

CHARACTERISTICS OF SOIL PROPERTIES AND PLANT UPTAKE OF  
METALLIC IONS IN MUNICIPAL SOLID WASTE SITES

BY

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A PROJECT SUBMITTED TO THE DEPARTMENT OF AGRICULTURAL AND BIO-  
RESOURCES ENGINEERING

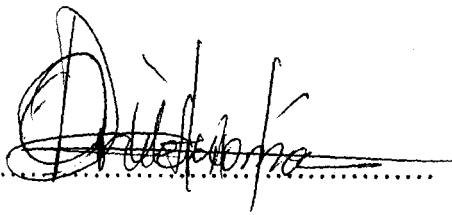
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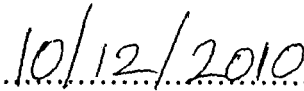
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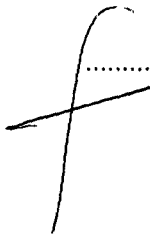
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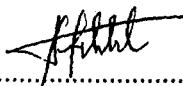
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## CERTIFICATION

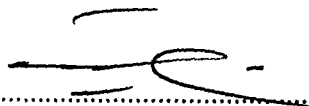
This is to certify that the project entitled "Characteristics of Soil Properties and Plant Uptake of Metallic Ions In Municipal Solid Waste Sites" by Orueri, Ufuoma Daniel meets the regulations governing the award of the degree of Bachelor of Engineering (B. ENG.) of the Federal University of Technology, Minna, and it is approved for its contribution to scientific knowledge and literary presentation.

  
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## **DEDICATION**

This thesis is dedicated to God Almighty who in His infinite mercies saw me through the period of my academic pursuit and also to my parents for their astounding support in all my endeavors.

## ACKNOWLEDGEMENT

Special appreciation goes to God Almighty for His protection and care throughout my academic pursuit.

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## ABSTRACT

This research work was conducted to determine the effects of metallic ions on the properties of soil in municipal solid waste sites and also to compare the uptake of these metallic ions by various plants, using Delta State as a case study. Soil samples obtained from two MSW sites and a control plot were used to grow two crop types, Tomato (Lycopersicon esculentum) and Okra (Abelmoschus esculentus). The plant and soil samples from the various sites were taken for analysis, and the following trace metals were discovered to be in the following order; Fe > Zn > Pb > Cu > Ni. The soils from the MSW sites were found to be richer in terms of organic matter content than those of the control plot. Tomato plant was discovered to bio-accumulate the metals excessively, showing its property as a metal hyper-accumulator and as a tool for phyto-remediation. Crops cultivated in areas of heavy metal contamination pose serious threat to man and animals, as such proper phyto-remediative processes need to be carried out before any cultivation is done.

# CHAPTER ONE

## 1.0 INTRODUCTION

Human activities create waste and it is the way these wastes are handled, stored, collected and disposed of, that constitutes risk to the environment and public health. In urban areas, especially in the rapidly urbanizing cities of the developing world, problems and issues of solid waste management are of immediate importance. This has been acknowledged by most government. However, rapid population growth overwhelms the capacity of most municipal authorities to provide even the basic services.

When wastes are collected, they are disposed off in uncontrolled dumpsites and/or burnt, polluting water resources, air (Onibokun et al., 2000).

Municipal solid wastes includes wastes generated from residential, commercial, industrial, institutional, construction, demolition, process and municipal services. Residential single and multi- family dwellings generate food wastes, paper, cardboard, plastic, textile, leather, yard waste, wood, glass, metals, ashes, special waste (e.g. bulky items, consumer electronics, batteries, oil, tires), and household hazardous wastes. Commercial stores, hotels, restaurants, markets, generates paper, cardboard, plastic, wood, food wastes, office wastes, e.t.c. (Tchobunoglous et al., 1993).

The Delta State Government, Nigeria, still endorses the use of open space dumping. The method is regarded as primitive, as most developed countries consider waste as a source of wealth and invest in its treatment and disposal. Hazardous wastes are not separated from municipal solid wastes disposed off at these dumpsites. The infectious medical wastes, toxic industrial wastes and domestic wastes are disposed together.

The soil is a primary recipient of solid wastes (Nyle and Ray, 1999). Millions of tons of these wastes from a variety of sources: industrial, domestic and agricultural find their way into the soil. These wastes end up interacting with the soil system thereby changing the physical and chemical properties (Piccolo and Mbiagwu, 1997). The accumulation of contaminants is aided by the capability of soil to bind them with clay minerals or organic substances. Their accumulation has multiple effects on the visibility and functions of the eco-system (Nielson, 1997).

Heavy metal is a general collective term applied to the group of metals and metalloids with an atomic density greater than  $6 \text{ g/cm}^3$ . They are metals commonly associated with pollution and toxicity problems. The inorganic pollutants from metals, metal salts, mineral substances, solid particulate matter and synthetic chemical compounds and their by-products pollute dump soils (Alloway, 1996). Heavy metal absorption is governed by soil characteristics such as pH and organic matter content (Salt et al., 1996). Heavy metal soil contamination is particularly problematic because they are not degraded in soil. Heavy metals in soil cannot be permanently eliminated. At best they can be locally reduced by redistribution in the eco-system or removed from circulation by immobilization (Baker et al., 1994).

## **1.1 Project Objectives**

This project focuses on the following specific objectives:

- a) To determine the effects of metallic ions on the properties of soils in municipal solid waste sites.
- b) Comparison between plants grown on MSW sites and those grown on normal agricultural lands (control plots).

## **1.2 Scope of the Project Work**

This project work is intended to cover the following;

- a) Assessment of the levels of heavy metal accumulation in soils and plants at municipal solid waste sites.
- b) Analysis of the effects of heavy metal accumulation in man and animals.
- c) Comparison between the soil properties and metallic ion content of soils in municipal solid waste sites and those of control plots.

## **1.3 Project Justification**

Solid waste handling and disposal is a major environmental problem in many urban centers in Nigeria. In a few cases, the municipal wastes, mostly garbage and wastes from food processing plants are incinerated or simply dumped. City dwellers have long contended that any form of waste with proper compositing and processing can be made into fertilizers that farmers will gladly pay for. However, the modern farmer is not willing to accept this position since he is an astute businessman who has to be convinced that the risk and cost involved are small enough to benefit him (Carlson, 1976).

