mg/kg, and in control site the mean concentration is  $16.7979 \pm 3.71$  mg/kg.

The results of ANOVA showed that there was a significant difference statistically in the mean concentration of Mn between the two sites. This is supported by the F-statistic which was more than the value of F-critical (47.4832 > 3.0984). Also, the p-value supports the rejections of nondirectional null hypothesis since p-value is less than 0.05 with the value of 2.99x10-09 < 0.05. This means that the concentration of Mn in these sites was statistically different.

# Copper (Cu)

Number of weeks	Site A-Portion A (ppm)	SiteA-Portion B (ppm)	SiteA-Portion C (ppm)	Site-B (ppm)
Week -1	16.2139	33.6197	33.9496	2.0317
Week -2	15.2846	14.3526	3.1289	1.5561
Week -3	3.3356	18.8688	2.7172	4.5241
Week -4	11.1055	19.2794	2.7314	0.8692
Week -5	58.0866	44.079	20.9497	3.261
Week -6	26.5587	20.9353	7.4709	3.7695
Mean	21.7642	25.1891	11.8246	2.6686
Standard deviation	±19.33	±11.30	±12.91	±1.41





For Cu in soil WHO recommended the permissible limits to range from 7.00 - 80 mg/kg [12]. The results obtained in this study shows that for all collected samples of soil the mean concentration was within the normal range, except for the control site which was recorded below the permissible limits.

In the dumpsite the Cu mean concentration was high at portion-B with a mean value of  $25.1892 \pm 11.30$  mg/kg, followed by portion-A ( $21.7642 \pm 19.33$ ) and lower at portion-C ( $11.8246 \pm 12.91$ ). Concentration in the control site was recorded below the normal range with a mean of  $2.6686 \pm 1.41$ .

The ANOVA results showed that there was statistically significant difference between the mean concentration of portions from site-A and site-B. This is supported by the value of F-critical which was less than the F-statistic value (3.0984 < 3.7164). The p-value was recorded as less than 0.05 with a value of 0.028 < 0.05. Therefore this means that the nondirectional null hypothesis is rejected, and this shows that the mean concentration between site-A and site-B is not the same.

## Mean concentration of heavy metals in soil samples.

Collection Sites	Cu	<u>Hg</u>	Mn	<u>Pb</u>	Mean	Standard deviation
Site A-Portion A (ppm)	21.764	8.454	30.122	1.575	15.3618	±10.18
Site A-Portion B (ppm)	25.189	6.68	29.359	2.297	5.471	±2.71
Site A-Portion C (ppm)	11.825	4.582	29.006	0.806	26.3213	±6.37
Site B (ppm)	2.669	2.168	16.798	0.435	1.2783	±0.83



Figure 10: The mean concentration (ppm) of selected heavy metals in soil.

In the collected soil samples from both sites (A and B) the mean concentration of these metals (Cu, Hg, Mn, and Pb) was determined. In the obtained results, the Mn mean concentration was found to be higher than other metals with a mean value of 26.3213  $\pm 0.83$  mg/kg, and the lowest mean concentration was recorded for Pb (1.2783  $\pm 6.37$ ). The maximum mean concentration of metals analyzed can be classified according to their relative abundance in soil sample as follows Mn > Cu > Hg > Pb.

The graph shows that for Cu the mean concentration was recorded high at portion-B and lower at the control site. The average concentration of Hg was found to be high at portion-A and less at the control site, while for Mn the concentration was found to be more at portion-A and low at the control site. For Pb, the highest mean concentration was recorded at portion-B and lower at the control site.

The ANOVA results indicated that there is statistically significant difference in mean concentration between the selected heavy metals. The F value and p-value provide evidence on the rejection of nondirectional null hypothesis. F-statistic > F-critical (13.0955 > 3.4903), the p-value is less than 0.05 (0.00043 < 0.05). This also shows that statistically, the concentration of these metals is not the same.

