COMPARATIVE STUDY OF HEAVY METAL CONCENTRATION IN VEGETABLES GROWN IN BENIN CITY, EDO STATE, NIGERIA.

BY

AKINWALERE OMOTEBI FAVOUR (MISS)
MATRICULATION NUMBER:
LSC2003053

AN UNDERGRADUATE DISSERTATION SUBMITTED TO THE DEPARTMENT OF ENVIRONMENTAL MANAGEMENT AND TOXICOLOGY, FACULTY OF LIFE SCIENCES, UNIVERSITY OF BENIN, BENIN CITY, EDO STATE, NIGERIA; IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR AWARD OF BACHELOR OF SCIENCE (B.Sc) DEGREE IN ENVIRONMENTAL MANAGEMENT AND TOXICOLOGY

DATE: 3RD NOVEMBER,2025

CERTIFICATION

This is to certify that this research titled “COMPARATIVE STUDY OF HEAVY METAL CONCENTRATION IN VEGETABLES GROWN IN BENIN CITY, EDO STATE, NIGERIA” was carried out by “AKINWALERE OMOTEBI FAVOUR (MISS)” and presented to the Department of Environmental Management and Toxicology, Faculty of Life Sciences, University of Benin, Benin City; in partial fulfilment of the requirements for the award of Bachelor of Science (B.Sc) in Environmental Management and Toxicology. It was conducted under suitable conditions, was carefully supervised and subsequently approved as having met the requirements for the award of a Bachelor of Science degree in Environmental Management and Toxicology.

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(PROJECT SUPERVISOR) **DATE**

Prof.(Mrs.) E.T. Aisien

______________________ ______________________

(HEAD OF DEPARTMENT) **DATE**

Prof.(Mrs.) E.T. Aisien

DECLARATION

I "**AKINWALERE OMOTEBI FAVOUR** (MISS)" declare that "**COMPARATIVE STUDY OF HEAVY METAL CONCENTRATION IN VEGETABLES GROWN IN BENIN CITY, EDO STATE,NIGERIA**" is my work and that all sources that I have used or quoted have been acknowledged using complete references and that this work has not been submitted before for any other degree at any other University.

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AKINWALERE OMOTEBI FAVOUR **DATE**

DEDICATION

This report is dedicated to God Almighty, for his guidance and protection during this project. I also want to dedicate this report to my beloved parents (Mr and Mrs Akinwalere) and my loving family, whose unwavering support and encouragement have been the foundation of my academic journey and their unwavering support, prayers, love and financial assistance throughout my academic journey.

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ABSTRACT

Vegetables are consumed in both the developing and developed countries of the world due to their high nutritive values, however they also contain some high levels of toxic substances including metals.This study assessed the comparative concentrations of selected heavy metals:cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn), and copper (Cu) in four commonly consumed leafy vegetables: fluted pumpkin (Telfairia occidentalis), bitter leaf (Vernonia amygdalina), water leaf (Talinum triangulare), and scent leaf (Ocimum gratissimum) cultivated in polluted (Oluku) and unpolluted (Iyowa) sites in Benin City, Edo State, Nigeria. Samples were analysed using Atomic Absorption Spectrophotometry (AAS), and results were compared with FAO/WHO permissible limits. The concentrations of all heavy metals were below recommended safety thresholds, with the general trend of accumulation being polluted site > unpolluted site. Statistical analysis ($p < 0.05$) revealed significant variations for some metals, particularly Zn, Cd, and Cu, across the two locations. Bitter leaf and scent leaf exhibited higher tendencies for metal accumulation compared to other vegetables. Although all concentrations were within safe limits, continuous cultivation near polluted areas may lead to long-term contamination risks. The findings highlight the influence of anthropogenic activities such as waste disposal and vehicular emissions on metal uptake in vegetables and underscore the need for regular environmental monitoring,improved waste management, and public awareness to ensure food safety.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Food safety has become an increasing global concern, especially in the face of rising environmental pollution and the demand for sustainable food production. During recent decades, the growing need for food security has stimulated research on the hazards associated with the consumption of foodstuffs contaminated by pesticides, heavy metals, and other pollutants (Gerhard and Franz, 2023). Food is the major source of heavy metal ingestion in humans, particularly vegetables. One of the most essential aspects of food quality assurance is the assessment of heavy metal contamination of food items (Rafi and Gowda, 2017).

Soil serves as the primary storage for solid waste and provides essential nutrients and water for plants, animals, and humans. As a result, contamination and degradation of soil health have widespread effects on ecosystems (Abdu *et al*., 2017). Human activities frequently lead to soil contamination, resulting in significant variability influenced by anthropogenic factors such as mining, industrial emissions, and the use of sewage sludge.

Vegetables establish basic parts of the diet routine, by contributing protein, nutrients, iron, calcium and other components, which are difficult to come by (Sadeghi *et al*., 2020). The human diet must include vegetables since they are essential for maintaining normal physiological functioning and supplying nutrients (Wuyep *et al*.,2021). Due to the presence of certain nutritional elements that are necessary for human survival, vegetables are consumed more often. They are also known as protective foods since they help prevent sickness in humans. They are known to be a vital part of our diet since they provide enough fiber, vitamins, minerals, and trace elements (Chacha and Laswai, 2020).However, some vegetables have the ability to accumulate high levels of toxic elements such as heavy metals from soil and the environment. Various factors influence the absorption and accumulation of heavy metals in vegetables, including environmental conditions, climate factors, the concentration of heavy metals in the soil, soil characteristics, and the growth stage of the plants at harvest (Ganiyat, 2021).

The contamination of vegetables with heavy metals poses significant risks to food quality and public health. High concentrations of metals like Cu, Cd, and Pb have been linked to health problems, including gastrointestinal cancers (Danjuma and Abdulkadir, 2019). Heavy metals such as cadmium and lead are of particular concern because of their ability to bioaccumulate and cause long-term damage to the kidneys, liver, bones, and nervous system.

In Nigeria, and specifically Edo State, local populations rely heavily on vegetables such as fluted pumpkin (Telfairia occidentalis), bitter leaf (Vernonia amygdalina), water leaf (Talinum triangulare), and scent leaf (Ocimum gratissimum) as part of their staple diet. However, limited awareness and regulation of environmental pollution may expose residents to significant health risks through the consumption of contaminated vegetables.

1.2 **Statement of the Problem**

The increasing urbanization and industrial activities in Benin City have led to widespread environmental pollution, including the contamination of agricultural soils with heavy metals and the lack of effective waste management infrastructure. The toxicity and cumulative nature of heavy metals make their excessive accumulation in ecosystems a major environmental concern (Ali *et al*. 2021; Tauqeer *et al*.,2022).Vegetables grown in these soils may accumulate toxic metals such as lead, cadmium, nickel, zinc, and mercury, which can enter the human food chain and pose serious health hazards. Despite the importance of vegetables in the daily diet of Edo State residents, there is limited scientific data on the extent of heavy metal contamination in commonly consumed leafy vegetables within Benin City. This knowledge gap makes it difficult for consumers, farmers, and policymakers to assess the risks and take appropriate actions to ensure food safety.

1.3 **Aim of the Study**

The aim of this study is to compare the concentration of selected heavy metals in commonly consumed vegetables grown in different areas of Benin City, Edo State, and assess potential public health risks.

1.4 **Objectives of the Study**

The objectives of this study are to:

1. Analyze samples of commonly consumed vegetables: fluted pumpkin (Telfairia occidentalis), bitter leaf (Vernonia amygdalina), water leaf (Talinum triangulare), and scent leaf (Ocimum gratissimum) from selected locations in Benin City.
2. Determine the concentrations of heavy metals in the vegetable samples using standard laboratory analytical techniques.
3. Compare the levels of heavy metal contamination in vegetable samples across different locations in Benin City.
4. Assess potential health risks associated with consuming these vegetables based on WHO/FAO intake guidelines.
5. Identify possible anthropogenic sources of heavy metals in the selected areas.
6. Recommend strategies to minimize health risks and improve vegetable safety in urban agriculture.

1.5 **Significance of the Study**

The findings from this study will provide baseline data on the levels of heavy metal contamination in vegetable grow in Benin City, which is valuable for food safety monitoring and policy making. It highlights the potential health risks associated with the consumption of contaminated vegetables, thereby raising awareness among consumers and farmers. The finding can guide environmental health authorities and agricultural extension workers in developing strategies to reduce contamination and promote safer urban farming practices

1.6 **Scope of the Study**

This study focuses on the comparative analysis of heavy metal concentrations in four commonly consumed leafy vegetables: fluted pumpkin (Telfairia occidentalis), bitter leaf (Vernonia amygdalina), water leaf (Talinum triangulare), and scent leaf (Ocimum gratissimum) cultivated within different locations of Benin City, Edo State. The research focused on five selected heavy metals (Pb, Cd, Zn, Ni, and Cu), which are of significant environmental and public health concern.

The study will provide a comparative evaluation between vegetables cultivated in residential gardens (representing unpolluted areas) and those grown around dumping sites (representing polluted areas), thereby reflecting the influence of urbanization and anthropogenic activities on contamination levels. In addition, the results will be assessed against WHO/FAO food safety standards to estimate potential health risks associated with vegetable consumption in the study area. The findings will provide a scientific basis for risk communication, consumer awareness, and regulatory interventions aimed at minimizing exposure to toxic metals through dietary intake.

CHAPTER TWO

LITERATURE REVIEW

2.1 **HEAVY METAL (definition and classification**)

Heavy metals commonly refer to a group of comparatively dense and harmful elements, even in very low concentrations.This group includes metals and metalloids with densities exceeding 5 g/cm³ and atomic masses ranging from approximately 60 to 200. (Burakov *et al*., 2018). Arsenic (As), chromium (Cr), cadmium (Cd) and copper (Cu) are a few instances of heavy metals present in different ecosystems and wastewater, with levels varying typically from ng·L-1 to mg·L-1(Fu *et al*.,2017). Such metals are non-biodegradable elements compared to other pollutants and are typically classified into two categories. Poisonous metals like As and Pb make up the first category,which are entirely unfavourable substances, have no biochemical advantages to human beings, and are hazardous regardless of their levels. The second category consists of important metals such as manganese (Mn) and zinc (Zn), which are beneficial to humans biologically and favourable in small amounts. However higher concentrations of these elements mayresult in toxicity and disruption of body homeostasis (Kennelly, 2018). Similarly, heavy metals are divided into non-essential and essential elements of living things in terms of their functions during biological activities. Essential elements are necessary for living things and usually in very small amounts, while there is no proven biochemical function for non-essential elements to living beings. Zn, Mn, and Fe are essential elements, whereas Pb and Cd are considered physiologically unnecessary and are hazardous metals (Ali *et al*., 2019). In contrast, others divided heavy metals into four more specific classes: toxic, nutrient, radionuclides, and precious group (Alalwan *et al*., 2020; Singh and Ambawat, 2020).

2.2 Heavy Metal Contamination in Benin City

Benin City, a major urban centre in Edo State, has experienced environmental contamination due to rapid urbanisation, poor waste management, and proximity of agricultural sites to pollution sources. Heavy metal contamination in Benin City, Nigeria, is of a significant environmental and public health concern, with studies indicating pollution in water bodies, soil, and even vegetables. This contamination poses risks of both carcinogenic and non-carcinogenic health effects, particularly for children. Studies have highlighted the risk posed by cultivation near dumpsites and busy roads, as vegetables from these areas often exceed permissible heavy metal limits

(Aisien, 2022).