Recently, many studies have shown that heavy metals from these wastes can accumulate and persist in soils at environmentally hazardous levels (Carlson, 1976; Alloway, 1996). Purves (1973), in a study of trace-element content of municipal wastes, reported wide ranges of B, 3.8 – 103ppm; Pb, 44 – 352ppm; Cu, 25 – 215ppm; Ni, 7 – 21ppm; and Zn, 400 – 655ppm. In spite of the foregoing, most abandoned waste dump sites in many towns and villages in Nigeria attract people as fertile ground for cultivating varieties of crops. The cultivated plants take up the metals either as mobile ions present in the soil solution through the roots (Davies, 1983) or through foliar adsorption (Chapel, 1986). The uptake of the metals by crops results in the bio-accumulation of these elements in plant tissues. This is known to be influenced by the metal species, plant species and plant part (Juste and Mench, 1992).

Indeed, it has been reported that plants grown on soils possessing enhanced metal concentration due to pollution have increased heavy metal ion content (Alloway, 1996). If the consumption of these metals through plant sources is not carefully regulated, it may lead to accumulation in man with attended health hazards. The information in this research study is expected to guide in formulating an appropriate land use and management policy for such unique eco-systems.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 Pollution

Pollution, contamination of Earth's environment with materials that interfere with human health, the quality of life, or the natural functioning of ecosystems (living organisms and their physical surroundings). Although some environmental pollution is a result of natural causes such as volcanic eruptions, most is caused by human activities.

There are two main categories of polluting materials, or pollutants. Biodegradable pollutants are materials, such as sewage, that rapidly decompose by natural processes. These pollutants become a problem when added to the environment faster than they can decompose. Non-degradable pollutants are materials that either do not decompose or decompose slowly in the natural environment. Once contamination occurs, it is difficult or impossible to remove these pollutants from the environment.

Non-degradable compounds such as dichlorodiphenyltrichloroethane (DDT), dioxins, polychlorinated biphenyls (PCBs), and radioactive materials can reach dangerous levels of accumulation as they are passed up the food chain into the bodies of progressively larger animals. For example, molecules of toxic compounds may collect on the surface of aquatic plants without doing much damage to the plants. A small fish that grazes on these plants accumulates a high concentration of the toxin. Larger fish or other carnivores that eat the small fish will accumulate even greater, and possibly life-threatening, concentrations of the compound. This process is known as bioaccumulation.



## **2.2 Impacts Of Pollution**

Because humans are at the top of the food chain, they are particularly vulnerable to the effects of non-degradable pollutants. This was clearly illustrated in the 1950s and 1960s when residents living near Minamata Bay, Japan, developed nervous disorders, tremors, and paralysis in a mysterious epidemic. More than 400 people died before authorities discovered that a local industry had released mercury into Minamata Bay. This highly toxic element accumulated in the bodies of local fish and eventually in the bodies of people who consumed the fish. More recently research has revealed that many chemical pollutants, such as DDT and PCBs, mimic sex hormones and interfere with the human body's reproductive and developmental functions.

In addition to its effects on the economy, health, and natural resources, pollution has social implications. Research has shown that low-income populations and minorities do not receive the same protection from environmental contamination as do higher-income communities. Toxic waste incinerators, chemical plants, and solid waste dumps are often located in low-income communities because of a lack of organized, informed community involvement in municipal decision-making processes (Microsoft Encarta Premium DVD, 2009).

## **2.3 Soil Pollution**

Soil is a mixture of mineral, plant, and animal materials that form during a long process that may take thousands of years. It is necessary for most plant growth and is essential for all agricultural production. Soil pollution is a buildup of toxic chemical compounds, salts, pathogens (disease-causing organisms), or radioactive materials that can affect plant and animal life.

Unhealthy soil management methods have seriously degraded soil quality, caused soil pollution, and enhanced erosion.

## 2.4 Soil Properties

Soils can be enormously complex systems of organic and inorganic components.

### 2.4.1 Soil Texture

Soil texture refers to the relative proportion of sand, silt and clay size particles in a sample of soil. Clay size particles are the smallest being less than .002 mm in size. Silt is a medium size particle falling between .002 and .05 mm in size. The largest particle is sand with diameters between .05 for fine sand to 2.0 mm for very coarse sand. Soils that are dominated by clay are called fine textured soils while those dominated by larger particles are referred to as coarse textured soils. Soil scientists' group soil textures into soil texture classes. A soil texture triangle is used to classify the texture class.

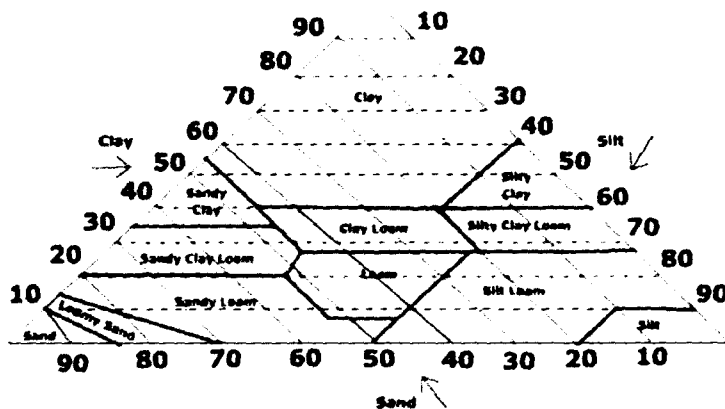


Fig 1.0 Soil Texture Triangle

The sides of the soil texture triangle are scaled for the percentages of sand, silt, and clay.

Clay percentages on the left side of the triangle are read from left to right across the triangle (dashed lines). Silt runs from the top to the bottom along the right side and is read from the upper right to lower left (light, dotted lines). The percentage of sand increases from right to left along the base of the triangle. Sand is read from the lower right towards the upper left portion of the triangle (bold, solid lines). The boundaries of the soil texture classes are highlighted in blue. The intersection of the three sizes on the triangle gives the texture class. For instance, if you have a soil with 20% clay, 60% silt, and 20% sand it falls in the "silt loam" class (Microsoft Encarta Premium DVD, 2009).

