HEAVY METALS (CADMIUM AND CHROMIUM) CONTENT IN SOILS IN THE VICINITY OF REFUSE DUMPSITES

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FACULTY OF AGRICULTURE

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BENIN CITY

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A RESEARCH PROJECT SUBMITTED TO THE
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CERTIFICATION

This is to certify that this research project **“Heavy metals (Cadmium (Cd) and Chromium (Cr) content in soils in the vicinity of Refuse Dumpsites** was carried out by **Ezeh Precious OLUEBUBE** of the Department of Soil Science and Land Management, Faculty of Agriculture, University of Benin City, Edo State, Nigeria.

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DEDICATION

I dedicate this project to God Almighty for his grace and strength throughout this program.

ACKNOWLEDGEMENTS

Gratitude fills my heart as I reflect on this remarkable journey, and I am moved to acknowledge the incredible individuals who have been instrumental in bringing my project to fruition.

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ABSTRACT

This study investigates the contents of some heavy metals (Cadmium (Cd) and Chromium (Cr)) concentrations in the soils of a dumpsite located within Egor Local Government Area in Benin City. Soil samples were randomly obtained from different locations within the dumpsite while the control soils were obtained from the Faculty of Agriculture University of Benin. A total of 18 samples were collected, with nine from the dumpsite and nine from the control site at three different depths (0-15cm, 15-30cm, and 30-45cm). The experiment was thereafter laid out in a Completely Randomized Design (CRD). Results from the investigations shows that the dumpsite soils exhibited higher organic matter content (47.73, 38.00 and 31.03 gkg^{-1}) that ranged from the topsoil to the subsoil while the control had 13.79, 10.57 and 10.51 gkg^{-1} respectively. The dumpsite also recorded reduced (5.04 – 6.13) acidity, which resulted in increased nutrient (N, P, K, Ca and Mg) release so was the cadmium (Cd) concentrations significantly elevated in the dumpsite soils, ranging from 5.14 - 8.18 mgkg^{-1}, compared with the content in the control (0.31 - 0.66 mgkg^{-1}.). The Cd (19.93 – 36.78 mgkg^{-1}) and Cr (5.14 – 8.18 mgkg^{-1}) contents in the dumpsite were highly above the permissible limit defined by World Health Organization. These findings underscore the potential impact of waste deposition, emphasizing the need for proper waste management practices to mitigate heavy metal contamination from getting into the food chain and as such it is recommended that the dumpsite investigated should not be used in the production of food crops intended for human consumption.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Soil contamination by heavy metals has become a significant environmental concern worldwide (Smith *et al.,* 2019). Heavy metals, such as cadmium (Cd) and chromium (Cr), are toxic pollutants that pose serious risks to human health and the ecosystem. The accumulation of these metals in soils, particularly in the vicinity of refuse dumpsites, has raised considerable alarm due to potential contamination of food crops, groundwater, and subsequent exposure to humans and animals (Fan *et al.,* 2016).

Soil, as a vital component of the environment, plays a crucial role in supporting the growth of plants and providing essential ecosystem services (Kabata-Pendias, 2011). Aboyeji and Eigbokhan (2016) in a study, revealed that the careless burning and disposal of waste could lead to the generation of leachates containing various substances, including melted organic matter and inorganic compounds like ammonium, calcium, magnesium, sodium, potassium, iron, sulphates, chlorides, as well as heavy metals such as cadmium, chromium, copper, lead, zinc, and nickel. These leachates have the potential to infiltrate the soil and contaminate groundwater, depending on the concentration and toxicity of the contaminants, the water table's type and depth, and the direction of groundwater flow. When municipal solid waste residues produce leachate, it can easily seep into water bodies and, subsequently, be consumed by animals and transferred to humans through the food chain, acting as a significant source of pollution for both soil and underground water (Adedara *et al.,* 2013; Ibrahim *et al.* 2020). Refuse dumpsites of most solid waste without proper management, are of particular concern due to the potential release of heavy metals into the surrounding soils (Akoto *et al.,* 2018). Ibrahim *et al*. (2020) emphasized on heavy metal pollution by stressing the pressing ecological issue of soil pollution caused by heavy metal presence. This environmental concern arises due to the possible negative impacts on ecosystems which is majorly caused by uncontrolled burning and refuse disposals. Although heavy metals do exist naturally in soils at minimal levels, their pervasiveness, along with their potential for acute and chronic harm, designates them as soil pollutants. These metals exhibit remarkable environmental persistence, being resistant to both biodegradation and thermal degradation. Consequently, they amass to hazardous concentrations, posing a prolonged threat to the biosphere without undergoing decomposition (Nwaichi *et al*. 2016; Onyejekwe *et al.,* 2019).

Cadmium and chromium are two prominent heavy metals known for their detrimental effects on soil and human health (Bakshi *et al.,* 2018). Thus, this thesis focuses on the non-essential heavy metals, like cadmium, chromium and the level of its availability in a refuse dumpsite.

1.2 Objectives of the Study

The research objective of the study was to assess the concentration of heavy metals (Cadmium and Chromium) pollution in dumpsite within University of Benin, Uselu, from 3 control site location in Benin City.

The objectives of the study were to determine the:

i. heavy metal content, specifically cadmium (Cd) and chromium (Cr), in soils in the vicinity of refuse dumpsites.

ii. spatial distribution, concentration levels, and potential sources of these heavy metals in the soils.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metal Overview

Heavy metals are a group of metallic elements that have high atomic weights and densities. They are naturally occurring elements found in the Earth's crust, but their concentration and distribution in the environment have been significantly influenced by human activities. Barceloux, (1999) grouped heavy metals under metals having a specific gravity higher than 5 gcm^{-3}, including copper (Cu), nickel (Ni), chromium (Cr), lead (Pb), cadmium (Cd), mercury (Hg), iron (Fe), and arsenic (As). While some heavy metals like iron and nickel are essential to life at low concentrations (Bakshi *et al.,* 2018), others such as lead, cadmium, and mercury are toxic even in low amounts and can lead to metabolic abnormalities in living organisms, especially those consuming food from plants grown in contaminated soil (Singh and Kumar, 2006). Heavy metal pollution in soils, water, and crops had become a serious global environmental issue, which is primarily caused by both natural sources and human activities (Bakshi *et al.,* 2018).

Heavy metals are characterized by their high specific gravity and can be divided into two main categories: essential and non-essential.

Essential heavy metals, such as iron and nickel, play vital roles in various physiological processes and are required for the survival of all life forms in small concentrations (Bakshi *et al.,* 2018). On the other hand, non-essential heavy metals, like lead, cadmium, chromium, and mercury, and can be harmful, even at low concentrations, causing various health and environmental problems (Bakshi *et al.,* 2018).

Heavy metal pollution poses a significant threat to the environment and human health. These pollutants can enter the ecosystem through various means, such as urban-industrial aerosols, solid and liquid waste, mining activities, industries, and agricultural chemicals (Singh and Kumar, 2006; Bakshi *et al.,* 2018). The concentrations of heavy metals in the soil around refuse dumpsites are influenced by factors such as the types of waste, topography, runoff, and scavenging levels (Singh and Kumar, 2006).

Improper waste disposal and uncontrolled leachate flow from landfills can contaminate the surrounding environment, soil, and groundwater (Umutesi *et al.,* 2018; Ekere *et al.,* 2017).

The environmental pollution caused by heavy metals presents significant health concerns globally. Human exposure to toxic heavy metals can occur through various pathways, including inhalation, ingestion of contaminated food and water, and dermal contact (Sridevi *et al.,* 2012). Even low levels of heavy metal exposure can have severe health implications, such as interfering with mitochondrial functioning, leading to respiratory problems and other health issues (Ramelli *et al.,* 2012).