2.3 Sources of Heavy Metal Contamination in Soil

The introduction of heavy metals into various environmental media, including soil, air, and water, can stem from both natural and human made sources.

2.3.1 Natural Source

Naturally, heavy metals can emanate from the following processes: leaching, weathering, volcanic eruptions, decomposition, and seismic activities amongst others.

(i) WEATHERING

Weathering refers to a process, which breaks down rocks, soil, and minerals via their contact with the atmosphere, water, and living organisms. Weathering is an on site process and it does not involve the movement of weathered materials. Weathering involves physical, biological, and chemical processes. Physical weathering refers to the breakdown of minerals containing heavy metals through direct exposure to microclimatic factors such as heat, water, ice, and pressure. On the other hand, chemical weathering entails the reaction of chemicals in the rocks with micro climatic conditions leading to the release of heavy metals from the host rock to the surrounding environment. Both physical and chemical weathering can occur subsequently in any given system. Biological process entails the breaking down of rocks and soil molecules in the quest for nutrients for plants growth or for microorganisms to survive. The abstraction of nutrients leaves the rock vulnerable to other reactions. Breaking of rocks by plant roots to anchor a tree also leads to rocks disintegration and weathering. Minerals will therefore be broken down into minute molecules and get converted to secondary minerals. Minerals from the weathered rocks comprise problematic heavy metals that are of paramount concern in the environment. Igneous and sedimentary rocks are regarded as the most common natural sources of heavy metals. The parent material, from which they were originally derived, is the main source of HMs in soils. The Earth's crust is composed of sedimentary rocks to a little extent (approximately 5%) and 95% igneous rocks (Sarwar *et al*., 2016). Different concentrations of HMs are present in igneous and sedimentary rocks. Heavy metals naturally arise in the soil as a result of the weathering process because they originate in the Earth's crust. Heavy metals in rocks may be released into the soil environment as a result of a variety of natural processes, such as erosion, leaching, volcanic eruptions, biological processes, terrestrial processes, and surface winds (Muradoglu *et al*.,2015).

(ii) LEACHING

Leaching is the release of heavy metals from soil matrices using different leachants.

A leachant may include water, acids, bases, and other organic compounds. Often, when rainfall interacts with surface rock fractures, the leachable fraction comes into contact with aqueous media, resulting in the leaching of metals from the surrounding geology. This process is influenced by various factors, including the pH of the leaching solution, the presence of buffering minerals, solubility, and the susceptibility of the rocks. In the chemical processing industry and metallurgical processes, leaching has numerous applications, including separation of metal from ore using acid, and other leachants. Leaching is affected by desorption and complexation processes, which are influenced by pH, redox conditions, dissolved organic matter, and microbial processes.

(iii) VOLCANIC ERUPTION

Volcanic eruption is a natural process. It leads to the emission of particles to the earth surface. The ash from volcanic eruptions contain heavy metals that are toxic to the environment and living organisms. They usually get transported to the environment during rainfall since they will be washed off to the environment. Volcanic dust which is a component of volcanic ash that gets ejected during volcanic eruptions usually fly under the influence of wind, and then fall onto the ground during rainfall and when conditions are favourable. Volcano is formed from the dissolution of metals from the earth crust hence the resultant product is rich in heavy metals. Volcanic ash may contain contaminants such as Pb, Zn, Cu, Cd, Cr, Fe, and Al (Huff and Owen, 2015). The trace metals in the volcanic dust that settles on the ground can migrate into the soil, where they dissolve in water based on redox conditions, temperature, and pH, and subsequently get adsorbed by soil particles.

(iv) SEISMIC ACTIVITIES

Seismic events, like earthquakes, contribute to the release of heavy metals into the environment. When an earthquake occurs, the underground geology fractures, bringing oxidizable and reactive materials into contact with oxygen. Rainfall and underground leakages can then cause water to interact with these fractured soil components, resulting in the release of heavy metals (Leclère *et al*. 2018; Simonen *et al*. 2018).

(v) DECAYING OF ORGANIC MATTER

Living organisms take up metals and other chemicals as essential nutrients.These nutrients or metals are essential for their growth. To a certain extent, plants can phytoremediate the soil hence accumulating all the metals on its matrices. When they die and decompose, those contaminants go back to soil and they also lead to a release of metals to the environment. Common heavy metals found at contaminated sites include Pb, Cr, As, Zn, Cd, Cu, and Hg, among others. These metals can bioaccumulate and biomagnify in the food chain since they are available in the body matrices of decaying organic matter (Zhang *et al*., 2018).

2.3.2 ANTHROPOGENIC SOURCES

Anthropogenic generally indicates sources that are man-made. Human activities, such as smelting, mining, and burning fossil fuels for energy, elevate the concentrations of heavy metals in soils.

(I) Agricultural Activities

The agricultural sector has many potential sources, including fertilizer, pesticides, livestock dung, and wastewater. The use of pesticides, soil amendments and fertilizers is required in order to meet the increased demands in food production. Organic soil amendments include the by-products of processing mills such as sawdust and waste such as bio-solid (sewage sludge). The use of these pesticides and soil amendments introduces heavy metals into the environment and the extensive use of them result in contamination of surface waters and aquifers during various erosion processes (Diagboya and Dikio 2018).

- Pesticides

Pesticides are harmful substances that can be created synthetically or naturally. They can also be hazardous compound combinations. Insecticides, bactericides, and fungicides are frequently used in agricultural fields to control harmful weed, fungus, bacterial, and insect infestations.Several common pesticides used fairly extensively in agriculture and horticulture in the past contained substantial concentrations of metals. Pesticides are chemicals or compounds that are designed to kill or stop the growth of pests (fungi, weed, and insects amongst others), with herbicides designed for weed, fungicide for fungi and insecticide for insects (Wallace 2015). Phenylmercuric acetate (fungicide) and lead arsenate (insecticide) are some of the many pesticides used in fruit plantations, and these pesticides contain heavy metals such as mercury, arsenic and lead which contaminate the environment upon exposure. The usage of metal based pesticides has since been discontinued due to their toxicity and adverse effects on human health. However, they drastically contribute to an increase in the concentration of heavy metals in the environment (Sophia and Lima 2018).

- Soil Enhancers (bio-solid and manure)

Soil amendments are important in replenishing nutrients in the soil and keeping it suitable for agriculture hence the use of biosolids, sewage effluents and fertilizers. Bio-solids are organic materials present in animal waste, sewage sludge and industrial waste such as pulp sludge from the production of paper. These solids are used for soil enhancement because of the nutrients they contain and their ability to improve the properties of soil such as pH, porosity, fertility, and water retention. Certain animal wastes such as poultry, cattle, and pig manures produced in agriculture are commonly applied to crops and pastures either as solids or slurries. While manures are often regarded as beneficial fertilizers, in the pig and poultry industries, the copper and zinc added to animal diets as growth enhancers, along with arsenic in poultry health products, may contribute to soil metal contamination.The application of solid agricultural wastes, including biosolids and farm manures, has increased the buildup of hazardous metals in soils, while their availability in soils is unlikely to change much in the near future (Urra *et al*.,2019; Taghipour and Jalali 2019). It has been noted that applying biosolids and agricultural manures repeatedly raises the amount of Ni, Cd, Zn, Cr, Cu, and Pb in soils (Prodipto *et al*.,2024)

Bio-solids are not only rich in soil-enriching nutrients but also contain heavy metals such as As,Cd, Cr, Cu, Pb, Hg, Ni, Se,Mo, Zn, Tl, Sb, which are toxic in high concentrations. The concentration of heavy metals present in bio-solids is determined by the source of waste. Bio-solids derived from domestic waste have lower heavy metal concentrations than those from industrial sources. The plant uptake or absorption of these metals is affected by the presence of natural organic matter within the soil as organic matter influences the solubility of these trace metals

- Fertilizer

Both organic (natural) and inorganic (synthetic) fertilizers can be sources of heavy metals.

The application of fertilizer is essential in improving the quality of soil and improving agricultural yields as they contain nutrients, which are important for plant growth and nutrition. However, Salem *et al*. (2020) disclosed that application of phosphate and urea fertilizers increased the levels of metals (Cr, Cu, Cd,Mn, Zn, Ni and Pb) in agricultural soil. The overuse of macro nutrient fertilizers (nitrogen, phosphate and potassium also known as NPK) leads to the leaching of the nutrients and the contamination of water resources and causing eutrophication. Another concern with the use of fertilizers is the presence of heavy metals within them such as Cd, As and Pb. The presence of these metals varies with each fertilizer, for instance phosphate based fertilizers demonstrate the presence of high levels of trace metals especially cadmium which is the most toxic heavy metal. Different types of rocks are utilized in the production of phosphate-based fertilizers and the type of rock used has an influence on the amount of heavy metals present, as sedimentary rocks tend to have higher cadmium concentrations than magmatic rocks. Biofertilizers, liming materials, and phosphate fertilizers are the most common inorganic fertilizer types responsible for HMs release in agricultural soil and subsequent uptake by plants (Fan *et al*.,2018).

2. Industrial Activities

Industrial activities are considered as major contributors of heavy metals towards environmental contamination. Heavy metals are released into the environment as a result of rising human activity, such as industrial advancements. Eventually, these contaminants build up in the soil, especially in areas that are rapidly industrializing(Jin *et al*.,2019;Liu *et al*.,2020)

3. Mining Activities

Mining is one of the most significant activities towards economic growth and development of many countries. Increased mining activities, poor mining methods, lack of research and lack of resources have led to mining being one of the major sources of contamination of water bodies (Mensah *et al*., 2015). Mining of valuable minerals lead to the exposure of minerals and associated fractions to different weathering conditions. This leads to the enrichment of the environment with heavy metals. This is attributed to the fact that miners attempt to unearth a number of other mineral resources associated with the desired minerals, hence exposing them to a number of earthly processes such as air and rain. These ingredients foster the weathering of mineral resources. For example, mining of gold, coal and other precious metals lead to the exposure of sulphide bearing minerals to oxidizing conditions (Fernando *et al*., 2018; Park *et al*., 2019).

4. Energy production

The rapid increase in population, industrialization, and urbanization has led to a high demand for energy, with fossil fuels like coal and petroleum remaining the primary sources despite their environmental and health impacts. Coal combustion, primarily used for power generation, produces fly ash as a by-product. The composition of fly ash varies depending on factors such as coal type (lignite, bituminous, anthracite), preparation methods, combustion conditions, and climate. Fly ash typically contains high concentrations of heavy metals and oxides of Al, Si, Fe, Ca, K, S, Mg, and Na, along with trace elements like As, Cd, Pb, Zn, and others.Although some fly ash is used in the construction industry, much of it is dumped, causing leaching of trace metals into groundwater. Volatile elements tend to be released during combustion and later condense on ash particles, forming amorphous spheres.