Soil texture effects many other properties like structure, chemistry, and most notably, soil porosity, and permeability. Soil porosity refers to the amount of pore, or open space between soil particles. Pores are created by the contacts made between irregular shaped soil particles. Fine textured soil has more pore space than coarse textured because you can pack more small particles into a unit volume than larger ones. More particles in a unit volume create more contacts between the irregular shaped surfaces and hence more pore spaces. As a result, fine textured clay soils hold more water than coarse textured sandy soils. Permeability is the degree of connectivity between soil pores. A highly permeable soil is one in which water runs through it quite readily. Coarse textured soils tend to have large, well-connected pore spaces and hence high permeability.

## **2.4.2 Soil Structure**

Soil structure is the way soil particles aggregate together into what are called peds. Peds come in a variety of shapes depending on the texture, composition, and environment.

Granular, or crumb structures, look like cookie crumbs. They tend to form an open structure that allows water and air to penetrate the soil. Platy structure looks like stacks of dinner plates overlaying one another. Platy structure tends to impede the downward movement of water and plant roots through the soil. Therefore, open structures tend to be better agricultural soils.

Bulk density of a soil is the mass per unit volume including the pore space. Bulk density increases with clay content and is considered a measure of the compactness of the soil. The greater the bulk density, the more compact the soil. Compact soils have low permeability, inhibiting the movement of water. The use of heavy agricultural equipment can cause compaction of soil, especially in wet clay soil. Soil compaction results in reduced infiltration and increase runoff and erosion.

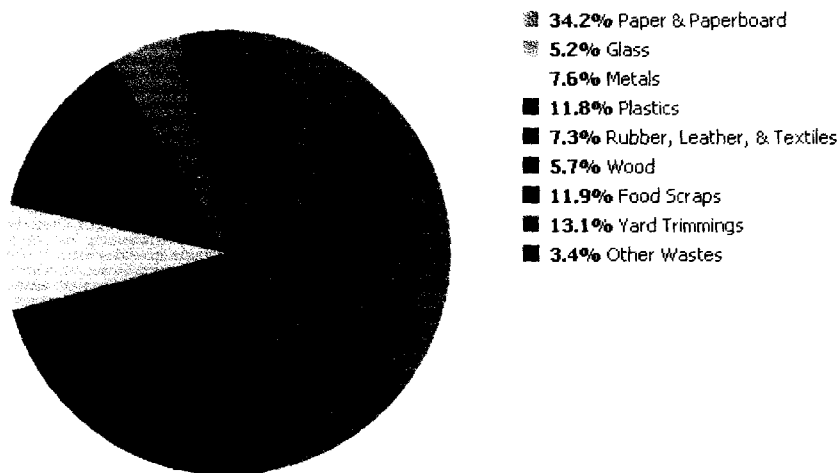
## **2.4.3 Soil Chemistry**

As plant material dies and decays it adds organic matter in the form of humus to the soil. Humus improves soil moisture retention while affecting soil chemistry. Cations such as calcium, magnesium, sodium, and potassium are attracted and held to humus. These cations are rather weakly held to the humus and can be replaced by metallic ions like iron and aluminum, releasing them into the soil for plants to use. Soils with the ability to absorb and

retain exchangeable cations have a high cation-exchange capacity. Soils with a high cation-exchange capacity are more fertile than those with a low exchange capacity.

Hydrogen ion concentration in the soil is measured in terms of the pH scale. Soil pH ranges from 3 to 10. Pure water has a pH of 7 which is considered neutral, pH values greater than seven are considered basic or alkaline, below seven acidic. Most good agricultural soils have a pH between 5 and 7. Though acidic soils pose a problem for agriculture due to their lack of nutrients, alkaline soils can pose a problem as well. Alkaline soils may contain appreciable amounts of sodium that exceed the tolerances of plants, contribute to high bulk density and poor soil structure. Alkaline soils are common in semiarid regions.

## 2.5 Municipal Solid Wastes



Source: Environmental Protection Agency, 2005 data.

Fig. 1.2 components of municipal solid waste

### **2.5.1 Solid Waste**

Solid wastes are unwanted solid materials such as garbage, paper, plastics and other synthetic materials, metals, and wood. Billions of tons of solid waste are thrown out annually. Moreover, waste from developed countries typically contains a high percentage of synthetic materials that take longer to decompose than the primarily biodegradable waste materials of developing countries.



Plate 1. an overflowing landfill

Areas where wastes are buried, called landfills, are the cheapest and most common disposal method for solid wastes worldwide. But landfills quickly become overfilled and may contaminate air, soil, and water. Incineration, or burning, of waste reduces the volume of

solid waste but produces dense ashen wastes (some of which become airborne) that often contain dangerous concentrations of hazardous materials such as heavy metals and toxic compounds. Composting, using natural biological processes to speed the decomposition of organic wastes, is an effective strategy for dealing with organic garbage and produces a material that can be used as a natural fertilizer. Recycling, extracting and reusing certain waste materials, has become an important part of municipal solid waste strategies in developed countries. According to the EPA, more than one-fourth of the municipal solid waste produced in the United States is now recycled or composted. Recycling also plays a significant, informal role in solid waste management for many Asian countries, such as India, where organized waste-pickers comb streets and dumps for items such as plastics, which they use or resell.

Expanding recycling programs worldwide can help reduce solid waste pollution, but the key to solving severe solid waste problems lies in reducing the amount of waste generated. Waste prevention, or source reduction, such as altering the way products are designed or manufactured to make them easier to reuse, reduces the high costs associated with environmental pollution.

