

**IMPACT ASSESSMENT OF CEMENT PRODUCTION ON VEGETATION AND
SOIL OF OBAJANA COMMUNITY, KOGI STATE, NIGERIA**

BY

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**BEING A Ph.D. THESIS SUBMITTED AND PRESENTED TO THE DEPARTMENT OF
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THE DEGREE OF Ph.D. IN PLANT BIOLOGY.SUPERVISOR:**

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MAY, 2021

CERTIFICATION

I certify that this research was carried out by Mrs. Owoleke Veronica Amina in the Department of Plant Biology, Faculty of Life Sciences, University of Ilorin, Ilorin, Nigeria, for the award of Doctor of Philosophy (Ph.D.) degree in plant Biology.

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Departmental Postgraduate
Programmes Coordinator
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APPROVAL PAGE

This thesis has been read and approved as having met the requirement of the Department of Plant Biology and Postgraduate School, University of Ilorin, Ilorin, Nigeria, for the Award of Doctor of Philosophy (Ph.D.) Degree in Plant biology.

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DEDICATION

I dedicate this work to the Almighty God whose mercies and grace have brought me thus far and to my late mother Mrs Charity Iyeh whose last words some thirty-two years ago propelled me academically to this point. May her gentle Soul continue to rest in peace (Amen).

DECLARATION

I declare that the work in this dissertation, titled “Impact Assessment of Cement Production on Vegetation and Soil of Obajana Community, Kogi State, Nigeria” has been carried out by me in the Department of Plant Biology, University of Ilorin, under the supervision of Prof. P.O. Fatoba. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this work was previously presented for another degree in this or other institutions.

OWOLEKE, Veronica Amina

Signature

Date

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ABSTRACT

The production activities of cement factories pollute the soil and vegetation in their environment with heavy metal-laden cement dust. Heavy Metals (HMs) are serious pollutants thus constituting threat to the biota. The study was designed to evaluate the impact of Obajana Cement Factory (OCF) on the environment. This study investigated the effects of cement dust on the vegetation and soil of Obajana community Kogi State, Nigeria. The objectives of the study were to: (i) evaluate the HMs contamination of soil around OCF; (ii) quantify the concentrations of HMs in *Zea mays*, *Abelmoschus esculentus*, *Mangifera indica* and *Carica papaya* growing around OCF; (iii) investigate the leaf epidermal responses of the studied plants to cement dust pollution; (iv) determine HMs mobility in the studied plants; and (v) assess the hazard quotient of HMs contamination of the studied plants.

Soil and plant samples were collected from the eastern, western and northern axes of OCF, at 1, 2 and 3 kilometres from the factory. Samples were digested using a mixture of concentrated HNO_3 : HCl (1:3), while Zn, Pb, Cr, Cd and Cu concentrations were determined using Atomic Absorption Spectrophotometry. Epidermal responses of the studied plants to cement dust pollution were assessed using standard method. Transfer factor, bioaccumulation index, ecological risk and potential health risk were calculated using standard models. Data generated were subjected to Analysis of Variance, Carl Pearson Correlation Coefficient and t-test with significance level at $p < 0.05$.

The findings of the study were that:

- i. the soil samples contained Zn (8.70-196.00 mg/kg), Cr (3.95-115.87 mg/kg), Pb (4.18-29.65 mg/kg), Cd (0.00-6.75 mg/kg) and Cu (5.70-34.00 mg/kg). Chromium content of soil samples (62.65-111.87 mg/kg) was much higher than the CCME permissible limit of 64 mg/kg;
- ii. the highest amounts of HMs (mg/kg) in the fruits of each of the studied plants were; *Z. mays*, Zn (67.01), Cr (5.97), Pb (3.02), Cd (1.00) and Cu (6.05); *A. esculentus*: Zn (90.54), Cr (2.43), Pb (2.84), Cd (0.50) and Cu (4.21); *M. indica*: Zn (60.31), Cr (2.65), Pb (1.83), Cd (0.05) and Cu (9.01); *C. papaya*: Zn (58.07), Cr (2.71), Pb (1.77), Cd (0.05) and Cu (10.03);
- iii. stomatal sizes and densities of plants from the polluted sites were significantly ($p < 0.05$) different from the control. Stomatal complex types remained unchanged;
- iv. *A. esculentus* and *M. indica* accumulated Cu and Zn and excluded Cr, Cd and Pb; *C. papaya* accumulated Cu, Zn and Pb and excluded Cr and Cd while *Z. mays* accumulated Cr, Cu and Zn and excluded Pb and Cd; and
- v. fruits of all the studied plants had Hazard Quotient values greater than 1 for Zn. Whereas, *Z. mays* fruit had Hazard Quotient values greater than 1 for Cr.

The study concluded that the soils of Obajana community had elevated levels of HMs, as evidenced by the accumulation of chromium in *Z. mays* grains. The study recommended

remediation of soil around OCF to reduce its HMs load in order to avert health hazards that may result from consumption of crops grown around the location.

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CHAPTER ONE

INTRODUCTION

1.1 Air pollution caused by industrial activities

Industrial activities have great impact on the environment as well as the health of humans and animals. All chemical compounds or elements released into the atmosphere primarily as a result of human activities and which can cause damage to living organisms, can be called air pollutants (Pacyna and Pacyna, 2001). Cement dust can be carried away for long distances and cause air pollution and soil degradation if it contains heavy metals. Small suspended solids particles (ranging between 0.01 - 200 Microns), remains in the air for a long period of time (Hashim, 2009). For this reason, these particles increases respiratory diseases, especially asthma, and may lead to lung tissue damage. Relatively bigger particles settles down more rapidly due to their weight because air turbulence cannot sustain their weight in suspension for a long period of time (Hashim, 2009). In addition, smaller particles seem to interact with other air pollutants, leading to more severe damaging influence on the environment. These suspended solids consists of suspended minerals and heavy metals (Leili *et al.*, 2008).

The source of these heavy metals may be natural or artificial. Natural sources are usually particles of soil and sediments that are transported by winds, while artificial sources includes industrial activities that emit heavy metals into the air and causing contamination of the atmosphere. In order to improve quality of life, man has tampered with the harmless state of some naturally occurring substances converting them into toxic wastes. This increasing amounts and concentrations of pollutants has caused the balance of nature to be affected. Thus, the environment's self-healing limits has been reached and the life-sustaining mechanisms of nature has been surpassed (Emberson, 2003).

The contribution of Portland cement production worldwide to the greenhouse gas emission is estimated to be around 7% of the total greenhouse gas emissions to the earth's atmosphere (Malhotra, 2002). The negative consequences of global warming are evident in melting of the polar ice, flooding, drought and changing flora and fauna of natural habitat for both plants and animals. The production and exploitation of resources by mining does not only change the environment, but also destroys and damages the natural ecosystem by destroying the original habitat (USEPA, 2003).

Airborne particles and gases, waterborne pollutants and deposition of waste materials in the soil have all impacted plants and animals. Elements produced in small quantities may become toxic to plants when present in large quantities and may also be transported by water and wind at high concentrations, thereby reducing the quality of air and water (Van Tienhoven, 2000). Heavy metals such as cadmium, copper, silicon, lead, mercury and so on are released into the environment by quarrying and smelting activities (Kumar and Singh, 1990). Heavy metal contamination has caused the death of plants and denudation of vegetation.

Industrialization has been strongly correlated with air pollution, which has increased in recent times. The bulk of heavy metals, sulphur and nitrogen compounds that causes pollution, comes from anthropogenic sources (Pacyna and Pacyna, 2001). The degree and extent to which emissions are distributed depends on the pollution source, the composition of the emissions and the weather conditions (Abatyough *et al.*, 2015). Cement manufacture is one activity that contributes to environmental pollution through the emission of gasses and cement dust El-Abssay *et al.*, 2011. This dust can spread over large areas through wind and rain and are accumulated in and on soils and plants (Cristina and Otilia, 2008).

Cement production has been widely associated with high emissions of pollutants, including particulate air pollutants, which pollute the entire area in the vicinity (Adejumo *et al.*, 1994).

Atmospheric emissions from industrial establishments is one of the major sources of environmental pollution. One type of industry that causes particle pollution is the cement industry (Zerrouqi, *et al* 2008). The main inputs of cement production activities on the environment are the broadcasts of dust and gases. Cement dust spreads along large areas through wind, rain etc. and are accumulated in and on soils, plants and animals and can affect human health badly (Isikli *et al.*, 2006).

1.2 Soil pollution caused by cement production activities

The occurrence of heavy metals in soil can be of natural and anthropogenic source. The anthropogenic sources includes cement production, smelting, mining, fossil fuel combustion and several other industrial activities. Cement production is a vital emission rout of heavy metals such as Cadmium, Chromium, Lead, Zinc and Copper (Al-Khashman and Shawabkeh, 2006). These heavy metals are deposited onto soil at various distances depending on wind velocity and particle size, through cement dusts and stack fumes. Heavy metals in cement dust originates mainly from raw materials.

Soil has been proven to be the major sink for anthropogenic heavy metal deposition through various pathways (Ogunkunle *et al.*, 2013a). The contamination of soil by heavy metals can pose challenges at several levels because they do not degrade biologically (Emmanuel *et al.*, 2009) and this causes several soil disfunctions leading to concerns about the environmental quality. Metal contaminated soil poses risks to humans and animals through ingestion of plants that have bio-accumulated toxic metals from contaminated soil (Turner, 2009). The host community of Obajana cement factory depends on the vast arable land surrounding this massive cement factory for their agricultural activities which include growing of fruit trees and crops like mango, pawpaw, maize and okra.

Environmental pollution caused by industrialization is inevitable unless proper measures are taken (Mohammad and Mohammad 2001). Heavy metals can affect both the yield of crops and their composition (Alloway *et al.*, 1990). These metals are important because they are capable of bio accumulating and biomagnifying in the food chain. There is also the risk of superficial and groundwater contamination. Therefore, knowledge of the basic chemistry of these metals in soil as well as the environmental and health risk they pose in soil is necessary in understanding their speciation and bioavailability (USEPA Report 1996). The fate and transport of heavy metals in soil depends significantly on the chemical form and speciation of the metal. Bioavailability of metals released from deposits is very complex and dependent on many interrelated chemical, biological and environmental factors. These processes may vary overtime and among micro - organisms, plants and animals. Field and laboratory studies of particular sites using soil, plants and selective chemical extraction methods may enhance understanding of this concept which is of environmental concern (Shiowatana *et al.*, 2001).

Soil contamination due to disposal and dispersal of industrial and urban wastes is a major environmental concern. This contamination is caused by the presence of a wide range of inorganic and organic compounds. These compounds may be heavy metals, combustible substances, explosives, petroleum products and hazardous wastes (Ghosh and Singh, 2005). Heavy metals are the main constituent of the inorganic contaminants. Though, some heavy metals are vital but at high concentrations, these metals can produce toxic effects as their free radicals causes oxidative strain. So elevated concentrations of heavy metals render the soil inappropriate for the growth of plants and could ultimately wipe out biodiversity (Alloway, 1990).

Dusts that escapes from cement factories is usually transported by wind and deposited in areas close and far away from the factories. The affected areas may natural vegetation,

include cultivated lands, towns and villages. These depositions of particulate matter and other pollutants interfere with normal metabolic activities of plants, causing direct injury and impairment of growth and decrease in plant yields (Ediagbonya *et al.*, 2013). Heavy metals are among the most harmful substances emitted during the process of cement manufacture. Among the metals present in cement dust, and known to have toxic effects in environmental matrices are cadmium, arsenic, lead, thallium, Aluminium, mercury, Chromium, Copper, Manganese, Zinc, Nickel and Beryllium (Schumacher *et al.*, 2002). Toxic substances such as lead, fluoride, zinc, copper, magnesium, hydrochloric acid and sulphuric acid were reported to be emitted by cement manufacturing factories (Iqbal and Shafiq, 2001).

Dangote cement factory produces 16.25 million metric tonnes of cement per annum across five lines (OCP 2020). In cement factories, dust is produced primarily from raw materials and clinkers broken by abrasion, impact, grinding, crushing and through the release of previously created dust during operations such as packing, dumping and transfer also, through the re-circulation of previously created dust by wind or through the movement of workers and machinery (CPCB, 2007). The amount of dust produced by these practices depends on the physical characteristics of the materials and the manner in which they were treated (CPCB, 2007). Cement production is an important emission source of heavy metals such as Cd, Cr, Cu, Pb and Zn, Cr, Pb, Cd and Cu (Al-Khashman and Shawabkeh, 2006). The majority of heavy metals in cement dust originates from raw materials. Soil has been recognized as the major sink for anthropogenic heavy metal deposition through various pathways (Ogunkunle *et al.*, 2013).

1.3 Soil physico-chemical parameters

Soil pH is a measure of a soil's acidity or alkalinity (Förstner, 1995). It is an important soil health indicator. Soil pH regulates both soil biology and biological processes. In several soil

processes, soil pH plays a significant role. This vital physicochemical property of soil regulates the interaction of xenobiotic, translocation and transformation within the three phases of the soil. Consequently, soil pH is a major determinant of the fate of substances in the soil system. This has consequences for the recycling and availability of nutrients for crop production, the environmental distribution of hazardous substances, and their removal or translocation (White, 2006).

For the remediation of polluted soils and the regulation of pollutant translocation and transformation in the environment, this functional role of soil pH in soils has been exploited. The solubility, mobility, and bioavailability of trace elements which determines their translocation in plants are all regulated by soil pH (Förstner, 1995). Basta *et al.* (2005) reported that the most important factor that controls plant metal uptake is soil pH. Cd absorption is inversely correlated to the pH of the soil (Alloway, 1992). Soil pH was considered by Alloway (1992) as the main factor that determines the presence of cadmium in soil, this is because pH affects both cadmium adsorption and speciation in soil solution.

Alloway and Jackson (1990) recorded that adding lime to increase the pH of a wide range of different sludge soils to pH 7.0 had the effect of reducing cabbage Cd concentrations by an average of 43% and lettuce Cd content by 41%. At low pH, because of high desorption and low adsorption, heavy metals are generally soluble. At intermediate pH, heavy metal adsorption increases within a small pH range called the pH-adsorption edge, from almost no adsorption to almost maximum adsorption (Bradl, 2004). Metals are completely adsorbed from this point forward (Bradl, 2004). For example, (Bradl, 2004) found that Cd, Cu, and Zn adsorption into a composite sediment consisting of Al-, Fe-, and Si-oxides was 60%, 62%, and 53%, respectively, at pH 5.3. He found, however, that 50 percent of Cd and Zn were adsorbed into humic acids between pH 4.8-4.9.9 (Bradl, 2004).

Slight increase or decrease in soil pH causes distinct effects on the solubility of metals. This will possibly depend on the metals' ionic species and the direction of the change in pH. Förster, 1995, found a 10-fold increase in metal solubility as a result of a decrease in soil pH by one unit. In an experiment, he found that only about $1\text{ mg Zn}\cdot\text{L}^{-1}$ of the total Zn content of $1200\text{ mg}\cdot\text{kg}^{-1}$ was present in soil solution at pH 7. The concentration reached $100\text{ mg Zn}\cdot\text{L}^{-1}$ at pH 6, while $40\text{ mg Zn}\cdot\text{L}^{-1}$ was present at pH 5. Heavy metal concentrations at high soil pH can also be caused by accumulation of carbonates, chlorides, hydroxides, phosphates, and sulphates in addition to adsorption (Cui, 2016).

Organic matter

Organic matter of the soil refers to the organic component of the soil. Soil organic matter affects the composition of the soil, the moisture retaining ability of the soil and the availability of nutrients.

In addition, the amount of soil organic matter affects the availability of heavy metals in the soil for plant uptake and soil pH regulates this. There are different components of soil organic matter, ranging from basic molecules such as amino acids, monomeric sugars, etc., to polymer molecules such as cellulose, collagen, lignin, etc. These occur alongside undecomposed and partially decomposed residues of plants and microbials (Baldock, 2007). During and after decomposition, the solubility and mobility of the fractions vary and could contribute to the leaching of dissolved organic carbon and nitrogen in some soils (Vogel *et al.*, 2000). By increasing the dissociation of acid functional groups, soil pH increases the solubility of soil organic matter (Anderson *et al.*, 2000) and decreases the bonds between organic components and clays (Cutin *et al.*, 1998). Thus, with soil pH and subsequently mineralizable C and N, the dissolved organic matter content of soil increases (Cutin *et al.*,

1998). This explains the powerful effects of alkaline soil pH conditions on dissolved organic carbon leaching and dissolved organic nitrogen found in many soils containing large amounts of organic matter (Anderson *et al.*, 2000; Evans *et al.*, 2012). A similar finding was reported by Oulehle *et al.*, 2016 on dissolved organic carbon content in peatland soils. Dissolved organic carbon concentration's pH dependency becomes more pronounced beyond pH 6 (Cutin *et al.*, 2016).

The solubility of organic matter within the pH condition of any soil is strongly affected by the type of base. It is especially higher in the presence of monovalent cations than with multivalent cations (Cutin *et al.*, 2016). Soil pH regulates the solubility of organic matter in two main ways; its effect on the charge density of humic compounds and enhancement/suppression of microbial activities (Andersson and Nilsson 2001; Andersson *et al.*, 2000).

Electrical conductivity (EC)

Electrical conductivity (EC) of a soil is an indicator of a soil's ability to conduct an electrical current. Its a pointer to the nutrient availability of a soil. The higher the EC, the more sites (organic matter) found in the soil that are negatively charged. Therefore, the more cations in the soil are preserved. Soil optimal EC levels vary from 110-570($\mu\text{S}/\text{Cm}$).

The physico-chemical properties of soil are influenced by; the type of parent materials that forms the soil and various human activities such as farming and deposition of materials such as industrial waste. One such industrial waste that affects the physico-chemical properties of the soil is cement dust. The manufacture of cement includes the mining and quarrying of raw materials, which are primarily oxides and metal carbonates. It also requires grinding the raw materials into fine particles and mixing them in suitable proportions. Cement processing is

one of the main anthropogenic activities that contributes to environmental emissions of particulate matter.

Cement production was listed as the highest source of ambient dust pollution by an inventory of air pollutants in Nigeria, accounting for around 22.4 million tonnes of emissions in 1988. (Adejumo *et al.*, 1994). Soil remains one of the largest sinks for emitted dust from cement production activities occasioned by direct dumping or atmospheric depositions of cement dust at distances close to or far away from the factories. The deposition of aerosols created by cement production, could have profound adverse effects on the physicochemical properties of the soil and which could eventually be transferred to the food chain. The physico-chemical properties and elementary compositions of soils around cement factories are therefore affected by the impact of dust produced from cement production. It has been documented that heavy metal absorption is regulated by soil factors such as pH and organic matter content (Csintalan and Tuba, 1991)

1.4 Heavy metals pollution

Heavy metals occur naturally in the environment at very low and tolerable limits. Nevertheless, human activities such as mining and cement manufacturing have resulted in increased environmental levels of these pollutants. Heavy metal, regardless of its atomic mass or density, can be described as any toxic metal (Doelsch *et al.*, 2005). Metalloids, basic metals, transition metals, lanthanides, actinides and metals of groups III to V of the periodic table all consists of heavy metals. Examples of heavy metals are: arsenic, vanadium, cadmium, bismuth, chromium, tin, copper, gold, thallium, lead, manganese, platinum, nickel, iron, silver, tellurium, gallium, cobalt, uranium, cerium, zinc, antimony and mercury (Mosby *et al.*, 1996).

Heavy metals are natural components of the earth's crust that cannot be destroyed or damaged, but are able to gain entrance into human bodies through water, air and food (Dung *et al.*, 2002). Heavy metals belong to a narrowly defined class of elements that exhibits metallic properties. They are mostly transition metals, some of which are metalloids, lanthanides and actinides. There is no standard definition of heavy metals, some definitions are based on a specific gravity greater than 4.0 or 5.0 while others makes reference to atomic weight. Although, Gardea-Torresdey *et al.* (2005) identified heavy metals as a group of elements with a specific gravity higher than 4 and an atomic weight between 63.54 and 200.59. More recently, the term 'heavy metal' is used to describe all metals and semi-metals with potential human or environmental toxicity (Menlenbelt *et al.*, 2001). These toxic metals, such as Cr, Cd, Pb, which enter the environment through human activities, can undergo bioaccumulation, geoaccumulation and biomagnification and are harmful to human health and the environment (Michael, 2010).

In small amounts, heavy metals such as copper, iron, zinc and manganese are nutritionally necessary for a healthy life. These essential elements occur naturally in vegetables, fruits and meats; and commercially available in multivitamin products (Jolly *et al.*, 2013). Some heavy metals play important roles in the body, such as helping essential enzymes work. Some heavy metals perform physiological roles; Copper (amine oxidases, dopamine hydrolase and synthesis of collagen), zinc (synthesis of proteins, DNA and RNA stabilization) and iron (hemoglobin and cytochrome hemoeties) Rengel, 2004. Heavy metals are present in pesticides, batteries, alloys, electroplating metal pieces, textile dyes, steel and several other domestic items (Flora *et al.*, 2008). Since the body does not metabolize them, heavy metals become toxic and accumulate in the soft tissues. Cadmium, lead, mercury, arsenic, aluminium, bismuth, antimony, uranium and barium are hazardous heavy metals. The heavy metals that are beneficial in small quantities are typically toxic in larger quantities. Heavy

metals that are toxic are capable of replacing essential metals. For example, cadmium which is located just below zinc in the periodic table and has an atomic weight very similar to zinc can displace zinc in binding sites of critical enzymes such as carboxypeptidase, alcohol dehydrogenase and RNA transferase in an organism's body (Siedleka and Kurpa, 1997). In the earth's crust, heavy metals occur naturally, and their environmental concentrations can vary in different areas, resulting in spatial differences in background concentrations.

Heavy metal distribution in the environments is determined by the metal's properties and some environmental variables (Kabata-Pendias and Mukherjee, 2007). Out of the 92 elements that exists naturally, about 30 metals and metalloids have the potential to be harmful to humans. Heavy metals may be of natural and anthropogenic origin in soils. Anthropogenic pollution is the addition of heavy metals to the environment by human activities, while the natural sources originates from parent materials containing high levels of heavy metals (Brown *et al.*, 1999).

In living organisms, some heavy metals in very small concentrations are essential to maintain different biochemical and physiological functions. However, these essential heavy metals becomes toxic when certain threshold concentrations are exceeded. Heavy metals are important environmental contaminants that have environmental, biological, nutritional and evolutionary impacts (Jaishankar *et al.*, 2013). Such metals bind to protein sites not intended for them by removing the original metals from their normal binding sites, causing cell malfunction and eventually toxicity (Flora *et al.*, 2008). Chromium, cadmium, lead, zinc and copper are the most frequently found heavy metals in soils and plants near cement factories, all of which pose risks to human health and the environment (Lambert *et al.*, 2000).

In our environment and diet, these heavy metals are constantly present. Some are needed in small quantities to maintain good health, but they can become harmful in larger quantities.

The functioning of the brain, kidney, liver, blood, lungs and other very vital organs may be affected by heavy metal toxicity. In most heavy metals, the toxicity threshold may be just above the background concentrations naturally present in the environment. Therefore, in order to be properly guided on the risk of exposure and hazardous concentrations, thorough knowledge of heavy metals is very necessary (Ferner, 2001).

Zinc

Zinc is a blue-white lustrous metal with atomic density 7.14g/cm^3 , atomic number 30 and atomic mass 65.38g/mol (Eisler, 1993). It is a trace element important for the growth of plants. Zinc is an integral part of most enzymes and proteins (Kupper and Kroneck, 2005). Zinc is released into the environment by anthropogenic activities such as vehicular pollution, mining, production of cement, corrosion of galvanized structures, production of iron and steel, disposal of waste, use of fertilizers, combustion of coal and fuel, and use of pesticides containing zinc. The stability of biological molecules such as DNA and biological structures such as ribosomes and membranes is assured by zinc (Leonard and Gerber, 1989).

In plants, the concentration of zinc varies directly to its concentration in the soil on which the plant is grown (Kupper and Kroneck, 2005). The ability of plants to take up other essential metals such as iron and manganese is affected by zinc concentrations above 500 ppm in the soil (Emsley 2001). Zinc helps to protect plants from cadmium toxicity by increasing the plants' protection against Cd-induced oxidative stress and competing with Cd for binding to critical cell constituents when zinc is in the moderate range in soils (Koleli *et al.*, 2004). In polluted soils, roots typically have higher concentrations of zinc than shoots, although the reverse is true in areas where zinc is an airborne pollutant (Gallego *et al.*, 1996). High levels of zinc in humans cause acute symptoms, such as gastrointestinal irritation, anorexia,

weakness, hair loss, anaemia, decreased use of food, serum enzymes, changes in the levels of liver and changes in brain morphology and enzymes.

Chromium

Chromium occurs in many oxidation states that ranges from Cr^{2+} to Cr^{6+} (Rodríguez *et al.*, 2009). Chromium is one of those heavy metals in the atmosphere with a steadily growing concentration due to industrial growth, especially the production of metals, tanning industries and cement plants (Adejumo *et al.*, 1994). The seventh most common element on earth is chromium (Mahaboob and Srinivas, 2013). In industries such as cement production, metallurgy, paint and pigment manufacturing, electroplating, tanning, chemical production, wood preservation, and paper manufacturing, chromium is commonly used. These sectors play an important role in chromium contamination of the environment with an adverse impact on biological and ecological ecosystems (Ghani, 2011).

In recent years, environmental contamination by chromium, particularly hexavalent chromium, has been the greatest concern (Zayed and Terry, 2003). For plant and animal scientists, pollution of soil and groundwater resulting in subsequent plant absorption due to the use of chromium in different anthropogenic activities has been a major source of concern for many decades. It has been found that chromium is highly toxic to plants and harms their growth and reproduction, although certain plants are not harmed by low Cr concentrations (Huffman and Allaway, 1973). There is no clear mechanism for Cr uptake due to the fact that Cr is a non-essential element (Shanker *et al.*, 2005), so its uptake is through carriers used for the uptake of essential metals for plant metabolism.

Diseases such as malignant neoplasia, lung cancer, skin ulcers and dermatitis are induced by chromium exposure (Salami *et al.*, 2014). The irrigation by Cr waste water and Cr dust results in soil pollution affecting the soil-vegetable system and also disturbs the production of

vegetables and their quality for human consumption (Duan *et al.*, 2010). The presence of excess chromium above the acceptable limit is harmful to plants as it seriously affects the plant's biological factors and reaches the food chain with the ingestion of the plant materials that are chromium polluted. Reduction in root development, seed germination inhibition, leaf chlorosis and depressed biomass are common features of Cr phytotoxicity. The biological processes in various plants such as wheat, maize, cauliflower, barley, and other vegetables are greatly affected by chromium toxicity. Chromium toxicity in plants triggers chlorosis and necrosis (Ghani, 2011).

Lead

Lead is a bright silvery metal which, in a dry atmosphere, is slightly bluish. On contact with air, it starts to tarnish, thus forming a complex mixture of compounds, depending on the prevailing environmental conditions (Sharma and Dubey, 2005). Lead is radioactive and has an atomic weight of 208.19, an atomic number of 82, a melting point of 27.50C and a basic gravity of 11.37. Industrial activities, drinking water, food, smoking, and household items are some routes of lead exposure. Vehicle pollution and house painting are other sources of lead (Thürmer *et al.*, 2002). Lead is a highly toxic metal whose widespread use in many parts of the world has caused extensive environmental pollution and health concerns.

Lead is an extremely toxic heavy metal that interferes with different physiological processes of plants and does not perform any biological functions unlike other metals, such as copper, zinc and manganese. Lead is not biodegradable and remains a long-term source of lead pollution after the soil has been contaminated by it according to Pehlivan *et al.* (2009). In both terrestrial and marine ecosystems, lead is a major pollutant and remains a significant pollution concern in urban environments (Olowoyo and Van Heerden, 2010). The development of reactive oxygen species (ROS) is high in plants with high lead concentration,

thus causing lipid membrane damage, damage to chlorophyll and photosynthetic processes and eventually suppresses the overall plant growth (Najeeb *et al.*, 2014). The negative impact of Pb depends on its concentration, the form of occurrence in the soil, soil properties and species of plants grown on the lead polluted soil (Patra *et al.*, 2004). Lead toxicity causes reduced rate of seed germination, decreased root and shoot dry mass (Munzuroglu and Geckil, 2002) and decreased cell division (Eun *et al.*, 2000).

Lead uptake is regulated by soil pH, particle size and cation exchange capacity, as well as root exudation and other physicochemical parameters (Irfan *et al.*, 2010). Excess Pb causes several plant toxicity symptoms, such as chlorosis, inhibits photosynthesis, stunted growth, disturbed mineral intake and water balance (Shafiq *et al.*, 2010). Lead toxicity ionic mechanism occurs primarily because of the ability of lead metal ions to replace other bivalent cations such as Mg^{2+} , Fe^{2+} , Ca^{2+} and monovalent cations such as Na^{+} , which eventually results in disturbance of the cell's biological metabolism. Lead can substitute calcium even at low concentrations and in turn affects protein kinase, which regulates neural excitation and memory storage (Flora *et al.*, 2008). Lead poisoning was treated as a conventional disease and the symptoms found in children and adults were generally related to the central nervous system and the gastrointestinal tract (Markowitz, 2000).

Lead has been reported to contaminate drinking water supplies; this could result from the pipes holding the water (Brochin *et al.*, 2008). Lead is believed to be a carcinogen, according to the Environmental Protection Agency (EPA). Lead toxicity, also referred to as lead poisoning, can be either acute or chronic. Hypertension, Loss of appetite, headache, renal dysfunction, abdominal pain, exhaustion, vertigo and arthritis may result from acute lead exposure. Chronic lead exposure can lead to birth defects, mental retardation, autism,

allergies, hallucinations, paralysis, hyperactivity, brain injury, muscle weakness, kidney damage and even death (Martin and Griswold, 2009).

Cadmium

Cadmium, according to the ATSDR list, is the seventh most toxic heavy metal. It is a dense, silver-colored, toxic heavy metal that exists naturally in the crust of the earth (Mutlu *et al.*, 2012). Owing to its high toxicity and low water solubility, it is regarded as a very critical pollutant (Pinto *et al.*, 2004). Cadmium is a highly toxic, non-essential heavy metal that is well known for its harmful effects on nutritional deficiency in plants, oxidative stress and cell enzymatic processes (Irfan *et al.*, 2013). Cadmium is commonly used in electroplating and has many uses, such as in pigments, batteries, metal coatings and plastics, (Martin & Griswold, 2009). Cadmium and its compounds are listed by the International Agency for Research on Cancer (IARC) as Category A human carcinogens (Henson and Chedrese, 2004).

Natural activities such as weathering, river transport, volcanic eruptions and certain human activities such as cement production, mining, industrial waste, cigarette smoking, fertilizer processing and incineration are responsible for releasing cadmium into the atmosphere. Cadmium (Cd) is one of the most dangerous elements for plants among heavy metals; it appears to have high soil mobility and is easily absorbed by plants than many other heavy metals, including Pb and Cu (Alloway, 1990). Due to its high rate of soil-to-plant transfer, cadmium is mainly present in fruits and vegetables (Satarug *et al.*, 2011). Low pH also affects the elevated levels of Cd in soil solution (Alloway, 1990). By altering membrane composition and function, stimulating free radical growth and inhibiting key enzymes of important metabolic pathways, Cadmium usually affects the overall metabolism of cells, which ultimately leads to oxidative stress. (Gratao *et al.*, 2005).

As a consequence, Cd affects the most important physiological processes such as photosynthesis or respiration, thus preventing plant development and growth (Gallego *et al.*, 1996). Cadmium is absorbed into edible leaves, fruits and seeds from the roots of plants. Cadmium taken from the soil is concentrated in the centre of the kernel during the growth of grains such as wheat and rice. Cadmium also accumulates in fatty tissues and animal milk (Figuerola, 2008). People are also exposed to cadmium by consuming cadmium-polluted foods. A source of cadmium exposure may also be seafood, such as molluscs and crustaceans (Gratao *et al.*, 2005).

Ingestion of cadmium in greater quantities can lead to diarrhoea, inflammation of the stomach and vomiting. It can be accumulated in the kidney at lower concentrations at very long exposure periods and eventually contributes to kidney failure, lung damage and fragile bones (Bernard, 2008). In contrast to other metals, cadmium and its compounds are extremely water soluble. Their bioavailability is very high and, thus, bioaccumulation is a continuous occurrence. Through food and some other pathways, humans are exposed to cadmium. However, the absorption of cadmium by other routes is much smaller (Mudgal *et al.*, 2010). Cadmium interacts with vital nutrients by which its toxicity effects are caused.

Copper

Copper is released during mining, agriculture and industrial activity into the environment (Harrison *et al.*, 1981). In soils, high levels of copper rarely occur naturally (Kupper and Kroneek, 2005), but copper may accumulate due to the use of sewage sludge, pig slurry or slag or, more generally, through the repeated use of agrochemicals such as fungicides or fertilizers containing copper (Sauve *et al.*, 1997). The toxicity of copper appears to have a primary effect on plant roots, so the concentration in the above ground parts may be a poor indicator of plant status (Marschner, 1995). Alva *et al.* (1995) found that the concentration of

copper in citrus trees did not increase significantly as soil Cu was increased to levels that decreased yield. Copper is used in very small quantities as a divalent ion (Cu^{2+}) and plays an important role in metabolic processes such as the production of enzymes and chlorophyll, photosynthesis, respiration, metabolism of carbohydrates and other proteins (Estifanos, 2014).

The useful Cu concentration range is said to be very narrow (Kupper and Kroneck, 2005), but for many proteins and enzymes, Cu is needed as an active core. Cu absorption is highly dependent on pH and Cu's bioavailability increases with decreasing pH (Sauve *et al.*, 1997). Cu is not readily leached from the soil profile due to its high affinity for organic matter and continues to settle on the soil surface (McBride *et al.*, 1997). The intra-plant movement direction of copper is still only partially understood, but long-range transport in plant xylem can be mediated by cu-complex ligands such as histidine and nicotinamide, both of which combines readily with Cu (Kupper and Kroneck, 2005). High doses of Cu could cause, abdominal pain, nausea, haemoglobinuria, haematuriad, diarrhoea, hypotension, jaundice, coma and death. Information on chronic copper toxicity is minimal. However, except for people suffering from Wilson's disease, copper does not seem to be a cumulative toxic threat to humans. Copper is not believed to be carcinogenic or mutagenic (Codex, 2011).

1.5 Production of cement in Nigeria

Cement is a basic component of constructions (Winmore *et al.*, 2012). Due to extensive construction works taking place across Nigeria, the demand for cement is on the increase. In both developed and developing countries, the manufacture of cement is considered to have many harmful effects on the environment and human health. Akande and Idris (2005) showed that the manufacture of cement has a number of socio-economic impacts on the local communities where cement factories are located. These effects include health issues, crime

growth, and infrastructural development. The Federal government had considered building a cement factory in Nkalagu in the early 1950s because of the discovery of significant amounts of limestone deposits in the area. However, this scheme was not completed and the Nigerian Cement Company was not incorporated until 1954. More cement factories have been built after this time. In Nigeria, there are currently 10 integrated cement manufacturing firms; Dangote Cement Plc (Obajana, Ibese, Gboko), West African Portland Cement Company Plc (Ewekoro, Sagamu), United Cement Company of Nigeria, BUA Cement (Okpella), Edo Cement Company (Okpella), Benue Cement Company Plc and Ashaka Cement Company Plc (Gombe).

Nigeria's Obajana cement plant in Kogi State is the largest cement plant in sub-Saharan Africa and is considered one of the world's largest cement plants with a production capacity of approximately 15.7 million tons of cement per year as of 2018, increasing to 16.25 million tons of cement per year across five lines as at 2020 (OCP 2020). Obajana cement plant is owned by Dangote Cement plc. The factory is situated in Lokoja local government area of Kogi state, Nigeria. Obajana is one of the towns in Oworo land. Obajana is located between Latitudes $6^{\circ}24'N - 7^{\circ}34'N$, Longitudes $7^{\circ}49'E - 8^{\circ}59'E$ of the Greenwich meridian. Obajana is about 220Km from Abuja, the Nigeria Federal Capital Territory, 43Km to Lokoja, 49Km to Okene and 40Km to Kabba.

The establishment of Cement industry in Obajana communities have heavily impacted the people, both physically and socio-economically. These impacts can be both positive and negative. Cement industries all over the world create dusts thereby giving room to lungs related diseases. Adamson (1996) reported that cement production is one of the worst air polluters in the world. Cement-based contaminants in the form of cement slurry stack spills and kiln dust emissions that contain particulate matter, heavy metals, SO_x, CO_x, NO_x and

smaller amounts of hydrocarbons, ketones and aldehydes are predominant in communities that host large cement facilities (Adamson, 1996). Dust and gases emitted from cement plants are the major environmental impacts of cement production (Bilen, 2010). Cement binding and calcination produces pollutants such as heavy metals, dioxins (Ade-Ademilua and Obalola, 2008) and causes many diseases, including respiratory diseases, cancers, genetic diseases etc. Furthermore, numerous residents around cement plants protest against the health problems they face, which they attribute to the state of the air they breathe (Fortune, 2011) and toxic components that are bioaccumulated in crops that later find their way through food chains into humans Ogunbileje *et al.*, 2013.

