THE IMPACT OF GAS FLARING FALLOUT ON CASSAVA FLOUR DRIED AROUND GAS FLARING SITES IN DELTA STATE.

BY

IKWUAKOLAM, INNOCENT MADUABUCHI (B.Eng.)
REG. NO: 20114774188

A THESIS SUBMITTED TO SCHOOL OF POSTGRADUATE STUDIES FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE (MASTER OF SCIENCE) M.Sc. DEGREE IN ENVIRONMENTAL TECHNOLOGY

DECEMBER, 2015

CERTIFICATION

I certify that this work entitled " THE IMPACT OF GAS FLARING FALLOUT ON CASSAVA FLOUR DRIED AROUND GAS FLARING SITES IN DELTA STATE " was carried out by IKWUAKOLAM, Innocent Maduabuchi (Reg No 20114774188) in partial fulfillment for the award of the degree of (M.Sc. in Pollution Control Technology in the Department of Environmental Technology) of the Federal University of Technology, Owerri.

---------------------------- 9/5/16
Dr. P. C. Njoku **Date**
(Supervisor)

---------------------------- 9/5/16
Dr C. O. Nwoko **Date**
(Head of Department)

---------------------------- ----------------------
Professor R. N. Nwanbueze **Date**
(Dean, School of Environmental Technology)

---------------------------- ----------------------
Engr. Prof. (Mrs) K. B. Oyoh **Date**
(Dean, Post Graduate Studies)

Prof. F. E. Ezeonu ----------------------
(External Examiner) **Date**

DEDICATION

This thesis is dedicated to Almighty God for His guidance and protection throughout my education.

ACKNOWLEDGMENT

A big thanks to my Supervisor, Dr. P. C. Njoku who has been there for me. Also I commend his academic prowess and patience. I thank you for your patience, understanding and thorough supervision of my work. I thank my ever ready Head of Department (HOD) Dr C. O. Nwoko for his leadership disposition, God bless you sir. I thank my lecturers who taught me in my masters programme Dr P.C.Njoku, Dr E.E. Nkwocha, Dr. (Mrs) S.M.O. Akhionbare, Dr A.O. Nnaji, Dr J.D. Njoku, Dr C.O. Nwoko and Dr. (Mrs.) C.G. Okoli and the entire academic staff of Environmental Technology Department. I also thank the non academic staff, my course mates, my course representative Edo Friday A and all my well wishers. I owe a lot to my parents Mr. and Mrs. Ikwuakolam and my siblings for their prayers and support. I thank my friends and well wishers. God bless you all.

TABLE OF CONTENTS

CHAPTER ONE

CHAPTER TWO

CHAPTER THREE

CHAPTER FOUR

CHAPTER FIVE

LIST OF TABLES

LIST OF FIGURES

Figure **page**

ABSTRACT

This study investigated the impact of gas flaring fallout on cassava flour (Tapioca/kpokpo garri) dried around gas flaring sites in Delta State was undertaken. The test samples used for the analysis were obtained from a farm at Ogbe Avenue off PTI Road; Effurun. Three (3) samples A, B and C were obtained. Sample A was dried at PAN OCEAN flare site Oghara, while sample B was dried at AGIP flare site Kwale and sample C, which is the control was dried in an oven in the laboratory. The processed (dried) samples were analysed for Nickel, Vanadium, zinc, arsenic, iron, copper and Carbon deposit, using Atomic Absorption Spectrophotometer (AAS) and Titrimetric Method. Nickel was 0.3ppm, zinc 0.001 ppm, arsenic 0.80ppm, copper 0.01ppm, iron 0.39ppm and that of vanadium was 0.03ppm; sample B, nickel was also 0.37ppm, zinc 0.001ppm, arsenic 0.9ppm, copper 0.02ppm, iron 0.29ppm and vanadium was 0.04ppm. However, that of carbon deposit had 6.85ppm in sample A and 8.32ppm in sample B. The Crowcon Gasman Air Monitor that had been pre-calibrated using air cylinder standard was used in the direct detection of oxides of sulphur, oxides nitrogen, volatile organic compounds and ozone (SOx, NOx, VOC and O_3) 0.001, 0.01, 0.018, 0_3 respectively. *In-situ* test was used to measure the ambient air around the flaring stack. Hand-held Testrel 4500 weather Tracker, a high precision *in-situ* weather monitoring equipment was used in the determination of ambient temperature, wind speed and relative humidity. The study was carried out at the sampling points and the readings were obtained. It was noticed that all the samples analysed were within the permissible limit. Though the analysed parameters were within permissible limits, constant monitoring should be done.

Key words; Impact, gas flaring, fallout, analysis, samples, ambient temperature, *in situ,* parameters, permissible limits, monitoring.

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND OF STUDY

The flaring of natural gas has continued to generate interest due to the widespread nature of its confirmed and imagined physical, biological and socio-cultural environmental impacts.

Flaring of natural gases in Nigeria by upstream oil producing companies happens to be a source of worry and a pertinent aspect of the global environmental concern. There can be no wholesome environmental protection if gas flaring and its resultant emissions are allowed to assume an increasing tempo.

Inhabitants of this gas flaring communities make use of heat generated from this flare for many things. The emitted gases and compounds in the atmosphere generate heat around flare stacks, a phenomenon that could induce insomnia, especially in the night (since the area is permanently bright red like day light). Depositions from the gas flaring could either be wet or dry, depending on the state of matter in which it is incorporated and transported (US EPA, 2003). Wet depositions are commonly in the forms of acid rain, fog, and snow, while dry depositions are in the forms of acidic gases and particles.

Acid rain refers to a precipitation that has a pH less than 5.6 (the pH of unpolluted water is <5.6) (Cowling, 1982). About half of the acidity in the atmosphere falls back to the earth through deposition. The dry depositions from the stack are blown farther away and could be washed by rainstorms. Runoff water add those acids to the acid rain, thus, making the combination more acidic than the falling rain alone and is introduced both in deeper soils and on the aquatic habitat (US EPA, 2003).The acidity of rainwater is increased by the presence of particulate matter, which may contain trace metals such as As, Pb, Cd, and Hg that could alter pH (Oghenejoboh, 2005). Overall, acid deposition causes a cascade of effects or kills individual edaphic or aquatic organisms (depending on the ecosystem), reduce their population, completely eliminate their species and decrease overall biodiversity (Ogwejifor, 2000; US EPA, 2003).

Various stages are undergone in the production of cassava flakes (tapioca). It involves the process of peeling a harvested cassava from the tuber. This peeled cassava tuber is washed thoroughly with water. After washing, the cassava tubers are ground with a milling machine which reduces the cassava tuber to fine, whitish slurry. This whitish slurry is a combination of starch and particulates substance. The solid substance is used to produce either tapioca or garri.

In producing tapioca, the starch content is extracted to a zero value if possible. This is achieved by putting this whitish grounded cassava into a sack and squeezed with the substance inside to extract the starch through the pores of the sack. The solid substance is cooked for about 10-15 minutes before it is then molded to different sizes and shapes (mostly of irregular shapes). These irregular shaped, molded substances are then spread on a mesh and spread around the flame from flare site. The molded substances when dried are referred to as TAPIOCA.

1.2 AIM AND OBJECTIVES

The aim of this research is to determine the presence of pollutant fallouts from the gas flaring sites at Oghara Efe and Kwale plants. The following objectives were used in achieving this aim:

1. To determine the quantity of carbon (carbon black) on the cassava flakes (tapioca) spread near gas flare sites for drying.

2. To determine the concentration of heavy metals (Nickel,vanadium, zinc, arsenic, iron and copper) deposited on cassava flakes (tapioca) as a result of drying it around gas flaring site.

3. To determine the levels of oxides of sulphur, oxides of nitrogen, volatile organic substance and ozone (SO_X, NO_X, VOC, O_3) and some physicochemical parameters such as pH and temperature.

4. To compare results with some regulatory standards

1.3 SIGNIFICANCE OF STUDY

The significance of this study cannot be over overemphasized, especially in the face of increasing oil exploration and exploitation and in the environment.

Results from this research could serve usefulness in the following areas:

- A guide to highlight the hazards or dangers associated with the consumption of contaminated food.
- A means to draw government's attention to enforce legislation on gas flaring activities of oil producing companies.
- An effort to provide relevant data to the company as a basis for advising their management to install an effective and efficient method in preference to the current management method used.

- A means to provide necessary information to government health workers in a bid to policing a sound and healthier environment for the people of Oghara Efe and Kwale communities in particular and the State in general.

1.4 SCOPE AND DELIMITATION

This project work is limited to the determination of carbon deposits (sooth), the concentration of heavy metals (Nickel,vanadium, zinc, arsenic, iron and copper) deposited on cassava flakes (tapioca) dried around gas flaring sites at Oghara Efe and Kwale and also levels of oxides of sulphur, oxides of nitrogen, volatile organic substance and ozone (SO_X, NO_X, VOC, O_3) and some physicochemical parameters such as pH and temperature of the ambient air around the gas flare sites.

CHAPTER TWO

2.0 LITERATURE REVIEW

Humans populate every corner of the earth, and change the environment to suit their needs. Technological advances, industrialisation, pollution and the population explosion cause the destruction of large parts of the natural environment. We build factories, industries and houses, and plant food. In the process we produce tons of waste. This waste must be disposed of and this is not always done with consideration for the environment and future inhabitants. Pollutants are dumped in the water, air and soil, affecting the biosphere. By contaminating our environment with pollutants, the health of all living organisms suffers. Pollutants cause many health problems like asthma, respiratory tract infections, allergic reactions, headaches, nasal congestion, eye and skin irritations, coughing and sneezing, fatigue, nausea and cancer. It is the responsibility of the national and local governments to ensure that the environment is kept pollution free, with policies which stipulate rules and regulations. They also conduct impact studies to establish how community practices impact the environment and formulate ways in which to ensure a sustainable and healthy environment and development (Fereidoun *et al*, 2007; Progressive Insurance, 2005). According to Ma *et al*. (1994), Calvert (1990) and Fergusson (1990), trace metal accumulation in soils is of concern in agricultural production due to the adverse effects on food quality (safety and marketability), crop growth (due to phytotoxicity), and environmental health (soil/fauna and terrestrial animals

The major problem is the reconcentrations of these harmful substances in natural food chain Osu *et al* (1990).

Contamination of food can take place at any stage in the production chain (i.e. from the raw materials, processing, packing, transportation, storage or marketing) to consumption. Because of improper processing, handling and storage of these foods could be subject to contamination by micro organism, metals as well as pesticides. Obviously, data on the concentrations of metals in food items at the point of consumption are necessary for estimation human exposure to metals (Iwegbue, 2011). The concentration of metals in foods are of great importance because of the wide role of metal ions in health and diseases which include the requirement for intake of essential trace elements to the toxicity associated with metal overload (Hague *et al*., 2008). Certain metals (e.g. Cd, Pb) cannot be tolerated at low concentrations because they are exceptionally toxic to human (Suppin *et al*., 2006). For example, the toxicity of heavy metals could be by the displacement of physiologically appropriate metal: Cd can replace Cu and Fe in cytoplasmic and membrane proteins. Especially in divalent form, the free metal ions can promote the generation of superoxide and hydroxyl radical which, in turn, can lead to oxidative damage of lipids, nucleic acids and proteins (Marias and Blackhurst, 2009). Cd has been linked to skeletal damage (Jarup, 2003). Cd and Pb are known to harm the reproductive system and embryonic development. The physiologic roles of essential metals are well known e.g. Fe (haem moieties of hemoglobin and cytochromes), Cu (amine oxidases, caeruloplasmin, dopamine hydrolase and collagen synthesis), Mn (superoxide dismutase), Zn (protein synthesis, stabilization of DNA and RNA) with low requirement of Cr (glucose homeostasis) (Marias and Blackhurst 2009). The physiologic roles of essential metals are due to the fact that these metals are components of enzymes and proteins. The deficiency of these elements could induce disease conditions e.g. Cu deficiency is known to induce hypertension, increase blood cholesterol (hypercholesterolemia) and low density lipoproteins fraction increment in blood which add to the conditions favouring heart attack. Deficiency of manganese has been associated with chronic disease like osteoporosis, epilepsy and diabetes mellitus. The intake of essential metals above threshold limits could cause toxicity problems. For example, epidemiological studies have shown that there is a link between excessive intake of dietary Zn and increase in prevalence of obesity and associated diseases (Singh and Taneja, 2010). As in Nigeria and many other countries, ready-to-eat foods (meat pie, sausage rolls, burger, moin-moin (black eyed pea cake) etc) make up a significant proportion of the daily food intake. A survey of literature reveals only a few studies of Nigerian foods for metal contents and these studies are limited in the scope of the elements and foods surveyed (Okoye 1994; Onianwa *et al.*, 1999; Onianwa *et al.*, 2001; Iwegbue 2011). Onianwa *et al*. (2001) examined the levels and daily intake of Cu and Zn from confectioneries (sweets, biscuits and breads). At present, there is paucity of information on the elemental composition of ready-to-eat foods consumed in southern Nigeria and no study has reported the individual and combined target hazard quotient values for common confectioneries. This study give a comprehensive evaluation of heavy metal concentrations, daily intake and long life exposure to metals from consumption of ready-to-eat food with a view to providing information on the risk associated with consumption of tapioca.