Lead (Pb), in particular, poses a significant risk to children's health, affecting their growth and development (Yilmaz, 2005). Developing countries, where environmental monitoring may not be prioritized, are particularly vulnerable to heavy metal contamination (Yilmaz, 2005).

2.2 Sources of Heavy Metals in the Environment

The presence of heavy metals in the environment can result from both natural and anthropogenic sources (Barceloux, 1999; Bakshi *et al.,* 2018). Anthropogenic sources include various human activities such as industrialization, waste disposal, agricultural practices, and vehicular emissions (Barceloux, 1999; Bakshi *et al.,* 2018).

Inadequate waste management, especially in developing countries, leads to the deposition of heavy metals in soil and water bodies, contributing to environmental pollution (Ekere *et al.,* 2017; Umutesi *et al.,* 2018). Additionally, the use of heavy metal-containing materials in industrial processes and products can release pollutants into the environment (Barceloux, 1999 and Sridevi *et al.,* 2012).

Industrial activities are major contributors to heavy metal contamination in soil. Industries such as mining, smelting, metal processing, and manufacturing release significant amounts of heavy metals into the environment (Alloway, 2013). These activities can lead to direct deposition of heavy metals onto soil surfaces or indirect contamination through atmospheric emissions and subsequent deposition. For example, a study by Smith *et al*. (2018) conducted in a region with extensive industrial activities found elevated concentrations of heavy metals, including lead (Pb), cadmium (Cd), and mercury (Hg), in the soil near industrial sites.

Agricultural practices, including the use of fertilizers, pesticides, and animal manure, can contribute to heavy metal contamination in soil. Fertilizers and pesticides may contain heavy metals as impurities or additives, and their repeated application can lead to the accumulation of these metals in the soil (Kabata-Pendias and Mukherjee, 2007). Animal manure from livestock farming can also introduce heavy metals into the soil if the animals were exposed to contaminated feed or bedding materials.

A study by Wang *et al*. (2015) investigated the impact of long-term agricultural practices on heavy metal accumulation in soil. They found that the use of fertilizers and manure significantly increased the concentrations of heavy metals, such as copper (Cu) and zinc (Zn), in agricultural soils.

Urbanization and the improper management of solid waste can contribute to heavy metal contamination in soil. Urban areas are characterized by human activities, infrastructure development, and the generation of various waste streams. Improper disposal of solid waste, including household waste and industrial waste, in landfills can lead to the leaching of heavy metals into the surrounding soil (Peng *et al.,* 2018). Urban runoff and the deposition of atmospheric pollutants can also contribute to heavy metal contamination in urban soils.

In a study conducted by Li *et al*. (2017) in an urbanized area, the researchers found elevated levels of heavy metals, such as chromium (Cr) and nickel (Ni), in soils near landfills and urban runoff areas.

Atmospheric deposition is another important source of heavy metal contamination in soil. Heavy metals can be released into the atmosphere through natural processes, such as volcanic eruptions and dust storms, as well as human activities, including the combustion of fossil fuels, industrial emissions, and vehicle exhaust (Alloway, 2013). These airborne pollutants can settle onto soil surfaces through dry deposition or can be washed down during rainfall events, leading to the accumulation of heavy metals in the soil.

A study by Zhang *et al*. (2019) investigated the impact of atmospheric deposition on heavy metal contamination in rural agricultural soils. The researchers found that atmospheric deposition, particularly from industrial emissions and vehicular exhaust, significantly contributed to the accumulation of heavy metals, such as lead (Pb) and arsenic (As), in the soil.

2.3 Behavior of Heavy Metals in Soils

Once heavy metals are released into the soil, their behavior is influenced by various physical, chemical, and biological processes. These processes determine the mobility, bioavailability, and potential for accumulation of heavy metals in soils.

The mobilization of heavy metals within the soil environment is influenced by various factors, including pH, properties of the heavy metals, redox conditions, soil chemistry, organic matter content, clay content, cation exchange capacity, and other soil properties (Sauve *et al.,* 2000). The solubility and mobility of heavy metals in soil are environmentally significant due to their potential toxicity to both humans and animals (Chirenje *et al.,* 2003). The transfer and chemical stability of metal contaminants in soil and sediments are governed by complex biogeochemical processes influenced by variables such as pH, clay content, and redox potential (Vanbroekhoven *et al.,* 2006). Trace metal mobility is closely linked to metal solubility, which is further regulated by adsorption, precipitation, and ion exchange reactions in soils (Ma and Dong, 2004).

The movement of heavy metals from soil to plants depends on three factors: the total potential amount of available elements, the activity and ionic ratios of elements in the soil solution, and the rate of element transfer from solid to liquid phases and plant roots (reaction kinetics) (Mo *et al.,* 1999). Changes in redox potential resulting from a decrease in oxidation state can lead to altered metal oxidation state, the formation of less soluble minerals, and the reduction of iron, which in turn releases associated metals (Baumann *et al.,* 2002). Generally, metal solubility increases as pH decreases, except for metals present in the form of oxyanions or amphoteric species. Additionally, soil solution properties can be time-dependent (Mo *et al.,* 1999).

Adsorption and desorption processes play a significant role in the behavior of heavy metals in soils. Heavy metals can bind to soil particles and organic matter through adsorption, which reduces their mobility and availability for uptake by plants or leaching into groundwater.

Desorption can release previously adsorbed heavy metals back into the soil solution, making them susceptible to transport.

The mobility and bioavailability of heavy metals depend on factors such as soil pH, organic matter content, clay mineralogy, and redox conditions. Changes in these factors can alter the solubility and speciation of heavy metals, affecting their availability for uptake by plants or their potential for leaching into groundwater.

Speciation and transformation processes also influence the behavior of heavy metals in soils. Heavy metals can exist in various chemical forms, including free ions, complexes with organic and inorganic ligands, and as precipitates. These forms determine their stability, solubility, and potential toxicity in the soil environment.

Leaching and transport of heavy metals in soils can occur through processes such as percolation, runoff, and erosion. The movement of heavy metals in the soil profile can lead to their vertical distribution and potential contamination of groundwater resources.

Numerous studies have investigated the behavior of heavy metals in soils. For example, a study by Alloway (2013) provides comprehensive information on the fate and behavior of heavy metals in soils, including their adsorption, mobility, speciation, and transport processes.

Cadmium is a lustrous white metal that has similarities in several characteristics to Zinc and Tin. It is not abundant in nature, with its presence in the earth's crust estimated to range between 0.15 to 0.11mg/g, making it the 67th most abundant element. The Zn/Cd ratio in the environment depends on the nature of rocks and is typically around 250:1.

Cadmium can be released into the environment through volcanic emissions and vegetation. While not essential for plant growth, it can accumulate in certain plants under specific conditions, reaching levels that pose hazards to animals and humans. Some sewage sludge may contain enough cadmium to promote its accumulation.

The behavior of cadmium in soil reactions is not fully understood. However, it is known that the uptake of this element is generally reduced by organic matter, silicate clay, hydrous oxides of iron and aluminum, and poor soil aeration. Cadmium uptake is higher in acidic soils but decreases when the soil is limed.

Cadmium is considered a hazardous air pollutant and can enter plants and animals through soil and water, ultimately affecting products. It has an inhibitory effect on antioxidant processes and interacts with the sulfuric groups of essential enzymes. Proper management of cadmium exposure is crucial to protect the environment and human health.

Cadmium can enter the soil through various anthropogenic and natural sources. Anthropogenic sources include industrial activities, such as metal mining and smelting, battery manufacturing, and waste incineration (Alloway, 2013). These activities release cadmium into the air, water, and soil, leading to contamination. Natural sources of cadmium include weathering and erosion of rocks and minerals containing cadmium

Anthropogenic activities are the primary contributors to cadmium contamination in soil. Industrial processes, especially those involving the production and disposal of electronic devices, batteries, and pigments, release substantial amounts of cadmium into the environment (Satarug *et al.,* 2010). In addition, the application of phosphate fertilizers derived from phosphate rock can contribute to cadmium accumulation in agricultural soils (Alloway, 2013).