1.6 Description of the studied plants

Abelmoschus esculentus

Abelmoschus esculentus commonly called okra, belongs to the Malvaceae family. It is a vegetable widely consumed in humid West and Central Africa, where its cultivated in subsistence and commercial agriculture. It is cultivated around Obajana cement factory for its edible green pods. The plant is a common vegetable that is eaten in almost every part of the world. It is high in vitamin C, high in fiber, high in antioxidants, a strong source of calcium and potassium and high in folate. Cancer and heart disease prevention due to consumption of *Abelmoschus esculentus* fruit has been reported (Idu, 2009). Different parts of the plant; pods, new leaves, flowers, buds, seeds and stems are used for varying purposes. Immature fruits are eaten as vegetables and can be used in soups, stews and salads. Okra has medicinal benefits; okra mucilage binds cholesterol and bile acid thus removing toxins from the liver. Okra seeds are a possible source of oil. Okra seed oil is also a rich source of a polyunsaturated fatty acid and linoleic acid, which are important for human nutrition.

Okra has been called "the vegetable of a perfect villager" because of its robust nature, dietary fibre and distinct seed protein balance of both lysine and tryptophan amino acids. Okra seed protein's amino acid composition is similar to that of soya bean and the protein efficiency ratio is higher than that of soya bean protein. The protein's amino acid pattern makes it an effective addition to diets deficient of legumes or meat protein. Okra seed is known to be rich in high quality protein, especially in relation to its content of essential amino acids as compared to other sources of plant proteins. Okra is a powerhouse of essential nutrients, almost half of which are gum and pectin-like soluble fibres that help lower serum cholesterol, decreasing the risk of heart disease. The insoluble fibre fraction of Okra, helps to keep the intestinal tract healthy. Many carbohydrates, minerals and vitamins are also abundant in Okra, which plays a crucial role in human nutrition and health.

Mangifera indica

Mangifera indica L. commonly called mango, belongs to the family Anacardiaceae. It is a very important tropical fruit (Ramayya, (1981). The tree is evergreen, often reaching heights of 15-18 meters. It is one of the world's most valuable and widely cultivated fruits. Mangoes are a rich source of vitamin A, C and D. Like other perennial fruit crops, it is in addition to being a carbon sink, a heavy nutrient forager.

Under various agropedological conditions, mango is cultivated across the length and breadth of the globe and is very much cultivated in all parts of Nigeria. *Mangifera indica* is one of the most popular and important tropical fruits eaten worldwide in fresh or processed form. Mango could be processed into canned slices, pickles, nectar, puree and chutney. These processed mango products have become popular all over the world and have become increasingly important in Nigerian markets. Mango, because of its health-promoting properties, has been listed at the top of the super fruits list. It is considered one of the best fruits in the tropics.

Ethnobotanical studies have shown that the plant is widely used for the treatment of diseases because it contains active substances with high therapeutic potentials. It has high sugar concentration (16-18 per cent w/v) and many organoleptic acids and its also very rich in antioxidants. Norfaizal and Latiff (2013) reported that *Mangifera* has been found to have anomocytic, anisocytic and staurocytic stomata. The height of the stomatum is 35.9 µm. Urban and Jannoyer (2004) stated that in terms of transpiration rate, the first striking characteristic of mango appears to be well covered leaves that protects the plant against excessive water loss. Stomatal frequency is high, but stomata are small, allowing relevant stimuli to be responded to quickly.

Zea mays

Zea mays, more commonly known as maize or corn is a member of the grass family Poaceae. It is cultivated more than any other crop on more parts of the world and is grown on every continent except Antarctica. Its extraordinary ability to genetically adapt to a wide range of conditions and produce very high yields of starch-rich grain and some protein and fat has led to its popularity as a world crop. It is believed to have originated from present day Central or South America some 55-70 million years ago. In terms of total production, it is the world's major grain crop, with recent worldwide production of around 1000 million tonnes per year as of 2016. Making it about 32% of the total world cereal production. Maize grain is used for food, animal feed and industrial products such as foams, plastics and adhesives that are biodegradable. In addition, maize stovers, maize plant leaves and stalks are used for forage production, biofuel production and chemical production. *Zea mays* is an important crop of staple cereals which naturally accumulates carotenoids of provitamin A in the seed

endosperm. It is an essential dietary ingredient in human nutrition and a significant source of nutrients in animal feed. Maize is a vital commodity for global food security.

Carica papaya

Carica papaya commonly called pawpaw is a herbaceous laticiferous succulent plant belonging to the family Caricaceae. It is widely cultivated in the tropics as food and cash crop. For the treatment of ailments, the entire plant, plant parts and extracts are traditionally used. Phytochemicals derived from *C. papaya* are increasingly being investigated and have shown great pharmacological promise. *Carica papaya*, originally from Central America and southern Mexico, is an especially high-yielding tropical crop. There are numerous phytoconstituents such as carbohydrates, protein, and lipids in papaya fruits. However, native to America, it is now commonly cultivated for its edible melon-like fruit that is available throughout the year in other tropical regions of the world. It is one of the largest tropical fruit crops, with an annual production of over eleven million metric tons (FAO, 2001).

1.7 Leaf anatomical features

Stomata

Stomata are pores in the epidermis of a leaf, they are surrounded by a pair of structurally and physiologically specialized cells called guard cells. The neighbouring epidermal cells are called subsidiary cells. The stomatal complex is a group of cells that promotes gas movement through the epidermis of plant leaves (Paiva *et al.*, 2006). Stomata serve as a connection between a plant's internal air spaces and the surrounding environment. Most herbaceous plants and woody plants have a compact waxy coating on their exterior surfaces that is not only impermeable to water vapour but also helps them to conserve water in dry air. This thick waxy layer of cuticle prevents carbon dioxide from entering the cell, which is necessary for

carbon fixation in photosynthesis, and oxygen from entering the cell, which is required for cellular respiration.

Stomata are the main gas exchange gates on leaves (Brent and Ram, 2000). Stomata regulates gas exchange between the interior of the leaf and the atmosphere (Hetherington and Woodward, 2003) and plays a key role in the transpiration process. Stomata also plays a role in innate immunity in plants (Melotto *et al.* 2006). This critical gate between the plant and the atmosphere ‘the stomata’ can play a key role in plant/vegetation responses to environmental conditions (Nilson and Assmann, 2007). They can be found in all organs of plants except the roots (Hoover 1986). The majority of stomata, however, are found in the leaves. The location of stomata on leaves varies from plant to plant. Stomata can be present on both the upper and lower leaf surfaces (amphistomatous), but certain plants only have stomata on their lower leaf surface (hypostomatous), and others only have on their upper leaf surface (epistomatous) (Brownlee 2001).

Some floating species, such as water lilies, have stomata only on the adaxial (upper) leaf surface (epistomatous) (Ohsinu *et al.*, 2007). Stomata play such an important role in the control of plant-water relationships such that they account for nearly 85-90 percent of water loss (Yousufzai *et al.*, 2009).

According to research on field crops such as rice and wheat, stomatal features have a major influence on physiological processes such as transpiration, photosynthesis, plant photosynthetic activities and responses to environmental stress (Sarwar *et al.*, 2013). In leaves, there are two types of guard cells: kidney-shaped and dumb-bell-shaped. Dicotyledons have kidney-shaped guard cells, while grasses/monocotyledons have dumb-bell-shaped guard cells. Since guard cells in grasses need less solutes and less water to

achieve a given unit increase in aperture, dumb-bell shaped guard cells are more advanced in evolutionary terms and more effective physiologically (Brownlee 2001).

Stomata are found in parallel rows in monocots, conifers, and some dicots, but they are scattered in leaves with netted venation. They are often sunken below the surface, but they are occasionally raised and expands into sub stomatal cavities in the mesophyll tissues. Because of the unusual shape of guard cells and the fact that guard cells, unlike other epidermal cells, normally contain chloroplasts, they are easily noticeable on leaf surfaces under microscopic magnifications (Dania-Ogbe and Osawaru, 1988)

Based on the number, location, and size of the Subsidiary cells, Franco (1939) outlined eight categories and 34 structural stomatal forms. More than 25 different types of stomata have been described in dicots based on the arrangement of epidermal cells adjacent to guard cells (Al Afas *et al.*, 2006). Stomatal frequency is typically higher on the lower leaf surface of amphistomatous leaves than on the upper leaf surface (Kapitonova, 2002). Stomatal density in trees usually ranges from 30 to 1190 mm⁻², with guard cell lengths varying from 10 to 50µm, and there is often a negative relationship between stomatal density and stomatal size (Hetherington and Woodward, 2003). Stomata can be found on stems, leaves, flowers, and fruits but not on aerial roots, and their size and frequency differ greatly (Kapitonova, 2002). Within a single species, stomatal density can differ between leaves, and individual plants (Al Afas *et al.*, 2006).

Environmental factors such as air pollution, sunlight, water supply, temperature, and atmospheric CO₂ concentration may also influence the functionality of stomata (Sukumaran, 2004). In general, stomatal density decreases as air pollution levels rises, and leaves exposed to high pollution levels have lower stomatal densities than leaves produced in less polluted environments (Sukumaran, 2004). Stomatal abundance is typically higher on the lower leaf

surface than on the adaxial side in amphistomatous trees, and the adaxial to total stomatal density ratio continues to decrease as atmospheric pollution increases (Sukumaran, 2004).

Trichomes

Trichomes are highly specialized epidermal structures that appear as extrusions or appendages on plant surfaces, as well as on lichens and algae (Hauser, 2014). Trichomes are epidermal protuberances found on the aerial parts of plants. Trichomes are also known as leaf hairs. They are specialized epidermal cells that improve the mechanical and chemical defence of plant tissues from external factors (Hauser, 2014). It protects them from pollution, high temperatures, herbivore attack, transpiration, and UV light (Wagner *et al.*, 2004). Trichomes may be clustered, solitary, or form small membranaceous thalli that lack sheaths (exceptionally with very fine mucilaginous layers around the trichomes). They don't move around. Typically up to 3µm high, with no constriction at the cross walls and only slightly attenuated ends.

Flavonoids, methyl ketones, triterpenoids, phenylpropenes, acyl sugars, and proteins are among the secondary metabolites that glandular trichomes store and secrete. These metabolites may be semivolatile, volatile or nonvolatile, and they play a role in plant protection against contaminants in a number of ways. Peltate and capitate glandular trichomes are the two styles of glandular trichomes usually found on leaves and stems. The main distinction is in their functions: peltate trichomes produce and store diterpenes and nonvolatile or poorly volatile organic compounds, whereas capitate trichomes produce and store diterpenes and volatile or fairly volatile organic compounds (Li *et al.* 2018).

Several studies have shown that trichomes are susceptible to modifications by environmental stressors. The importance of glandular trichomes in a changing environment has been extensively studied in silver birch (*Betula pendula*), where the leaves formed a thick cover of

peltate glandular trichomes in response to environmental stress. In birch leaves exposed to increased UVB radiation and dust pollution, Kostina *et al.* (2001) found an increase in the density of glandular trichomes. Frost treatment in young birch seedlings caused a rapid increase in glandular trichome density indicating that even young plants can adapt their epidermal tissue to environmental stress, according to Prozherina *et al.* (2003). In a related study, Lihavainen *et al.* (2017) found that high atmospheric humidity decreased glandular trichome density both in the lab and on the field.

1.8 Bioavailability of heavy metals

Metal bioavailability was described by Brun *et al.*, 2001 as a fraction of the total amount of metal available for incorporation into the biota. The bioavailability of metals, on the other hand, is defined by Mishra *et al.* (2009) as the fraction of heavy metals in the soil that is accessible to the food chain and plants. Metal bioavailability in soil is a complex process affected by a number of chemical, biological, and environmental factors. According to Silva *et al.*, 2006 adding organic matter of soils during the flowering period of plants increases the bioavailability of metal ions. Heavy metals are redistributed into various chemical components with varying mobility, toxicity, and bioavailability once they enter the soil (Shiowatana *et al.*, 2001). The fate of different metals in nature is a major source of concern. Soils and organic materials in areas near former mine sites, dumps, industrial and urban centres that have a higher than normal abundance of heavy metals can produce more bioavailable heavy metals for plant uptake (Brun *et al.*, 2001).

1.9 Mobility of heavy metals in plants

Bioaccumulation factor (BF) is used to investigate metal transfer from soil to plant roots. It's measured as a ratio of a particular metal's concentration in a plant root to the same metal's concentration in soil, both expressed in the same units Rangnekar *et al.* (2013a). Higher (>1)

BF values suggest that the plant can absorb more metal from the soil and is more suitable for phyto-extraction and phytoremediation. Lower values (<1), on the other hand, suggests that plants have a weak response to metal absorption (Rangnekar *et al.*, 2013b).

Plants' ability to uptake and remove toxic materials, as well as their need for micronutrients, regulates the supply of metals. This ability varies depending on the plant species and their adaptation to their environment. Plants can be grouped into three groups based on this: excluders, indicators and accumulators. Heavy metal concentrations vary in different plant parts; the highest concentrations are found in roots and leaves, while the lowest concentrations are found in fruits and seeds. Lead accumulation in seed coats is a defensive mechanism against the detrimental effects of high concentrations of lead in the seed's inner parts. An examination of the roots may reveal the amount of heavy metals accumulated from a contaminated soil and also provides information about the level of soil metal pollution, whereas an examination of the leaves may reveal the level of atmospheric metal pollution.

Some plants are immune to certain metals and, as a consequence, they can efficiently uptake, accumulate and translocate significant amounts of these metals in their biomass. Metals are concentrated in aboveground sections of such plants, and they are referred to as metal accumulators Baker 1993. According to Nan *et al.*, 2002, the uptake and transfer of heavy metals from soil to plants is a critical process, and determination of bioaccumulation factor and transfer factor (TF) are a key parameters for assessing element availability in soil and plant hyper-accumulation capability. According to D'Souza *et al.* (2013), not all plants with phytoremedial potential are alike; some are metal-specific, while others work well for multiple metals. The mobility and availability of heavy metals in soil and plants have been shown to affect plant phytoremediation capacity.

As a result, the bioaccumulation factor (ratio of bioavailable metal content in root to that in soil) and transfer factor (TF) (ratio of metal content in shoot to that in root) can be used to determine plant accumulation potential and thus phytoremediation potential (Ogunkunle *et al.*, 2014). The high toxicity of Cd, according to Barcelo and Poschenrieder (1992), is due to its high mobility and the low concentration at which its effects on plants begin to manifest. High translocation is caused by active transport, a lack of metal absorption by fixed or soluble chelators in the root, or an association with Ca, Mn, and Zn passing through the roots (Varun *et al.*, 2012).

1.10 Uptake of heavy metals by plants

Heavy metal contamination of soil is a major concern due to its toxicity and danger to human life and the environment (Begum *et al.*, 2009). Cement dusts are rich in heavy metals and other contaminants including polycyclic aromatic hydrocarbons. Heavy metals in the soil can cause bio-magnification, geo-accumulation and bioaccumulation as well as negative effects on plant physiological functions like nutrient absorption, gas exchange and photosynthesis (Takac *et al.*, 2009).

Fast-growing plants like spinach, tobacco and carrots takes up less metal than trees Smical *et al.*, 2008. Heavy metals gets into plants by absorption (the penetration of metals into the inner matrix) or adsorption (the binding of materials to a surface) or both. In small quantities, heavy metal residues in plants and animals are not harmful (De-vries *et al.*, 2007). Lead, cadmium and mercury, are exceptions since they are toxic even at low levels (Galas-Gorcher, 1991). Since heavy metals remain in the top soils and do not leach deeper, they have a greater impact on plants that are not deeply rooted (Yu *et al.*, 2002) Heavy metals are taken up by plants via, redox reactions, ionic exchange, precipitation-dissolution and other processes. The distribution of metals in plants is very diverse, and it is affected by metal toxicity factors,

genetics and environmental factors. Heavy metal dynamics in plant-soil interactions are primarily dictated by soil pollution levels and plant species Guala *et al.*, 2001. Plants absorb heavy metals from the soil and the environment by their roots and above-ground vegetative organs Mmolawa *et al.*, 2011. Plant species that accumulate high concentrations of Al, As, Cu, Ni, Pb, and Zn in contaminated mine soil were found to have a lower tolerance to toxic metal uptake Freitas *et al.*, 2004. Similarly, different plant species grown in the same soil can have differing amounts of the same metal Ibrahim *et al.*, 2014. Differences in heavy metal accumulation have been identified in plant organs Jolly *et al.*, 2013, plant age Naser *et al.*, 2011, and plant cultivars Krstic *et al.*, 2007. Plants also evolved a system for extracting relatively scarce micronutrients such as Cu, Zn, Ni, and Mn from the soil.

According to Kochian *et al.*, 1993, the absorption and accumulation of these micronutrients by plants is highly organized and controlled by necessity. Many of these plant micronutrients are also heavy metals, posing a problem in terms of soil pollution due to either high levels of micronutrients (Zn, Mn, Cu, and Ni) or metals that may serve as analogues or substitutes (such as Cd, Pb or Hg) Kochian, 1993. As a result, plants have developed mechanisms such as metal detoxification in the roots and true resistance to heavy metal stress, which may include avoiding toxic concentrations at vulnerable sites Kochian, 1993. Another technique used by plants to avoid metal toxicity is to reduce their absorption of heavy metals.

Plants have ability to change their internal structure, external morphology ecological and physiological characteristics in response to environmental stress. Several authors have looked into the interactions between plants and various forms of pollutants: most works on the effects of environmental contamination concentrates on physiological and ultrastructural aspects (Psaras and Christodoulakis, 1987; Velikova *et al.*, 2000). There have also been

studies into the anatomy of the vegetative organs in polluted environments. (Ahmad *et al.*, 2005; Silva *et al.*, 2005, 2006, Verma *et al.*, 2006).

The structural and functional characteristics of different species are closely associated with their responses to altered environmental conditions. According to Christodoulakis and Fasseas (1990), there were no significant changes in the leaf structure of *Laurus nobilis* (a resistant xerophytic plant) exposed to air pollutants in Athens. Plants produce various morphological and anatomical changes when exposed to contaminants, according to studies. In highly polluted areas where lichens and mosses are often absent, higher plants have been used to regulate air pollution (Mulgrew and Williams, 2000). Owing to their bioaccumulation capabilities, higher plants could act as biomonitors in the assessment of aerial heavy metal pollution (Mulgrew and Williams, 2000). Higher plants accumulate metals from the soil as well as absorb pollutants from the atmosphere. Plants remove heavy metal deposits from the soil through their root systems and move them to other areas of the plant. Particle deposition on the surface of the leaf, according to Bache *et al.* (1991), may be influenced by a number of factors, which includes; wind speed, particle size and mass, leaf surface characteristics, leaf orientation and size and moisture level. Particles that have accumulated in the soil can be re-suspended, washed away by rain or stuck to plant foliage. Plant surface characteristics, environmental conditions, pollutant composition and particle size, influences the extent of heavy metal retention according to Harrison and Chirgawi (1989). They used experiments to show that foliar depositions and translocation of air-derived metal pollutants are important, and that foliar pathways are just as important as soil-root pathways. The amount of accumulation and toxicity, however, can vary depending on the plant species and heavy metals of concern. Pilegaard and Johnson (1994) investigated the absorption of Cd, Cu, Ni, and Pb by *Ichillea millefolium* and *Hordeum vulgare* from the atmosphere and soil in

Denmark, they concluded that Cu and Pb plant concentrations were linked more to aerial deposition than soil depositions.

Cho *et al.* (2003) discovered that plant exposure to heavy metals is mediated by a complex network of physiological and molecular mechanisms, which includes metal absorption and accumulation through extracellular exuding cell wall constituents and heavy metal ion complexing inside the cell. Heavy metal toxicity has a wide effect on the biosphere, with soil concentrations ranging from less than 1 mg/kg to more than 100,000 mg/kg, resulting from natural or anthropogenic sources (Blaylock and Huang, 2000). Some plant species native to metallurgical soils have been found to be able to tolerate higher than average levels of heavy metals or other toxic compounds, according to research (Blaylock and Huang, 2000).

Uptake of Zinc by plants

Zn absorption is affected by the concentration of Zn in the soil and the plant species. Since plant roots primarily absorb Zn from soil solutions, the concentration in the soil solution is crucial in determining its bioavailability (Marschner, 1995). Zinc is transported to the roots xylem via symplast and apoplast pathways (Broadley *et al.*, 2007), but high levels of Zn have been found in the phloem, indicating that this metal is transported through both xylem and phloem tissues (Haslett *et al.*, 2001).

Zn has an intermediate mobility relative to other extremely mobile elements like potassium or Phosphorus, and immobile elements like Calcium (Kabata-Pendias and Pendias, 2001). Apart from Zn^{2+} uptake kinetics, the mechanisms regulating zinc transport across root and other cell membranes tend to be metabolically regulated. This process is triggered by an electrochemical gradient through ionic gradients and carrier proteins, or by electrogenic pumps working against the electrochemical gradient (Weiss *et al.*, 2004).

Uptake of Chromium by plants

According to Shanker *et al.* (2005), Chromium makes its first interaction with a plant during its absorption period, and since it is toxic and non-essential to plants, they lack specific mechanisms for uptake. As a result, carriers used for the uptake of useful metals for plant metabolism are used to transport Cr (Shanker *et al.*, 2005). Chromium compounds are highly toxic to plants, hindering their growth and development (Shanker *et al.*, 2005). The uptake and accumulation of Cr by various crops has been thoroughly researched. According to Golovatyj *et al.* (1999), the distribution of Cr in crops has a predictable path that is dependent on soil properties and metal concentration. They also claimed that the highest concentrations of metal pollutants were often found in the roots, while the lowest concentrations were found in the vegetative and reproductive organs. Cr is immobilized in the vacuoles of root cells, making it less toxic. This may be a normal toxicity reaction of plants (Shanker *et al.*, 2004).

Uptake of Lead by plants

Since root absorption of Pb is passive, its uptake from the soil is poor, and plant transfer is limited, usually with a large amount of root accumulation (Kabata-Pendias and Mukherjee, 2007). While Godzik (1993) believed that duck leaves absorb heavy metals from the air, it was generally accepted that the majority of the Pb in the plants was retained in the roots (Kumar *et al.*, 1995).

After absorption, the concentration of lead in plants is higher in roots than in other areas of the plant and Pb attaches strongly to carboxyl groups in carbohydrates and galacturonic acid in the cell wall, limiting its transpiration by apoplast pathways (Rudakova *et al.*, 1988). Dicots accumulate slightly more Pb in their roots than monocots, according to Guala *et al.*, 2001, and Pb passes mostly into the root apoplastly and accumulates near the endodermis.

According to Verma *et al.*, 2006), the endodermis acts as a partial barrier to the movement of Pb from root to shoot, which may explain why roots accumulate more Pb than shoots.

Uptake of Cadmium by plants

Cd absorption by roots from soil is affected by factors such as Cd concentration in the soil, soil pH and organic matter content (Nazar *et al.*, 2012). The low molecular weight of organic acids secreted by roots, according to Mench and Martin (1991), played an important role in the solubility and availability of Cd as well as its absorption by plants. They also claimed that certain plants' ability to secrete organic acids that chelate with Cd ions in soil reduces its bioavailability and absorption as seen in wheat and buckwheat, which secretes malic acid, citric acid and oxalic acid that chelates with Cd to prevent its entry into roots.

Uptake of Copper by plants

The total amount of soluble Cu in a soil solution influences its mobility, but the amount of free Cu^{2+} in the solution determines Cu bioavailability to plants (Bolan *et al.*, 2013b). Plants takes up the least amount of Cu from the soil of all the essential elements (Kabata-Pendias and Pendias, 1992). Cu absorption by plant roots is a complex mechanism influenced primarily by Cu species. Cu was most readily available at or below pH 6.0, according to Alva *et al.*, 1995 and bioavailability decreased at pH above 7.0.

1.11 Environmental impact of cement production

Cement producers now produces higher quantities of cement than in the past, all thanks to technical advancements. Higher output levels, on the other hand, have been attributed to being the primary source of increased cement dust emissions. Excavation operations, kiln emissions, conveyer belts and crushing mills, are the key sources of air pollution in cement industry. Utilizing suitable technologies in the cement industry will go a long way towards reducing waste and emissions on-site. Our needs should be met in a way that does not negate

the future generations' ability to meet their own needs, according to the UN Brundtland Report (2008). This point of view emphasizes how today decisions and behavior can have a long-term effect on natural resource availability, environmental protection and the degradation of local and global ecosystems.

1.12 Health risk of human exposure to heavy metals

Some metals are important for life and play critical roles in the functioning of body organs as sources of vitamins and minerals. Metals are needed by all living organisms in varying quantities, but they become toxic at higher concentrations Lane and Morel 2010. Although some of these metals, such as mercury, lead, arsenic, cadmium and chromium have no useful role in human physiology. Also at very low levels of exposure, these metals can be harmful. They are widely regarded as the most harmful to humans and animals (Turdogan *et al.*, 2003). Heavy metals accumulate in vital organs such as the kidney, brain, bones and liver for years or decades after being introduced into the body, causing severe health effects Kabata-Pendias, 2011. Arsenic, mercury, cadmium, and lead are widely distributed in the atmosphere. Contamination of the atmosphere by potentially toxic elements is a major risk to human health and environmental quality. While some people are exposed to these pollutants primarily at work, majority of people are exposed to these toxic elements primarily through their diet. Heavy metal pollution typically follows a cyclic pattern: manufacturing, environment, soil, water, foods, and humans. While contaminant's toxicity and resultant danger to human health is a function of concentration, it is well-known that prolonged exposure to heavy metals and metalloids at relatively low levels may also have negative consequences (Agency for Toxic Substance and Disease Registry [ATSDR], 2008).

Chromium toxicity has already been reported in target organs such as the lung when inhaled, but oral and dermal pathways may also affect the immune systems, kidney, skin, and liver

(Ogunbileje *et al.*, 2013). Edible plants grown on polluted soils is of great health concern because of the possible harm to humans. Asthma and shortness of breath can be caused by inhaling excessive levels of chromium (VI). Compounds containing chromium (VI) are considered to be mutagenic and carcinogenic. The liver and kidneys can be harmed as a result of long-term exposure. Bosso and Enzweiler (2008) observed elevated blood Pb levels in children living near former smelter. Miners' health was harmed as a result of heavy metal accumulation in their bodies, according to Liu *et al.* (2005). Heavy metal exposure of soil, meat, and vegetables in the Van region of Turkey has been linked to a high prevalence of gastrointestinal cancer (Turdogan *et al.*, 2003). Dose-dependent Pb toxicity has been shown to cause a number of health complications in children and adults, including renal failure, coma, convulsions and high-dose associated deaths (USATSDR, 1998). Children have been identified as the category most vulnerable to the neurotoxic effects of Pb (Banks, 1997). According to Sajjad *et al.*, 2009 lead is a human mutagen and a possible carcinogen. It causes renal cancer and interferes with the normal functioning of the kidneys, reproductive and nervous systems Ogwuegbu and Muhanga, 2005.

The relative inability of humans to excrete Cd contributes to the health effects of Cd exposure (Benoff *et al.*, 2000). Acute high-dose Cd exposure can cause extreme respiratory irritation, and occupational Cd exposure is a recognized risk factor for chronic lung disease and testicular degeneration (due to airborne exposure) (Hu, 2002). The basic structural and functional unit of the kidney is impaired by cadmium toxicity, as demonstrated by the leakage of low molecular weight proteins and important ions such as calcium into the urine, which ultimately contributes to kidney failure, which eventually contributes to renal failure (Satarug *et al.*, 2000).

The ingestion of heavy metals such as Cd and Pb has been related to neurophysiological disorders such as the high prevalence of intrauterine growth retardation in humans, according to Fu *et al.* (2008). Cadmium is considered to be harmful at low concentrations and is also suspected of being carcinogenic. Cadmium poisoning can cause bronchiolitis, emphysema and alveolitis in the lungs, according to Kabata-Pendias (2011). Cadmium may also cause bone fractures, kidney failure, hypertension, and cancer. Long-term effects include arthritis, diabetes, anemia, cardiovascular disease, cirrhosis, reduced fertility, headaches, and strokes Harrison, 2001. Cu overdose in humans has been linked to severe pigmentation loss and liver damage (Al-Subu *et al.*, 2003). Even though Zn and Cu are important to human life, excessive consumption can have non-carcinogenic effects on human health. Copper in excess has been linked to liver damage, while Zn has been linked to growth and reproduction issues Nolan, 2003.

The hazard quotient (HQ), which is the ratio of average daily intake to the reference dosage (RFD) or reference concentration in air (RfC) for an individual pathway and chemical, is typically used to identify the human health risks caused by heavy metal exposure. A quotient of less than one is considered safe. When the HQ value reaches one, there might be questions about overexposure-related health risks. Summing HQs across metals should be used as a conservative evaluation tool to measure high-end risk rather than low-end risk to protect the public while evaluating the total potential for health effects posed by more than one metal.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Heavy metals and other contaminants accumulates significantly in the atmosphere, plants and soil as a result of anthropogenic activities. These contaminants are generated by industrial processes such as mining, smelting, refining, and cement production. Effluents from these factories are released into the air, water bodies and soil, ultimately resulting in bioaccumulation and bio-magnification in living organisms in the food chain. Particulate air pollution is a characteristic feature of cement manufacturing, which is emitted and discharged during raw material blasting, cement grinding, packing, and loading of finished cement. The majority of heavy metals in cement dust comes from raw materials. Particulate and related metal pollution from the cement industry have the potential to harm the environment and human health. This chapter summarizes researches on the effects of cement dust emissions on air, soil, plants, and humans conducted by several of researchers.

2.2 Air quality around cement industries

Owing to reliance on coal and petroleum products to power the kilns for clinker production, cement production is a major source of CO₂. According to Marland, (2003) cement factories account for around 3.4 percent of global CO₂ emissions from fossil fuel combustion. Carbondioxide levels near cement plants have been found to be higher than pollution control agencies' recommended limits (Kabir and Madugu, 2010). Cement production contributes significantly to the degradation of air quality in the vicinity of cement factories. The cement manufacturing process produces a large amount of dust particles (both coarse and fine), which degrades the quality of the surrounding air by increasing gases in different meteorological conditions. Otaru *et al.*, 2013 investigated particulate pollutant concentrations at Obajana cement Plc in Nigeria and found that the highest value of particulate matter for the

year 2012 was 448.16g/Nm³, which was lower than the Nigerian Federal Ministry of Environment Standard but significantly higher than the World Health Standard. This may be due to a lack of proper use of the control strategies or poor performance of the dust collecting instruments, a sign that the dust collecting systems haven't been adequately maintained.

Mehrotra *et al.*, (2001) and Rajasekhar *et al.*, (2001) investigated the suspended particulate matter (SPM) levels in ambient air around cement industries and recorded cement dust contamination and degraded air quality at a distance of about 100 meters from the cement facility. Abimbola *et al.* (2007) found that SPM (suspended particulate matter) concentrations near cement plants exceeded guideline values. This raises significant concerns about the impact of cement production on the environment and human health.

According to studies by Yu, (2011); Tajudeen, (2011) and Sabah, (2006), particulate matter discharged into the atmosphere degrades air quality. They found a higher concentration of total suspended particulate matter at a limestone quarry, which provides the factory with its main raw material. At a cement plant, Ideriah (2008) found a major difference ($P < 0.05$) between the indoor and outdoor mean concentrations of suspended particulate matter. Cement manufacturing leads to emissions by releasing gases and cement particles into the atmosphere (El-Abssawy 2011). Wind and rain will disperse this dust over vast areas, and it accumulates in and on soils and plants. Cadmium, chromium, copper, Arsenic, mercury, zinc, thallium and lead are among the metals commonly present in cement plant dust emissions (Schuhmacher, 2002).

Cement processing has been shown to be a significant source of heavy metal emissions by many researchers [Adejumo *et al.*, (1994); Isikli *et al.*, (2006); Khashman and Shawabkeh, (2006)]. Carrasco *et al.*, (2002) and Koptsik *et al.*, (2007) both confirmed the release of volatile contaminants such as cadmium, arsenic, mercury and lead into the atmosphere

around cement plant kilns. Environments contaminated by cement kiln dust has higher concentrations of lead and mercury, according to Bapat (2001) and Canpolat *et al.*, (2002). Sharma and Pervez (2004) discovered an enrichment of toxic elements such as Zn, Ni, Cd and Cr in the vicinity of a slag-based cement plant in Chhattisgarh. Cadmium is released into the atmosphere through cement kiln operations and waste incineration (Boyd *et al.*, 2009).

Coal and oil combustion during cement manufacturing process are the primary sources of chromium discharge into the atmosphere (Gbadebo and Bankole, 2007). According to Banat *et al.*, (2005), soils near cement plants were polluted with Cd and moderately contaminated with Zn, Pb and Hg.

2.3 Chemical composition of cement dust

According to a study by the American Concrete Institute (1990), cement dust is made up of Fe_2O_3 , SiO_2 , CaO and Al_2O_3 . Polat (2004) and Carlson *et al.*, 2011 discovered that the majority of cement clinker dust produced during the grinding process is composed of Al_2O_3 (2.86-3.76%), Fe_2O_3 (1.77-2.66%), SiO_2 (14.02-21.56%), and CaO (60%). Frias *et al.*, (2002), Kookos, (2011) and Mahaboob, (2013) found a high concentration of heavy metals in raw Portland cement.

Cement dust also includes heavy metals such as lead, chromium, cobalt, mercury and nickel as documented by Baby *et al.*, (2008). A study by Kakareka and Kukharchyk (2011) have established a connection between cement production and heavy metal pollution of the environment. Primary raw materials (limestone, marble, clay and chalk) and secondary raw materials are the key sources of heavy metals in the production chain of cement. The prevalence of heavy metals in cement dust has also been affirmed by Gbadebo and Bankole (2007).

2.4 Effect of cement dust on soil heavy metal content

With increasing distance from the factory, comes a dramatic decrease in soil pollution by heavy metals. Banat *et al.*, (2005) studied the linings of rotaries in the cement industry and discovered that they contain chromium, which can be liberated by wear and tear. As a result, the cement factory is suspected of being the source of Cr in the soil near cement plants. According to some researchers, heavy metals are deposited into soil at different distances depending on wind velocity and particle size via cement dusts and stack fumes, as stated by Schuhmacher *et al.*, (2009); Sakalauskaite *et al.*, (2009) and Majolagbe *et al.*, (2004) and Ogunkunle *et al.*, 2013a. Cristina *et al.* (2008) studied the spatial and temporal effects of dust emissions in the vicinity of a cement plant in a dry environment. They discovered that the source of Cd in the top soil was linked to cement factory emissions. In an analysis of the amounts and origins of heavy metal and trace elements in agricultural and residential areas, Kashem and Singh, 1999 implicated a cement factory as a source of Cr in the soil. Heavy metals showed soil enrichment along the wind path, according to Maina *et al.*, (2013), who analyzed the major elemental components in soil around a cement factory.

Sabah and Abdul-Wahab (2006). examined the effect of cement dust on soil health and found that the cement industry contributes significantly to environmental imbalances and poses air pollution risks. Cement dust is a possible phytotoxic pollutant in the vicinity of a cement factory, causing serious pollution issues and significant ecosystem harm. The contaminants emitted by the kiln are dispersed over a wide area, affecting plants, soil, and other natural resources.

Higher concentrations of metals were found in sites closer to the cement factory, as stated by Odoh *et al.*, 2018 in their study of heavy metals profile and variations of soil properties in a vicinity of a cement factory. The concentrations of heavy metals in soil samples in the

vicinity of a cement factory in Ewekoro, Nigeria, decreased as the distance from the cement factory increased, according to a study by (Ogunkunle and Fatoba, 2014) using pollution indices. The study found that dust pollution from the cement factory had an effect on the soils around the factory, as shown by the very low concentrations of heavy metal content in the control samples.

In the soils surrounding the Rochfort Cement plant in Jamaica, Mandal and Voutchkov (2011) found high levels of chromium, lead and zinc. According to Ade-Ademilua and Umebese (2007), soil around cement factories contains high levels of calcium, iron, silica and chromium with contamination levels decreasing as the distance from the factory increases. Adekola *et al.*, (2012) investigated metal deposition in soils surrounding a mega-cement plant in Nigeria, and discovered that Pb and Cu were the most mobile metals in the soil. Heavy metal distribution in the soil profile could reveal information about their source (Chen *et al.*, 2005). Heavy metal enrichment in soil could be as a result of past human activities (Mazurek *et al.*, 2017). Other anthropogenic emission sources, such as agriculture, manufacturing and transportation, have profound effect on heavy metal accumulation in the soil (Fatoba and Iyeh, 2012; Ogunkunle and Fatoba, 2014). Heavy metals can be extracted from both near and distant sources of pollutants, thus can be deposited in situ or transported over long distances due to their ability to be bound to dust particles (Mazurek *et al.*, 2017). The majority of anthropogenic contaminants are released into the atmosphere before being deposited on the surface of the soil (Ripin *et al.*, 2014; Liu *et al.*, 2016).

