

**HEAVY METALS CONCENTRATION OF AMARANTH
(*Amaranthus cruentus*) RAISED ON DUMP SITE
SOILS IN BENIN CITY**

BY

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AGR1700312

**DEPARTMENT OF SOIL SCIENCE AND LAND
MANAGEMENT**

FACULTY OF AGRICULTURE

UNIVERSITY OF BENIN

BENIN CITY

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

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AWARD OF BACHELOR OF AGRICULTURE DEGREE B. AGRIC. (SOIL
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OCTOBER, 2023

CERTIFICATION

This is to certify that this research project “**HEAVY METALS CONCENTRATION OF AMARANTH (*Amaranthus cruentus*) RAISED ON DUMP SITE SOILS IN BENIN CITY**” was carried out by **Peace Oghenekeno EDEGWARE** of the Department of Soil Science and Land Management, Faculty of Agriculture, University of Benin City, Edo State, Nigeria.

MR. E.O. AIRUEGHIAN
Project Supervisor

Signature and Date

Dr. (Mrs) A.O. Bakare
Head of Department

Signature and Date

DEDICATION

To Almighty God for his divine guidance. To my beloved mother for her boundless love and support. To my late father whose memory lives on in my heart. I dedicate this work as a tribute to your wisdom, values.

ACKNOWLEDGMENT

Foremost, I acknowledge the Almighty, God, whose divine guidance and blessings have been the foundation of my journey throughout this academic endeavor.

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ABSTRACT

This experiment was conducted in the green house of the Department of Soil Science and Land Management, Faculty of Agriculture, University of Benin, Benin City. The aim of the study was to ascertain the heavy metal (Pb, Cd, Cr and As) contents of *Amaranthus cruentus* raised on soils from dumpsites from different land uses in the University of Benin. The experiment was laid out in a Completely Randomized Design (CRD) with three replicates. Six different dumpsites were carefully selected in the Ugbowo campus of the University of Benin, three from learning centers and the other three from residential areas (students hostel). Soils collected from the dumpsites were filled into buckets and *Amaranthus* seeds were planted in them, and harvested at maturity. Soil and plant samples were taken to the laboratory to determine the physicochemical characteristics and heavy metal content present. Data obtained were subjected to Analysis of Variance (ANOVA) while LSD was used to separate means at 5% level of probability. Results obtained shows that soils from the dumpsites belong to the textural class: sand. Their pH was moderately acidic and their TOC contents were 19.60 and 21.50 g/kg in the Learning center and Residential area respectively. The heavy metal studied were present in both soils, and there was no significant difference between the heavy metal content across the two dumpsites. The peak lead (Pb) content (1.30 mg/kg) was obtained in the learning center while the peak Cd, Cr, and As contents (0.037 mg/kg, 0.040 mg/kg and 0.040 mg/kg respectively) were recorded in the residential area. The contents of the heavy metals in the soil were below their standard permissible limits. Similarly, the highest Pb (0.083 mg/kg) content in plant (*Amaranthus*) was found in learning center. Pb in *Amaranthus cruentus* from the learning center was above the permissible standard and is a potential health risk. While the other heavy metals (Cd, Cr and As) had their highest values in *Amaranthus cruentus* planted on soils from residential area. Their values (0.033 mg/kg, 0.017 mg/kg and 0.013 mg/kg) were below the standard permissible limit and did not pose any health risk.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Solid waste management has remained an intractable environmental sanitation problem in Nigeria. This problem has manifested in the form of piles of indiscriminately disposed heaps of uncovered waste and illegal dumpsites along major roads and at street corners in cities and urban areas, this problem is compounded by rapid urbanization and population growth which have led to generation of enormous quantities of solid waste which are often discarded by open dumping (Uwakwe, 2017). Poor waste management poses a great challenge to the well-being of city residents, particularly those living around the vicinity of the dumpsites due to the potential of the waste to pollute water, food sources, land, air and vegetation. The poor disposal and handling of waste thus leads to environmental degradation, destruction of the ecosystem and may cause great risks to public health. The resultant accumulation of waste poses a health hazard to urban inhabitants, and also threatens the surrounding environment (UNEP, 2020). Wastes from agriculture and industries can also cause serious health risks. Other than this, co-disposal of industrial hazardous wastes with municipal wastes can expose people to chemical and radioactive hazards. Uncollected solid waste can also obstruct stream water runoff, resulting in the formation of stagnant water bodies that become breeding grounds for disease causing organisms. Wastes dumped near a water source also cause contamination of the water body or the ground water source. The direct dumping of untreated wastes in land fills rivers, seas and lakes result in the accumulation of toxic metals and organic pollutants in man through the food chain (Medina, 2022). This clearly shows how waste disposal seriously affects the health of

residents located closer to dumpsites. The smelly and unsightly conditions of dumpsites are worse in dry season, because of extreme temperatures, which speed up the rate of bacterial action on biodegradable organic material. Disposal of solid wastes on land without careful planning and management can present a danger to the environment and the human health (USEPA, 2022).

Like many cities in South-South Nigeria, Benin City in Edo State faces problems of environmental sanitation such as improper disposal of refuse near residential areas; poor refuse collection and handling, it is common to find huge refuse dumpsite within residential areas and farmers use them as fertilizers. This however, leads to accumulation of heavy metals in plants grown on dumpsite soils or fertilised with dumpsite manure, which on subsequent transfer through food chain end up in man, posing potential health risk.

The rise in population and civilization in Benin metropolis has increased the number of dumpsite due to poor waste management schemes, thereby contaminating the environment. It is based on these facts that this study is aimed at determining the total concentration of heavy metals of *Amaranthus cruentus* raised on dumpsite soil in Benin metropolis, Edo State, Nigeria.

