BIOACCUMULATION OF HEAVY METALS IN SOILS AND *Celosia argentea* LEAVES GROWN AROUND TEMBOGA RIVER BANK

BY

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BENIN CITY

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A PROJECT SUBMITTED TO THE DEPARTMENT OF SOIL SCIENCE AND LAND MANAGEMENT, FACULTY OF AGRICULTURE, UNIVERSITY OF BENIN, BENIN CITY, NIGERIA

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF AGRICULTURE (B. AGRIC. HONS) DEGREE IN SOIL SCIENCE.

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CERTIFICATION

This is to certify that this Project work titled **Bioaccumulation of Heavy metals in soils and *Celosia argentea* leaves grown around the Temboga river bank** was carried out by **Oghenemine Faith IGHURE (Miss)** with Matriculation Number **AGR2000147** in the Department of Soil Science and Land Management, Faculty of Agriculture, University of Benin, Benin City, Nigeria.

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Prof. E. R. Orhue	Dr. (Mrs.) V. I. O. Edosa
Project Supervisor	Head of Department
……………………..…	………………………….
Date	Date

DEDICATION

I dedicate this project to God Almighty, whose boundless blessings and unfailing protection have sustained me throughout my course of study at the University of Benin. To You, Heavenly Father, I remain forever grateful.

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My deepest gratitude is to God Almighty, who has remained ever-present throughout my studies and by whose grace I have successfully completed the final phase of my undergraduate program.

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ABSTRACT

Heavy metals are naturally occurring metallic elements with high atomic weights and densities at least five times greater than water which due to their persistence, toxicity, and bio-accumulative nature, they pose significant environmental and health risks. The study aimed at assessing bioaccumulation of heavy metals (Cd, Pb and Ni) in soils and *Celosia argentea* leaves grown around the Temboga River Bank in Benin City, Nigeria. Auger soil samples (0-30 cm) and *C. argentea* leaves were collected randomly from Temboga riverbank, 60 m (60MRB), and 120 m (MRB) from riverbank, in triplicates to make a total of 9 soil and 9 *C. argentea* leaves samples. The soil and *C. argentea* lea samples were analyzed for some physical, chemical, and heavy metal content using standard laboratory methods. The results showed that cadmium (Cd) content of the soils had values of 0.14 mg/kg at riverbank, 0.19 mg/kg at 60MRB, and 0.09 mg/kg at 120MRB. The levels of Cd were still within soil tolerance levels. The Nickel (Ni) content in the soils was low and had values of 0.06, 0.70, and 0.07 mg/kg at the riverbank, 60MRB and 120MRB respectively. The results also showed that Ni content of 2.883 mg/kg at riverbank, 60MFB and 2.717 mg/kg at 120MRB have reached toxic levels while Cd and Pb content of *C. argentea* leaves were still within tolerance levels for consumption. The *C. argentea* leaves grown around Temboga riverbank is not fit for consumption owing to the toxic levels of Ni, which could negatively impact human health.

CHAPTER ONE

1.0 INTRODUCTION

Heavy metals are naturally occurring metallic elements with high atomic weights and densities at least five times greater than water which due to their persistence, toxicity, and bio-accumulative nature, they pose significant environmental and health risks (Ali *et al.,* 2020). Lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) are toxic even at low concentrations (Tchounwou *et al.*, 2020**).** Heavy metal bioaccumulation refers to the progressive increase in concentration of toxic metals (e.g., Pb, Cd, Hg, As) in living organisms over time, primarily through uptake from contaminated water, soil, or food, exceeding environmental levels due to slow excretion rates (Ali *et al*., 2023). This process involves the absorption and retention of heavy metals in tissues of organisms, leading to higher internal concentrations than their surroundings, with potential transfer across food chains (biomagnification) (Javed *et al.,* 2022).

These heavy metals get into rivers and soils in various ways; industrial wastewater discharge, agricultural runoff (e.g., pesticides and fertilizers), mining activities, atmospheric deposition, and natural weathering of rocks (Briffa *et al.,* 2020). Heavy metals enter crops primarily through root absorption from contaminated soils and irrigation water, with secondary pathways including atmospheric deposition on leaves and agrochemical residues (Rai *et al*., 2019).

Heavy metal pollution in Nigerian rivers and farmlands has become a major environmental and public health concern due to rapid industrialization, improper waste disposal, and unsustainable agricultural practices (Orisakwe *et al*., 2021). Many Nigerian communities depend on river water for irrigation, drinking, and fishing, yet these water bodies are increasingly contaminated with toxic metals such **as** lead (Pb), cadmium (Cd), arsenic (As), and mercury (Hg) from industrial effluents, mining activities, and urban runoff (Ezekwe *et al*., 2022). Vegetables grown along polluted riverbanks, such as Lagos Spinach (***Celosia argentea*),** fluted pumpkin **(***Telfairia occidentalis***),** waterleaf **(***Talinum triangulare)***,** and spinach **(***Spinacia oleracea)* are known to accumulate these metals, posing serious health risks to consumers which can affect the kidney, liver adversely (Oluwasanya *et al*., 2021).

This study is necessary as it provides current evidence on heavy metal contamination in soils and vegetables. It will raise public awareness on food safety and sustainable farming near polluted rivers. There is paucity of information on heavy metal status in soils and crops grown around riverbanks in Benin, hence this study.

1.1 Objectives of the Study

The broad objective of the study was to evaluate the bioaccumulation of heavy metal (Cd, Ni, Pb) in soils and *Celosia argentea* leaves grown around the Temboga River bank, Benin city, Edo State, Nigeria while specific objectives were to determine some;

I. heavy metal content of the soils,
II. heavy metal contents of *C. argentea* leaf grown around Temboga River bank
III. relationship between some soil properties and some heavy metals in *C. argentea* leaf.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Concept of Heavy Metals

Heavy Metals are naturally occurring metallic elements with high atomic weights (typically > 20u) and densities greater than 5 g/cm³. They are characterized by their; toxicity (harmful even at trace concentrations e.g. lead, cadmium, mercury), persistence (non-biodegradable, accumulating in ecosystems over time), bioaccumulation potential (stored in living tissues, increasing in concentration up the food chain) (WHO, 2021). Heavy metals can be categorized based on their biological roles into essential and non-essential heavy metals. Essential heavy metals are those that are required by organisms in small amounts for metabolic functions, e.g. zinc, copper, iron (Kabata-Pendias, 2020). Non-Essential heavy metals are purely toxic and not known to have any biological function (WHO, 2020). Heavy metals can be classified as essential (e.g., Zn, Cu, Fe), which are biologically required but toxic in excess, or non-essential (e.g., Pb, Cd, Hg, As), which are harmful even at trace concentrations, as in Table 1 below.

The ecological impacts of heavy metal pollution are equally concerning. In terrestrial systems, metal contamination degrades soil quality by disrupting microbial communities essential for nutrient cycling, ultimately reducing fertility and agricultural productivity (Ezekwe *et al*., 2023). Aquatic ecosystems suffer from metal bioaccumulation in food chains, where top predators often contain dangerous concentrations, while sensitive species face population declines (USEPA, 2022). This contamination contributes to broader biodiversity loss, as many organisms cannot tolerate elevated metal concentrations in their habitats (Oluwasanya *et al*., 2024). The persistence

Table 1: Classification of Heavy Metals Based on Utilization, role and toxicity.

Type	Examples	Role	Toxic Threshold
Essential	Zn, Cu, Fe	Required for biological functions	Toxic above optimal range
Non-essential	Pb, Cd, Hg, As	Purely toxic	Harmful at any level

Sources : Kabata-Pendias (2020), Tchounwou *et al.* (2020).

of these metals means such environmental damage can persist for decades even after pollution sources are controlled.