2.5 Effect of cement dust on soil physicochemical parameters

The physicochemical properties of the soil are affected by pollutants present in cement dust. The effects of cement dust on soils' physical and chemical properties have been studied through extensive field surveys and laboratory investigations.

According to Buba *et al.*, 2014, who investigated the quality evaluation and physico-chemical properties of soils around a cement factory in Gombe State, Nigeria, soil around cement factories suffers physicochemical damage and may not be suitable for the cultivation of millet, maize, groundnut and sorghum unless large quantities of fertilizers are applied. The pH and EC of soil are altered by cement kiln dust. Cement dust contamination is accountable for elevated soil pH according to Adak and Purohit, 2007 and Abdullahi and Usman (2010).

Bayhan *et al.*, (2002) attributed Changes in some soil characteristics to dust produced by cement plants. They recorded 22% increase in lime, 15.93% increase in exchangeable cations, 2.66% increase in pH, and 7.86% increase in electrical conductivity. Valdo *et al.*, (2003) and Iniobong *et al.* (2008) investigated the electrical conductivity and exchangeable salt contents of soil polluted with cement dust and reported an alteration of electrical conductivity and exchangeable salt contents of the soil occasioned by the cement dust pollution. Coal fly ash used as a raw material for cement manufacturing, according to Gbadebo and Bankole, (2007), Prakash *et al.*, (2002) and Ogedengbe and Oke, (2011), also modifies the physico-chemical and biological properties of soil.

Soil is the primary source of minerals necessary for plant growth and productivity. Gupta and Sharma (2012) looked into how the emission of calcium and magnesium ions from cement dust affects the soil's cation exchange ability. They discovered that the natural nutritional contents and physical properties of soil have been adversely affected as a result of industrial activities. Abatyough *et al.*, 2015 investigated the effect of cement dust emissions on some physical and chemical properties of agricultural soils in Gboko, Benue State, Nigeria. They said that the soils around the cement factory was prone to salinity as a result of continuous cement dust depositions onto the soil's surface, resulting in pollution and an increase in soil

metal (Na, Mg, K and Ca) levels when compared to unpolluted sites. Borgna (2009) discovered that soil heavy metal content and soil pH have a positive relationship.

Cement dust particles are very alkaline, according to Mandre *et al.* (1999), causing elevated pH levels in soils around cement factories, especially in downwind areas, affecting photosynthesis, growth rate, transpiration, respiration and vegetation development. Ibanga *et al.*, (2008) found a decrease in total nitrogen and organic matter content in soils surrounding the Calabar Cement Company in a study. Cutin *et al.*, (1998) found that the quantity of soil organic matter was affected as a result of direct biosolids application, and that this biosolids serves as a source of trace metals that should be monitored. Soils around cement factories have particularly high pH levels, according to Mandre *et al.*, (1999). Mandal and Voutchkov (2011) studied the concentration of Zn in soil near a cement factory in Rockfort, Jamaica, and discovered that soil pH has a major impact on heavy metal bioavailability.

2.6 Effects of cement dust pollution on plants

Plants in close proximity to the cement factory were harmed more than those further away. Numerous studies have been conducted on the impact of air pollutants on key physiological processes in plants, including transpiration, photosynthesis, stomatal activities, translocation and respiration (Darall, 1989; Barker, 1993). An investigation into the impact of cement dust pollution on *Azadirachta indica* in the Ariyalur area, which is rich in limestone and has many cement factories in and around it, revealed a decrease in the content of chlorophyll 'a' and chlorophyll 'b' in *Azadirachta indica* leaves grown in that area (Ramanathan and Jeyakavitha, 2006).

Onder *et al.* (2007) discovered that high levels of Zn in plants caused poor yield and growth, while low levels caused leaf deformation. Leguminous plants' pod formation and ripening were significantly delayed due to high levels of aluminum in plant leaves in the vicinity of a

cement plant (Ade-Ademilua and Umebese, 2007). According to Ade-Ademilua and Obala (2008), as the concentration of Fe and Ca originating from cement dust on their test plants grown around a mega cement factory increased, there was a significant reduction in leaf area, vitamin levels and shoot length. Kumar and Pandey, (2011) discovered a maximum reduction of total chlorophyll in 60-day-old leaves and lower nitrogen content in maize plant grains exposed to cement dust in a contaminated region. Princiwill *et al.* (2011) investigated the highest concentrations of Zn and Fe in *Andropogon*, as well as Cadmium in *Mangifera indica*, and found a strong connection between heavy metals in soil and plants.

Different sections of the rice plant were studied by Singh and Upadhyay (2011) (root, straw and grain). Except for Cu, all sections of the plants obtained from the cement dust contaminated site had higher heavy metal concentrations than the control samples. Chromium, Nickel and lead concentrations in *Celosia argentiana* leaves and stems have also been reported to rise due to cement dust contamination. Apple trees growing near a cement factory accumulated a lot of Mg and Ca according to Genon and Brizio (2008). Impact of cement production activities over time and space was studied in regards to Mg, Cr, Fe and Ca concentrations in *Xanthoria parietina*. The Cr levels observed reflected a significant pollution impact caused by the cement factory.

Except for Cd in soil, metal concentrations in soil and plants in an abandoned cement factory NIGERCEM by Princewill *et al.*, 2011 showed that heavy metal concentrations in soil and plants were below toxicity levels. Heavy metals in soils and plants, on the other hand, had strong positive correlations. Estifanos *et al.* (2014) investigated apple tree leaves growing in a cement factory in Lithuania and found that plants closer to the cement factory had a higher concentration of P, K, Pb, Cr and Cd. Metal concentrations were found to be more in plants

growing in areas 0-100m from the cement factory, as compared to plants growing 2000m away from the factory, according to Mutlu *et al.*, (2013).

Idakwoji *et al.*, 2016 assessed heavy metal contamination of soil and cassava plants near a cement factory in north central Nigeria and found that metal levels in both soil and cassava leaf samples were below WHO/FAO recommended limits. Studies have shown that cement dust reduces the productivity and chlorophyll concentration of a number of annual non-leguminous crops (Satao *et al.*, 1993). Furthermore, research on the effect of cement dust on plants have been conducted, such as the analysis of cement dust on conifers growing in Central European forests (Mandre *et al.*, 1999). Response of maize to cement dust in India (Salami *et al.*, 2002), and effects of cement dust on vegetation in South West Nigeria (Salami *et al.*, 2002). Cement dust reduced the yield of grapes and rice in the vicinity of a cement factory in China, according to Liu *et al.* (2016). Prasad and Inandar (1991) observed a decrease in the number of flowers and yield of black gram (*Vigna mungo*) due to cement dust contamination. Lerman and Darley (1975) observed a significant reduction in the growth of poplar trees one mile away from the cement factory as a result of cement production activities.

According to Anda, (1986) cement dust pollution resulted in a significant reduction in the amount of *Azadirachta indica* and *Delonix regia* foliage. The production activities of the Duna cement factory have been shown to influence the growth, metabolic processes and yields of winter barley (Borka, 1986). Topie (1999) said that the cement industry was to blame for the destruction of vegetation and environmental degradation in Solin and Kastela, Croatia, near Spilt. Mandre and Tuulmets (1999) both confirmed damage to coniferous trees caused by cement dust.

Experiments on the impact of different heavy metal concentrations on plants have been carried out (Reeves and Baker, 2000). Baycu and Tolunay (2005) concluded from a lead concentration study in Istanbul that the use of *Robinia* and *Aesculus* species should be controlled because they accumulate high concentrations of lead. Wide-leaved tree species are susceptible to metal pollution, according to Kovacs (1992a), and *Populus nigra* was explicitly recommended as an important bioindicator for heavy metal burdens in Europe (Kovacs, 1992b). Coniferous trees are also thought to be a strong indicator of environmental pollution, according to Zayed *et al.*, (1991).

According to Sawidis *et al.*, (1995), the best metal accumulator had rougher surfaced leaves, which resulted in effective particle trapping and retention. Herbs / grasses, according to Kovacs (1992a) and Awofolu (2005), are strong accumulative indicators because they can accumulate large quantities of metals without harming themselves. Pilegaard and Johnson (1994) used Milfoil (*Achillea millefolium*) for metal analysis because of its wide surface area, which made it a good accumulative indicator. According to studies, metal content varies depending on which section of the plant is sampled. Herbaceous plant roots and leaves retain a higher concentration of metal than stems and fruits, according to Csintalan and Tuba (1991).

Depending on the species and composition of the pollutant, the degree of accumulation in various parts of the plant varies. Analyses of tree bark could give an insight into long-term air quality (Kuik and Wolterbeek, 1994). Air pollution enters tree bark either directly from the atmosphere or by stem flow. In the Netherlands, Kuik and Wolterbeek (1994) proposed using tree bark samples as biomonitors of heavy metal contamination, though the sampling of bark was criticized for not distinguishing between soil and airborne inputs.

Plant absorption of heavy metal is typically the first step in its entry into the food chain, with mass flow, solute movement and diffusion promoting transport through the root of the plant (Nafiu, 2010). Roots excrete products such as high molecular weight organic acids that form complexes and chelate with metal ions, according to Wang *et al.* (1997), thus altering the movement and fixation of heavy metals in soils. Because of variations in root morphology, plants' ability to absorb heavy metals differs (Schierup and Larsen, 1981). It is also believed that a plant with more thin roots would accumulate more metal than one with more of thick roots.

2.7 Effects of cement dust on leaf anatomy

In the presence of moisture, cement dust forms crust on leaves, blocking stomatal pores and affecting photosynthesis and plant growth (Mandre *et al.*, 1999). The effect of cement and stone dust on the stomatal clogging of *Iphonia Grantioides* leaves was studied by Abdullah and Igbal (1991). Cement dust emitted by cement manufacturing facilities is one of the most dangerous pollutants that affect the environment, according to Ramesh *et al.*, (2014). They found that increased pollutant concentrations can cause progressive reductions in plant growth, closure of leaf stomata and most importantly, a reduction in leaf photosynthetic capacity.

Ogunkunle *et al.*, (2013b) reported that there were significant modifications in the stomatal size, density and index of leaves of *S. acuta* exposed to cement dust pollution. These anatomical adaptations could enable the plants thrive in cement polluted environment. The leaves of *Pennisetum purpureum* and *Sida acuta* growing around a cement factory, showed anatomical adaptive responses to the influence of cement dust pollution as reported by Ogunkunle *et al.*, 2013b. Plant tissues have been shown to be an effective indicator of atmospheric pollution (Kapitonova, 2002).

Sukumaran *et al.* (2004) investigated how air pollution affects the anatomy of tropical plants and discovered that different tissues of the same plant responds differently to the same pollutant. Continuous cement factory pollution obstructs gaseous exchange by clogging the stomata. It was clear that emissions from the cement industry has a negative impact on photosynthetic activity and chlorophyll content (Rajeev *et al.*, 2010). Dust deposition influenced photosynthesis, stomata opening and productivity of *Oleaneur opaea*, according to Nonas and Illas (2007). Cement dust has an alkaline pH of 10 to 12; because of this, it induces a shift in osmotic potential and increased permeability in the membrane system, resulting in plasmolysis and denaturation of plants' stomata.

2.8 Effects of cement dust pollution on the environment

Certain toxic heavy metals such as cobalt, nickel, zinc, arsenic and copper were substantially enriched in soils around cement factories in Nigeria, according to Adejumo *et al.* (1994). Because of the critical importance of food production and protection, the problem of high heavy metal concentrations, especially in agricultural soils, has become a global environmental issue (Chen *et al.*, 2005; Kabata-Pendias, 2011).

Heavy metals' incorporation into the food chain can have an effect on animal and human health (Begum *et al.*, 2014). An understanding of the impact of ever-increasing industrialization and intensive agricultural soil use on the content of heavy metals in the soil necessitated the proper assessment and determination of their ecological risk (Kowalska *et al.*, 2016). A large database of heavy metals' impact on the environment has been created as a result of numerous geochemical studies, which can now be used to assess environmental quality (Gong *et al.*, 2008; Wu *et al.*, 2010). However, determining the total amount of heavy metals in the soil may not always be a reliable method of evaluation (Caeiro *et al.*, 2005; Kowalska *et al.*, 2016). As a result, several computational methods have been used to

determine heavy metal enrichment and its relationship with soil properties (Gong *et al.*, 2008; Mazurek *et al.*, 2017).

2.9 Effects of cement dust pollution on human health

Cement dust causes crisis for people with asthma and other respiratory diseases, according to a study by Chaulya *et al.*, (2004); Chaurasia *et al.*, (2003). They investigated the high levels of air pollution in the regions around cement plants and reported negative health effects on the people who live there. Babu *et al.*, (2006) and Mishra *et al.*, (2013) computed the air pollution tolerance index at polluted and unpolluted sites around multiple cement plants (under various metrological conditions) and found that the obtained values were substantially higher at polluted sites than at control sites. Excessive deposition of these heavy metals in agricultural soils, which results in increased heavy metal uptake by food crops, is a major source of concern due to the possible health risks to humans and animals (Adriano, 2001).

2.10 Justification for the study

Industrialization is often viewed as the basic reason for a country's economic development and growth. Nigeria, like many other developing countries, has long adopted the idea of industrialization as a means of achieving economic growth and development. The presence of industries in previously undeveloped areas has been observed to have some negative effects on those areas. As a result, several studies on the prospects and effects of cement production on the majority of Africa's population have been conducted. Cement, according to Winmore *et al.*, (2012), is a fundamental building material. Because of the vast infrastructural constructions taking place around the world, there is a strong demand for cement.

Cement consumption has increased at an unprecedented rate around the world. Cement production in Africa increased from 1.2 billion tonnes per annum in 2005 to 2 billion tonnes per annum at the end of 2010. The rapid growth of cement factories in Africa is due to the

persistent increase in the price of building materials and the steady importation of cement (Afeni *et al.*, 2008). However, Harley (2007) pointed out that, while the cement manufacturing industry provides numerous benefits, it is also known to have a number of harmful effects on the soil, plants and humans in the surrounding environments, in both developed and developing countries (Ogunkunle *et al.* 2013a). Some of the negative consequences includes pollution, land degradation and the extinction of wildlife and crops.

Inyinbor *et al.*, 2012 evaluated the heavy metal pollution of the Onyi river in Obajana, Kogi state; Afeni *et al.*, 2008 evaluated the socio-economic impact of limestone quarrying and processing in Obajana, Kogi state; Idakwoji, 2014 investigated heavy metal contamination of soil and cassava plants in the vicinity of the Obajana cement factory; and Otaru *et al.*, 2013 investigated the particulate pollutant concentration of Obajana cement factory.

They all linked the contamination of the studied environmental matrix to the massive cement factory's cement production activities. They conducted their studies, however, when the cement factory had three production lines and a production capacity of 10.25 million metric tonnes per year. Obajana cement factory currently has five production lines and a production capacity of 16.25 million metric tons per year. As a result, a lot of changes must have occurred between these times, both in the soil, which is the ultimate recipient of pollutants emanating from the factory and in plants that are at the mercy of adaptation to survive the pollution load of their environment. While their research focused on how the factory's emissions affected air and water quality, this study aims at investigating the impact of the factory's cement production activities on the soil, annual and perennial crops and by extension on humans that feeds on these plants. Aribigbola *et al.*, (2012) investigated the health and environmental effects of a cement factory on residents of the Ewekoro community in Ogun State. Aigbedion and Iyayi (2007) investigated the environmental effects of mineral

exploitation in Nigeria and concluded that mining causes a variety of environmental damages, including ecological disturbances, destruction of natural flora and fauna, pollution of air, land and water, soil and rock mass instability, landscape degeneration, and radiation. They went on to say that the environmental damage has resulted in the loss of arable land, as well as economically valuable crops and trees.

Although their research focused on mining in general, this study will focus on a specific aspect of mining: cement production and how it affects the soil and crops in the study area. The effect of cement dust exposure on haematological and liver function among cement factory workers in Sokoto was studied by Mojiminiyi *et al*, (2008). Their tests were carried out on 23 members of staff and 46 people who were not exposed. The findings revealed that occupational exposure to cement dust can impair haemopoietic function while protecting the liver. This research will focus on cement factory workers, residents of the Obajana community, and travellers who ply the ever-bustling road that connects Abuja to several other states in the country through Lokoja-Obajana. All these people at one point or the other purchases boiled/roasted maize, mangoes and pawpaw fruits grown around the factory and sold along that stretch. Hence, it becomes imperative to focus on assessing the impact of this cement factory on the soil and some crops grown on the vast arable land around this gigantic factory, in order to suggest possible remediations if the pollution rates is alarming and to fill the existing gap in knowledge.

2.11 Scope of the study

The scope of this study is to assess the impact of Obajana Cement Factory on soil and selected plant species grown around the factory. As a result of the vastness of the study area, sampling will be limited to 3km from the factory. The study will also be carried only in the north, east and west axis of the factory. This is because the southern axis of the factory has a

rocky terrain and the plant species of interest were not readily available there. Soil and plant samples collection was in the rainy and dry seasons of the year 2018 and 2019 so that seasonal variations can be compared.

2.12 Aim and objectives

One major challenge presently trailing Obajana community is the impact of cement production on the overall wellbeing of its soils, plants and inhabitants and that is what this study attempts to elucidate. This study is aimed at investigating the impact of cement production on the soils and vegetation of Obajana community.

Its objectives are to assess/investigate;

- i. the impact of cement production on the heavy metal content of soil around Obajana cement factory,
- ii. the physicochemical parameters of soil around Obajana cement factory,
- iii. the mobility of heavy metals in *Zea mays*, *Abelmoschus esculentus*, *Mangifera indica* and *Carica papaya* grown around Obajana cement factory,
- iv. the leaf epidermal responses of the studied plant species to cement dust pollution,
- v. the ecological risk posed by heavy metals present in the vicinity of OCF,
- vi. the potential health risk of human consumption of the studied plants species grown around this mega factory.

CHAPTER THREE

MATERIALS AND METHODS

3.1 The Study Area

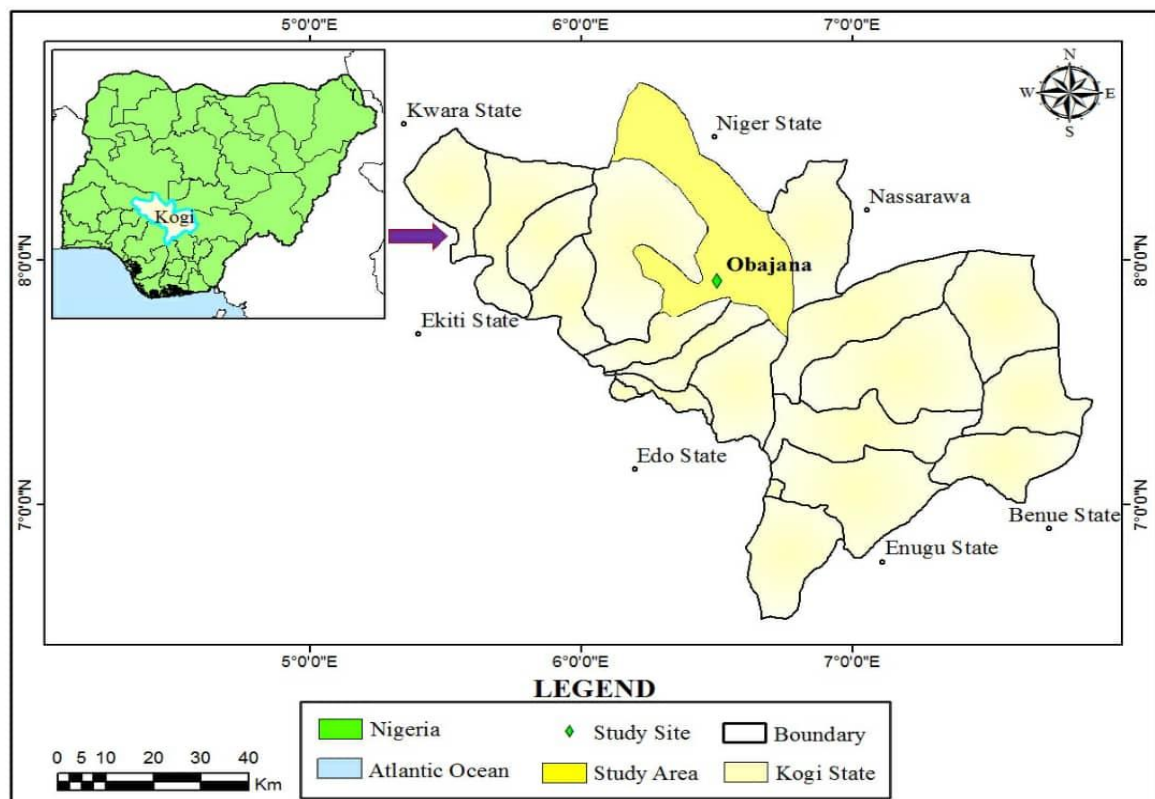


Figure 1: Map of Nigeria showing Kogi state and the study area (Obajana)



Figure 2: Aerial Photo: Obajana Cement factory. Source: Wikipedia Encyclopedia.

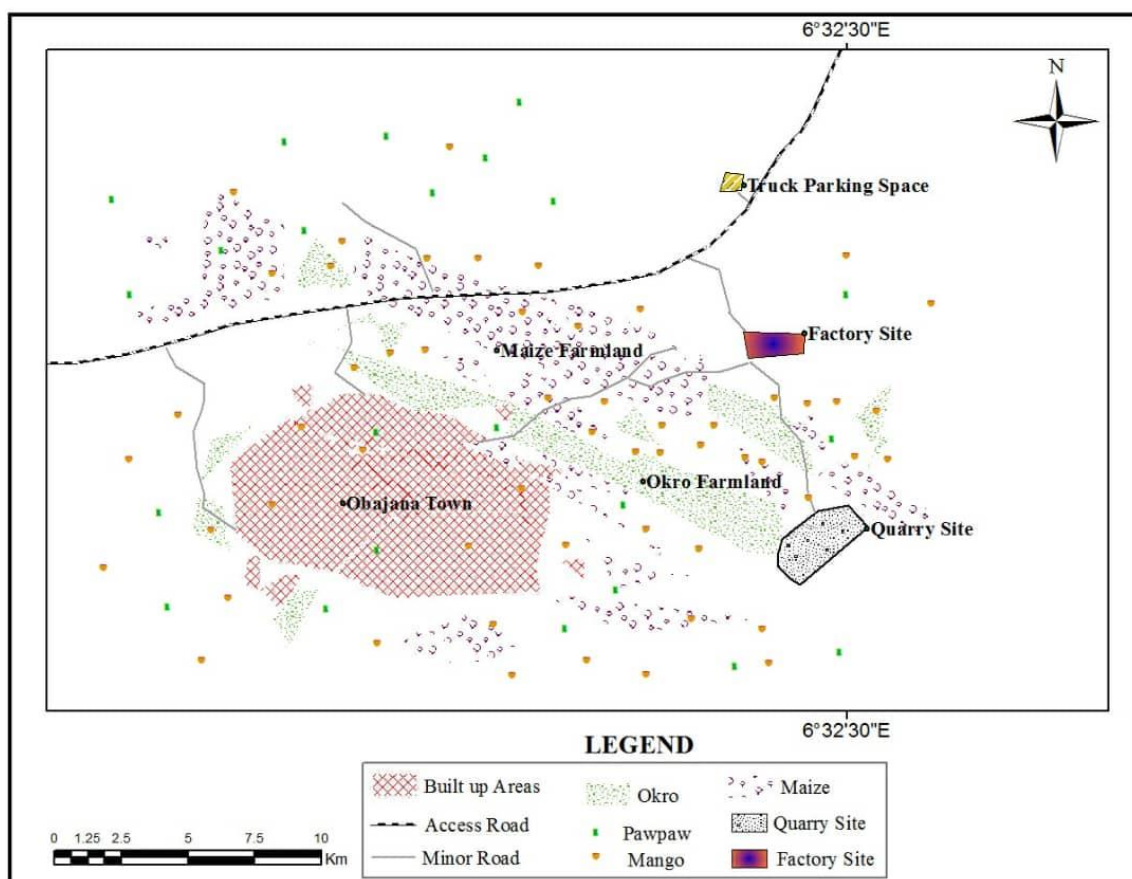


Figure 3: Map of Obajana showing sample collection points

Obajana cement factory is situated in Lokoja local government area of Kogi state, Nigeria. Obajana is one of the towns in Oworo land. Located between Latitudes $6^{\circ}24'N - 7^{\circ}34'N$, Longitudes $7^{\circ}49'E - 8^{\circ}59'E$ of the Greenwich meridian. Obajana is about 220Km from Abuja, the Nigeria Federal Capital Territory, 43Km to Lokoja, 49Km to Okene and 40Km to Kabba.

The study area is underlain by basement complex rocks, mainly folded gneisses. Limestone, quartzite, pegmatite, Schist, granite and granulites are some of the region's most common rock types. Two types of landforms characterize the region: residual dome-shaped hills and river valleys (Afeni *et al.*, 2008). The establishment of this mega cement factory in Obajana was necessitated by the high concentration of limestone, which is used as a raw material in cement production. The limestone deposit in the study area is projected to be about 647 million metric tonnes, which should make limestone sufficiently available to the factory for about 45 years. The mine and quarry sites are approximately 9 kilometers from the cement plant, thus crushed limestone is transported from the quarry to the factory via an 8.5-kilometer conveyor belt OCP (2005). A fleet of 2,370 trucks transports cement from the factory to all states in Nigeria.

Obajana has an average maximum temperature of 33 degrees Celsius and is hot almost all year. There are wet and dry seasons in the region. The average annual rainfall in the study area varies from 1,100 to 1,320mm. The rainy season spans from May to October. The predominant wind direction in June/July and December/January is south to southwesterly and northeasterly, respectively. In 2007, the soils of Obajana were slightly acidic to slightly alkaline, with a mean pH of 5.82. The organic matter content of the top soil ranged from 0.69 percent to 4.21 percent, with organic matter content ranging from 1.14 percent to 2.35 percent. Except for lead and iron, which tended to be high, the heavy metals content of its soil

was relatively low. Farmers don't need to use fertilizers to get good crop yields because the soils are very fertile (OCP, 2005).

Obajana cement factory began producing cement in 2007 with two production lines and a capacity of 5 million metric tonnes per year (Vetiva, 2010). It currently has five production lines with a combined capacity of 16.25 million metric tonnes per year (OCP, 2020). The Obajana cement plant was built to operate on natural gas with low pour fuel oil (LPFO) as a backup fuel, but all five lines have now been converted to run on coal as a primary and backup fuel (OCP, 2020).

The main occupations of the locals include subsistence farming, cattle rearing, and petty trading. The region's primary agricultural system is a rain-fed intensive small-holder system. The main crops grown there are maize, millet, mango, pawpaw, banana, okra, pepper, Sweet potatoes, cassava, and cowpea.

3.2 Sample Collection

Wet season Samples were collected in the month of July 2018 and July 2019 while dry season samples were collected in December 2018 and December 2019. *Zea mays* and *Abelmoschus esculentus* samples were collected in the rainy season while *Mangifera indica* and *Carica papaya* were sampled in the dry season. Specimens were identified in the Herbarium of the Department of Plant Biology, Federal University Lokoja, Lokoja, Nigeria. These plants were chosen because they were readily available around the factory and they produce fruits that serves as food to man and animals. Samples were collected from the Northern, Western and Eastern axes of the factory at 1km, 2km and 3km distances from the factory. The root, leaves and fruits of the plants were collected. All samples were collected in triplicates. Also at every point where plant samples were collected, soil samples were also

collected in triplicates and homogenized to get a soil sample that represents that point. GPS of all sampling points was noted.

Soil Samples Collection

Soil samples were collected at depth (0 – 20cm) using a soil auger. Three sub-samples were collected for each sampling location, thoroughly mixed in a plastic bowl to make a composite sample that represented that location. Collected soil samples were transferred into cellophane bags (Bamgbose *et al.*, 2000), labelled and taken to the laboratory for processing/pre-treatment and analysis.

Pre-treatment of Soil Samples

Soil samples was processed according to Awofolu (2005). In the lab, soil samples was air dried for two weeks until a constant weight was attained. Dried soil samples was pulverized using a ceramic mortar and pestle then passed through 2mm sieve. All physicochemical parameters and metallic determinations from soil samples was based on the fine particles obtained after sieving.

Treatment of Sample Containers and Crucibles

Glass wares, crucibles and plastic containers were washed and rinsed with distilled water then soaked in 10% (v/v) HNO₃ solution for 24h; after which they were rinsed with double distilled water to eliminate absorbance due to detergent. Crucibles that were used in determination of organic matter content through loss of weight on ignition method were heated in a furnace at 650 degrees for one hour and cooled before use. This is to ensure that materials that could interfere with its weight were completely burnt off.

3.3 Determination of Physico-Chemical Parameters of Soil

Determination of soil pH

The pH of soil samples was measured with a soil:water ratio of 1:2(w/v) using Crison MicropH 2000, pH meter. 5g of air-dried and sieved soil sample was weighed into 50ml plastic beaker. 10ml of distilled water was measured using a pipette and added. The mixture was stirred with the use of a glass rod. The soil suspension was allowed to stand for 30mins undisturbed. The electrode of the pH meter was then inserted into the settled suspension and the pH of the soil measured. Before use, the pH meter was calibrated with standard buffer solutions of pH 4.0, 7.0 and 9.0.

Determination of Electrical Conductivity

The electrical conductivities of soil samples were measured with a soil:water ratio 1:2 (w/v) using Digital Conductivity meter model No PT360 as follows: 5g of 2 mm sieved air-dried soil samples were weighed into plastic containers and 10cm³ of distilled water added. The mixture was stirred several times. The soil suspension was allowed to stand for 30minutes. The electrodes of the conductivity meter was inserted into the settled suspension and the electrical conductivity of the soil measured. Before use, the electrical conductivity meter was calibrated using 0.1M KCl.

Organic Matter Determination

The organic matter of the soil samples was determined using loss on ignition method. One (1g) of the air-dried soil sample was weighed into a crucible of known weight. The sample was then ashed in a furnace at the temperature of 650°C for 24 hours, after which the sample was again weighed. The soil organic matter content was determined according to the expression below.

$$\text{Organic matter (OM)} = [M_o/M_d] \times 100 \text{ -----Equation 1}$$

Where OM=Organic matter

$$M_O = M_d - M_a$$

M_d ----- Mass of dried soil

M_a -----Mass of ashed soil

3.4 Determination of Total Zn, Cr, Pb, Cd and Cu, content of soil.

Digestion of soil Samples

Wet digestion method was used for digestion of the soil samples. Soil samples for determination of Zn, Cr, Pb, Cd and Cu, was digested using; Aqua regia (prepared from 3:1 ratio of analytical grade HCl and HNO₃) (Jaing *et al.*, 2011). One (1) gram of each soil sample was weighed using electric weighing balance (Mettler Toledo mb-8310) into a 250 ml glass conical flask and 10ml of concentrated HNO₃ (70% Sigma-Aldrich Corp, Germany) was added. The mixture was boiled gently in a fume chamber for 45minutes. It was then allowed to cool for 12hours. After cooling, 5ml of 70% HCl (Sigma Aldrich Corp Germany) was added and the mixture was again boiled gently until dense white fumes appeared. All the digests were cooled and filtered using a whattman filter paper No. 42 and diluted to 50ml by adding double distilled water. Each digest was transferred into acid-washed stoppered glass bottle, appropriately labelled and kept for metal analysis.

3.5 Determination of Bioavailable (exchangeable) Zn, Cr, Pb, Cd and Cu content of soil

To determine the exchangeable soil metals, one (1) gram each of the air dried soil sample was weighed into a test tube with the use of an electronic weighing balance (Mettler Toledo mb-2610). 8ml of 0.5M magnesium chloride (MgCl₂) was added to the sample in the test tube. The test tube was subjected to continuous agitation at 1000 revolutions per minute for 20 minutes under normal room temperature with the use of a motorized shaker Chojnacka *et al.*,

2005. The test tube and its content was then allowed to stand for 12 hours. The supernatant was filtered using a Whatman No 42 filter paper and transferred into acid-washed stoppered glass bottle, made up to 25ml with double distilled water, appropriately labelled and kept for bioavailable metal analysis. Quantification of Bioavailable Pb, Cu, Cr, Cd and Zn in the samples was carried out by analyzing the extract with Atomic Absorption Spectrophotometer.

3.6 Plant Samples Collection

Fresh matured *Zea mays*, *Abelmoschus esculentus*, *Mangifera indica* and *Carica papaya* plants were randomly sampled from farms that were located at distances 1, 2 and 3 kilometres from the factory. The choice of these plants were influenced by their abundance and prevalence around the cement factory also the fact that they are sources of food to people living around the factory, passers-by and travellers plying the major road that passes right in front of the factory. Samples of these plants were randomly collected at distances 1 to 3 kilometres from the factory. Co-ordinates of each of the sampling locations were noted using a Global Positioning System (GPS) device. The root, leaves and fruits of these plants were collected with the use of a stainless steel knife. The samples were wrapped in big brown envelopes with adequate room for air movement within the bag and appropriately labelled (Mumba, *et al.*, 2008).

To determine the total Zn, Cr, Pb, Cd and Cu, content of the plant samples, the following procedures were followed.

3.7 Digestion of plant samples

In the laboratory, plant samples i.e. root, leaves and fruits were washed with distilled water to remove all soil particles. It was then air dried to constant weight at room temperature. The dried plant samples were ground in a ceramic mortar. 0.5g of the ground plant sample was weighed using a weighing balance into a conical flask. 7ml of concentrated HNO₃ was then

added. The mixture was boiled for 15 minutes to oxidize all organic matter. It was then left to cool. After cooling 3 ml of 70% HClO_4 was added and the mixture boiled until dense white fumes appeared. This shows the end of the process of digestion. The solution was allowed to cool then filtered using Whatman No. 42 filter paper. The filtrate was then made up to 50 ml by adding double distilled water. The total concentration of Pb, Cr, Cd, Zn and Cu in the digest was analyzed with Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP).

3.8 Quality Validation and Control

In order to validate the results obtained from the analysis, the following validation parameters were taken into consideration.

- i. Care was taken to avoid contamination in the process of sampling, extraction and analysis. All equipment and containers were soaked in 10% HNO_3 for 24 hours then rinsed thoroughly in double distilled water before use.
- ii. Reagent blanks were used. Blank samples were digested, subjected to the same extraction procedure as (3.4 and 3.7) above and analysed using the same metal analyses procedure for soil and plant samples. This helps to validate the purity of chemicals used for digestion.
- iii. Certified reference material IAEA-SL-1 (lake sediment) and certified reference material IAEA-Cabbage-359 were subjected to same digestion procedure as (3.4) and (3.7) above and analysed accordingly using Atomic absorption Spectrophotometry. The percentage recoveries of the standard reference materials were calculated to evaluate the accuracy of the analytical procedure.
- iv. the detection limit of the AAS used was noted to help ascertain the limit of detection of heavy metals in the samples.

3.9 Studies on the Adaptive Features of Plants Growing around Obajana Cement Factory.

Collection of plant samples

Fresh leaves of four plants species; *Zea mays*, *Abelmoschus esculentus*, *Mangifera indica*, and *Carica papaya* grown around Obajana cement factory (Latitudes 6°24'N – 7°34'N, Longitudes 7°49'E – 8°59'E) were collected for leaf anatomical studies. Samples were collected around 9am. Control samples was collected from Agbaja village (an agerian community with no cement dust pollution) a distance of about 50km from the cement factory. The samples collected were identified and authenticated at the Herbarium of Federal University Lokoja.

Isolation of Leaf Epidermal Layers

A sizeable portion of the fresh mature leaf was taken from the standard median levels (that is midway between the apex and the base) and immersed in concentrated HNO₃ for 8 minutes. The upper (adaxial) and lower (abaxial) epidermis of the leaves were then separated using a dissecting needle and forceps and rinsed with water. The epidermal layer was stained with 1% safranin for 25 minutes and rinsed in water (Olofinobinu and Oladele 1997). The samples were mounted on clean slides in 25% glycerol and the edges of the cover slip were sealed to prevent them from drying out. Both abaxial and adaxial surfaces of the leaves were used for the study. Microscopic observations were done using Olumpus microscope fixed with Accu-Scope digital image 9.0 camera. Stomata, epidermal cells and trichome counts was taken from 15 plants for each studied species at x400 magnification.

The following were determined;

- i. Stomata type using Metcalf and Chalk (1988) terminologies
- ii. Stomatal density (S) i.e the number of stomata per square millimetre (Stace, 1965).

- iii. Stomata index (SI). The stomata index was estimated for the leaf surfaces using Cutter (1978) formula i.e. by expressing the number of stomata per unit area as a percentage of the total number of epidermal cells.

$$SI = \{S/E + S\} \times 100 \text{ -----Equation 2}$$

Where SI = Stomatal Index

S = Number of stomata per unit area

E = Number of ordinary epidermal cells per unit area

Stomatal index for amphistomatous leaves was obtained from the mean of values from both surfaces, while for hypostomatous leaves, it was obtained from values on either of the surface where stomata was present.