1.2 Aim and Objectives

The aim of this work was to determine the heavy metals concentration of amaranth (*Amaranthus cruentus*) raised on dump site soils in Benin City. The specific objectives were to determine:

- (i) Gravimetric and chemical properties of soil samples collected from dumpsites in Benin City, Edo State, Nigeria;
- (ii) The concentrations of heavy metals in amaranth (*Amaranthus cruentus*) raised on dump site soils in Benin City.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Soil Pollution

Soil is an important natural resource to man, as it serves as one of the main source of agricultural production. However, anthropogenic activities such as agricultural practices, industrial operations and waste disposal methods causes soil pollution ensuing the release of toxicants in the soil, which invariably affects soil health and crop production (Zukowska and Biziuk, 2018). Materials that find their entry into the soil system, persist and accumulate in toxic levels, hence becoming heavy metals in the soil. These heavy metals include, iron, lead, zinc and cadmium. The concentration of these heavy metals in soil and their impact on ecosystems varies and it is influenced by factors such as the parent rock, climate and anthropogenic activities (Jia *et al.*, 2020).

2.2 Heavy Metals

Heavy metals are defined as metallic elements that have relatively high density and is toxic at low concentrations (Tchounwou *et al*, 2012). They are common pollutants in the soil environment, namely arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni). Their type of contamination is biologically toxic, widely distributed, and persists long-term in soil environment (Zhao, *et al*, 2020). They are also regarded as agricultural soil contaminants because if present at high levels in the soil, they negatively impact crop health, growth and productivity. Heavy metals are known to be the bane of soil and crop productivity as they are recalcitrant to degradation, and if not taken up by plants or removed by leaching, they can accumulate in the soil and persist for long periods (Rashid *et al*,

2023). When heavy metals accumulate to toxic levels in agricultural soils, these non-decomposable elements adversely affect crop's agronomic performance. They disrupt the normal structure and function of cellular components in plants/crops and impede their various metabolic and developmental processes (Rai *et al*, 2019). The toxicity of heavy metals on crops depends upon factors such as crop type, growth condition, and developmental stage. Also, the nature of toxicity of the specific elements involved, soil physical and chemical properties; occurrence and bioavailability of heavy metal ions in the soil solution; and soil rhizosphere chemistry (Rashid *et al*, 2023). Globally, heavy metal contamination is a serious issue especially in developing countries, as results of rapid urbanization, increased industrial operations, alongside municipal, agricultural, and domestic activities. Also, the lack of awareness on the toxic consequences of these elements to soil and crop health adds to its rapid proliferation and distribution (Jarup, 2003).

2.3 Heavy Metal contamination

Heavy metal contamination is described as the presence and accumulation of toxic heavy metals in the soil beyond natural levels which can be harmful to soil health and environment (Bose and Hemantaranjan, 2015). Heavy metal contamination is regarded to be common in dumpsites, and its widespread distribution has received the attention of researchers all over the world, mainly due to their harmful effects on the environment, crops and soil health (Misra and Mani, 2019). Alma *et al*. (2020) in a study conducted on two plant species grown at three different stations, indicated that heavy metals enter the biological cycle through the roots and leaves of plants and are enriched in various plant organs. They directly affect the growth of plants, and also increases the level of the element in the plant. An excess dietary intake of contaminated plants could also be dangerous to the health of humans and animals; due to the fact that the chemical composition of plants reflects almost the elemental composition of the soil. Elaigwe, (2017) carried out the

biomonitoring of vegetables and reported that farming in dumpsites – which is common in developing nations – has a negative impact on human health due to high concentration of trace metals in plants grown from the environment which subsequently enters the food chain.

Adeleken and Abegunde (2021) noted that heavy metals have low environmental mobility, as a result of this a single contamination could set a stage for a long term exposure of heavy metals to human, microbial, fauna, flora and other edaphic communities. The mobility, bioavailability and liability of some heavy metals in soils around automobile waste dumpsites in Northern part of Niger Delta were assessed by Osakwe and Otuya (2018) using Tessier *et al.* (1968) five step sequential chemical extraction procedure. The results showed that the mobility factors for the metals in all the sites ranged from 20.37 - 90.90 for cobalt, 15.83 - 62.07 for nickel, 25.50 - 60.43 for manganese and 16.49 - 32.13 for iron, following the order: Co > Ni > Mn > Fe.

2.4 Heavy Concentration in Dumpsites

Dumpsites are typically where levels of heavy metals are most concentrated. Assessment of the levels of copper, zinc and lead in soils and vegetation around solid waste dumpsites in Port Harcourt and environs were carried out in 2005 using atomic absorption spectrophotometry. Physical parameters such as pH and particle size were also determined. The results show that the mean concentrations of copper in transect and profile soils and vegetation were 1.20 ± 0.83 mg/kg, 2.57 ± 1.87 mg/kg, 1.48 ± 1.61 mg/kg respectively at the East – West road dumpsite and 2.42 ± 1.87 mg/kg, 1.40 ± 0.61 mg/kg, 1.39 ± 0.67 mg/kg respectively at the Kaduna/Afam street dumpsite. The mean concentrations of zinc in soil and vegetation along the transect were 12.83 ± 4.65 mg/kg, 2.68 ± 1.82 mg/kg, 1.33 ± 0.64 mg/kg, 0.80 ± 0.60 mg/kg respectively at the Kaduna/Afam street dumpsite. The mean concentrations of lead in the soil and vegetation were

0.26 ± 0.21 mg/kg, 0.28 ± 0.24 mg/kg, 1.48 ± 0.12 mg/kg respectively at the East – West road dumpsite and 0.45 ± 0.37 mg/kg, 0.20 ± 0.08 mg/kg, 0.39 ± 0.17 mg/kg respectively at the Kaduna/Afam street dumpsite.