2.2 Concept of Bioaccumulation

Bioaccumulation refers to the gradual buildup of toxic substances (e.g., heavy metals) in living organisms over time, exceeding environmental concentrations (USEPA, 2022). Bioaccumulation occurs when the rate of uptake from the environment exceeds the organism's ability to eliminate the substance (WHO, 2021). This process occurs through; direct uptake (e.g., plants absorbing metals from soil) and **t**rophic transfer (e.g., humans consuming contaminated vegetables) (Orisakwe *et al*., 2021). In riverbank ecosystems, bioaccumulation is exacerbated by persistent pollution and low degradation rates of metals (Ezekwe *et al*., 2022). Trophic level is a critical factor that influences bioaccumulation of contaminants in organisms, as top predators consistently accumulate the highest concentrations of substances, exemplified by the high levels of mercury found in shark muscle (Driscoll et al., 2021). The chemical persistence of a substance also plays a major role; non-degradable heavy metals like lead and cadmium can accumulate indefinitely within tissues, such as lead sequestered in bone (Jarup & Akesson, 2020; Tchounwou et al., 2020). Lipid solubility is also known to be a primary determinant for organic compounds, with fat-soluble contaminants like PCBs accumulating preferentially in adipose tissue, similar to how mercury bioaccumulates in fish liver (Scheuhammer et al., 2022). The duration of exposure is directly related to tissue concentrations, where longer exposure periods lead to greater accumulation, as observed with cadmium in the kidneys of long-term smokers (Jarup & Akesson, 2020).

2.3 Concept of Riverbanks

Riverbanks are dynamic interface zones between aquatic and terrestrial ecosystems, composed of sedimentary deposits and biologically active surfaces that: serve as natural levees during flood events (Kondolf and Piégay, 2022), function as ecological transition corridors (Naiman *et al*., 2023), act as biochemical reactors for nutrient processing (Gurnell *et al*., 2023). Riverbanks are dynamic ecosystems where soil, water, and vegetation interact. They are particularly vulnerable to heavy metal contamination due to: flooding (deposits polluted sediments onto soils (Ezeh *et al*., 2023)) and agricultur**e** (frequent irrigation with contaminated water (Ogunkunle *et al*., 2022)). In Nigeria, riverbanks like the Niger Delta and Ikpoba River are high-risk zones (Adekunle *et al*., 2023). Riverbanks are natural landforms that border flowing water bodies, formed through the interplay of hydrological forces (erosion/deposition cycles), sediment transport dynamics, biological stabilization by vegetation. These transitional zones serve as critical ecotones between aquatic and terrestrial ecosystems (Wohl, 2020). Riverbanks provide vital ecological services that sustain both aquatic and terrestrial ecosystems. These transitional zones serve as essential habitat for approximately 60% of aquatic species during critical life stages, functioning as nurseries for fish and breeding grounds for amphibians (Naiman *et al*., 2021). Their natural filtration capacity is remarkably efficient, with research demonstrating that intact riverbank systems can remove 40-60% of water pollutants through physical filtration and biochemical processes (Mayer *et al*., 2022). This includes trapping sediments, absorbing excess nutrients, and breaking down contaminants. Furthermore, riverbank soils play a significant role in climate regulation, storing about 25% more organic carbon compared to adjacent upland soils due to frequent nutrient deposition and waterlogged conditions that slow decomposition (Duval *et al*., 2023).

2.4 Sources of Heavy Metals in River Banks

Riverbanks act as long-term sinks for heavy metals, accumulating pollutants from upstream and adjacent land sources. Below is a detailed breakdown of their presence, behavior, and ecological impacts. Heavy metals accumulate in riverbanks through three primary pathways:

2.4.1 Direct Deposition from Water

During flood events, heavy metals adsorbed onto fine sediment particles (particularly clay and silt) are transported by river currents and gradually settle onto riverbanks as floodwaters recede. This process leads to the long-term accumulation of metals in bank soils. A striking example of this can be seen in the Niger Delta, where riverbanks contain 500-1,200 mg/kg of lead (Pb) deposited through historical flood events (Ezekwe *et al*., 2023). The finest particles tend to carry the highest metal concentrations due to their large surface area and strong adsorption capacity.

2.4.2 Contaminated Groundwater Seepage

The hyporheic exchange process, where groundwater interacts with riverbank sediments, serves as another significant entry route for heavy metals. Polluted groundwater carrying dissolved metals like arsenic (As) and chromium (Cr) gradually discharges into riverbank sediments. This is particularly problematic in areas with industrial groundwater contamination, where metals can persist for decades (Du Laing *et al*., 2022). The mixing of groundwater and surface water in this zone facilitates chemical reactions that may increase metal bioavailability.

2.4.3 Surface Runoff and Erosion

Surface runoff from agricultural and urban areas transports metal contaminants directly to riverbanks. Agricultural runoff often carries cadmium (Cd) from phosphate fertilizers, while urban runoff frequently contains lead (Pb) from road dust and vehicle emissions (Ogbeide *et al*., 2023). During rainfall events, these contaminants are washed into waterways and subsequently deposited on riverbanks. Erosion of contaminated soils upstream further contributes to this metal loading, creating a continuous input of pollutants to riverbank ecosystems.

2.5 Heavy Metals in Plants Around River Banks

Heavy metals from contaminated riverbanks are absorbed by plants, leading to bioaccumulation

in edible crops and ecological risks. Below is a detailed breakdown of the process, impacts, and examples from Nigeria. Plants growing along contaminated riverbanks may absorb toxic heavy metals through two primary pathways:

2.5.1 Root Uptake

The most significant route of metal absorption occurs through plant root systems. When heavy metals like cadmium (Cd), lead (Pb), and arsenic (As) dissolve in soil water from contaminated riverbank sediments, they are taken up through root membranes via both passive and active transport mechanisms (Oluwasanya *et al*., 2023). Certain metal ions chemically resemble essential nutrients - for instance, cadmium mimics calcium - allowing them to enter through nutrient uptake channels (Kabata-Pendias, 2020). A documented example includes waterleaf (*Talinum triangulare*) cultivated near Nigerian riverbanks, which showed cadmium concentrations up to 0.9 mg/kg due to root absorption from flooded, contaminated soils (Oluwasanya *et al.*, 2023).

2.5.2 Foliar Deposition

Plants also accumulate metals through direct atmospheric deposition on leaf surfaces. Airborne particulate matter containing lead (Pb) and mercury (Hg) from industrial emissions, vehicular exhaust, and contaminated dust settles on leaf cuticles and enters through stomatal pores (Uzu *et al.*, 2022). This pathway contributes significantly to metal accumulation in leafy vegetables, with studies showing up to 40% of total lead content in urban-grown spinach originating from foliar absorption (Schreck *et al.*, 2020).

2.6 Key Factors Influencing Metal Uptake Efficiency

Several environmental and biological factors regulate metal absorption:

- **Soil pH**: Acidic conditions (pH <5.5) dramatically increase the bioavailability of cadmium and lead by enhancing their solubility in soil water (Rinklebe *et al.*, 2022). For every unit decrease in pH, cadmium uptake in lettuce increases by approximately 30% (McBride, 2021).
- **Organic Matter Content**: Riverbank soils rich in organic compounds (≥5% organic carbon) can bind up to 80% of available copper and mercury ions, significantly reducing plant uptake (Du Laing *et al.*, 2021). However, under anaerobic conditions during flooding, some organometallic complexes may become more mobile.
- **Plant Species Differences**: Hyperaccumulator species like sunflower (*Helianthus annuus*) can concentrate metals 50-100 times more effectively than non-accumulators (Ali *et al.*, 2020). Among food crops, leafy vegetables (e.g., spinach, waterleaf) typically accumulate 3-5 times

more cadmium than grain crops (WHO, 2021). Table 2 below shows plants in Nigeria that are commonly contaminated.