- i. Stomatal area was determined by measuring the length and breadth of the guard cells. Then calculated using the formula below.

$$SA = L \times B \times K \text{-----Equation 3}$$

Where SA = Stomatal area

L = Length of guard cell

B = Breadth of guard cell

K = Franco's constant = 0.78524 (Franco, 1939)

- ii. Trichome types; the shapes of trichomes was observed and named following Dilcher 1974
- iii. Frequency of trichome types was computed following the formular;

$$\text{Frequency (\%)} = \{Nt/Tt\} \times 100 \text{ -----Equation 4}$$

(Metcalf and Chalk, 1988)

Where N_t = number of particular trichome type

T_t = total number of trichome type

3.10 Determination of metal mobility in the studied plants

- i. Determination of Bioaccumulation factor (BF) of heavy metals from soil to plant root
- ii. Determination of Transfer factor (TF) of heavy metals from root to shoot

Bioaccumulation factor of heavy metals from soil to plant root

Bioaccumulation factor seeks to predict the concentration of elements in plant that has been taken up from the soil on which the plant grows. The concentration of some elements in the plant has linear relationship with the concentration in the soil at equilibrium (Chojnacka *et al*; 2005).

$$BF = C_p \text{ (mg kg}^{-1}\text{)} / C_{ts} \text{ (mg kg}^{-1}\text{)} \text{ -----Equation 5}$$

Where C_p is the metal content in root

C_{ts} is the bioavailable metal content of the soil

$$\text{Bioaccumulation factor (BF)} = \frac{\text{Concentration of metal in plant root}}{\text{Concentration of metal in soil}}$$

If $BF > 1.0$ Good phytostabilizer and has high metal transfer rate (Garba *et al.*, 2012).

$BF < 0.5$ low metal transfer rate

Transfer factor (TF) of heavy metals from root to shoot

Transfer factor (TF) is the ability of plants to translocate metal species from root to shoot at different concentrations (Ghosh and Singh 2005).

$$TF = \frac{\text{Metal content of shoot (mg/kg)}}{\text{Metal content of root (mg/kg)}} \text{ -----Equation 6}$$

Metal content of root (mg/kg)

TF < 1.0 implies limited mobility of metal within the plant

TF < 0.7 implies that the metals are immobilized within the root

TF < 1.0 plant is a phytostabilizer and an excluder of heavy metals

TF > 1.0 plant is an accumulator of heavy metals (Garba *et al.*, 2012)

3.11 Models used in determination of pollution status of the environment

Contamination Factor

Contamination factor is used to determine the level contamination caused by a given toxic substance in an environmental matrix (Hakanson, 1990). Contamination factor (Cf) was calculated using the formula

$$Cf = C_i / C_n \text{ ----- Equation 7}$$

Cf is contamination factor

C_i is the mean concentration of the heavy metal

C_n is the Concentration of the heavy metal in the Control samples.

Contamination factor is categorized as follows:

Cf ≤ 1 is low pollution

Cf > 1 ≤ 3 is moderate pollution

Cf > 3 ≤ 6 is high pollution

Cf > 6 is very high pollution (Maanan *et al.*, 2014).

Geo Accumulation Index

Geo accumulation index is an indicator used to assess the presence and intensity of anthropogenic contaminant deposition on surface soil. It describes the degree of pollution in soils posed by heavy metal contaminations with reference to the background concentrations of these metals.

It is computed using the formular

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \cdot B_n} \right) \text{ -----Equation 8}$$

Where C_n is the mean heavy metal concentration

B_n is the background values (i.e metal concentration in the background reference samples)

1.5 is the correction values occasioned by human influences or possible variations in the background values.

$$\log_2 = 0.3010$$

The geo accumulation index is grouped into six classes according to (Buccolieri *et al.*, 2016):

$I_{geo} < 0$: unpolluted

I_{geo} between 0-1: unpolluted to moderately polluted

I_{geo} between 1-2: moderately polluted

I_{geo} between 2-3: moderately to strongly polluted

I_{geo} between 3-4: strongly polluted

I_{geo} between 4-5: strongly to very strongly polluted

I_{geo} between >5 : very strongly polluted

Ecological Risk Factor

Ecological risk factor is the product of the contamination factor and the toxicity of individual metal. It expresses the potential ecological risk of each given contaminant (Hakanson, 1990).

It can be expressed as:

$$E = Tr \times Cf. \quad R = \sum E \text{ -----Equation 9}$$

Where;

E is the individual potential risk factor,

Cf is the contamination factor,

Tr is the toxic response factor

The toxic response factor for Zn, Cr, Pb, Cd, and Cu is 1, 2, 5, 30 and 5 respectively (Nouri and Haddioui, 2016)

The following terminologies are also used to describe the ecological risk (Ri)

$R_i < 95$ indicates a low potential ecological risk

$95 < R_i < 190$ is a moderate ecological risk

$190 < R_i < 380$ is a considerable ecological risk

$R_i \geq 380$ is a very high ecological risk (Maanan *et al.*, 2014).

3.12 Human health implications from ingestion of heavy metal laden vegetables/fruits growing around the factory

Health risk assessment of human exposure to industrial chemical agent is computed by the hazard quotient (HQ). The systemic toxicity or non-carcinogenic hazard for a single element is expressed as the hazard quotient;

$$HQ = \frac{DOI \times C_{\text{metal}}}{Rfd \times Bw} \text{-----Equation 10}$$

HQ – Hazard quotient (unitless)

DOI – Daily oral intake of fruit/ vegetables (0.086Kg/day)

C_{metal} – Concentration of metal in vegetable/fruit (Mg/Kg)

Rfd – Refrence oral dose of metal (mg/kg of body weight/day) as provided by USEPA 2010.

BW – Body weight (body weight of adult was be taken as 70kg)

Human health risk is described on the basis of the HQ values. If $HQ > 1$ or if $HQ < 1$.

The greater the value of HQ above 1, the greater the level of concern/risk since the accepted standard is 1.0 at which there will be no significant health hazard (Grzetic and Ghariani, 2008). The probability of experiencing long-term health hazard effects increases with the increasing HQ value (Wang *et al.*, 2012) and according to Lemly (1996) and Grzetic and Ghariani (2008): $HQ = 1.1-10$ refer to moderate hazard while $HQ > 10$ refer to high hazard.

3.13 Data Analysis

The results obtained from heavy metal analysis were subjected to statistical using SPSS 23.0 (SPSS Inc., USA) software. The means of the replicates and the evaluation of significant differences among sampling sites, sampling distances, sampling depth (soil samples) and different organs(plant samples) were be determined using descriptive statistics and analysis of variance (ANOVA). Linear correlations between plant organs, metals in soils and metals in plants, metal concentrations in soil samples at various distances and depth were be tested through the Pearson's r coefficient. Data generated were also be subjected to student t-test for significant difference between the variables under consideration. All statistical calculation were performed using the software Statistical Package for Social Sciences (SPSS) version 23.0.

CHAPTER FOUR

RESULTS

4.1 Percentage recoveries and permissible limits of heavy metals

The percentage recovery of heavy metals in the standard reference material IAEA-SL-1(lake sediment) used for quality control and confirmation of the accuracy of the analytical process are presented on table 1. The percentage recoveries of the heavy metals in the soil samples ranged from 91.9% to 110.8% in the rainy season. While in the dry season it ranged from 90.67% to 110.8%. Whereas, the percentage recovery of metals in reference material (IAEA-Cabbage-359) used for quality control of the plant samples ranged from 95.8% to 109.8% in the rainy season. While in the dry season it ranged from 91.7% to 107.7% as shown on table 2. The detection limit of the atomic absorption spectrophotometer used in analysing the samples for heavy metal content is presented on table 3 with Cd having the lowest (0.001mg/l) detection limit and Pb with the highest (0.08mg/l) detection limit. The internationally allowable limits of heavy metals in soils and plants as given by Canadian Council of Ministers of the Environment (CCME) 2007 and Food and Agriculture Organisation (FAO)/ World Health Organisation (WHO) in 2001 is presented on table 4. These permissible limits are in agreement with our local standards as such, they were adopted as the benchmark with which the results obtained for this research was compared.

Table 1: Percentage recovery of metals in reference material (lake sediment)

Rainy season IAEA-SL-1(lake sediment)				Dry season IAEA-SL-1(lake sediment)		
Metal	Mean value (study)	Mean value (certified)	% recovery	Mean value (study)	Mean value (certified)	% recovery
Zn	207.1	223.0	92.9	211.4	223.0	94.79
Cr	95.62	104.0	91.9	94.6	104.0	90.9
Pb	35.50	37.70	94.2	34.5	37.7	91.5
Cd	5.10	4.60	110.8	5.1	4.6	110.8
Cu	27.8	30.0	92.7	27.2	30.0	90.67

Table 2: Percentage recovery of metals in reference material (IAEA-Cabbage-359)

Metal	Rainy season IAEA-Cabbage-359			Dry season IAEA-Cabbage-359		
	Mean value (study)	Mean value (certified)	% recovery	Mean value (study)	Mean value (certified)	% Recovery
Zn	42.2	38.6	109.8	40.5	38.6	104.9
Cr	1.4	1.3	107.7	1.4	1.3	107.7
Pb	NA	NS	NA	NA	NS	NA
Cd	0.12	0.12	100.0	0.1	0.12	91.7
Cu	5.43	5.67	95.8	5.32	5.67	93.8

NA- Not applicable; NS- Not specified in the certified sample

Table 3: Detection limit of AAS used for determination heavy metal levels

Heavy metal	AAS (Buck Scientific 210 VGP)
Zn	0.005mg/l
Cr	0.04mg/l
Pb	0.08mg/l
Cd	0.001mg/l
Cu	0.005mg/l

Table 4: International allowable limits for heavy metals (mg/kg) in plants and soils.

Metal	CCME(2007)^a	FAO/WHO(2001)^b
Cu	63.0	40.0
Cd	1.4	0.2
Pb	70.0	0.3
Zn	200.0	60.0
Cr	64.0	2.3

^a; Permissible limit for heavy metals in agricultural soils,

^b; Permissible limit for heavy metals in plants.

4.2 Physicochemical parameters of soil around Obajana cement factory in the rainy and dry seasons.

Table 5 shows the Descriptive statistics of pH, organic matter and electrical conductivity of soil samples from the polluted and unpolluted sites in 2017 and 2018 rainy season. The pH values in the polluted site ranged from 5.1 (slightly acidic) to 9.3 (slightly alkaline). In the northern axis of the factory mean pH value was between 5.1- 8.8. In the eastern flank, pH values ranged from 7.4-9.0. Whereas, in the western side of the factory, pH ranged from 6.8 – 9.3. pH had a wider range in the northern axis and the soil acidity was highest there. While, soil of the western axis is the most alkaline of the 3 axis investigated. pH of soil from the control site was lower (4.7 ± 0.5) than what was obtainable at the study area. Organic matter content of soils of the study area ranged from 6.2% to 12.0%, with the highest (12.0%) occurring at E3 and the least (6.2%) at N2. Organic matter content of the unpolluted site was (10.0%). Electrical conductivity ranged from 100.5 us/cm to 119.7 us/cm. The unpolluted site had EC value of 95.0 us/cm.

Table 6 shows the Descriptive statistics of pH, organic matter and electrical conductivity of soil in 2017 and 2018 dry season. The pH values in the polluted site ranged from 4.3 ± 0.2 (acidic) to 11.5 ± 1.4 (alkaline). In the northern axis of the factory mean pH value was between 5.2 ± 0.2 - 10.5 ± 1.5 . In the eastern flank, pH values ranged from 10.5 ± 1.7 - 11.5 ± 1.4 . Whereas, in the western side of the factory, pH ranged from 4.3 ± 0.2 – 10.1 ± 1.5 . pH had the narrowest range in the eastern axis and the soil alkalinity was highest there. pH of soil from the control site was lower (4.4 ± 0.5) than what was obtainable at the study area. Organic matter content of soil of the study area ranged from 6.4% to 15.3%, with the highest (15.3%) occurring at N3 and the least (6.4%) in E2. Organic matter content of the unpolluted site was

8.5%. Electrical conductivity ranged from 102.3 ± 12.6 us/cm to 123.5 ± 12.5 us/cm. Electrical conductivity decreased with increasing distance from the factory.

4.3 Total heavy metal levels in soil samples in the rainy seasons

Mean values of the total Zn concentrations in soil samples from different locations ranged from 8.42 to 89.87. The highest (89.87) occurred at N2 but its concentration is not significantly greater than N1, N3, W1 and W2. The least concentration (8.72) around the factory occurred in E3 which was also not significantly different from SC, W3, E1 and E2 at $P \leq 0.05$. Although, the concentration of Zn in the unpolluted/control site was still slightly lower (8.42) than what was obtainable at E3. Whereas, highest (115.87) mean total concentration of Cr was found at E1 but its concentration was not significantly greater than N1, N2, N3, W1, W2, and E2. While the lowest (46.42) concentration was at SC although it was not significantly different from E3 at $P \leq 0.05$. On the other hand, highest (29.65) concentration of Pb was found at W2 but its concentration was not significantly greater than N1, N2, and N3. While the lowest (6.77) concentration of lead was at SC which was also not significantly different from E3 at $P \leq 0.05$. Likewise, the highest (2.75) concentration of Cd was found at W2 but its concentration is not significantly greater than E1. While the lowest concentration of Cd was at E3 (0.00) which was also not significantly different from E2, E1, W3, SC, N2 and N1 at $P \leq 0.05$. In the same vein, highest (34.00) concentration of Cu was found at N2 but its concentration is not significantly greater than E1, W1, W2, N1, N3. While the lowest concentration of Cu was at SC (8.00) which was also not significantly different from E2, E1, E3, W3, and N1 at $P \leq 0.05$. Total Cu concentrations in soils samples from different locations ranged from 8.00 to 34.00. As shown on table 7.

Legend; N-north, W-west, E-east, 1, 2,3 implies one, two, three Kilometers from OCF.

N₁ ---- 1 km from the factory in the northern axis of the factory

N₂ ---- 2 km from the factory in the northern axis of the factory

N₃ ---- 3 km from the factory in the northern axis of the factory

W₁ ---- 1 km from the factory in the western axis of the factory

W₂ ---- 2 km from the factory in the western axis of the factory

W₃ ---- 3 km from the factory in the western axis of the factory

E₁ ---- 1 km from the factory in the eastern axis of the factory

E₂ ---- 2 km from the factory in the eastern axis of the factory

E₃ ---- 3 km from the factory in the eastern axis of the factory

Sc-----Control sample (soil)

Rc-----Control sample (roots)

Lc-----Control sample (leaves)

Fc-----Control sample (fruits)

Table 5: Descriptive statistics of soil physicochemical parameters in the rainy seasons.

Locations	pH	Organic matter (%)	EC(μ S/Cm)
N1	8.8 $\pm$ 0.7 ^a	9.0 $\pm$ 1.0 ^b	115.4 $\pm$ 14.3 ^a
N2	7.4 $\pm$ 0.8 ^{ab}	6.2 $\pm$ 0.8 ^{bc}	100.7 $\pm$ 11.6 ^c
N3	5.1 $\pm$ 0.5 ^{bc}	10.2 $\pm$ 1.0 ^a	118.6 $\pm$ 20.5 ^a
W1	9.3 $\pm$ 1.0 ^a	10.2 $\pm$ 2.5 ^a	119.7 $\pm$ 16.3 ^a
W2	9.0 $\pm$ 0.8 ^a	11.2 $\pm$ 2.1 ^a	110.5 $\pm$ 10.4 ^{ab}
W3	6.8 $\pm$ 0.7 ^b	13.1 $\pm$ 2.3 ^a	112.8 $\pm$ 10.8 ^{ab}
E1	9.0 $\pm$ 1.3 ^a	8.5 $\pm$ 0.7 ^b	116.5 $\pm$ 12.5 ^a
E2	8.8 $\pm$ 1.0 ^a	10.2 $\pm$ 1.2 ^a	111.4 $\pm$ 12.8 ^{bc}
E3	7.4 $\pm$ 0.8 ^{ab}	12.0 $\pm$ 2.5 ^a	112.1 $\pm$ 10.7 ^{ab}
Control	4.7 $\pm$ 0.5 ^c	10.0 $\pm$ 0.5 ^a	95.0 $\pm$ 10.0 ^{cd}

Values with the same superscript along the column are not significantly different at $p < 0.05$

Table 6: Descriptive statistics of soil physicochemical parameters in the dry seasons

Locations	pH	Organic matter (%)	EC ($\mu\text{S}/\text{Cm}$)
N1	10.5 $\pm$ 1.5 ^a	10.7 $\pm$ 1.4 ^a	123.5 $\pm$ 12.5 ^a
N2	9.4 $\pm$ 1.4 ^a	12.6 $\pm$ 2.3 ^a	118.2 $\pm$ 10.6 ^a
N3	5.2 $\pm$ 0.2 ^c	15.3 $\pm$ 2.1 ^a	112.4 $\pm$ 15.3 ^{ac}
W1	10.1 $\pm$ 1.5 ^a	8.6 $\pm$ 1.5 ^b	116.8 $\pm$ 12.6 ^b
W2	9.2 $\pm$ 0.7 ^a	10.0 $\pm$ 1.2 ^a	105.3 $\pm$ 10.3 ^c
W3	4.3 $\pm$ 0.2 ^c	12.4 $\pm$ 2.0 ^a	102.4 $\pm$ 12.6 ^c
E1	11.5 $\pm$ 1.4 ^a	9.3 $\pm$ 0.4 ^b	120.0 $\pm$ 13.7 ^a
E2	10.5 $\pm$ 1.7 ^a	6.4 $\pm$ 0.2 ^c	118.4 $\pm$ 10.4 ^a
E3	10.7 $\pm$ 1.2 ^a	10.5 $\pm$ 1.0 ^a	115.2 $\pm$ 14.3 ^a
Control	4.4 $\pm$ 0.5 ^c	8.5 $\pm$ 0.6 ^b	96.4 $\pm$ 10.5 ^c

Values with the same superscript along the column are not significantly different at $p < 0.05$

Table 7: Descriptive statistics of soil total heavy metal contents (mg/kg) in the rainy seasons.

Location	Zn	Cr	Pb	Cd	Cu
N1	86.65±1.8 ^a	100.57±5.5 ^a	26.87±3.57 ^{ab}	0.500±.70 ^b	22.00±4.24 ^{ab}
N2	89.87±5.25 ^a	104.25±4.06 ^a	28.15±3.42 ^a	0.00±0.00 ^b	34.00±5.21 ^a
N3	86.82±6.56 ^a	105.85±5.54 ^a	26.20±1.34 ^{ab}	0.00±0.00 ^b	19.25±3.01 ^{ab}
W1	72.90±4.54 ^a	108.35±6.59 ^a	19.77±3.36 ^{abc}	.000±0.00 ^b	20.25±1.77 ^{ab}
W2	77.55±8.48 ^a	111.70±8.31 ^a	29.65±3.08 ^a	2.75±2.59 ^a	15.75±3.98 ^{ab}
W3	59.77±2.99 ^b	76.32±2.25 ^b	12.47±2.54 ^{abc}	0.00±0.00 ^b	8.75±1.76 ^b
E1	30.90±2.32 ^b	115.87±7.23 ^a	27.92±5.37 ^a	2.25±1.41 ^{ab}	21.50±4.49 ^{ab}
E2	66.10±7.37 ^b	77.95±1.52 ^a	14.10±1.69 ^{abc}	0.500±0.70 ^b	11.25±0.35 ^b
E3		58.57±4.89 ^c	9.60±2.35 ^{bc}	0.00±0.00 ^b	10.25±0.35 ^b
	8.72±2.77 ^{bc}				
SC	8.42±1.30 ^b	46.42±6.76 ^{cd}	6.77±2.68 ^c	0.00±0.00 ^b	8.00±2.43 ^b

Values with the same superscript along the column are not significantly different at p<0.05

4.4 Total heavy metal levels in soil samples in the dry seasons

Table 8 shows the mean values of total heavy metal contents (mg/kg) in the dry seasons soil samples. Zn concentrations in soil samples from different locations ranged from 8.11 to 94.93. The highest (94.93) occurred at N2 but its concentration is not significantly greater than N1, N3, W1 and W2. The least concentration (8.11) around the factory occurred in SC which was also not significantly different from E3 at $P \leq 0.05$. Whereas, highest (119.49) mean total concentration of Cr was found at E1 but its concentration was not significantly greater than N1, N2, N3, W1, W2, and E2 at $P \leq 0.05$. While the lowest (47.42) concentration was at SC. On the other hand, highest (38.15) concentration of Pb was found at N2 but its concentration was not significantly greater than N1. While the lowest (8.37) concentration of lead was at SC which was also not significantly different from E3, E2 and W3 at $P \leq 0.05$. Likewise, the highest (1.15) concentration of Cd was found at W2 but its concentration is not significantly greater than E1. While the lowest concentration of Cd was at E3 (0.00) which was also not significantly different from E2, E1, W3, SC, N2 and N1 at $P \leq 0.05$. In the same vein, highest (30.00) concentration of Cu was found at N2 but its concentration is not significantly greater than E1, W1 and N1 at $P \leq 0.05$. While the lowest concentration of Cu was at SC (6.00).

Table 8: Descriptive statistics of soil total heavy metal contents (mg/kg) in the dry seasons.

Location	Zn	Cr	Pb	Cd	Cu
N1	90.24±5.63 ^a	103.57±2.57 ^a	34.35±3.57 ^a	0.05±0.00 ^b	20.50±4.24 ^a
N2	94.93±7.23 ^a	107.25±1.39 ^a	38.15±7.42 ^a	0.05±0.00 ^b	30.00±5.21 ^a
N3	88.80±6.53 ^a	108.85±2.59 ^a	26.20±1.34 ^b	0.00±0.00 ^b	14.15±2.01 ^b
W1	82.90±4.54 ^a	110.35±3.59 ^a	25.45±3.36 ^b	.05±0.00 ^b	18.25±1.77 ^{ab}
W2	71.59±8.74 ^a	112.70±2.31 ^a	28.45±13.08 ^b	1.15±0.05 ^a	14.75±3.98 ^b
W3	49.36±2.23 ^b	86.32±2.60 ^b	18.47±2.54 ^{bc}	0.05±0.00 ^b	10.75±1.76 ^b
E1	47.90±5.34 ^b	119.49±3.23 ^a	26.52±15.37 ^b	1.05±0.50 ^a	17.50±2.49 ^{ab}
E2	48.10±8.37 ^b	100.95±1.58 ^a	24.10±1.69 ^{bc}	0.50±0.00 ^b	10.25±0.50 ^b
E3		86.57±4.65 ^b	19.60±2.35 ^{bc}	0.00±0.00 ^b	10.00±1.35 ^b
	12.78±2.38 ^c				
SC	8.11±1.36 ^c	47.42±6.76 ^{cd}	8.37±2.68 ^c	0.00±0.00 ^b	6.00±1.40 ^c

Values with the same superscript along the column are not significantly different at $p < 0.05$

4.5 Bioavailable metal levels in soil around Obajana Cement Factory in the dry season

Descriptive statistics of bioavailable heavy metal contents (mg/kg) of soil around Obajana Cement Factory in the dry seasons is shown on Table 9. The mean bioavailable Zn concentrations in soils samples from different locations ranged from 6.40 to 68.00 mg/kg. The highest bioavailable concentration of Zn (68.00 mg/kg) was in W1 but was not significantly greater than N1, N2, N3, W1 and W2. While the lowest (6.40 mg/kg) concentration is in E1 which was also not significantly different from W3, E1 E2, SC and E3 at $P \leq 0.05$. Also, highest (77.90 mg/kg) bioavailable concentration of Cr was found at N2 but not significantly greater than N1, N3, W1, W2, W3, E1 and E2. While the lowest (11.72 mg/kg) concentration was in SC this is not significantly different from E3 at $P \leq 0.05$. That is the bioavailable Cr concentrations in soil samples from different locations ranged from 11.72 mg/kg to 77.90 mg/kg. Similarly, highest bioavailable concentration of Pb (23.52 mg/kg) was found in N3 but its concentration is not significantly greater than N1, N2, W1, W2, W3, E1 and E2. While the lowest (1.22 mg/kg) concentration of Lead was in SC which was also not significantly different from E3 at $P \leq 0.05$. Bioavailable Pb concentrations in soil samples from different locations ranged from 1.22 to 23.47 mg/kg. Cd had its peak (1.00 mg/kg) bioavailable concentrations in W2 and the least (0.00 mg/kg) concentration in most of the sampled locations. The highest (11.50 mg/kg) bioavailable concentration of Cu was found at N3 but its concentration is not significantly greater than E1, W1 and N2. While the lowest (1.50 mg/kg) concentration of Cu was at SC which was also not significantly different from W3 at $P \leq 0.05$. Bioavailable Cu concentrations in soils samples from different locations ranged from 1.50 mg/kg to 11.50 mg/kg.

4.6 Bioavailable metal levels in soil around Obajana Cement Factory in the rainy season

Descriptive statistics of bioavailable heavy metal contents (mg/kg) of soil around Obajana Cement Factory in the rainy seasons is shown on Table 10. The mean bioavailable Zn concentrations in soils samples from different locations ranged from **5.05** to 54.00 mg/kg. The highest bioavailable concentration of Zn (54.00mg/kg) was in W1 but was not significantly greater than N1, N2, N3, W1 and W2. While the lowest (5.05 mg/kg) concentration is in SC which was also not significantly different from E3 at $P \leq 0.05$. Also, highest (58.42 mg/kg) bioavailable concentration of Cr was found at N2 but not significantly greater than N1, N3, W1, W2, W3, E1 and E2 at $P \leq 0.05$. While the lowest (9.64 mg/kg) concentration was in SC. That is the bioavailable Cr concentrations in soil samples from different locations ranged from 9.64mg/kg to 58.42 mg/kg. Similarly, highest bioavailable concentration of Pb (20.73 mg/kg) was found in N3 but its concentration is not significantly greater than N1, N2 and W1. While the lowest (1.00 mg/kg) concentration of Lead was in SC which was also not significantly different from W2, W3, E2 and E3 at $P \leq 0.05$. Bioavailable Pb concentrations in soil samples from different locations ranged from 1.00 to 20.73 mg/kg. Cd had its peak (0.50 mg/kg) bioavailable concentrations in W2 and the least (0.00 mg/kg) concentration in most of the sampled locations. The highest (9.50 mg/kg) bioavailable concentration of Cu was found at N3 but its concentration is not significantly greater than E1, E2, W1 and N2. While the lowest (1.00 mg/kg) concentration of Cu was at SC which was also not significantly different from W3 at $P \leq 0.05$. Bioavailable Cu concentrations in soils samples from different locations ranged from 1.00 mg/kg to 9.50 mg/kg.

Table 9: Descriptive statistics of bioavailable heavy metal contents (mg/kg) in the dry seasons.

Location	Zn	Cr	Pb	Cd	Cu
N1	57.96±3.14 ^a	63.30±7.64 ^a	21.65±4.59 ^a	0.25±0.35 ^b	3.50±0.70 ^b
N2	64.80±6.15 ^a	77.90±1.41 ^a	23.47±2.18 ^a	0.00±0.00 ^b	8.50±1.94 ^{ab}
N3	58.57±4.70 ^a	69.80±4.03 ^a	23.52±1.30 ^a	0.00±0.00 ^b	11.50±2.36 ^a
W1	68.00±5.55 ^a	76.25±4.36 ^a	17.77±4.27 ^a	0.00±0.00 ^b	11.00±2.82 ^{ab}
W2	49.32±6.24 ^a	75.60±0.59 ^a	6.52±0.17 ^{abc}	1.00±0.70 ^a	5.50±2.32 ^b
W3	15.52±0.42 ^b	65.17±4.57 ^a	7.40±0.95 ^{ab}	0.00±0.00 ^b	2.50±0.70 ^{bc}
E1		77.52±8.94 ^a	11.57±2.94 ^a	0.00±0.00 ^b	7.50±4.94 ^a
	19.40±0.82 ^b				
E2	17.25±3.22 ^b	75.12±4.20 ^a	7.70±1.48 ^{ab}	0.25±0.35 ^b	5.00±1.41 ^b
E3	7.62±2.99 ^b	25.70±3.39 ^b	1.92±0.29 ^c	0.00±0.00 ^b	5.50±0.70 ^b
SC	6.40±2.58 ^b	11.72±2.81 ^b	1.22±0.49 ^b	0.00±0.00 ^b	1.50±0.70 ^c

Values with the same superscript along the column are not significantly different at $p < 0.05$

Table 10: Descriptive statistics of bioavailable heavy metal contents (mg/kg) in the rainy seasons

Location	Zn	Cr	Pb	Cd	Cu
N1	53.36±2.17 ^a	44.30±7.64 ^a	18.65±4.59 ^a	0.05±0.35 ^b	2.50±0.70 ^b
N2	53.30±3.10 ^a	58.42±1.41 ^a	17.47±2.18 ^a	0.00±0.00 ^c	7.50±1.90 ^a
N3	48.57±4.00 ^{ab}	49.80±4.03 ^a	20.73±1.30 ^a	0.00±0.00 ^c	9.50±2.50 ^a
W1	54.00±5.45 ^a	50.25±4.36 ^a	15.77±4.27 ^a	.00±0.00 ^c	8.00±2.82 ^a
W2	42.32±2.24 ^{ab}	51.60±0.59 ^a	5.52±0.17 ^{bc}	0.50±0.70 ^a	3.50±2.32 ^b
W3	30.00±1.40 ^c	45.17±4.57 ^a	6.40±0.95 ^{bc}	0.00±0.00 ^c	1.50±0.70 ^{bc}
E1	35.40±1.89 ^c	47.52±8.94 ^a	10.57±2.94 ^b	0.00±0.00 ^c	5.50±1.94 ^a
E2	37.25±1.20 ^c	45.12±4.20 ^a	5.70±1.48 ^{bc}	0.20±0.35 ^a	5.00±1.01 ^{ab}
E3	16.62±2.00 ^d	23.70±3.39 ^b	1.00±0.29 ^c	0.00±0.00 ^c	3.50±0.50 ^b
SC	5.05±2.43 ^d	9.64±2.81 ^c	1.00±0.49 ^c	0.00±0.00 ^c	1.00±0.00 ^c

Values with the same superscript along the column are not significantly different at $p < 0.05$

Correlation of total soil metal and physicochemical parameters in the rainy season.

Table 11. Shows Pearson correlation coefficient (r) between physicochemical parameters (pH, organic matter) and total metal contents of the soil around Obajana cement factory in the rainy and dry seasons.

Pearson correlation coefficient is a measure of the strength of the linear relationship between two variables. A Pearson correlation analysis was conducted to investigate the relationships between soil pH, soil organic matter content and total heavy metal concentration in the soil during the wet and dry seasons. The results as shown on table 11 revealed a weak negative correlation with significance ($p < 0.05$) between; pH and OM (-.124), Cr (-.028), Pb (-.250) and Cd (-.125). This negative correlation shows that increase in pH caused a decrease in the other variables during the two seasons while the correlation between pH and Zn (.023) was positive but weak. Whereas, the correlation between pH and Cu was positive and strong at ($p < 0.05$). Revealing a possible common source of metals with high correlation. This shows that increase in pH resulted in increased total Zn and Cu levels during the two seasons. There was a positive correlation between OM and Zn (.029), Pb (.240), Cd (.035) and Cu (.083) at ($p < 0.05$). Though the correlation between OM and Cr (-.170) was negative. Strong correlations existed between: Zn and Cr (.423), Pb (.657), Cd (.540), Cu (.414) at ($p < 0.05$). Likewise, strong correlations existed between Cr and Pb (.599), Cr and Cd (.340), Pb and Cd (.528), and Cd and Cu (.584). While the correlation between Cr and Cu (.157), Pb and Cu (.195) was weak at ($p < 0.05$).

Table 12 shows the Pearson correlation coefficient (r) between physicochemical parameters (pH, organic matter) and bioavailable metal contents of the soil around Obajana cement factory in the rainy and dry seasons.

There was positive correlation between pH, OM and all the heavy metals with the exception of Cr which was negatively correlated. This indicates increase in pH had a positive impact on all the other parameters except chromium. The correlations between OM and Pb (.662); OM and Cd (.651) were the strongest at ($p < 0.05$). There was a strong positive correlation between the bioavailabilities of all the studied metals with the exception of Zn and Pb (.260), Zn and Cd (.215) that was weak at ($p < 0.05$).

Table 11: Pearson correlation coefficient (r) between pH, organic matter and total metal contents of the soil around Obajana cement factory in the rainy season.

		Pearson correlation coefficient (r)						
		pH	OM	Zn	Cr	Pb	Cd	Cu
pH	Pearson Correlation	1						
OM	Pearson Correlation	-.124	1					
Zn	Pearson Correlation	.023	.209	1				
Cr	Pearson Correlation	-.028	-.170	.423	1			
Pb	Pearson Correlation	-.250	.240	.657**	.599**	1		
Cd	Pearson Correlation	-.125	.035	.540*	.340	.528*	1	
Cu	Pearson Correlation	.391	.083	.414	.157	.195	.584**	1

** Correlation is significant at the 0.01 level

* Correlation is significant at the 0.05 level

OM - Organic matter

Table 12: Pearson correlation coefficient (r) between pH, organic matter and bioavailable metal concentrations of the soil around Obajana Cement Factory in the dry season.

		Pearson correlation coefficient (r)						
		pH	OM	Zn	Cr	Pb	Cd	Cu
Ph	Pearson Correlation	1						
OM	Pearson Correlation	0.323	1					
Zn	Pearson Correlation	.272	.211	1				
Cr	Pearson Correlation	-.137	.320	.342	1			
Pb	Pearson Correlation	.295	.662**	.260	.527**	1		
Cd	Pearson Correlation	.463*	.651**	.215	.780**	.524*	1	
Cu	Pearson Correlation	.295	.477*	.366	.341	.525*	.574*	1

** Correlation is significant at 0.01 level

*Correlation is significant at 0.05 level

OM – Organic matter

4.7 Comparison of metal levels in the rainy season and dry season

Table 13 shows the difference between the total heavy metals concentrations during dry and wet seasons. There were significant differences between the total concentration during the wet and dry seasons for Zn, Cr and Pb while there was no significant difference between wet and dry season concentrations of Cd and Cu.

Table 14 shows the t-test of bioavailable Heavy Metals during the dry and wet seasons. There was significant difference between dZn and wZn, dCr and wCr , dPb and wPb, which shows that the bioavailable concentrations of these Heavy Metals in the soil during the dry season are quite different from those of rainy season. But there was no significant difference between dCd and wCd, dCu and wCu which were the bioavailable Cd and Cu during the dry and wet seasons.

Table 13: Differences between the total H.M in the soil during the dry and wet season

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	dZn wZn	66.57	58.21	13.01	39.33	93.82	5.11	19	0.00
Pair 2	dCr wCr	-86.97	24.17	5.40	-98.29	-75.66	-16.08	19	0.00
Pair 3	dPb wPb	-10.77	9.82	2.19	-15.37	-6.18	-4.90	19	0.00
Pair 4	dCd wCd	-0.77	2.87	0.64	-2.12	0.56	-1.21	19	0.24
Pair 5	dCu wCu	-1.75	9.95	2.22	-6.41	2.90	-0.78	19	0.44

Significant at $p < 0.05$ d – dry season w – wet season

Table 14: Differences between the bioavailability of heavy metals in the soil during the dry and wet seasons

		Paired Differences						t	df	Sig.(2tailed)
		Mean	Std. Deviation	Std.Error Mean	95% Confidence					
					Interval of the Difference					
					Lower	Upper				
Pair 1	dZn wZn	26.18	26.03	5.82	14.00	38.36	4.49	19	.000	
Pair 2	dCr wCr	-58.08	24.05	5.37	-69.34	-46.82	-10.79	19	.000	
Pair 3	dPb wPb	-8.33	7.34	1.64	-11.77	-4.89	-5.07	19	.000	
Pair 4	dCd wCd	0.06	0.65	0.14	-.24	0.36	0.40	19	.687	
Pair 5	dCu wCu	2.10	5.28	1.18	-.37	4.57	1.77	19	.091	

Significant at $p < 0.05$ d – dry season w – wet season

4.8 Relationship among heavy metal levels in the soil during the wet and dry seasons

The Pearson correlation coefficient is a measure of the strength of the linear relationship between two variables. A Pearson correlation analysis was conducted to investigate the relationships between the the total heavy metal concentration in the soil during the wet and dry seasons. The results as shown on table 15 revealed a high correlation with significance ($p < 0.05$) between; dPb and dCu (.657), wZn and wPb (.639), wCu and wPb (.650), wPb and wCu (.738). Revealing a possible common source of metals with high correlation. This shows that increase in one led to increase in other(s) during the two seasons. Weak correlations exists between: dZn and dCr (-.124), dZn and dCd (-.028), dZn and dCu (-.250), dZn and wZn (-.125); dCr and dCd (-.170), dCr and wCd (-.097); dPb and wCd (-.155); dCu and wCd (-.283). This negative correlation is indicative of a different sources of the metals. This shows that increase in one led to a decrease in other(s) during the two seasons

Table 16 shows the relationship among the bioavailable heavy metal concentration in the soil during the wet and dry seasons. There was positive correlation among most of the heavy metals with the exception of; dCu and dZn , wZn and dZn which were negatively correlated. This indicates that most of the correlations between the studied metals are significant. The correlations between dCu and wPb (.887) was the strongest followed by dCu and wZn (.780).