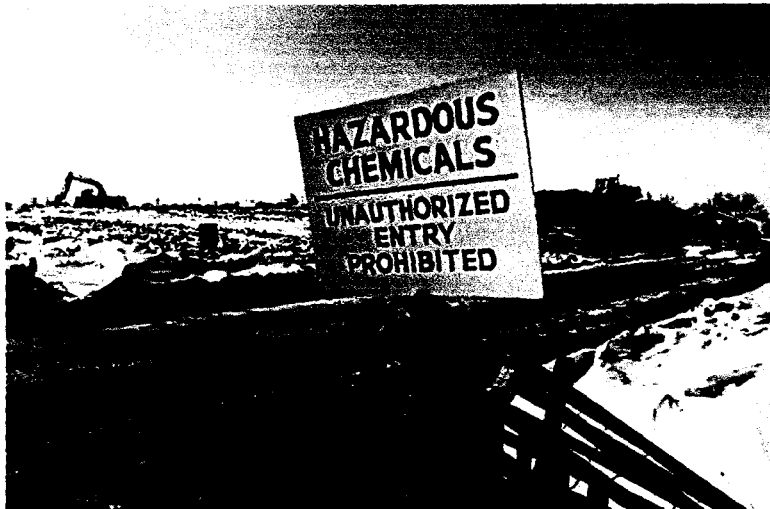


Plate 1.1 Toxic Wastes in Love Canal

### **2.5.2 Hazardous Waste**

Hazardous wastes are solid, liquid, or gas wastes that may be deadly or harmful to people or the environment and tend to be persistent or non-degradable in nature. Such wastes include toxic chemicals and flammable or radioactive substances, including industrial wastes from chemical plants or nuclear reactors, agricultural wastes such as pesticides and fertilizers, medical wastes, and household hazardous wastes such as toxic paints and solvents.

About 400 million metric tons of hazardous wastes are generated each year. The use, storage, transportation, and disposal of these substances pose serious environmental and health risks. Even brief exposure to some of these materials can cause cancer, birth defects, nervous system disorders, and death. Large-scale releases of hazardous materials may cause thousands of deaths and contaminate air, water, and soil for many years.



Until the Minamata Bay contamination was discovered in Japan in the 1960s and 1970s, most hazardous wastes were legally dumped in solid waste landfills, buried, or dumped into lakes, rivers, and oceans. Legal regulations now restrict how such materials may be used or disposed, but such laws are difficult to enforce and often contested by industry. It is not uncommon for industrial firms in developed countries to pay poorer countries to accept shipments of solid and hazardous wastes, a practice that has become known as the waste trade. Moreover, cleaning up the careless dumping of the mid-20th century is costing billions of dollars and progressing very slowly, if at all. The United States has an estimated 217,000 hazardous waste dumps that need immediate action. Cleaning them up could take more than 30 years and cost \$187 billion.

Hazardous wastes of particular concern are the radioactive wastes from the nuclear power and weapons industries. To date there is no safe method for permanent disposal of old fuel elements from nuclear reactors. Most are kept in storage facilities at the original reactor sites where they were generated. With the end of the Cold War, nuclear warheads that are decommissioned, or no longer in use, also pose storage and disposal problems (Huang, 2000).

## **2.6 Micro and Macro-Nutrients in Soil**

Plants require both macro nutrients and micro nutrients for their growth. The essential micronutrients for plants required are boron, chlorine, sodium, copper, iron, manganese, zinc, vanadium and molybdenum. They are required at trace levels and if present at higher levels, have a toxic effect. Most of these serve as components of essential enzymes. Some of these such as chlorine, manganese, iron, zinc and vanadium are likely to take part in photosynthesis. The essential macronutrients required for the plants are carbon, hydrogen, oxygen, nitrogen,

Vitamin A	623 IU
Vitamin E	0.38 mg
Niacin	0.628 mg

Source: USDA Nutrient Data Base

### 3.1.3 Experimental Plots

The soil samples were obtained from three different locations; plot A- solid waste site at Otor-Udu, behind Shell petroleum Gas plant in Udu L.G.A; plot B- a dumpsite at Okwagbe waterside along the creek in Ughelli south L.G.A; plot C- a control plot at DSC Aladja in Udu L.G.A. All three sites are well located within Delta State.

### 3.1.4 Sample collection and set-up

Six representative top soil (0-15 cm depth) samples (5 kg each) were collected randomly from each of the sites, and divided into three parts. As such, total samples collected were eighteen (18).

#### First part

The first part of plots A, B, and C consisting of six different samples were analyzed separately without planting on it.

#### Second part

The second set of six soil samples were used in the cultivation of the okra plant.

% organic matter in soil = % organic carbon x 1.729 (Anderson and Ingram, 1993)

### **3.1.7 Heavy Metals Analysis (soil)**

Analysis for the heavy metal content was carried out using the atomic absorption spectrophotometer. The soil samples were air-dried, crushed and passed through a 20 mm sieve. A portion (1 g) of the soil sample was digested in a 1:1 mixture of concentrated nitric acid and perchloric acid by heating the mixture plus sample on a water bath in a fume cupboard. The solution was heated to dryness while the residue was re-dissolved in 5 cm<sup>3</sup> of 2.0 M HCl (Alloway, 1996).

### **3.1.8 Plants Analysis**

In the laboratory, the plant samples were placed under running tap water to wash off soil particles from the leaves, fruits and roots. Stainless steel knife was used to cut the plant samples into different parts. The plant parts were dried in an oven maintained at 80 °c, and then pulverized to fine powder using a laboratory stainless grinder. The ground samples were placed in polythene bags and labeled accordingly before being kept in a dessicator. The plant parts were analyzed separately for heavy metal content. 1 g of < 2 mm fraction plant samples was weighed into porcelain crucibles and was ignited in a muffle furnace for 6hrs at a temperature between 450 – 500°C. Grey white ash was obtained at the completion of the ashing. The ash samples were allowed to cool and then 10mL of 2 M HNO<sup>3</sup> was added to each sample. The solution was evaporated to near dryness on a hot plate and the cooled residues were re-dissolved in 10mL 2 M HNO<sup>3</sup>. The solutions were then filtered into 25mL volumetric flasks. Both the crucible and the filter paper were washed into the flasks, made up with de-ionized water and then stored in polyethylene tubes for instrumental analysis. Atomic absorption Spectrophotometer (Buck

Scientific 200) was used to analyze soil and plant digests for heavy metals.