Cadmium is naturally present in the Earth's crust, and its release into the environment occurs through geological processes. Weathering of rocks and minerals containing cadmium results in the release of cadmium ions into soil (Lindsay, 1979). However, natural sources typically contribute a smaller proportion of cadmium contamination compared to anthropogenic sources.

Cadmium (Cd) causes abnormalities in different plant parts and alters the dry-to-fresh mass ratio (DM/FM) in all organs. It can also impact sugar content and amino acids in certain plant species, indicating inhibition of starch hydrolysis (Singh *et al.,* 2020).

Cd can disrupt the balance between macro and micronutrients in plants, leading to imbalances in nutrient uptake in certain species (Barceloux, 1999).

Cadmium interacts with photosynthetic complexes and reduces the assimilation of photosynthetic carbon. Cd also affects guard cell regulation, which influences water status in plants (Singh *et al.,* 2020). Cadmium interferes with the production of phytochelatins, affecting plant nutrient stability and inhibits the transportation of other elements (Barceloux, 1999).

According to Sprynskyy *et al*. (2007), heavy metals uptake by plants and their subsequent accumulation in food chains pose risks to both animal and human health. Mobile heavy metals are easily absorbed by plants and can contaminate groundwater or enter food chains, resulting in serious pollution problems. As documented by several earlier scientists, vegetables, especially leafy vegetables grown in heavy metal-contaminated soil, accumulate high amounts of metals through their leaves (Yongsheng *et al.,* 2011). Excessive levels of heavy metals are harmful to plant growth, causing oxidative stress, damage to cell structures, and inhibition of photosynthetic reactions (Barceloux, 1999). Furthermore, heavy metals can also affect seed germination and reduce harvest production. According to Tang *et al.* (2017), heavy metals have a more detrimental effect on plant growth compared to other environmental stresses. For example, nickel (Ni) toxicity delays enzymatic activities, leading to plant height reduction, reduced chlorophyll content, and the accumulation of certain ions in plants (Barceloux, 1999). Heavy metals and metalloids pose significant threats as pollutants commonly found in industrial wastewater, exerting adverse effects on both human health and the environment (Nakkeeran *et al.,* 2018). Among these pollutants, chromium (Cr) stands out as one of the most toxic heavy metals occurring naturally and extensively utilized in industrial processes. Its release from natural sources, particularly the earth's crust, results in two principal forms: trivalent chromium [Cr (III)] and hexavalent chromium [Cr (VI)] (McCartor and Becker, 2010; Stambulska *et al.,* 2018). Trivalent chromium [Cr (III)] is crucial for the well-being of living organisms, including humans, as its deficiency or excess significantly impacts their metabolic processes (Rojas-Romero *et al.,* 2015). On the other hand, the Cr(VI) form is highly soluble, mobile, and exceedingly toxic, causing more severe and devastating effects on animals and humans compared to Cr(III) (Nakkeeran *et al.,* 2018). In contrast, Cr(III) remains relatively immobile under ambient conditions, as it typically binds to organic matter, making it less poisonous than Cr (VI) (Shankar and Venkateswarlu, 2011; Jiang *et al.,* 2019).

The majority of environmental chromium releases stem from industrial sources, particularly from various industrial processes such as chemical manufacturing, mineral extraction, steel production, metal plating, leather tanning, textile dyeing, electroplating, cement manufacturing, metallurgical works, and other related activities (Nakkeeran *et al.,* 2018; Lian *et al.,* 2019). Understanding the sources, health effects, and behavior of chromium in soil is important for assessing its environmental impact and developing appropriate management strategies.

Chromium enters the soil through different sources and emission pathways. Industrial processes, such as electroplating, leather tanning, and stainless steel production, are significant sources of chromium contamination (Alloway, 2013). These activities release chromium compounds into the environment through effluents, waste disposal, and atmospheric emissions.

Industrial processes play a major role in chromium contamination of soil. Electroplating, for example, involves the use of chromium compounds in metal coating processes, resulting in the release of chromium into the surrounding soil and water (Bian *et al.,* 2011). Tanneries, which process animal hides and skins, utilize chromium salts in leather tanning, leading to the discharge of chromium-containing wastewater that can contaminate nearby soil (Hassan *et al.,* 2011).

Tannery waste is a significant source of chromium in soil. The use of chromium salts in the tanning process contributes to the accumulation of chromium in the soil through the disposal of untreated or poorly treated wastewater (Hassan *et al.,* 2011). Improper management of tannery waste can result in the leaching of chromium compounds into the soil, posing risks to both human health and the environment.

Stainless steel production is another important contributor to chromium contamination in soil. The manufacturing process involves the use of chromium-containing alloys, and the disposal of waste materials, such as slag and dust, can lead to the release of chromium into the soil (Alloway, 2013). Effluent discharges and airborne emissions from stainless steel production facilities can also contribute to the deposition of chromium in nearby soil.

Chromium exposure can have detrimental effects on human health. The specific health effects depend on the valence state of chromium, with hexavalent chromium (Cr (VI) being of particular concern due to its toxicity and carcinogenicity.

Hexavalent chromium is the most toxic and bioavailable form of chromium. It can enter the body through inhalation, ingestion, or dermal contact. Inhalation of airborne Cr (VI) compounds can lead to respiratory effects, such as asthma, bronchitis, and lung cancer (Agency for Toxic Substances and Disease Registry, 2012). Ingestion of contaminated water or food can also result in gastrointestinal effects, kidney damage, and an increased risk of developing gastrointestinal cancers.

Hexavalent chromium has been classified as a human carcinogen by multiple regulatory agencies, including the International Agency for Research on Cancer (IARC, 2012). Prolonged exposure to Cr (VI) compounds has been associated with an increased risk of developing lung cancer, nasal sinus cancer, and certain gastrointestinal cancers (ATSDR, 2012).

Inhalation of chromium compounds, particularly Cr(VI), can cause various respiratory effects. Occupational exposure to airborne Cr (VI) has been linked to respiratory symptoms, such as coughing, wheezing, and shortness of breath (ATSDR, 2012). Chronic exposure to high levels of Cr (VI) can result in irreversible lung damage and an increased risk of developing respiratory diseases.

Dermal contact with chromium compounds can lead to skin irritation and allergic reactions. Occupational exposure to Cr (VI) through direct skin contact or contact with contaminated objects can cause skin ulcers, dermatitis, and allergic sensitization (ATSDR, 2012). Individuals with pre-existing skin conditions or compromised skin barriers may be more susceptible to the adverse effects of chromium exposure.

The accumulation and distribution of chromium in soil are influenced by various factors, including its sources, soil properties, and environmental conditions.

The accumulation of chromium in soil is influenced by factors such as the type and concentration of chromium compounds, pH, organic matter content, and redox conditions (Alloway, 2013). Chromium tends to accumulate in soils with higher pH levels and organic matter content. The presence of certain minerals and clay minerals in the soil can also affect the adsorption and retention of chromium.

Chromium distribution in soil can vary both vertically and horizontally. Vertical distribution refers to the concentration of chromium at different soil depths, while horizontal distribution refers to the spatial variation of chromium within a given area. Factors such as leaching, runoff, and soil erosion can influence the vertical and horizontal distribution of chromium in soil (Alloway, 2013). High concentrations of chromium are often found near the contamination source or in areas where the disposal of chromium-containing wastes has occurred.

2.4 Soil Contamination near Refuse Dumpsites

Refuse dumpsites are potential sources of soil contamination, as they often contain various types of waste materials that can release heavy metals into the surrounding environment. Understanding the characteristics of refuse dumpsites and the extent of heavy metal contamination in nearby soils is crucial for assessing the environmental risks and developing effective remediation strategies.