Table 15: Relationship among the total heavy metal concentrations in the soil during the wet and dry seasons

		dZn	dCr	dPb	dCd	dCu	wZn	wCr	wPb	wCd	wCu
dZn	Pearson Correlation	1									
dCr	Pearson Correlation	-.124	1								
dPb	Pearson Correlation	.023	.209	1							
dCd	Pearson Correlation	-.028	-.170	.423	1						
dCu	Pearson Correlation	-.250	.240	.657**	.599**	1					
wZn	Pearson Correlation	-.125	.035	.540*	.340	.528*	1				
wCr	Pearson Correlation	.391	.083	.414	.157	.195	.584**	1			
wPb	Pearson Correlation	.435	.052	.315	.147	.281	.639**	.650**	1		
wCd	Pearson Correlation	.572*	-.097	-.155	.067	-.283	.032	.320	.421	1	

wCu	Pearson Correlation	.115	.017	.099	.116	.395	.515*	.442	.738**	.125	1
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** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Table 16: Relationship among the heavy metal bioavailability during the dry and wet seasons

		dZn	dCr	dPb	dCd	dCu	wZn	wCr	wPb	wCd	wCu
dZn	Pearson Correlation	1									
dCr	Pearson Correlation	233	1								
dPb	Pearson Correlation	175	.272	1							
dCd	Pearson Correlation	253	-.137	.320	1						
dCu	Pearson Correlation	-312	.295	.662**	.260	1					
wZn	Pearson Correlation	-218	.463*	.651**	.215	.780**	1				
wCr	Pearson Correlation	384	.295	.477*	.366	.341	.525*	1			
wPb	Pearson Correlation	295	.422	.659**	.182	.887**	.774**	.523*	1		
wCd	Pearson Correlation	163	.020	.059	.034	-.183	.195	.157	-.187	1	
wCu	Pearson Correlation	301	.567**	.094	-.064	.433	.502*	.436	.583**	-.142	1

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

4.9 Heavy metal levels in *Zea mays* samples

Heavy metal levels in *Zea mays* root samples

As Shown on table 17, Zn concentrations in maize root samples from different locations ranged from 6.20 to 69.8 mg/kg. The highest (69.82 mg/kg) Zinc concentrations in maize root was in E2. The least (6.20 mg/kg) Zn concentration is in RC at $P \leq 0.05$. Chromium concentrations in maize roots ranged from 1.85 to 5.10 mg/kg. The highest (5.10 mg/kg) Cr concentration in maize root was found in N2 but it was not significantly greater than W1. While the lowest concentration was in RC (1.85 mg/kg) this is not significantly different from E3, W3 and E2 at $P \leq 0.05$. On the other hand, Lead concentrations in maize roots ranged from 0.35 to 2.70 mg/kg. Maize root with the highest (2.70 mg/kg) Pb concentrations occurred in W1 its concentration is not significantly greater than N1 and E1. The least concentration (0.35 mg/kg) of Pb in maize root was recorded in RC. Similarly, highest (1.0 mg/kg) Cd concentrations occurred in W2 its concentration is not significantly greater than Cd concentrations at all the other locations at $P \leq 0.05$. The highest (1.5 mg/kg) Cu concentrations occurred in W2 its concentration is not significantly greater than Cd concentrations at all the other locations at $P \leq 0.05$.

Heavy metal levels in *Zea mays* leaf samples

Table 18 Shows Zn concentrations in maize leaf samples from different locations it ranged from 5.80 to 53.32. The highest (53.32) Zinc concentrations in maize leaf was in N1 but not significantly greater than W1 and N3 at $P \leq 0.05$. The least (5.80) Zn concentration is in LC. While, Chromium concentrations in maize leaf ranged from 1.30 to 8.70. The highest (8.70) Cr concentration in maize root was found in E1. While the lowest concentration was in LC (1.30) this is not significantly different from N2 and E2 at $P \leq 0.05$. Meanwhile, Lead concentrations in maize leaf ranged from 0.57 to 3.01. Maize leaf with the highest (3.01) Pb

concentrations occurred in E1. The least concentration (0.57) of Pb in maize root was recorded in LC at $P \leq 0.05$. Similarly, The highest (1.50) Cd concentrations occurred in W1. The least concentration (0.00) of Cd in maize root was recorded in its concentration is not significantly greater than Cd concentrations at all the other locations at $P \leq 0.05$. The highest (1.49) Cu concentrations in maize leaf occurred in E1. The least concentration (0.00) of Cu in maize leaf was recorded in LC its concentration is not significantly greater than CU concentrations in E3 and W3 at $P \leq 0.05$.

Table 17: Concentration of some selected heavy metals (mg/kg) in *Zea mays* (root) samples collected at different locations

Location	Zn	Cr	Pb	Cd	Cu
N1	51.40±1.41 ^c	3.20±0.28 ^b	2.40±0.46 ^{abc}	0.00±0.00 ^a	1.00±0.00 ^a
N2	60.55±1.41 ^b	5.10±0.14 ^a	1.32±0.62 ^{cd}	0.00±0.00 ^a	0.50±0.00 ^a
N3	53.15±0.70 ^c	2.40±0.56 ^c	1.65±0.13 ^{cd}	0.00±0.00 ^a	0.50±0.00 ^a
W1	61.25±0.70 ^b	4.37±0.53 ^a	2.70±0.84 ^a	0.00±0.00 ^a	1.00±0.00 ^a
W2	51.55±0.70 ^c	3.25±0.35 ^b	1.30±0.24 ^{cd}	1.00±0.00 ^a	1.50±0.00 ^a
W3	53.55±0.70 ^c	1.35±0.49 ^d	1.02±.06 ^{de}	0.00±0.00 ^a	0.00±0.00 ^a
E1	20.00±0.70 ^d	2.65±0.70 ^c	2.60±0.71 ^{ab}	0.00±0.00 ^a	0.50±0.00 ^a
E2	69.82±0.24 ^a	2.28±0.23 ^{bcd}	1.50±0.51 ^{cd}	0.00±0.00 ^a	0.50±0.00 ^a
E3	13.85±0.70 ^d	2.30±0.36 ^{bcd}	1.71±0.23 ^{bcd}	0.00±0.00 ^a	0.50±0.00 ^a
RC	6.20±1.69 ^e	1.85±0.71 ^d	0.35±0.84 ^e	0.00±0.00 ^a	0.00±0.00 ^a

Values with the same superscript along the column are not significantly different at $p < 0.05$

Table 18: Concentration of some selected heavy metals (mg/kg) in *Zea mays* (leaf) samples collected at different locations

Location	Zn	Cr	Pb	Cd	Cu
N1	53.32±0.45 ^a	4.02±0.06 ^f	2.25±0.35 ^c	0.00±0.00 ^c	1.00±0.00 ^b
N2	51.20±0.24 ^b	2.03±0.08 ^h	1.57±0.02 ^d	0.00±0.00 ^c	0.50±0.00 ^c
N3	52.27±0.38 ^{ab}	5.37±0.53 ^d	1.64±0.00 ^d	0.00±0.00 ^c	0.50±0.00 ^c
W1	52.28±0.40 ^{ab}	4.57±0.02 ^e	2.55±0.07 ^b	1.50±0.07 ^a	0.50±0.00 ^c
W2	46.20±0.28 ^c	7.20±0.01 ^c	1.01±0.02 ^f	1.00±0.07 ^b	1.02±0.36 ^b
W3	40.62±0.036 ^e	8.07±0.03 ^b	1.15±0.21 ^{ef}	0.00±0.00 ^c	0.00±0.00 ^d
E1	15.51±0.21 ^f	8.70±0.07 ^a	3.01±0.01 ^a	0.00±0.00 ^c	1.49±0.07 ^a
E2	44.08±0.04 ^d	1.71±0.02 ^h	1.53±0.02 ^d	0.00±0.00 ^c	0.50±0.00 ^c
E3	12.35±0.49 ^g	2.90±0.07 ^g	1.42±0.03 ^{de}	0.00±0.00 ^c	0.00±0.00 ^d
LC	5.80±1.13 ^h	1.30±0.07 ^h	0.57±0.03 ^g	0.00±0.00 ^c	0.00±0.00 ^d

Values with the same superscript along the column are not significantly different at $p < 0.05$

Heavy metal levels in *Zea mays* fruit samples

Zinc concentrations in maize fruit samples from different locations ranged from 4.80 to 52.08. The highest (52.08mg/kg) Zinc concentrations in maize fruit was in E1. The least (4.80) Zn concentration is in FC at $P \leq 0.05$ (Table 19). Likewise, Chromium concentrations in maize fruit ranged from 1.30 to 5.91. The highest (5.91) Cr concentration in maize fruit was found in W1. While the lowest (1.30) concentration was in FC at $P \leq 0.05$. Also, Lead concentrations in maize fruit ranged from 0.07 to 2.95. Maize fruit with the highest (2.95) Pb concentrations occurred in E1. The least concentration (0.07) of Pb in maize fruit was recorded in FC at $P \leq 0.05$. Meanwhile, The highest (1.00) Cd concentrations in maize fruit occurred in W2. This concentration is significantly the same as Cd concentrations at all the other locations at $P \leq 0.05$. The highest (1.05mg/kg) Cu concentrations in maize fruit occurred in N1. The least concentration (0.00) of Cu in maize fruit was recorded in W3 its concentration is not significantly greater than Cu concentrations in FC and W3 at $P \leq 0.05$.

Table 19: Concentration of some selected heavy metals (mg/kg) in *Zea mays* (fruit) samples collected at different locations

Location	Zn	Cr	Pb	Cd	Cu
N1	51.41±0.71 ^d	1.23±0.11 ^g	1.50±0.08 ^d	0.00±0.00 ^a	1.05±0.07 ^a
N2	50.93±0.035 ^c	4.61±0.01 ^d	1.30±0.28 ^e	0.00±0.00 ^a	0.50±0.00 ^c
N3	51.67±0.03 ^d	4.91±0.01 ^c	1.60±0.00 ^d	0.00±0.00 ^a	0.50±0.00 ^c
W1	50.53±0.03 ^b	5.91±0.01 ^a	2.41±0.01 ^b	0.00±0.00 ^a	0.50±0.00 ^c
W2	51.83±0.04 ^d	4.15±0.07 ^e	1.01±0.01 ^f	1.00±0.00 ^a	1.00±0.00 ^b
W3	50.03±0.04 ^d	1.25±0.07 ^g	1.08±0.04 ^f	0.00±0.00 ^a	0.00±0.00 ^d
E1	52.08±0.04 ^a	5.23±.03 ^b	2.95±0.07 ^a	0.00±0.00 ^a	0.50±0.00 ^c
E2	10.25±0.07 ^e	2.20±0.07 ^f	1.73±0.04 ^c	0.00±0.00 ^a	0.50±0.00 ^c
E3	5.25±0.36 ^f	2.11±0.01 ^f	1.43±0.03 ^d	0.00±0.00 ^a	0.00±0.00 ^d
FC	4.80±2.55 ^f	1.30±0.07 ^g	0.07±0.02 ^g	0.00±0.00 ^a	0.00±0.00 ^d

Values with the same superscript along the column are not significantly different at $p < 0.05$

4.10 Heavy metal levels in *Abelmoschus esculentus* samples

Heavy metal levels in *Abelmoschus esculentus* root samples

Table 20 Shows Zn concentrations in okra root samples from different locations which ranged from 6.4 to 69.93. The highest (69.93) Zinc concentrations in okra root was in E2. This concentration is significantly the same as Zn concentrations in E1. The least (6.4) Zn concentration is in RC at $P \leq 0.05$. Likewise, chromium concentrations in okra root ranged from 1.40 to 3.75. The highest (3.75) Cr concentration in okra root was found in W1. This concentration is significantly the same as Cr concentrations in W2. While the lowest (1.40) concentration was in RC This concentration is significantly the same as Cr concentrations in E2 at $P \leq 0.05$. Also, Lead concentrations in Okra root ranged from 0.08 to 3.03. Okra root with the highest (3.03) Pb concentrations occurred in E1. The least concentration (0.08) of Pb in Okra fruit was recorded in RC at $P \leq 0.05$. Similarly, the highest (0.50) Cd concentrations in maize fruit occurred in W1. This concentration is significantly the same as Cd concentrations at all the other locations at $P \leq 0.05$. The highest (1.05). Cu concentrations in Okra root occurred in W1. The least concentration (0.25) of Cu in Okra root was recorded in RC its concentration is not significantly greater than Cu concentrations in E3, E2, E1 and W3 at $P \leq 0.05$.

Heavy metal levels in *Abelmoschus esculentus* leaf samples

Table 21 Shows Zn concentrations in okra leaf samples from different locations which ranged from 5.4 to 91.34. The highest (91.34) Zinc concentrations in okra leaf was in N1. The least (5.4) Zn concentration is in LC at $P \leq 0.05$. However, Chromium concentrations in okra leaf ranged from 1.38 to 5.30. The highest (5.30) Cr concentration in okra leaf was found in N2. Whereas the lowest (1.38) concentration was in LC at $P \leq 0.05$. Also, Lead concentrations in Okra leaf ranged from 0.8 to 2.93. Okra leaf with the highest (2.93) Pb concentrations occurred in E1. The least concentration (0.80) of Pb in Okra leaf was recorded in LC at

$P \leq 0.05$. However, the highest (0.5) Cd concentrations in Okra leaf occurred in W2. This concentration is significantly the same as Cd concentrations at all the other locations at $P \leq 0.05$. While, the highest (0.50mg/kg) Cu concentrations in Okra leaf occurred in W1. The least concentration (0.00) of Cu in Okra leaf was recorded in LC its concentration is not significantly greater than Cu concentrations in E3, E2, E1 and W3 at $P \leq 0.05$.

Table 20: Concentration of some selected heavy metals (mg/kg) in *Abelmoschus esculentus* (root) samples collected at different locations

Location	Zn	Cr	Pb	Cd	Cu
N1	53.15±0.06 ^c	3.23±0.04 ^{bc}	2.03±0.04 ^c	0.00±0.00 ^a	1.00±0.00 ^b
N2	62.05±1.42 ^b	3.13±0.04 ^{bcd}	1.83±0.04 ^d	0.50±0.00 ^a	1.00±0.00 ^b
N3	51.55±0.71 ^c	2.80±0.14 ^d	1.65±0.07 ^e	0.00±0.00 ^a	0.50±0.00 ^c
W1	61.31±0.71 ^b	3.75±0.07 ^a	2.55±0.07 ^b	0.50±0.00 ^a	1.50±0.00 ^a
W2	51.71±0.71 ^c	3.45±0.07 ^{ab}	1.03±0.04 ^f	0.00±0.00 ^a	1.50±0.00 ^a
W3	53.45±0.07 ^c	2.25±0.07 ^e	1.10±0.07 ^f	0.00±0.00 ^a	0.50±0.00 ^c
E1	62.55±0.07 ^a	2.90±0.07 ^{cd}	3.03±0.04 ^a	0.00±0.00 ^a	0.50±0.00 ^c
E2	69.93±0.04 ^a	1.35±0.07 ^f	1.75±0.07 ^e	0.00±0.00 ^a	0.50±0.00 ^c
E3	34.14±0.72 ^d	1.15±0.07 ^f	1.69±0.01 ^e	0.00±0.00 ^a	0.50±0.00 ^c
RC	6.40±1.70 ^e	1.40±0.42 ^f	0.08±0.04 ^g	0.00±0.00 ^a	0.25±0.35 ^c

Values with the same superscript along the column are not significantly different at $p < 0.05$

Table 21: Concentration of some selected heavy metals (mg/kg) in *Abelmoschus esculentus* (leaf) samples collected at different locations.

Location	Zn	Cr	Pb	Cd	Cu
N1	91.34±0.72 ^a	2.84±0.05 ^e	2.12±0.17 ^c	0.00±0.00 ^a	0.50±0.00 ^a
N2	57.20±0.070 ^d	5.30±0.00 ^a	1.62±0.27 ^d	0.50±0.00 ^a	0.50±0.00 ^a
N3	9.82±0.02 ^h	2.85±0.00 ^e	1.55±0.00 ^d	0.00±0.00 ^a	0.00±0.00 ^a
W1	61.25±0.07 ^b	4.90±0.00 ^b	2.50±0.07 ^b	0.00±0.00 ^a	0.50±0.00 ^a
W2	51.35±0.71 ^d	4.42±0.02 ^c	1.08±0.04 ^e	0.50±0.00 ^a	0.50±0.00 ^a
W3	34.65±0.07 ^e	3.35±0.00 ^d	1.06±0.08 ^e	0.00±0.00 ^a	0.00±0.00 ^a
E1	16.93±0.04 ^f	2.65±0.00 ^e	2.93±0.04 ^a	0.00±0.00 ^a	0.50±0.00 ^a
E2	58.15±0.71 ^b	2.16±0.05 ^f	1.70±0.07 ^d	0.00±0.00 ^a	0.00±0.00 ^a
E3	6.38±0.03 ^h	2.08±0.35 ^f	1.50±0.07 ^d	0.00±0.00 ^a	0.00±0.00 ^a
LC	5.40±0.50 ⁱ	1.38±0.46 ^g	0.80±0.28 ^f	0.00±0.00 ^a	0.00±0.00 ^a

Values with the same superscript along the column are not significantly different at $p < 0.05$

Heavy metal levels in *Abelmoschus esculentus* fruit samples

Table 22. Shows Zn concentrations in okra fruit samples from different locations it ranged from 6.00 to 90.15. The highest (90.15) Zinc concentrations in okra fruit was in N1. The least (6.0) Zn concentration is in FC at $P \leq 0.05$. Also, Chromium concentrations in okra fruit ranged from 1.01 to 2.53. The highest (2.53) Cr concentration in okra fruit was found in W1. Whereas the lowest (1.01) concentration was in FC at $P \leq 0.05$. However, Lead concentrations in Okra fruit ranged from 0.14 to 2.73. Okra fruit with the highest (2.73) Pb concentrations occurred in E1. The least concentration (0.13) of Pb in Okra leaf was recorded in FC at $P \leq 0.05$. Also, Cadmium was not present in Okra fruit at all sampled locations at $P \leq 0.05$. Copper concentrations in Okra fruit was highest (5.0mg/kg) occurred in W1.

Table 22: Concentration of some selected heavy metals (mg/kg) in *Abelmoschus esculentus* (Fruit) samples collected at different locations.

Location	Zn	Cr	Pb	Cd	Cu
N1	90.15±0.07 ^a	1.72±0.02 ^c	2.03±0.04 ^c	0.00±0.00 ^a	0.00±0.00 ^a
N2	56.28±0.39 ^d	1.35±0.07 ^e	1.54±0.02 ^d	0.00±0.00 ^a	0.50±0.00 ^a
N3	9.10±0.14 ^h	1.08±0.03 ^f	1.53±0.04 ^d	0.00±0.00 ^a	0.00±0.00 ^a
W1	60.83±0.04 ^b	2.53±0.04 ^a	2.52±0.03 ^b	0.00±0.00 ^a	5.00±0.00 ^a
W2	50.22±0.02 ^e	2.13±0.04 ^b	1.07±0.03 ^e	0.50±0.00 ^a	0.00±0.00 ^a
W3	18.05±0.07 ^f	2.09±0.02 ^b	0.92±0.02 ^f	0.00±0.00 ^a	0.00±0.00 ^a
E1	15.61±0.01 ^g	2.05±0.07 ^b	2.73±0.04 ^a	0.00±0.00 ^a	0.50±0.00 ^a
E2	57.52±0.03 ^c	1.55±0.07 ^d	1.63±0.04 ^d	0.00±0.00 ^a	0.00±0.00 ^a
E3	6.63±0.03 ⁱ	1.10±0.07 ^f	1.53±0.04 ^d	0.00±0.00 ^a	0.00±0.00 ^a
FC	6.00±1.41 ⁱ	1.01±0.01 ^f	0.14±0.12 ^g	0.00±0.00 ^a	0.00±0.00 ^a

Values with the same superscript along the column are not significantly different at $p < 0.05$

4.11 Heavy metal levels in *Mangifera indica* samples

Heavy metal levels in *Mangifera indica* root samples

Table 23 the highest (62.92) Zinc concentrations in Mango root was in W1. The least (22.30) Zn concentration is in RC at $P \leq 0.05$. However, the highest (3.14) Cr concentrations in Mango root was in W1. This is not significantly different from Cr concentrations in N1. The least (0.77) Cr concentration is in RC at $P \leq 0.05$. While the highest (1.73) Pb concentrations in Mango root was in E1. The least (0.23) Pb concentration is in RC at $P \leq 0.05$. However, the highest (0.17) Cd concentrations in Mango root was in N2. . The least (0.03) Cd concentration is in RC. This is not significantly different from Cr concentrations in Rc, E2, E1, W3, W2 at $P \leq 0.05$. The highest (10.82) Cu concentrations in Mango root was in N1. The least (1.55) Cu concentration is in RC at $P \leq 0.05$.

Heavy metal levels in *Mangifera indica* leaf samples

Table 24. The highest (52.72) Zinc concentrations in Mango leaf was in N1. This was not significantly different from Zn concentrations in N2. The least (12.45) Zn concentration is in LC at $P \leq 0.05$. However, the highest (2.44) Cr concentrations in Mango Leaf was in W1. This was not significantly different from Cr concentrations in N1, W2. The least (0.76) Cr concentration is in RC at $P \leq 0.05$. Likewise, the highest (1.53) Pb concentrations in Mango leaf was in N2. The least (0.05) Pb concentration is in LC at $P \leq 0.05$. Also, the highest (0.16) Cd concentrations in Mango Leaf was in W1. The least (0.00) Cd concentration is in N3 at $P \leq 0.05$. The highest (12.82) Cu concentrations in Mango Leaf was in N1. The least (1.33) Cu concentration is in LC at $P \leq 0.05$.

Heavy metal levels in *Mangifera indica* fruit samples

Table 25. The highest (59.25) Zinc concentrations in Mango fruit was in N3. The least (19.88) Zn concentration is in FC at $P \leq 0.05$. Also, the highest (2.35) Cr concentrations in

Mango Fruit was in W1. The least (0.35) Cr concentration is in FC at $P \leq 0.05$. Moreso, The highest (1.63) Pb concentrations in Mango fruit was in W2. The least (0.10) Pb concentration is in FC it was not significantly different from Pb concentrations in E3, E2 at $P \leq 0.05$. However, the highest (0.05) Cd concentrations in Mango fruit was in W1. It was not significantly different from Cd concentrations in N2, W2, E1, E2, FC The least (0.00) Cd concentration is in E3. It was not significantly different from Cd concentrations in FC, W3, N1 at $P \leq 0.05$. The highest (11.08) Cu concentrations in Mango fruit was in N1. The least (1.73) Cu concentration is in W3 at $P \leq 0.05$.

Table 23: Concentration of some selected heavy metals (mg/kg) in mango (root) samples collected at different locations

Location	Zn	Cr	Pb	Cd	Cu
N1	56.83±0.04 ^c	3.03±0.03 ^a	1.32±0.02 ^c	0.04±0.01 ^b	10.83±0.04 ^a
N2	53.43±0.03 ^d	1.03±0.04 ^e	1.53±0.04 ^b	0.17±0.02 ^a	9.42±0.02 ^b
N3	41.93±0.04 ^f	1.93±0.04 ^c	0.52±0.03 ^g	0.07±0.02 ^b	9.14±0.02 ^b
W1	62.93±0.04 ^a	3.14±0.01 ^a	1.24±0.02 ^d	0.06±0.01 ^b	7.16±0.01 ^c
W2	60.53±0.04 ^b	2.42±0.03 ^b	0.87±0.02 ^e	0.06±0.01 ^b	3.56±0.01 ^d
W3	52.53±0.03 ^d	1.44±0.01 ^d	0.71±0.01 ^f	0.06±0.01 ^b	3.08±0.04 ^e
E1	47.03±0.04 ^e	1.12±0.03 ^e	1.73±0.04 ^a	0.06±0.01 ^b	3.42±0.03 ^{de}
E2	37.63±0.03 ^g	2.03±0.04 ^c	0.83±0.03 ^e	0.06±0.01 ^b	3.16±0.01 ^{de}
E3	34.53±0.04 ^h	1.05±0.01 ^e	0.34±0.06 ^h	0.06±0.01 ^b	2.41±0.01 ^f
RC	22.30±1.77 ⁱ	0.78±0.25 ^f	0.23±0.03 ⁱ	0.03±0.03 ^b	1.55±0.57 ^g

Values with the same superscript along the column are not significantly different at $p < 0.05$

Table 24: Concentration of some selected heavy metals (mg/kg) in mango (leaf) samples collected at different locations

Location	Zn	Cr	Pb	Cd	Cu
N1	52.72±0.02 ^a	2.34±0.02 ^{ab}	1.32±0.03 ^b	0.00±0.00 ^d	12.82±0.03 ^a
N2	51.06±0.01 ^{ab}	1.1200±0.03 ^g	1.53±0.04 ^a	0.11±0.01 ^b	9.42±0.03 ^b
N3	43.62±0.02 ^{cd}	2.05±0.03 ^{cd}	0.53±0.04 ^f	0.00±0.00 ^d	9.17±0.02 ^c
W1	40.02±0.03 ^d	2.44±0.02 ^a	1.27±0.03 ^b	0.16±0.01 ^a	8.92±0.02 ^d
W2	47.33±0.03 ^c	2.23±0.02 ^{abc}	1.08±0.04 ^c	0.06±0.01 ^c	3.84±0.03 ^e
W3	42.93±0.04 ^d	1.75±0.02 ^e	0.31±0.01 ^g	0.06±0.00 ^c	2.37±0.04 ^h
E1	30.34±0.02 ^e	2.15±0.01 ^{bcd}	0.73±0.04 ^e	0.06±0.01 ^c	3.95±0.02 ^e
E2	29.06±0.01 ^e	1.48±0.01 ^f	0.87±0.02 ^d	0.06±0.01 ^c	2.5600±0.01 ^g
E3	22.72±0.03 ^f	1.92±0.01 ^{de}	0.21±0.01 ^h	0.06±0.01 ^c	2.82±0.03 ^f
RC	12.45±7.21 ^g	0.76±0.37 ^h	0.05±0.00 ⁱ	0.04±0.02 ^c	1.33±0.18 ⁱ

Values with the same superscript along the column are not significantly different at $p < 0.05$

Table 25: Concentration of some selected heavy metals (mg/kg) in mango (fruit) samples collected at different locations.

Location	Zn	Cr	Pb	Cd	Cu
N1	52.54±0.02 ^b	2.12±0.02 ^b	1.12±0.02 ^b	0.05±0.00 ^b	11.08±0.04 ^a
N2	47.66±0.01 ^c	1.54±0.05 ^e	0.66±0.01 ^d	0.05±0.00 ^a	5.80±0.07 ^c
N3	59.25±0.07 ^a	2.12±0.03 ^c	0.52±0.03 ^e	0.00±0.00 ^b	5.23±0.04 ^d
W1	34.60±0.14 ^f	2.35±0.03 ^a	1.03±0.03 ^c	0.05±0.00 ^a	9.13±0.03 ^b
W2	49.23±0.04 ^c	2.34±0.04 ^a	1.63±0.04 ^a	0.05±0.00 ^a	3.21±0.01 ^g
W3	37.63±0.03 ^e	1.73±0.04 ^d	0.45±0.01 ^f	0.00±0.00 ^b	2.21±0.02 ^h
E1	52.88±0.02 ^b	1.53±0.04 ^e	0.57±0.03 ^e	0.05±0.00 ^a	5.06±0.01 ^e
E2	41.08±0.02 ^d	1.73±0.04 ^d	0.10±0.01 ^g	0.05±0.00 ^a	4.66±0.01 ^f
E3	37.06±0.02 ^e	1.92±0.03 ^c	0.09±0.01 ^g	0.00±0.00 ^b	1.53±0.04 ^j
FC	19.88±2.91 ^g	0.35±0.14 ^f	0.10±0.07 ^g	0.03±0.04 ^{ab}	1.73±0.18 ⁱ

Values with the same superscript along the column are not significantly different at $p < 0.05$

4.12 Heavy metal levels in *Carica papaya* samples

Heavy metal levels in *Carica papaya* root samples

Table 26. The highest (62.00) Zinc concentrations in Pawpaw root was in W2. This was not significantly different from Zn concentrations in N2 and W1. The least (24.49) Zn concentration is in RC at $P \leq 0.05$. Also, the highest (3.76) Cr concentrations in Pawpaw root was in W1 which was not significantly different from N1 at $P \leq 0.05$. The least (0.95) Cr concentration is in RC. Likewise, the highest (1.92) Pb concentrations in Pawpaw root was in W1. The least (0.25) Pb concentration is in RC at $P \leq 0.05$. Yet, the highest (0.12) Cd concentrations in Pawpaw root was in N2, it was not significantly different from Cd concentrations in E1. The least (0.10) Cd concentration is in RC. It was not significantly different from Cd concentrations in E2, W2, W1, N3, W3, N1 at $P \leq 0.05$. While, the highest (9.8) Cu concentrations in Pawpaw root was in N, this is not significantly different from Cu concentrations in N3 and W1. The least (1.00) Cu concentration is in RC at which is not significantly different from E3 and W3 at $P \leq 0.05$.

Table 26: Concentration of some selected heavy metals (mg/kg) in pawpaw root samples collected at different locations

Location	Zn	Cr	Pb	Cd	Cu
N1	46.82±0.02 ^b	3.76±0.09 ^a	1.83±0.04 ^b	0.06±0.01 ^b	9.82±0.02 ^a
N2	52.46±0.04 ^a	1.49±0.01 ^d	1.62±0.03 ^c	0.13±0.04 ^a	5.72±0.02 ^b
N3	40.64±0.01 ^b	1.99±0.01 ^d	0.85±0.01 ^e	0.06±0.01 ^b	8.67±0.03 ^a
W1	61.63±0.04 ^a	3.76±0.03 ^a	1.92±0.03 ^a	0.03±0.00 ^b	7.07±0.03 ^a
W2	62.00±0.04 ^a	2.83±0.02 ^b	0.72±0.01 ^f	0.05±0.00 ^b	3.00±0.03 ^b
W3	50.53±0.04 ^a	1.47±0.02 ^d	0.93±0.01 ^d	0.05±0.00 ^b	1.20±0.02 ^c
E1	42.08±0.04 ^b	1.57±0.02 ^d	1.82±0.01 ^b	0.11±0.01 ^a	3.74±0.01 ^b
E2	40.63±0.03 ^b	2.31±0.01 ^c	0.85±0.01 ^e	0.05±0.00 ^b	3.97±0.04 ^b
E3	32.82±0.03 ^c	1.72±0.03 ^d	0.63±0.01 ^g	0.06±0.01 ^b	2.76±0.04 ^c
RC	24.50±1.90 ^h	0.95±0.01 ^h	0.26±0.02 ^h	0.01±0.00 ^b	1.00±0.01 ^g

Values with the same superscript along the column are not significantly different at $p < 0.05$

Heavy metal levels in *Carica papaya* leaf samples

Table 27. The highest (54.70) Zinc concentrations in Pawpaw leaf was in N1. The least (13.90) Zn concentration is in LC at $P \leq 0.05$. Also, the highest (2.51) Cr concentrations in Pawpaw leaf was in N1. The least (0.88) Cr concentration is in LC at $P \leq 0.05$. Likewise, the highest (1.72) Pb concentrations in Pawpaw leaf was in N1. The least (0.06) Pb concentration is in LC at $P \leq 0.05$. It was not significantly different from Pb concentrations in W3. On the other hand, highest (0.19) Cd concentrations in Pawpaw leaf was in W1. The least (0.02) Cd concentration is in LC at $P \leq 0.05$. The highest (9.15) Cu concentrations in Pawpaw leaf was in N3, its not significantly different from N1, and W1 at $P \leq 0.05$. The least (1.31) Cu concentration is in LC.

Heavy metal levels in *Carica papaya* fruit samples

Table 28, the highest (50.07) Zinc concentrations in Pawpaw fruit was in N1 its not significantly different from N2 and N3 at $P \leq 0.05$. The least (11.93) Zn concentration was in FC. Also, the highest (2.42) Cr concentrations in Pawpaw fruit was in N1 and this is not significantly different from W1 and W2 at $P \leq 0.05$. The least (0.42) Cr concentration was in FC. However, the highest (1.51) Pb concentrations in Pawpaw fruit was in N1. The least (0.03) Pb concentration is in FC. Meanwhile, the highest (0.05) Cd concentrations in Pawpaw fruit was in W1. It was not significantly different from Cd concentrations in N1, N2, W2, E1,E2,FC. The least (0.00) Cd concentration is in E3 It was not significantly different from Cd concentrations in W3, N3 at $P \leq 0.05$. The highest (7.10) Cu concentrations in Pawpaw fruit was in W1 its not significantly.

Table 27: Concentration of some selected heavy metals (mg/kg) in pawpaw leaf samples collected at different locations

Location	Zn	Cr	Pb	Cd	Cu
N1	54.70±0.07 ^a	2.51±0.01 ^{ab}	1.72±0.03 ^a	0.00±0.00 ^e	8.80±0.14 ^a
N2	52.08±0.00 ^b	1.92±0.02 ^c	1.52±0.02 ^b	0.11±0.01 ^b	4.35±0.07 ^b
N3	45.35±0.06 ^c	2.28±0.01 ^b	1.01±0.01 ^e	0.00±0.00 ^e	9.15±0.03 ^a
W1	42.54±0.05 ^d	2.38±0.02 ^b	1.31±0.01 ^c	0.19±0.01 ^a	8.23±0.02 ^a
W2	41.92±0.03 ^d	2.81±0.01 ^b	1.14±0.02 ^d	0.06±0.00 ^c	3.37±0.03 ^b
W3	37.47±0.03 ^e	1.02±0.02 ^d	0.71±0.01 ⁱ	0.06±0.01 ^c	2.10±0.01 ^{bc}
E1	30.36±0.02 ^f	2.57±0.02 ^{ab}	1.04±0.01 ^e	0.06±0.00 ^c	4.97±0.05 ^b
E2	27.22±0.02 ^g	1.27±0.03 ^d	0.89±0.01 ^f	0.07±0.02 ^c	2.59±0.01 ^{bc}
E3	28.71±0.02 ^g	1.06±0.01 ^d	0.26±0.01 ^h	0.06±0.01 ^c	2.33±0.01 ^{bc}
LC	13.91±2.24 ^h	0.89±0.43 ^e	0.07±0.02 ⁱ	0.03±0.01 ^d	1.31±0.33 ^d

Values with the same superscript along the column are not significantly different at $p < 0.05$

Table 28: Concentration of some selected heavy metals (mg/kg) in pawpaw fruit samples collected at different locations

Location	Zn	Cr	Pb	Cd	Cu
N1	50.07±0.02 ^a	2.42±0.03 ^a	1.51±0.01 ^a	0.05±0.01 ^a	6.05±0.00 ^a
N2	49.67±0.03 ^a	1.83±0.04 ^b	0.84±0.01 ^d	0.04±0.01 ^a	3.91±0.00 ^b
N3	45.33±0.04 ^a	1.13±0.04 ^b	0.75±0.01 ^e	0.00±0.00 ^b	5.21±0.00 ^a
W1	36.69±0.03 ^b	2.11±0.01 ^a	1.08±0.01 ^b	0.05±0.00 ^a	7.10±0.00 ^a
W2	29.75±0.07 ^b	2.11±0.01 ^a	1.02±0.02 ^c	0.05±0.00 ^a	3.17±0.00 ^{bc}
W3	27.67±0.02 ^b	1.00±0.04 ^c	0.23±0.04 ^g	0.00±0.00 ^b	2.05±0.00 ^c
E1	20.44±0.03 ^c	1.92±0.02 ^b	0.51±0.00 ^f	0.05±0.00 ^a	4.05±0.00 ^b
E2	16.08±0.02 ^c	1.22±0.02 ^b	0.17±0.03 ^h	0.05±0.00 ^a	2.00±0.00 ^d
E3	33.06±0.03 ^b	1.01±0.01 ^c	0.12±0.02 ⁱ	0.00±0.00 ^b	1.95±0.00 ^{de}
FC	11.93±0.42 ^d	0.42±0.08 ^d	0.03±0.04 ^{hi}	0.03±0.04 ^{ab}	1.30±0.41 ^e

Values with the same superscript along the column are not significantly different at $p < 0.05$ different from N1 and N3. The least (1.30) Cu concentration is in FC its not significantly different from E3 at $P \leq 0.05$.