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSION

#### 4.1 Result of Soil Analysis

The chemical characteristics of the soils at the various plots are given in the table below;

Table 4.1 Heavy metal concentration (mg/kg) in soils

Elements	A (Otor- Udu)	B (Okwagbe)	C (Aladja)
Cu	19.17 21.11	58.23 64.03	12.49 16.05
Ni	1.79 2.43	4.46 6.00	3.72 4.62
Pb	143.24 134.80	141.73 156.85	105.56 99.00
Zn	174.11 156.41	373.12 332.36	86.44 98.38
Fe	701.17 725.69	925.04 89.16	459.71 499.17

**Table 4.2 Comparative mean concentration of metals in the soil samples of the three plots**

<b>METALS</b>	<b>PLOT A (mg/kg)</b> <b>(Otor-Udu)</b>	<b>PLOT B (mg/kg)</b> <b>(Okwagbe)</b>	<b>PLOT C (mg/kg)</b> <b>(Aladja)</b>
Copper	20.14	61.13	14.27
Nickel	2.11	5.23	4.17
Lead	139.02	149.29	102.28
Zinc	165.26	352.74	92.41
iron	713.43	912.10	479.44

**Table 4.3 Organic matter content and pH value of soils**

	<b>A</b> <b>(Otor-Udu)</b>	<b>B</b> <b>(Okwagbe)</b>	<b>C</b> <b>(Aladja)</b>
<b>pH</b>	7.02	7.22	6.91
	7.28	7.70	6.03
<b>Org. Matter (%)</b>	16.74	21.09	11.01
	15.50	22.39	9.95

**Table 4.4 Comparative mean of pH and organic matter of soil samples**

	<b>A (Otor-Udu)</b>	<b>B (Okwagbe)</b>	<b>PLOT C (Aladja)</b>
<b>pH</b>	7.15	7.46	6.47
<b>Organic matter %</b>	16.12	21.74	10.48

#### **4.1.1 Heavy Metal Content of the Soils**

The investigation of the total content of heavy metals in the soils was restricted to the top 15 cm since previous studies showed that surface soils are better indicators of metallic burdens (Nyangababo and Hamya, 1986).

The results show that the heavy metal content in plot B is highest followed by that of plot A, with the control, which is plot C, having the least in terms of heavy metal content. Plot B was a major dumpsite for over fifteen years before it was abandoned. Its location close to petroleum pipelines may have contributed to its higher degree of heavy metals as compared to the other two plots.

The reduction in the metallic ion content of plot A as compared to plot B could also be thought to be as a result of the differences in the living standards, consumption patterns and industrial development between cities/towns and rural communities. Modern and highly developed communities generate wastes that contain less leaves and food remnants but more paper, rag,

plastic/polythene, tins and metals, bottles, glasses, industrial and/or laboratory wastes/chemicals, and a variety of miscellaneous materials (Ademoroti, 1996).

In other to minimize those wastes that may increase the heavy metal load of the dump site soils while the wastes decompose or corrode, careful sorting at source should be encouraged among the general public in towns and cities particularly in Nigeria. The current statutory regulation on waste management in Nigeria focuses on industrial and/or corporate institutions, and compliance is enforced by the Federal and the State Environmental Protection Agencies. There is also the need for an enabling statutory regulation and means of enforcing compliance, to ensure proper waste management/handling by the general public. To ensure enforcement and compliance, a unit of the Health Department of the Local Government Council could be assigned this responsibility. Those wastes that pose greater health hazards need to be properly land-filled so as to reduce the incidence of environmental pollution and/or degradation.

#### 4.2 Result of Crop Analysis

**Table 4.5 Heavy metal concentration in plants**

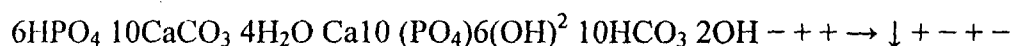
Elements	A (mg/kg)		B (mg/kg)		C (mg/kg)	
	Okra	Tomato	Okra	Tomato	Okra	Tomato
Cu	4.20	11.73	5.91	42.02	3.98	6.56
	4.08	11.25	6.63	46.70	4.04	6.24
Ni	0.11	1.05	0.78	2.13	0.29	1.96
	0.15	0.99	1.16	2.87	0.23	1.62
Pb	33.29	35.41	39.21	44.14	21.03	25.04
	28.95	40.93	35.77	41.68	28.11	30.24
Zn	9.07	42.11	27.12	104.77	5.07	23.29
	8.57	48.27	30.90	98.67	3.69	22.33



rate of release of nitrogen to plants roughly parallels plant growth. Plants use  $\text{NO}_3^-$  from soil in general. When nitrogen is applied to soils as  $\text{NH}_4^+$  (fertilizer), nitrifying bacteria converts it into  $\text{NO}_3^-$  for use by plants. Certain leguminous plants, e.g. Soya beans, alfalfa, clover etc. possess the unique ability to fix atmospheric nitrogen through nitrogen fixing bacteria on their root modules. Legumes can add considerable quantities of nitrogen to soil (Logan et al., 1992).

### 2.7.1 Phosphorous

Even though the percentage of phosphorous in plant material is very low, it is an essential component of plants. The assimilable phosphate species by the plants are  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  which exist at the soil pH. Orthophosphate is most available to plants at pH values near neutrality. In acidic soils, the orthophosphate ions are either precipitated or sorbed by cations, viz,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , etc. In alkaline soils, the following reaction occurs with  $\text{CaCO}_3$ , whereby hydroxyapatite is precipitated:



Since phosphorous is fixed as hydroxyapatite very little phosphorous, added as fertilizer, leaches from the soil (Epstein et al., 1992).

### 2.7.2 Potassium

Potassium is one of the three major fertilizer elements required by plants. In general potassium status of soils is satisfactory only when enough potassium is added to compensate for the potassium removed in the crops. This is because any excess potassium added is largely retained in the soil by sorption on clays and organic matter. In areas where crops have been grown for many years without the addition of adequate potassium containing fertilizers, yield gradually

decrease as the potassium from between the illite layers is slowly removed. If potassium fertilizer is then added, the increase in yield is not as great as might be expected. This is because the potassium returns to the illite structure rather than remaining immediately available for plant growth. As a consequence the farmers are faced with the high costs of potassium fertilizers without receiving a comparable increase in crop yield. High yields of any crop can be sustained only by replacing the nutrients removed with the crop (Epstein et al., 1992).