2.7 Review of Selected Heavy Metals

2.7.1 Cadmium (Cd)

Cadmium is a soft, bluish-white heavy metal with atomic number 48 and atomic weight 112.41 g/mol. It is classified as a transition metal, cadmium exhibits several concerning properties: high toxicity even at trace concentrations (0.001-0.1 mg/L in water), extreme persistence in the environment (biological half-life of 10-30 years in humans), strong bioaccumulation potential, particularly in kidneys and liver. It also has chemical similarity to zinc, allowing it to mimic essential nutrients in biological systems (WHO, 2021). Cadmium enters ecosystems through natural processes and human activities. The natural sources are volcanic emissions which release cadmium into the atmosphere, weathering of cadmium-containing minerals (e.g., greenockite), forest fires contributing to atmospheric cadmium deposition. The anthropogenic sources (which are more significant) include; phosphate fertilizer production (commercial fertilizers contain 5-300 mg/kg cadmium as impurity), **z**inc mining and smelting (major byproduct of zinc ore processing), battery manufacturing (nickel-cadmium batteries account for 75% of industrial use), waste incineration (releases airborne cadmium particles) f**ossil** fuel combustion (coal contains 0.1-3 ppm cadmium (ATSDR, 2022). Cadmium demonstrates complex environmental dynamics: in soil**s**; mobility depends on pH (more soluble below pH 6) and organic matter content, in water; it exists as Cd^{2+} ion, forming complexes with chlorides and sulfates, **i**n air; particulate matter carries cadmium over long distances and in biological systems; accumulates in organisms due to lack of effective excretion mechanisms. The metal persists indefinitely, moving through:

Table 2: Common contaminated Plants in Nigeria

Plant	Heavy Metals Found	Source of contamination	Health Risk
Fluted Pumpkin (Ugwu)	Pb, Cd	Floodplain Farming	Kidney damage
Spinach	As, Hg	Polluted irrigation water	Cancer risks
Root Vegetables (potatoes, carrots)	Cd, Pb	Direct uptake from contamnated soil	Liver toxicity, anemia

Sources: WHO (2021), NESREA (2023).

atmospheric deposition → soil absorption → plant uptake → food chain, industrial wastewater → river sedimentation → aquatic organisms, agricultural runoff → groundwater contamination → drinking water (Nordberg *et al.*, 2022).

2.7.2 Chromium (Cr)

Chromium is a transition metal (atomic number 24) that exists in multiple oxidation states, with trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) chromium being the most environmentally significant. Chromium has high melting point (1,907°C) and corrosion resistance, Cr^{6+} is highly toxic and mobile in water, while Cr^{3+} is less toxic and binds to soils, it is used extensively in industrial applications due to its hardness and durability (IARC, 2020). Chromium enters ecosystems through: natural sources such as weathering of chromium-rich minerals (e.g., chromite $FeCr_2O_4$) and volcanic emissions and wildfires and anthropogenic sources (primary contributors) such as tanneries (release Cr^{6+} in wastewater (up to 500 mg/L)), **s**tainless steel production (accounts for 80% of industrial chromium use), electroplating (generates Cr-laden sludge), textile dyeing (chromium-based dyes contaminate water bodies) leather tanning (uses chromium sulfate ($Cr_2(SO_4)_3$)) (ATSDR, 2021). Chromium's fate depends on its oxidation state. As Cr^{6+} (Chromate)**,** it is highly soluble in water, making it mobile in aquifers, and toxic to aquatic life at concentrations >0.1 mg/L. As Cr^{3+}**,** it is insoluble and binds to soil particles (clay, organic matter) and less bioavailable but can oxidize to Cr^{6+} under certain conditions. The factors affecting chromium availability include pH (Cr^{6+} dominates in alkaline conditions (pH >8)), redox potential (reducing environments convert $Cr^{6+} \rightarrow Cr^{3+}$), organic matter (enhances Cr^{3+} stability) (Barrera-Díaz *et al.*, 2022).

2.7.3 Cobalt (Co)

Cobalt is a transition metal (atomic number 27) with a high density (8.9 g/cm^3) that exhibits both essential and toxic properties depending on concentration and exposure route (IARC, 2020). While cobalt serves as a crucial component of vitamin B_{12} (cobalamin) in humans, required for red blood cell formation and neurological function, excessive exposure poses significant health and environmental risks (Li *et al*., 2021). Cobalt enters ecosystems through multiple pathways: weathering of cobaltiferous minerals (e.g., cobaltite, erythrite) contributes approximately 8-15% of environmental cobalt (Gonzalez *et al*., 2022), mining operations in the Democratic Republic of Congo (DRC) account for 70% of global production (Sovacool *et al*., 2022), lithium-ion battery production has increased cobalt demand by 300% since 2018 (International Energy Agency, 2023), industrial applications including superalloys, catalysts, and pigments (USGS, 2023). Cobalt's environmental fate depends on: soil chemistry (mobility increases in acidic conditions (pH <6) and in soils with low iron/manganese oxide content) (Tóth *et al*., 2020), oxidation states (Co^{2+} dominates in reducing environments while Co^{3+} forms stable complexes in oxidizing conditions) (Smith *et al*., 2021), organic matter (humic substances can either mobilize or immobilize cobalt depending on pH) (Yang *et al*., 2022). Primary routes of exposure include: seafood and leafy vegetables from contaminated areas may contain >1 mg/kg cobalt (Khan *et al*., 2021), metal-on-metal hip implants can release 100-500 µg cobalt daily (Matusiewicz *et al*., 2023), battery factory workers show blood cobalt levels 50× higher than controls (Bucher *et al*., 2022). Health effects associated with bioaccumulation of cobalt includes; cardiomyopathy (blood cobalt >7 µg/L associated with heart failure in hip implant patients) (Leyssens *et al*., 2021), respiratory effects (Hard metal lung disease prevalence of 5-15% in exposed workers) (Naqvi *et al*., 2022), neurotoxicity (developmental delays in children from mining communities) (Banza *et* *al*., 2023), endocrine disruption (alters thyroid function at 50 µg/L in drinking water) (Chen *et al*., 2023). In aquatic systems, 0.1 mg/L reduces daphnia reproduction by 50% (De Schamphelaere *et al*., 2020), in soil microbiota, cobalt alters nitrogen-fixing bacteria communities at 100 mg/kg (Rajkumar *et al*., 2021), in plants, hyperaccumulators like Crotalaria cobalticola store >1000 mg/kg (Faucon *et al.,* 2022).

2.7.4 Lead (Pb)

Lead (Pb) is a bluish-gray heavy metal with atomic number 82 and atomic weight 207.2 g/mol, classified among the most toxic environmental pollutants. It has high density (11.34 g/cm^3) and malleability**.** It is also known for its **e**xtreme persistence in soils (half-life >500 years). It has the tendency to accumulate in bones and soft tissues. Mercury has n**o** known biological function in humans (WHO, 2021). Mercury has multiple oxidation states (Pb^0, Pb^{2+}, Pb^{4+}), with Pb^{2+} being most common in environmental systems (ATSDR, 2020). Contemporary lead pollution stems from both legacy and ongoing sources. Anthropogenic sources of lead include**;** lead acid batteries **(**account for 85% of global lead use (ILA, 2022)**),** legacy leaded gasoline **(**still contaminates soils near roads (Pb levels 500–2,000 mg/kg) (Ezeh *et al*., 2023**),** mining/smelting **(**releases particulate lead into air and water**),** electronic waste recycling **(**informal processing contaminates soils (Pb >5,000 mg/kg) (Ogundele *et al*., 2021)**),** paints/pigments(older buildings contain 10–50% lead by weight (EPA, 2022)**).** The natural sources include; weathering of lead-bearing minerals (e.g., Galena), volcanic emissions (minor contributor) (Kabata-Pendias, 2020). Lead exhibits complex environmental dynamics. In air, its fine particulates (<2.5 µm) travel long distances, **i**n water, it forms insoluble compounds (e.g., $PbCO_3$, $PbSO_4$) at neutral pH. It is known to bind strongly to organic matter and clay particles in soil and its bioavailability increases at pH < 6 (Rinklebe *et al*., 2022). In biological systems, it mimics calcium (Ca^{2+}), accumulating in bones and also biomagnifies in food chains, especially in urban areas (Taylor *et al*., 2021). Modern populations face lead exposure through soil/dust ingestion (mostly in children). This occurs through hand-to-mouth behavior which results in 50-200mg/day intake (WHO, 2021). Food contamination through crops grown in Pb-contaminated soils like leafy greens and game meat from lead-shot animals is also another way people are exposed to lead. Lead pipes/solder leach Pb into water (as it was reported in Flint, Michigan crisis), also battery recycling workers inhale Pb dust (Blood Lead Leves (BLLs) >30 µg/dL) (NAS, 2022).