### **3.2 Water results**

### **3.2.1** Physicochemical properties of water samples

Number of Weeks	рН	Temperature (°C)	Electrical conductivity (ms/cm)	Total hardness (mg/L)	Total dissolved solids (mg/L)
Week 1	6.91(±0.10)	25.9(±0.28)	35.15(±6.72)	57.5(±2.12)	600(±84.85)
Week 2	7.02(±0.12)	21.15(±1.34)	30.3(±1.41)	58(±1.41)	720(±56.57)
Week 3	6.67(±0.16)	19.6(±3.25)	21.65(±0.78)	54(±2.83)	615(±49.50)
Week 4	6.86(±0.18)	18.3(±4.10)	44.45(±2.33)	54(±1.41)	545(±49.49)
Week 5	6.39(±0.61)	15.75(±7.28)	40.7(±0.71)	51.5(±6.36)	420(±169.71)
Week 6	5.41(±0.53)	14.05(±2.47)	53.85(±27.65)	50(±1.41)	485(±63.64)

<u>**Table 5**</u>: The physicochemical properties of water (mean ±standard deviation)

**Alkalinity**: Alkalinity is the measure of the ability of a solution to neutralize acids the equivalence point of bicarbonates and carbonates. Alkalinity was determined in this experiment. A few drops of phenolphthalein was added to water samples and showed no development of pink color in the solution, the samples remained unchanged. This indicated the absence of alkalinity in the collected water samples [13].

This showed that a number of ions were present in water samples but at a very small amount. It also meant that water samples have low capability in neutralize acids, therefore some aquatic animals such as fish won't be able to survive in this water because there will be rapid changes in pH. The results of alkalinity in this study were slightly different from previously conducted studies. Mane et.al reported a study where the alkalinity of water samples was quite high with the highest value of 296 mg/L. High alkalinity amount might be favoured by dissolution of carbon rock and the presence of  $CO_2$  from the atmosphere [7].

**pH**: pH, as one of the most important water quality properties used to measure the acidity and alkalinity of water. The normal drinking water pH range revealed by WHO guidelines are between 6.5 and 8.5 respectively. pH for all the collected water samples was recorded within the normal range, except for samples of week 6 which were below the normal range and acidic [7]. The pH amounts of all the waste water samples were found to be in the range between the slightly acidic ( $5.41 \pm 0.53$ ) and neutral ( $7.02 \pm 0.12$ ) range. The lower the pH value the higher the corrosive nature of water is. The range from slightly acidic to neutral is due to the presence of dissolved carbon dioxide and organic acids (fulvic and humic acids), which result from the decay and leaching of plant materials. A low pH can cause corrosion of water-carrying metal pipes, thereby releasing poisonous metals such as Zn, Pb, Cd, and Cu. Furthermore, low pH values in natural water can result in gastrointestinal disorders like hyperacidity, ulcers and stomach pain with burning sensation [14].

**Temperature**: temperature plays an important role in physicochemical and biological behaviour. Water temperature controls the rate of all chemical reactions and affects the growth of organisms such as fish, reproduction, and immunity. The temperature in water samples was recorded to range from 25.9 °C to 14.1 °C. Every week of sampling the water temperature was observed to be decreasing. This is due to seasonal and weather change. Extreme temperature changes can be fatal to fish. Wastes often increase water temperatures. This leads to poorer oxygen levels and weakens many insects and fish [14].

**Electrical conductivity**: EC is a quantity of water salt content in the form of ions and is measured in microSiemens/cm ( $\mu$ S/cm). In the present study, EC values ranged from 21.65 ( $\pm$ 0.78) mS/cm to 53.85 ( $\pm$ 27.65) mS/cm. The normal range of EC in water was determined to range between 400 to 600 $\mu$ S/cm by WHO [7].
In the entire collected water sample, values of EC were recorded as higher than permissible limits. This might be due to the high amount of dissolved ions and salts such as Ca, Cl and Mg. Also, the evaporation of water from the dam surface due to high temperatures can concentrate dissolved solids in the remaining water. High levels of EC in water cause corrosion of metal equipment like boilers; eliminates food plant and habitat-forming plant species [14], and again since the site is allocated next to the road, the road runoffs can also have influence. EC is an indicator of water quality and soil salinity, hence the relatively high values observed in some water samples showed high salinity; thus the waters might not be very suitable for domestic and agricultural use [15].