## **2.8 Wastes and Pollutants in Soil**

Large quantities of untreated industrial municipal and agricultural wastes are dumped into the soil. Heavy metals like mercury, lead, cadmium, nickel and arsenic cause serious land pollution problems. For example wastes from mines and factories located in agricultural areas have been found to have contaminated the soil with heavy metals. In some cases, land disposal of degradable hazardous organic wastes is practiced as a means of disposal and degradation.

In soil a pesticide may be transported into various sectors of the environment by different physical processes, such as adsorption by the soil, leaching by rain water or be taken up by plants and animals or carried away by wind. But the processes that actually play important roles in reducing their total amount of residues, are those mediated by microorganisms, animals, plants and sunlight. Other factors are pH and heat. Catalytic agents in the soil and soil enzymes also play important roles in degrading relatively unstable pesticides. The major group of soil microorganisms such as actinomycetes, fungi and bacteria, degrade pesticides through oxidation, ether cleavage, ester and acid hydrolysis, oxidation, epoxidation etc. The notable characteristics of degradation systems in microorganisms are the reductive systems. Combustion of sulfur-containing fuels emits  $\text{SO}_2$  and finally leaves sulphate in the soil. Atmospheric nitrogen oxides

are converted into nitrates in the atmosphere and the nitrates eventually are deposited on the soil. Particulate lead from automobile exhausts also settles on soil along with rides of highway with heavy automobile traffic. High levels of Pb, Zn etc, are absorbed on soils near lead and zinc mines, etc. All these result in deterioration of soil quality, due to effects on the micro fauna, bacteria, fungi, etc. Biological degradation is also associated with lowering or depletion of soil organic matter.

## **2.9 Heavy Metals**

A heavy metal is a member of an ill-defined subset of elements that exhibit metallic properties, which would mainly include the transition metals, some metalloids, lanthanides and actinides. Many different definitions have been proposed- some based on density, some on atomic number or atomic weight and some on chemical properties or toxicity. The term “Heavy Metal,” has been called “meaningless” and “misleading” in an IUPAC technical report due to the contradictory definitions and its lack of “coherent scientific basis.”

There is an alternative term “Toxic Metals,” for which no consensus of exact definition exists either. As discussed below, depending on context, heavy metal can include elements lighter than carbon and can exclude some of the heaviest metals. Heavy metals occur naturally in the ecosystem with large variations in concentration. In modern times, anthropogenic sources of heavy metals, i.e. pollution have been introduced to the ecosystem (Hart, 1999).

Living organisms require varying amounts of “heavy metals.” Iron, cobalt, copper, manganese, and zinc are required by humans. Excessive levels can be damaging to the organism. Other heavy metals such as mercury, plutonium and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can

cause serious illness. The fact still remains that certain elements that are normally considered toxic for some organisms are for others under certain conditions, beneficial. Examples include vanadium, tungsten and even cadmium.

Some of these elements are actually necessary for humans in minute amounts (Co, Cu, Cr, Ni) while others are carcinogenic or toxic, affecting among others, the central nervous system (Hg, Pb, As), the liver or kidney (Hg, Pb, Cu, Cd) or skin, bones and/or teeth (Ni, Cd, Cu, Cr).

Heavy metals can get into the soil through precipitation of their compounds or by ion exchange and lay dormant. Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation. In some places, plants or micro-organisms are tentatively used to remove some heavy metals such as mercury. Plants which exhibit hyper-accumulation can be used to remove heavy metals from soils by concentrating them in their bio-matter (Baker et al., 2000).

## **CHAPTER THREE**

### **3.0 METHODOLOGY**

#### **3.1 Location Of The Project Area**

Delta state is one of the oil producing states in Nigeria, located on latitude  $5^{\circ}30^1$  N and longitude  $6^{\circ}$ E. It has a total land area of  $17,698\text{km}^2$  (6,833.2sq mi) with twenty-five (25) Local Government Areas.

Delta State comprises mainly Igbo (Anioma people), Urhobo, Isoko, Ijaw, and Itsekiri. The whole ethnic groups that make up the Delta are administratively grouped into three senatorial districts namely Delta North, Delta South and Delta Central for easy administrative purposes.

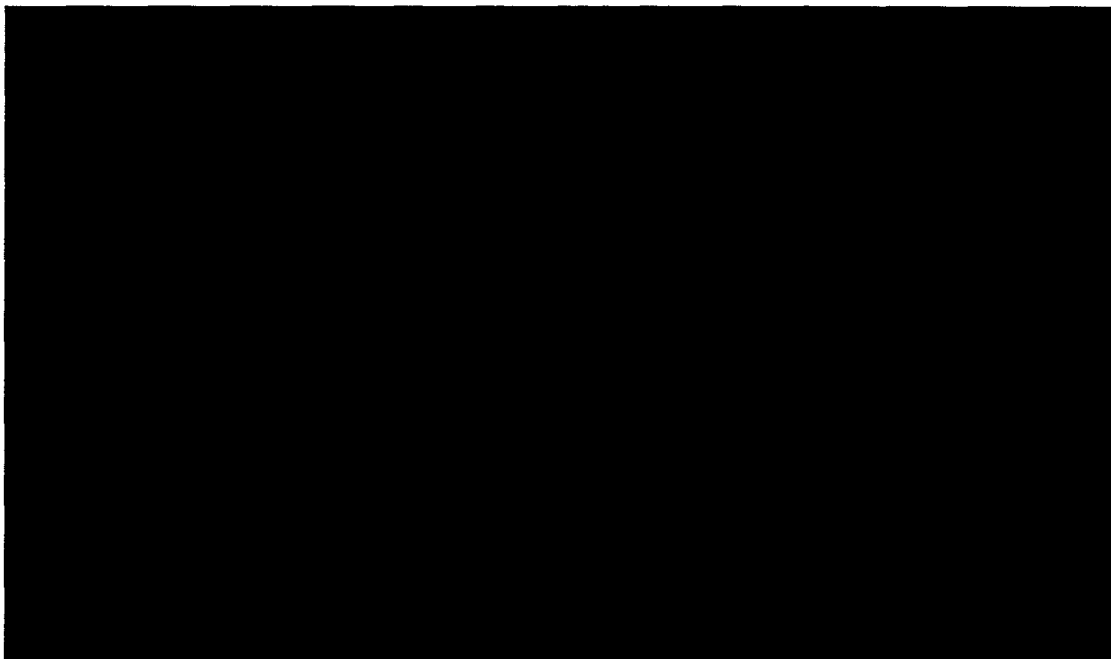


Fig. 1.3 Map of Delta State

## 3.2 Crops Used

### 3.2.1 Okra (Abelmoschus esculentus)

Okra is primarily a hot-weather tropical vegetable that can be grown in both northern and southern gardens. The fruits can be harvested from fifty-five (55) to sixty-five (65) days after seeding, depending on the variety. Okra thrives in any well-drained, good garden soil in full sunlight. If the soil is wet, the seed tend to rot, so good drainage is necessary. Although okra will do well in any kind of ground, thorough preparation of the soil is very important. Poultry manure is splendid material for okra beds.