Several factors influence heavy metal contamination near refuse dumpsites. Waste disposal practices, including waste composition and handling, affect the potential for heavy metal leaching into the surrounding soil (Sarkar *et al.,* 2021). Leachate percolation and runoff can transport heavy metals from the dumpsites to nearby soil (Sarkar *et al.,* 2021). Soil properties and characteristics, such as texture and organic matter content, influence the retention and distribution of heavy metals (Sarkar *et al.,* 2021).

Refuse dumpsites consist of a wide range of waste materials originating from domestic, industrial, and commercial sources. The composition of waste can vary significantly, depending on the activities and practices in the area. Common types of waste found in dumpsites include municipal solid waste, construction and demolition waste, electronic waste, and industrial waste (Awasthi *et al.,* 2017). These waste materials can contain various heavy metals, including cadmium and chromium, which can leach into the surrounding soil.

One of the significant concerns associated with refuse dumpsites is the generation and migration of leachate. Leachate is a liquid that forms as a result of water percolating through the waste materials, extracting dissolved and suspended substances, including heavy metals. Leachate can contain high concentrations of heavy metals and other contaminants, posing a risk to nearby soil and water resources (Fan *et al.,* 2016). The migration of leachate can occur through the soil matrix, potentially reaching groundwater sources and further spreading heavy metal contamination.

In addition to leachate generation, refuse dumpsites can also emit gases, including methane (CH4) and volatile organic compounds (VOCs). Methane is a potent greenhouse gas and is generated as a byproduct of anaerobic decomposition of organic waste (Awasthi *et al.,* 2017). VOCs can be released from various waste materials and can have harmful effects on both human health and the environment. These gases can interact with the surrounding soil, affecting its physicochemical properties and potentially facilitating the transport of heavy metals.

Understanding the extent and distribution of heavy metals in soils near refuse dumpsites is crucial for assessing the potential risks to human health and the environment. Various studies have investigated the heavy metal content in soils in the vicinity of dumpsites, focusing on factors such as sampling and analysis methods, spatial distribution, and comparison with background levels.

2.5 Spatial Distribution and Hotspots

The spatial distribution of heavy metals in soils near refuse dumpsites can vary depending on factors such as waste composition, leachate migration, and soil properties. Studies have shown that elevated concentrations of heavy metals are often found in the immediate vicinity of dumpsites, with decreasing levels observed with increasing distance (Xiong *et al.,* 2019). Hotspots, characterized by significantly higher concentrations of heavy metals, can occur within the contaminated area. Identification of these hotspots is crucial for effective remediation and risk management strategies.

2.5.1 Permissible levels of heavy metals

Comparing the heavy metal concentrations in soils near refuse dumpsites with background levels is essential for assessing the extent of contamination and determining the potential sources of contamination. Background levels represent the natural or baseline concentrations of heavy metals in the absence of anthropogenic influence. By comparing the concentrations, it is possible to differentiate between naturally occurring heavy metals and those originating from dumpsite activities (Xiong *et al.,* 2019). This comparison helps in understanding the magnitude of the problem and identifying the areas that require immediate attention and remediation efforts.

The concentration of chromium in the soil was found in the range of 10.57 to 77.10 mg/kg, permissible limit recommended by Dutch standard is 100 mg/kg for chromium. All the soil samples were within the permissible limit. The higher concentration in the plant may be as a result of the different kinds of Chromium that differ in their effects and upon which they enter air, water and the soil. Cr3+ and Cr6+ form through natural processes and human activities. Chromium is not essential for plant growth, it was not detected in some plant sites due to the fact that uptake of Cr by plant shoot is generally low (WHO, 1996; Ogundele *et al.,* 2015) Heavy Metal Concentrations in Plants and Soil along Heavy Traffic Roads in North Central

Nigeria. The permissible limit of cadmium in plant recommended by WHO (1996), is 0.02 mg/kg.

According to the findings on the concentration of cadmium in the soil samples from various sites by Osmani *et al.* (2015) found in low range of ND to 0.36 mg/kg (Tables 2-10) in the soil. The maximum level of Cadium in the soil according to the Dutch standard is 0.8 mg/kg

Umoh and Etim (2013) conducted a study comparing the concentration of metals in soils at a decomposed biodegradable waste dumpsite with soils 100m away at a control site. The results revealed a notable increase in the concentration of heavy metals at the dumpsite when compared to the control site, which is consistent with findings from a similar study by Amusan *et al*. (2005). This increase can be attributed to the presence of metals containing wastes at the dumpsite, which eventually leach into the underlying soils.

The metals analyzed in this study include micro-nutrients like iron, zinc, and copper, as well as non-essential/toxic heavy metals, which can be harmful to plants when present in concentrations exceeding tolerance levels. These elements are crucial for the normal growth of plants. The concentration of lead at the dumpsites ranged from 9.46 mg/kg to 18.83 mg/kg, while at the control sites, it ranged from 5.21 mg/kg to 7.53 mg/kg. Both the dumpsites and control sites fell within the normal range of 2-200 mg/kg, as reported by Ebong *et al*. (2008).

The higher concentration of lead at the dumpsites can be attributed to the decomposition of lead-containing wastes present in that area.

Ebong *et al*. (2008) reported that plants growing in soil near dumpsites accumulate significantly higher levels of heavy metals compared to those in normal soil. This increased concentration of heavy metals in the soil can easily surpass tolerance levels, leading to severe issues in the food chain. Cadmium is categorized as a soft acid and has a preference for forming complexes with sulphides (Moore, 2006). The accepted range of cadmium in soil, as reported by Ebong *et al*. (2008), is (0.01 - 300) mg/kg. However, both the dumpsite and control site in the current study fall below this accepted range for cadmium in soil. The analytical results indicate that the cadmium levels at the dumpsite range from (0.09 to 0.42) mg/kg, while the control site shows levels between (0.04 to 0.08) mg/kg. Cadmium is considered one of the 129 priority pollutants by the EPA (1991) and is among the 25 hazardous substances. Ingesting high levels of cadmium can cause severe irritation to the stomach, leading to vomiting and diarrhea. Cadmium and its compounds are known human carcinogens, and smokers are exposed to significant amounts of cadmium compared to non-smokers. Other health effects associated with cadmium exposure include lung damage, fragile bones, and kidney disease (Sabine and Wendy, 2009). As a result, this issue demands the attention of environmental chemists, government agencies, and other private bodies.

Umoh and Etim (2013) furthermore, investigated on the levels of heavy metals in soils around a designated municipal solid waste dumpsite and a control site in Port Harcourt and its environs. The results showed that the soil samples from the waste dumpsite had higher levels of heavy metals compared to the control site. Continuous dispersion of heavy metals from the waste dump by run-off water, wind, and scavengers contributed to the contamination of soils around the waste dump. The concentrations of metals in soils ranged from 0.50 g/g to 20.5 g/g for As, 0.20 g/g to 13.0 g/g for Cd, 0.50 g/g to 100.0 g/g for Cr, 2.50 g/g to 910.0 g/g for Cu, 0.50 g/g to 34.0 g/g for Ni, and 1.0 g/g to 127.5 g/g for Pb. The difference in mean concentrations of Cd, Cu, and Pb between the waste dump and the area outside the dump was not statistically significant in the wet season ($p > 0.05$ Pb). However, the concentrations of As, Cr, and Ni showed significant differences between the two areas in the dry season ($P < 0.05$). Cd, Cr, and Cu demonstrated a positive correlation with distances across the waste dump (r =

0.9236, 0.9338, 0.3586 respectively). The mean concentrations of Cd and Cu in soils from the waste dumpsite exceeded tolerable limits, raising environmental concerns (Ideriah *et al.,* 2005; Nkop *et al.,* 2016).