5.Metallurgical Processes

Post mining activities, desired minerals are taken to a metallurgical house for purification. This process involves the extraction of valuable minerals for further processing. During the process, unwanted materials known as residues are also produced and they include heavy metals. Reclamation or remaining of minerals from tailings can also lead to production of a stream of heavy metals that are problematic to the environment.Different solvent extraction, leaching and digestion processes are used to harness the desired mineral from the mineral of interest. These processes lead to the generation of residues that are rich in heavy metals. For instance, gold tailings are rich in minerals that can lead to the generation of AMD. During reprocessing or remining, the liquid phase used for reprocessing will acquire heavy metals. Heavy metals such as Zn, Cu, Ni, and Hg amongst others can be present in the tailings. This will then be the main routes at which these metals are leached into the environment. Leaching of tailings can also enrich the environment with heavy metals (Masindi *et al*. 2018)

6. Run-Offs

Urban, peri-urban and rural activities lead to the release of heavy metals to the environment. This is mainly caused by exhaust from moving vehicles, leakages from moving vehicles, domestic septic tanks and other manufacturing processes. Advancements in infrastructures such as housing, roads and railways have significantly contributed in the transportation of heavy metals to different receiving environments. This led to elevated levels of contaminants

in the receiving streams nearby. Heavy metals from the moving vehicles, petrol spillages, light industries emission and many more contribute to the emission of heavy metals in urban areas. Fertilisers and chemicals used to enhance the greener areas in urban and rural areas lead to the enrichment of the environment with heavy metals. During rainfall, heavy metals will be washed away to nearby environments (Hashim *et al.,* 2017). Illegal dumping and misuse of dumping sites in urban and rural areas lead to the discharge of heavy metals into the environment. Essentially, these metals from different urban and rural facets get washed off by run-offs to nearby environments hence enriching the environment with heavy metals. This makes it unsuitable for myriads of defined uses (Vardhan *et al*., 2019).

2.4 HEAVY METAL CONTAMINATION OF VEGETABLES

Vegetables are the most important components of the human diet and it is well known that consumption of these food items on a regular basis is one of the possible health improving practices (Sultana *et al*., 2017). They have a wide variety of nutrients such as vitamins, dietary fibre, minerals, proteins and starch. The consumption of vegetables as food offers rapid and least means of providing adequate vitamins, supplies, minerals and fibers (Asaduzzaman *et al*., 2015). Heavy metals in soils may gain entry into plants via active transport or passive diffusion (Yan *et al*.,2020) . They are absorbed by plant roots and are either stored in the roots or transported through the xylem cells of the roots to other parts of the plants such as the shoots or leaves (Jan and Parry, 2016). Vegetables may also contain some amount of toxic elements (Pan *et al*.,2016).

Many chemical elements found in vegetables are vital for human metabolic functions, but they can become toxic when consumed in high concentrations, and some are harmful even in very low amounts. The presence of metals in plants is influenced by several factors, including clay minerals, soil pH, oxides, carbonates, and organic matter. The chemical form and binding characteristic of metals are a key determining factor for the mobility and bioavailability of heavy metals in soil.The consumption of vegetables contaminated with heavy metals poses risk to the health of humans. It is evident that continuous consumption of food containing unsafe levels of heavy metals concentrations may lead to chronic accumulation of heavy metals in the kidney and liver of human beings causing various disorders in numerous biochemical processes, leading to cardiovascular, bone, kidney and nervous diseases. Heavy metals are persistent in the environment and can bioaccumulate within food chains. Generally, broad-leaved vegetables tend to accumulate more heavy metals than fruiting or non-leafy vegetables due to the large surface area of the leaves enhancing evapotranspiration rate and also adsorption capacity for atmospheric deposits (Gan *et al*.,2017; Pérez-Figueroa *et al*.,2023). Therefore, heavy metal contamination in vegetables is a significant issue because these foods are critical to human diets. Ensuring the safety of food regarding heavy metal contamination is a key aspect of food quality control. Diet is the main way by which the non-occupational population gets exposed to trace elements (Antoine *et al*., 2017).

2.5 FAO/WHO Recommended Limits for Heavy Metals in Vegetables

International organizations like WHO and FAO have established maximum allowable concentrations for heavy metals in vegetables. These guidelines help assess the safety of food and protect public health.

Heavy Metal FAO/WHO permissible limit for vegetables	Mg/Kg
Zinc (Zn)	60
Cadmium (Cd)	0.2
Lead (Pb)	0.3
Nickel (Ni)	68
Copper (Cu)	40

Table 1: FAO/WHO permissible limit
FAO/WHO (2007 /2011)

2.6 SELECTED HEAVY METALS

(i) ZINC

Zinc(Zn) metal, represents one of the commonly found transition elements on the planet's surface and a necessary minor element to nearly every living thing (Lee, 2018). Zinc is a bluish-white, brittle, shiny metal that remains solid at room temperature. It is typically known as a mildly reactive metal regarding its reaction with metals and O2 and easily becomes mouldable and flexible once heated to higher than 110°C. Zn is a naturally existing metal in the form of a sphalerite (ZnS) material with five isotopes, ^{64}Zn being the most commonly abundant isotope among them (Audi *et al*., 2017). It is an essential element present in many protein structures, particularly zinc-finger proteins, and plays numerous roles in biological processes. Zinc is crucial for over 300 enzymes, acting as a catalyst and/or coenzyme (Rahman and Karim, 2018). Zn is essential for the regulation of numerous metabolisms and physiological activities within biological tissues. On the other hand, excessive Zn levels have adverse effects on health (Abbas *et al*., 2016). The commercial uses for Zn Include brass coating, brass and Zn metals related working activities, manufacturing of wood related pulp, steel work activities related to pipe coating, paper manufacturing, painting industry, dyes manufacturing, and pharmaceutical and cosmetic products (Tóth *et al*., 2016). Zinc enters ecosystems through various means including metal waste, fertilizers, electroplating, plating iron and steel, galvanization, mining and metallurgy and silt remobilization

(ii) CADMIUM

Cadmium (Cd) is a non essential heavy metal, one of the most dangerous heavy metal toxins, and lacks any known essential biological role. In its compounds, cadmium typically exists as the divalent Cd (II) ion. Positioned directly below zinc in the periodic table, cadmium shares chemical similarities with zinc, an important micronutrient for both plants and animals. This resemblance may contribute to cadmium's toxicity, as substituting zinc with cadmium can disrupt metabolic processes. Despite it being uncommon metal, it is found naturally within sediments, water, and minerals such as carbonate compounds (Balali-Mood *et al*., 2021). Cadmium and its ions are highly soluble in water, allowing for rapid movement through soil and water resources and featuring a tendency for bioaccumulation (Qi *et al*., 2018). Increased levels of cadmium may arise naturally from volcanic activity, as well as from human activities, including those in fertilizer manufacturing, power generation, wastewater disposal, waste management, mining, battery production, electroplating, and dye industries (Dou *et al*., 2017). Cadmium (Cd) and essential micronutrients have a strong interaction in gastrointestinal absorption. Fe and Zn are the most critical micronutrients associated with these interactions. Cd metal accumulates mainly in the human kidneys, with a comparatively lengthy half-life of 10 to 35 years (AlKhaldi *et al*., 2015). Cd accumulation also impacts the bones and promotes cancer at its high levels. However, the most serious kind of Cd exposure seems to be intense bone pain which is known as “itai-itai” illness. In addition, Cd has been linked to liver disease and high blood pressure. Moreover, Cd in polluted water may interfere with vital bodily functions and cause short-term and/or long-lasting issues (Jiang *et al*., 2015; Richter *et al*., 2017).

(iii) LEAD

Lead (Pb) is a non-degradable chemical element recognized as one of the most hazardous substances among heavy metals in ecosystems (Charkiewicz and Backstrand, 2020). It is a bluish-gray metal that naturally occurs in trace amounts in the earth's crust. Lead has features including softness, flexibility, plasticity, weak conductivity, and corrosion resilience, which pose a challenge to abandoning this substance (Saeed *et al*., 2017). Because of its non-biodegradable nature and continuing usage, Pb accumulates in the ecosystems, its concentrations increase and thus, the incidence of linked health problems increases dramatically (Irawati *et al*., 2022). Pb exists in various forms on the earth, including metallic, Pb salts, and Pb-organic compounds (Assiet *et al*., 2016). Pb is employed for a wide variety of applications nowadays and has a long history of industrial usage. It could be estimated that Pb applications are found in about 900 various industries, some of which include metal processing, mining, and battery industries. In the environment, the major sources of Pb release include electroplating, smelting and its related combustion, painting and dyes manufacturing, the plastics industry, fabrics, yachts manufacturing, printing industry, Pb contained tubes, and preservative materials (Ara and Usmani, 2015;Ince *et al*., 2017).

(iv) NICKEL

Nickel (Ni) is a poisonous heavy metal, it counts as the twentyfourth-most common mineral on the earth. It is considered one of the trace metals that poses a major danger to public health and ecology (Sule *et al*., 2020). Its concentration is estimated at 50 ppm within the earth’s crust layers, It is silverwhite in appearance, with various valence states ranging between -1 and +4. The primary manufacturing activities that lead to nickel (Ni) contamination in the environment include battery production, certain alloy production, the printing sector, metal coatings, smelting processes, waste incineration, and emissions from fossil fuel combustion, such as those from power plants and vehicles (Hassan *et al*., 2019). Such industries employ different Ni related substances, including nickel acetate (Ni(CH3CO2)2·4H2O), nickel oxide (NiO), nickel hydroxide (Ni(OH)2), and nickel carbonate (Ni4CO3(OH)6(H2O)4). The mentioned substances eventually accumulate in different ecosystems (water resources and soils), and therefore they could be readily absorbed by the plants. As a result, these compounds may become part of the food chain and harm living things.

(V) COPPER

Copper (Cu) is an abundant mineral that may exist within a wide range of rock types at trace levels. It also presents inside the human body in several cells and organs at trace levels, where the liver has its most considerable amount. Copper is an essential nutrient required for numerous biochemical and physiological functions, and an insufficient amount of copper may result in the disruption of metalloenzyme incorporation and hemoglobin formation. However, a surplus quantity of copper has been associated with cellular and tissue damage and has numerous deleterious effects on human health (Taylor *et al*., 2020; Haque *et al*., 2021). Various industrial and agricultural activities utilize copper (Cu) compounds, which can subsequently leak into ecosystems, ending up in different water bodies (Poole, 2017). Such practices raise copper concentrations above normal levels, leading to ecosystem contamination. Textile industry, metal plating, paints and pigments, rayon, mining and metallurgy, pesticides, mining and metallurgy, explosives, electrical and electronics waste are major sources of Cu release to the environment (Izydorczyk *et al*.,2021).

2.7 SELECTED VEGETABLES

(i) Fluted Pumpkin (Telfairia occidentalis)

Fluted pumpkin (Telfairia occidentalis) is a leafy vegetable belonging to the Cucurbitaceae family. It is a large perennial plant that climbs using bifid tendrils that are typically coiled. It is a tropical vine grown in West Africa mainly as a leaf vegetable and for its edible seeds. The leaves of the plant are compound, usually 3-5 foliate, with blades and petioles also covered with multicellular hairs. The fruits are marked by 10 conspicuous longitudinal ridges and are among the largest known (16-50 cm length, 9 cm diameter). The seeds which are embedded within a bright-yellow fibrous endoscarp are large, non endospermic and usually dark red in colour. Telfairia occidentalis has various common names across languages and regions, including Fluted pumpkin, oyster nut, oil nut, fluted gourd, and Telfairia nut (English); Costillada (Spanish); Krobonko (Ghana); Oroko, pondokoko, and Gonugbe (Sierra Leone); Ugwu (Igbo-Nigeria); and Aworoko, Eweroko (Yoruba-Nigeria) and Ikong (Efik/Ibibio-Nigeria). Telfairia occidentalis is popular in the diets of households in all economic classes for its nutritional properties being a rich source of protein and fat at 29% and 18% respectively as well as minerals and vitamins up to 20% (Amao *et al*., 2018). It is rich in antioxidants, thiamin, riboflavin, and ascorbic acid. The young shoots and leaves of this vegetable are used in preparation of several delicacies in southern Nigeria, including Edikang Ikong Soup, a popular delicacy of the Efiks and Ibibios in Cross River and Akwa Ibom States, Nigeria.