**Total hardness of water**: Hardness of water is the amount of dissolved calcium and magnesium in water and is measured in mg/L equivalent calcium carbonate (CaCO<sub>3</sub>). WHO has classified drinking water with a total hardness of CaCO3 less than 50 mg/L as soft water, 50 - 150 mg/L as moderately hard water and water with 150 mg/L CaCO<sub>3</sub> as hard. Based on this classification all collected water samples ranged from 50  $\pm$ 1.41 to 58  $\pm$ 1.41 mg/L. This meant that all the water samples investigated were moderately hard water, thus the waters are suitable for domestic use in terms of hardness. This is because moderately hard water is preferred to soft water for drinking purposes [13].

**Total dissolved solids (TDS):** TDS are the inorganic matters and small amounts of organic matter, which are present as solution in water. WHO normal values of total dissolved solids (TDS) of soil ranges from 5 to 1000 mg/L and for water it range from 500-1000 mg/L. The TDS for this study was recorded to fall within the permissible limits from WHO, and they range from  $420\pm169.71$  mg/L to  $720\pm56.57$  mg/L. These results indicate the presence of solid materials and solutes in water. The low TDS values found can be attributed to high rainfall prevailing, which causes significant dilution [16].

## 3.2.2 Selected heavy metals in water samples

Collection Weeks	Cu	<u>Hg</u>	Mn	<u>Pb</u>
Week -1	***	11.4202	0.0233	0.0017
Week -2	***	55.0353	0.931	0.0024
Week -3	***	46.0588	1.1056	0.0015
Week -4	***	38.9057	0.7448	0.0021
Week -5	***	33.6642	0.5909	0.0044
Week -6	***	28.2811	0.1609	0.0011
Mean =		35.5609	0.5928	0.0022
Standard deviation=		±15.10	±0.43	±0.001

*Note:* \*\*\* = not detected



Figure 11: The concentration of selected metals in water.

## a. Mean concentration of Cu in water samples

The permissible limits drafted by WHO for Cu element in water is 2.0 mg/L. In all collected water samples, the Cu was undetected because the resulted value from AAS was below the detection limit of the instrument (below zero ppm). This may be due to the fact that in water Cu travels large distances either suspended on dust particles or as free ions.

The above findings are supported by other conducted studies where no detection for Cu in water samples was found [7], while Brigden *et.al*, (2008) detected Cu from sediments but no Cu concentration was detected in water. The pH of the water might also cause low levels of Cu since the solubility of some metal ions in water increases with a decrease in pH (acidic condition) [17].

### b. Mean concentration of Hg in water samples

WHO suggested that the normal limits of Hg in water must be 0.01 mg/L [10]. In this study for all collected water samples, the mean concentration for Hg was found to be extremely above the normal range. The mean concentration of Hg in water ranged from  $11.4202 \pm 8.08$ to  $55.0353 \pm 39.14$  mg/L. Mercury is a naturally occurring metallic element found in trace amounts in water, soil, and air. Additionally, inorganic mercury is present in rocks and soil and occurs naturally. Mercury is released through erosion and weathering of surface water. Most Hg in water remains inorganic but in certain environments which have low pH, low dissolved oxygen, and high organic matter, some of it is converted to a much poisonous organic form called MeHg [18].

#### c. Mean concentration of Mn in water samples

The normal limits of Mn concentration in water recommended by WHO range at 0.05 mg/L [10]. For all collected water samples the Mn mean concentration was found to range from  $0.0233 \pm 0.02$  mg/L to  $1.1056 \pm 0.78$  mg/L. The obtained results were recorded above the normal range, except for the samples which were collected in the first week; the concentration was below the normal standard with a mean concentration of  $0.0233 \pm 0.02$  mg/L. Mn occurs naturally in water, soil, and plants. It is present most frequently as a manganous ion (Mn<sup>+1</sup>) in water and manganese salts are more soluble in acidic water than alkaline water [19].

### d. Mean concentration of Pb in water samples

According to WHO standards limit for Pb in water is 0.05 mg/L [7]. In the collected water samples, the Pb mean concentration was recorded to be below the normal range. The Pb concentration was found to range from  $0.0011 \pm 0.001$  to  $0.0044 \pm 0.003$  mg/L.

The ANOVA analysis for the water samples shows that between the mean concentrations of selected heavy metals in the water, there is a statistically significant difference; their mean concentration is different from one element to the other. This is supported by the value of p > 0.05 and F-critical which is less than F-statistics with the value of 3.0984 < 32.8897. P-value is  $6.3 \times 10^{-08} < 0.05$ ; therefore the nondirectional null hypothesis is rejected.