Nkop *et al*. (2016) in a study disclosed a significant difference between the mean concentration of Cd in soil at dumpsites and the control. The concentration of Cd in the dumpsites ranged from1.80 to 9.25 mg/kg. The dumpsite B records the highest with means 9.25 mg/kg, dumpsites A has the lowest with concentration of 1.80 mg/kg while dumpsite C records 2.12 mg/kg. The control sample recorded 0.06, 2.04 and 0.23 mg/kg for dumpsite A, B and C respectively. The result obtained indicates that dumpsites contributed significant amount of Cd to the environment.

2.6 Risk Assessment and Remediation Strategies

2.6.1 Human health risk assessment

Human health risk assessment is essential to evaluate the potential risks associated with heavy metal contamination in soil. Exposure pathways, such as ingestion, inhalation, and dermal contact, are considered in assessing the health risks (Khan *et al.,* 2018). Risk assessment models and guidelines provide frameworks for evaluating and managing these risks (Khan *et al.,* 2018).

2.6.2 Remediation techniques for heavy metal in soils

Remediation techniques aim to mitigate the effects of heavy metal contamination in soils. Physical methods, such as soil excavation and containment, are used to remove or isolate contaminated soil (Kumar *et al.,* 2021). Chemical methods involve the use of amendments or chelating agents to immobilize or extract heavy metals from soil (Kumar *et al.,* 2021).

Biological methods utilize microorganisms or plants to degrade or accumulate heavy metals in the soil (Kumar *et al.,* 2021).

Remediation approaches can be classified into three main categories: physical methods, chemical methods, and biological methods.

Physical methods involve the physical removal or containment of contaminated soil to reduce heavy metal concentrations. Excavation and disposal of the contaminated soil in designated repositories is a common physical remediation technique (Liu *et al.,* 2018). This method is effective for removing localized hotspots of contamination but may be impractical for large-scale remediation projects due to high costs and potential disruption to the surrounding environment.

Soil washing is another physical method that utilizes water or other solvents to extract heavy metals from contaminated soil (Wu *et al.,* 2019). The soil is mixed with the washing solution, and the resulting leachate is treated to remove the heavy metals before the soil is returned to its original location. Soil washing can achieve significant reductions in heavy metal concentrations and is particularly effective for soils with high contaminant mobility.

Soil capping or sealing involves covering the contaminated soil with an impermeable layer, such as clay or geomembranes, to prevent the leaching and migration of heavy metals (Xiong *et al.,* 2019). This method is commonly used for managing contaminated sites with low to moderate levels of contamination. However, long-term monitoring and maintenance are essential to ensure the effectiveness of the cap in preventing the release of heavy metals.

Chemical methods involve the use of chemical agents or amendments to alter the chemical properties of heavy metals, thereby reducing their mobility and bioavailability in the soil. One commonly used chemical remediation technique is soil stabilization, which aims to immobilize heavy metals by changing their chemical form or binding them to less soluble compounds (Tangahu *et al.,* 2011). Common stabilization agents include lime, cement, and phosphate-based materials. These agents react with heavy metals to form stable compounds, reducing their potential for leaching and uptake by plants.

Another chemical method is soil flushing, which involves the application of chemicals or solvents to enhance the desorption and subsequent removal of heavy metals from the soil matrix (Kumar *et al.,* 2019). Chelating agents, such as ethylenediaminetetra-acetic acid (EDTA) and citric acid, can effectively mobilize heavy metals and facilitate their removal through leaching. However, careful consideration should be given to the proper disposal of the resulting metal-laden leachate.

Biological methods utilize living organisms, such as plants and microorganisms, to remediate heavy metal-contaminated soils. Phytoremediation, a popular biological remediation technique, utilizes plants to extract, stabilize, or degrade heavy metals (Ma *et al.,* 2015). Different mechanisms, such as phytoextraction, phytostabilization, and rhizoremediation, are employed by various plant species to remediate contaminated soils. Plants can accumulate heavy metals in their tissues, immobilize them in their root zones, or promote microbial activity to enhance metal degradation.

Microbial remediation techniques involve the use of specific microorganisms that have the ability to metabolize or transform heavy metals in the soil. These microorganisms can facilitate the biodegradation or immobilization of heavy metals through processes such as biosorption, bioleaching, and biomineralization (Rajapaksha *et al.,* 2016). Bioremediation strategies often involve the addition of microbial inoculants or amendments to enhance the activity of native microorganisms or introduce specific metal-resistant strains.

It is important to note that the selection of an appropriate remediation technique depends on various factors, including the characteristics of the contaminated soil, the type and concentration of heavy metals, site-specific conditions, and economic considerations. Often, a combination of different remediation techniques may be required to achieve optimal results in addressing heavy metal contamination in soils.

CHAPTER THREE

MATERIALS AND METHOD

3.1 Study Area

The study was conducted sampling from a dumpsite located within Egor Local Government Areas in Benin City, Edo State while the control samples were obtained from the research filed of Faculty of Agriculture, University of Benin. The area lies within latitude 6 ° 24′ 7.947 ″ N and longitude 5 ° 37′ 9.64884″ E for the dumpsite while the control was within latitude 6 ° 23′ 28.02156 ″ N and longitude 5 ° 37′ 46.66908″ E.

3.2 Sample Collection

Soil sample were obtained from two different areas in Edo State which were from a dumpsite located within Egor L.G.A and on geographical coordinate of; Latitude 6 ° 24′ 7.947 ″ N and longitude 5 ° 37′ 9.64884″ E, while that of the Control samples were obtained from the research filed of Faculty of Agriculture, University of Benin. The area lies within latitude 6 ° 23′ 28.02156 ″ N and longitude 5 ° 37′ 46.66908″ E. Replicate samples were obtained from each of the selected areas at three different depths (0 - 15, 15 - 30 and 30 - 45 cm) using an auger (Wilding, 1985). The soil samples were thereafter carefully bagged in a well labelled polythene bag then taking to the laboratory and analyzed for some physical and chemical properties.

3.3 Sample Preparation / Laboratory Analysis

The soil samples were air-dried for 7 days indoors to reduce the moisture contents. The samples were crushed in a mortal after drying. They were thereafter passed through a 2mm sieve. The sieved samples were analyzed for some physical and chemical properties using standard laboratory procedures. The sieved particles were then stored for digestion and subsequent analysis.

3.4 Soil pH

pH 1:1 in H_2O

Twenty grams (20 g) of fine air dried soils was weighed into 50 ml beaker after which, 20 ml of distilled water was added and the mixture was stirred intermittently for 30 minutes. The pH was measured by immersing the glass electrode into the partially settle suspension and pH was recorded as soil pH in H_2O 1:1 by Udoh (2009).

3.5 Particles Size Distribution

The particle size distributions were determined using the hydrometer method of Bouyoucos (1951) as modified by Day (1965). 51 g of air- dried or 50 g of oven-dried soils Weighed into a soil shaking bottle while 100 ml of calgon was added and was allowed to soak for 30 minutes. The mixture was stirred with a mechanical stirrer. The soil suspension was transferred into a sedimentation cylinder and was filled to mark with distilled H_2O.

A plunger was inserted and moved up and down to mix the content thoroughly, while the sediment was dislodged with their upward strokes of the plunger near the bottom, the hydrometer was lowered carefully into the suspension and readings were taken after 40 seconds (R 40 sec.).

The temperature reading was taken thereafter with a thermometer.

The second reading was taken at about 120 minutes after the commencement of the experiment, while the first (R 40 sec.) reading was calculated for % silt + clay, the second reading was done for % clay and subtracted from % silt clay and both subtracted from 100 to get % sand.

3.6 Organic Carbon

Organic carbons were determined using Walkley-Black wet oxidation methods (Walkley and Black (1934).