The order of occurrence of the heavy metals in the top soils of the study areas was Zn > Cu > Pb. The levels of copper and zinc in soils from the waste dumpsite were significantly different ($P < 0.05$) from soil sample elsewhere. The differences in the levels of copper, zinc and lead in soils and vegetation's as well as dumpsite and outside dumpsite were not significant ($P < 0.05$). The results indicate that solid wastes contributed to the levels of heavy metals in soils and vegetation. Also the concentrations of the metals in soils do not depend on the age of the dumpsite rather it depends on the source, composition and the topography of the dumpsite (Ideriah *et al.*, 2015).

A study of speciation of Cu, Cd, Pb, Ni, Zn, Mn, Fe, Cr and Hg was carried out by Olanipekun and Fagbote (2020) on soils of Agbabu, Nigeria, using sequential extraction procedure with atomic absorption spectroscopy. From the results obtained in the two seasons, most of the metals had high abundance in the residual fractions indicating lithogenic origin and low bioavailability of the metals considered. The average potential mobility for the metals studied in the two seasons gave the order: Zn > Cr > Cu > Mn > Cd > Fe > Ni > Pb > Hg (Olanipekun and Fagbote, 2020).

Study on the effect of leaching of heavy metals at dumpsites was conducted by analyzing samples of soil collected from different dumpsites located within Ikere and Ado Ekiti metropolis, South Western Nigeria. The samples were analyzed for concentrations of Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni, Sn and Zn. The results of the analyses showed a significant difference in the concentration of these metals from the centre of each dumpsite at interval of 10 – 70 m down the

slope ($p < 0.05$). The dumpsites were found to contain significant amount of toxic heavy metals (Awokunmi *et al.*, 2020).

Geochemical implication of heavy metals was evaluated on groundwater surrounding a municipal solid waste dumpsite at Olusosun waste disposal site in Lagos. Twenty groundwater samples and a leachate were investigated around the dumpsite and analysed. The results revealed dominance of Pb, Fe and, Mn when compared with to WHO and SON standard, while all the metals were found to be high in the leachates. Contamination assessment revealed that Fe and Pb extremely contaminated the groundwater, while geoaccumulation factor showed that farther away from the dumpsite the contamination reduced significantly. Pb, Mn, Fe found to be from anthropogenic source and their levels correlated significantly Pb - Cd (0.84), Mn - Pb (0.90), Fe - Cd (0.76). Thus, if the levels of Pb, Fe and Mn is not checked it could lead to major health problems like tooth decolouration, low mental development and kidney problems in the populace (Laniyan *et al.*, 2021).

Study was carried out by Odukoya *et al.* (2015) to assess the trace element concentrations in soils of active and abandoned dumpsites in Lagos, Nigeria. Thirty-six trace and rare earth elements were analysed in the soil samples using Inductively Coupled Plasma Mass Spectrometry. From the results, only Pb, Cd, Zn, Cr, Cu, As, Mo and Mn were at significant amounts for both active and abandoned dumpsites. Geo accumulation index showed that soil samples were within low to moderate contamination with As, Cr, Mn, Mo, and Fe while Cd, Pb, Zn and Cu were in the class of moderate to strong contamination for all the samples.

Waste dumpsites can transfer significant levels of toxic and persistent metals into the soil environment (Udosen *et al.*, 2016). These metals are taken up by plants and transferred into the

food chain (Benson and Ebong, 2015). Cultivated plants take up these metals either as mobile ions in the soil solution through their roots (Udosen *et al.*, 2016) or through their leaves thereby making them unfit for human consumption (Yusuf *et al.*, 2013). Consequently, higher levels of heavy metal in soil can result to higher uptake level by plants (John *et al.*, 2019). The rate of metal uptake by a plant could be influenced by factors such as metal species, plant species, plant age and plant part (Singh *et al.*, 2020).

2.5 Effects of Heavy Metals on the Soil

Various physical and chemical techniques were used to investigate the characteristics and heavy metal concentration of soils in some selected waste dumpsites in Port Harcourt (David *et al.*, 2019). The results showed that the soils are moderately acidic with a mean pH value of 5.5 for the 1 m subsoil and 5.8 for 30 cm soil depth in the various dumpsites. In addition, the total organic carbon (TOC) levels of the soil was low with 3.41% and 2.90% for depths 30 cm and 1 m respectively. The cation exchange capacity (CEC) of the soils had the range 21.36 – 28.79 meq/100g for a depth of 30 cm and 20.94 – 26.44 meq/100g for the depth 1m soil across the dumpsites. The textural class of the soils was observed to be a mixture of sand, clay and loam in all the sites. Low sand fractions (> 40%) was observed for almost all the sites except for Elekahia and Eleme roads that had 64.7% and 56.4%, respectively. The results of the heavy metal concentration in all the locations of the dumpsites were above the permissible limits set by World Health Organization (2020). However, in this study the soil did not meet up with the moisture requirement for a waste land filling and could therefore be prone to porosity, surface flooding and underground water pollution. The use of impermeable geo-membrane is suggested to minimize seepage of leachates from causing pollution of both surface and groundwater resources (David *et al.*, 2019)

Heavy metals affect the pH of the soil, where soils with elevated levels of heavy metals tend to have lower pH and soils less level of heavy metals have higher ph. Furthermore, with increasing pH, the solubility of most metals decreases due to their increased adsorption (Takac *et al.*, 2019). pH is generally acknowledged to be the principal factor governing concentration of soluble and plant available metals (Brallier *et al.*, 2021). Metal solubility tends to increase at lower pH and decrease at higher pH values (Garcia *et al.*, 2019).