(ii) Scent leave (Ocimum gratissimum)

Ocimum gratissimum commonly referred to as "scent leaf" or African basil" is a herbaceous perennial plant. It is pan tropical and widely naturalized in many regions of Africa. Scent leaves, also known as efirin in Yoruba, nchanwu in Igbo and daidoya in Hausa Nigeria, are not only aromatic additions to culinary delights but also harbours a treasure trove of health benefits. It is widely used in traditional medicine across various cultures, most especially in Nigeria. Some chemical compounds and active ingredients from this plant that make it exhibit strong antimicrobial properties include eugenol, thymol, camphor, pinene, and limonene are responsible for many of its medicinal properties (Akpoghelie *et al*., 2022). It is a common perennial herbaceous plant with a potent aroma that is also commercially viable. Scent leaf, found in Africa, Asia, and South America, is a member of the Lamiaceae family (Ugbogu *et al*., 2021). It is commonly used to flavor fish, meat, soups, and stews, and it is also utilized for treating various health issues such as pain, fever, inflammation, anemia, diarrhea, and infections from fungi and bacteria (Shedoeva *et al*., 2019). It has enough macronutrients in it that is valuable to the body. The leaf has a lot of nutritional value when taken in the right quantity and in moderation.

(iii)Water Leaf (Talinum Triangulare)

Waterleaf (T. triangulare) is a perennial herb belonging to the Portulacaceae family that has its own medicinal benefits and is still utilized in many traditional medicines in West Africa and

Southeast Asia in particular. Because of its nutritional and therapeutic potential, it is quite popular among the Nigerian people. In traditional medicine, T. triangulare Due to its nutritional and medicinal benefits, scent leaf is especially popular among Nigerians. Popularly considered a weed, it is an unconventional food plant with many nutritional and socio-economic potentials that needs to be rescued for invasive farming. The plant leaves are traditionally utilized either as condiments or spices in human diets or as supplementary feeds for livestock such as poultry, cattle, swine, and rabbits.

(iv) Bitter Leaf (Vernonia Amygdalina)

Bitter leaf (Vernonia amygdalina) is a perennial shrub named for the bitter flavor of its leaves. The plant originates from the Asteraceae (compositae) family and usually presents as a shrub of about 2.5–3 m height (Achuba, 2018).V. amygdalina has a rough bark with dense black straits, it comprise of green colored elliptic leaves that have a characteristic odor and bitter taste (Akpoghelie *et al*., 2022). V. amygdalina goes by other African names as well for example; ewuro (Yoruba), etidot (Efik), ityuna (Tiv), Congo Bololo (D. R. Congo), oriwo (Edo), onugbu (Igbo), grawa (Amharic), shuwaka or chusar-doki (Hausa), Awɔnwono (Akan), mululuza (Luganda), olusia (Luo) and labwo. Research has shown that bitter leaf contains substantial amounts of lipids, carbohydrates, proteins with high essential amino acid profiles (Edo *et al*., 2022), fiber, iron, phosphorus, copper, calcium, potassium, cobalt and manganese, appreciable amounts of biologically active compounds like ascorbic acid, saponins, alkaloids, steroids terpenes, flavonoids, coumarins, lignans, phenolic acids, peptides, xanthones, anthraquinone, sesquiterpenes and carotenoids (Erhonyota *et al*., 2022). Bitter leaf extracts can be used as tonics for various conditions, including vomiting, nausea, diabetes, loss of appetite, diarrhea, dysentery, and other gastrointestinal issues (Adebukola *et al*., 2022) which explains why many herbalists and indigenous doctors in Africa recommend that their patients take the aqueous preparations of these leaves against certain health maladies (Usai *et al*., 2022).

2.8 UPTAKE AND ACCUMULATION TENDENCIES IN LEAFY VEGETABLES

Leaf vegetables typically exhibit faster growth and higher transpiration rates compared to non-leaf vegetables. This heightened activity can enhance the uptake of metals by their roots, allowing for the transfer of these metals to other tissues within the plant. Due to their broad leaf surfaces, leaf vegetables are more prone to accumulating pollutants from soil dust and rainwater. The accumulation of metals in vegetable tissues is affected by various factors such as soil characteristics (including pH, organic matter content, clay content, and metal concentration), plant characteristics (such as type and planting method), and environmental conditions (including atmosphere and industrial pollution). Environmental variables like rainfall, temperature, and humidity can impact heavy metal migration; for instance, heavy rainfall can leach metals from the soil, increasing their concentrations in soil solutions and thereby enhancing plant uptake. On the other hand, dry conditions can constrain metal mobility, making them less available for plants (Chen *et al*., 2021; Su *et al*., 2023). Seasonal changes can also influence both plant growth and metal accumulation, with varying growth stages possibly resulting in different levels of metal uptake. Additionally, proximity to industrial activities significantly affects heavy metal levels in nearby soil, as emissions, wastewater discharge, and contaminated irrigation can introduce heavy metals, thereby heightening the risk of accumulation in crops.

2.9 Previous Comparative Studies on Heavy Metal Contamination in Nigeria

Sakiyo *et al*. (2020) investigated the health risks associated with heavy metal accumulation in vegetables cultivated near dumpsites in Jimeta and Ngurore, Adamawa State. The vegetables assessed spinach (Spinacia oleracea) and lettuce (Lactuca sativa) were analyzed using Atomic Absorption Spectrophotometry (AAS) to determine the concentrations of Iron (Fe), Lead (Pb), Copper (Cu), Chromium (Cr), and Cadmium (Cd). The results indicated that iron (Fe) was the most prevalent metal found, particularly in lettuce. Among spinach samples taken from the Jimeta dumpsite, metal concentrations followed this order: Fe > Pb > Cu > Cr. A similar order was observed in samples from Ngurore: Fe > Pb > Cu > Cr. Cadmium was below the limit of detectable in any of the samples. Statistical analysis using a paired t-test at a 0.05 significance level revealed that Fe and Pb showed significant differences in concentrations between the two sites, whereas Cu and Cr did not. The study concluded that the presence of heavy metals in edible vegetables poses potential health risks to consumers and recommended continuous environmental monitoring and increased public awareness to discourage vegetable cultivation in contaminated areas.

A laboratory based study conducted by Dada *et al*.,(2024) in Ibadan metropolis investigated the levels of heavy metals in five commonly consumed leafy vegetables: Celosia argentea (soko), Corchorus olitorius (ewedu), Amaranthus viridis (tete), Talinum triangulare (water leaf), and Telfairia occidentalis (fluted pumpkin). The vegetables were collected over a 12-week period from different markets and analysed for concentrations of lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni), and copper (Cu) using Atomic Absorption Spectrophotometry.The results indicated that certain vegetables exceeded World Health Organization/Food and Agriculture Organization (WHO/FAO) permissible limits for specific metals. Notably, water leaf showed elevated levels of lead and copper, while fluted pumpkin also recorded a concerning lead concentration. Some samples showed high levels of cadmium, zinc, and nickel, though others remained within acceptable limits. Additionally, the study observed that vegetables collected in the evening had significantly higher heavy metal concentrations than those obtained in the morning, suggesting possible environmental or handling-related accumulation during the day.The study concluded that vegetables sold in urban markets may pose a public health risk due to contamination with toxic heavy metals, and it strongly recommended ongoing monitoring and intervention by regulatory agencies to safeguard food safety.

CHAPTER THREE

METHODOLOGY

3.1 Study Area

The study was carried out in Benin city, Edo State. Edo State is located in the South-South geopolitical region of the Federal Republic of Nigeria and has 18 Local Government Areas. Edo State has a total land area of 19,559km2. It has a tropical wet and dry or savanna climate with a yearly temperature of 28.78oC (83.8oF). The vegetable samples were collected from Oluku waste dumpsite (Latitude 6°27′53″N and Longitude 5°36′4″E) and iyowa community(Latitude 6°29′18″N and Longitude 5°36′25″) near Benin in Ovia North East Local Government Area of Edo State, Nigeria.

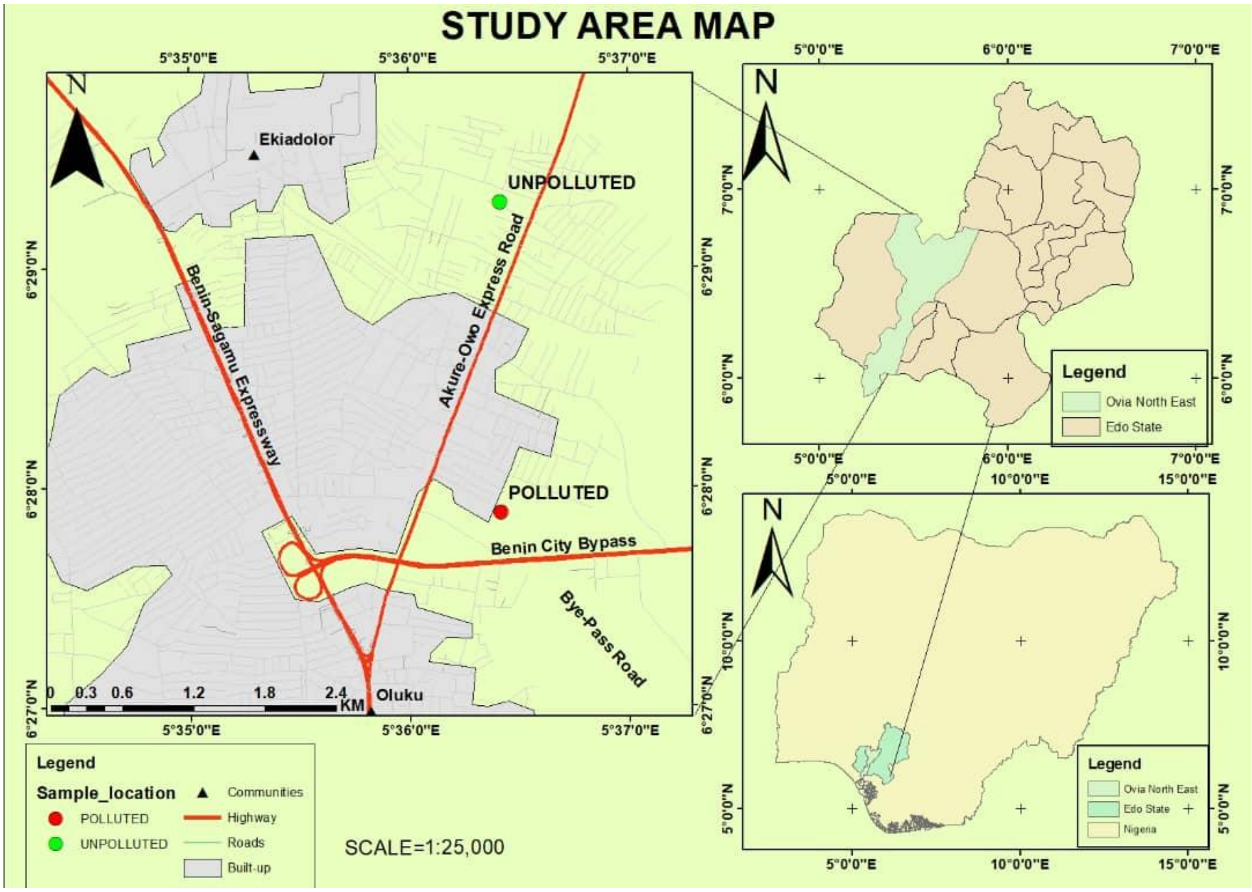

Fig 3.1: map showing the area of study

3.2 Apparatus

Glasswares, foil paper, fitter paper, samples bottles, weighing balance, drying oven, funnel, fume cupboard, pipette, atomic adsorption spectrophotometer.