1g of soil sample was weighed into 250 ml conical flask, 10 ml of 1N $K_2Cr_2O_7$ solution was added and the mixture swirl for proper mixing. Thereafter, 20 ml of concentrated H_2SO_4 was added carefully. The mixture was again swirl to mix up and was left for 30 minutes and thereafter 100 ml of distilled water was added. The mixture was again swirl round. 5 drops of ferroin indicator was also added.

The excess chromic acid was titrated with 0.5 N ferrous sulphate to dirty brown end-point (Tml).

A blank was run, using the sample procedure, but without soil sample (Bml).

The blank will measure the amount of reducing substance present in the reagents as impurities.

-% organic carbon was calculated as follows:

3.7 Organic Matter

The organic matter was computed by multiplying the value of the organic carbon by a standard value of 1.724.

3.8 Exchangeable Bases

Exchangeable cations, Ca, Mg, K and Na were extracted with 1N ammonium acetate solution (1N NH_4OAc) buffered at pH 7.0 the Ca and Mg were determined from the extract using 0.01m EDTA (ethylenediaminetra-acetic acid) titration method as described by Black (1965), while K and Na were determine using flame photometer (Jackson, 1962).

10 g of soil sample was weighed into 250 ml soil shaking bottle and left overnight after adding 1M NH_4OAC,

The mixture was filtered using Whatman No. 1 filter paper into 100ml volumetric flask and was made up to mark with NH_4OAC. From the leachate, Ca and Mg were determined titrimetrically, while Na and K were read in a flame photometer, and each element is expressed in cmol/kg.

3.9 Determination of Ca and Mg (EDTA Titration Method)

10 ml of the 1MNH_4OAC extracted Leachate was pipetted into a 250 ml conical flask (V_2).

50 ml of distilled water was added.

8ml of NH_3 solution (conical) was added.

5 drops of 2 % KCN was also added; followed by 5 drops of 5% hydroxyl ammonium chloride ($OHNH_3Cl$).

3 drops Eriochrome Black T indicator (EBT) was added. The mixture was then titrated with 0.01M EDTA, from red-wine-blue.

3.9.1 Ca Determination

10 ml of extract was pipetted into 250 ml conical flask (V2)

50 ml of distilled water was added.

2 ml 2 % KOH was also added.

5 drops of % KCN followed by 5 drops of $OHNH_3Cl$.

5 drops of calgmit was added and the mixture titrated also using EDTA (0.01M).

Calculation:

Ca in mmol / 100 subscript 5 = M×T (EDTA) ×V1/V2×100/wt of sample × 40

Where:

T- Titre value

M (EDTA) - Molarity of EDTA

V_1- Volume of extract

V_2- Volume of aliquot

40- Molecular weight of Ca

While that of Mg go with same.

3.10 Total Nitrogen

Total Nitrogen was determined using the regular macro Kjeldahl method as reported by Bremmer and Mulvaney (1982)

0.5 g of fine air dry soil was weighed into 10 ml conical flask.

A catalyst mixture of K_2SO_4 + $CUSO_4$ + ScO_2 was added to aid quick digestion.

15ml of conc.H_2SO_4 was added and a glass curved funnel (specially made to prevent direct escape of ammonia (NH_3) the heating was done on an electric cooker till the solution became very clear.

It was left to cook down to room temperature.

The digested soil was filtered into 100ml volumetric flask and was made up to mark.

The mixture was turned thoroughly and severally and was kept waiting for distillation.

During distillation, 10 ml aliquot was taken into a 500 ml Kjeldahl flask.

30 ml of distilled water was added.

15 ml of 10 N NaOH was added and it was set-up in the distillation apparatus.

25 ml distillate was collected and titrated back with 0.01 N HCl.

Total % nitrogen was calculated as follows:

$$M\,x\,T\,x\,\frac{14}{100}\,x\,\frac{V1}{V2}\,x\,\frac{100}{wt.of\;sample}$$

Where:

M -Molarity of acid

T- Control titre value

V_1- Final Volume of digest.

V_2- Volume of digest used for distillation

3.11 Available Phosphorus

The available phosphorus was determined by colorimetric method after extracting with Bray 1solution (Murphy and Riley 1962).

Weigh 5 g of soil was weighed into a 250 ml shaking bottle.

Add 35 ml of extracting solution (1M NH_4F).

The mixture was shaken for 3 minutes and was filtered into 100ml volumetric flask and the leachate determined in a spectrometer.

Calculation:

Weight of sample used – 5 g

Volume of extract used (V) – 35 ml

Volume of extract used - 250 ml diluted to 50ml

Therefore ppm soil = $ppm\ graph\ x\ \frac{35}{35}\ x\ \frac{50}{2.5}$

3.12 Heavy Metals Determination

The double acid extraction method was used to determine the micronutrients, One gramme (1.0 g) of the soil sample was digested with 15 mL of (0.05N HCl in 0.125N H_2SO_4) The extract was filtered through Whatman No 1 filter, the samples were subsequently analyzed for Zn, Cr, Fe, Mn, Cd, Pb, Ni, and Cu, using flame atomic adsorption spectrophotometry (Udo *et al.,* 2009).

3.13 Statistical Analysis

The data obtained from the physical and chemical analysis were further analyzed statistically using Genstat Statistical Package Version 8.0. The differences between the means were separated using Least Significant Differences (LSD) at 5% level of probability.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Soil Physical and Chemical Properties from Refuse Dumpsites and Control Soils

The results for some of the chemical and physical properties of the soils obtained from the dumpsite and areas away from the dumpsite (Control) are presented in Table 4.1. It shows that, the control soil had a pH value that ranged from 4.46 at the top (0 – 15 cm) soil to 4.10 at the subsoil (30 – 45 cm). These pH values (4.46, 4.50 and 4.10) imply that the soils of the control according to the pH classification by Chude *et al.* (2011) are generally very strongly acid. Whereas, the pH of the soils in the dumpsite ranged from 6.13 at the top soil to 5.04 at the subsoils. However, these pH values (6.13, 5.63 and 5.04) falls under the class of moderately acid. These results agree with the findings of Ogbemudia *et al.* (2015) which reported similarity (5.17 – 6.53) in pH of soils from a dumpsite. OC (8.00 – 6.10 gkg^{-1}), OM (13.79 – 10.51 gkg^{-1}), TN (0.66 – 0.30 gkg^{-1}), Av.P (10.98 – 8.35 mgkg^{-1}) and all the basic cations (K, Ca, Mg and Na) were all higher in amount at the top soils than the subsoils. This result aligns with the findings of Xiao *et al.* (2012) who reported differences in soil nutrients between top soils and subsoils and their influencing factors. On the other hand, the dumpsite had OM (27.69 – 18.00 gkg^{-1}) that ranged from topsoil to subsoils, OC (47.73 – 31.03 gkg^{-1}), T.N (2.73 – 1.43 gkg^{-1}) and Av.P (44.13 – 28.81 mgkg^{-1}).

The relatively higher amount of the chemical properties could be attributed to the organic matter richness of the dumpsite coupled with the less acidity which allows for abundance of nutrient release compared to the pH status of the control soils. This results are further explained by the facts that the textual class of the soils both at the dumpsite and control were Loamy sand from the topsoil down to the subsoils which means that the changes in the chemical richness of the dumpsite is actually due to the higher amount of organic matter input to that particular site than the control soils.

4.2 Heavy Metal (Cr and Cd) Contents in Control and Refuse Dumpsites

The concentrations of Cr in soil ranged from 19.93 to 36.78 mg/kg (Table 4.2), which was higher than that of the control (7.78 to 12.51 mg/kg). Allowable limits of Cr concentrations vary widely with country, being 150mg/kg in France; 100mg/kg in Austria and Spain; 60mg/kg in Germany and Sweden; and 30mg/kg in Denmark and the Netherlands. Therefore, most of the values obtained in this study conform to the acceptable limits. The values of Cr obtained in this study were lower than the 900–2000mg/kg reported by Adefemi and Awokunmi (2009) in dumpsites within Ado-Ekiti town in South West Nigeria. The elevated concentrations were ascribed to deposited wastes which contained high concentrations of Cr. As observed by Adelekan and Abegunde (2011), Chromium is one of the heavy metals whose concentration in the environment is steadily increasing due to industrial growth, especially the development of metal, chemical and tanning industries. Cd was more concentrated at the 0-15 cm depth.