In planting, the seeds could be scattered in drills or planted loosely and covered to a depth of one to two inches, according to the compactness of the soil. The seed could be separated three or four inches to allow space for the development of the stems. If the weather is warm, germination should take place within a few days.

For continuous production, pods should be gathered everyday when they are one to four inches long, depending on the variety. They should still be soft and the seed should be half grown if pods are to be eaten. If it is necessary to keep the pods over 24 hours, they should be spread out in a cool place and slightly moistened. They should be given ventilation because they become heated when heated when kept in closed crates or boxes.

Some of the varieties of okra are; the Dwarf green long pod, the Perkins mammoth, the White velvet, the Clemson spineless okra and the Emerald.

### 3.2.2 Tomato (Lycopersicon esculentum)

Tomatoes are propagated from seeds and belong to the family `solanaceae`. They do best in well-fertilized, sandy loams, but they also grow well in almost any type of fertile, well-drained soil. Tomato, because of its properties is used in phyto-remediation. Some of the compositions of fresh tomatoes are given below;

Table 1.0 Composition of tomato per each 100 gm

Water	93.76 g
Energy	21 Kcal
Fat	0.33 g
Protein	0.85 g
Carbohydrate	4.64 g
Fiber	1.1 g
Potassium	223 mg
Phosphorus	24 mg
Magnesium	11 mg
Calcium	5 mg
Vitamin C	19 mg

Vitamin A	623 IU
Vitamin E	0.38 mg
Niacin	0.628 mg

Source: USDA Nutrient Data Base

### 3.1.3 Experimental Plots

The soil samples were obtained from three different locations; plot A- solid waste site at Otor-Udu, behind Shell petroleum Gas plant in Udu L.G.A; plot B- a dumpsite at Okwagbe waterside along the creek in Ughelli south L.G.A; plot C- a control plot at DSC Aladja in Udu L.G.A. All three sites are well located within Delta State.

### 3.1.4 Sample collection and set-up

Six representative top soil (0-15 cm depth) samples (5 kg each) were collected randomly from each of the sites, and divided into three parts. As such, total samples collected were eighteen (18).

#### First part

The first part of plots A, B, and C consisting of six different samples were analyzed separately without planting on it.

#### Second part

The second set of six soil samples were used in the cultivation of the okra plant.



Fe	91.33 98.07	82.10 76.12	127.16 118.72	89.40 109.18	38.85 43.99	38.17 41.87
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**Table 4.6 Comparative mean of heavy metal concentration in okra plant**

Heavy Metal	Plot A (mg/kg)	Plot B (mg/kg)	Plot C (mg/kg)
Copper	4.14	6.27	4.01
Nickel	0.13	0.97	0.26
Lead	31.12	37.49	24.57
Zinc	8.82	29.01	4.38
Iron	94.70	122.94	41.42

**Table 4.7 Comparative mean concentration of heavy metal in tomato plant**

Heavy metal	Plot A (mg/kg)	Plot B (mg/kg)	Plot C (mg/kg)
Copper	11.49	44.36	6.40
Nickel	1.02	2.50	1.79
Lead	38.17	42.91	27.64
Zinc	45.19	101.72	22.81
Iron	79.11	99.29	40.02

#### 4.2.1 Transfer ratio

The transfer ratio is the level of the metal in the plants as a fraction of the soil total in the dump soil (Oyedele et al., 1995).

##### For Okra:

$$\text{Cu (plot A)} = 4.14/ 20.14 = 0.21; \quad \text{Cu (plot B)} = 6.27/ 61.13 = 0.10;$$

$$\text{Cu (plot C)} = 4.01/ 14.27 = 0.28;$$

$$\text{Ni (plot A)} = 0.13/ 2.11 = 0.10; \quad \text{Ni (plot B)} = 0.97/ 5.23 = 0.19;$$

$$\text{Ni (plot C)} = 0.26/ 4.17 = 0.10;$$

$$\text{Pb (plot A)} = 31.12/ 139.02 = 0.22; \quad \text{Pb (plot B)} = 37.49/ 144.29 = 0.26;$$

$$\text{Pb (plot C)} = 24.57/ 102.28 = 0.24;$$

$$\text{Zn (plot A)} = 8.82/ 165.25 = 0.10; \quad \text{Zn (plot B)} = 29.01/ 352.74 = 0.10;$$

$$\text{Zn (plot C)} = 4.38/ 92.41 = 0.05;$$

$$\text{Fe (plot A)} = 94.70/ 713.43 = 0.13; \quad \text{Fe (plot B)} = 122.94/ 912.10 = 0.14;$$

$$\text{Fe (plot C)} = 41.42/ 479.44 = 0.10;$$

##### For Tomato:

$$\text{Cu (plot A)} = 11.49/ 20.14 = 0.57; \quad \text{Cu (plot B)} = 44.36/ 61.13 = 0.73;$$

$$\text{Cu (plot C)} = 6.40/ 14.27 = 0.45;$$

$$\text{Ni (plot A)} = 1.02/ 2.11 = 0.48; \quad \text{Ni (plot B)} = 2.50/ 5.23 = 0.48;$$

$$\text{Ni (plot C)} = 1.79/ 4.17 = 0.43;$$

$$\text{Pb (plot A)} = 38.17 / 139.02 = 0.28;$$

$$\text{Pb (plot B)} = 42.91 / 149.29 = 0.29;$$

$$\text{Pb (plot C)} = 27.64 / 102.28 = 2.27;$$

$$\text{Zn (plot A)} = 45.19 / 165.26 = 0.27;$$

$$\text{Zn (plot B)} = 101.72 / 352.74 = 0.29;$$

$$\text{Zn (plot C)} = 22.81 / 92.41 = 0.25;$$

$$\text{Fe (plot A)} = 79.11 / 713.43 = 0.11;$$

$$\text{Fe (plot B)} = 99.29 / 912.10 = 0.11;$$

$$\text{Fe (plot C)} = 40.02 / 479.44 = 0.10;$$

**Table 4.8 Transfer ratio for Okra plant**

Heavy Metals	Plot A	Plot B	Plot C
Copper	0.21	0.10	0.28
Nickel	0.10	0.19	0.10
Lead	0.22	0.26	0.24
Zinc	0.10	0.10	0.05
Iron	0.13	0.14	0.10