## 3.3 Acacia karroo Analysis

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Collection Weeks	<u>Cu</u>	<u>Hg</u>	<u>Mn</u>	<u>Pb</u>
Week -1	***	10.6019	0.3038	0.009
Week -2	***	13.2667	0.347	0.0032
Week -3	***	5.6659	0.3161	0.0013
Week -4	***	2.3837	0.5462	0.0022
Week -5	***	1.7121	0.1354	0.0011
Week -6	***	2.4801	0.4132	0.0025
Mean =	***	6.0184	0.3436	0.0032
Standard deviation =	***	±4.87	±0.14	0.003

3.3.1 Mean concentration of heavy metals in Acacia karroo.

*Note:* \*\*\* = *not detected* 



Figure 12: The concentration of selected metals in Acacia karroo

### a. Mean concentration of Cu in Acacia karroo

In the collected *Acacia karroo* samples, the Cu element was not detected. This might be caused by pH of the soil which has influence on the solubility and availability of nutrients in the soil.

## b. Mean concentration of Hg in Acacia karroo

For medicinal plant (*Acacia karroo*) samples the recommended standard limits for Hg from WHO is said to range 0.03 mg/kg [10]. In all collected *Acacia karroo* samples, the concentration was recorded as extremely above permissible limits. The mean concentration of Hg in *Acacia karroo* samples ranges between  $1.7121 \pm 1.21$  mg/kg and  $13.2667 \pm 9.38$  mg/kg. This may be due to the burning of municipal waste and medicinal waste; emissions from coal-using power plants may also contribute to high levels of mercury [11].

### c. Mean concentration of Mn in Acacia karroo

The standard limits recommended by WHO for Mn concentration in medicinal plants ranges between 2 mg/kg to 685 mg/kg [10]. In this study, it was found that for all collected *Acacia karroo* samples the mean concentration was recorded below the normal standard. *Acacia karroo* mean concentration for Mn ranged from 0.1354  $\pm$ 0.10 mg/kg to 0.5462  $\pm$ 0.39 mg/kg.

### d. Mean concentration of Pb in Acacia karroo

According to WHO, the standard permissible limits of Pb concentration in medicinal plants is 2.0 mg/kg [7]. For all collected *Acacia karroo* samples, the Pb mean concentration was been detected and found to be below the normal range. The Pb concentration ranged from 0.009  $\pm 0.01$  mg/kg to 0.0032  $\pm 0.002$  mg/kg. Therefore all collected *Acacia karroo* samples were recorded below permissible limits.

The ANOVA test results show that between mean concentrations of the metals there is the statistically significant difference and that the means are not the same. This is supported by the p-value which is less than 0.05 (0.000607 < 0.05), and the value of F-statistic which is more than the value of F-critical (8.8820 > 3.0984). Therefore the nondirectional null hypothesis is rejected.

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### **CHAPTER FOUR**

## 5.0 CONCLUSION AND RECOMMENDATION

### 4.1 Conclusion

The aim of this study was to assess the concentration of some toxic heavy metals and also some chemical properties including pH, EC, and hardness of water. The physicochemical properties of both water and soil were recorded within the normal range acclaimed by WHO, apart from EC of water which was recorded above permissible limits. The metal concentration in soil samples was found to be within the normal range, except for Pb and Hg which were recorded above normal limits as specified by WHO. The high concentration of metals has been observed to be high at the landfill site compared to the control site. The soil samples collected at the control site had fewer metal concentration compared to those collected at the dumpsite. The high concentration of metals in samples from the landfill site is caused by the type of waste, topography, and scavengers on the site. For water samples, Cu was not detected, while the concentration of Hg and Mn were recorded to be above normal limits suggested by WHO, and the Pb was found to fall below the normal range. Also in Acacia karroo sample, the Cu element was not detected. The Hg in Acacia karroo has been found above normal standards while Mn and Pb were below the normal limits. High levels of metal concentration in Acacia karroo are in this study considered normal because of the composition of waste in the dumpsite, which is changing due to increasing population and consumption pattern. Heavy metals in the dumpsite may not seem to cause very serious environmental problems at the moment but continuous accumulation of metal concentration may later results in a threat to human health and the environment. Specifically, the accumulation of Pb and Hg is concerning. The water quality flowing to the municipal treatment plant could increasingly become polluted and will cost the municipality more financial resources to deliver portable water to homes around the affected place.