CARBON DEPOSIT (sooth)

Sooth consist of elemental carbon with variable amounts of volatile matter and ash, It is produced by the partial combustion or the thermal decomposition of natural gas or petroleum distillates and residues.

TOXICITY OF CARBON DEPOSIT (sooth)

The biggest problem associate with carbon black emitted when fuel or natural gas is burnt is the presence of substances other than the carbon that gives its fuel value. This substance associated with the carbon black is about 3% sulphur and 10% ash. This sulphur combines with Oxygen to make sulphur dioxide.

The sulphur in this carbon black ultimately becomes sulphuric acid.

This is shown in the equation below:

$S + O_2 \qquad SO_2$

$SO_2 + \frac{1}{2} O_2 \qquad SO_3$

$SO_3 + H_2O \qquad H_2SO_4$

This sulphuric acid produced is detrimental to health andshould not be in contact or come to contact with food materials or drinking water.

Heavy metals such as lead, Mercury, Cadmium and Nickel have not been shown to be essential for human life but due to man's activities, re found in large amount in the environment. Heavy metals can be classified as toxic and non-toxic depending on its role in the function of human body and other biological systems. Organiometallic derivates of mercury, calcium, Nickel and leads are often volatile and may get into human tissue through inhalation. Toxic heavy metals are associated with various forms of diseases of the brain, cardiovascular, nervous system, kidney and general behaviour disorder.

Heavy metals such as copper, zinc, cobalt, selenium and nickel have received much attention because of their toxic effect on fishes, crops and livestock. The direct negative impact of these heavy metals on man has arisen much interest largely because they are often present in food and drinking water in levels that may be required for nutritional purposes.

It refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration (Agarwal, 2009). The term “trace” metals identifies the low concentrations that these elements are required for biological utilizations. However, the two terms could be inter-used. Example of heavy metals include Mercury (Hg), Nickel (Ni), cadmium (Cd), Aluminum (Al), chromium (Cr), lead (Pb), copper (Cu), Arsenic (As), Zinc (Zn), iron (Fe), etc. Heavy metals are natural components of the earth’s crust and cannot be degraded or destroyed.

To a small extent they enter our bodies through food, drinking water, and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body (Sharma, 2006).

However, at higher concentrations, they can result to poisoning. Heavy metal poisoning could result, for instance, from drinking water contamination (e.g. lead pipes), high ambient air concentrations near emission sources (Oghenejoboh, 2005) or intake via the food chain (Aremu *et al.*, 2010).

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological, compared to the chemical's concentration in the environment. According to Idodo-Umeh and Ogbeibu, (2010), heavy metal compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Increasing urbanization and technological advancement are twin contributors of pollutants, including heavy metals in the environment at high concentrations.

Soil represents the major repository of trace element over geologic time. On a worldwide basis, soil exhibits an average composition close to the crust, but the near surface parent materials from which soils are derived are not uniform and soil forming processes differ markedly from one climatic region to another (accounting for considerable overall variability in heavy metals concentration) (Arun *et al*., 2005).

Heavy metals, such as Cd, Cu, Pb, Cr and Hg are important environmental pollutants, particularly in areas with high anthropogenic pressure. Their presence in the atmosphere, soil and water, even in traces, can cause serious problems to all organisms. Heavy metal accumulation in soils is of concern in agriculture production due to the adverse effects on food quality (safety and marketability), crop growth (due to phytotoxicity) and environmental health (soil flora/fauna and terrestrial animals)(Zhuang *et al*., 2009).

The mobilization of heavy metals into the biosphere by human activities has become an important process in the geochemical cycling of these metals. This is acutely evident in urban areas where various stationary and mobile sources release large quantities of heavy metals into the atmosphere and soil, exceeding the natural emission rate (Ogbonna *et al.*, 2009). Heavy metal bioaccumulation in the food chain can be highly dangerous to human health. These metals enter the human body mainly through two routes namely, inhalation and ingestion; with ingestion being the main route of exposure to these elements in human population (Aremu, *et al.*, 2010). Heavy metals in-take by human population through the food chain has been reported in many countries with this problem receiving increasing attention from the public as well as governmental agencies, particularly in developing countries, (Idodo-Umeh and Ogbeibu, 2010).

Aerosols contain different toxic metals which fall on the soil and are retained in the top few centimeters and are subsequently carried down by leaching, presumably due to their interaction with soil colloids (Arun *et al.*, 2005). They are therefore liable to be quite persistent in the soil. Once deposited, metal-containing materials are subject to chemical and microbial modifications. With metal solubility, ultimately approach in the thermodynamic equilibrium with native soil minerals and organic matter, the rate and extent of solubilization are governed by the physicochemical properties of the deposited mineral, soil processes and properties (Graig, 1987).

Particulates arising from fossil fuel combustion, metal smelting operation etc may be expected to be largely insoluble in soil solution. Hydrolyzable metals (for example nickel, cadmium) or metal forming insoluble precipitate with sulphur and phosphorous on entering the soil-soluble form may be expected to be rapidly solubilized at near neutral pH of most soil due to hydrolysis on dilution and subsequent precipitation on, or reaction with particle surface (Graig, 1987). Certain elements (for example iron) may also form precipitates with sulphur or phosphorus.

Metals with low ionic potential tend to form primarily simple soluble ion while metals with intermediate and high ionic potentials tend to form soluble complex. Common inorganic complex forming ions in the soil solution include CO_3^{2-}, HCO_3^- SO_4^{2-}, HS^-, OH^- and Cl^-. Soil microorganism may play an important role in this process through the production of soluble ligands with high affinity for metals (Arun,*et al.*, 2005).

Soil physicochemical parameters that are most important in influencing the solubility of metals include soil composition (inorganic or organic), pH, type and density of change on soil colloids and reactive surface area (Graig, 1987). These phenomena will be dependent upon soil properties, including metal concentration and form; particles size distribution, quantity and reactivity of hydrous oxides, mineralogy, degree of aeration and microbial activity (Sharma, 2006).

Observation shows that the mobility of heavy metals decrease in soil with inorganic matter, as compared to the soil will decomposed organic matter. This may be due to the high adsorption capacity of the soil organic matter associated with clay particles due to clay-meal soil-organic matter interaction (David and Peter, 1987). The mobility order observed was Ni <Mn Cr < Cu <pb. This trend in the reverse order of their binding capacities with soil organic matter means that there will be decrease in mobility (Sharma, 2006).

Disposal of industrial, as well as domestic sewage sludge and domestic wastes on land is a common practice. One of the major problems with land disposal of sludge is the likely introduction of heavy metal in the soil. In general, sludge solution appears to increase the mobility of trace element in soil. Increase in mobility of trace elements is often attribute to a combination of factors, including complexation by dissolved organic, inorganic ligand, high background concentration of metals and other ions and high ionic strength of amended soil solution.

The bioavailability and mobility of metals in soil system are functions of the metal species in soil solution and the distribution of metals in the soil solid component (Zhuang *et al.*, 2009).

2.1. Heavy Metals and Soils

Heavy metals are considerable environmental concern due to their toxicity and accumulative behaviour (Purves, 1985; Omgbu, 1992). Trace quantities of certain heavy elements are essentially assimilable and accumulate in ecological materials (Nurnberg, 1984) such as soil. According to Kakulu (1985) and Omgbu and Kokogho (1993), comprehensive studies of trace metals in various Nigerian crude oils have shown them to contain relatively high concentrations of Fe, Cu, Zn, Pb and Hg. Associated gases, when flared could release these pollutants as outfalls on soil (Ademoroti 1996; Ogundipe, 2006) and such could exert adverse effects on edaphic variables and biota necessary for soil health (Adesiyan, 2005). The contaminants could further infiltrate ground water aquifers (Ogbonna *et al.,* 2006) and so pose public health hazards (Ogbonna *et al*., 2008). A salient case of public health danger from trace metals poisoning of the environment is the recent leadpoisoning reported by the June 26th edition of the Saturday Sun Newspaper; whereby many deaths were recorded (and still counting) (Saturday Sun, 2010).

Contaminated soils could result in decline in crop productivity and sustainability (Hart *et al.*, 2005). Trace metals have bioaccumulation potential due to their persistence in the environment. This attribute enables them to get translocated along the food chain, albeit in small doses. Over time they accumulate and magnify across the trophic levels to pose serious health hazards to tertiary consumers such as man (Agbaire and Esiefarienrhe, 2009).

Heavy metals absorption is governed by soil characteristics such as pH ands organic matter content (Agbogidi *et al.*, 2006). This thus portend that high levels of trace metals in soil may not always indicate similar high concentrations in plants, as the extent of accumulation will depend on the plant and trace metal species under consideration (Hart *et al.*, 2005). In an investigation of the uptake of Cd, Cu. Ni and Pb from air and soil by milfoil (*Achilleamillefolium*) and barley (*HordeumVulgare*) in Denmark, it was concluded that Cu and Pb plant concentrations correlated with aerial deposition but not with soil concentrations. In contrast, Ni and Cd contents in plant correlated with deposition and soil content (Hart *et al*., 2008).

According to Ma *et al*. (1994), Msaky and Calvert (1990) and Fergusson (1990), trace metal accumulation in soils is of concern in agricultural production due to the adverse effects on food quality (safety and marketability), crop growth (due to phytotoxicity), and environmental health (soil/fauna and terrestrial animals). The mobilization of these metals into the biosphere by human activities has become an important process in the geochemical cycling of these pollutants. This is acutely evident in urban areas where various stationary and mobile sources releases large quantities of trace metals into the atmosphere and soil, exceeding the natural emission rates (Nriagu, 1989; Bilos *et al.*, 2001).