2.7.5 Nickel

Nickel is a transition metal (atomic number 28) with a density of 8.9 g/cm³ that exhibits both essential biological functions and significant toxicity at elevated concentrations (Genchi *et al.*, 2020). While nickel serves as a cofactor for several microbial enzymes, it has been classified as a Group 1 carcinogen by IARC when in certain compound forms (IARC, 2020). Modern nickel pollution originates from: weathering of ultramafic rocks contributes approximately 150,000 metric tons annually (Ermolin *et al*., 2022), stainless steel production accounts for 68% of global nickel use (USGS, 2023), lithium-ion battery manufacturing has increased demand by 40% since 2020 (IEA, 2023), fossil fuel combustion releases 8,000-10,000 tons of nickel particles yearly (ATSDR, 2021). Recent studies reveal that nickel's mobility in soil increases five-fold in acidic conditions (pH <5.5) with low organic matter (Tóth *et al*., 2022), in aquatic systems, Ni2+ is the dominant species in freshwater, while NiCO3 forms in marine environments (Barceloux, 2021). additionally, microorganisms play a key role in mediating nickel's oxidation and reduction reactions (Hao *et al*., 2023). Current research identifies key human exposure pathways to nickel through occupational settings, with welders exhibiting significantly higher urinary nickel levels (Bucher *et al.,* 2022); consumer products like e-cigarettes, which release microgram quantities per puff (Olmedo *et al*., 2021); and dietary sources such as chocolate and nuts, potentially containing over 2 mg/kg(Khan *et al.,* 2023). Recent findings indicate that nickel exposure is associated with various health effects, including respiratory issues like chronic rhinosinusitis in refinery workers (Naqvi *et al*., 2023), dermatological concerns such as nickel allergy affecting a notable percentage of Europeans (Thyssen *et al.,* 2022), carcinogenic effects due to DNA hypermethylation induced by nickel compounds (Cheng *et al.,* 2023), and developmental impacts, including reduced fetal growth from in utero exposure (Wang *et al*., 2021). Furthermore, contemporary research reveals significant ecological impacts, demonstrating aquatic toxicity where low concentrations inhibit algae photosynthesis (De Schamphelaere *et al.,* 2021) and lead to high bioaccumulation factors in mollusks (Jiang *et al.,* 2022), as well as terrestrial effects where 100 mg/kg reduces soil microbial biomass by 30% (Rajkumar *et al.,* 2023) and certain plants act as hyperaccumulators (Alyssum spp.), storing substantial amounts (>1%) of nickel in their leaves (Van der Ent *et al*., 2023).

2.7.6 Selenium

Selenium is a metalloid element (atomic number 34) that exhibits dual characteristics of both essential nutrient and environmental toxicant, with its effects being highly dose-dependent (Winkel *et al.,* 2021). This chalcogen element has a density of 4.81 g/cm^3 and exists in several oxidation states (-II, 0, IV, VI) that determine its environmental behavior and biological interactions (Lenz *et al.,* 2022). Modern selenium contamination stems from; weathering of selenium-rich Cretaceous shales releases 2,000-10,000 metric tons annually (Schilling *et al*., 2023), coal combustion contributes 40% of atmospheric selenium emissions (Vriens *et al*., 2020), agricultural irrigation in arid regions mobilizes selenium from soils (Lin *et al*., 2021), mining operations generate selenium-laden wastewater (Santos *et al*., 2022). Selenium exists in multiple oxidation states (-II, 0, IV, VI) that determine its environmental mobility and bioavailability; selenate (SeO_4^{2-}) dominates in oxidized environments with mobility 10× greater than selenite (Nakamaru and Sekine, 2021), selenite (SeO_3^{2-}) strongly adsorbs to iron oxides, reducing bioavailability (Wang *et al*., 2023), nanoparticulate Se^0 (emerging concern due to unique transport properties) (Lampis *et al*., 2022). Optimal intake of selenium is 55-400 µg/day, with selenoprotein P as key biomarker (Roman *et al*., 2021). A blood selenium concentration exceeding 300 µg/L indicates the toxicity threshold associated with selenosis (Vinceti *et al*., 2023). In aquatic systems: 5 µg/L causes teratogenic deformities in fish embryos (Janz *et al*., 2021), trophic magnification factors reach 3.8 in food chains (Presser and Luoma, 2023). In terrestrial systems: selenium hyperaccumulators (e.g., Astragalus spp.) contain >1,000 mg/kg (El Mehdawi *et al*., 2022), soil microbial diversity decreases at >10 mg/kg (Stolz *et al.,* 2023).

2.7.7 Arsenic

Arsenic is a metalloid with characteristics of metals and non-metals, but is commonly classified as a heavy metal due to its: high atomic weight (74.92 g/mol), density (5.73 g/cm³) and toxicity at low concentrations (WHO, 2021). Arsenic exists in organic form, which is less toxic and can be found in seafood and inorganic form, which is highly toxic and can be found in soil/water. Arsenic enters the environment through natural and human-made sources, with its chemical form determining its mobility and toxicity. Natural sources primarily include the weathering of arsenic-rich minerals such as arsenopyrite in rocks and sediments, which releases inorganic arsenic forms (As(III) and As(V) into surrounding ecosystems (Smedley and Kinniburgh, 2020). Volcanic activity also contributes to atmospheric arsenic emissions, which eventually deposit onto land and water surfaces. On the anthropogenic side, gold mining operations generate arsenic-laden tailings that contaminates nearby soil and water bodies, while historical use of arsenic-based pesticides has left persistent residues in agricultural areas (Adekunle *et al.*, 2023). Industrial processes, particularly smelting and electronics manufacturing, release arsenic trioxide (As_2O_3), a highly toxic byproduct that accumulates in the environment. The environmental fate of arsenic depends strongly on redox conditions and chemical interactions. In aquatic systems, soluble arsenite (As(III)) becomes the dominant form under reducing, anaerobic conditions commonly found in groundwater and flooded soils (Zhao *et al.*, 2021). When exposed to oxygen-rich environments, arsenic typically oxidizes to arsenate (As(V)), which strongly binds to iron oxides in soil particles, reducing its mobility but creating long-term reservoirs of contamination. Biological systems play a crucial role in arsenic transformation through methylation processes, where microorganisms and plants convert toxic inorganic arsenic into less harmful organic forms such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) (Cullen and Reimer, 2021). Global populations face arsenic exposure through multiple interconnected pathways, with drinking water representing the most significant threat. The World Health Organization (2023) estimates over 50 million people worldwide consume water containing unsafe arsenic levels, exemplified by groundwater in Bangladesh where concentrations reach 1,000 µg/L - 100 times the WHO's recommended limit of 10 µg/L. The food chain serves as another critical exposure route, particularly through rice cultivation, which accumulates 10 times more arsenic than other cereal grains due to its growth in flooded paddies that mobilize arsenic (Meharg and Zhao, 2022). Leafy vegetables irrigated with contaminated water also efficiently absorb arsenic, while occupational exposure remains a serious concern for gold miners who inhale arsenic-containing dust during ore processing, significantly increasing their risk of developing lung cancer.