3.3 Collection of samples

Vegetable samples of water leaves (Talinum triangulare), Scent leave (Ocimum gratissimum), Fluted pumpkin leaves (Telfairia occidentalis) and bitter leaves (Vernonia amygdalina) were randomly collected from Oluku waste dumpsite and a farm in Iyowa community in Benin, Edo State, Nigeria. Samples were collected with a clean stainless knife into a sterilized labelled polythene bag for each vegetable. Four vegetable samples were collected from the two sites, making a total of eight (8) from the study areas mentioned.

3.4 Sterilization of Work Bench and Material

All laboratory work was carried out under aseptic conditions while following laboratory rules and regulations. The work bench was disinfected with 70% ethanol, glass wares were properly washed and sterilized in an autoclave at 121°C at 15 mmHg for 15 minutes before use. Laboratory coats, face masks and hand gloves were worn throughout the practical procedures and good hygiene was maintained during the procedure.

3.5 Preparation of Samples

The vegetable samples collected from the experimental site were brought to the laboratory where they were washed and rinsed with deionized water. These were carefully chopped into smaller portions (root, stem and leave) with a clean stainless steel knife. The chopped vegetable samples were air dried and reduced in size by grinding to a fine powder using cleaned mortar and pestle. Each sample was sieved using 2mm plastic sieve and stored in a labeled container.1 gram of each samples were measured using a weigh balance and immediately introduce into a clean sterilised beaker.Acid digestion of the samples were immediately carried out using a heating mantle in a fume cupboard until digestion of sample is completed. Each sample was subject to filtration using a whatman fitter paper into a 100mL volumetric flask and filled to mark with distilled water,the filtered samples were introduced into clean and sterilized sample bottles.

3.6 Digestion of Sample

1g of the dried sample was mixed with a mixture of HNO3 and HCl (ratio 1: 1) and it was heated in a fume cupboard that has a heating mantle until a transparent solution was obtained. The solution was filtered using a Whatman no. 42 filter paper into 100 mL volumetric flask and stored for analysis . The concentrations of the metals namely: Zn, Cd, Cu, Ni, and Pb were determined using an Atomic Adsorption Spectrophotometer.

3.7 Preparation of Standard for Atomic Absorption Spectrophotometer.

1mL were pipetted from the Original standard of a particular element into 100 mL volumetric flask and immediately filled to mark to make the stock solution. 10mL,20mL and 30mL from the stock solution were pipetted into a clean 100mL volumetric flask respectively and fill to mark to make 1,2 and 3ppm concentration standards,the elements analyzed were zinc, cadmium,lead,copper,and nickel. Experimental study of the vegetable samples were carried out in the University of Benin (UNIBEN), Central Research Laboratory in Edo State, Nigeria using an Atomic Absorption Spectrophotometer (AA320N).

3.8 Instrumental Analysis Using Atomic Absorption Spectrophotometer (AAS)

The concentrations of Cadmium (Cd), Lead (Pb), Zinc (Zn), Nickel (Ni), and Copper (Cu) were determined using an Atomic Absorption Spectrophotometer (AAS). The instrument operates based on the principle that free atoms in the gaseous state absorb light energy at characteristic wavelengths. When the sample solution is aspirated into the flame, the metallic elements are atomized, and each absorbs light corresponding to its unique wavelength. The amount of light absorbed is directly proportional to the concentration of the metal in the sample.

The standard solutions which are 1ppm, 2ppm and 3ppm of each metal were prepared from certified stock solutions by serial dilution. Calibration curves were plotted for each element using the prepared standard solutions, and absorbance readings for the samples were measured at the corresponding wavelengths. Deionized water was aspirated between samples to prevent carry-over. The concentration of each metal was determined by comparing sample absorbance values with those of the calibration standards.

3.9 Quality Assurance and Quality Control (QA/QC)

To ensure the accuracy and reliability of analytical results, standard quality assurance and quality control (QA/QC) procedures were adopted. All reagents used were of analytical grade, and deionized water was used for all rinsing and dilutions. Glasswares were properly washed and sterilized in an autoclave at 121°C at 15 mmHg for 15 minutes before use to prevent contamination.

Sample collection, handling, and storage were done using clean, non-metallic tools and pre-cleaned polyethylene bags to avoid external metal interference. Analytical-grade hydrochloric acid (HCl) and nitric acid (HNO_3) were used for digestion, while the Atomic Absorption Spectrophotometer (AAS) was calibrated with standard solutions prepared from certified stock solutions for each metal (Cu, Pb, Cd, Ni, Zn). Calibration curves with correlation coefficients

($R^2 \geq 0.995$) were obtained before analysis

Procedural blanks and duplicate samples were analyzed alongside test samples to check for contamination and precision. Each vegetable sample was analyzed in duplicate, and the mean values were recorded to enhance precision. Replicate measurements were performed at intervals to monitor the stability of the instrument. Metal concentrations were expressed on a dry-weight basis to ensure comparability.

3.10 Statistical Analysis

The mean of heavy metal concentrations were calculated for each vegetable species and sampling site. The results were compared with the FAO/WHO permissible limits for heavy metals in vegetables. Statistical analysis was performed using the t-test analysis method to test for significant differences ($p < 0.05$) in heavy metal concentrations among vegetables and between sampling locations.

3.10.1 T-test Statistical Analysis Method

T-test was employed to determine whether there were significant differences in the concentrations of heavy metals in vegetables collected from the polluted and unpolluted locations. T-test is a parametric statistical method used to compare the means of two groups. It assumes that the data are approximately normally distributed and that the variances of the two groups are similar.The method compares the mean values of two groups to assess if observed variations are statistically significant or due to random chance. The test was conducted at a 5% level of significance ($p = 0.05$), where $p \leq 0.05$ indicates a significant difference, and $p > 0.05$ indicates no significant difference. The t-value was calculated using standard formulas and verified using Microsoft Excel and SPSS statistical software.

CHAPTER FOUR

RESULTS

4.1 **Results from Analysis of Heavy Metal Concentration from Oluku (polluted) and Iyowa (unpolluted) sites**

Vegetable	Analysis	Cadmium (Cd)	Zinc (Zn)	Nickel (Ni)	Lead (Pb)	Copper (Cu)
Water Leaf	**Analysis 1**	0.008	0.064	0.013	0.008	0.011
	Analysis 2	0.014	0.051	0.012	0.006	0.011

Bitter Leaf	**Analysis 1**	0.016	0.084	0.007	0.009	0.062
	Analysis 2	0.014	0.077	0.004	0.010	0.057
Scent Leaf	**Analysis 1**	0.017	0.032	0.008	0.006	0.040
	Analysis 2	0.015	0.033	0.006	0.005	0.042
Pumpkin Leaf	**Analysis 1**	0.012	0.023	0.036	0.012	0.009
	Analysis 2	0.012	0.022	0.034	0.014	0.007

Table 4.1: Heavy Metal Concentration (mg/kg) in Vegetable from Oluku (Polluted Site)

NOTE: Each vegetable sample from Oluku (polluted site) was analyzed twice using Atomic Absorption Spectrophotometry (AAS). The two sets of results are shown as Analysis 1 and Analysis 2 to confirm repeatability and accuracy of measurements.

Table 4.2 Heavy Metal Concentration (mg/kg) in Vegetable from Iyowa (unpolluted site)

Vegetable	**Analysis**	**Cadmium (Cd)**	**Zinc (Zn)**	**Nickel (Ni)**	**Lead(Pb)**	**Copper (Cu)**
Water Leaf	**Analysis 1**	0.001	0.005	0.002	0.001	0.003
	Analysis 2	0.001	0.003	0.002	0.001	0.001
Bitter Leaf	**Analysis 1**	0.002	0.001	0.001	0.001	0.001
	Analysis 2	0.001	0.003	0.001	0.002	0.002

Scent Leaf	**Analysis 1**	0.003	0.002	0.001	0.001	0.001
	Analysis 2	0.001	0.002	0.002	0.001	0.003
Pumpkin Leaf	**Analysis 1**	0.001	0.002	0.002	0.001	0.001
	Analysis 2	0.001	0.001	0.002	0.001	0.002

NOTE: Each vegetable sample from Iyowa (unpolluted site) was analyzed twice for consistency. The values are reported as Analysis 1 and Analysis 2, representing independent tests carried out under the same laboratory conditions.

4.2 The statistical comparison results between the mean heavy metal concentrations in vegetables obtained from the polluted (Oluku) and unpolluted (Iyowa) sites using T-test

Vegetable	Heavy Metal	Mean (Oluku – Polluted Site)	Mean (Iyora – Unpolluted Site)	p-value (Two-tail)	Significant ($p < 0.05$)
Water Leaf	Cadmium (Cd)	0.011	0.001	0.18	No
	Zinc (Zn)	0.0575	0.004	0.07	No
	Nickel (Ni)	0.0125	0.002	0.03	Yes
	Lead (Pb)	0.007	0.001	0.10	No

	Copper (Cu)	0.011	0.002	0.07	No
Bitter Leaf	Cadmium (Cd)	0.015	0.0015	0.05	Yes
	Zinc (Zn)	0.0805	0.002	0.02	Yes
	Nickel (Ni)	0.0055	0.001	0.20	No
	Lead (Pb)	0.0095	0.0015	0.01	Yes
	Copper (Cu)	0.0595	0.0015	0.02	Yes
Scent Leaf	Cadmium (Cd)	0.016	0.002	0.01	Yes
	Zinc (Zn)	0.0325	0.002	0.01	Yes
	Nickel (Ni)	0.007	0.0015	0.12	No
	Lead (Pb)	0.0055	0.001	0.07	No
	Copper (Cu)	0.041	0.002	0.00	Yes
Pumpkin Leaf	Cadmium (Cd)	0.012	0.001	#NUM!	
	Zinc (Zn)	0.0225	0.0015	0.00	Yes
	Nickel (Ni)	0.035	0.002	0.02	Yes
	Lead (Pb)	0.013	0.001	0.05	Yes
	Copper (Cu)	0.008	0.0015	0.11	No

Table 4.3: The statistical comparison between the mean heavy metal concentrations in vegetables obtained from the polluted (Oluku) and unpolluted (Iyowa) sites. The comparison was conducted using a two-tailed t-test to determine whether differences in metal concentrations between the two sites were statistically significant

NOTE: “Yes” in the Significant ($p < 0.05$) column indicates that the difference between the two locations is statistically significant, meaning pollution had a measurable effect on the concentration of that metal.

"No" indicates no statistically significant difference ($p > 0.05$), implying that the concentrations at both sites were statistically similar.