2.6 Effects of Heavy Metals on Crop Production

Study of heavy metals in the abandoned Isolo dumpsite soil and *Amaranthus cruentus* planted on the dumpsite soil indicated that the concentration of heavy metals in *Amaranthus* at the dumpsite and the control were: Pb (35.00 and 23.68 mg/kg); Zn (8.70 and 4.00 mg/kg); Cu (7.68 and 4.34 mg/kg); Cr (0.08 and 0.05 mg/kg) and Fe (98.00 and 24.50 mg/kg) respectively. Also, the concentrations of heavy metals in the tomato planted at the dumpsite were: Pb (46.75 mg/kg); Zn (85.64 mg/kg); Cu (13.35 mg/kg); Cr (0.25 mg/kg) and Fe (86.94 mg/kg). The levels of heavy metals in the dumpsite soil and the soil after harvesting the tomato plant were: Pb (127.50 and 56.75 mg/kg); Zn (157.60 and 65.80 mg/kg); Cu (27.60 and 12.25 mg/kg); Cr (3.60 and 1.50 mg/kg) and Fe (785.50 and 653.75 mg/kg) respectively. The *Amaranthus* species on the dumpsite soil were found to accumulate more heavy metals than that of the control. The level of heavy metal in the dumpsite soil decreased drastically after harvesting the tomato plant (Oyelola *et al.*, 2019).

Okoronkwo *et al.* (2016) carried out the risk and health implications of metals in polluted soils used for crop production. The results of the analysis showed heavy metal contaminations of the dumpsite soils. The study concluded that there is higher risk of exposure of the consumer to

heavy metals due to plant uptake of these toxic elements from polluted soils, abandoned waste dumpsite soil and any other form of polluted soil for agricultural purposes. Of all the five heavy metals studied by Okoronkwo *et al.* (2016), the highest mean concentration (mgkg^{-1}) was 133.74 ± 10.60 recorded for Pb followed by 22.27 ± 3.03 for Cr, 8.14 ± 0.33 for Ni and 5.97 ± 0.32 for As in the soils; while the least mean concentration of 1.64 ± 0.11 was recorded for Cd. Sand, organic matter and cation exchange capacity (CEC) correlated significantly and positively with Cr and Pb, indicating that these factors largely control the concentration of these elements in the soils.

2.7 Effect of Heavy Metals on Amaranth

Amaranth is a genus of annual herbs belonging to the family *Amaranthaceae* (Stephens, 2019). It consists of 60–70 species (Xu and Sun, 2019) and include at least 17 species with edible leaves and three grain amaranths grown for their seeds (Grubben and Denton, 2020). Although, several species are often considered weeds, people around the world and in Nigeria value amaranths as leafy vegetables (Trucco and Tranel, 2019). The local names in Nigeria are *alayyafoo* in Hausa, *efoo* in Yoruba, *imine olu* in Igbo and *Ebe afor in* Edo. Contemporarily, there is no distinct separation between all the types of amaranth since the leaves of their young plants can be eaten as both human and animal food (Muyonga *et al.*, 2018; Yarger, 2018). They are very good sources of vitamins, protein and dietary minerals including calcium, iron, magnesium, phosphorus, potassium, zinc, copper and manganese (Ofitserov, 2018). They are regarded as important source for food, feed and raw materials for the agri-system value chain. According to Onyango (2020), improvement of amaranths through research and development could produce an easy and cost-effective way of eliminating malnutrition and promoting people 's health as well as achieving food security. However, due to the proliferation of irregular dumpsites,

especially in the south-south region of Nigeria, the capacity for adequate production of quality leafy vegetables such as Amaranth is on decline (Okpara *et al*, 2021). An assessment of the uptake of heavy metals by *Amaranthus cruentus* grown on abandoned dumpsites in Effurun, Nigeria showed that the soil samples exhibited high levels of the heavy metals Zn(59-214), Pb (0.9-4.2), Cu (301-714), Fe (712-2186), Ni (7.1-14.9) and Hg (0.61-1.14) expressed in mg/kg dry weight basis, while parts of the plant showed low concentrations, with leaves having the highest levels of Zn, Cu, Fe, and Ni, stem contain the highest levels of Pb and Hg and the fruit had a low safe limits. The study provided nutritional data on heavy metal composition *Amaranthus cruentus* grown on abandoned dump sites and serves as a pathway for investigating how such elements enter the food chain and will finally be ingested by humans (Akpofure, 2021). The toxic and detrimental impacts of heavy metals become apparent only when long-term consumption of contaminated vegetables occur.

Summarily, the problem of heavy metal pollution is not going to disappear overnight. On the contrary it will remain a legacy of mass industrial activity for many generations and is likely to escalate further in the future (Shrivastav, 2021). In this regard, the compilation of past and present catalogues of heavy metal concentration is an activity of great importance, alongside continual research on the effects to crop production.

2.8 Effects of Some Heavy Metals on the Environment

2.8.1 Lead

Lead (Pb) is a well-known neurotoxin. Impairment of neurodevelopment in children is the most critical effect of lead poisoning. Exposure in the uterus, during breastfeeding and in early childhood may all be responsible for the effect. Lead accumulates in the skeleton and its transfer

from bones during pregnancy and lactation causes exposure to fetuses and breastfed infants (ATSDR, 2017). Chronic exposure to Pb can affect physical growth and cause anemia, kidney damage, headache, hearing problems, speaking problems, fatigue or irritable mood (Simeonov *et al.*, 2020). The toxicity by Pb has multiple biochemical effects. It has the ability to inactivate enzymes, compete with calcium for incorporation into bones and interfere with nerve transmission and brain development (Ediin *et al.*, 2020). It has been suggested that lead on a cellular and molecular level may permit or enhance carcinogenic events involved in DNA damage, DNA repair and regulation of tumor suppressor and promoter genes (Silbergeld, 2020).