2.7.8 Mercury

Mercury is a unique heavy metal that exists in liquid form at room temperature, with an atomic number of 80 and atomic weight of 200.59 g/mol. This silvery-white metal exhibits several concerning properties; high volatility (evaporates at 20°C), exceptional ability to bioaccumulate and bio-magnify in food chains, it exists in three primary forms: elemental (Hg^0), inorganic (Hg^+, Hg^{2+}), and organic (methylmercury), forms amalgams with other metals, historically used in mining and dentistry (WHO, 2021). Mercury enters ecosystems through both natural processes and human activities. The natural sources include volcanic eruptions (accounts for approximately 10% of atmospheric mercury), weathering of mercury-containing rocks (e.g., cinnabar), natural degassing from oceans and soils. The anthropogenic sources (dominant) include artisanal gold mining (uses mercury to extract gold (37% of global emissions)), coal combustion (releases gaseous mercury (24% of emissions)), industrial processes (chlor-alkali plants, cement production), waste incineration (especially electronic and medical waste), dental amalgams (slowly release mercury vapor) (UNEP, 2023). Mercury demonstrates complex environmental dynamics; atmospheric transport (elemental mercury vapor can circulate globally for 6-24 months), methylation (anaerobic bacteria convert Hg^{2+} to methylmercury (CH_3Hg^+) in water bodies), bioaccumulation (methylmercury concentrates in fish muscle tissue), persistence (remains in ecosystems for decades to centuries). The global mercury cycle involves Atmospheric emission → deposition → methylation → bioaccumulation, aquatic systems → fish → humans/birds/mammals, soil accumulation → plant uptake → terrestrial food chains (Driscoll *et al*., 2022). People encounter mercury through multiple routes. One is primary exposure routes which include; fish consumption, occupational exposure and other routes such as dental amalgam fillings, contaminated rice (in mercury polluted areas), broken fluorescent lights/thermometers (WHO, 2021).

2.8 General Effects of Heavy Metals

Heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) are non-biodegradable, persist indefinitely in ecosystems, and bioaccumulate in food chains. Their toxicity—even at trace levels—poses severe risks to human health (e.g., neurotoxicity, carcinogenicity) and environmental integrity (Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., and Beeregowda, K. N. 2021). Exposure to these contaminants leads to severe neurological effects, particularly in vulnerable populations. Lead and mercury, for instance, disrupt neurodevelopment in children, with studies showing a reduction of 2-5 IQ points for every 1 µg/dL increase in blood lead levels (Lanphear *et al.,* 2020). Methylmercury exposure during pregnancy has been linked to lasting motor and sensory impairments in offspring (Grandjean and Landrigan, 2021). Beyond cognitive impacts, heavy metals cause substantial organ damage, with cadmium accumulating in kidneys and inducing tubular dysfunction, while arsenic exposure through contaminated drinking water contributes to liver fibrosis and cardiovascular disease (Satarug *et al*., 2020; WHO, 2021). The carcinogenic potential of these metals is equally concerning, as hexavalent chromium and inorganic arsenic are classified as Group 1 carcinogens, directly linked to lung, skin, and bladder cancers through various exposure routes (IARC, 2020; Naujokas *et al.,* 2021). The ecological consequences of heavy metal pollution are equally devastating, disrupting soil health, aquatic systems, and biodiversity.

Contaminated soils experience reduced microbial activity and plant growth inhibition, with lead and cadmium levels exceeding 100 mg/kg decreasing microbial diversity by half (Adekunle *et al*., 2023). Arsenic interferes with root development, while mercury bioaccumulates in aquatic food chains, reaching toxic concentrations in fishes and threatening piscivorous wildlife (Driscoll *et al*., 2021). Mining activities exacerbate these issues, with runoff eliminating sensitive species and altering ecosystem dynamics (Eisler, 2020). Regional case studies highlight the urgency of addressing heavy metal pollution. In Nigeria's Niger Delta, fishes contain lead concentrations eight times higher than WHO limits due to oil industry contamination (Ezekwe *et al*., 2023). The Zamfara gold mining crisis resulted in hundreds of child deaths from acute lead poisoning, underscoring the human cost of improper metal management (Dooyema *et al*., 2021).

2.8.1 Effects of Heavy Metals in Soils

Heavy metal contamination in soils poses significant threats to both ecosystem health and agricultural productivity. Studies have documented that excessive concentrations of metals like lead (Pb), cadmium (Cd), and arsenic (As) disrupt soil microbial communities, reducing biodiversity and impairing essential nutrient cycling processes (Ayangbenro and Babalola, 2020, Xiao *et al.,* 2021). These metals alter soil enzyme activities, particularly those involved in decomposition and nitrogen transformation, ultimately decreasing soil fertility and organic matter turnover (Tóth *et al*., 2020). The presence of heavy metals also induces oxidative stress in soil microorganisms, leading to reduced populations of beneficial bacteria and fungi that support plant growth (Rajkumar *et al.,* 2020). The phytotoxic effects of heavy metals manifest through multiple mechanisms that compromise plant health and crop yields. Research shows that metal accumulation in agricultural soils inhibits seed germination, reduces root elongation, and disrupts photosynthesis by interfering with chlorophyll synthesis (Rizwan *et al*., 2020). Some metals like cadmium and lead compete with essential nutrients for plant uptake, causing nutrient deficiencies even in fertile soils (Antoniadis *et al*., 2020). This not only reduces crop productivity but also facilitates the transfer of toxic metals into the food chain, creating potential health risks for consumers (Wuana and Okieimen, 2020). Heavy metal contamination also alters the physical and chemical properties of soils, with long-term consequences for land use. Studies indicate that chronic metal pollution increases soil acidity and reduces cation exchange capacity, diminishing the soil's ability to retain nutrients (Alloway, 2020). These changes can persist for decades, as most heavy metals resist degradation and remain biologically available in soils (Bolan *et al*., 2020). The resulting degradation of soil structure and water-holding capacity further exacerbates the challenges of revegetation and ecological restoration in contaminated areas (Khalid *et al*., 2020). Recent research emphasizes that these combined effects make heavy metal pollution one of the most persistent and challenging forms of soil degradation worldwide (Yang *et al*., 2020).

2.8.2 Effects of Heavy Metals in Riverbanks

Heavy metal contamination in riverbank ecosystems poses significant ecological and environmental challenges. These transitional zones between aquatic and terrestrial environments accumulate metals through hydrological processes, leading to long-term impacts on soil quality and biological communities. Studies have shown that riverbank soils contaminated with lead (Pb), cadmium (Cd), and other heavy metals exhibit reduced microbial diversity and impaired nutrient cycling functions (Bai *et al*., 2020). The unique hydrology of riverbanks, characterized by periodic flooding and sediment deposition, facilitates the accumulation and redistribution of metal contaminants along watercourses (Du Laing *et al*., 2020). The presence of heavy metals in riverbank soils significantly affects vegetation establishment and growth. Heavy metal contamination may alter plant community composition, favoring metal-tolerant species while suppressing sensitive riparian vegetation (Pandey *et al*., 2020). This shift in plant biodiversity can disrupt the structural integrity of riverbanks, increasing erosion susceptibility and compromising their natural flood mitigation capacity (Grabowski *et al*., 2020). Furthermore, the bioaccumulation of metals in riparian plants creates pathways for contaminants to enter terrestrial food webs, potentially affecting higher trophic levels (Bonanno and Lo Giudice, 2020). Riverbank heavy metal contamination also poses risks to aquatic ecosystems through leaching and sediment transport. Studies demonstrate that during high-flow events, contaminated riverbank soils contribute substantially to the metal load in water columns (Bing *et al*., 2020). This dynamic exchange between riverbanks and water bodies creates persistent contamination cycles that affect aquatic organisms and water quality downstream (Zhao *et al*., 2020). The ecological consequences are particularly severe in urban river systems, where industrial and stormwater runoff have created metal hotspots in riparian zones (Väänänen *et al*., 2020). These findings underscore the importance of riverbanks as both sinks and sources of heavy metal pollution in aquatic ecosystems.