The symbol "#NUM!" indicates that the t-test could not be computed because one or both datasets contained identical or single mean values, resulting in zero variance. In such cases, there is no measurable difference within the data, and the statistical software cannot calculate a valid p-value.

4.3 **Interpretation of the Statistical Comparison of Mean Heavy Metal Concentrations in Vegetables from Oluku (Polluted Site) and Iyora (Unpolluted Site)**

The comparison of mean heavy metal concentrations in vegetables collected from Oluku (polluted site) and Iyowa (unpolluted site) revealed varying levels of contamination across the sampled vegetables and metals. The results of the two-tailed t-test ($p < 0.05$) are:

Water Leaf

- Cd, Zn, Pb, Cu: No significant difference ($p > 0.05$), indicating similar levels at both sites.
- Ni: Significant difference ($p = 0.03$), showing higher nickel accumulation in samples from the polluted site.
  Interpretation: Water leaf appears less sensitive to most metals except for nickel, which may accumulate more readily under polluted conditions.

Bitter Leaf

- Cd, Zn, Pb, Cu: Significant differences ($p < 0.05$), meaning concentrations were significantly higher in samples from Oluku.
- Ni: No significant difference ($p = 0.20$).
  Interpretation: Bitter leaf shows strong evidence of heavy metal contamination, especially for cadmium, zinc, lead, and copper, confirming pollution impact at the dumpsite.

Scent Leaf

- Cd, Zn, Cu: Significant differences ($p \leq 0.01$), indicating marked contamination in polluted samples.
- Ni, Pb: No significant difference ($p > 0.05$).
  Interpretation: Scent leaf accumulated cadmium, zinc, and copper significantly more in polluted environments, reflecting its potential as a bioindicator of metal pollution.
-

Pumpkin Leaf

- **Zn, Ni, Pb:** Significant differences ($p \leq 0.05$), showing higher levels in polluted site samples.
- **Cu:** No significant difference ($p = 0.11$).
- **Cd:** Result error (#NUM!) The #NUM! result for cadmium in pumpkin leaf indicates that the t-test could not be computed due to identical or single mean values in both groups, resulting in no variance within the dataset.
  Interpretation: Pumpkin leaf shows significant variation for zinc, nickel, and lead between sites, but cadmium could not be analyzed due to insufficient variability.

Implication: The t-test results confirm that pollution significantly influences heavy metal accumulation in edible leafy vegetables, with potential health implications for consumers near dumpsites.

4.3 Graph

The first graph shows the comparison between the mean value of the polluted site to the mean of the unpolluted site for each metal.

The second graph shows the comparison between the mean value of the polluted and unpolluted site to the joint FAO/WHO standard for each metal

Note: Some bars representing the measured heavy metal concentrations do not appear prominently in the graphs. This is because the WHO/FAO permissible limits for heavy metals are much higher than the concentrations obtained in this study. When plotted on the same scale, the sample values appear very small compared to the standard limits.

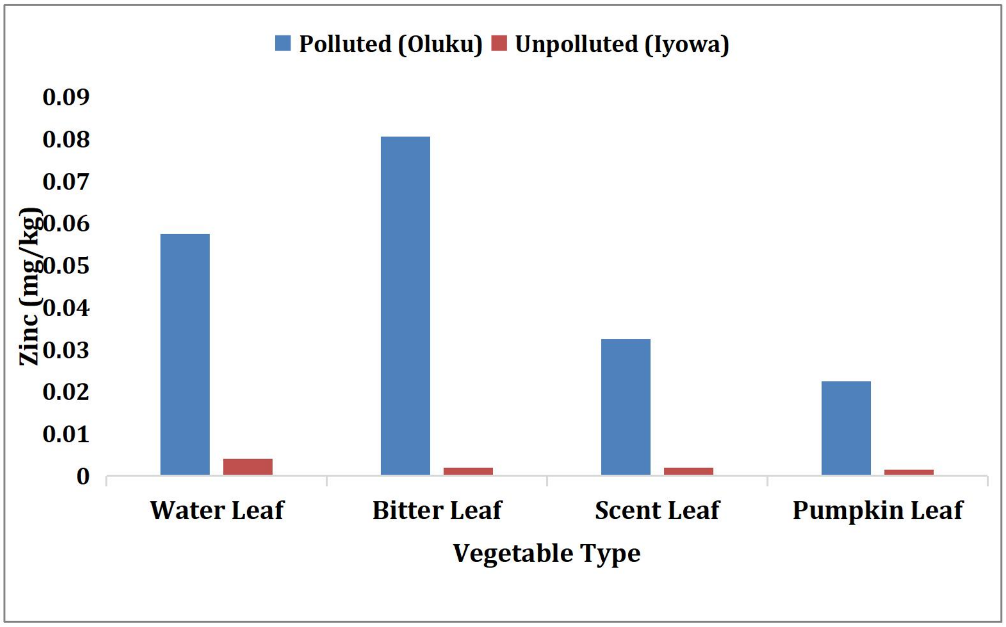

fig 4.1: Zinc concentration level across different vegetables from polluted and unpolluted site

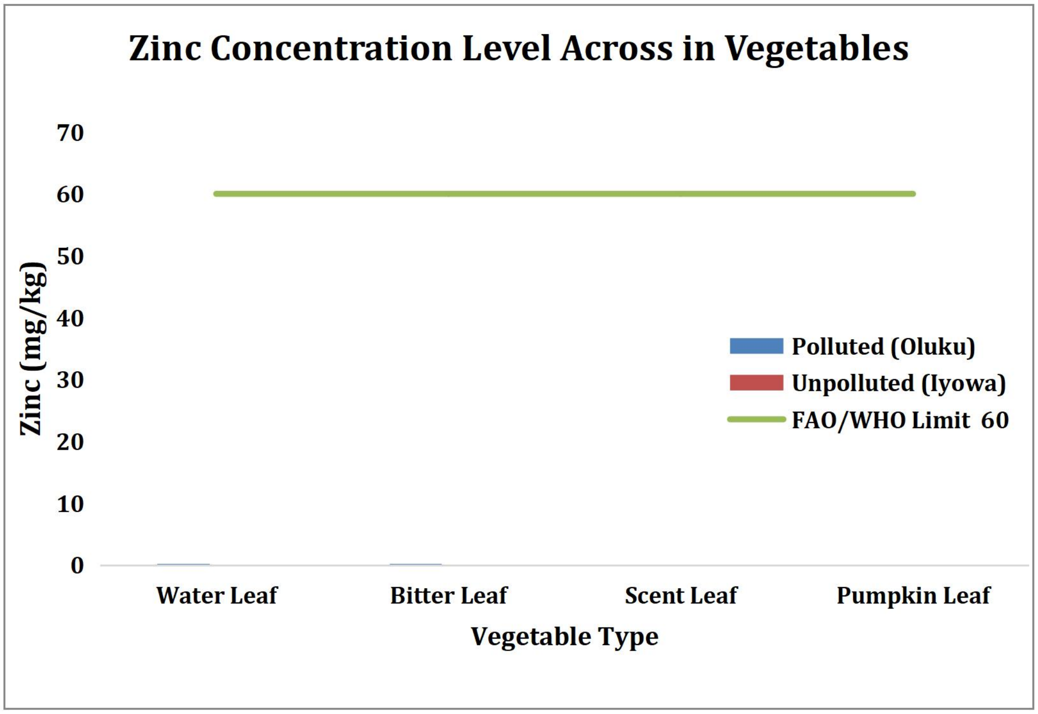

Fig 4.2: Zinc concentration level across different vegetables from polluted and unpolluted sites in comparison with FAO/WHO standard

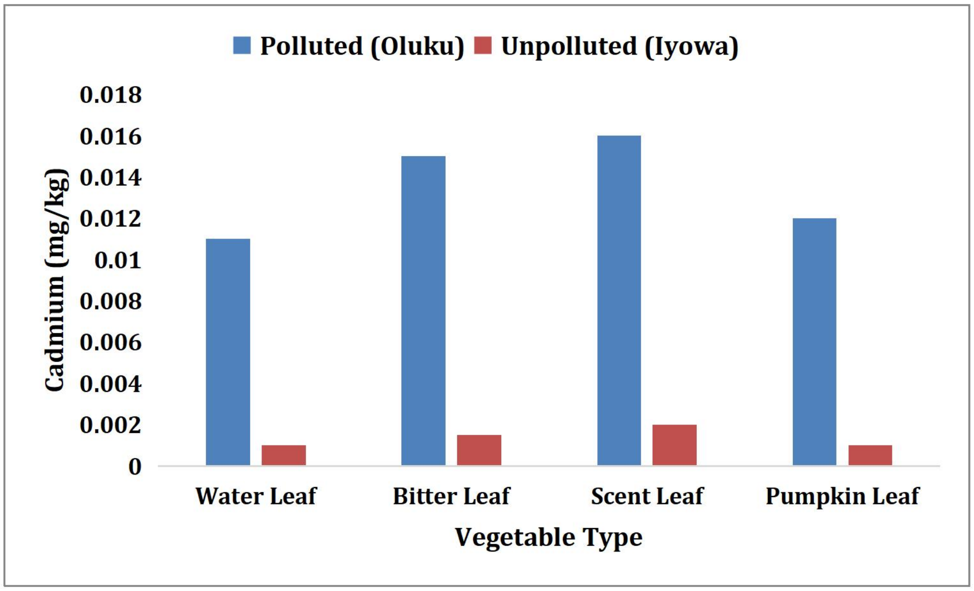

Fig 4.3: Cadmium concentration level across the different types of vegetables from polluted and unpolluted site

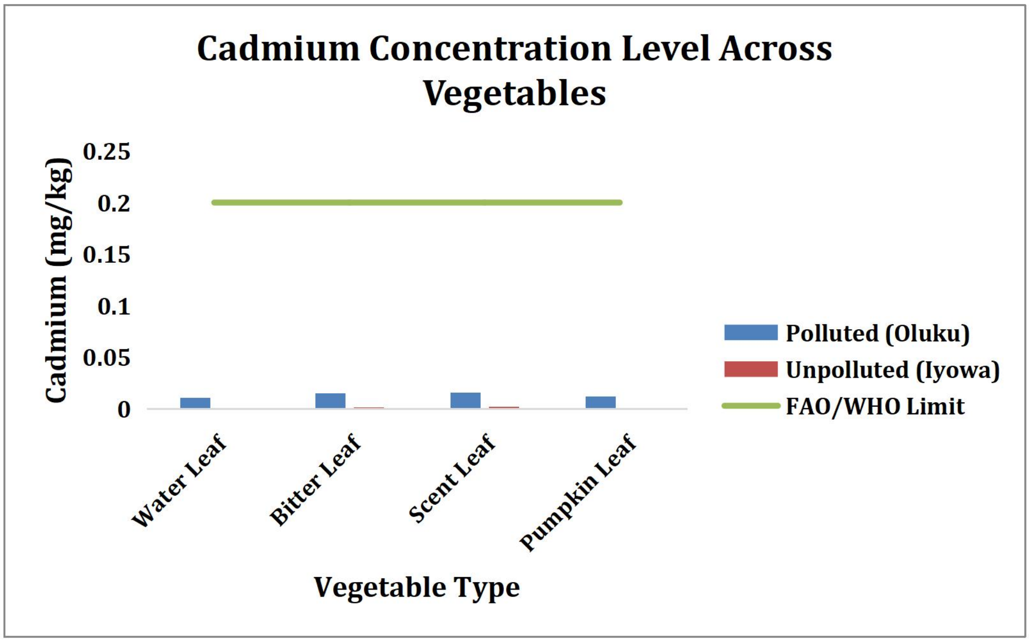

Fig:4.4: Cadmium concentration level across the different types of vegetables from polluted and unpolluted sites in comparison with FAO/WHO standard