2.2. Heavy Metals uptake and Accumulation in Vegetable parts

Plant species and varieties vary in their capacity for heavy metal accumulation. Long *et al*. (2003) showed that zinc uptake and accumulation by shoots and roots varied with Zn levels in growth media and vegetable types. Both shoot and root Zn concentrations increased sharply with increasing Zn concentrations for Chinese cabbage, celery and pakchoi. However, shoots contained over 3-fold less Zn than roots when grown under nutrient solution culture conditions. The three vegetable crops differed greatly in their ability to take up Zn from the growth media and to transport it to the shoots. At an external Zn level of 25 mg/L, shoot Zn concentration of Chinese cabbage was almost 2-fold lower than that of pakchoi or celery. Zinc concentration in the edible part of celery was nearly 2-fold higher than that of the other two species when grown at higher Zn levels (50 mg/L). Moreover, under soil culture conditions, the zinc accumulation coefficient (AF) in shoots increased for pakchoi, but decreased for celery and Chinese cabbage when soil available Zn was raised from 10 to 172 mg/L. However, root Zn AF increased to varied extents, with increasing soil Zn for all the vegetables. Celery showed highest AF in edible parts at low soil Zn (i.e. in control), where as pakchoi had the higher AF of Zn at higher soil available Zn levels. The AF for zinc in edible parts of the three vegetable crops decreased in the order pakchoi>celery (stem)>Chinese cabbage. Significant positive correlations were noted between shoot Zn and soil available Zn level (long *et al*., 2003). Zn threshold for human health has been established to be 20mg/kg (Chinese Department of Preventive Medicine, 1995).

Ni *et al*. (2002) studied the effect of Cd on the growth of three vegetable crops i.e. Chinese cabbage (*Brassica chinensis* L cv. Zao-Shu 5), winter greens (*B. rosularis* var. Tsenet Leecv. Shang-Hai-Qing), and celery (*Apiumggraveolens* L. var. dulce DC). Their results indicated that the Cd concentration in shoots and roots varied both with different Cd levels and type of vegetable. Generally Cd accumulation in various plant parts in vegetable crops increased with the increasing cadmium concentrations in the growth medium. Root Cd increased more sharply than shoot Cd. Celery contained higher Cd in edible parts than other vegetable species.

Yang *et al*. (2002) studied the response of three vegetables to Cu toxicity and found that Cu levels in both root and shoot increased, but root Cu concentration increased more sharply than shoot with increasing Cu levels in growth media. Cu mainly accumulated in roots while a small fraction (10-20%) of absorbed Cu was transported to shoot. Celery accumulated higher Cu content both in roots (1557 mg/L) and shoot (166.7 mg/L in leaves).

Copper AFs in the shoots of vegetable species were relatively small when grown at soil addition Cu levels of 200-400 mg/kg and dramatically increased at soil addition Cu levels above 600 mg/kg.

While investigating copper toxicity and bioaccumulation in Chinese cabbage (*Brassica pekinensis*Rupr),Xiong and Wang (2005) found that Cu concentration on the shoots was significantly influenced by Cu treatment ($P<0.001$). Cu concentration increased markedly with an increase in the soil Cu concentration. With a background level of 13.6 Cu (the control, 13.6 mg/kg dry soil), Cu concentration in the shoots was 9.9 mg/kg. with the 0.2 mmol/kg treatment, shoot Cu concentration rose to 42.5 mg/kg. With the 1.0 mmol/kg treatment, shoot Cu concentration was 119.0 mg/kg (1.9 mmol/kg). According to the LSD test, shoot Cu concentration in both treatments was significantly higher than that in the control. These facts showed that when Chinese cabbage (cultivar Xiayangbai) plants were exposed to certain levels of Cu pollution, the shoots could accumulate a relatively high amount of Cu.

2.3. Soil-Plant-Man Relations in Heavy Metal Toxicity

Soil-to-plant transfer is one of the key components of human exposure to metals through the food chain. Lacatusu *et al*. (1996) studied soil-plant-man relationships in heavy metal polluted areas in Romania and detected significant overclark levels of Cd and Pb from the geogenic abundance viewpoint. Although the polluted soils were neutral to slightly alkaline and well supplied with organic matter, the soluble forms of heavy metals in EDTA-CH_3COONH_4, pH=7.0 represented on average 37% Cd, 17% Cu, 28% Pb and 14% Zn, respectively of their global concentration, exceeding the maximum allowable limits (MAL), for soluble forms, by on average up to 14.8 (Pb), 4.2 (Cd) and 2.1 (Zn) times. The relationship between their contents in plants and in soil (soluble forms) showed significant correlations for Cd, Cu, Pb and Zn. As a result, the contents of these elements in vegetable often exceed those allowable for normal human and animal consumption. In this case, if an adult consumed 2 kg potatoes, 2 kg tomatoes and 1 kg carrots in a week, his/her food would exceed by 12% the MAL for Cd (0.525 mg). The daily maximum allowable rate of ingested Pb (0.430 mg) could be reached by consuming 880 g of vegetables (equal parts of potatoes, tomatoes, carrots and cucumbers). The higher acidity of soils enhances the transfer of large amounts of heavy metals in soluble forms, exceeding MAL on average up to 23.4 (Pb), 2.1 (Cd), 2.8 (Cu) and 2.7 (Zn) times. As a result, the average Pb content in carrots was 10 times higher than the

MAL and the Pb accumulation in the lettuce, parsley and garden orach, significantly above the critical contents. At the same time, the Cd content in the analyzed vegetables exceeded by 5 times the MAL, while the Cu and Zn contents were close to critical levels (Lacatusu *et al*., 1996). Ingestion of vegetables containing high concentrations of heavy metals is one of the main ways in which these elements enter the human body. Typical diseases recorded were Pb and Cd intoxication, saturnine encephalopathy, radial nerve paralysis and saturnine colic. The most affected group of inhabitants was children (Lacatusu *et al*., 1996). Estimates form various countries showed that the dietary intake for lead in adults is between 54 mg per day (Dabeca *et al*., 1987) and 412 mg per day (Dick *et al*., 1978), and that of cadmium is between 10 and 30 mg per day (Reilly, 1991). For zinc and copper, the estimated daily intake is from 1 to 3 mg, and 10 to 20 mg, respectively (Fox, 1982). Lacatusu *et al*. (1996) found that their estimations for lead and zinc were above those reported from other countries, whereas the estimations for cadmium were within the range. The levels of copper were observed to be below the estimation. Bahemuka and Mubofu (1999) suggested that a large daily intake of these vegetables is likely to cause a detrimental health hazard to the consumer.

Since the dietary intake of food may constitute a major source of long-term low-level body accumulation of heavy metals, the detrimental impact becomes apparent only after several years of exposure. Regular monitoring of these metals from effluents, sewage, in vegetables and in other food materials is essential for preventing excessive build-up of the metals in the food chain (Bahemuka and Mubofu, 1999).

2.4. Effects of Heavy Metals on Human Health

Chronic low-level intakes of heavy metals have damaging effects on human beings and other animals, since there is no good mechanism for their elimination. Metals such as lead, mercury, cadmium and copper are cumulative poisons. These metals cause environmental hazards and are reported to be exceptionally toxic (Ellen *et al*., 1990). Vegetables take up metals by absorbing them from contaminated soils, as well as from deposits on parts of the vegetable exposed to the air from polluted environments (Zurera-Cosano *et al*., 1989).

In this region, the industry operates over a thousand producing wells, gas plants, a network of thousands of kilometers of pipelines, criss-crossing the delta, carrying crude oil to flow stations, terminals and refines spread a cross the region (Onosode 2003). Several petroleum services and hydrocarbon dependent industries, including petrochemical, nitrogenous fertilizer and other plants have also sprung up in the

Niger Delta region to take advantage of ancillary opportunities created by the oil industry.

During the process of extraction of crude oil at the flow stations, associated gases are vented through open flares, and according to Oghenejoboh (2005), gas flaring is a major contributor to the emission of toxic gases into the atmosphere. Gas flares produce oxides of carbon (COx), sulphure (SOx) and nitrogen (NOx), water vapour, volatile and non-volatile trace elements (such as Pb, Hg, Cd and As) (WHO, 1988). Incomplete combustion of flare gases could also produce greenhouse gases (e.g. CH_4), other pollutants (e.g. CO), and organic elemental particles (e.g. Coke) (Oyekunle, 1999).

The emitted gases and compounds in the atmosphere are deposited on the earth as acid depositions. Acid depositions could either be wet or dry, depending on the state of matter in which it is incorporated and transported (EPA, 2003). Wet depositions are commonly in the forms of acid rain, fog, and snow, while dry depositions are in the forms of acidic gases and particles.

Acid rain refers to a precipitation that has a pH less than 5.6 (the pH of unpolluted water is <5.6) (Cowling, 1982). About half of the acidity in the atmosphere falls back to the earth through deposition. The dry depositions are blown farther away and could be washed by rainstorms. Runoff water adds those acids to the acid rain, thus, making the combination more acidic than the falling rain alone and is introduced both in deeper soils and on the aquatic habitat (US EPA, 2003).The acidity of rainwater is increased by the presence of particulate matter, which may contain trace metals such as As, Pb, Cd, and Hg that could alter pH (Oghenejoboh, 2005). In the overall, acid deposition causes a cascade of effects or kills individual edaphic or aquatic organisms (depending on the ecosystem), reduce their population, completely eliminate their species and decrease overall biodiversity (Ogwejifor, 2000; US EPA, 2003).

Aerosols contain different toxic metals which fall on the soil and are retained in the top few centimeters and are subsequently carried down by leaching, presumably due to their interaction with soil colloids (Arun *et al.*, 2005). They are therefore liable to be quite persistent in the soil. Once deposited, metal-containing materials are subject to chemical and microbial modifications. With metal solubility, ultimately approach in the thermodynamic equilibrium with native soil minerals and organic matter, the rate and extent of solubilization are governed by the physicochemical properties of the deposited mineral, soil processes and properties (Graig, 1987).

Particulates arising from fossil fuel combustion, metal smelting operation etc may be expected to be largely insoluble in soil solution. Hydrolyzable metals (for example nickel, cadmium) or metal forming insoluble precipitate with sulphur and phosphorous on entering the soil-soluble form may be expected to be rapidly solubilized at near neutral pH of most soil due to hydrolysis on dilution and subsequent precipitation on, or reaction with particle surface (Graig, 1987). Certain elements (for example iron) may also form precipitates with sulphur or phosphorus.

Metals with low ionic potential tend to form primarily simple soluble ion while metals with intermediate and high ionic potentials tend to form soluble complex. Common inorganic complex forming ions in the soil solution include CO_3^{2-}, HCO_3^- SO_4^{2-}, HS^-, OH^- and Cl^-. Soil microorganism may play an important role in this process through the production of soluble ligands with high affinity for metals (Arun,*et al*., 2005).

Soil physicochemical parameters that are most important in influencing the solubility of metals include soil composition (inorganic or organic), pH, type and density of change on soil colloids and reactive surface area (Graig, 1987). These phenomena will be dependent upon soil properties, including metal concentration and form; particles size distribution, quantity and reactivity of hydrous oxides, mineralogy, degree of aeration and microbial activity (Sharma, 2006).

Observation shows that the mobility of heavy metals decrease in soil with inorganic matter, as compared to the soil will decomposed organic matter. This may be due to the high adsorption capacity of the soil organic matter associated with clay particles due to clay-meal soil-organic matter interaction (David and Peter, 1987). The mobility order observed was Ni <Mn Cr < Cu <pb. This trend in the reverse order of their binding capacities with soil organic matter means that there will be decrease in mobility (Sharma, 2006).

Disposal of industrial, as well as domestic sewage sludge and domestic wastes on land is a common practice. One of the major problems with land disposal of sludge is the likely introduction of heavy metal in the soil. In general, sludge solution appears to increase the mobility of trace element in soil. Increase in mobility of trace elements is often attribute to a combination of factors, including complexation by dissolved organic, inorganic ligand, high background concentration of metals and other ions and high ionic strength of amended soil solution.

The bioavailability and mobility of metals in soil system are functions of the metal species in soil solution and the distribution of metals in the soil solid component (Zhuang *et al.*, 2009).