4.13 Anatomical studies on the leaves of *Abelmoschus esculentus*, *Zea mays*, *Mangifera indica* and *Carica papaya*.

The results of epidermal studies on the leaves of the studied plants are summarised in tables 29-32 and plate 1-13. This includes; stomata type, stomata frequency, trichome type, trichome density, stomatal density and stomatal size.

Stomatal complex types

Abelmoschus esculentus stomata were composed of two bean shaped guard cells and a stomatal pore as shown on plate 1. Plate 2, shows Anisocytic stomata, Branchyparacytic stomata, Paracytic stomata and Tetracytic stomata types in *Abelmoschus esculentus* leaf samples collected from the unpolluted site whereas *Abelmoschus esculentus* sampled from the polluted site only had Anisocytic and Paracytic stomata types. *Zea mays* samples from the polluted and unpolluted sites had paracytic stomata type (plate 7&8, table 1) *Carica papaya* samples from the unpolluted site had Anisocytic, tetracytic and paracytic stomata types (plate 12, table 1) but samples from the polluted site only had anisocytic and paracytic stomata types. As shown in plate 13 numerous Anomocytic and paracytic stomata types were in *M. indica* samples from the unpolluted site while samples from the polluted site had only paracytic stomata type.

Trichome density

Many long unicellular trichomes were observed on the epidermis of *Abelmoschus esculentus* leaf samples obtained from the surroundings of OCF (polluted site) as shown on (plate 6). Trichome density in *Abelmoschus esculentus* samples from the polluted sites was higher (6) than trichome density in *Abelmoschus esculentus* samples from the control site. Trichome type in *Zea mays* was also unicellular in all the samples. Just like in *Abelmoschus esculentus* trichome density in *Zea mays* was higher in the samples from the polluted site when compared to samples from the control site (plate 9&10). Stellate and

unicellular trichome types were seen on *Carica papaya* leaves samples from the unpolluted site while only unicellular trichomes occurred in the polluted site samples (Table 29). Trichome density was generally higher in samples collected from the vicinity of OCF (polluted site) than samples from the unpolluted site.

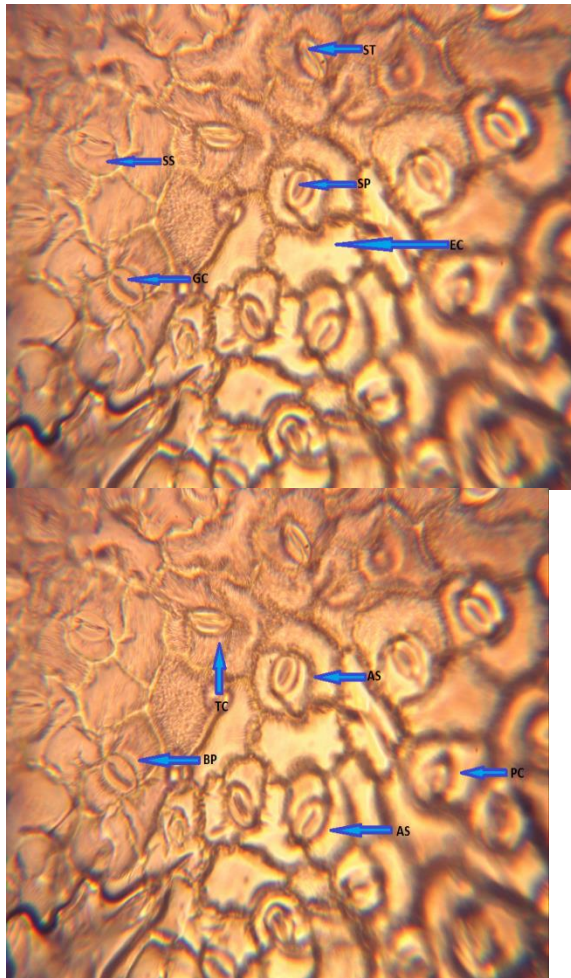


Plate 1: Abaxial epidermis of *A. esculentus* leaf showing ST, SP, EC, GC.

Plate 2: Abaxial epidermis of *A. esculentus* Leaf showing AM, AS, BP, PC,

TC

ST- stomata, SP- stomatal pore, EC- Epidermal cell, GC- Guard cell. AM – Anomocytic stomata, AS - Anisocytic stomata, BP -Branchyparacytic stomata, PC -Paracytic stomata and TC - Tetracytic stomata.

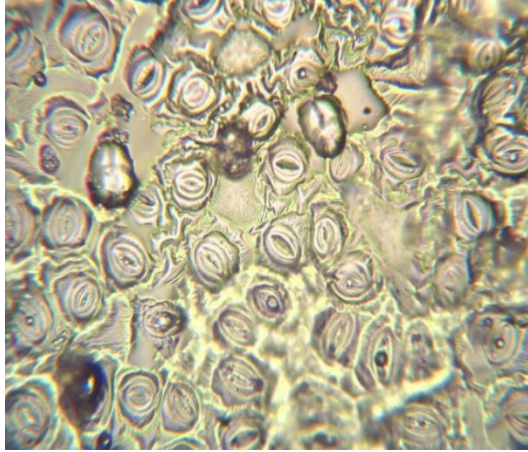


Plate3: More number of stomata on abaxial
leaf surface of *A. esculentus* from the
polluted site (400x).

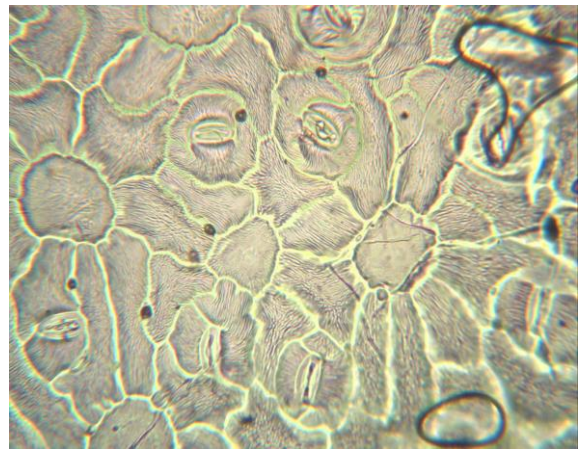


Plate 4: fewer number of stomata on
leaf surface of *A. esculentus* from
the unpolluted site (400x).

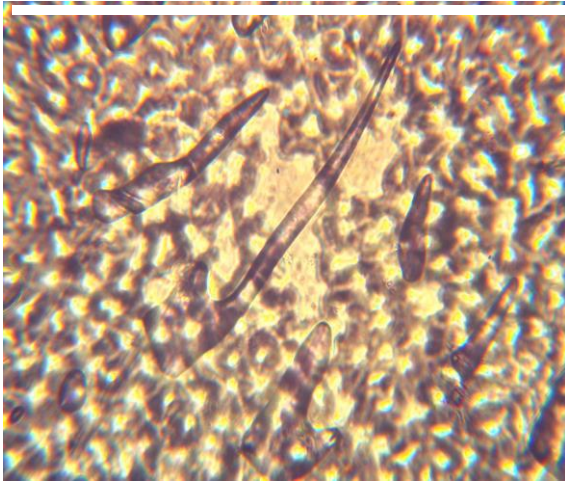


Plate 5: more number of trichomes on abaxial
leaf surface of *A esculentus*
unpolluted site (400x).

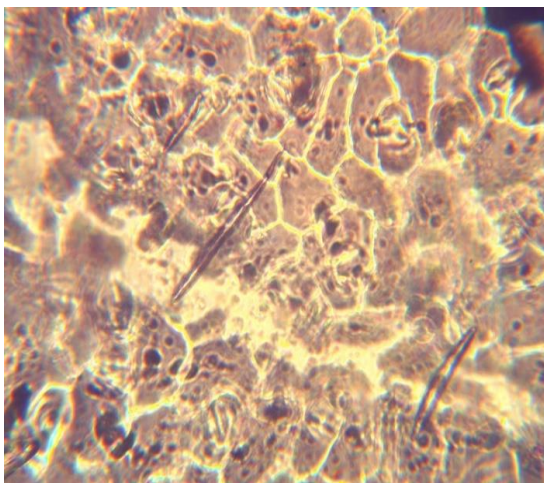


Plate 6 : fewer number of trichomes on
of *A esculentus* from the
(400x).

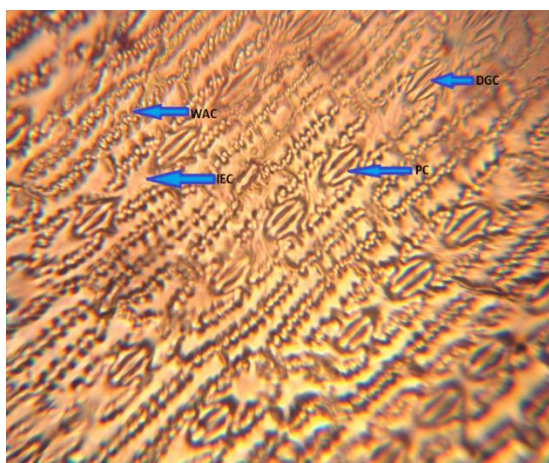


Plate 7: Many stomata on abaxial leaf surface of *Zea mays* from the polluted site (400x) .

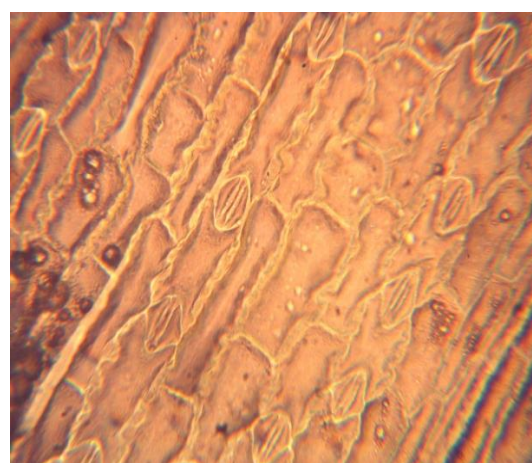


Plate 8: Fewer stomata on abaxial leaf of *Zea mays* from the (400x).

(WAC, IEC, PC, DGC) WAC; Wavy anticlinal cell wall, IEC- Irregular shaped epidermal cell, PC-Paracytic stomata, DGC-dumb shaped guard cell.



Plate 9: Many trichomes on abaxial leaf surface of *Zea mays* from the polluted site (400x).

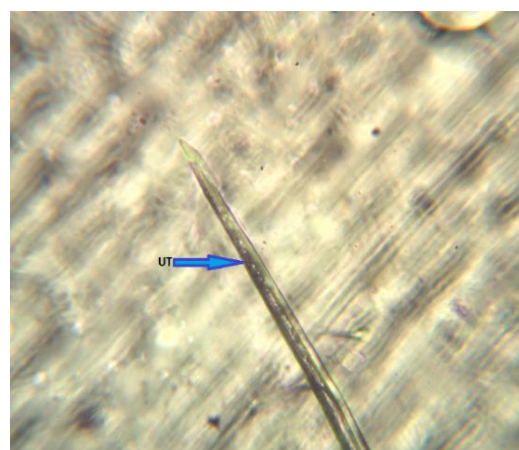


Plate 10: Single trichome on abaxial leaf of *Zea mays* from the unpolluted site (400x).

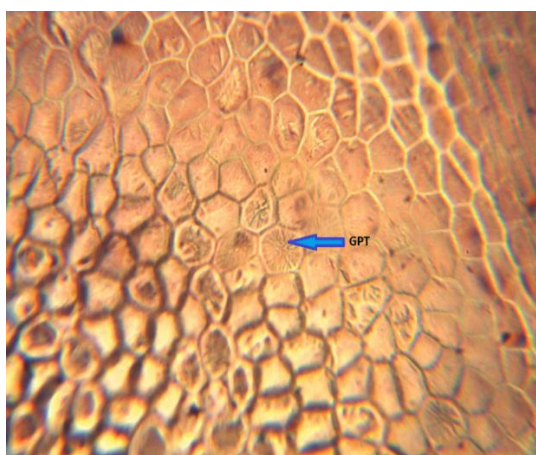


Plate 11: Adaxial epidermis of *C. papaya* leaf Showing Glandular peltate trichome. stomata

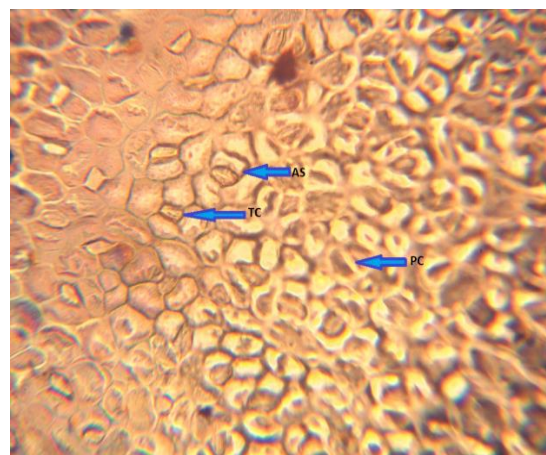


Plate 12: Abaxial epidermis of *C. Papaya* leaf Showing AS, TC,PC types



Plate 13: Abaxial epidermis of *Mangifera indica* Leaf showing numerous, small anomocytic stomata

Table 29: Stomata type, Stomata frequency, Trichome type and Trichome density

Plant	Location	Stomata type	Stomatal frequency (%)	Trichome type	Trichome density(mm^{-2})
<i>A. esculentus</i>	Polluted	AS, PC	68%, 32%	Unicellular	6
	Control	AS,BP,	42%,12%,	Unicellular	3
		PC,TC	20%,16%		

<i>Z. mays</i>	Polluted	PC	100%	Unicellular	5
	Control	PC	100%	Unicellular	3
<i>M.indica</i>	Polluted	PC	100%	–	–
	Control	AM, PC	46%, 54%	–	–
<i>C.papaya</i>	Polluted	AS, PC	44%, 56%	Unicellular	2
	Control	AS, PC ,TC	30%, 30%, 40%	Unicellular Starlate	1

AM – Anomocytic stomata, AS - Anisocytic stomata, BP -Branchiparacytic stomata,
PC -Paracytic stomata and TC -Tetracytic stomata.

Stomata density

There were variations in the stomata density of samples collected from the vicinity of the cement factory and samples of same plant species collected from the unpolluted site. In *Abelmoschus esculentus*, stomata density on the abaxial epidermis (polluted site) ranged from 24.43-42.17 and 19.63-35.94 on the adaxial epidermis. Whereas, stomata density on the abaxial epidermis (unpolluted site) ranged from 16.63-19.62 and 12.25-14.93 on the adaxial epidermis (Table 30). In *Zea mays*, stomata density on the abaxial epidermis (polluted site)

ranged from 21.47-28.50 and 16.37-24.56 on the adaxial epidermis. In the same vein, stomata density on the abaxial epidermis (unpolluted site) ranged from 15.48-16.62 and 12.43-15.48 on the adaxial epidermis (table 31). *Mangifera indica* had abaxial and adaxial stomata densities ranging from 28.51-37.78 and 23.70-31.54 for samples from the polluted sites while samples from unpolluted site had abaxial and adaxial stomata densities ranging from 21.62-25.38 and 17.59-21.63 respectively as shown on table 32. Whereas, *Carica papaya*, stomata density on the abaxial epidermis (polluted site) ranged from 17.49- 29.43. While, stomata density on the abaxial epidermis (unpolluted site) ranged from 11.54-14.28 (Table 33). Stomata density were found to be higher on the abaxial epidermis than the adaxial epidermis. Likewise, stomata density was higher in samples from the polluted sites than the unpolluted sites for the studied plant species.

Stomatal size

Metcalf and Chalk (1988) and Beerling and Woodward (1997) reported that larger stomata gave lower stomatal density, while, smaller stomata gave higher stomatal density. As shown on table 29, stomata size in *Abelmoschus esculentus* collected from the vicinity of OCF had stomata size ranging from 31.59µm to 37.64µm and 41.67µm to 44.35µm for samples from the unpolluted site (Table 30). In *Zea mays*, stomatal size ranged from 41.79µm to 47.09µm in samples from the polluted site and 54.81µm to 57.36µm in samples from the control (Table 31). Stomatal size in *Mangifera indica* ranged from 23.85µm to 27.96µm (in samples from the polluted site) and 32.83µm to 34.26µm (in samples from the unpolluted site) as shown on table 32. Likewise, *Carica papaya* leaf samples collected from the polluted site had stomatal size ranging from 22.67µm to 28.31µm. and 32.81µm to 35.33µm in the unpolluted site (table 33).

Table 30: Stomatal density and stomata size in *A. esculentus* leaves

Samples	Stomatal density (mm ⁻²)		Stomatal Size (μm)
	Abaxial	Adaxial	
1	28.43±2.25	21.43±1.93	32.53±3.54
2	24.45±2.06	21.65±2.43	37.64±3.43

3	39.87 $\pm$ 3.62	35.94 $\pm$ 2.54	34.28 $\pm$ 2.94
4	26.51 $\pm$ 2.64	22.05 $\pm$ 2.70	33.12 $\pm$ 3.54
5	42.17 $\pm$ 2.04	33.62 $\pm$ 3.54	35.37 $\pm$ 2.54
6	27.04 $\pm$ 2.50	24.73 $\pm$ 2.41	34.65 $\pm$ 2.48
7	26.93 $\pm$ 2.32	22.40 $\pm$ 2.34	31.59 $\pm$ 2.98
8	40.62 $\pm$ 3.64	31.51 $\pm$ 2.04	33.66 $\pm$ 3.76
9	29.41 $\pm$ 2.43	19.63 $\pm$ 2.47	36.39 $\pm$ 1.54
10	27.30 $\pm$ 2.12	21.08 $\pm$ 2.50	31.93 $\pm$ 2.65
11	24.43 $\pm$ 1.63	20.80 $\pm$ 1.56	34.56 $\pm$ 2.54
12	28.38 $\pm$ 2.30	23.65 $\pm$ 2.41	33.75 $\pm$ 1.97
C ₁	19.62 $\pm$ 1.83	14.93 $\pm$ 1.75	42.40 $\pm$ 3.65
C ₂	17.94 $\pm$ 1.43	12.25 $\pm$ 2.54	41.67 $\pm$ 3.54
C ₃	16.63 $\pm$ 2.01	13.05 $\pm$ 1.44	44.35 $\pm$ 2.65

Values given are means $\pm$ standard deviation Significant at p<0.05

Table 31: Stomatal density and stomata size of *Zea mays* leaves

Samples	Stomatal density (mm ⁻²)		Stomatal Size (μm)
	Abaxial	Adaxial	

1	21.47 $\pm$ 1.30	19.62 $\pm$ 1.04	43.65 $\pm$ 3.05
2	27.17 $\pm$ 2.04	23.37 $\pm$ 1.50	46.97 $\pm$ 2.84
3	23.40 $\pm$ 1.08	18.95 $\pm$ 1.07	42.73 $\pm$ 2.49
4	25.57 $\pm$ 0.43	19.05 $\pm$ 0.74	41.79 $\pm$ 2.70
5	25.17 $\pm$ 2.85	20.39 $\pm$ 2.59	43.56 $\pm$ 1.39
6	23.83 $\pm$ 2.30	22.86 $\pm$ 0.53	45.10 $\pm$ 3.96
7	25.73 $\pm$ 1.60	24.56 $\pm$ 1.96	44.82 $\pm$ 2.69
8	22.05 $\pm$ 0.43	16.37 $\pm$ 2.06	43.97 $\pm$ 2.40
9	24.62 $\pm$ 1.36	20.94 $\pm$ 1.60	42.85 $\pm$ 1.02
10	23.49 $\pm$ 1.70	22.40 $\pm$ 1.04	47.09 $\pm$ 2.48
11	22.83 $\pm$ 2.12	19.42 $\pm$ 0.82	44.65 $\pm$ 2.05
12	28.50 $\pm$ 1.44	22.69 $\pm$ 2.94	42.79 $\pm$ 2.40
C ₁	15.48 $\pm$ 1.56	12.43 $\pm$ 1.05	54.81 $\pm$ 3.79
C ₂	16.40 $\pm$ 0.52	13.60 $\pm$ 0.92	57.36 $\pm$ 2.46
C ₃	16.62 $\pm$ 0.97	15.48 $\pm$ 1.23	55.99 $\pm$ 3.17

Values given are means $\pm$ standard deviation Significant at $p < 0.05$

Table 32: Stomatal density and stomata size in *Mangifera indica* leaves

Samples	Stomatal density (mm ⁻²)		Stomatal Size (μm)
	Abaxial	Adaxial	

1	32.43±3.54	27.67±2.45	25.53±1.45
2	37.78±2.08	30.47±2.68	23.85±2.58
3	29.47±2.56	24.83±1.68	26.39±1.95
4	30.09±3.60	26.76±2.54	26.75±2.06
5	29.84±2.05	25.73±2.09	24.70±2.85
6	31.60±2.70	25.90±1.60	26.96±1.57
7	28.51±1.56	24.54±2.78	24.83±2.00
8	33.60±3.06	26.62±2.86	25.64±2.05
9	35.53±2.64	31.54±2.05	27.07±2.68
10	30.39±2.94	23.70±1.57	26.56±1.59
11	29.70±1.70	24.94±2.49	24.48±1.06
12	32.60±2.05	25.85±1.89	27.96±2.50
C ₁	21.62±2.50	19.98±2.36	34.05±2.73
C ₂	25.38±2.59	21.63±2.07	32.83±2.97
C ₃	23.64±1.94	17.59±2.84	34.26±3.57

Values given are means ± standard deviation

Significant at p<0.05

Table 33: Stomatal density and stomata size in *C arica papaya* leaves

Samples	Stomatal density	Stomatal
	(mm ⁻²)	Size (µm)

1	21.35 $\pm$ 1.45	24.82 $\pm$ 2.54
2	22.86 $\pm$ 1.85	25.36 $\pm$ 2.93
3	25.30 $\pm$ 2.59	22.71 $\pm$ 1.83
4	21.16 $\pm$ 2.43	23.90 $\pm$ 1.40
5	29.43 $\pm$ 1.05	26.31 $\pm$ 2.05
6	19.70 $\pm$ 1.94	23.75 $\pm$ 1.04
7	20.50 $\pm$ 1.45	25.94 $\pm$ 2.40
8	21.95 $\pm$ 0.93	22.67 $\pm$ 1.95
9	17.49 $\pm$ 0.37	28.31 $\pm$ 1.79
10	18.05 $\pm$ 1.94	25.80 $\pm$ 1.04
11	20.54 $\pm$ 1.64	26.35 $\pm$ 2.95
12	19.35 $\pm$ 0.63	24.90 $\pm$ 1.57
C ₁	11.54 $\pm$ 0.32	32.81 $\pm$ 2.94
C ₂	14.28 $\pm$ 1.43	35.33 $\pm$ 1.94
C ₃	13.45 $\pm$ 0.63	33.85 $\pm$ 2.45

Values given are means $\pm$ standard deviation Significant at $p < 0.05$

4.14 Bioaccumulation factor of heavy metals from soil to plant root.

The values of bioaccumulation factor of heavy metals from soil to plant root is used to assess the mobility of metals from the soil on which the plant grows into the plant root. It was determined as;

$$\text{Bioaccumulation factor (BF)} = \frac{\text{Concentration of metal in plant}}{\text{Concentration of metal in soil}}$$

Abelmoschus esculentus recorded peak BF of Zn (2.42) in the East, 1.93 Zn transfer in the North and 0.69 in the control locations. Likewise transfer of Cu from soil to its root exceeded one at the 3 axes of the factory but less than unity at the control site. Cr had least transfer of 0.01 at the control and highest 0.04 in the North. Pb transfer was highest in the East with a value of 0.31 and lowest in the North (0.08). Cd transfer was highest in the west (0.25) and lowest in the east (0.01). (Table 34).

The BF in *Zea mays* ranged from 0.08 – 2.40 across the different locations. Highest 2.40 transfer was recorded in the East and 0.08 (lowest) in the North and the control values ranged from 1.01 to 0.67. the highest 2.40 transfer rate was of Zn in the east axis. While the North and west both recorded transfers value for Zn as 1.29. Cr had its peak 1.05 transfers in the north and west axes while the east was slightly lower (1.04). Pb had highest transfer factor of 0.31 in the East, 0.08 in the North and 0.02 at the control. Cd had transfer value of 0.75 in the west and 0.26 at the control location. Bioaccumulation factor of the studied heavy metals from soil to the root of *Z. mays* was generally less than one in all the control samples except for Cu. (Table 35).

Table 34: Bioaccumulation Factor (BF) of Heavy metals in the root of *Abelmoschus esculentus* around Obajana cement factory

Location	Zn	Cr	Pb	Cd	Cu
North	1.93±0.13	0.04±0.01	0.08±0.02	0.19±0.06	1.11±0.01
West	1.29±0.42	0.04±0.01	0.15±0.03	0.25±0.03	1.18±0.02
East	2.42±0.34	0.03±0.00	0.31±0.01	0.01±0.00	1.08±0.01
Control	0.69±0.05	0.01±0.02	0.09±0.02	0.03±0.00	0.50±0.04

Values given are means ± standard deviation

Table 35: Bioaccumulation Factor (BF) of Heavy metals in the root of *Zea mays* around Obajana cement factory

Location	Zn	Cr	Pb	Cd	Cu
North	1.29±0.04	1.05±0.01	0.08±0.01	0.63±0.06	1.08±0.01
West	1.29±0.02	1.05±0.01	0.15±0.02	0.75±0.03	1.13±0.02
East	2.40±0.01	1.04±0.00	0.31±0.02	0.63±0.07	1.08±0.00
Control	0.67±0.05	0.42±0.01	0.02±0.01	0.26±0.03	1.04±0.04

Values given are means ± standard deviation

Bioaccumulation factor in *Mangifera indica* for Zn had highest (1.6) values in the East and lowest (1.04) values in the North. The control had transfer value of 1.38. Cr uptake by *Mangifera indica* root peaked at 0.05 in the east and 0.02 in the control. The North had the highest (0.15) lead uptake by *Mangifera indica* root and the lowest (0.05) by the same species grown in the control site. Cd was most (0.57) transferred by mango root in the west while least (0.06) transfer occurred in the control. Cu was highly (1.33) taken up by the control mango root while its least (1.05) transfer was in the east (Table 36).

Carica papaya had highest (1.79) Zn uptake from the east while least (1.13) transfer of Zn from soil to plant root occurred in the control site. Bioaccumulation factor of Cr ranged from 0.01 (control) to 0.04 (west). Pb uptake by *Carica papaya* root also ranged from 0.4 (control) to 1.11 (West). Meanwhile, Cd had highest (0.10) BF in the north and lowest (0.03) in the control locations. Whereas, BF for Cu had its peak (1.24) in the north and its minimum (1.05) value in the east (Table 37).

Table 36: Bioaccumulation Factor (BF) of Heavy metals in the root of *Mangifera indica* around Obajana cement factory.

Location	Zn	Cr	Pb	Cd	Cu
North	1.04±0.10	0.03±0.01	0.15±0.01	0.38±0.05	1.25±0.03
West	1.37±0.30	0.03±0.00	0.09±0.02	0.57±0.02	1.12±0.02
East	1.60±0.60	0.05±0.00	0.13±0.02	0.06±0.01	1.05±0.05
Control	1.38±0.21	0.02±0.01	0.05±0.03	0.07±0.07	1.03±0.03

Values given are means ± standard deviation

Table 37: Bioaccumulation Factor (BF) of Heavy metals in the root of *Carica papaya* around Obajana cement factory

Location	Zn	Cr	Pb	Cd	Cu
North	1.19±0.03	0.03±0.01	1.06±0.01	0.10±0.00	1.24±0.12
West	1.40±0.01	0.04±0.01	1.11±0.00	0.06±0.01	1.07±0.03
East	1.79±0.11	0.03±0.01	0.16±0.01	0.09±0.02	1.05±0.03
Control	2.13±0.04	0.01±0.01	0.04±0.01	0.03±0.00	1.16±0.21

Values given are means ± standard deviation

4.15 Heavy metal transfer factor (TF) from root to shoot.

The TF of Zn in the leaves of *Abelmoschus esculentus* was less than 1 and ranged from 0.94 – 0.94. Cr translocation to leaves was higher than 1 across the locations while Pb translocation was below 1 in all four locations. Cd translocation was higher than 1 while Cu was less than 1 (Table 38).

In *Zea mays*, transfer factor of Cr and Cu had TF >1 across all the four locations (Table 39). While Zn, Pb and Cd had TF values < 1. Table 40 shows the TF of the studied heavy metals in the leaves of *Mangifera indica*. Zn and Cu had TF >1 while Cr, Pb and Cd has TF < 1. TF in the leaves of *Carica papaya* was such that Zn, Cr, Pb and Cu had TF < 1 while Cd had TF that ranged from 1.71 – 2.50 (Table 41).

Table 38: Transfer Factor (TF) of Heavy metals in the shoot of *Abelmoschus esculentus* around Obajana cement factory

Location	Zn	Cr	Pb	Cd	Cu
North	0.94±0.07	1.18±0.07	0.93±0.12	1.42±0.02	0.52±0.12
West	0.89±0.38	1.32±0.15	0.96±0.11	1.42±0.02	0.28±0.05
East	0.89±0.11	1.24±0.09	0.95±0.13	1.00±0.01	0.02±0.01
Control	0.84±0.04	1.00±0.04	0.58±0.42	1.00±0.01	0.03±0.01

Values given are means ± standard deviation

Table 39: Transfer Factor (TF) of Heavy metals in the shoot of *Zea mays* around Obajana cement factory

Location	Zn	Cr	Pb	Cd	Cu
North	0.95±0.03	1.04±0.06	0.93±0.21	0.30±0.02	1.21±0.05
West	0.84±0.12	1.48±0.02	0.98±0.03	0.52±0.15	1.60±0.03
East	0.81±0.04	1.60±0.01	0.92±0.02	0.40±0.10	1.34±0.02
Control	0.94±0.11	0.84±0.10	0.41±0.51	0.30±0.06	1.01±0.13

Values given are means ± standard deviation

Table 40: Transfer Factor (TF) of Heavy metals in the shoot of *Mangifera indica* around Obajana cement factory

Location	Zn	Cr	Pb	Cd	Cu
North	1.97±0.23	0.68±0.11	0.00±0.03	0.38±0.02	1.07±0.06
West	1.74±0.13	0.91±0.10	0.93±0.04	0.80±0.02	1.10±0.02
East	1.39±0.41	0.34±0.31	0.61±0.02	0.00±0.01	1.04±0.08
Control	1.12±0.05	0.26±0.21	0.75±0.06	0.09±0.01	1.81±0.03

Values given are means ± standard deviation

Table 41: Transfer Factor (TF) of Heavy metals in the shoot of *Carica papaya* around Obajana cement factory

Location	Zn	Cr	Pb	Cd	Cu
North	0.92±0.03	0.93±0.07	0.97±0.13	2.38±0.04	0.99±0.52
West	0.68±0.04	0.77±0.06	0.88±0.12	2.50±0.73	0.94±0.31
East	0.30±0.07	0.88±0.08	0.71±0.10	1.71±0.05	0.95±0.25
Control	0.87±0.02	0.73±0.10	0.00±0.52	2.00±0.83	0.62±0.21

Values given are means ± standard deviation

4.16 Pollution status of the environment

Pollution status of soil of the study area as revealed by the contamination factor of the studied heavy metals, geoaccumulation index and risk factors are presented on table 42. The contamination factor for Zinc showed low pollution at the 2km [W2 (0.84), N2 (0.73), E2 (0.93)] and 3km [W3(0.73), N3(0.64), E3(0.34)] distances from the factory while Zinc pollution was moderate at W1(1.28), N1 (1.24) and E1 (1.44). Whereas, contamination factor for chromium showed moderate chromium pollution at all axes and distances considered except for N3 (0.76) that had low chromium pollution. Lead contamination had moderate [W1 (1.89), W2 (1.07), W3(1.93), N1 (2.04), N2 (1.11), N3 (1.71)] pollution in the west and north axis while the eastern axes had low [E1 (0.92), E2(0.72), E3(0.57)] lead pollution. Cadmium contamination was low in all the locations with the exception of E2 (1.08) and E3 (1.02). Copper contamination was low in all the sampled locations. The soil lead pollution of the study area had moderate pollution at W1 (0.07), N1 (0.43) and E1 (0.37) while soil of all other locations were unpolluted by lead. The potential ecological risk of soils in the assessed vicinity of Obajana cement factory was such that; the potential ecological risk for Zn and Cd was low for all samples collected. Whereas potential ecological risk was moderate for chromium at N1 (98.60) and E1 (127.80) and lead at E1 (99.60).

Table 42: Showing the Pollution status of the environment of OCF

HM	PM	SC	W1	NI	EI	W2	N2	E2	W3	N3	E3
Zn	Cf	0.50	1.28	1.24	1.44	0.84	0.73	0.93	0.73	0.64	0.34
	Igeo	-0.57	-0.23	-0.33	-0.07	-0.43	-0.04	-0.13	-0.47	-0.53	-0.27
	Ri	41.00	76.28	64.21	77.44	73.11	62.16	51.37	57.01	64.03	51.26
Cr	Cf	0.56	1.94	1.93	1.91	1.01	1.02	1.07	1.01	0.76	1.08
	Igeo	-0.59	0.87	0.77	0.63	1.10	0.40	0.33	0.20	0.17	0.10
	Ri	30.00	76.30	98.60	127.80	72.60	82.20	80.40	64.80	66.30	42.60
Pb	Cf	0.23	1.89	2.04	0.92	1.07	1.11	0.72	1.93	1.71	0.57
	Igeo	-0.57	0.07	0.43	0.37	-0.23	-0.43	-0.43	-0.97	-0.20	0.07
	Ri	48.00	94.45	68.20	99.60	55.35	80.05	90.10	91.65	60.55	57.85
Cd	Cf	0.04	0.21	0.12	0.26	0.42	0.74	1.08	0.16	0.21	1.02
	Igeo	-0.57	-0.53	-0.83	-0.50	-0.67	-0.83	-0.83	-0.50	-0.53	-0.10
	Ri	20.00	37.88	63.88	41.82	23.22	41.44	32.74	24.42	51.32	40.16
Cu	Cf	0.20	0.65	0.08	0.85	0.55	0.83	0.62	0.26	0.57	0.33
	Igeo	-0.57	-0.13	-0.47	-0.30	-0.03	-0.27	-0.10	-0.27	-0.07	-0.17
	Ri	35.00	48.25	40.40	43.25	47.75	39.15	38.10	46.30	37.85	41.65
	R		94.16	119.27	151.91	100.03	106.00	103.71	90.18	87.05	61.52

HM- heavy metals, PM-pollution models SC-control samples (soil)

Contamination Factor (Cf), Geoaccumulation Index (Igeo), Ecological Risk index (Ri)

4.17 Human Health risk resulting from consumption of crops grown around OCF.

Table 43: Parameters used for the calculation of the Health Risk (HQ)

Parameter	Values adopted	References
C _s concentration of contaminant in soil	Chemical specific	a, b
IR-ingestion rate	0.0001kg/day-adult	a, b
Ef- exposure frequency (day/yr)	350 day/year	c
ED-exposure duration (year)	30 years for adult 6 years for child	a, b
AT-Average time for non-carcinogens (day/yr)	365days/year/child or adult	a
BW-body weight (kg)	70kg for adult, 15 kg for child	a, b

^aGreztic and Ghariani, 2008; ^bDumitrescu *et al*, 2012; ^c Wang *et al*. (2012); ^d USEPA 2010.

Table 44: Some Toxicological Characteristics of the Investigated Heavy Metals

Characteristics	Pb (mg/kg/day)	Cu (mg/kg/day)	Cr (mg/kg/day)	Cd (mg/kg/day)	Zn (mg/kg/day)
Oral minimal	-	0.01	-	0.0002	0.03 ^b
Risk Level ^a (MRL)					
Oral chronic	0.004	0.04	0.003	0.001	0.02
Reference dose					

^aMinimal Risk Level^a (MRL) is an estimate of the daily human exposure to a hazardous substance that is likely to be without an appreciable risk of adverse non-cancer health effects over a specified route and duration of exposure (USEPA, 2010). ^bImray and Langley (2001).

Figure 4 shows the health risk resulting from human consumption of *Abelmoschus esculentus* fruit grown around Obajana cement factory. The hazard quotient is greater than 1 for zinc content in *Abelmoschus esculentus* fruit grown in the North (3.46), west (2.85) and east (1.75). Likewise, hazard quotient for chromium in *Abelmoschus esculentus* fruit exceeded unity in the west (1.08) and eastern axis (1.69) of the factory. Whereas, hazard quotient for chromium in *Abelmoschus esculentus* fruit was less than 1 in the north (0.61). in the same vein, hazard quotient for Pb, Cd and Cu was less than one *Abelmoschus esculentus* fruit grown around Obajana cement factory.