Cd values at the dumpsites ranged from 5.14 to a high of 8.18 mg/kg (Table 4.2), while the control samples had <0.66 mg/kg.

Table 4.1: Some Physical and Chemical Properties of Soils from Control and Refuse Dumpsites

Treatments	Depth	pH	EC	Org.C	Org. M	T. N	AV.P	K	Ca	Mg	Na	Ea	CEC	Sand	Silt	Clay
		(1:1)	µs/cm		g/kg		$Mgkg^{-1}$	Coml/kg							g/kg	
Control	0-15cm	4.46a	85.70a	8.00a	13.79a	0.66a	10.98a	0.34a	0.12a	0.81a	0.64a	10.98a	0.857a	841.30a	42.33a	116.30a
	15-30cm	4.50a	67.59b	6.13b	10.57b	0.50b	10.49a	0.26b	0.07b	0.74a	0.35b	10.49a	0.6759b	837.70b	33.00ab	129.30a
	30-45cm	4.10b	50.75c	6.10b	10.51b	0.30c	8.35b	0.21c	0.06b	0.66b	0.31b	8.35b	0.5075c	832.30c	28.33b	139.30a
Dumpsite	0-15cm	6.13a	341.80a	27.69a	47.73a	2.73a	44.13a	0.86a	0.36a	2.42a	1.84a	44.13a	3.418a	836.30a	47.00a	116.70c
	15-30cm	5.63a	215.20b	22.04b	38.00b	2.00b	34.64b	0.69b	0.24b	1.83ab	1.65b	34.64b	2.152b	834.00a	42.67a	123.30b
	30-45cm	5.04b	203.60b	18.00c	31.03c	1.43b	28.81b	0.55c	0.16c	1.40b	1.41c	28.81b	2.036b	827.70a	37.00a	135.30a

Means in the same column having the same letter are not significantly different from one another at 5% level of probability using Duncan Multiple Range Test (DMRT)

Table 4.2: Heavy metal (Cr and Cd) contents in Control and Refuse Dumpsites

Location	**Depth**	**Cr** **mg/kg**	**Cd**
Control	0-15cm	12.51a	0.66a
	15-30cm	10.10b	0.46ab
	30-45cm	7.78c	0.31b
Dumpsite	0-15cm	36.78a	8.18a
	15-30cm	23.06b	7.18a
	30-45cm	19.932c	5.14b

4.3 Comparative Analysis of the Physical and Chemical Properties of Soils from Control and Dumpsite

The data presented in Table 4.3 illustrates correlation coefficients (r) between various soil physical and chemical properties observed at the Dumpsite located within Egor Local Government Areas in Benin City, Edo State. The significance level was set at ($P<0.05$). The comparative analysis of heavy metal contents between the dumpsite located within Egor Local Government Areas in Benin City, Edo State and the control site, the research filed of Faculty of Agriculture, University of Benin, provides critical insights into the potential impact of waste deposition on soil quality and heavy metal concentrations. Specifically, chromium (Cr) exhibited higher concentrations at the 0-15 cm depth within the dumpsite, possibly attributed to the disposal of waste materials containing elevated levels of Cr. This finding suggests a direct association between waste deposition and increased Cr concentrations in the soil.

The concentrations of Cr in the dumpsite soil ranged from 19.93 to 36.78 mg/kg, notably higher than those observed in the control site (7.78 to 12.51 mg/kg). When compared to international allowable limits for Cr concentrations, the values obtained in this study generally conform to acceptable limits, indicating that Cr contamination in the studied area is within permissible levels (100mgkg soil). This stands in contrast to the extremely high Cr concentrations reported in some dumpsites within Ado-Ekiti town in South West Nigeria, which were in the range of 900–2000 mg/kg. These elevated concentrations in the dumpsite located within Egor Local Government Areas in Benin City, Edo State could be attributed to the deposition of waste materials rich in Cr, likely from various industrial activities, including metal, chemical, and tanning industries.

Similarly, cadmium (Cd) exhibited notable differences between the dumpsite and the control site. Cd concentrations in the dumpsite soils ranged from 5.14 to a high of 8.18 mg/kg, which were higher than the permissible level [0.8mg/kg soil] as defined by Ogundele et al.,[2015]. whereas the control samples contained less than 0.66 mg/kg of Cd. The significant disparity in Cd concentrations indicates a substantial contamination of Cd within the dumpsite, likely due to the presence of Cd-rich waste materials.

The comparison of heavy metal concentrations in the dumpsite located within Egor Local Government Areas in Benin City, Edo State and the control site highlights the potential environmental implications of waste disposal practices. The elevated levels of Cr and Cd in the dumpsite soils, likely attributed to the deposition of industrial waste, emphasize the need for effective waste management strategies to prevent further contamination and mitigate potential adverse effects on the environment and human health. These findings underscore the importance of responsible waste disposal practices and monitoring of heavy metal concentrations in dumpsite soils to safeguard the surrounding ecosystem.

Table 4.3: Comparative Analysis of the physical and chemical properties of soils from control and dumpsite

Treatments	Depth(cm)	pH	EC	Org.C	Org. M	T. N	AV.P	K	Ca	Mg	Na	Ea	Sand	Silt	Clay
		(1:1)	µs/cm	g/kg			Mgkg^{-1}	Cmol/kg					g/kg		
Control	0 - 15	4.47^{b}	85.70^{b}	8.00^{b}	13.79^{b}	0.67^{b}	11.00^{b}	0.12^{b}	0.81^{b}	0.64^{b}	0.35^{b}	1.75^{a}	841.3^{a}	42.30^{a}	116.30^{a}
Dumpsite	0 - 15	6.13^{a}	341.8^{a}	27.69^{a}	47.73^{a}	2.73^{a}	44.10^{a}	0.36^{a}	2.42^{a}	1.85^{a}	0.87^{a}	0.47^{b}	836.6^{a}	47.00^{a}	116.70^{a}
	SED	0.14	15.55	0.62	1.06	0.24	2.05	0.02	0.13	0.06	0.04	0.06	6.21	5.52	8.99
	LSD$_{(0.05)}$	0.38	43.18	1.71	2.95	0.67	5.70	0.06	0.37	0.16	0.11	0.16	17.24	15.32	24.97
Control	15 - 30	4.50^{b}	67.60^{b}	6.10^{b}	10.50^{b}	0.50^{b}	10.50^{b}	0.07^{b}	0.74^{b}	0.35^{b}	0.26^{b}	1.47^{a}	837.70^{a}	33.00^{a}	129.30^{a}
Dumpsite	15 - 30	5.63^{a}	215.2^{a}	22.04^{a}	38.00^{a}	2.00^{a}	34.60^{a}	0.24^{a}	1.84^{a}	1.65^{a}	0.69^{a}	0.40^{b}	834.00^{a}	42.70^{a}	123.30^{a}
	SED	0.17	2.28	1.39	2.40	0.15	2.160	0.02	0.27	0.07	0.03	0.07	6.82	4.14	7.56
	LSD$_{(0.05)}$	0.49	6.33	3.86	6.66	0.42	6.00	0.05	0.75	0.18	0.09	0.19	18.92	11.48	21.00
Control	30 - 45	4.10^{b}	50.70^{b}	6.13^{b}	10.57^{b}	0.30^{b}	8.35^{b}	0.06^{b}	0.66^{b}	0.31^{b}	0.21^{b}	1.20^{a}	832.3^{a}	28.3^{b}	139.3^{a}
Dumpsite	30 - 45	5.28^{a}	204.30^{a}	18.93^{a}	32.63^{a}	1.47^{a}	29.33^{a}	0.18^{a}	1.47^{a}	1.44^{a}	0.57^{a}	0.31^{b}	826.7^{a}	38.7^{a}	134.7^{a}
	SED	0.22	3.36	1.00	1.73	0.07	0.77	0.01	0.13	0.01	0.03	0.01	5.73	3.09	6.60
	LSD$_{(0.05)}$	0.61	9.32	2.79	4.81	0.19	2.15	0.02	0.37	0.02	0.09	0.02	15.92	8.58	18.32