2.8.4 Effects of Heavy Metals in Plants

Heavy metal contamination significantly impacts plant physiology, growth, and productivity through multiple mechanisms. When plants absorb metals like cadmium (Cd), lead (Pb), arsenic (As), and mercury (Hg) through their roots, these toxic elements disrupt critical metabolic processes and cellular functions (Raza *et al*., 2020). The presence of heavy metals induces oxidative stress by generating reactive oxygen species (ROS), which damage cellular membranes, proteins, and DNA, ultimately impairing plant growth and development (*Adrees et al.,* 2020). Studies have demonstrated that metal toxicity reduces chlorophyll synthesis and photosynthetic efficiency, leading to visible symptoms such as chlorosis, stunted growth, and reduced biomass accumulation (Emamverdian *et al.,* 2020). The uptake and translocation of heavy metals in plants varies depending on the specific element and plant species. Some plants exhibit metal hyperaccumulation capabilities, storing exceptionally high concentrations in their tissues without showing toxicity symptoms, while most crops suffer severe physiological damage at relatively low metal concentrations (Yan *et al*., 2020). Heavy metals interfere with nutrient uptake by competing with essential elements for transport proteins and binding sites, resulting in nutrient deficiencies even in fertile soils (Shahid *et al*., 2020). For instance, cadmium disrupts calcium and zinc homeostasis, while lead interferes with iron and manganese absorption, creating complex nutritional imbalances (Gupta *et al*., 2020). These disruptions affect enzyme activities, hormone regulation, and water relations, collectively reducing crop yields and agricultural productivity (Hussain *et al*., 2020). At the molecular level, heavy metals alter gene expression and protein synthesis in plants. Research has shown that metal stress triggers the upregulation of stress-responsive genes and the production of protective compounds like phytochelatins and metallothioneins (Clemens and Ma, 2020). While these defense mechanisms help plants tolerate moderate metal exposure, excessive contamination overwhelms these systems, leading to cellular damage and plant death (Ghori *et al*., 2020). The presence of heavy metals in edible plant parts also poses significant food safety concerns, as contaminants enter the human food chain through consumption of metal-laden crops (Antoniadis *et al*., 2020). This dual impact on both plant health and food security underscores the importance of understanding and mitigating heavy metal effects in agricultural systems (Rizwan *et al*., 2020).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of The Study Area

The study was conducted between April-October, 2025 on soils collected around Temboga River bank, Benin City, Edo state, Nigeria. The coordinates of the points where the soils were collected is shown in Table 3. The area was sloppy and swampy closest to the river bank and planted to various vegetables, including *Celosia argentea* (lagos spinach), *Amaranthus hybridus* (green leaf), *Telfairia occidentalis* (pumpkin leaf), *Talinum triangulare* (water leaf) and *Corchorus Olitorius* (Ewedu) and other arable crops like *Zea mays* (Maize plant). The area is also used for growing plantains and for fish farming activities. The soil in the area has a history of being treated with organic and inorganic fertilizers, as well as herbicides.

3.2 Collection of Samples

Soil and *Celosia argentea* leaves samples were collected in 3 replicates at the river bank, 60 m and 120 m away from the river bank respectively, making a total of nine soil samples and nine *C. argentea* leaves samples.

3.3 Sample preparation

3.3.1 Soil sample preparation

Soil samples were air-dried for about 1-2 weeks. The samples were later grounded/crushed, sieved through a 2 mm sieve, analyzed and stored in a polythene bag for laboratory analysis.

Table 3: Coordinates of points where soil samples were collected

Location	Replicate	Cordinate
Riverbank	1	6.372510°N, 5.646845°E
Riverbank	2	6.372582°N, 5.646745°E
Riverbank	3	6.372659°N, 5.646662°E
60MRB	1	6.3709° N, 5.6506° E
60MRB	2	6.372623°N, 5.646612°E
60MRB	3	6.372467°N, 5.646612°E
120MRB	1	6.32062°N, 5.646252°E
120MRB	2	6.371958°N, 5.646452°E
120MRB	3	6.371932°N, 5.646683°E

MRB = meters from river bank

3.3.2 *Celosia argentea* sample preparation

C. argentea leaves was harvested from the crop, washed with water several times, washed with 0.2% detergent solution (2 g detergent in 1 L of water) to remove greasy or waxy particles/coating on leaf surface, washed with 0.1 M HCl followed by thorough washing with plenty water and finally double washed with distilled water. The leaves were dried with tissue paper and air dried on a perfectly clean surface at room temperature for 2 to 3 days in a dust free atmosphere. The leaves were oven dried at 70 °C for 48 hours grinded, sieved using 0.5 mm sieve, oven dried again for 1 hour to obtain constant weight, and stored in a paper bag for analysis.

3.4 Laboratory analysis

3.4.1 Particle Size Determination

This was determined using the Hydrometer method of Bouyocuos (1951) as modified by Day (1965). 51 g of the soil sample was weighed into a soil shaking bottle, 100 ml Sodium hexameta phosphate (calgon) was added and allowed to soak for 35 minutes to ensure dispersion. The mixture was stirred using a stirring rod, dispersed using a dispersing machine for 5 minutes and transferred into a 1000 ml sedimentation flask, made up to mark with distilled water and the soil particles were set in motion with the palm covering the sedimentation flask. The first hydrometer (H_1) and temperature (T_1) readings was taken after 40 seconds while the second hydrometer (H_2) and temperature (T_2) readings was taken after 2 hours, using the standard soil hydrometer with Bouyoucos scale in g/L and thermometer respectively. The first reading was used to calculate the percentage of clay and silt in the soil while the second reading was used to calculate the percentage of clay in the soil, according to the formula below:

%(Clay+ Silt) = $\frac{H1 \pm 0.3\ (T1 - 20°C) \times 100}{w}$

%Clay = $\frac{H2 \pm 0.3\ (T2 - 20°C) \times 100}{w}$

%Sand = 100% - % (Clay + Silt)

Where;

H_1= first hydrometer reading, T_1= first temperature reading, H_2= second hydrometer reading, T_2= second temperature reading, w =weight of soil sample used.

3.4.2 Textural Classification

Textural classification was determined using the textural triangle (soil survey staff, 2003).

3.4.3 pH in Water (1:2)

The soil pH (1:2) was determined in 1:2 soil to water suspension ratio, using a glass electrode pH meter (Tan, 1996). 10 g of the sample was weighed into an extraction cup, 20 ml water was added and the mixture was stirred intermittently with a stirring rod for 30 minutes. The pH meter was then inserted and the pH recorded.

3.4.4 pH in Calcium Chloride ($CaCl_2$)

The soil pH (1:2) was determined in 1:2 soil to Calcium chloride suspension, using a glass electrode pH meter (Tan, 1996). 10 g of the sample was weighed into an extraction cup, 20 ml of 0.01 M CaCl was added and the mixture was stirred intermittently with a stirring rod for a period of 30 minutes. The pH meter was then inserted and the pH recorded.

3.4.5 Soil Organic Carbon (OC)

The soil organic carbon (OC) content was determined by the wet oxidation method of Walkley and Black (1934). 1 g soil was weighed into a conical flask. 10 ml 0.167 M $K_2Cr_2O_7$ was added and swirled, 20 ml of concentrated H_2SO_4 was added and swirled for 1 minute to allow proper mixture and the mixture was allowed to cool for 30 minutes after which, 100 ml distilled water was added and the conical flask was swirled. 4 drops of ferroin complex indicator was added. The mixture was swirled and titrated against 0.5 N $FeSO_4.7H_2O$ to a dirty brown end point (T). Blank was prepared and titrated (B) following same procedure without soil. OC contents of the soil was calculated as;

$$\% \text{ OC} = \frac{(B-T)5\times 0.003F}{w} \times 100$$

Where;

B = blank titre value, T = sample titre value, F = correction factor, w = weight of soil

3.4.6 Exchangeable Bases

Exchangeable bases (Ca, Mg, Na, K) were extracted with 1 N ammonium acetate (1 N NH_4OAc), buffered at pH 7. 10 g of soil was weighed into an extraction cup. 100 ml of 1 N NH_4OAc was added and placed in a mechanical shaker for 1 hourr and filtered through Whatman No. 42 filter paper, from the filtrate, Na and K were read using flame photometer, while Ca and Mg were determined using EDTA Titration method.