Figure 5 shows the health risk resulting from human consumption of *Zea mays* fruit grown around Obajana cement factory. The hazard quotient is greater than 1 for zinc content in *Zea mays* fruit grown in the North (3.55), west (3.65) and east (1.78). Likewise, hazard quotient for chromium in *Zea mays* fruit exceeded unity in the North (1.59), west (1.68) and eastern axis (1.42) of the factory. Whereas, hazard quotient for chromium and zinc in *Zea mays* fruit sampled from the contrl location was less than 1 control [zinc (0.45). chromium (0.58)].Likewise, hazard quotient for Pb, Cd and Cu was less than one *Zea mays* fruit grown around Obajana cement factory.

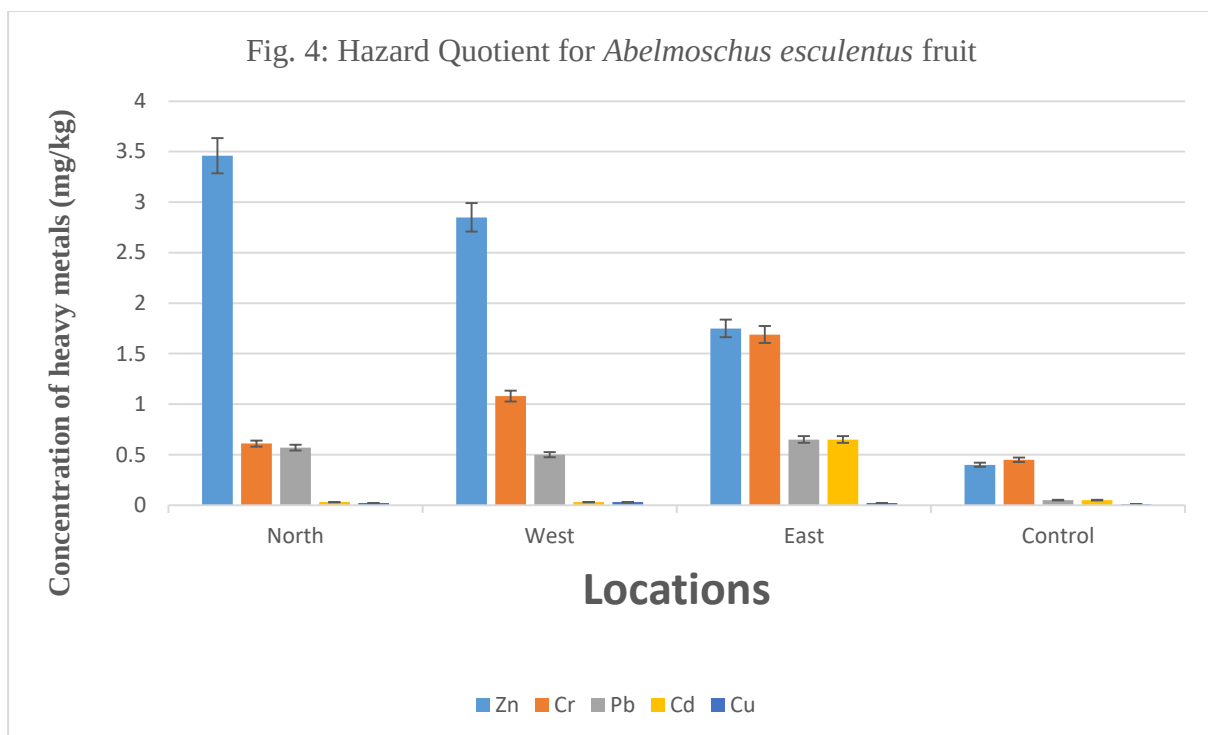


Figure 4: Hazard Quotient for *Abelmoschus esculentus* fruit

HQ>1- Potential health risk HQ<1- No potential health risk

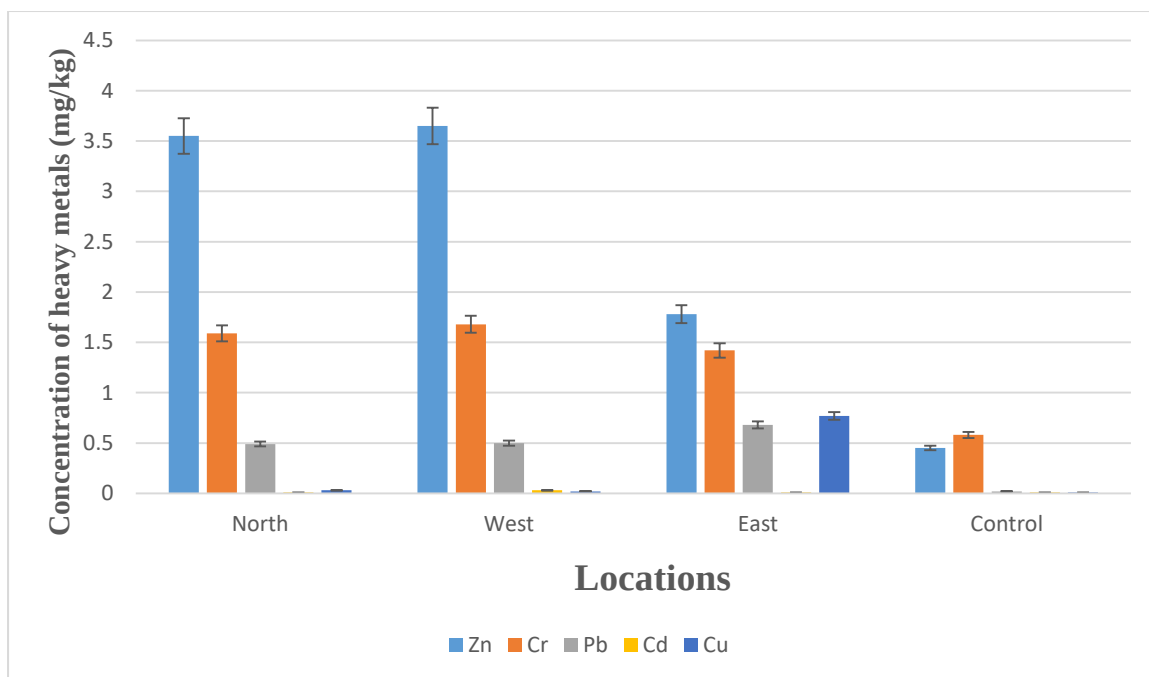


Figure 5: Hazard Quotient for *Zea mays* fruit

HQ>1- Potential health risk HQ<1- No potential health risk

Figure 6 shows the health risk resulting from human consumption of *Mangifera indica* fruit grown around Obajana cement factory. The hazard quotient is greater than 1 for zinc content in *Mangifera indica* fruit grown in the North (3.55), west (2.70) and east (2.91). Likewise, hazard quotient for lead in *Mangifera indica* fruit exceeded unity in the North (1.26) but less than one in the west (0.85) and in the east (0.08). Whereas, hazard quotient for chromium, cadmium and copper in *Mangifera indica* fruit sampled from the north, west and eastern axis of this mega cement factory were all less than one.

Figure 7 shows the health risk resulting from human consumption of *Carica papaya* fruit grown around Obajana cement factory. The hazard quotient is greater than 1 for zinc content in *Carica papaya* fruit grown in the North (3.36), west (1.47) and east (2.87). Likewise, hazard quotient for lead in *Carica papaya* fruit exceeded unity in the North (1.34) and west (1.24) but less than one in the east (0.09). While, hazard quotient for chromium, was less than one in all sampled locations except for west (1.97) which had hazard quotient greater than one. Cadmium and copper in *Carica papaya* fruit sampled from the north, west and eastern axis of this mega cement factory all had hazard quotient values all less than one.

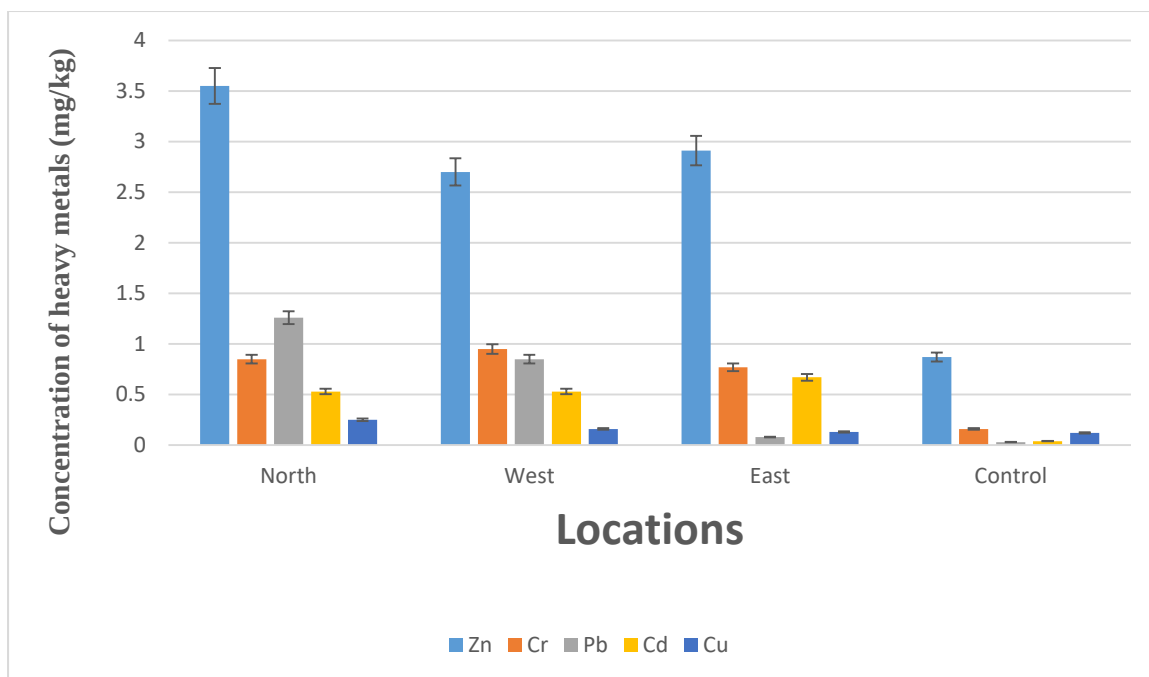


Figure 6: Hazard Quotient for *Mangifera indica* fruit

HQ>1- Potential health risk HQ<1- No potential health risk

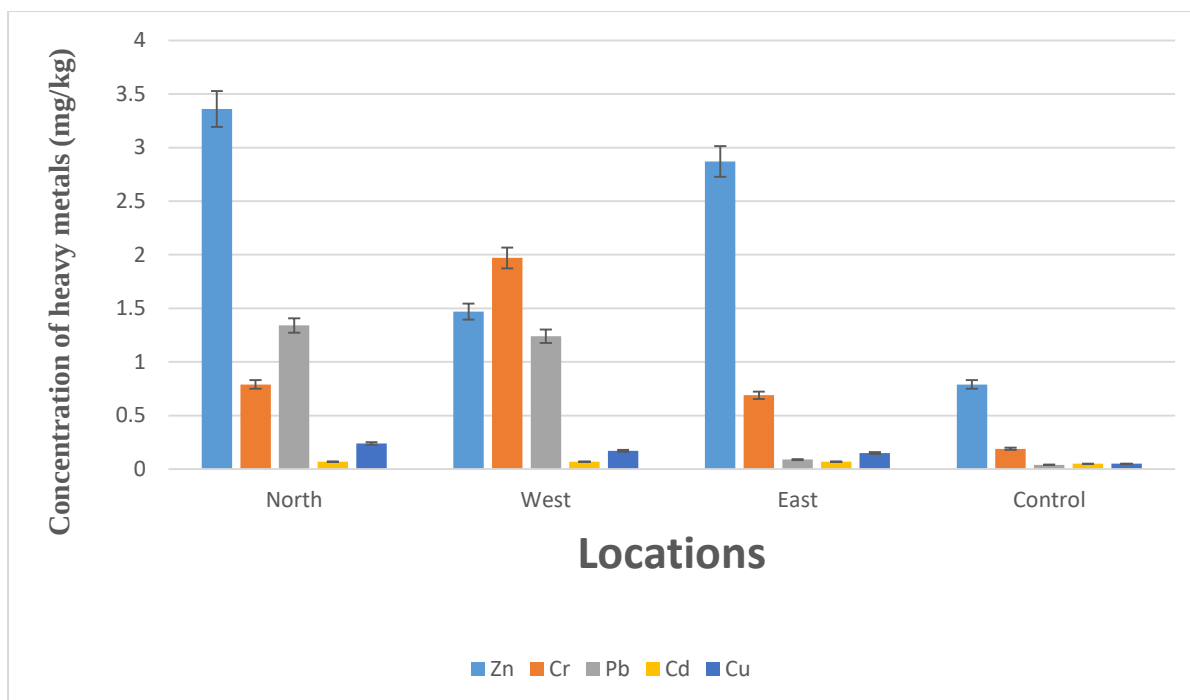


Figure 7: Hazard Quotient for *Carica papaya* fruit

HQ>1- Potential health risk

HQ<1- No potential health risk

CHAPTER FIVE

DISCUSSION

5.1 Physicochemical Parameters of Soil around Obajana Cement Factory

Soil pH around Obajana cement factory

Soil pH is an important parameter that directly influences sorption/desorption, precipitation/dissolution, complex formation and oxidation reduction reactions (Oyedele *et al.*, 1990). Soil pH at the 3km distance varied from acidic to slightly alkaline. Whereas, in the vicinity of the cement factory (1Km) pH varied from slightly alkaline to moderately alkaline. That is, the impacts of cement dusts on soil pH reduces with increase in distance from the factory. The soil pH in the vicinity of the factory as shown in the EAA report before the commencement of full operation of the factory was slightly acidic. This change is probably due to liming effect of cement dust (Maina, 2013). Cement dust contains CaCO_3 , resulting in alkalinity when it comes in contact with soil (Fortune, 2011). When cement dust released from the factory comes in contact with soil, it has indirect effect on soil quality (Buba *et al.*, 2004). Another finding also confirmed that soil surrounding the cement plants was alkaline in nature, this is chiefly due to the influence of cement dust (Tajudeen and Joy, 2011). Gradual decrease in soil pH with increasing distance from a cement factory has also been reported by some researchers (Ibanga, 2008).

The soil pH differed from one season to the other across the axes. The soils were moderately acidic to slightly alkaline and slightly acidic to moderately alkaline during the rainy and dry seasons respectively. During the dry season, cement dust deposition is more severe in the absence of rain (Iniobong *et al.*, 2008), thus the higher soil pH recorded in the dry season in this study. These values were relatively higher compared to the average pH values recorded at the control site. Although, the pH of most soils in the tropics ranged from acidic to slightly neutral (Alloway and Aryes, 1997). At acidic soil pH, plant nutrients are readily available and

microorganisms are mostly active. The modification of the soils in some sites from acidic to alkaine during the dry season could be attributed to the deposition of liming materials {CaO and Ca (OH)₂} which are often used for cement production. During the rainy seasons, the soil across the sites were observed to be more acidic than in the dry season. This may be attributed to the fact that there are more hydrogen ions in the soil solution during the rainy season. As soil pH is usually lowered by precipitation (Oyedele *et al.*, 1990). An increase in soil pH closer to the factory could be as a result of soil amendment with low proportions of cement.

Organic matter of soil around Obajana cement factory

There was slight variations in soil organic matter from season to season, distances from the factory and the three axes of the factory that were assessed. The relatively higher organic matter content in the dry season could be due to lower soil moisture in the soil during the dry season. Thus, microbial decompositions of organic matter was retarded during the dry season. On the other end, soils in the control site had moderate amount of organic matter content. The higher quantity of organic matter at the control site indicated that it could support better plant growth than those that are closer to the factory.

The soil organic matter content for the three axis was in the order of North > West > East in the dry season and West > East > North in the rainy season. The relatively higher organic matter content in the Northern axis could be attributed to less cement dust, occasioned by the prevailing northeasterly wind direction (Afeni, 2008) in the dry season. Thus microbial decompositions of organic matter was more owing to less cement dust deposition (Odoh *et al.*, 2018) in the Northern axis of the factory in the dry season. In the same vein, soil organic matter was slightly higher in the western axis of the factory in the rainy season because of the

prevailing southwesterly wind direction in the study area in the rainy season (Odoh *et al.*, 2018).

Soil organic matter was found to gradually increase in percentage as distance from factory increases in both seasons. Cement dust is alkaline in nature and when it comes in contact with soil it interferes with both the synthesis and decomposition of soil organic matter (Rawat and Katiyar, 2015) resulting in lower soil organic matter closer to the cement factory where cement dust deposition is higher. A similar trend has been reported severally around cement factories (Oludoye and Ogunyebi 2017; Magray, 2012). That is soil organic matter was generally lower at sites nearest to the factory and increased with increasing distance from the cement factory.

Electrical conductivity of soil around Obajana cement factory

Soil electrical conductivity (EC) is a measure of the amount of salt in soil (salinity of soil). It is an important indicator of soil health. It reflects the extent to which the soil is suitable for growing crops. Too low EC indicates low available nutrients. Dry season concentrations of electrical conductivity were slightly higher than the wet season concentrations. This may be attributed to rainfall and weathering intensities as well as to leaching and lateral translocations which lowered the EC (Bayhan, 2002) in the rainy season.

In relation to distance from the factory, the level electrical conductivity decreases with increasing distances from the factory with few exceptions in the rainy season. This can be attributed to the significant amount of cement dust deposited on the soil surface around the vicinity of the cement factory. From this finding, the level of soil electrical conductivity was found to increase under the influence of cement dust. Variations of soil EC due to influence of cement dust has been confirmed by (Carlson *et al.*, 2011). The irregular pattern of EC recorded during the rainy seasons may be chiefly due to the wash off of the cement dusts

deposited on the top soil layer by rainfall. Also, EC was higher in the polluted site than the control site in both seasons. Cement dust contaminated sites have been reported to have significantly higher EC than in the control soil (Bhatty, 1995).

5.2 Heavy Metal Contamination of soil around Obajana Cement Factory

The mean values of metal concentrations in the soil samples from the polluted site were found to be higher than the average concentrations in the soil samples from the unpolluted site. This is in line with the report of Galkus *et al.*, 2012.

Heavy metal pollution at varying distances from the factory

The average concentrations of Pb varied along the sampling distances. Similarly, Cu and Cr average concentrations also varied with sampling distances. This decrease in metal concentrations as distance from the factory increases is an indication that the metals are being discharged from the activities of the factory. In cement industries, the linings for the rotaries contain Cr, Co and Cu which could be liberated to the environment by wears and frictions (Banat *et al.*, 2005). Generally, higher concentrations of heavy metals were observed in the 1km distance than in the 3km distance. The heavy metals analysis inculcates cement dust originating from the cement facility for being partly or wholly responsible for metal contamination of soil around the factory. The decrease in the quantity of the metal concentrations as distance from the factory increases could indicate a link between the cement production and soil metal concentrations around the factory. Metals originating from industrial activities are distributed in soils by the atmosphere within a distance that depends on the size of particles (Mandal and Voutchkov, 2011).

The highest concentrations of Pb, Cr, Cd and Cu in soil around the factory were obtained at 1Km distance and this may be attributed to the size of the particles vis-à-vis the proximity of this sampling distance in comparison to the others (2Km and 3Km). Metal contaminants from

cement factories are released as constituents of dusts discharged from the exhaust kilns and can be deposited and retained in the soil at distances from the source depending on wind velocity, direction and particle size distribution of soil particles. The contamination of the soil may be due to the close proximity of the farm lands to the cement factory. At close distance (1Km) from the cement factory, the soil exhibited lower Zn levels than farther away from the factory, this can be attributed to the mobility of Zn in the soil. The fact that Zn is known to have high mobility in soils has been reported by Luke *et al.*, 2010. All the heavy metals studied were found in significant amounts at the three different distances from the factory. However, the metals were concentrated more at the 1Km distance than at the 2Km and 3Km distances. At the 2Km distance, metal content was quite high but not as high as in the 1Km distance and was slightly lower than concentrations at the 3Km distance from the factory.

The recorded concentrations of chromium at the 3 distances sampled, was such that chromium concentrations progressively reduced as distance from the factory increased. 1Km had the highest concentration while 3Km from the factory had the least chromium concentrations. In the cement factory (as reported by Banat *et al.*, 2005) the linings for the rotaries contain Cr, which could be liberated by wear and tear of the machine due to friction. Hence the source of Cr in the soil samples may be as a result to this process. Thus, the decreasing trend in Cr concentrations can be attributed to recent deposition of the polluting dust. The recorded values for lead in relation to distance from the factory did not strictly follow any particular trend as its concentration was highest at the 1Km distance at some points, and highest at the 2Km and 3Km distances at other point. Although, the concentrations recorded at the study area far exceeds what was observed at the control site. The influence of the cement factory on the observed lead concentrations around the cement factory cannot be ruled out as the production of cement requires a substantial amount of energy supplied by burning fossil fuel which in turn releases lead pollutant into the

environment. This has been corroborated by several reports (Al-Kashman and Shawabkeh (2006); Ogunbileji *et al.*, 2013). The irregularity in the concentrations of lead as it relates to distance could be attributed to an interplay between discharge from the cement factory and vehicular emissions from the high traffic density road that transverses from the North, through the west to the southern axis of the factory. The concentrations of Zn and Pb could be attributed to the emissions from fossil fuels and vehicular emissions (tyre abrasions and wears) because of the high traffic density road that passes right in front of the cement factory (Fatoba and Iyeh, 2012; Asubiojo *et al.*, 1992). The higher concentrations of these heavy metals in the polluted site is majorly as a result of cement production as Bhatti (1995) affirmed that introduction of heavy metals into cement dust was related to combustion processes in cement production. Also, Ogunbileje *et al.*, (2013) stated that the source of fuel and raw materials used in the production of cement determines the amount of heavy metals in cement dust.

Heavy metal levels in soil of the different axes of the factory

Samples were collected from the western, eastern and northern axes of the factory. Samples were not collected in the southern axis of the factory as it was basically a rocky terrain. The quarry is in the eastern axis while a high traffic density road transverses the north, through the west to the southern axes of the factory. It is worth mentioning that over 5,000 trucks load cement in the northern and western flank of the factory for onward delivery to consumers. Chromium, cadmium and copper levels of the sampled soil was high in the eastern axis, where the quarry is located. This finding is in agreement with the results reported by Al-Omran *et al.*, 2011 who noticed a similar trend in metal concentrations in the direction of the quarry relative to the cement factory. Zinc contamination occurred in the northern, western and eastern axes of the factory at a comparable degree. This is not suggestive of Zn pollution source being the same aside from discharge from the factory. Rather, it is indicative of the

fact that external pollution sources of Zn occurs in the three axes. The observed contamination of the eastern axis by Zn could be as a result of quarrying activities that is extensively carried out there to feed the factory with the required raw materials. It has been reported that quarry topsoil are normally abundantly rich in Zn more than other toxic metals (Pb, Cu, Cd, Cr) (Etim and Adie, 2012). In the same vein, additional Zn pollution of the soil in the northern and western axes can be attributed to the high traffic density road in that axes. Zinc and lead in soils could be derived from industrial sources as well as from abrasion from tyres of motor vehicles (Al-Khashman and Shawabkeh, 2006; Carreras and Pignata, 2002).

The highest concentrations of Pb and Zn were found in the samples from the north and west axes of the factory. This could be premised on the high traffic density road that transverses the north and west of the factory. That is, in addition to discharge from the cement factory. Likewise, the truck packing lot where loading and offloading activities which mostly re-suspends heavy metals laden dusts that eventually settle in the soil is located in the north/western axes of the factory. Thus, high concentration of Pb in the north/western part of the factory was expected because of the synergy of depositions from cement production with the release from vehicular activities (Carerras and Pignata, 2002; Al-Khashman and Shawabkeh, 2006). Cadmium also showed a similar distribution as Zn and Pb as regards to the axis of the factory. Cd is also derived from the mechanical abrasion of vehicles and is associated with tyre wear Kakareka and Kukharchyk (2011). The highest concentrations of chromium was recorded in the samples collected nearest to the cement factory and had no bias for axes to the cement plant. This is because Cr pollution of soil around the vicinity of cement factories chiefly emanates from the operations of the cement factory. In cement industries the linings of rotaries contain chromium, which could be liberated by wear and friction (Banat *et al.*, 2005).

5.3 Seasonal Variation of Heavy Metal Concentrations around the Factory

During the dry season, the concentrations of the studied heavy metals were higher in the soils around the cement factory than in the rainy season. This could be as a result of their association with the raw materials (limestone, clay, laterite, sandstone and gypsum) used for cement production. As the deposited cement dust were not washed away by rain water in the dry season. The elemental concentrations were slightly lower in the rainy season than values obtained in the same location during the dry seasons probably due to rain induced heavy metals dilutions and leaching into the sub-soil layers as researchers have indicated these heavy metals have the potential of being leached out when weakly adsorbed to topsoil (Zanders, 1999). Imray and Langley (2001) also reported that changes in concentration of heavy metals overtime in soil stratum may occur as a result of factors such as breakdown and leaching. This was noticed at all the sampled sites as the concentrations of all the elements (Zn, Cr, Pb, Cd and Cu) tested for were lower than in the rainy season than their corresponding values in the dry season. This evidently could be suggestive of leaching. Leaching of these metals from the soil in the rainy season could have been enhanced by the higher acidity of the soil in the rainy season. Hernandez *et al.*, 2003 proved that heavy metals like Pb, Cd and Cu tend to leach out of soil when the soil pH is low. In addition to leaching, reduction in Cd concentrations between the dry and rainy seasons can be attributed to its high mobility (Vamerali *et al.*, 2009) and solubility in water (Salt *et al.*, 1995). The fact that most Cd in tropical soils is always present in soluble form (Olaide, 1987) makes it to be fairly mobile within profiles of tropical humid soils of Nigeria (Olaide, 1987). Cadmium has also been reported to be most mobile under oxidizing condition at pH levels below 8, hence the leaching of the solubilized Cd. Also, seasonal variation in concentrations of heavy metals in soils could result from breakdown and volatilization (Imray and Langley, 2001). The levels of Cr is of significant interest as it was far higher than what Ogunkunle and Fatoba 2013a

recorded in a similar study around a cement factory located in Ogun state Nigeria . However, except for Cr and Pb, the concentrations recorded for other elements were similar to the values reported around the soils of a mega Cement Factory in Gboko, Benue State, Nigeria (Abatyough *et al.*, 2015).

5.4 Comparism of Soil Metal Levels with CCME Standards

Permissible limit is the minimum toxicity levels for heavy metals in agricultural soils. Soils whose heavy metal content exceeds the permissible limit are regarded as contaminated for agricultural activities (Toth *et al.*, 2015) and are associated with ecological risks or human health risks. Nigeria has no national guideline limits for heavy metals in soil. As a result, heavy metal levels in this study were compared with the target values for remediation by the Department of Petroleum Resources (DPR, 2002), and the Canadian Council of Ministers for Environment (CCME) guidelines for heavy metals in agricultural soils. On comparison with these references, Cr levels far exceeded the CCME permissible limits. While Cr concentrations in the unpolluted site (a distance of 50Km from the factory) were below the DPR, 2002 and CCME permissible limits. This is an indication that cement production could be a major contributor to soil heavy metal content in the study area. Since there were no other sources of contamination in the area. The source of Cr pollution in the soil may be attributed to dust particles from Obajana cement factory. In cement industry the linings for the rotaries contain chromium, which could be liberated by wear and friction (Banat *et al.*, 2005). Consequently, the cement factory is implicated as the source of Cr in the sampled soil. Soils around cement factories show high concentrations of metals sespecially Cr on top soils of 0-10 cm deep (Al-Khashman and Shawabkeh, 2006). In a similar study, Al-Kashman and Shawabkeh (2006) also reported the presence of Cr and Cd in surface soil around Rashadiya

cement factory in Southern Jordan which was higher than the permissible limits for agricultural soils.

The concentration of Pb in the soil of the study area is about the same as the permissible limits of the standards used for comparison. This findings corroborates the reports of several studies around cement factories (Ogunkunle and Fatoba 2013a; Abimbola *et al.*, 2007 and Gabdebo and Bankole 2007) in which Pb was found to be one of the greatest pollutant of dusts around Lafarge-Cement WAPCO cement factory. Odoh *et al.*, 2018 reported similar Pb levels in the vicinity of Obajana cement factory. The concentration of Pb in soil of the study area is substantially higher than reported by Sakalauskaite *et al.*, (2009) in the vicinity of a cement factory in Lithuania probably due to the presence of a high traffic density road in the study area and soil chemical composition. Lead is a classical chronic or cumulative poison, thus the need to ensure its concentration does not exceed the permissible limit. The high concentrations of lead in the vicinity of the factory can be attributed to the cement factory since the process of cement production requires a substantial amount of energy supplied by burning fossil fuel coupled with traffic activity on the nearby road. Deposition of Pb on roadside soils by vehicular emissions have been reported by Fatoba and Iyeh 2012. This implies that the areas surrounding the factory cannot be safely utilized for agricultural purpose. Though, the reality is that fallow areas around the factory are extensively used for subsistent farming of crops and fruit trees. Thus, there is the need for remediation of soil around OCF for Cr and Pb, since their total contents were greater than the CCME limits. When total metal content in agricultural soil is higher than the permissible limits, such soil requires remediation (Dao *et al.*, 2012).

The average concentrations of the other quantified heavy metals (Zn, Cd and Cu) were below the CCMCE limits. Zinc is known to cause less environmental concern for soil as many

studies have regarded Zn as a non-critical factor in the pollution of soil (Chen *et al.*, 2005; Wu *et al.*, 2010). Among all the heavy metals evaluated, zinc is the least toxic and is an essential element in human diet as it is required to maintain the functioning of the immune system. The deficiency of Zn may be more fatal to human health than the excess of it. Although the level of Zn in this study is still within safe limits for soils. However, this contradicts the findings of Ogunkunle *et al.*, 2013 around a cement factory in Ogun state, Nigeria.

Copper and Cd levels were below critical limits. The estimated concentrations of Cd in the soil samples even though below the CCME permissible limit, were slightly higher than those from the control sites. With these observations, there is no fear of acute toxicity since the concentration is below the permissible limits. The concentration of Cd in soil is significantly lower than what was reported by Gabdebo and Bankole (2007); Mandal and Voutchkov (2011) around some cement factories. The source of Cd in the top soils may be associated with emission sources from the cement factory. This study did not observe any risk of Cu toxicity. Cu concentration in the soil samples is below the maximum permissible concentration set by CCME but higher than the concentration obtained at the control site.

One possible reason for Zn, Cd and Cu levels being less than the permissible limits is the fact that the factory has only been in operation for about ten years as at the time of collection of soil samples for this study. The highest concentration of Cd, Cr, Cu and Pb were found closest (1Km) to the factory, while the highest concentration of Zn was found at 2Km and 3Km from the factory. Cement industry plays a vital role in the imbalances of the environment by producing toxic substances such as Cr, Pb and Zn (Sakalauskaite *et al.*, 2009), thus, OCF is the source of increased metal concentrations in soil around the factory. Mousavi *et al.*, evaluated the concentration of heavy metals in the dust caused by Karun

cement factory and concluded that Cr had the highest concentration while Cd had the lowest concentration (Mousavi *et al.*, 2013), which is consistent with the results of the present study and a study by (Ogunkunle and Fatoba, 2014). Generally, the concentrations of metals in soil followed the decreasing order: Cr>Pb>Zn>Cu>Cd.

5.5 Bioavailability of heavy metals in the soil

Bioavailability of the heavy metals in the soil varied slightly between the rainy season and the dry season in all the three axes. The change in the bioavailability of these heavy metals can be as a result of the total concentration of heavy metals available in the soil. The reduction in the soil metal contents in the rainy season has a pronounced influence on their soil bioavailability. Nevertheless, pH is the major factor that dictates the bioavailability of the metals in the soil but the higher the soil total metal content, the greater their bioavailabilities. This explains the decrease of soil bioavailability in the rainy season. There was no significant difference in the soil bioavailability of Zn, Pb, Cr, Cd and Cu in the three axes during the rainy season. This could be attributed to the fact that the soils of the three axes had lower pH values in the rainy season as bioavailability of these heavy metals is mainly controlled by pH (Takac *et al.*, 2009) and to a lesser extent by organic matter as the organic matter content was higher in the rainy season than the dry season. A closer look at the amount of heavy metals extracted in the soil shows that Cr had the highest concentration while Cd had the least concentration, Cr concentration was highest (with respect to their permissible limits) at N2 this co-incides with a location with the lowest soil alkalinity. Bioavailability of heavy metals in soil decreases with increasing organic matter content of the soil (Zia *et al.*, 2011). Although, Cr was more bioavailable in the soil for both North and West axes most likely because those axes are not rich in organic matter content as bioavailability of Cr in soil is largely controlled by organic matter (Zia *et al.*, 2011); therefore, the relative high bioavailable Cr content in the soils can be pegged on the quantity of organic matter. The study indicated

high bioavailability of Cu and Zn in the cement-polluted soil in the study area, in relation to the total Cu and Zn concentrations. The high bioavailability of Cu and Zn may be due to the low soil pH, which can increase solubility (Hess and Schmid, 2002). There have been reports that low pH increases solubility of Cu in soil, making it phyto-bioavailable and reducing complexation with organic matter and chem.-sorption on oxides and silicate clays (Bolan *et al.* 2003^a, 2003^b). The organic matter content of soil can favour bioavailability of Zn, making it more abundant for uptake by vegetables, as metals associated with organic matter have high mobility due to decomposition and oxidation of organic matter with time (Salomone, 1995). McLeean and Bledsoe (1992) reported that high mobility of Cu in soil can be attributed to its high complexing nature with soluble soil organic matter which leads to easy leaching from the soil. Amrhein *et al.* (1992) also reported increased mobility of Cu in the presence of dissolved organic matter, which was consistent with the result of this study. The relatively low organic matter content of the soil may not be able to explain the high bioavailability of Cu; but the high acidity of the soil can do.

5.6 Heavy metal uptake by the plants

The accumulation of metals has been described as their content or concentration in different parts on the basis of their amount per unit dry weight of tissues (mg/kg dry weight). Heavy metals are mobile and easily taken up by plants grown in metal contaminated environments. Since the plants have high ability to accumulate metals in their different parts from the environment, metals taken up by the crop plants may pose risks to human health when they are grown on or near contaminated areas through various food chains. The amount of heavy metals absorbed and the proportion of their distribution to different edible and non-edible parts of the investigated crop plants are briefly discussed below.

Metal accumulation in different plant parts of studied crops

Heavy metal concentrations in the examined species (*A. esculentus*, *Z. mays*, *M. indica*, *C. papaya*) vary as previously reported by Alloway *et al.*, (1990) that plant species type determines the degree of accumulation of metals in plant tissues. Heavy metal concentrations in the examined crop species showed some variations even at the same location. This is due to the difference in physiological properties of the plant species. Kumar *et al.*, (1995) found that metal concentrations in different plant species grown on soil with the same pollution level exhibited variations in metals uptake, this suggests that the accumulation effect depends to a large extent on the crop's physiological properties. Irrespective of the different plant species and plant parts, the total uptake of metals by the crops was recorded in the order of Zn>Cr>Pb>Cu>Cd.

Certain plants have evolved the capacity to take up and accumulate selected metals in their shoots and roots at levels that are toxic to ordinary plants (Dong, 2006; Fagbote and Olanipekun, 2010). Generally, plant samples collected from the vicinity of the factory had higher metal concentrations than their counterparts from Control sites, this is in agreement with the findings of Idakwoji, 2016 when similar studies were undertaken. This could be attributed to the high metal contents of the polluted site soils which are eventually taken up by the plants grown on them. This also indicates that the Heavy metal contents of plants grown around cement factories are dependent upon the metal concentrations of the habitual soil environment and this is in agreement with the findings by Idakwoji, 2016.

The concentration of Zn, Cr, Pb, Cd and Cu in *Zea mays* root, leaves and fruit was highest at the 1km distance from the factory. Generally, the results showed that among the metals studied, the accumulation levels of Zn and Cr in *Zea mays* plant parts were above the maximum levels as stipulated by FAO/WHO 2001 which is 60.0 mg/kg and 2.3 mg/kg respectively. This could suggest that the cement dust pollution have caused an increase in the

Zn and Cr content of the *Zea mays* growing at distances 1km to 3km from the cement factory. Since the concentration of Zn and Cr in *Z. mays* collected from the unpolluted site is well below the permissible limit. Cr is a toxic metals that can accumulate in various parts of the plant without any particular function (Kabata-Pendias and Pendias, 2001). Thus, heavy metal contaminants (particularly, Cr and Zn) found in soils on which *Zea mays* was cultivated constitutes to its heavy metal pollution levels. The sequence of metal accumulation in decreasing order was: root>leaves> fruit. With root and leaves showing a higher tendency of metal accumulation as compared to the fruit. According to Hopkins (1999) metals such as Fe, Mn, Cu and Zn are found in plants because they are nutrients which are required for photosynthesis and various metabolic processes in the plant (Hopkins, 1999).