While investigating copper toxicity and bioaccumulation in Chinese cabbage (*Brassica pekinensis*Rupr), Xiong and Wang (2005) found that Cu concentration on the shoots was significantly influenced by Cu treatment ($P<0.001$). Cu concentration increased markedly with an increase in the soil Cu concentration. With a background level of 13.6 Cu (the control, 13.6 mg/kg dry soil), Cu concentration in the shoots was 9.9 mg/kg. with the 0.2 mmol/kg treatment, shoot Cu concentration rose to 42.5 mg/kg. With the 1.0 mmol/kg treatment, shoot Cu concentration was 119.0 mg/kg (1.9 mmol/kg). According to the LSD test, shoot Cu concentration in both treatments was significantly higher than that in the control. These facts showed that when Chinese cabbage (cultivar Xiayangbai) plants were exposed to certain levels of Cu pollution, the shoots could accumulate a relatively high amount of Cu.

Metal contamination of garden soil may be widespread in urban areas due to past industrial activity and the use of fossil fuels (Chronopoulos *et al*., 1997; Sanchez-Camazano *et al*., 1994; Sterrett *et al*., 1996; van Lune, 1987; Wong, 1996). Heavy metals may enter the human body through inhalation of dust, direct ingestion of soil, and consumption of food plants grown in metal-contaminated soil (Cambra *et al*., 1999; Dudka and Miller, 1999; Hawley, 1985). Potentially toxic metals are also present in commercially produced foodstuffs (DEFRA, 1999). Exposure to potentially toxic metals from dust inhalation or soil ingestion is usually modeled simply as the concentration of contaminant measured in the soil multiplied by the quantity of dust inhaled or soil ingested (Konz *et al*., 1989). This is a conservative approach to estimate dose, because the bioaccessibility of heavy metals adsorbed on ingested soil is not 100% (Ruby et al., 1999). However, predicting exposure to potentially toxic metals from consumption of food crops is more complicated because uptake of metals by plants depends on soil properties and plant physiologic factors. This leads to much larger uncertainties associated with estimating potential doses through food chains compared to the uncertainties associated with other exposure pathways such as soil ingestion and dust inhalation (McKone, 1994).

Lead is toxic element that can be harmful to plants, although plants usually show ability to accumulate large amounts of lead without visible changes in their appearance or yield. In many plants, Pb accumulation can exceed several hundred times the threshold of maximum level permissible for humans (Wierzbicka, 1995). The introduction of Pb into the food chain may affect human health, and thus, studies concerning Pb accumulation in vegetables have increasing importance (Coutate, 1992). Although a maximum Pb limit for human health has been established for edible parts of crops (0.2 mg/kg) (Chinese Department of

Preventive Medicine, 1994), soil Pb threshold for producing safe vegetable are not available.

Zn toxicity in humans is minimal. The most important information reported is its interference with Cu metabolism (Barone *et al*., 1998; Gyorffy and Chan, 1992). The symptoms that an acute oral Zn dose may provoke include tachycardia, vascular shock, dyspeptic nausea, vomiting, diarrhea, pancreatictis and damage of hepatic parenchyma (Salgueiro *et al*., 2000). Although maximum Zn tolerance for human health has been established for edible parts of crops (20 mg/kg) (Chinese Department of Preventive Medicine, 1995), soil Zn threshold for producing safe vegetable is not available.

According to Hough *et al*., (2004) under Part IIA of the Environmental Protection Act 1990, the UK government favors a "suitable for use" approach to redevelopment (DETR, 2000): Land is contaminated only if the current or intended use of a site has the potential to cause an unacceptable health risk to human occupants or to the environment. Under the UK Town and Country Planning Act 1990 (DETR, 2000), this approach requires that land be assessed for redevelopment on a site-specific basis. At present, concentrations of metals in the soil are compared to metals-specific "trigger values" (termed "maximum contaminant levels or maximum contaminant concentrations” in North America). In the past these trigger values were based on total contaminant concentration in the soil (ICRCL, 1987). More recently, the introduction of Contaminated Land Exposure Assessment (CLEA) (DEFRA and Environment Agency, 2002a) in April 2002 has replaced these trigger values with generic soil guidance values (SGVs) (DEFRA and Environment Agency, 2002b). The SGVs are considered a significant improvement on the previous ICRCL values and for Cd at least, soil pH categories are employed where food plants are to be grown. Where a soil exceeds the SGV, it is recommended that a risk assessment or remediation measure be conducted for the site in question (DEFRA and Environment Agency, 2002b). Additionally exceeding of an SGV indicates that some further risk management action be undertaken. However, the use of single trigger values of SGVs for most scenarios may represent a poor indication of the risk associated with a specific site. There is therefore requirement for site-specific risk assessment based on commonly measured geochemical and population parameters (Hough *et al*., 2004).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of the Study Area

Oghara Efe is a village of about 6,000 people in Ethiope West Local Government Area of Delta State. The main occupation of Oghara Efe people is farming of which cassava is one of the main products of their farming. The neighbouring villages are Apapa, Ajagbodude, Ogharesi and Ejenesan (Olomo, 1993)

Agip flow station in Kwale (Okpai Gas plant) is situated between Ndokwa east and West Local Government Area of Delta State. The people of these areas are mainly farmers and traders. They have population of about 1 million people residing in this area. The neighbouring villages are Orogun, Ejeme-aniogo, Isoko Oronigwe in Edo State, Abavo in Ika (Olomo,1993).

3.2. Geology

Niger Delta consists of massive, very porous and permeable freshwater bearing sandstones with minor clay intercalations (Olomo,1993). The formation is generally water bearing and so it is the main source of portable groundwater in the area. The aquifers are recharged mainly by surface precipitation and nearby drainage. Sediments deposition and groundwater flow are generally in the NE-SW trend in line with the regional trend of the basin (Soronnadi *et al*., 2012).

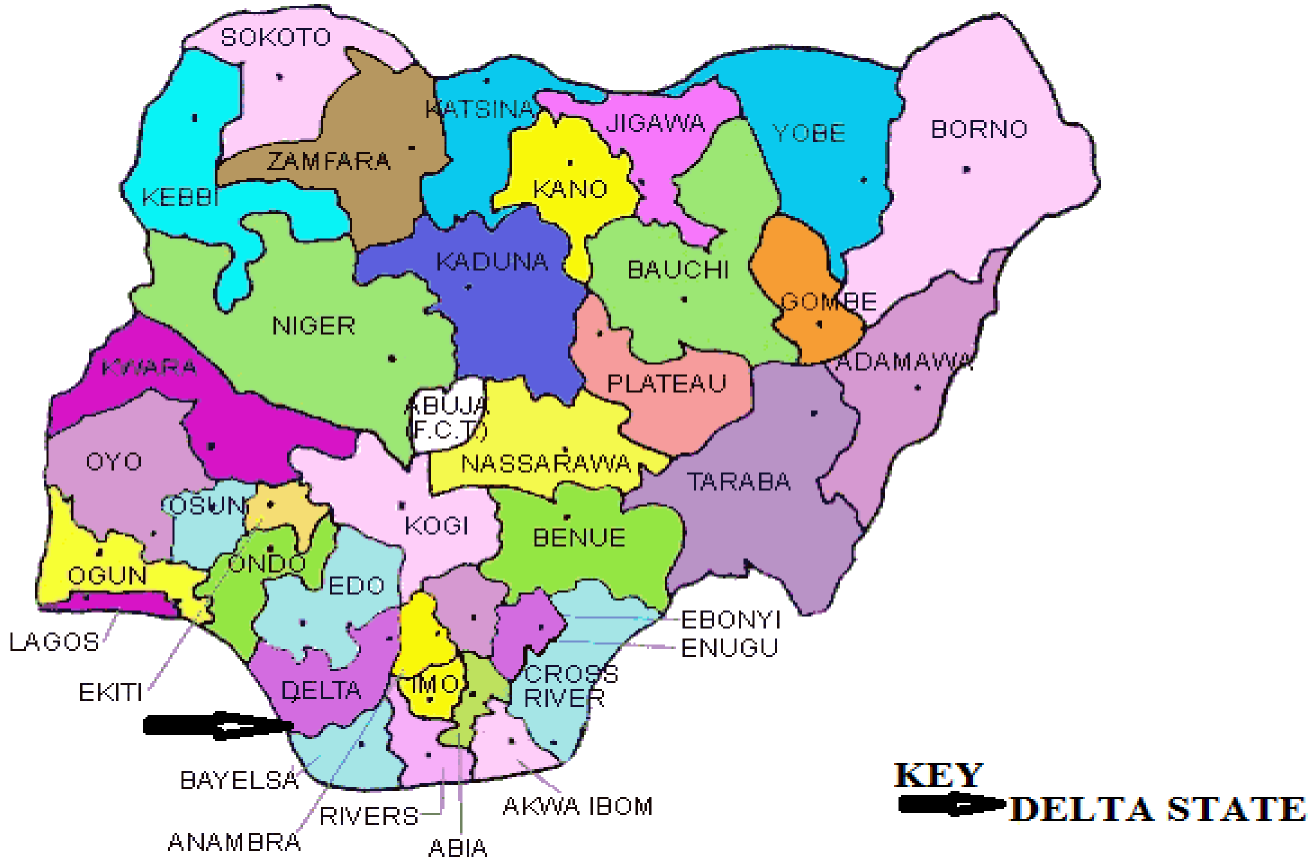

FIG 3.1 Map of Nigeria State showing Delta State

Source; Delta State Ministry of Lands and Survey

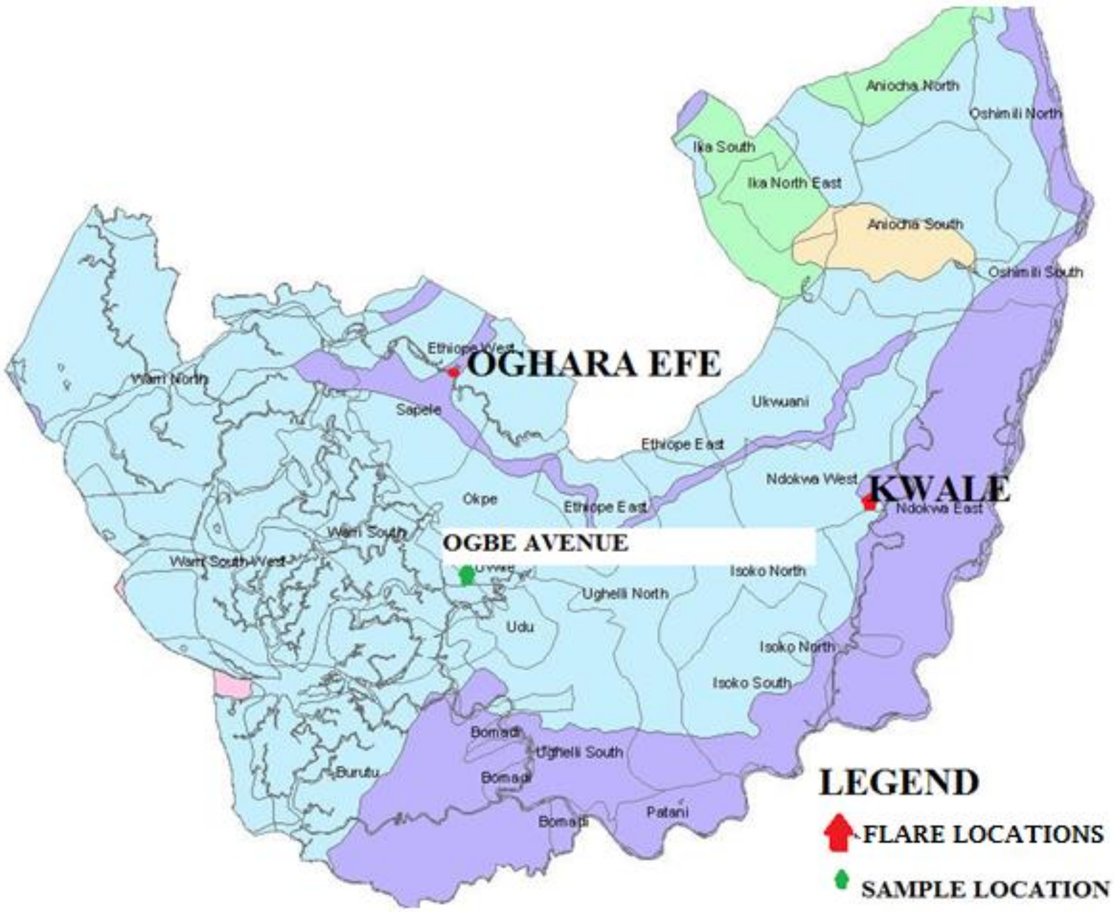

FIG 3.2 Map of Delta State showing Ethiope West, Kwale the flare locations and Ogbe Avenue the sample location

Source; Delta State Ministry of Lands and Survey

3.3. **Climate**

The area is characterized by lengthy and heavy rainfall typically known as Tropical monsoon. It has two seasons Dry and Wet or raining Season. It has its peak precipitation in September, with an average of 730mm of rainfall (Soronnadi *et al*., 2012). December is the month with the lowest precipitation of the year, with rainfall of about 20mm.