3.4.7 Cation Exchange Capacity (CEC)

The cation exchange capacity (CEC) was determined by summation methods. CEC was calculated by summation of values of Ca, Mg, K and Na. (Udo *et al.,* 2009).

3.4.8 Exchangeable acidity (EA)

Exchangeable acidity was determined by extracting soils with 1 M KCl as reported by Juo (1979). 5 g of soil was weighed into a soil shaking bottle, 100 ml 1 M KCl was added, shaken for 1 hour and filtered using whatman No. 42 filter paper. 10 ml filtrate was measured into a conical flask, 5 drops of phenolphthalein was added, 50 ml distilled water was added, titrated against 0.01 M NaOH to a permanent pink endpoint end point, and the EA was calculated using the formula below;

$$\text{EA} = \frac{T \times M \times V1}{V2} \times \frac{100}{w}$$

Where:

EA = Exchangeable Acidity, T = titre value, M = molarity of acid used (0.01 M), V_1 = volume of extractant (100 ml), V_2 = final volume of extract used for titration (10 ml), W = weight of soil

3.4.9 Effective Cation Exchange Capacity (ECEC)

Effective Cation Exchange Capacity (ECEC) was calculated by summation of Exchangeable bases (CEC) and Exchangeable acidity (EA).

3.4.10 Base Saturation

Percentage base saturation was determined by the equation given below:

$$\% \text{ Base saturation} = \frac{Total\ exchangeable\ basic\ cation}{ECEC} \times 100$$

3.5 DETERMINATION OF HEAVY METALS IN SAMPLED SOIL

3.5.1 Preparation of Diethylene triamine penta acetic acid–Triethanol amine (DTPA-TEA)

DTPA-TEA extracting solution was prepared by dissolving 1.957 g diethylene triamine penta acetic acid (DTPA), 14.914 g triethanol amine (TEA) and 1.4702 g $CaCl_2.2H_2O$ in about 590 ml distilled water, the solution was mixed thoroughly and pH adjusted to exactly 7.30 using HCl before making up to 1 liter mark with distilled water (Behera, 2022).

3.5.2 Determination of Available heavy metals (Cd, Pb, and Ni)

Available heavy metals (Cd, Pb, and Ni) were extracted with diethylene triamine penta acetic acid-triethanol amine (DTPA-TEA) extractant according to the procedures described by Behera (2022). 10 g soil was weighed into a polyethylene bottle, 20 ml DTPA-TEA extracting solution was added and stoppered well, the content was shaken in a mechanical shaker for 120 minutes, filtered through Whatman No. 42 filter paper, the filtrate was analyzed for available heavy metals (Cd, Pb, and Ni), using Atomic absorption spectrophotometer (AAS), in central research Laboratory, University of Benin.

3.6 DETERMINATION OF HEAVY METALS IN *Celosia argentea* LEAVES SAMPLE

3.6.1 Preparation of di-acid

It involves digesting leaves samples with a mixture of two acid which include Nitric acid (HNO_3) and Perchloric acid ($HClO_4$) in a ratio for 9 to 4.

3.6.2 Digestion of *Celosia argentea* leaves sample

One gram of sample was weighed into a 100 ml cornicle flask, 10 ml di-acid was added and swirled, content was placed in a fume cupboard and heated continuously until the production of red $N0_2$ fume seizes and content was reduced to ¾ ml and become colorless, but was not allowed to dry up, it was cooled, made up to 100 ml mark with distilled water and filter through a Whatman no. 42 filter paper. Cd, Ni and Pd contents of the extract was read using the Atomic absorption spectrophotometer.

3.6.3 Determination of Heavy Metals in *Celosia argentea* (Lagos Spinach) leaves digest

The filtrate was analyzed for available heavy metals (Cd, Pb, and Ni) using Atomic Absorption spectrophotometer (AAS) Buck Scientific Model: VGP 210, in Central Research Laboratory, University of Benin.

3.7 Determination of relationship between Heavy metal content in soils and *C. argentea* leaf

The relationship between the Cd, Ni Pb content in soils and *C. argentea* leaves was determined by simple linear correlation.

3.8 Statistical Analysis

Data obtained from soil and C. *argentea* leaves analysis were statistically analyzed using the Genstat statistical package (12th edition), while Duncan Multiple Range Tests was used to separate means at 5% level of probability descending order.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Physical and Chemical Properties of Soils Around Temboga Riverbank

Sand was the dominant soil fraction and had some value of 834 g/kg for Riverbank (RB), 60m away from Riverbank (60 MRB) and 120 m away from Riverbank (120 MRB), and had same value of 834 g/kg. Silt content of the soils increased slightly with values of 57.8 g/kg, 63.4 g/kg and 67.6 g/kg for RB, 60 MRB and 120 MRB respectively (Table 4). While clay was slightly inconsistent but we're not significantly different amongst the distances away from Riverbank. Values of 108.2 g/kg, 102.6 g/kg and 98.4 g/kg clay were obtained for RB, 60 MRB and 120 MRB respectively. It was observed that the various soil separates (Sand, Silt and clay) where not significantly different amongst the various distances away from the RB. The textural classification of the soils across the three distances (RB, 60 MRB and 120 MRB) were loamy sand.

High value of sand content at the RB observed in this study aligns with the findings of Nwosu (2018), and could be due to sediment deposition where flowing water carries soil particles and deposit them along the RB. The pH (H_2O) of the soil was significantly different with distances from riverbank and had values of 5.55 (moderately), 5.99 (slightly) and 6.5 (slightly) acidic for RB, 60 MRB and 120 MRB respectively. The moderately and slightly acidic pH range obtained for soils around Temboga Riverbank found in this study aligns with the findings of Belay *et al,* (2023). Organic carbon content ranges between 27.5 g/kg (120 MRB) and 34.2 g/kg (RB) could be said to be very high when compared to greater than 20 g/kg reported by Chude *et al.,* (2011).

Table 4: Some Physical and Chemical Properties of Samples Collected

Location	Sand	Silt	Clay	TC	pH	pH	OC	TON	Ca+Mg	EA
	———	g/kg	———		(H_2O)	($CaCl_2$)	——	g/kg ——	——	cmol/kg——
RB	834.00a	58.7a	108.2a	LS	5.55c	5.01c	34.2a	1.70a	0.1b	0.37a
60MRB	834.00a	63.4a	102.6a	LS	5.99b	5.41b	33.4a	1.70a	0.26a	0.29a
120MRB	834.00a	67.6a	98.4a	LS	6.51a	5.92a	27.5a	1.40a	0.34a	0.4a
Mean	834.00	62.9	103.1	-	6.02	5.45	3.17	0.16	0.23	0.36
cv	2.0	16.8	12.4	-	3.1	2.0	29.4	29.4	33.3	40.7
SEM	0.95	0.61	0.74	-	0.11	0.06	0.54	0.03	0.04	0.08
SED	1.35	0.86	1.04	-	0.15	0.09	0.76	0.04	0.06	0.12

RB = river bank, MRB = meters from river bank, TC = Textural classification, OC = Organic carbon, TON = Total Organic Nitrogen, EA = Exchangeable Acidity, LS= Loamy sand, means with the same alphabets within columns are not significantly different at $p \leq 0.05$, using Duncan Multiple Range Tests.

Higher organic content of 34.2 g/kg and 33.4 g/kg obtained at RB and 60 MRB could be due to deposit of organic materials from the river and the use of organic manure by farmers raising vegetables around the RB soils observed. Total organic nitrogen (TON) content of 1.70 g/kg was obtained for soils of RB and 60 MRB while 120 MRB had values of 1.40 g/kg. However significant differences were not observed amongst the soils around the RB. These trends of TON could be due to the influence of organic carbon on nitrogen in line with the findings of Emomu *et al.* (2022), they reported higher nitrogen content in soils containing higher organic carbon levels. Exchangeable acidity (EA) characteristics of the soils were not significantly different from RB, 60 MRB and 120 MRB respectively.