The common sources of lead are car batteries, tyre materials, coals, plastics and insecticides. The high level of Pb in soil, could be attributed to Pb from car exhaust fumes, derived from leaded petrol (Alloway, 2019). The main sources of Pb in the environment include, dust from leaded paints of older houses, leaded gasoline and tap water from soldered pipes (Ediin *et al.*, 2000). The maximum allowable limits of lead in the soil in UK and USA are 100 mg/kg and 200mg/kg respectively (Mamtaz and Chowdhury, 2016), while it is 0.05 mg/kg in Nigeria (FEPA, 2019).

2.8.2 Cadmium

Cadmium (Cd) is a heavy metal characterised by high mobility in biological systems. It is emitted to the atmosphere in combustion processes, mainly in the form of oxides (Wieczorek *et al.*, 2014). Cd uptake by plants is partly limited by presence of calcium, phosphorus and chelating compounds in the soil (Wieczorek *et al.*, 2014). Cadmium has atomic number of 48, atomic mass 112.4, density 8.7gcm⁻³, melting point 321°C and boiling point 767°C. The metal is a lustrous, silver-white, ductile, very malleable metal. It is soluble in acids, but not in alkalis. It is usually found as a mineral combined with other elements such as oxygen as cadmium oxide,

chlorine as cadmium chloride, or sulphur as cadmium sulphate and cadmium sulfide (Schult-Schrepping and Piscator, 2020). The sources of Cd in the environment include: mining and smelting of metal ores, fossil fuel combustion and also phosphate fertilizers (Challa and Kumar, 2019). Cd is used in the production of Nickel-Cd rechargeable batteries when this is deposited in sewage sludge, it raises the levels of Cd in the environment (Challa and Kumar, 2019). Farming practices such as tobacco growing also increases the level of Cd in the environment, as tobacco is known to accumulate Cd in its tissues (Selinus and Alloway, 2015). The sources of Cd in the urban areas are much less well defined than those of Pb, but metal plating and tire rubber are considered the likely sources of Cd (Jaradat and Momani, 2019). Cd is also found in lubricating oils as part of many additives and car tyres as a result of the vulcanization process. The industrial activities; the metal is widely used in electroplating, pigments, plastics, stabilizers and battery industries (Mehbrahtu and Zebrabruk, 2021). Cd is highly toxic and responsible for several cases of poisoning through food. Small quantities of Cd cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures and kidney damage (Mehbrahtu and Zebrabruk, 2021). The recommended concentration of cadmium in soil is 3kg/mg (EU, 2019).

2.8.3 Chromium

The most common forms of chromium are chromium (VI) and chromium (III) (Hilgenkamp, 2016). Although chromium toxicity in the environment is rare. It still presents some risks to human health since chromium can be accumulated on skin, lungs, muscle, fat, in liver, dorsal spin, hair, nails and placenta where it is traceable to various health conditions (Adeleken and Abegunde, 2021).

The health effects brought about by the exposure to chromium (VI) include lung cancer, malignant neoplasia, chromium dermatitis and skin ulcers (Sarkar, 2015). Perforations and ulcerations of the nasal septum and bronchial asthma have also been reported. In one of the studies, a four-fold increase in childhood leukemia was attributed to possible consumption of water with chromium (VI) levels above standard recommended value of 300 mg/kg (Sarkar, 2015). The sources of chromium in the environment include, cement, leather, plastics, dyes, textiles, paints, printing ink, cutting oils, photographic materials, detergents, wood preservatives among others (Hilgenkamp, 2016). Other sources of chromium are power plants, liquid fuels, brown and hard coal and industrial and municipal wastes. Non biodegradability of chromium is responsible for its persistence in the environment and once mixed with soil, it undergoes transformation into various mobile forms before ending into environmental sink (Adeleken and Abegunde, 2021). The maximum allowable limit of chromium in the soil set by United Kingdom is 300 mg/kg (EU, 2019) while the limit set by FEPA (2019) is 0.03 mg/kg in Nigeria.

2.8.4 Nickel

Nickel is an essential trace element in animals, although the functional importance of nickel has not been clearly demonstrated. However, there is evidence of uptake and accumulation in certain plants. Nickel deficiency is manifested primarily in the liver. Its effects include abnormal cellular morphology, oxidative metabolism and increase and decrease in lipid levels. The essentiality of nickel in humans has not been established and nickel dietary recommendations have not been established for humans (ATSDR, 2013). Nickel compounds are known carcinogens in both human and animal models (Feder *et al.*, 2019). There is evidence that the Geno-toxic effects of nickel compounds may be indirect through the inhibition of DNA repair systems. As a result of

this inhibition it has been suggested that accumulation of nickel in breast tissue may be closely related to malignant growth process (ATSDR, 2015).