Means in the same column having the same letter are not significantly different from one another at 5% level of probability using Duncan Multiple Range Test (DMRT)

4.4 Comparative Analysis in the Amount of Heavy Metals in Soils

The comparative analysis in the heavy metal contents between the control and dumpsite are presented in Figure 1 and 2. Cr was more concentrated at the 0 - 15 cm depth. The elevated concentrations in the dumpsite can be ascribed to the deposited wastes which contained high concentrations of Cd. Cd showed a significant difference of occurrence in the treatment dumpsite to the control site.

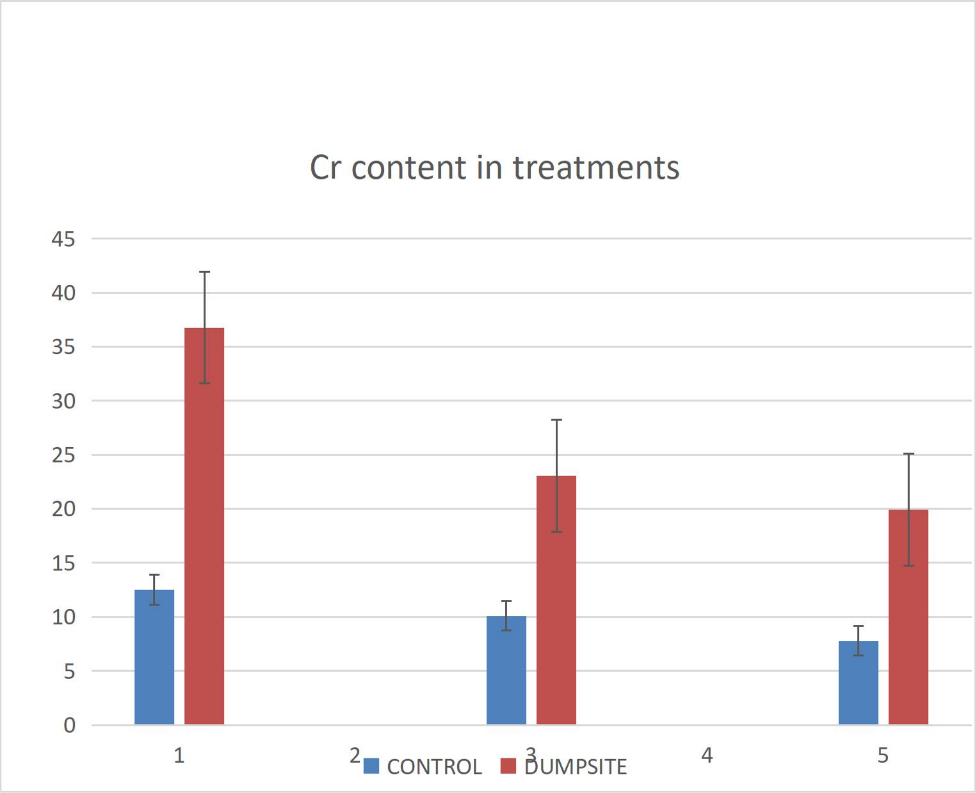

Figure 1: Cr content in treatments

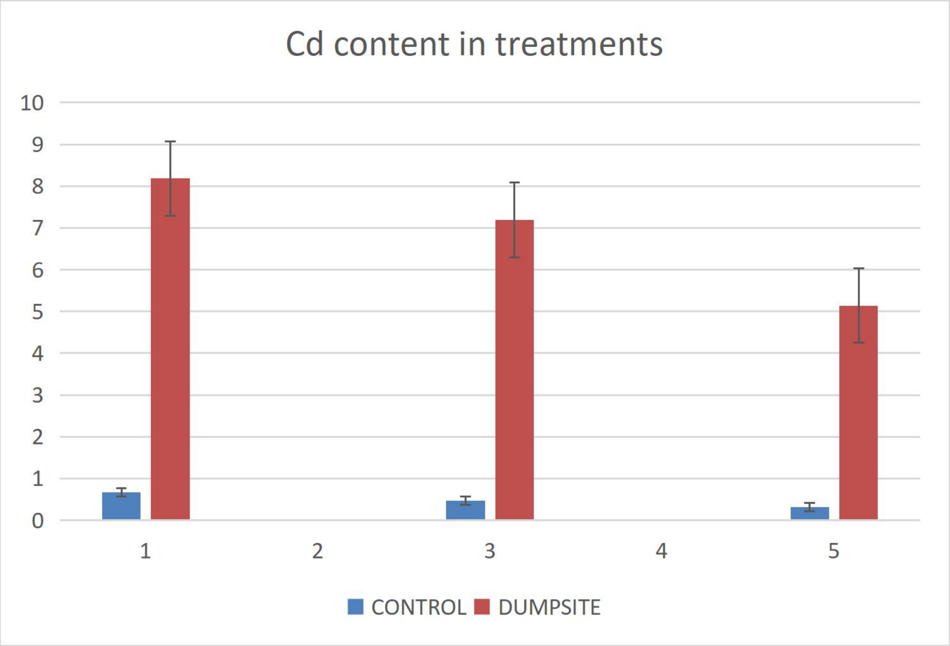

Figure 2: Cd content in treatments

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

High levels of heavy metals in the soil indicate pollution from human activities coming from industry and waste disposal. With careful analysis of heavy metal concentration from soil samples from depth 0 - 15cm, 15-30 and 30 -45cm, this study focused on assessing the availability of cadmium and chromium concentrations in a waste dumpsite. Chromium was the most prominent heavy metal, while cadmium was least detected. These findings disclosed that the soil from the dumpsite have more concentration of Cd and Cr and compared to control site in the study area. While this raises urgent action to prevent further contamination of the soils, it will be essential to tackle human activities and policies aimed at reducing the use of dumpsites or dumpsite soils for food production in Edo state and Nigeria without a proper soil test because minor deviations from safe levels of this heavy metals can lead to significant ecological and health problems if not managed adequately.

5.2 Recommendations

Based on the findings from this research, it recommends as follows: that;

1. there are higher amount of Cd and Cr in the dumpsite relative to the control soils of the study area.
2. Chromium and Cadmium contents in the dumpsite soils are not only concentrated in the topsoil (0 -15 cm) but its distributed down the soil profile in an amount that is above the permissible limits defined by WHO.
3. Furthermore, a concerted effort towards waste recycling should be championed as a means to curtail the escalation of heavy metal pollution. Governmental agencies

should collaborate to institute policies that deter the unrestricted disposal of waste materials. This could involve the meticulous identification and categorization of materials at specific sites, facilitating more effective waste management strategies.

4. Central to these recommendations is the establishment and strict enforcement of directives prohibiting agricultural activities on dumpsites. As a pivotal measure, the relocation of dumpsites from urban areas is paramount to prevent the continual accumulation of heavy metals within these regions. Concurrently, stringent adherence to existing environmental protection regulations should be enforced to counteract the ongoing buildup of heavy metal pollutants.

By embracing these recommendations, society can pave the way towards a more sustainable and resilient environment for present and future generations.

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