3.4. **Vegetation**

Oghara Efe and Kwale are located in the rainforest region of Nigeria; though anthropogenic activities such as deforestation have altered this regime in some areas. The common vegetation types include palm trees, banana trees, shrubs and grasses. Other economic trees include the Abura, mango and raffia palm trees.

3.5. **Economic activities**

The inhabitants of the area are mainly subsistent farmers and petty traders. However, some people are civil servants and industrial workers, while others are craftsmen.

Materials

In carrying out this project work, the following materials and equipment were used.

1. Mortar and pestle
2. Muffle furnace
3. Conical flasks (250ml)
4. Desiccators
5. Electric oven
6. Weighing balance
7. Measuring cylinder (100ml)
8. Beakers (250ml, 600ml)
9. Hot plate
10. Atomic Absorption Spectrophotometer (AAS)
11. Concentrated nitric acid
12. Concentrated sulphuric acid
13. Pechloric acid
14. Sieve (2mm filter)
15. Fume cupboard

16. Tapioca samples
17. Distilled water
18. Knife
19. Milling machine
20. Whatman 42 filter paper
21. Thermometer
22. Aluminium foil
23. Aluminium pot
24. Sack
25. Hand-held Testrel 4500 weather Tracker
26. Digital Automatic Gas Monitors (DAGMs).

The samples used for the analysis carried out in this project work were of two types:

a. Test samples
b. Control

3.6. **Field Procedures**

Sample Collection

The test samples used for the analysis were tapioca (cassava flake) obtained from cassava tubers harvested from a farm at Ogbe Avenue, off PTI Road, Effurun. A large quantity of the same species of cassava was harvested from the same place. The cassava tubers, after harvesting were peeled and thoroughly washed. The peeled cassava tubers were ground with milling machine which reduced them to fine, whitish particles The starch- contents will be extracted by putting it into a sack and squeezing it. The starch was removed or extracted through the pores of the sack. The remnant of the ground cassava, which was the solid substance was cooked for about 10-15 minutes and allowed to cool. It was then molded to different sizes of irregular shapes. These irregular shaped pulps were shared into three portions and labeled A, B, C.

Sample “A” was dried at Pan Ocean Flaring site, Oghara; Sample “B” was dried Agip flaring site, Kwale; and Sample “C” was used as control.

Sample “A” and “B” were spread on a mesh and spread around the flame form flare site (Pan Ocean flaring site, Oghara and Agip flaring site, Kwale respectively) with temperature of about $35.24^{O}C$ for two days in three places 100 meters from the flaring sites respectively. This was done so that a representative sample could be obtained.

The control sample used for the analysis was collected from the same source as the test samples as earlier stated (i.e. the same specie of cassava and from the same farm land). This was done to overcome the problem of variation in the heavy metals content of the cassava and other parameters of interest. The only difference between the test samples and the control was that the test samples were dried around flame from flare site while the control sample was dried in an oven set at the same temperature as of the flaring site (i.e. 32.0 degree centigrade (for two days).

The representative samples for this project work was collected from the three different points around the two flaring sites respectively. It was put in a plastic container and stored in a cool dry place in the laboratory for analysis.

The control sample was also put in a separate plastic container after drying and stored in a cool dry place in the laboratory.

3.8. PREPARATION OF THE SAMPLES

Preparation of the samples involved the preparation of the test samples from the different sampling locations (Oghara and Kwale) respectively, preparation of the control, and also preparation of the blank along with the samples for vanadium and nickel analysis.

Again the samples were also prepared for carbon deposits (sooth) analysis.

a. PREPARATION OF THE TEST SAMPLES, CONTROL AND BLANK FOR VANADIUM, ZINC AND NICKEL ANALYSIS. APHA (1998)

A 30g of the dried cassava flake (tapioca) from each flaring site was crushed/ground in a mortar with pestle to a coarse powder respectively; the control was also crushed/ground in a mortar with pestle to a coarse powder. These samples and the control were sieved with a 2mm sieve respectively with filter paper (after sieving of each sample, the remnant with larger size was further subjected to more grinding until a uniform size was obtained, and the sieve was thoroughly cleaned before sieving another sample).

10g of each of the ground samples was weighed in an electronic weighing balance and put in a 250ml conical flask respectively. 20ml well mixed perchloric acid, sulphuric acid and nitric acid in the ratio 1:2:2 was measured and transferred into the flask containing the samples respectively in a fume cupboard. These mixtures containing the different samples were heated for about one hour (1hr) in a hot plate until a white fume was observed. Before the observation of the white fume, in about 15 minutes of heating, brown fumes were observed. After about 28 minutes of heating, the white fumes were observed. When the white fume was observed, digestion was stopped and the digest allowed to cool. After cooling, 20ml of distilled water was added and boiled for about 20 minutes to bring the metals into solution. It was allowed to further cool and filtered through Whatman 42 filter paper in a 100ml volumetric flask, and made to mark with distilled water. Then it was transferred to 100ml plastic can for analysis of vanadium and nickel width Atomic Absorption Photo spectrometer (AAS).

The blank also was prepared along with these samples. The difference between the samples and the blank was that the blank contained only 6.0ml distilled water while the samples contained 40ml distilled water and 20ml mixture of pechloric acid, nitric acid and sulphuric acid in the ratio of 1:2:2 before they were made to mark of 100ml.

b. **PREPARATION OF SAMPLES FOR CARBON DEPOSIT ANALYSIS APHA (1998)**

0.05 g of the sample was weighed and put into 250ml conical flask. 10ml of potassium dichromate (1N) was put into the flask containing the quantity 0.05g of the sample. Then 20ml of concentrated H_2SO_4 was added into the flask, swirled, mixed and allowed to cool. I added 60ml of distilled water was added into the flask and its content. I added 5ml of orthophosphoric acid was also added. Then 8drops of diphenylamine indicator was also added and titrated with 0.4N ammonium ferrous sulphate to greenish end point. This procedure was carried out in the two samples (sample A and sample B) and the control.

c. **DIGITAL AUTOMATIC GAS MONITORS (DAGMs)**. The Crowcon Gasman Air Monitor that had been pre-calibrated using air cylinder standard (SPDC, 2002) was used in the direct detection of oxides of sulphur, nitrogen, volatile organic compounds and ozone (SOx, NOx, VOC and O_3). This method was used to measure the ambient air around the flaring stack.

d. METEOROLOGICAL VARIABLES

Hand-held Testrel 4500 weather Tracker, a high precision in-situ weather monitoring equipment was used in the determination of ambient temperature, wind speed and relative humidity then the mean of the sampling points taken. The experiment was carried out at the sampling points and the readings were read off the Liquid Crystal Display (LCD) screen of the equipment at each given interval.

Statistical Analysis

Simple bar charts where also used to analyze the level of each parameter and descriptive statistics was also used.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION OF RESULTS

Table 4.1. Descriptive statistics of the Impact of Gas Flaring Fallout on Cassava Flour Dried Around Gas Flaring Sites in Delta State.

	Concentrations				
Parameters (ppm)	**Minimum**	**Maximum**	**Range**	**Mean**	**SE**
Ni	0.24	0.61	0.37	0.47	0.115902
V	0.01	0.05	0.04	0.033333	0.012019
Zn	0.001	0.002	0.001	0.001333	0.000333
As	1.3	2.2	0.9	1.866667	0.2848
Cu	0.00	0.02	0.02	0.01	0.005774
Fe	0.01	0.4	0.39	0.236667	0.116952
C	0.00	8.32	8.32	5.00	2.544432

Nickel varied from 0.24-0.61 (0.47 ± 0.12) PPM, Vanadium varied from 0.01- 0.05 (0.03± 0.01)PPM, Zinc varied from 0.001- 0.002 (0.001 ± 0.00) PPM respectively. However Arsenic varied from 1.3 – 2.2 (1.87 ± 0.28)PPM, while Copper varied 0.0 – 0.02 (0.01 ± 0.005)PPM, Iron from 0.01- 0.4 (0.24 ± 0.12) PPM, and Carbon varied from 0.00 – 8.32 (5.0 ± 2.54) PPM.

4.10 HEAVY METALS RESULTS

Table 4. 2; Heavy Metals

	Ni Ppm	V ppm	Zn ppm	As ppm	Cu ppm	Fe ppm	Carbon ppm
CONTROL	0.24	0.01	0.001	1.30	0.00	0.01	
SAMPLE A	0.56	0.04	0.002	2.10	0.01	0.40	6.68
SAMPLE B	0.61	0.05	0.001	2.20	0.02	0.30	8.32
NAFDAC RANGE	-	-		10		40-45	-
EU RANGE			10		10		-

***ppm = PARTS PER MILLION**

***EU= European Commission**

***NAFDAC=National Agency for Food and Drug Administration Control**

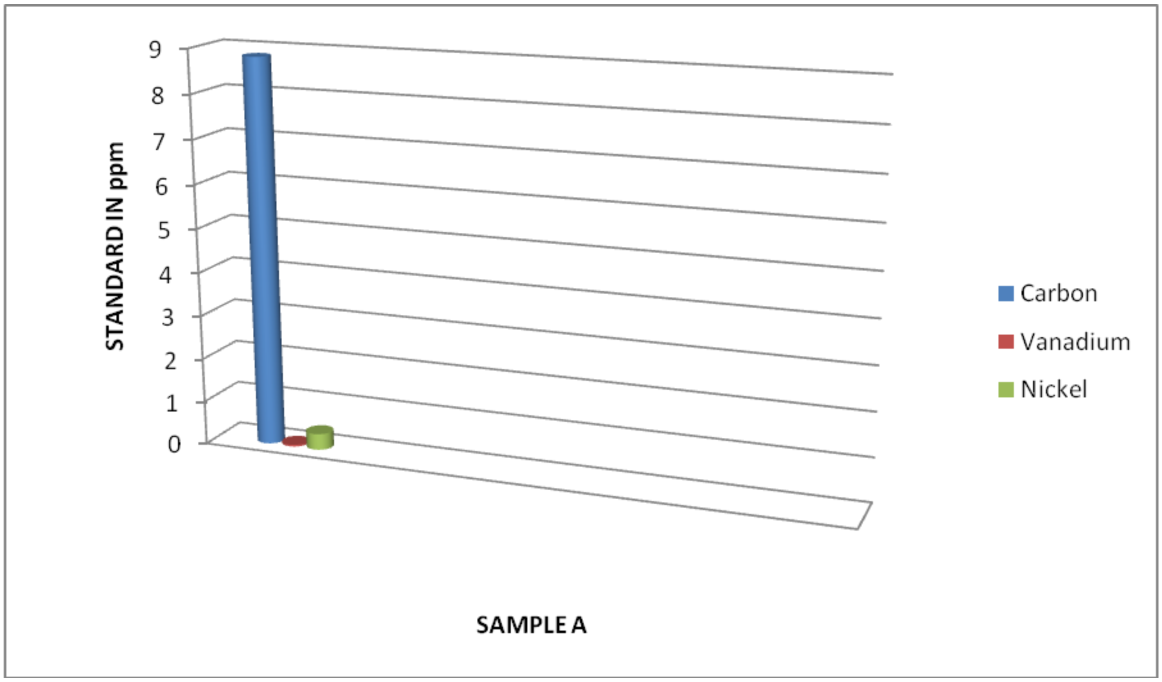

Fig. 4.1 Values of sampled parameters of study area for sample A (carbon, vanadium and nickel)