2.8.5 Copper

Copper is an essential nutrient that is incorporated into a number of metalloenzymes involved in hemoglobin formation, drug/xenobiotic metabolism, carbohydrate metabolism, catecholamine biosynthesis, the crosslinking of collagen, elastin and hair keratin, and the antioxidant defense mechanism. Copper-dependent enzymes, such as cytochrome C oxidase, superoxide dismutase, ferroxidases, monoamine oxidase and dopamine β -monooxygenase, function to reduce activated oxygen species or molecular oxygen. Symptoms associated with copper deficiency in humans include normocytic, hypochromic anemia, leukopenia, and osteoporosis (ATSDR, 2014). Although copper homeostasis plays an important role in the prevention of copper toxicity, exposure to excessive levels of copper can result in a number of adverse health effects including liver and kidney damage, anemia, immune toxicity and developmental toxicity. Many of these effects are consistent with oxidative damage to membranes or macromolecules. Copper can bind to the sulfhydryl groups of several enzymes, such as glucose-6-phosphatase and glutathione reductase, thus interfering with their protection of cells from free radical damage (ATSDR, 2014). A few examples of human activities that contribute to copper release are mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activity, it is very widespread in the environment. The metal is often found near mines, industrial settings, landfills and waste disposals (Schult and Kelling, 2019).

CHAPTER THREE

MATERIALS AND METHOD

3.1 Study Area

The study was carried out at the Ugbowo Campus of the University of Benin, Benin City in Edo State, Nigeria., which lies between latitude 06°23' 37" to 06°24' 26" North and longitude 00536' 25" to 00538' 09" East, which falls within the rain forest ecological zone of Nigeria with an annual rainfall of about 2000 mm and annual average temperature of about 27C (Molindo and Nwachokor, 2010). The topography of the area is a gentle slope, which falls eastwards while soils in the area are ultisols derived from recent coastal plain sands known as Benin formation (Umweni, 2007).

3.2 Sample Collection

Six (6) different dump sites were carefully collected in the Ugbowo campus of University of Benin. Three (3) each from Learning centers, and student's hostel (residential areas). The coordinates of the six dumpsites were taken, using a global positioning system (GPS). Soil samples from the dumpsites were collected and filled into plastic buckets, for the cultivation of *Amaranthus cruentus*.

Cultural Practices

Amaranthus cruentus seeds were planted at 4 seeds per bucket, and later thinned to 2 seedlings per bucket. Weeds were handpicked at intervals and adequate water was supplied when deemed necessary. At maturity, *Amaranthus cruentus* were harvested. Soil and plant samples were collected at the termination of the experiment.

Experimental Design

The experiment was conducted in the Greenhouse of the Department of Soil Science and Land Management, Faculty of Agriculture, University of Benin, Benin City. The experiment was laid out in Completely Randomized Design (CRD) with three treatments (soils from dumpsites) and three replicates.

Parameters Measured/Determined

Collected soil and plant samples were taken to the main laboratory Faculty of Agriculture, University of Benin, where standard procedures to determine: pH, TOC, N, P, K, Exchangeable bases, exchangeable acidity, sand, silt, clay and trace/heavy metal contents of the soil. The trace elements/heavy metal contents of the shoots of *Amaranthus cruentus* were also determined.

3.3 Soil Laboratory Analysis

Soil samples from refuse dumps in the different land uses were filled into buckets pots and Amaranth seeds were planted in them. After harvest, soil and plant samples were taken. Standard laboratory procedures were used in the analysis to determine selected physical and chemical characteristics. The analysis of the soil physical and chemical properties was carried out at the Faculty of Agriculture Main Laboratory.

1. Particle size determination (Hydrometer method)

The particle size distribution was determined by the hydrometer method (Boyucos, 1962) as modified by Gee and Bauder (1986). 51 g of air dried soil was weighed into a 250 ml beaker and 50 ml of Calgon solution (sodium hexameta phosphate) was added to the soil. Then 100 ml of distilled water was added and stirred vigorously for minute using the glass rod and allowed it to

stand for 30 minutes. The sample was transferred quantitatively into 100 ml measuring cylinder and made up to mark with distilled water. The first and second readings were taken at 40 seconds, and 2 hours respectively.

2. pH

The pH of the air dried soil was determined using an electronic pH meter of ratio 1:1 and (10 g soil to 10 ml distilled water). 10 g of air dried soil was weighed into 50 ml beaker, 10 ml of distilled water was added and the mixture was stirred intermittently for 30 minutes with a stirring rod. The pH meter was standardized with buffer pH 4.0 and 9.0, before the pH of the soil was taken. The reading was taken by dipping the electrode into the liquid mixture and the reading recorded.

3. Organic Carbon Content

This was determined by the chromic acid wet oxidation procedure of Walkey and Black as described by (Black, 1965). 1 g air dried soil was weighed into 250 ml conical flask, 10 ml of 1 N potassium heptaoxidochromate (vi) $K_2Cr_2O_7$ solution was added using a 10 ml pipette and the flask gently swirled to effect proper mixing. Thereafter, 20 ml of concentrated tetraoxosulphate (vi) acid H_2SO_4 was added violently but carefully to avoid dissipation of heat of the reaction and to enhance complete oxidation, after 30 minutes, 100 ml of distilled water was added with 100 ml measuring cylinder followed by 5 drops of ferroine indicator. The content of the flask was titrated with 0.5 N ferrous sulphate solution ($FeSO_4 \cdot 7H_2O$). The colour changed from dirty brown to a wine color. A blank titration was carried out (without soil sample) thus, organic carbon was calculated as;

$$\{B \text{ (ml)} - T \text{ (ml)}\} \times N \times 0.003F / \text{Weight of soil sample} \times 100/1$$

Where B (ml) = Titre value of blank

T (ml) = titration value

N = normality of FeSO₄ Solution

F = Correction factor (1.33) %

Organic Carbon (%) was converted to g/kg by multiplying the values by 10.

4. Exchangeable Bases (Ca, K, Na and Mg) determination (Ammonium Saturation Method)

10 g of air dried soil was weighed into a 250 ml soil shaking bottle. 100 ml of 1 N ammonium acetate was added and was shaken in a mechanical shaker for 1 hour. The soil suspension was filtered through whatman No 45 filter paper into 100 ml volumetric flask and made up 100 ml mark with ammonium acetate solutions and stored in a 100 ml plastic reagent bottle. K and Na were read in Jenway model flame photometer and Ca and Mg were read in a Unicam series 969 model.