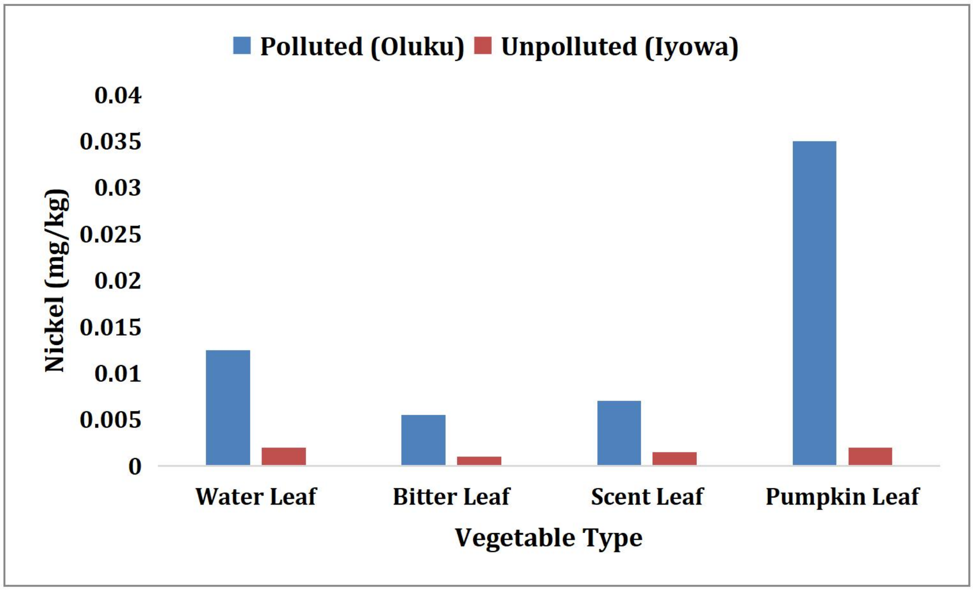

Fig 4.5: Nickel concentration level across the different types of vegetables from polluted and unpolluted sites

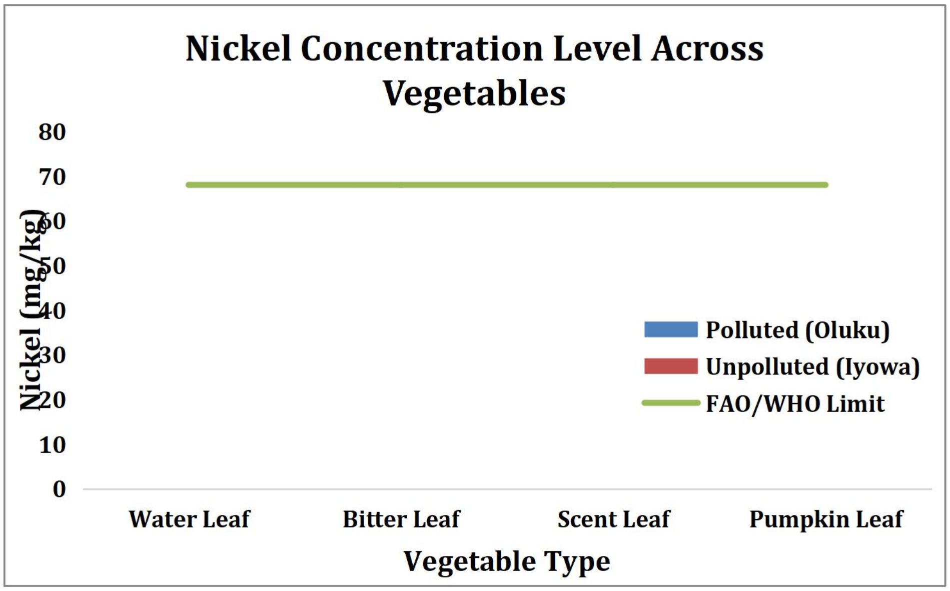

Fig4.6: Nickel concentration level across the different types of vegetables from polluted and unpolluted sites in comparison with FAO/WHO standard

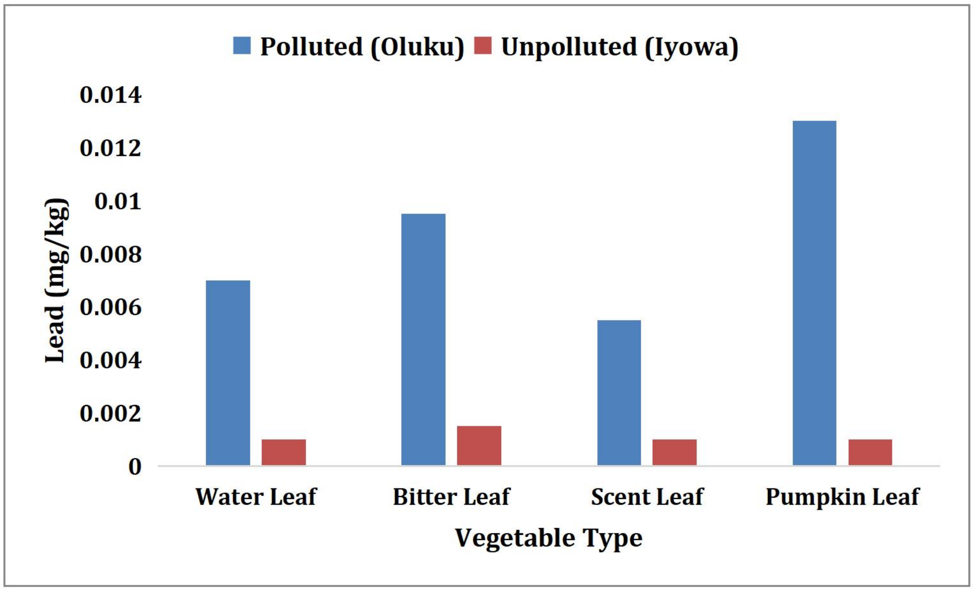

Fig 4.7: Lead concentration level across the different types of vegetables from polluted and unpolluted sites

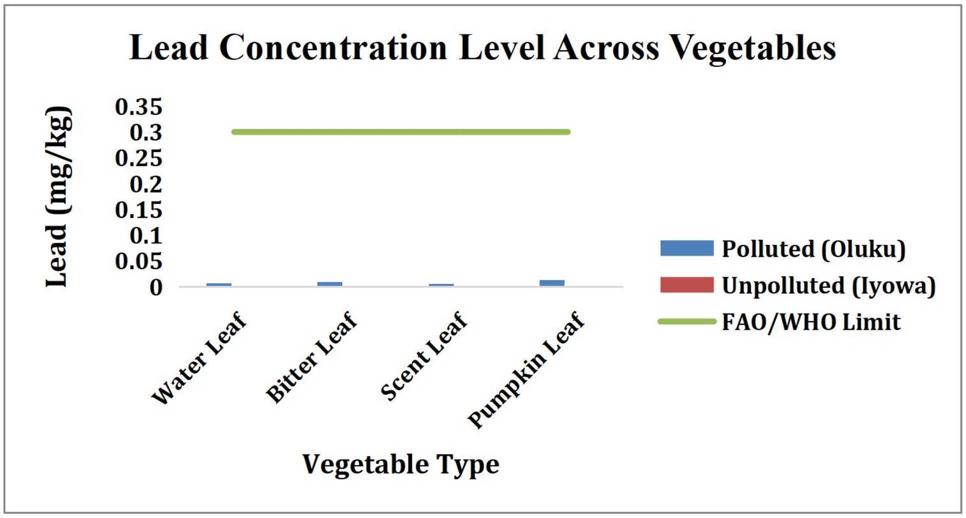

Fig 4.8: Lead concentration level across the different types of vegetables from polluted and unpolluted sites in comparison with FAO/WHO standard

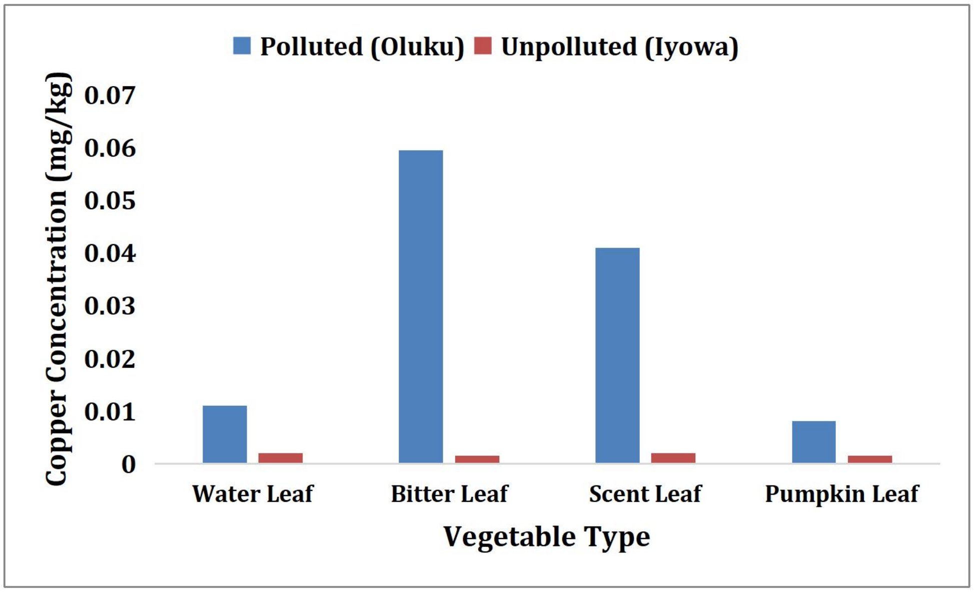

Fig 4.9: Copper concentration level across the different types of vegetables from polluted and unpolluted sites

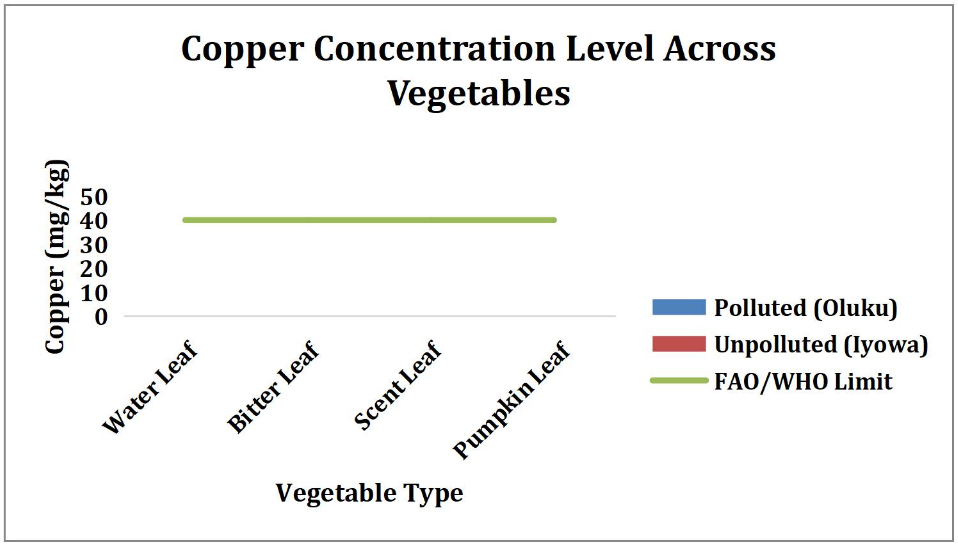

Fig 4.10: Copper concentration level across the different types of vegetables from polluted and unpolluted sites in comparison with FAO/WHO standard

CHAPTER FIVE

5.1 DISCUSSION

This study assessed the comparative concentration of selected heavy metals (Cadmium, Lead, Nickel, Zinc, and Copper) in four commonly consumed vegetables which are water leaf (Talinum triangulare), bitter leaf (Vernonia amygdalina), scent leaf (Ocimum gratissimum), and fluted pumpkin (Telfairia occidentalis) cultivated in polluted (Oluku) and unpolluted (Iyowa) sites in Benin City, Edo State. The results obtained were compared with the permissible limits set by the FAO/WHO (2007/2011) and subjected to statistical analysis ($p < 0.05$) to determine the significant differences between the two sites.