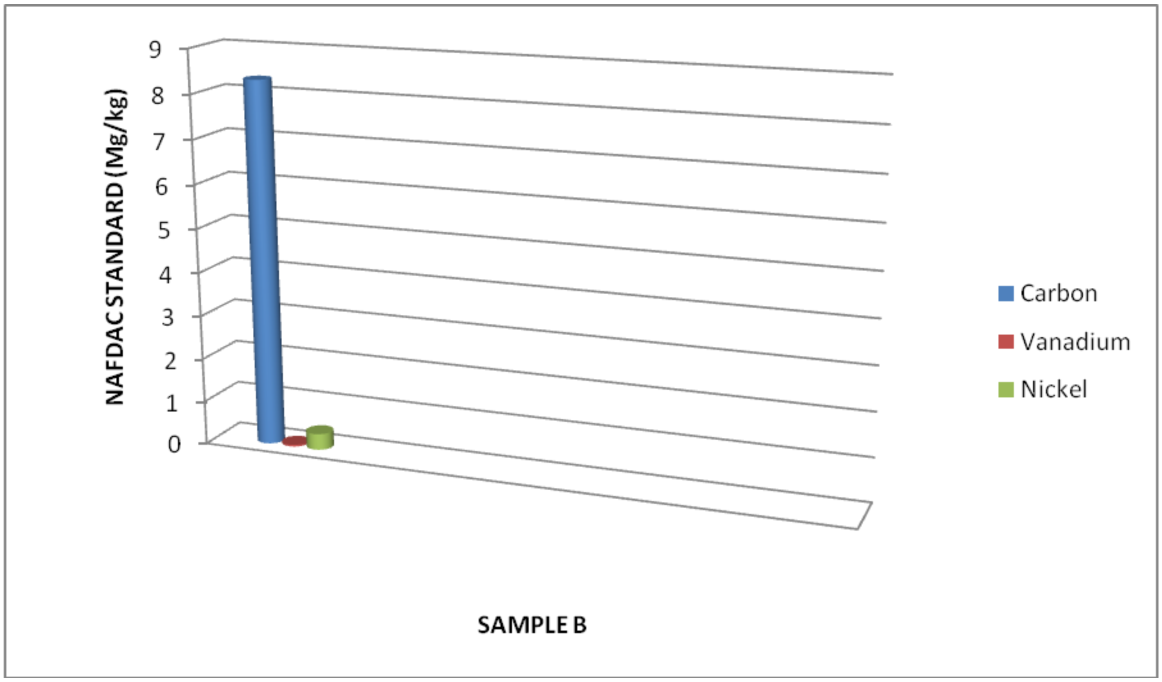

Fig. 4.2 Values of sampled parameters of study area for sample B (carbon, nickel and vanadium)