5. Exchangeable Acidity Determination (Titration method)

5 g of air dried soil was weighed into a shaken bottle. 50 ml of 1 M KCl was added and shaken for 1 hour on a mechanical shaker. The soil was thereafter filtered into a 100 ml volumetric flask and was made up to 100 ml mark with 1M KCl solution. 25 ml of soil extract was measured into a 250 ml conical flask and 5 drops of phenolphthalein indicator was added. Mixture was titrated with 0.05 N NaOH to pink end point. Results were expressed as cmol/kg Calculation $\text{Meq}/100 \text{ g} = \frac{N \times V \times 100}{W}$ Where N=Normality; V= Litre Volume; w = Weight of soil in aliquot $\text{meq}/100 = (\text{mol}/\text{kg})$.

6. Available Phosphorus Determination

The available phosphorus in the soil samples was determined using Bray-1 method. Here a 5 g soil sample that passed through 2 mm sieve was weighed into an extracted cup. 30 ml of Bray-1 (1945) solution was added and was stirred on a mechanical shaker for 5 minute. The soil suspension was then filtered through whatman 42 filter paper. 1 ml extract (aliquot) was pipette into a 50 ml volumetric flask. 6 ml of distilled water was added. 2 ml of colour developing reagent was added and was well mixed. 1 ml of Ascorbic acid solution was added and was left for 10 minutes so that the colour can develop. The solution was measured at 650 m in visible range spectrometer. A graph of absorbance (ppm) against standard (ppm) for P interpolation was done. Calculation ppm of P (mg of P/ kg soil).

7. Total Nitrogen (Kjeldahl method)

1 g of air dried soil sample of fine tilth was weighed into a 250 ml micro kjeldahl flask followed by the addition of 1 g of catalyst tablet (comprising of CuSO_4 , K_2S and a pinch of Selenium). 20 ml of concentrated H_2SO_4 was added and the flask was heated in a fume cupboard until digestion was completed and the digest had become light green in colour. The flask was cooled and about 10 ml of distilled water was added. The digest was filtered through whatman No. 42 filter paper into 100 ml volumetric flask. It was made up to mark and shaken together for proper mixing.

Distillation

10 ml aliquot was transferred into 500 ml Kjeldahl flask. 30 ml of water was added. 15 ml of NaOH (excess base) was added. Heat was applied, and 25 ml distillate was collected in 5 ml

boric acid indicator. The NH. Nitrogen was determined by titration distillate with 0.01 M standard HCL. Color changed from green to pink.

Heavy Metal Determination

1 g of air dried soil sample was weighed into a digestion tube 10 ml of concentrated HNO was added and heated in block digester for 1 hour. 5 ml of HClO₄ was added and heated for another 1 hour The flask was cool and 5 ml of 2.0 M HCL was added, the solution was diluted with 10mls distilled water and filtered using whatman No 1 filter paper into 100 ml volumetric flask and made up to make with distilled water. The extraction was then stored in a plastic reagent bottle for instrumental determination using AAS.

Plant Analysis

At harvest, plants were randomly selected from each treatment plot and oven dried for forty-eight hours at 75°C. The plants were then ground to powder and placed in Muffle furnace for about eight hours at 450°C to completely turn samples into ashes. Ashes were treated with both 0.1 M HCl and 1M HCl and filtered (A.O.A.C., 1990). The filtrate was used for determination of P, K, Ca and Mg. P was determined by the molybdenum-blue colorimetric procedure of Murphy and Riley, (1962). K was determined using flame photometer. Ca and Mg content were determined volumetrically by EDTA titration procedure (Black, 1965). The N content was determined by Micro-Kjedahl digestion method (Bremner, 1996).

Statistical Analysis

Data collected were subjected to Analysis of variance (ANOVA), using Genstat software, while Least Significant Difference (LSD) was used to separate means at 5% level of significance.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Physical Properties

4.1.1 Particle Size Distribution

The results (Table 1) of the particle size distribution under the different dump sites showed Sand fraction of 881.7 g/kg in learning centers, 884 g/kg in hall of residence. Silt fractions was 69 g/kg in learning centers, while hall of residence had 70 g/kg. Clay fraction of 49.3 g/kg in learning centers and 45 g/kg in halls of residence was observed. The soil textural class of the dump sites studied was sand.

4.2 Chemical Properties

4.2.1 Total nitrogen

The result on Table1 shows that halls of residence had the highest total nitrogen (1.13 g/kg) as compared to learning centers which had 1.09 g/kg. The relatively high N content may be due to the composition of the wastes which decomposed over time, therefore increasing the level of microbial activity. The activities of soil organisms in the decomposition of these wastes may have accounted for the rich N contents of the soil (Obute *et al.*, 2010; Amos-Tautua *et al.*, 2014).