4.2 Heavy Metals content of Soils grown around Temboga Riverbank

The result show that the different soil heavy metals (Ni, Pb and Cd) levels studied at Riverbank (RB), 60 meter away from Riverbank (60MRB) and 120 meter away from Riverbank (120 MRB) varied with distances away from the riverbank but was not significantly different from one another (Table 5). However, Cd contents of the soils were 0.14 mg/kg at RB, 0.19 mg/kg at 60 MRB and 0.09 mg/kg at 120 MRB. The levels of soil Cd where within critical value of 0.01-0.70 mg/kg reported by Allaway, (1968). The Ni content of the soil were 0.06, 0.70 and 0.07 mg/kg at RB, 60MRB and 120MRB respectively, which could be said to be very low in the soil when compared to the critical levels of 10-100 mg/kg reported by Allaway, (1968). Orhue *et al.* (2025), have earlier reported Ni and Pb level to be within tolerance level in soils around Temboga Riverbank.

Table 5: Heavy Metal Contents (Cd, Ni, Pb) of Soils Grown Around Temboga Riverbank

LOCATION	Cd mg/kg	Ni mg/kg	Pb mg/kg
RB	0.140a	0.0607a	0.267a
60MRB	0.193a	0.0653a	0.213a
120MRB	0.093a	0.0680a	0.233a
Mean	0.142	0.0647	0.238a
cv	32.8	5.6	16.0
SEM	0.0269	0.00211	0.0219
SED	0.0381	0.00298	0.0310

means with the same alphabets within columns are not significantly different at $p \leq 0.05$, using Duncan Multiple Range Tests, RB = river bank, MRB = meters from river bank.

4.3 Heavy Metal Content of *Celosia argentea* Leaves Grown Around Temboga Riverbank

The result (Table 6) showed that heavy metal (Cd, Ni and Pb) levels varied in *C. argentea* leaves grown around the RB, although significant statistical differences were not observed amongst *C. argentea* leaves grown at RB, 60MRB and 120MRB. Cd levels of 0.167 mg/kg, 0.267 and 0.167 mg/kg was obtained in *C. argentea* leaves grown at riverbank, 60MRB and 120MRB respectively. The Cd content of the *C. argentea* could be said to be within tolerance levels when compared with critical values of 0.2 – 0.8 mg/kg Cd reported by Allaway 1968. The low Cd content of *C. argentea* leaves could be due to selective absorption by the growing *C. argentea*. However, the low Cd content levels found in *C. argentea* grown around RB is in line with the findings of Kihampa and Nwegoha (2010), who reported low Cd content in vegetables grown around riverbanks.

The Ni content of *C. argentea* leaves had the same value of 2.883 mg/kg at RB and 60MRB and decreased slightly to a value of 2.717 mg/kg at 120MRB. The Ni content of *C. argentea* at the RB and surrounding soils could be said to have reached toxic levels when compared with critical values of 1.00 mg/kg Ni reported by Allaway 1968. The toxic levels of Ni in the *C. argentea* leaf could be due to excessive absorption from the soils. Toxic levels of Ni in *Telfaria occidentalis* leaf grown around the study area have been reported (Orhue *et al*., 2025). Lead content of *C. argentea* was observed to have the same value of 0.167 mg/kg at RB and 60MRB but increased to 1.300 mg/kg at 120MRB, although significant statistical differences were not observed amongst the various locations around the riverbank. These values obtained for Pb in *C. argentea* leaf, could was within tolerance level when compared with critical values of 0.1-10 mg/kg Pb (Allaway, 1968). Similar levels of Pb found in *Telfaria occidentalis* have been reported by Orhue

Table 6: Heavy metal contents of *C. argentea* Leaves grown around Temboga Riverbank

Location	Cd	Ni	Pd
		mg/kg	
RB	0.167a	2.883a	1.167a
60MRB	0.267a	2.883a	1.167a
120MRB	0.167a	2.717a	1.300a
Mean	1.200	2.828	1.211
cv	24.8	8.7	14.6
SEM	0.1716	0.1427	0.1018
SED	0.2427	0.2018	0.1440

RB = riverbank, MRB = meters from river bank, cv = coefficient of variation, SEM = standard error of means, SED = standard error of difference, means with the same alphabets within columns are not significantly different at ($p \leq 0.05$), using Duncan Multiple Range Tests.

et al. (2025), when they reported bioaccumulation of heavy metals in soils and *Telfaria occidentalis* leaf grown around a riverbank and dumpsite. The lower content of Ni in *T. occidentalis* leaf reported by Orhue *et al.* (2025), compared to higher content of Ni in *C. argentea* leaf found in this study is an indication of higher tendency of *C. argentea* to absorb Ni compared to *T. occidentalis* reported by Orhue and colleagues.

4.4 Relationship between heavy metals in Soil and *C. argentea* Leaf

The result showed that heavy metals (Cd, Ni and Pb) in soils and *C. argentea* leaf were both positively and negatively related although, no statistical significance was detected (Table 7). Cd showed negative relationship between soil and *C. argentea* leaves at 60MRB ($r = -0.528$, $p \leq 0.05$) and 120MRB ($r = -0.082$), while Ni also showed negative relationship between soil and *C. argentea* leaf at 60MRB ($r = 0.500$) and 120MRB ($r = 0.982$). Pb content in soil and *C. argentea* only had negative relationship at 120MRB (-0.7206). Several authors have reported significant relationship between heavy metal content in soils and vegetables grown around riverbanks (Emurotu and Onaiwu, 2017; Orhue *et al.*, 2025).

Table 7: Relationship Between Heavy Metals In Soils and *C. argentea* leaves

LOCATION	Cd	Pb	Ni
RB	0.9820	0.5000	0.9948
60 MRB	-0.528	0.1429	-0.500
120 MRB	-0.082	-0.7206	-0.9820

RB = river bank, MRB = meters from river bank

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The study showed that the soil texture around the RB, 60MRB, 120MRB were loamy sand with sand constantly decreasing and clay increasing with distances away from the RB. However, the chemical properties studied were within levels suitable for crop production. The heavy metal content of the soils around the RB varied with distances away from the RB, although statistical difference was not observed amongst the heavy metal content around the RB. However, the level of Cadmium in the soils were within critical values reported in literature while Ni and Pb content of the soil were within tolerance levels for crop production.

The Cd, Ni and Pb content in *C. argentea* leaf grown around the RB varied with distances from the RB. The Cd content of *C. argentea* leaf of 0.167 mg/kg at RB and 120MRB and Pb content of *C. argentea* leaf of 1.167 mg/kg at RB and 60 MRB were within tolerance levels indicating *C. argentea* leaves were not contaminated with Cd and Pb. However, the Ni content of 2.88 mg/kg obtained for *C. argentea* leaf in RB and 60MRB and 2.72 mg/kg at 120MRB have reduced toxic levels indicating that Celosia leaves grown around the RB is contaminated with Ni and hence not fit for consumption by humans who regularly consume vegetables grown around the RB. Toxic levels of Ni found in *C. argentea* around the RB might have been absorbed from the soils around the RB.

The positive and negative relationship between some soil properties and Cd, Ni and Pb is an indication of the influence of soil properties on heavy metals bioaccumulation by plants growing around contaminated soils, although no significant difference was observed.

5.2 Recommendations

1. Regular monitoring and assessment of heavy metal contents in soils and vegetables grown around Temboga riverbank, is recommended to prevent excessive accumulation of heavy metals such as; Cd, Ni and Pb, in soil and vegetables grown around Temboga riverbank, which can pose health risks to humans and the environment.
2. There should be a check and regulation, on consumption of *C. argentea* grown around Temboga Rivebank as it has been found to contain toxic levels of Nickel.

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