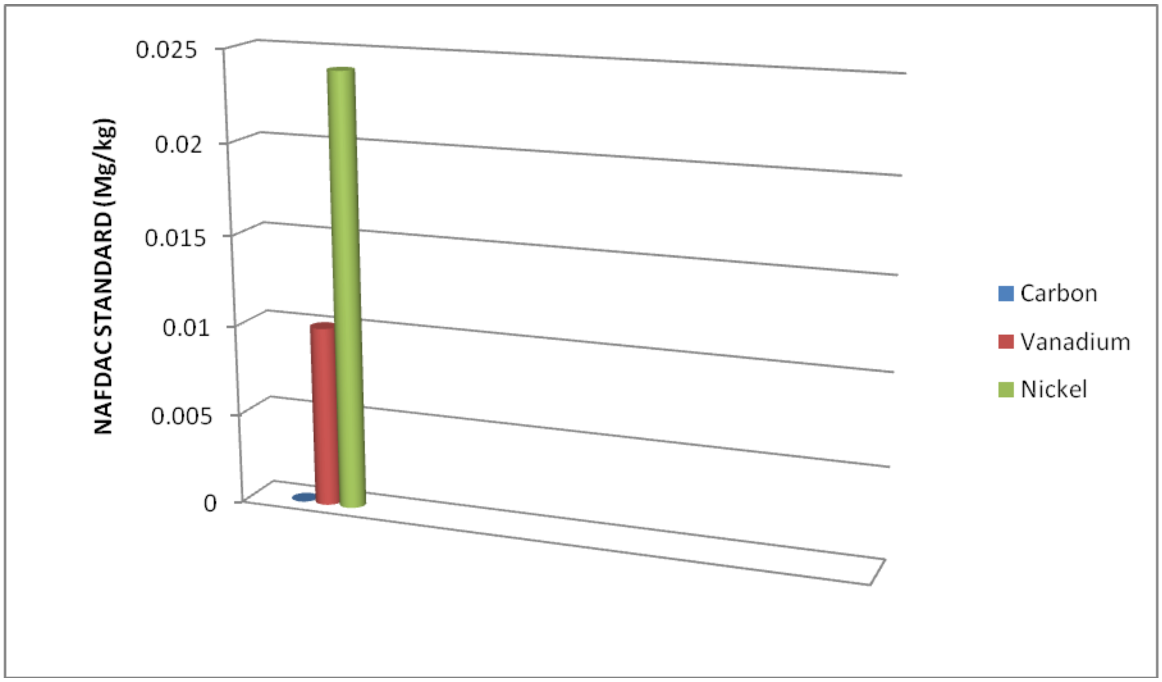

Fig. 4.3 Values of sampled parameters of study area for sample control

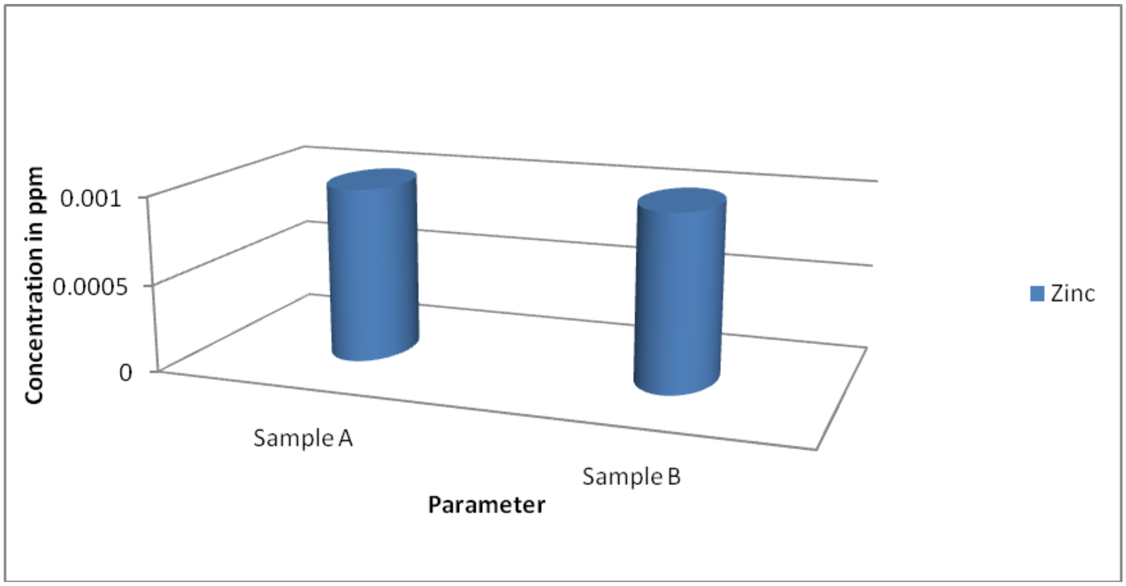

Fig. 4.4 Values of sampled parameter (Zinc) of study area for sample A and B

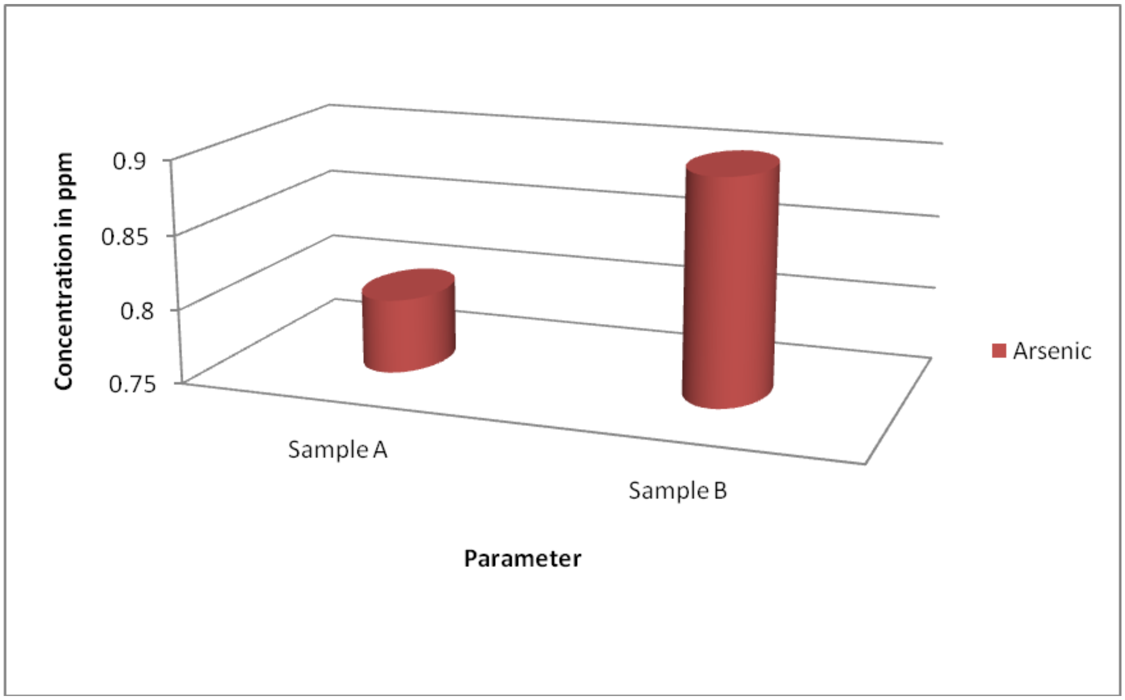

Fig. 4.5 Values of sampled parameter (Arsenic) of study area for sample A and B

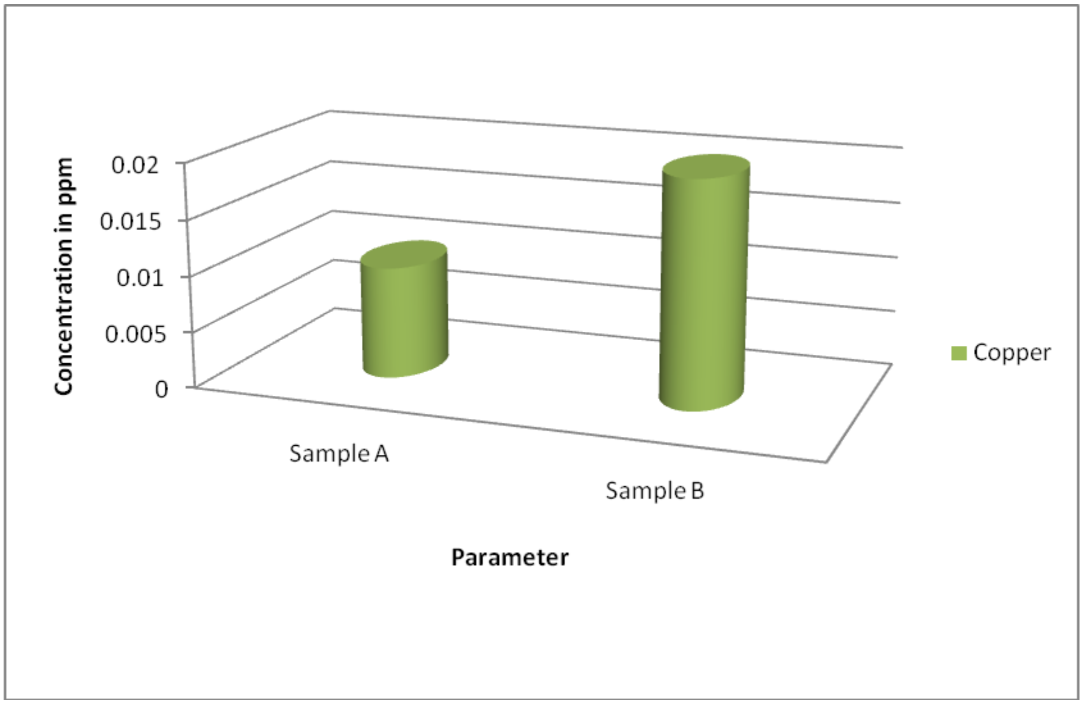

Fig. 4.6 Values of sampled parameter (Copper) of study area for sample A and B

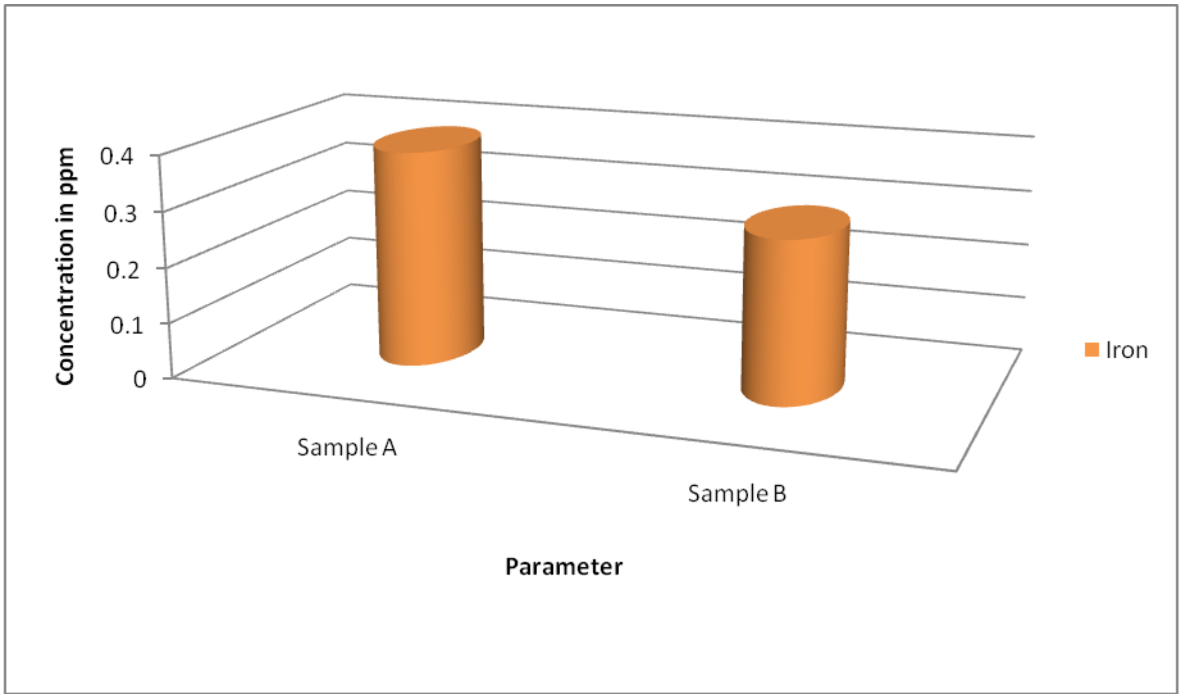

Fig. 4.7 Values of sampled parameter (Iron) of study area for sample A and B

4.2 COMPARATIVE REPRESENTATION OF THE RESULT

The table and the charts above showed the results of the analysis. In sample A, the concentration of nickel was 0.56 ppm, vanadium was 0.04 ppm and carbon was 6.68ppm. In sample B, nickel was 0.61 ppm, vanadium was 0.05 ppm, and carbon was 8.32 ppm respectively. The results showed no impact of the fallout on ppthe sampled parameters.

4.3 COMPARATIVE ANALYSIS OF THE RESULT

From the table and the charts above showed that the results of the analysis in sample A and sample B, had the following concentrations of nickel was 0.56 ppm, vanadium was 0.04 ppm and carbon was 6.68ppm. While in sample B, the concentration of nickel was 0.61ppm, vanadium was 0.05 ppm, and carbon was 8.32 ppm respectively.

These concentrations were compared with standards which set upper limit for some heavy metals, that levels of these elements should not exceed some certain range. It was observed that the sampled parameters in the study were all within the permissible limits. This could be as a result of wind dispersion of the flared gases farther away from the flaring stark.

Chemicals like cyanide, mercury, lead and copper, are non-biodegradable. Organisms are poisoned as the concentrations of toxins increase, and are passed through the food chain. The poisonous chemicals can cause cancer and damage internal organs in people and animals. The non exceedances of the various parameters sampled shows that the tapioca under study was not impacted by the flared gases of the sites.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

From the result of the analysis carried out in this project work, it can be concluded that the elements that are emitted from flaring sites of Oghara Efe and Kwale have not reached lethal level. This is because the required level of these sampled metals in food (tapioca) was low when compared with some standards. Though it has no immediate effect or impact now, it is likely that continued usage or consumption may cause health impacts, through bioaccumulation and biomagnifications.

5.2 RECOMMENDATIONS

1. A constant environment monitory should be given proper attention.
2. More test/analysis should be carried out and periodic revisting of the site should be encouraged
3. The effects of seasonal variation should be considered. That is to say, there should be sampling in the raining season as well as dry season to carter for seasonal variation.

4. Routine analysis should be carried out in flare sites to monitor any change in concentration.

5. A further analysis and study should be carried out on other heavy metals and compounds that are not included in this project work.

REFERENCES

Ademoroti, C.M.A. (1996). *Environmental Chemistry and Toxicology.*Foludex Ltd: Ibadan, Nigeria, p.186-204.

Adesiyan, S.O. (2005) *Man and his biological environment.*Ibadan University Press, Ibadan, Nigeria. 196pp.

Agarwal, S.K. (2009).*Pollution Management: water pollution*. A.P.H publishing corporation New Delhi. 384p.

Agbaire, P.O. and Esiefarienrhe, E. (2009).Air pollution tolerance indices (APTI) of som plants around Otorogun gas plant in Delta State, Nigeria.*Journal of Applied Science and Environmental Management,* 13:11-14.

Agbogidi, O.M., Eruotor, P.G. and Akparobi, S.O. (2006). Effects of soil contaminated with crude oil on the germination of maize (*Zea mays* L.). *Nigerian Journal of Science and Environment,* 5:1-10.

Agency (2002a).*Contaminated Land Exposure Assessment Model (CLEA): Technical Basis ans Algorithms.* Bristol, UK.

American Public Health Association, (APHA) (1998). *Standard Methods for the Examination of Water and Wastewater*. 20th Ed; Washington DC. PP 143-146, 248-252

Aremu, M.O., Atolaiye, B.O. and Labaran, L. (2010).Environmental implication of heavy metal concentrations in soil, plant foods and pond in area around the derelict Udege Mines of Nasarawa State, Nigeria.*Bulletin of Chemical Society of Ethiopia,* 24(3): 351-360.

Arun K.J., Ashok K.J. and Punmia.B.C. (2005).*Soil Mechanics and Foundation*. 6th ed. London: McGraw Hill.

Asthan, D.K & Asthana, M; (2003). *Environment problems & solutions*; S. chand & Company Ltd. Pgs 166-181.

Bahemuka, T.E. and Mubofu, E.B. (1999).Heavy metals in edible green vegetables grown along the sites of the Sinza and Msimbazi rivers in Dar es Salaam, Tanzania.*Food Chemistry,* 66(1):63-66.

Barone, A., Ebesh, O., Harper, R.G. and Wapnir, R.A. (1998). Placental copper transport in rats: effects of elevated dietary zinc on fetal copper, iron and metallothionin. *Journal of Nutrition,* 128(6): 1037-1041.

Bilos, C., Colombo, J.C., Skorupka, C.N. and Rodriguez, P.M.J. (2001). Source, distribution and variability of airborne trace metals in La Plata City area, Argentina. *Environmental Pollution,* 111(1): 149-158.

Carter, O.E. and Fernando, Q. (1979).Chemistry.*Toxicological Journal of Chemical Education*, 56:491-523.

Cambra, K., Martinez, T., Urzelai, A. and Alonso, E. (1999).Risk analysis of a farm area near a lead- and cadmium-contaminated industrial site.*Journal of Soil Contamination*, 8(5): 527-540.

Chinese Department of Preventive Medicine.(1994) *Threshold for food Hygiene*. Beijing, China: Standard Press.

Chinese Department of Preventive Medicine.(1995) Threshold for food Hygiene. Beijing, China: Standard Press.

Chronopoulos, J., Haidouti, C., Chronopoulou-Sereli, A. and Massas, I. (1997).Variation in plant and soil lead and cadmium content in urban parks in Athens, Greece.*Science and Total Environment*, 196(1): 91-98.

Codex Committee of Food Additives and Contaminants (CCFAC). 2001. Comments submitted on draft maximum levels for lead and cadmium.

Agenda 16 c/16d, Joint FAO/WHO Food Standards Programme, thirty-third sessions, The Hague, The Netherlands, 12-16 March, 2001

Coutate, T.P. (1992). *Food, the Chemistry of its component.*2nd ed. Cambridge: Royal Society of Chemistry, p.265.

Cowling, E.B. (1982).*Environmental Science and Technology.*Vol. 16. John Wiley Inc., London.

Dabeca, R.W., McKenzie, A.D. and Lacroix, G.M.A. (1987). Dietary intakes of lead, cadmium, arsenic and fluoride by Canadian adults, a 24 hours duplicate diet study. *Food Additive Contaminants,* 4:89-102.

David R., and Peter L.B. (1987).*Introduction to Soil Mechanics,* London: McGraw-Hill Book.

Department of Environment, Food and Rural Affairs (DEFRA) (1999).*Total Diet Study- Aluminum, Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Selenium, Tin and Zinc.*London: The Stationery Office.

Department of Environment, Food and Rural Affairs (DEFRA) and Environment Department of Environment, Food and Rural Affairs (DEFRA) and Environment Agency (2002b).*Assessment of Risks to Human Health from*

Land Contamination: An Overview of the Development of Soil Guideline Values and Related Research, CLR7, Bristol, UK.

Department of Environment, Transport and Regions (DETR) (2000).*Contaminated land: Implimentation of Part IIA of the Environmental Protection Act 1990.* London: Stationery Office.

Dick, G.L., Hughes, J.T., Mitchell, J.W. and David, F. (1978).Survey of trace elements and pesticides in New Zealand.*Journal of Science*, 21: 57-69.

Dudka, S. and Miller, W.P. (1999).Permissible concentrations of arsenic and lead in soils based on risk assessment.*Water, Air and Soil Pollution,* 113(1/4): 127-132.

Ellen, G., Loon, J.W. and Tolsma, K. (1990).Heavy metals in vegetables grown in the Netherlands and in domestic and imported fruits.*Z LebensmUntersForsch.*, 190(1): 34-39.

European Commission (EC). (2006). Setting maximum levels for certain contaminants in foodstuffs. Official Journal of the European Union L364/5 Commission Regulation(EC) No 1881/2006.