Table 1: Soil Parameters

TRT	pH (1:1) in water	TOC (g/kg)	TN (g/kg)	Av. P (mg/kg)	Exchangeable Bases				Exch. Acidity					Sand	Silt	Clay	TC		
					K	Ca	Mg	Na	H	Al	Pb	Cd	Cr					As	
L.C	5.76	19.60	1.090	12.80 ^a	0.223	0.87	0.256	0.157	0.18	0.067	0.13	0.03	0.01	0.03	881.7	69.0	49.3	Sand	
Res	5.97	21.50 ^a	1.130	13.80	0.27	1.01	0.29	0.177	0.123	0.03	0.123	0.034	0.04	0.04	884.3	70.7	45.0	Sand	
SEM	0.13	2.26	0.01	1.51	0.023	0.09	0.034	0.0101	0.02	0.01	0.01	0.001	0.001	0.001	1.65	2.39	2.39		
SED	0.19	3.20	0.14	2.13	0.04	0.123	0.05	0.015	0.03	0.011	0.01	0.001	0.001	0.012	2.33	3.38	3.38		
LSD	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	N.S	
CV (%)	3.9	19.1	15.6	19.7	20.6	16.7	24.4	11.2	27.8	40.8	13.9	30.6	30.6	53.3	0.3	5.9	8.8		

Means with the same alphabets in the same column are not significantly different at P = 0.05

4.2.2 pH

The pH of the soils (Table 1) were moderately acidic (5.763 and 5.970 respectively) in the soils from dumpsites in learning centers and residential areas. There was no significant difference between the pH of the two dumpsites at 5% level of significance. The moderately acidic pH observed is similar to the findings of Obianefo *et al.*, 2017 who also reported that the pH of dumpsites was moderately acidic.

4.2.3 Organic Carbon

The result on Table 1 shows that the TOC of the dumpsites was 19.60 g/kg in learning centers and 21.50 g/kg in residential areas. There was no significant ($p < 0.05$) difference between the TOC contents of the two dumpsites. The relatively high TOC contents of the dumpsites may be connected with the wastes deposited on the dumpsites. This is similar to the findings of Airueghian *et al.*, 2018 who reported high TOC contents from the dumpsites.

4.3 Heavy Metals Concentration of Dumpsites

Cadmium

As shown on Table 1, the cadmium concentration of the dumpsites soils reveals that the learning Centre had 0.033 mg/kg while the residential area had 0.037 mg/kg. there was no significant difference between Cd contents of both dumpsites at 5% level of significance. The values from the dumpsites were below the WHO maximum permissible values of 0.2 mg/kg. This indicate that concentration of Cd in the soils from dumpsites were low.

Lead

The lead (Pb) content of the soils from the dumpsites were 0.127 mg/kg and 0.130 mg/kg from the residential area and learning centers respectively. There was no significant difference

between the Pb levels of the soils from the dumpsites at 5% level of probability. The pb content from the dumpsites were below the FAO/WHO maximum permissible value of 0.3 mg/kg.

Chromium

The chromium content in the soil were significantly below the maximum permissible limit set by WHO. There was no significant difference observed in both soils of residential and learning centers dumpsites in terms of chromium concentration. However, chromium content was higher in residential soils than that of learning centers, with values of both ranging from 0.013 to 0.040 mg/kg.

Arsenic

The Arsenic (As) content in the soil were 0.03 mg/kg and .04 mg/kg for learning centers and residential area respectively. There was no significant difference observed in both soils and the As content were below the maximum permissible limit.

4.4 Heavy Metals Concentration in *Amaranthus Cruentus*

Cadmium

Residential areas had the highest level of Cd (0.037mg/kg) and it observed too in the uptake of Cd by the amaranth plant (0.33mg/kg). The concentration of cadmium (Table 2) in *Amaranthus cruentus* grown on the soil from these dumpsites studied were generally higher than the standard limit of 0.01 - 0.03 mg/kg as reported by Fatoba *et al.* (2012). The high concentration obtained may be due to deposition of the metal from non - ferrous metal activities, combustion, etc. There was no significant difference between Cd concentrations in *amaranthus cruentus* grown on soils from dumpsites in learning centers and residential areas respectively.

Arsenic

The Arsenic (As) content in the plant, *Amaranthus cruentus* were 0.010 mg/kg and 0.013 mg/kg for learning centers and residential area respectively. There was no significant difference observed zof As content in plants and the As content were below the maximum permissible limit set by thze WHO.

Table 2: Plant parameters for *amaranthus*

	Pb	Cd	Cr	As
Dump site	←————— (mg/kg) —————→			
Learning Centers	0.08	0.02	0.001	0.01
Residential	0.04	0.03	0.011	0.01
SEM	0.001707	0.002	0.004	0.001
SED	0.01	0.003	0.001	0.001
LSD	0.04	0.01	0.02	0.023
CV (%)	19.3	15.3	60.6	70.0

Chromium

From Table 2 chromium concentration in the Amaranth plant were 0.007 mg/kg in learning centers and 0.017 mg/kg in residential areas. The values were generally below the standard limits (0.03 mg/kg) set by Federal Environmental Protection Agency (FEPA) 1991. There was no significant difference in chromium concentrations. Sources of Cr in the soils could be due to automobiles, colored polythene bags, discarded plastic materials, empty paint containers and electronic waste (Jung and Casher, 2006).

Lead

Lead had lower values of 0.043 mg/kg and high values of 0.083 mg/kg in residential areas and learning centers respectively. The pb content of the dumpsite from residential areas was above the permissible limit while that of the learning centers was below the permissible limit of 0.05 mg/kg as recommended by Federal Environmental Protection Agency (FEPA) 1991. The high levels of lead in the learning centers and residential areas could be attributed to the release of

exhaust from generators and also burning of wastes (ATSDR, 2007). This indicate that this metal is readily bio-available to the environment (Uzairu *et al.*, 2013).

CHAPTER FIVE

5.0 CONCLUSION

The soils from the dumpsites belong to the textural class: sand. Their pH was moderately acidic and have high TOC contents. The heavy metals studied were detected in both dumpsite soils. Their concentration in the dumpsites did not differ significantly at 5% level of significance and their levels were below the permissible limits allowed in the soil. Also, the heavy metals were also found in the plant samples. Pb content in the plant samples were above the permissible limit but other heavy metals were below the levels of permissible limit in plant tissues.

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