5.1.1 Heavy Metal Concentrations in Vegetables

- Cadmium (Cd)

Cadmium concentrations ranged from 0.001 to 0.016 mg/kg across all vegetables. The highest mean value (0.016 mg/kg) was observed in scent leaf from the polluted site, while the lowest (0.001 mg/kg) was recorded in water leaf and pumpkin leaf from the unpolluted site. All recorded values were below the FAO/WHO permissible limit of 0.2 mg/kg, indicating that cadmium accumulation in these vegetables poses no immediate health risk. However, statistical analysis showed a significant difference ($p < 0.05$) between the polluted and unpolluted sites for scent leaf ($p = 0.01$), bitter leaf ($p = 0.05$), and water leaf ($p = 0.18$, not significant). This suggests that cadmium accumulation is site-dependent and likely influenced by anthropogenic activities such as vehicular emissions, waste disposal, and agricultural runoff in the polluted area.. These low concentrations are consistent with findings from Latif *et al.* (2018), who reported a similar safe pumpkin concentration of 0.045 mg/kg.Also a study conducted on vegetables from markets in Tamale, Ghana reported Cd levels which ranged from 0.01 to 0.07 mg/kg (Ametepey,2018).

- Lead (Pb)

Lead concentrations varied between 0.001 and 0.013 mg/kg. The highest level (0.013 mg/kg) was recorded in pumpkin leaf from the polluted site, while the lowest (0.001 mg/kg) occurred in all vegetables from the unpolluted site. All values were well below the FAO/WHO permissible limit of 0.3 mg/kg. Although some samples (bitter leaf and pumpkin leaf) showed statistically significant differences (p = 0.01 and 0.05 respectively), the overall concentrations suggest low bioavailability of lead in the studied soils. The slightly higher values in the polluted site may be attributed to atmospheric deposition from vehicle exhaust and open waste burning, which are common in the area of study. Sakiyo *et al*., (2020) research on heavy metals in vegetables grown near dumpsites of Jimeta and Ngurore areas shows the concentrations of Pb in vegetables were found to be within the safe limits prescribed by FAO/WHO. Similarly research done by Abata *et al*.,(2024) the assessment of metal concentrations in vegetable plants examined in the vicinity of the disposal sites remained below the maximum permissible levels for metals in plants set by FAO/WHO. Beniah and Christian research on the concentration of Pb in T. occidentalis, P. mildbraedii, G. latifolium and V. amygdalina are presented here ranging from 0.006±0.005 mg/kg to 0.012±0.002 mg/kg. The findings revealed that Pb levels in the four vegetables were below 0.3 mg/kg, the limit set by FAO/WHO.

- Nickel (Ni)

Nickel levels ranged from 0.001 to 0.035 mg/kg. The highest mean value was observed in pumpkin leaf from the polluted site, whereas the lowest occurred in unpolluted site samples. All values were below the FAO/WHO standard limit of 68 mg/kg, indicating safe levels. Only water leaf and pumpkin leaf showed statistically significant differences (p = 0.03 and 0.02 respectively). Nickel enrichment in polluted areas may be linked to contaminated irrigation water, metal corrosion, or industrial effluents, although the observed values remain within safe limits for consumption. These findings align with Ezeonyejiaku *et al*. (2023), who also observed low nickel concentrations in vegetables which includes highest in green leaf (0.337), followed by fluted pumpkin (0.299) while least in water leaf (0.148) from Eke-Awka market, noting that these levels were similarly well below the WHO/FAO acceptable limit, corroborating the safe consumption status observed in this study.

- Zinc (Zn)

Zinc concentrations ranged between 0.002 and 0.0805 mg/kg. Bitter leaf from the polluted site showed the highest accumulation (0.0805 mg/kg), while unpolluted site vegetables showed much lower levels. Despite these variations, all zinc values were far below the FAO/WHO permissible limit of 60 mg/kg. Significant differences ($p < 0.05$) were observed in bitter leaf, scent leaf, and pumpkin leaf, suggesting that zinc accumulation is influenced by site conditions such as soil nutrient composition, fertilizer use, and vehicular emissions. Zinc, though an essential micronutrient, can become toxic at elevated levels; however, the observed concentrations here are within safe nutritional ranges. Latif *et al*. 2018 reported Zn levels ranging from 19.5mg/kg to 41mg/kg in vegetables. Dada *et al*., 2024 also reported Zn level ranging from 0.03mg/kg to 0.40 mg/kg commonly consumed leafy vegetables sold in major markets within Ibadan metropolis, southwestern,Nigeria. Nkop *et al*.,(2016) noted that the Zn level in water leaf and bitter leaf from dumpsite around the University of Uyo is below the joint FAO/WHO standard

- Copper (Cu)

Copper levels ranged from 0.0015 to 0.0595 mg/kg, with the highest value recorded in bitter leaf from the polluted site. All results were below the FAO/WHO permissible limit of 40 mg/kg, suggesting no copper toxicity risk. Significant differences ($p < 0.05$) were observed in scent leaf ($p = 0.00$) and bitter leaf ($p = 0.02$), while water leaf and pumpkin leaf showed no significant differences. The higher copper levels in the polluted area may be associated with the use of copper-based pesticides, vehicle parts corrosion, or runoff from nearby workshops.Ogbole *et al*.,(2024) research on the assessment of heavy metal in vegetables grown in irrigated land in Butura,Bokkos LGA, Plateau State shows the mean copper concentration in all the analyzed vegetable(pepper, cabbage, and Irish potato)samples was within the value given by the FAO/WHO. Anowar *et al*.,2024 study on heavy metal contamination in selected leafy vegetables in Dhaka, Bangladesh indicate that the concentration level of Cu were obtained below the permissible limit recommended by WHO

5.1.2 Comparative Analysis Between Polluted and Unpolluted Sites

Across all vegetables, higher concentrations of heavy metals were recorded in samples from the polluted site (Oluku) compared to the unpolluted site (Iyowa). This pattern indicates that environmental contamination and anthropogenic activities significantly influence the accumulation of heavy metals in edible plants. Despite these differences, all measured concentrations were below international safety thresholds, implying that the vegetables remain safe for human consumption. However, continuous exposure or bioaccumulation over time could pose health risks if pollution persists.

Although the levels of heavy metals detected are within permissible limits, the consistent trend of higher concentrations in polluted areas suggests potential contamination risks in the long term. Prolonged consumption of vegetables cultivated in contaminated soils can lead to gradual metal accumulation in human tissues, potentially resulting in kidney, liver, and nervous system disorders. Therefore, regular monitoring and control of agricultural practices, wastewater management, and roadside farming should be encouraged to maintain food safety.

5.2 SUMMARY

This study assessed the bioavailability of selected heavy metals (Cadmium, Zinc, Nickel, Lead, and Copper) in four commonly consumed leafy vegetables fluted pumpkin (Telfairia occidentalis), bitter leaf (Vernonia amygdalina), water leaf (Talinum triangulare), and scent leaf (Ocimum gratissimum) cultivated in two different locations within Benin City, Edo State which is Oluku (polluted site) and Iyowa (unpolluted site).

Results from the analyses revealed that all the heavy metals examined were present in the vegetables, though in varying concentrations across the two sites. Heavy metal concentrations followed the general trend: Polluted Site > Unpolluted Site. All heavy metals analyzed (Cd, Pb, Ni, Zn, Cu) were below FAO/WHO (2007 and 2011) permissible limits.Statistically significant differences ($p < 0.05$) were observed in several vegetables, particularly for Zn, Cd, and Cu. Bitter leaf and scent leaf showed higher accumulation tendencies, possibly due to their broad leaves and high adsorption capacity. Vegetables from both sites are safe for consumption,however, the elevated concentrations in vegetables grown near the polluted site suggest potential long-term contamination risks if such areas are continuously used for farming so preventive measures against pollution are essential.

5.3 CONCLUSION

The vegetables cultivated close to polluted sites such as waste dumps (Oluku) tend to accumulate higher concentrations of heavy metals compared to those grown in unpolluted environments

(Iyowa). This demonstrates that anthropogenic activities such as waste disposal and environmental pollution influence the uptake of heavy metals by edible plants. Although the concentrations of cadmium, lead, nickel, zinc, and copper detected in the analyzed vegetables were below the WHO/FAO maximum permissible limits, their presence indicates ongoing contamination that could pose a potential health risk to consumers if exposure continues over time. The study concludes that continuous monitoring of heavy metal levels in food crops is essential, particularly in urban and peri-urban areas where pollution sources are prevalent. Proper land use planning and public awareness are crucial to prevent cultivation in contaminated areas.

5.4 RECOMMENDATIONS

Regular Monitoring:

Continuous environmental monitoring of heavy metal concentrations in agricultural soils and vegetables, especially near waste dumpsites and industrial zones, should be carried out by environmental agencies. Periodic monitoring helps to identify heavy metal concentrations in vegetables and soils and it should be carried out by relevant authorities and research institutions to detect contamination trends and ensure food safety.

Public Awareness:

Farmers and local residents should be educated on the dangers of cultivating and consuming vegetables grown in polluted areas to prevent long-term health effects. Farmers should be educated and encouraged to adopt good agricultural practices such as using clean irrigation water, avoiding cultivation close to busy roads or waste dumps, and applying organic manure to reduce metal uptake by crops.

Waste Management:

The government and relevant stakeholders should strengthen waste management practices in Benin City to minimize pollution from dumpsites and open waste burning.

Soil Remediation and Pollution Control

Contaminated farmlands should undergo appropriate remediation techniques such as phytoremediation, soil washing, or organic amendment with compost to reduce heavy metal concentrations. Simultaneously, pollution sources such as waste dumps, effluents, and vehicle emissions should be effectively managed and controlled.

Policy Enforcement:

Government agencies should develop and enforce regulations limiting cultivation in contaminated areas and ensure regular inspection of irrigation sources and farmlands.Enforcement of environmental regulations that restrict farming close to waste disposal sites should be intensified to protect food safety and public health.

Further Research:

Future studies should include soil and water analysis from the same locations to better understand the pathway of heavy metal uptake in vegetables and the extent of contamination in the surrounding environment.

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