### **4.2 Recommendations**

The above study implies that there is a need for recycling, proper and thorough sorting of waste before disposal. Though recycling and waste sorting before disposal is not enough, it will help to reduce the metal load at the landfill site. The dams or sitting wells near the dumpsite should be taken care of, because of health risks associated with water pollution. Modern waste disposal facilities should be acquired by designated government agencies and appropriate waste disposal sites chosen by experts to avoid indiscriminate dumping of waste within the community. Proper education and legislation on how to handle waste in the society needs to increase and there is a need for visible signs to mitigate indiscriminate dumping of certain potential toxic wastes in the site.

## APPENDICES

# <u>Appendix 1</u>

# <u>**Table A1**</u>: The ANOVA results of Pb in soil

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Site A-Portion A	6	9,4494	1,5749	0,688933		
Site A-Portion B	6	13,7843	2,297383	0,498764		
SiteA-Portion C	6	4,8344	0,805733	0,276127		
SiteB	6	2,6108	0,435133	0,064696		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	12,36451	3	4,121503	10,7856	0,000198	3,098391
Within Groups	7,642601	20	0,38213			
Total	20 00711	23				

# Appendix 2

# .<u>Table A2:</u> The ANOVA results for Hg in soil samples

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Site A-Portion A	6	50,7231	8,45385	69,08199		
Site A-Portion B	6	40,0779	6,67965	38,64295		
SiteA-Portion C	6	27,492	4,582	17,08648		
SiteB	6	6,503	1,083833	1,491156		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	180,6099	3	60,20331	1,906638	0,161051	3,098391
Within Groups	631,5129	20	31,57564			

## <u>Appendix 3</u>

# <u>**Table A3**</u>: The ANOVA results for Mn in soil samples

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Site A-Portion A	6	180,7319	30,12198	0,130024		
Site A-Portion B	6	176,1513	29,35855	2,665196		
SiteA-Portion C	6	174,0356	29,00593	3,953116		
SiteB	6	100,7873	16,79788	13,73432		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	729,4368	3	243,1456	47,48323	2,79E-09	3,098391
Within Groups	102,4133	20	5,120663			
Total	831,8501	23				

## Appendix 4

## <u>**Table A4**</u>: The ANOVA results for Cu in soil samples

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Site A-Portion A	6	130,5849	21,76415	373,6632		
Site A-Portion B	6	151,1348	25,18913	127,6597		
SiteA-Portion C	6	70,9477	11,82462	166,5968		
SiteB	6	16,0116	2,6686	1,977387		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1867,173	3	622,3911	3,716338	0,028376	3,098391
Within Groups	3349,486	20	167,4743			
Total	5216,659	23				

# <u>Appendix 5</u>

Table A5:	The ANOVA	results of all	selected	metals in	ı soil
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Anova: Single Factor						
SUIVIIVIARY						
Groups	Count	Sum	Average	Variance		
Cu	4	61,447	15,36175	103,7261		
Hg	4	21,884	5,471	7,353367		
Mn	4	105,285	26,32125	40,5246		
Pb	4	5,113	1,27825	0,686668		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1495,746	3	498,5822	13,09554	0,00043	3,490295
Within Groups	456,8721	12	38,07267			
Total	1952,619	15				

# <u>Appendix 6</u>

<u>**Table A6**</u>: The ANOVA results for selected metals in water

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Cu	6	0	0	0		
Hg	6	213,3653	35,56088	228,0024		
Mn	6	3,5565	0,59275	0,182264		
Pb	6	0,0132	0,0022	1,37E-06		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	5628,7	3	1876,233	32,88973	6,3E-08	3,098391
Within Groups	1140,924	20	57,04618			
Total	6769,624	23				

## Appendix 7

# Table A7: The ANOVA results for selected metals in Acacia karroo

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Cu	6	0	0	0		
Hg	6	36,1104	6,0184	23,58908		
Mn	6	2,0617	0,343617	0,018318		
Pb	6	0,0193	0,003217	8,63E-06		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	157,261	3	52,42034	8,882016	0,000607	3,098391
Within Groups	118,037	20	5,901852			
Total	275,2981	23				