EVM. 2003. Safe upper levels for vitamins and minerals of the Export Group on Vitamins and Minerals. Food Standard

Agency.http://www.food.gov.uk/multimedia/pdfs/vitmin200

Fergusson, J.E. (1990). *The heavy elements: chemistry, environmental impact and health effects.* Oxford: Pergamin Press, pp.382-399.

Fox, B.A. (1982). *Food Science, 3rd ed.* London: Holder and Stoughton.

Graig, R.K. (1987).*Soil Mechanics*, 4th ed. London: Chapman and Hall.

Gyorffy, E.J. and Chan, H. (1992).Copper deficiency and mycrocystic anemia resulting from prolonged ingestion of over-the-counter zinc.*American Journal of Gastroenterology*, 87:1054-1055.

Hart, A.D. ,Oboh, C.A., Barimalaa, I.S. and Sokari, T.G. (2005). Concentrations of trace metals (Lead, Iron, Copper and Zinc) in crops harvested in some oil prospecting locations in Rivers State, Nigeria. *African Journal of Food and Nutritional Sciences*, 5(2): 1-14.

Hawley, J.K. (1985). Assessment of health risk from exposure to contaminated soil.*Risk Analysis*, 5(4): 289-302.

Hough, R.L., Breward, N., Young, S.D., Crout, N.M., Tye, A.M., Moir, A.M. and Thornton, I. (2004).Transformation of TNT by aquatic plants and plant tissue cultures.*Environmental Science and Technology*, 31(1): 266-271.

Kokogho M. A.(1993). Determination of Zn, Pb, Cu and Hg in soils of Ekpan, Nigeria. 19: 531-644

Kupolokun, F. (2003-2004) Selected *New scientist inside science; the green house effect* Speech of Group Managing Director; NNPC publication; pg 28

Gribbin, J. (1988);. Pg3

Kieffer, E.F. (1976); *Chemistry Today;* Harper & Row Publisher Inc. New York pg. 241.

Idodo-Umeh, G. and Ogbeibu, A.E. (2010). Bioaccumulation of the heavy metals in cassava tubers and plantain fruits grown in soils impacted with petroleum and non-petroleum activities. *Research Journal of Environmental Science,* 4: 33-41.

Kakulu, S.E. (1985). Heavy metals in the Niger Delta: impact of the petroleum industry on the baseline levels. PhD Thesis, Department of Chemistry, University of Ibadan, Nigeria.

Konz, J..Lisi, K. and Friebele, E. (1989).*Exposure Factors Handbook* .Washington DC: US Environmental Protection Agency, Office of Health and Environmental Assessment, EPA/600/8-89/043.

Lacatusu, R., Rauta, C., Carstea, S. and Ghelase, I. (1996). Soil-plant-man relationships in heavy metal polluted areas in Romania. *Applied Geochemistry,* 11(1-2): 105-107.

Long, X.X., Yang, X.E., Ni, W.Z., Ye, Z.Q., He, Z.L., Calvert, D.V. and Stoffella, J.P. (2003). Assessing zinc thresholds for phytotoxicity and potential dietary toxicity in selected vegetable crops. *Communications of Soil Science and Plant Analysis,* 34(9&10):1421-1434.

Ma, Q.Y., Traina, S.J. and Logan, T.J. (1994). Effects of aqueous Al, Cd, Fe(II), Ni and Zn on Pb immobilization by hydroxyapatite. *Environmental Science and Technology*, 28(7): 1219-1228.

McKone, T.E. (1994). Uncertainty and variability in human exposures to soil contaminants through homegrown food: a Monte Carlo assessment. *Risk Analysis,* 14(4): 449-463.

Msaky., J.J. and Calvert, R. (1990). Adsorption behavior of copper and zinc in soils: influence of pH on adsorption characteristics. *Soil Science*, 150(2): 513-522.

Ma, Q.Y., Traina, S.J. and Logan, T.J. (1994). Effects of aqueous Al, Cd, Fe(II), Ni and Zn on Pb immobilization by hydroxyapatite. *Environmental Science and Technology*, 28(7): 1219-1228.

Nwasike P.O. (2006) *Handout on Air pollution and control*, petroleum training institute, Pg 29 (An unpublished work)

Nriagu, J.O. (1989) A global assessment of natural sources of atmospheric trace metals. *Nature*, 338(6210): 47-49.

Nurnberg, II. W. (1984).The voltametric approach in trace metal chemistry of natural waters and atmospheric precipitation.*Analytical Chemistry Acta*, 164: 1-21.

Ogbonna D.N., Kii, B.L. and Youdeowei, P.O. (2009). Some Physicochemical and heavy metal level in soils of waste dumpsites in Port Harcourt Municipality and environs. *Journal of Applied Science and Environmental Management*, 13(4): 65-70

Ogbonna, D.N., Kii, B.L. and Youdeowei, P.O. (2008).Land disposal of hazardous wastes and heavy metal concentration in soils of waste dumpsites in Port Harcourt Municipality ans environs.*International Journal of Environmental Science*, 4(3): 61-68.

Ogbonna, D.N., Miebi, I. and Isirimah, N.O. (2006).Studies on the inorganic chemicals and microbial contaminants of health importance in groundwater resources in Port Harcourt, Rivers State, Nigeria.*Journal of Applied Sciences,* 6(10): 2257-2262.

Ogbuagu, D.H, Okoli, C.G; Emereibole, E.I; Anyanwu, I.C; Onuola, O; Ubah, N.D; Ndugbu, C.D; Okoroama, O.N; Okafor, A; Ewa, E; Ossai, R. and Ukah, F. (2011a). Trace metals accumulation in biofilms of the upper and middle reaches of Otamiri River in Owerri, Nigeria, *Journal of Biodiversity and Environmental Science (JBES),* 1(3): 19-26.

Oghenejoboh, K.M. (2005).The impact of acid rain deposition resulting from natural gas flaring on the socio-economic life of the people of Afiesere community in Nigeria's Niger Delta.*Journal of Industrial Pollution Control*, 21(1):83-90.

Oguejoifor, G.G. (1998); *Environmental revolution* vol. 2. Pg 92 Centre London pg 1

Ogundipe, O. (2006). *Introduction toEnvironmental Issues: causes, effects and solutions.* Lagos: Ikofa Commercial Press Ltd. 88pp.

Ogwejifor, G.C. (2000). Counting the cost of gas flaring and venting for enhanced gas resources management in Nigeria.*A paper delivered in a government forum on environmental degradation in Nigeria*, Abuja.

Olomo O. R. (1993); Compilation and Dissemination of Information on Tourist Environment in Nigeria. *The Role of the Cartographer chapter 4 in Environment and Tourism in Nigeria*, Edited by B. A. Chokor

Omgbu, J.A. (1992). The distribution of Fe, Hg, Zn, Cd, Cu and Pb in soils of Forcados terminal and its environs.MSc Thesis, Department of Chemistry, University of Port Harcourt, Nigeria.

Omgbu, J.A. and Kokogho, M.A. (1993) Determination of Zn, Pb, Cu and Hg in soils of Ekpan, Nigeria.*Environment International,* p.1-3.

Onosode, G.0 (2003). *Environmental Issues and Challenges of the Niger Delta: Perspective from the Niger Delta Environmental Survey Process.* B. A. Chokor (Ed.), Lilybank Property & Trust Ltd, Lagos, pp.204.

Osu, C.J. and Odoemelam, S.A. (2007). Heavy metals (Pd, Cd, As, Ag) contamination of edible grain grown and marketed in Nigeria.*Research Journal of Applied Science,* 2:192-195.

Oyekunle, L.O. (1999). Gas flaring in Nigeria and environmental pollution control.*Proceedings of the 29th Annual Conference of the NSChE,* Port Harcourt.

Porteous, A. (1976); *Dictionary of Environmental Science and Technology;* low & pry done, 2nd Edition, Pg 89

Purves, D. (1985). Trace element contamination of the environment. Amsterdam: Elsevier.

Reilly, C. (1999). *Metal contamination of food.*2nd. Ed., London: Elsevier Applied Science.

Ruby, M.V., Schoof, R., Brattin, W., Goldade, M., Post, G., Harnois, M., Mosby, D.E., Casteel, S.W., Berti, W. and Carpenter, M. (1999).Advances in evaluating the oral bioavailability of inorganics in soil for use in human risk assessment.*Environmental Science and Technology*, 33(21): 3697-3705.

Salgueiro, M.J., Zubillaga, M., Lysionek, A., Sarabia, M.I., Caro, R., Paoli, T.D., Hager, A., Weill, R. and Boccio, J. (2000). Zinc as an essential micronutrient: a review. *Nutrition Research*, 20(5): 737-755.

Sanchez-Camazano, M., Sanchez-Martin, M.J. and Lorenzo, L.F. (1994).Lead and cadmium in soils and vegetables from urban gardens of Salamanca (Spain).*Science and Total Environment*, 146/147:163-168.

Sivaperumal P, Sankar TV, Viswanathan Nair RG. 2007. Heavy metal concentrations in fish, shellfish and fish products from internal markets of India vis-à-vis international standard. Food Chem 102(2): 612–630.

Sharma, B.K. (2006). *Environmental Chemistry*.10th ed. Goel Publishing House, Mecrut.

Shell Petroleum Development Company of Nigeria (SPDC) (2002). Report on

Fourth Quarter 2002-Gaseous Emission Monitoring Report. Quality Environmental

Management Company Limited.

Sterrett, S.B., Chaney, R.L., Gifford, C.H. and Meilke, H.W. (1996). Influence of fertilizer and sewage sludge compost on yield of heavy metal accumulation by lettuce grown in urban sopils. *Environmental Geochemistry and Health,* 18(4): 135-142.

Soronnadi-Ononiwu C.G; Omoboriowo A.O and Alozie B.E. (2012) *Quality Status of groundwater in Igwuruta area, Ikwerre L.G.A, Rivers state Nigeria. International Journal of Earth Sciences and Engineering.* 2(3): 1-18

United Nations Environmental Programme (2005). “Freshwater pollution”, UNEP/GEMS Environmental Library, 5(6): 5-6

United States Environmental Protection Agency (US EPA) (2003). Effects of acid rain: Lakes and streams. Retrieved from http://www.epa.gov/airmarkets/acidrain/effects/surfacewater.html. (Accessed 19th October, 2015)

van Lune, P. (1987). Cadmium and lead in soils and crops from allotment gardens in the Neterlands. *Netherland Journal of Agricultural Science,* 35:207-210.

Wierzbicka, M. (1995). How lead loses its toxicity to plants. *Acta Soc. Bot. Pol,* 64:81-90.

Wong, J.W.C. (1996). Heavy metal contents in vegetables and market garden soils in Hong Kong. *Environmental Technology,* 17(4): 407-414.

Xiong, Z.T. and Wang, H. (2005). Copper toxicity and bioaccumulation in Chinese cabbage (*Brassica pekinensis* Rupr). *Environmental Toxicology*, 20(2): 188-194.

Yang, X.E., Long, X.X., Ni, W.Z., Ye, Z.Q., He, Z.L., Stoffella, P.J. and Calvert, D.V. (2002).Assessing copper thresholds for phytotoxicity and potential dietary toxicity in selected vegetable crops.*Journal of Environmental Science and Health*, B37(6): 625-635.

Zhuang, P., Zou, B., Li, N.Y. and Li, Z.A. (2009). Heavy metal contamination in soils and food crops around Dabaoshan mine in Guangdong, China: implication for human health. *Environmental Geochemistry and Health*, 31: 707-715.

Zurera-Casano, G., Moreno-Rojas, R., Salmeron-Egea, J. and Pozo, L.R. (1989). Heavy metal uptake from greenhouse border soils for edible vegetables. *Journal of Science*, *Food and Agriculture*, 49(3): 307-314