**Table 4.9 Transfer ratio for Tomato plant**

Heavy Metals	Plot A (Otor-Udu)	Plot B (Okwagbe)	Plot C (Aladja)
Copper	0.57	0.73	0.45
Nickel	0.48	0.48	0.43
Lead	0.28	0.29	0.27
Zinc	0.27	0.29	0.25
Iron	0.11	0.11	0.10

**Table 4.9 Transfer ratio for Tomato plant**

<b>Heavy Metals</b>	<b>Plot A (Otor-Udu)</b>	<b>Plot B (Okwagbe)</b>	<b>Plot C (Aladja)</b>
Copper	0.57	0.73	0.45
Nickel	0.48	0.48	0.43
Lead	0.28	0.29	0.27
Zinc	0.27	0.29	0.25
Iron	0.11	0.11	0.10

#### **4.2.2 Heavy Metal Content of the Plants**

The data presented were restricted to the edible parts of the crop plants. Generally, crops harvested in the soils of the refuse dumpsites presented higher levels of the metals when compared to those crops from the control site (plot C). This is interpreted to mean that if the level of these metals in soils is significantly increased, the test crops have the potential of showing increased uptake of the metals. Alloway and Davies (1991) and Grant and Dobbs (1991) reported that plants grown on soils possessing enhanced metal concentrations have increased heavy metal ion content. The uptake of metal ions has been shown to be influenced by the metal species and plant parts (Juste and Mench, 1992). From the results obtained, it is observed that the tomato plant accumulates more metals than the okra plant from the dump soils as well as those from the control.

It was observed that the okra plant has more affinity for Iron (Fe) than tomato. The transfer ratios obtained for tomato were particularly high. This shows the ability of tomato being used in the

process of phyto-remediation. With increasing metal load in the dump soils where these plants are cultivated, there is a greater tendency for their bio-accumulation.

Tomato plant was able to extract high concentrations of heavy metals from the soils. In view of this, tomato plant can be used to clean up dump soil by farmers. This will decrease some of the metal elements present in the dump soil before the soil can be used as compost or for agricultural purposes. It is therefore recommended that dump soil should not be used for agricultural purpose until after a cleaning process with metal hyper-accumulation plants such as tomato, which must not be consumed by man or animal after harvesting.

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## APPENDIX (TABLES)

Table A1	Comparative mean concentration of metals in the soil samples of the three plots
Table A2	Comparative mean of pH and organic matter of soil samples
Table A3	Comparative mean concentration of heavy metal in okra plant
Table A4	Comparative mean concentration of heavy metal in tomato plant
Table A5	Transfer ratio for okra plant
Table A6	Transfer ratio for tomato plant

**Table A1: Comparative mean concentration of metals in the soil samples of the three plots**

<b>METALS</b>	<b>PLOT A (mg/kg)</b> <b>(Otor-Udu)</b>	<b>PLOT B (mg/kg)</b> <b>(Okwagbe)</b>	<b>PLOT C (mg/kg)</b> <b>(Aladja)</b>
Copper	20.14	61.13	14.27
Nickel	2.11	5.23	4.17
Lead	139.02	149.29	102.28
Zinc	165.26	352.74	92.41
iron	713.43	912.10	479.44

**Table A2: Comparative mean of pH and organic matter of soil samples**

	<b>A</b> <b>(Otor-Udu)</b>	<b>B</b> <b>(Okwagbe)</b>	<b>PLOT C</b> <b>(Aladja)</b>
<b>pH</b>	7.15	7.46	6.47
<b>Organic matter %</b>	16.12	21.74	10.48

**Table A3: Comparative mean of heavy metal concentration in okra plant**

<b>Heavy Metal</b>	<b>Plot A (mg/kg)</b>	<b>Plot B (mg/kg)</b>	<b>Plot C (mg/kg)</b>
Copper	4.14	6.27	4.01
Nickel	0.13	0.97	0.26
Lead	31.12	37.49	24.57
Zinc	8.82	29.01	4.38
Iron	94.70	122.94	41.42

**Table A4: Comparative mean concentration of heavy metal in tomato plant**

<b>Heavy metal</b>	<b>Plot A (mg/kg)</b>	<b>Plot B (mg/kg)</b>	<b>Plot C (mg/kg)</b>
Copper	11.49	44.36	6.40
Nickel	1.02	2.50	1.79
Lead	38.17	42.91	27.64
Zinc	45.19	101.72	22.81
Iron	79.11	99.29	40.02

**Table A5: Transfer ratio for Okra plant**

<b>Heavy Metals</b>	<b>Plot A</b>	<b>Plot B</b>	<b>Plot C</b>
Copper	0.21	0.10	0.28
Nickel	0.10	0.19	0.10
Lead	0.22	0.26	0.24
Zinc	0.10	0.10	0.05
Iron	0.13	0.14	0.10

**Table A6: Transfer ratio for Tomato plant**

<b>Heavy Metals</b>	<b>Plot A</b>	<b>Plot B</b>	<b>Plot C</b>
	<b>(Otor-Udu)</b>	<b>(Okwagbe)</b>	<b>(Aladja)</b>
Copper	0.57	0.73	0.45
Nickel	0.48	0.48	0.43
Lead	0.28	0.29	0.27
Zinc	0.27	0.29	0.25
Iron	0.11	0.11	0.10