All five Zn, Pb, Cr, Cd, Cu heavy metals accumulated in different amounts in the root, leaves and fruit of *Abelmoschus esculentus* plants. Heavy metal accumulation was significantly higher ($p < 0.01$) in all the samples from the vicinity of the factory in comparison to samples from the unpolluted site. Lead, zinc and copper accumulation was relatively higher in the roots than the leaves and fruits. Whereas, Cr levels in *Abelmoschus esculentus* leaves exceeds concentration in the root. This corroborates the report of Motior *et al.*, 2013 on the efficient uptake of Cr by *Abelmoschus esculentus* grown on polluted soil. The amount of metal translocated into different parts of the plant, especially into the edible portion, are crucial as intake of this metals via consumption of polluted *Abelmoschus esculentus* have negative health consequences.

The concentrations of Zn, Cu and Cd in *Mangifera indica* samples from the polluted site was well below the FAO/WHO 2001 permissible limit. This agrees with the findings of Edori and Kpee (2016) in their studies of the prevalence of Some Heavy Metals in Mango and Pawpaw Found growing in Eleme Local government area of Rivers state.

Higher concentrations of heavy metals recorded in *Carica papaya* samples from the vicinity of the cement factory was higher than samples from the unpolluted sites. This is in agreement with the findings reported by Mench and Martin, 1991 that plant species can significantly influence the rate of metal uptake by plants. The fact that Cd recorded higher concentrations in the leaves than in the root and fruits whereas Cu, Cr, Zn and Pb recorded higher concentrations in roots than other parts investigated, is in conformity with the results reported from similar studies by Schuhmacher *et al.*, 2002. Likewise, Moreno *et al.*, 2002 reported higher metal concentrations of Cu, Zn and Cd in the roots of some fruit trees grown around a mega cement factory. The lower concentrations of Cd in *C. papaya* roots which consequently indicates its low level of utilization is in agreement with the report by Udosen *et al.*, 2012 in *Manihot utilissima* obtained from a heavy metal polluted site in Nigeria. This could be occasioned by the low level of the metal in the earth's crust and the fact that its a non-essential element for plants. These observations may also be caused by the unavailability and scarcity of Cd in the soil on which the plant is grown which could also affect their uptake by the plant. However, the large difference between root and fruit concentrations of Cu in the vegetables showed that the plants have restricted internal transport of metals from roots towards aerial parts, as reported by Dahmani-Muller *et al.* (2000).

Uptake of Zinc by the plant species

Among the different crops and various plant parts, *Abelmoschus esculentus* leaves showed the highest Zn accumulation followed by leaves of *Carica papaya* and *Zea mays* while the leaves of *Mangifera indica* had the least Zinc concentrations. This could be as a result of the glossy nature of mango leaves that will not readily allow for adsorption of zinc laden cement dust that settled on it. Edori and Kpee, 2016 also reported lower Zinc levels in *Mangifera indica* than in *Carica papaya* leaves. There has been reports that Zn, being extremely soluble and mobile, can be readily transported from soil to shoots of plants, thereby making its

assimilation easy by plants leading to phytotoxicity (Brun *et al.*, 2001; Nafiu, 2010). The distribution of Zinc in the studied plants, shows that the crops were tolerant to Zn, but the mechanism of their tolerance differs, which may not be physiological alone but an innate adaptation to their polluted environment (Ernst, 1975).

Uptake of Chromium by the plant species

Among the crops, *Zea mays* recorded greatest accumulation of Cr in comparison to the other crops investigated. Plant uptake of heavy metals from soil occurs either passively with the mass flow of water into the roots or through active transport across the plasma membrane of root epidermal cells (Yoon *et al.*, 2006) and this process varies in different plant species which could also translate into different rates of metal uptake. The high uptake of Cr from the soil by *Zea mays* suggests the plants' ability to efficiently absorb Cr from contaminated soils (Yoon *et al.*, 2006). This indicates that this species can be used in phyto-extraction and phyto-stabilization of Cr in polluted soil (Mendez and Mairer, 2008; Garba *et al.*, 2012). This also implies that *Zea mays* grown around Obajana cement factory is chromium polluted. The concentrations of Cr in *Zea mays* recorded in his study is similar to that reported by Matina *et al.*, (2003) and Nafiu (2010), who showed that *Zea mays* intensively absorbed and conducted Cr from the soil to its shoot.

Uptake of Lead by the plant species

As regarding lead accumulation in the different crops and their different parts. Leaves of *Zea mays* showed highest content of lead. Whereas, highest Pb concentrations in *Abelmoschus esculentus*, *Mangifera indica* and *Carica papaya* was recorded in the roots.

Uptake of Zinc by the plant species

Uptake of cadmium by the investigated plant species was generally low as no species or plant part had cadmium levels beyond the FAO/WHO 2001 benchmark. This could be attributed to

the low cadmium levels in the soil of the study area. On an average Cd content was found highest in roots, followed by leaves and fruits of all the crops. This findings was consistent with the reports of Garba *et al.*, (2013) who observed reduction in Cd concentration in the shoot of *Pennisetum pedicellatum* despite its high concentrations in the plant root.

Uptake of Copper by the plant species

Copper is an essential element required for metabolism of plant cells. However, elevated levels in food can cause irritation of the nervous system, depression, necrotic changes in liver and kidney. Among the various plant parts, roots showed highest accumulation of copper followed by leaf and fruits. Heavy metals can also be recycled back to the roots via the phloem when they are getting towards toxicity threshold in plants as observed for Cu by Patsikke *et al.*, (1998). However, the large difference between root and shoot concentrations of Cu in the studied crops showed that the plants have restricted internal transport of metals from roots towards aerial parts, as reported by Dahmani-Muller *et al.*, (2000). The concentrations of Cu observed in this research is similar to the concentrations reported by Matina *et al.* (2003), Nafiu (2010) and Ondo *et al.* (2012), who showed that vegetables intensively absorbed and conducted Cu into the shoot. Concentration of Cu in the investigated plants is also comparable to that reported by Shilev and Babrikov (2005) from industrial polluted soil.

Hetero-geneous accumulation of heavy metals in different crop species, and different plant parts of same crop species as seen in the present investigation have also been reported by Singh *et al.* (2011) which could be attributed to their diverse morphological characteristics and position of leaves and fruits on the plants in respect of their distance from roots and the selective uptake of metal by each crop (Mohamed and Mohammad, (2001). Low metal accumulation in fruit trees (*Mangifera indica* and *Carica papaya*) as compared to annual

crops (*Abelmoschus esculentus* and *Zea mays*), and in vegetative parts than in reproductive organs have also been reported by Singh *et al.* (2011). This may possibly be due to poor metal mobility within the plants. In contrast, however, Barman and Lal (1994) reported higher accumulation of heavy metals (Cu, Zn, Pb, Cd) in edible parts than in non-edible plant parts. In general, lower levels of heavy metals particularly Pb and Cd in reproductive organs than in vegetative parts, may be due to their poor mobility in plants as compared to essential metal nutrients that is, Cu and Zn. Very low concentration of Cd in fruits of fruit type vegetable and their poor uptake indicates the possibility of safe cultivation of such type of vegetables on cadmium contaminated fields. Such variation in metals uptake and their distribution/compartmentalisation between different parts of different crop plants may be useful for selecting crop species suitable for cultivation on metal contaminated soils to reduce the movement of metals into the food chains.

5.7 Adaptations of *Abelmoschus esculentus*, *Zea mays*, *Mangifera indica* and *Carica papaya* to cement dust pollution around Obajana cement factory

Leaf epidermis is usually the first target for air pollutants. These pollutants pass through stomata during exchange of gases thereby initiating responses in several plant species (Duldulao and Gomez, 2008). How plants respond to air pollutants varies from species to species and depending on the nature of pollutant present in the atmospheric environment. Plants growing under stress of air pollution show some modifications/adaptations in the anatomical characteristics of their leaves as observed in this study. The leaf epidermal modification or responses in trichome density, stomatal density, stomatal index and stomata size of *Abelmoschus esculentus*, *Zea mays*, *Mangifera indica* and *Carica papaya* are good indications that the level of atmospheric pollutants has become hazardous to the species. These responses could be adaptive features to tolerate the high cement dust pollution of their environment.

Leaf epidermal studies of *Abelmoschus esculentus*, *Zea mays*, *Mangifera indica* and *Carica papaya* leaves collected from the cement dust polluted site (OCP) were compared to the same species collected from the control site. The control samples were used in order to evaluate the responses of the diagnostic species to cement dust pollution in the study area. Folia uptake through the stomata may be the principal routes for accumulation of air-borne pollutants in plants growing around such polluted areas. Reports have it that pollution stress alters leaf epidermal structures of plants exposed to air pollution (Gostin, 2009).

Stomatal complex types

Anisocytic stomata, branchyparacytic stomata, paracytic stomata and tetracytic stomata types were observed in *Abelmoschus esculentus* leaf samples collected from the unpolluted site whereas *Abelmoschus esculentus* sampled from the polluted site only had Anisocytic and Paracytic stomata types. *Carica papaya* samples from the unpolluted site had Anisocytic, tetracytic and paracytic stomata types while samples from the polluted site only had anisocytic and paracytic stomata types. Anomocytic and paracytic stomata types were observed in *M. indica* samples from the unpolluted site while samples from the polluted site had only paracytic stomata type. The absence of some stomata types in plants of the same species collected from the polluted site can be attributed to the ability of cement dust to denature and destroy plant stomata. Though these stomata types ought to have been naturally present in the sampled plant species, they are likely to have been destroyed or denatured by cement dust which was prevalent in the study area. This is in agreement with the findings of Vijaywargiya and Pandey (2003) who observed clogging of stomata, loss of one or both guard cells or total destruction of stomata apparatus caused by cement dust pollution in all the three species of flowering plants studied by them. Likewise, Kumar and Singh (1990) investigated the impact of stone crusher dust on *Mangifera spp* and reported absence of some

stomata types in plants grown on the polluted locations. Perhaps, some stomata types are more likely to be readily clogged, destroyed and denatured than others.

Trichome density

Trichome density was generally higher in samples collected from the vicinity of OCF (polluted site) than samples from the unpolluted site. This response could be an adaption to tolerate the high cement dust pollution in the area. Sharma and Davis (2001) reported increased trichome density and reduction in epidermal wall undulation as responses of *Parthenocissus quinquefolica* to cement pollution which enhanced its survival. Moreover, increased number of trichomes could be helpful in filtering out particulate matter and protects the leaf surface from detrimental pollutants which otherwise may enter the leaf and disrupt metabolic activities in the plant tissues. Meanwhile, increased number of long glandular, unicellular and stellate trichomes in *S. acuta* leaf has been reported by Ogunkunle *et al.* (2013a) as an adaptation to stress of cement dust pollution. In *Zea mays* it was observed that the trichomes were completely absent in the non-polluted region but in the polluted region unicellular trichomes were developed in the abaxial surface and their development were maximum at epidermal cells near stomata (Kumar and Pandey, 2011). This suggests that trichomes acts as protective cover against atmospheric pollutants especially particulate matter, so the pollutant could not gain entrance through the stomatal opening.

Stomata density

There were variations in the stomata density of samples collected from the vicinity of the cement factory and samples of same plant species collected from the unpolluted site. Stomata density were found to be higher on the abaxial epidermis than the adaxial epidermis. Likewise, stomata density was higher in samples from the polluted sites than the unpolluted sites for the studied plant species. The significantly higher stomatal density observed in both

leaf surfaces of samples from the cement polluted site is yet another adaptive response to the cement dust pollution. Increased stomatal density is considered an adaptability indicator to polluted environment (Kapitonova, 2002; Gostin, 2009). According to Yunus and Ahmad (1979), high stomatal density on plant leaves growing around polluted environments may be a response of the plants to the loss of matured and healthy stomata through the process of degradation caused by air pollution.

Stomatal size

Metcalf and Chalk (1988) and Beerling and Woodward (1997) reported that larger stomata gave lower stomatal density, while, smaller stomata gave higher stomatal density. This statement holds true in the plants examined, as samples collected from the polluted site which had higher stomata density were observed to have smaller stomatal size while samples from the unpolluted site earlier reported to have lower stomatal density had larger stomatal size. A reduction in the stomatal size of leaves has been reported to be responses to environmental stress. This seems to be an important strategy for controlling the absorption of pollutants by plant leaves (Gostin, 2009). The studied plants have shown response to the air pollution status of the study area by the reduction of their stomatal size. This most likely is a strategy of reducing the amount of pollutants entering the stomata during gaseous exchange. This modification has been reported to be peculiar to plants growing in environment with polluted atmosphere (Ogunkunle *et al.*, 2013a). The decrease in the stomatal size may also be an evasion mechanism against the suppression effect of pollutants on physiological activities such as photosynthesis and also portends quicker response to external stimuli (Verma *et al.*, 2006). According to Melo *et al.*, (2007) increased stomatal density coupled with decreased stomatal size can serve as an adaptive strategy for plants growing in environments with high atmospheric pollution. Thus, the higher stomatal density and the reduced stomatal size observed in this study are responses to the effects of cement dust pollution in the study area.

5.8 Soil-to-root transfer (Bioaccumulation Factor) of heavy metals in the studied plants

Some plant species have developed tolerance to heavy metal pollution and others (hyperaccumulators) are characterised by their ability to accumulate high quantities of metals in their tissues (Smical *et al.*, 2008) without visible damage to the plants. Hyperaccumulators are plants that achieve a soil to plant root metal-concentration ratio (bioaccumulation factor) and root to shoot metal-concentration ratio (transfer factor) greater than one. The accumulation of these metals may vary from one plant species to another and the physicochemical characteristics of the soil on which the plant is grown. The metal availability to plants depends on total concentration of metals in the soil and the forms in which they occur, pH, organic matter content, cation-exchange capacity, stage of growth of plants and microorganisms around the root zone (Lasat 2000). If these factors are constant, the uptake of a metal by different plant species may be comparable.

The ability of a metal species to migrate from the soil into plant roots is referred to as bioaccumulation factor (BF). Accumulation and distribution of heavy metals in plants depends on the plant species, the levels of the metals in the soil, the element species, bioavailability, and multiple other factors (Ogunkunle and Fatoba 2013). If the $BF > 1$, the plants have accumulated elements and $BF < 1$ show that plants exclude the elements from uptake (Olowoyo *et al.*, 2010). If the plants have higher BF values, they can be used for phytoremediation.

Bioaccumulation factor of *Abelmoschus esculentus*, indicated that Zn and Cu had $Bf > 1$. That is *Abelmoschus esculentus* has high Zinc and Copper accumulation from the soil to its root but less bioaccumulation of Cr, Cd, and Pb. The low uptake of Cr, Cd, and Pb from the soil to *A. esculentus* root indicates that the plant can tolerate high contaminations of Cr, Cd, and Pb in the soil. That is, there was restriction in the transfer of Cr, Cd and Pb into the roots

of *A. esculentus* despite the high bioavailability of these metals in the soil. This could be because of the high organic matter in the soil as there have been previous reports of organic matter playing an important role in limiting plant uptake of metals from the soil (Bolan *et al.*, 2003a). This implies that, *Abelmoschus esculentus* cannot be used in phytoextraction of Cr, Cd, and Pb since the bioaccumulation factor of these metals is less than 1.0 but can be used in phytoextraction of Zn and Cu since the BF is greater than 1.0. The Zn and Cu accumulation capacity of *A. esculentus* root reveals that *A. esculentus* can be used as a possible bioindicator of Zn and Cu pollution. Efficient uptake of Zn and Cu by plants of the Malvaceae family has been reported (Prasad and De Oliveira, 2003). Soil-root transfer of Cu and Zn in *A. esculentus* was above 1.0, indicating that *A. esculentus* is a good phyto-extractor of these heavy metals, this corroborates the findings of (Mendez and Maier, 2008; Garba *et al.*, 2012).

In *Zea mays* Bioaccumulation factor for Zn, Cu and Cr exceeded 1. That is Zn, Cu and Cr were efficiently taken up by *Zea mays* root, from the soil. Just as observed in *A. esculentus*, Zn and Cu are also efficiently transferred from soil to the root of *Zea mays*. The high Zn and Cr by *Zea mays* from the surroundings of the cement factory is in agreement with the high top soils Zn and Cr concentrations recorded around the mega factory. Cd had BF values that was above 0.5 in the polluted site and below 0.5 in the control an indication that Cd concentrations in the polluted soil has an influence on its uptake in the polluted sites. According to Sajjad *et al.*, 2009 if the BF of a metal is greater than 0.5, the plant will have a greater chance of the metal contamination caused by anthropogenic activities.

Transfer of metals from soil to the root of *Mangifera indica* was higher than 1 across the locations for Zn and Cu indicating that Zn and Cu had high transfer rate from soil to root. Zn and Cu are essential elements needed for plant growth. Chromium, lead and cadmium had transfer values < 1. The capacity of accumulating different heavy metals by different plant

species is related to the heavy metal content in soil and the alternative absorptivity to heavy metals Sajjad *et al.*, 2010. In this case, *Mangifera indica* being a perennial plant is more likely to have high absorptivity for the essential metals. Moreover, trees absorb less metal than fast growing plants like maize and okra according to Smical *et al.*, 2008. This can be attributed to activities of the woody root, which seems to act as a barrier for uptake of metals Khan *et al.*, 2009.

In *Carica papaya* Zn, Cu and Pb had BF values that exceeded 1 while Cr and Cd BF values were < 1. The BF for lead exceeded unity in the North and West axis of the factory. This can be justified by the presence of a high traffic density road that transverses through the northern and western axis of the factory. It has been reported by Fatoba and Iyeh, 2013 that uptake of lead by plants is enhanced by vehicular emissions on high traffic density road sides, since lead is an additive in fuel. Generally, as the distance from the source of pollution that is the cement factory increased, the bioaccumulation factor of most of the studied heavy metals in the plant sampled decreased.

Abelmoschus esculentus and *Mangifera indica* accumulated Cu, Zn excluded Cr, Cd, Pb; *Carica papaya* accumulated Cu, Zn, Pb excluded Cr, Cd while *Zea mays* accumulated Cr, Cu, Zn and excluded Pb, Cd. The present result agrees with the report by Jolly *et al.*, 2013 where the bioaccumulation factors for heavy metals were significantly higher for annual plants than perennial plants.

5.9 Transfer factor (TF) of heavy metals in the studied plants

The TF is an essential indicator that allows the assessment of mobility of heavy metals in plants (Zhao *et al.*, 2002).

TF = Concentration of metal in plant shoot

Concentration of metal in plant root

If the ratios >1 , the plant accumulated elements, if the ratio is 1 it indicates that the plants are not influenced by the elements, while ratios <1 show that plants excluded the elements from the been transferred from root to the aerial parts of the plant Olowoyo *et al.*, 2010. If the plants have higher TF values, it indicates higher suitability of the plant for phyto-extraction and phytoremediation of polluted soil. On the contrary, lower TF values indicates poor response of plants towards metal absorption and the plant can be used for human consumption Rangnekar *et al.*, 2013a.

The transfer of Zn and Pb from the root to the shoot of *Abelmoschus esculentus* in this study is less than one that is Zn and Pb have limited mobility within the plant body of *Abelmoschus esculentus*. Whereas the transfer factor of Cr and Cd from root to shoot of *Abelmoschus esculentus* is greater than one an indication that *Abelmoschus esculentus* in this study has high mobility of Cr and Cd within the plant body. These findings agreed with study carried out by Motior *et al.*, 2013. Thus there is no treat of Zn and Pb contamination via the consumption of A. esculentus grown around OCF. The high TF of Cr and Cd in A. esculentus indicates it can be used to phyto-extract Cr and Cd from polluted soils.

The transfer factor values of Zn, Pb and Cd in *Zea mays* is < 1 , this shows that these metals have limited mobility within the plant body. Cr and Cu had TF values that are > 1 an indication that Cr and Cu have high mobility within the plant body of *Zea mays*. This translates to Zn and Cu being highly mobile in *Zea mays* while Cr, Pb and Zn having limited mobility within the plant body. Which indicates that *Zea mays* plant can function as hyperaccumulator for Cr and Cu. The high level of these metals in the plant shoot might be due to direct deposition and foliar absorption in addition to translocation from roots to the upper part of the plant. This agrees well with the findings of Hong *et al.*, 2015 who reported

Zea mays as an accumulator of Cr, Ni and Cu when irrigated with waste water. Similar finding was also reported by Omolara *et al.*, 2019. Oladejo *et al.*, 2017 grew maize on dumpsites and had similar findings too. The annual plants had higher transfer factor among the studied plants.

The transfer factor of the studied heavy metals from the root of *Mangifera indica* to its shoot was such that, TF values were greater than 1 for Zn and Cu while TF values was less than 1 for Cr, Pb and Cd. Zn and Cu are essential for metabolism in plants, this may have necessitated their efficient transfer to the shoot of *Mangifera indica*. *Carica papaya* had Zn, Cr, Pb and Cu showing limited mobility owing to the fact that their $TF < 1$ while Cd was efficiently transmitted from root to the shoot of *Carica papaya* in this study because its TF value is > 1 . The concentration of heavy metals in soil depended mainly on the characteristics of the soil sample and the distance from the source of contamination. Uptake and accumulation of heavy metals by shoots and roots varied with heavy metal type and plant species. As these plants are widely consumed by humans, it is apparent that toxic elements can be easily transferred to human's body creating disruption in various biological systems.

5.10 Pollution status of the environment

The following deductions were made from the computed result for:

Geoaccumulation index of soils around Obajana cement factory. The soil of the study area is not Zn polluted as the Igeo values of Zn in the soil at all the locations were less than zero. In the same vain, the soil of the study area is not Cu and Cd polluted since the computed Igeo values were all less than zero. Conversely, soil of the study area has moderate chromium pollution, as the computed Igeo values for Cr at all sampled locations were greater than zero, this is in tandem with the Igeo values reported by Ogunkunle and Fatoba, 2014 around

Larfarge cement factory. The soil lead pollution of the study area had moderate pollution at W1 (0.07), N1 (0.43) and E1 (0.37) while soil of all other locations were unpolluted by lead.

The potential ecological risk of soils in the assessed vicinity of Obajana cement factory was such that; the potential ecological risk for Zn and Cd was low for all samples collected. Whereas potential ecological risk was moderate for chromium and lead. Soil samples the vicinity of Obajana cement factory were uncontaminated with Cd and Cu this agrees with the report of Loska *et al.*, 2003 who assessed the enrichment of heavy metals in cultivated soils around south Poland cement factory. Based on the Igeo result for Cd, all the samples were classified as unpolluted. Only Zinc, chromium and lead showed low to moderate contaminations in the various soil samples collected. Notably, the Cr and Pb pollution status in agricultural soil around the factory could possibly pose serious risks implication to human consumers that depends on crops grown on this soil as source of food. Previous studies reported the potential toxicity effects of Cr to exposed humans by its accumulation in food crops around industrial regions (Ordonez *et al.*, 2011; Zhao *et al.* 2018). However, the results of the CF showed that the soils in the area ranged from low contamination by Cd, Cu and Zn to moderate contamination by Pb and Cr. Overexposure to Cr by man could lead to kidney damage, bone loss and disruption of the olfactory system. Therefore, strategic action plans are needed to effectively deal with this emerging Cr pollution source.

5.11 Human health implications from ingestion of heavy metal laden vegetables/fruits growing around OCF

The daily oral intake (DOI) of a particular element must be below the chronic reference dose of that particular element because adverse health effects is not expected to occur except the human contamination is present at levels well in excess of response levels (Imray and Langley, 2001). From the computed HQ values, Zn and Cr portends adverse toxicological effects on humans through the consumption of *Abelmoschus esculentus* fruit grown around

OCF. This is evident in the Non-carcinogenic Hazard Quotients (HQ) for Cr and Zn that were greater than unity in the varying axis of the factory. The resultant exposure level to these metals (Cr and Zn) were greater than the toxicity values (USEPA, 2010) thus making the single hazard quotient to exceed unity. The people living in the vicinity of OCF are at health risk of Zn and Cr toxicity through oral exposure by ingesting *Abelmoschus esculentus* fruit grown around the factory. This is because the daily oral ingestion estimated was a little greater than the oral chronic reference dose (RFD) for Cr and Zn (USEPA, 2010). This translates into non-carcinogenic hazard quotient (HQ) that was greater than unity which poses high-non carcinogenic risk. A similar finding was reported by Benoff *et al.*, 2000 in their study of human health implications from exposure to some heavy metals taken up by crops grown on polluted soil. Although, Zn is essential to humans but high doses especially above reference doses can cause acute effects such as; gastrointestinal irritation, weakness, anorexia, anaemia, diminished growth, loss of hair, lowered food utilization, changes in the levels of liver and serum enzymes, morphological and enzymatic changes in the brain, and histological and functional changes in the kidney (Wuana and Okieimei, 2011). There was no health risk to the inhabitants around OCF to Pb, Cd and Cu toxicity through oral exposure by ingesting *Abelmoschus esculentus* fruit grown around the factory. This is because the daily oral ingestion estimated was less than the oral chronic reference dose (RFD) for Pb, Cd and Cu (USEPA, 2010). This translates into non-carcinogenic hazard quotient (HQ) that was less than unity which poses low-non carcinogenic risk.

Consumption of *Zea mays* fruit grown around Obajana cement factory, possess the risk of Zn and Cr toxicity through oral exposure by ingestion. This is because the daily oral ingestion estimated was greater than the oral chronic reference dose (RFD) for Cr and Zn (USEPA, 2010). This translates into non-carcinogenic hazard quotient (HQ) that was greater than unity which poses high-non carcinogenic risk. There was no health risk to the inhabitants around

OCF to Pb, Cd and Cu toxicity through oral exposure by ingesting *Abelmoschus esculentus* fruit grown around the factory. This is because the daily oral ingestion estimated was less than the oral chronic reference dose (RFD) for Pb, Cd and Cu (USEPA, 2010). This translates into non-carcinogenic hazard quotient (HQ) that was less than unity which poses low-non carcinogenic risk. This findings agree with the report of Caspah et al., 2016 who assessed the human health risk occasioned by the consumption of some annual crops grown around kpako cement factory, South Africa

Health risk resulting from human consumption of *Mangifera indica* fruit grown around Obajana cement factory could occur due to Zn mainly and Pb for *Mangifera indica* fruit grown in the northern axis of the factory. This agrees with the report of El-Abssay *et al.*, 2011 who observed high Zn and Pb levels in cement industry workers that eats fruits grown around the cement facility. While the consumption of *Carica papaya* fruit grown around Obajana cement factory exposes the consumers to the risk of zinc toxicity, lead toxicity from *Carica papaya* fruit grown grown in the north and west axis of the factory and chromium for *Carica papaya* fruit grown grown

In the western axis of the factory, the daily oral intake of Cr in the population was higher than the RfD (0.003 mg/kg/day) (USEPA, 2010) and this ought to be urgently attended to as Cr is a highly toxic heavy metal; its mutagenic and carcinogenic and its high oxidation state enhance its ability to move into living cells (USATSDR, 2000). (Tadesse *et al.*, 2006; El Nemr *et al.*, 2008). Chromium is an essential micronutrient for the normal energy metabolism of humans and animals (Kabata-Pendias and Mukherjee, 2007), however, people exposed to chromium at high doses can suffer from dermatitis and many allergic and eczematous reaction (Isikli *et al.*, 2003).

There was no health risk for Cd and Cu toxicity in the human populations around OCF through ingestion of crops grown around the factory. This was evidently observed in the daily oral intakes for Cd and Cu which was less than the reference oral dose and consequently resulted in HQs that were less than one indicating that there is no health risk associated with Cd and Cu in the assessed crops grown around the factory. Normally, when the daily dose is less than the RfD there will be no likely associated adverse health risks, thus it's less likely to pose a regulatory concern (enHealth, 2002). As the magnitude of the exposures exceeding the RfD increases, the probability of adverse effects in a human population increases (enHealth, 2002).

Oral ingestion in addition to dermal contact and inhalation of contaminated dust might have contributed significantly to the spread of diseases in the area as reported by Afolabi *et al.* 2012.

CHAPTER SIX

SUMMARY, CONCLUSION, RECOMMENDATIONS AND CONTRIBUTIONS TO KNOWLEDGE

6.1 Summary of findings

The result of the physicochemical analysis of soil collected from the vicinity of the cement factory shows that; Soil in the vicinity of the cement plant was moderately acidic to slightly alkaline and slightly acidic to moderately alkaline during the rainy and dry seasons respectively. Soil organic matter content was higher in the rainy season than in the dry season. This could be occasioned by lower soil moisture during the dry season, thus, microbial decompositions of organic matter was retarded during the dry season. The soil

organic matter content for the three axis was in the order of North > West > East in the dry season and West > East > North in the rainy season. Soil organic matter was found to gradually increase in percentage as distance from factory increases in both seasons.

Cement production also impacted the heavy metal levels in soil obtained from the vicinity of the factory as the concentration of heavy metals in this study exceeded what was obtainable in the soil of the surroundings of this mega factory before the commencement of cement production by the factory as contained in the EIA report. Generally, higher concentrations of heavy metals were observed in the 1km distance than in the 3km distance except for Zn whose peak concentrations was at 3km distance from the factory. This can be attributed to the efficient mobility of Zn in the soil as reported by some study. The decrease in metal concentrations as distance from the factory increases is an indication that the metals are being discharged from the activities of the factory. Chromium, cadmium and copper levels of the sampled soil was high in the eastern axis, where the quarry is located. The highest concentrations of Pb and Zn were found in the samples from the north and west axes of the factory. This could be premised on the high traffic density road that transverses the north and west of the factory. The highest concentrations of chromium was recorded in the samples collected nearest to the cement factory and had no bias for axes to the cement plant. Also, the concentrations of the studied heavy metals were higher in the soil around the cement factory in the dry season than in the rainy season

Comparison of metal levels in the soil of the study area to target values for remediation by the Department of Petroleum Resources (DPR, 2002), and the Canadian Council of Ministers for Environment (CCME) guidelines for heavy metals in agricultural soils showed that; Chromium levels far exceeded the CCME permissible limits. While Cr concentrations in the unpolluted site (a distance of about 50Km from the factory) were below the DPR, 2002 and

CCME permissible limits. The concentration of Pb in the soil of the study area is about the same as the permissible limits of the standards used for comparison. The average concentrations of the other quantified heavy metals (Zn, Cd and Cu) were below the CCME and DPR limits.

Heavy metal concentrations in the examined plant species (*A. esculentus*, *Z. mays*, *M. indica*, *C. papaya*) varied. Uptake of metals by the crops was recorded in the order of Zn>Cr>Pb>Cu>Cd. Generally, the results showed that among the metals studied, the accumulation levels of Zn and Cr in *Zea mays* plant parts were above the maximum levels as stipulated by FAO/WHO 2001. Thus, heavy metal contaminants (particularly, Cr and Zn) found in soils on which *Zea mays* was cultivated constitutes to its heavy metal pollution levels

All five Zn, Pb, Cr, Cd, Cu heavy metals accumulated in different amounts in the root, leaves and fruit of *Abelmoschus esculentus* plants. Heavy metal accumulation was significantly higher ($p < 0.05$) in all the samples from the vicinity of the factory in comparison to samples from the unpolluted site. The concentrations of Zn, Cu and Cd in *Mangifera indica* samples from the polluted site was well below the FAO/WHO 2001 permissible limit.

Anatomical studies of the leaves of the examined plants showed some adaptations to the cement dust pollution in their environment. The absence of some stomata types in plants of the same species collected from the polluted site can be attributed to the ability of cement dust to denature and destroy plant stomata. The leaf epidermal modification or responses were evident in trichome density, stomatal density, stomatal index and stomata size. Trichome density was generally higher in samples collected from the vicinity of OCF

(polluted site) than samples from the unpolluted site. Increased number of trichomes could be helpful in filtering out particulate matter and protects the leaf surface from detrimental pollutants which otherwise may enter the leaf and disrupt metabolic activities in the plant tissues.

Computed Bioaccumulation factor (BF) of the studied plant species shows that *Abelmoschus esculentus* has high Zinc and Copper accumulation from the soil to its root but less bioaccumulation of Cr, Cd, and Pb. That is *A. esculentus* can tolerate high contaminations of Cr, Cd, and Pb in the soil. This implies that, *Abelmoschus esculentus* cannot be used in phytoextraction of Cr, Cd, and Pb since the bioaccumulation factor of these metals is less than 1.0 but can be used in phytoextraction of Zn and Cu since the BF is greater than 1.0. Zn, Cu and Cr were efficiently taken up by *Zea mays* root, from the soil. *Abelmoschus esculentus* and *Mangifera indica* accumulated Cu, Zn excluded Cr, Cd, Pb; *Carica papaya* accumulated Cu, Zn, Pb excluded Cr, Cd while *Zea mays* accumulated Cr, Cu, Zn and excluded Pb, Cd. The annual plants (*Abelmoschus esculentus* and *Zea mays*) had higher transfer factor than the perennial plants (*Mangifera indica* and *Carica papaya*). It was generally observed that Zn, Cu and Cd posed very minimal ecological risk while moderate ecological risk was recorded for Pb and Cr in the vicinity of Obajana cement factory.

From the computed HQ values, Zn and Cr portends adverse toxicological effects on humans. This is evident in the Non-carcinogenic Hazard Quotients (HQ) for Cr and Zn that were greater than unity in the varying axis of the factory.

The people living in the vicinity of OCF are at health risk of Zn and Cr toxicity through oral exposure by ingesting crops grown around the factory. This is because the daily oral ingestion estimated was a little greater than the oral chronic reference dose (RFD) for Cr and Zn (USEPA, 2010). There was no health risk to the inhabitants around OCF to Pb, Cd and Cu

toxicity through oral exposure by ingesting crops grown around the factory. This is because the daily oral ingestion estimated was less than the oral chronic reference dose (RFD) for Pb, Cd and Cu (USEPA, 2010).

6.2 Conclusions

The results of soil physico-chemical parameters revealed that the soil samples from the control site possess better soil quality compared to that collected from different sites around the cement plants. The soil pH of the study area before the commencement of cement production was generally acidic. However, due to the continuous deposition of cement dust soil pH is currently, slightly alkaline. The values of soil organic matter increased significantly with increasing distance from the factory sites whereas there was a decrease in pH, electrical conductivity with increasing distance from the factory. The effect of dust deposition on soil was more pronounced in the areas nearer to the cement plants. Based on this findings, it can be concluded that if such trend of dust deposition continues, soil properties of a vast area around the cement plants are likely to change in terms of its physico-chemical properties. These changes will in turn have multiple deleterious effects particularly on agriculture, flora and fauna of the area in the near future.

The heavy metal pollution of soil around Obajana cement factory was found to be slightly higher in the dry seasons than in the rainy season. Metal concentration of the soil was generally within the permissible limits except for Chromium and lead in some hot spots.

Crops grown around the factory (*Abelmoschus esculentus*, *Zea mays*, *Mangifera indica* and *Carica papaya*) all bioaccumulated heavy metals from the soil at varying degrees. The soil of the study area is moderately Zn and Chromium polluted and showed lead pollution at some hot spots mostly located in the north and west axis of the factory. There is health concern arising from the consumption of *Zea mays* fruit because of its observed Cr content and the

other investigated crops owing to Zinc contamination and lead contaminations mainly in crops grown on the northern axis of this mega factory. This portends hazard not only to Obajana community but also to commuters who buys and consume some of these fruits sold along the ever busy Lokoja/ Kabba road that transverses right infront of this mega cement factory.

6.3 Recommendations

- Planting of food crops should not be carried out at distances less than 4Km from the factory to avert the health hazards that could occur from consuming heavy metal laden crops.
- Remediation process be put in place to reduce Zn, Cr and Pb levels in vast agrarian soil around Obajana cement factory.
- The operators of the factory should be encouraged to take environmental protection measures that will mitigate the quantity of cement dust discharged into the atmosphere by from their cement production activities.

6.4 Contributions to knowledge

1. The present study provides comprehensive information on the heavy metal pollution status of soil around Obajana cement factory, in Kogi state. Studies on the metal pollution status of agrarian soil around the factory is unavailable before now despite the gigantic size of this cement producing facility.
2. The comparison of physicochemical parameters of the soil in the vicinity of the cement factory with what was reported during the EIA of the same factory gives credence to the fact that cement production alters the physicochemical parameters of soil in the environs of the factory.

3. It has been confirmed by this study that annual plants (*Abelmoschus esculentus* and *Zea mays*) bio accumulates heavy metals more than perennial plants (*Mangifera indica* and *Carica papaya*) grown on same metal polluted soil.
4. Information has been provided on some anatomical modifications in (*Abelmoschus esculentus*, *Zea mays*, *Mangifera indica* and *Carica papaya*) leaves occasioned by cement dust pollution. A bio indication that the dust load is beginning to affect sedentary life forms around the factory.
5. Earlier before now, it has not been proven that consumption of *Zea mays* grown around Obajana cement factory could cause Cr poisoning; this vital information has been revealed by this study.
6. This study discovered that the Pb level of soil around Obajana cement factory, is at the verge of exceeding the permissible limit thus measures should be put in place to check and avert impending lead poisoning in Obajana community.
7. The present work is the first to report heavy metal status of commonly consumed food crops (*Abelmoschus esculentus*, *Zea mays*, *Mangifera indica* and *Carica papaya*) grown in the immediate vicinity of Obajana cement factory, Kogi State.

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