

**ASSESSMENT OF HEAVY METALS CONCENTRATION IN
SOIL AND FOOD CROPS GROWING AROUND ETELEBOU
FLOW STATION IN BAYELSA STATE, NIGERIA**

BY

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Assessment of heavy metals concentration in soil and food crops growing around etelebou flow station in Bayelsa State, Nigeria by Agbalaje
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CERTIFICATION

We certify that this project "**ASSESSMENT OF HEAVY METALS CONCENTRATION IN SOIL AND TUBER CROPS GROWING AROUND ETELEBOU FLOW STATION IN BAYLELSA STATE, NIGERIA**" was carried out by AGBALAJE O. LUCKY with Registration Number 20085632138 in the department of Environmental Technology. Federal University of Technology, Owerri.

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DEDICATION

This project work is dedicated to God Almighty who gave me the inspiration strength and power beyond what is normal to achieve success in my academics.

And to all members of my family most especially my mother Mrs. Agbalaje Margaret and my Sweet Heart Justina Lucky who gave me their total support throughout the critical period of my academics pursuits and to all lovers of clean environment.

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ABSTRACT

The concentration of Zinc, Lead, Copper, Iron and Chromium in soils, tuber crops (cassava, cocoyam and plantain fruit), within the vicinity of Etelebou flow station operated by Shell Petroleum Development Company (SPDC) were determined in order to assess the concentration level of heavy metals around the flow station. Twenty (20) soil samples were collected from the flow station environment, 50m apart. This consists of 10 top soils (0cm to 15cm) and 10 bottom soils (15cm to 30cm). Also Tuber crops cocoyam tuber (*Xanthosoma mataffa*), cassava tuber (*Manihot esculenta*), and plantain fruit (*Musa sapientum*) grown within the farmlands of the flow station were collected 3 samples each. Samples were prepared (Digested) and analyzed with the aid of Atomic absorption spectrophotometry technique. The result obtained showed the concentration level of 6.82mg/kg to 8.3mg/kg for Zn 0.64mg/kg to 2.3mg/kg for Pb, 1.81mg/kg to 3.3mg/kg for Cu, 16.02mg/kg to 27.10mg/kg for Fe and 0.1mg/kg to 0.81mg/kg for Cr for top soil sample. Bottom soil samples contain as much as 6.30mg/kg to 9.90mg/kg Zn, 0.91mg/kg to 3.33mg/kg Pb, 3.01mg/kg to 4.41mg/kg Cu, 18.50mg/kg to 27.10mg/kg Fe, 0.40mg/kg to 1.02mg/kg Cr. The levels reported on soil samples had an abundance ratio in the order of Fe, > Zn > Cu > Pb > Cr. The result of the concentration levels of heavy metals on food crops were found to be relatively high and gradually accumulating. Their accumulation in tuber crops were found to be higher than the background values (or controls). Furthermore, the concentration level in the soil samples were found to be higher compared to heavy metal concentration in tuber crops.

CHAPTER ONE: INTRODUCTION

1.0 BACKGROUND OF STUDY

Crude oil, a natural occurring complex mixture of liquids and gases, mainly hydrocarbon contents, is found thousands of meters below the earth crust and brought to the surface by drilling (Ifeadi and Nwankwo, 1989; Ake, 1979). Crude oil is accompanied by varying quantities of extraneous substances such as water, inorganic matters and gases. The removal of such substances does not change the state of the crude oil. (Wills, 2000; Bailey et al, 2000). Nigeria like other oil producing countries benefit as well suffers from its positive and negative effect of crude oil drilling such as gas flaring (Ake, 1979; Owobajo, 1981; Adeniyee et al, 1983). After the initial separation of crude oil into gas, oil and water, the oil is sent to refineries for fractional distillation, the gas is usually flared while the water is discharged into the environment (Wills, 2000; Zara and Paul, 2000). Gas flaring is the controlled burning of natural gases associated with oil production. The consistent flaring has left a devastating effect on the

surrounding environment of the Niger Delta Area, where the activities of oil exploration and exploitation is greatest (Adeniye et al; 1983). With a daily crude oil output in excess of two million barrels per day, Nigeria has over 200 gas flaring sites, some of which have been on continuously for over 20 years, while about 22 billion standard cubic feet (SCF) of natural gas is produced daily, about 5% of this quantity is being flared (Bailey et al; 2000).

Heavy metals are of considerable environmental concern due to their toxicity and accumulative behaviour (Purves, 1985; Omgbu, 1992). Trace quantities of certain heavy metals are essential to animal and plant growth. However, they are easily assimilable and accumulate in ecological materials (Nurnbery, 1984).

Comprehensive studies of heavy metals in various Nigeria crude oils have shown them to contain relatively high concentrations of Fe, Cu, Zn, Pb and Hg (Kakulu, 1985). Although petroleum exploration and processing in Nigeria started in the late fifties, government organized research and monitoring programs are less than fully operational, thus long

term and sustained studies of particular ecological and processing areas are few. With increased petroleum exploration and processing, large quantities of these heavy metals are released through the waste effluent into the restricted environment. They accumulate in the ecological material, and eventually get to the bodies of inhabitants over long periods.

With increased petroleum production there has been a continuous increased in processed oil products that are transported between points of production, processing and distribution or export terminals. (Imevbore and Adeyemi, 1981) or more than 90% of these activities takes place in the Niger Delta, the richest in mineral resources along the west African and Nigeria coastal line (imovbore 1979). The Niger Delta is also a rich source of shell fish and fin fish as well as of the coastal mangroves swamps, another of the Nigeria important natural resources.

This valuable Niger Delta ecosystem is however, vulnerable to destruction by industry operational activities, within the area (Imevbore and Adeyemi 1981). (Ekweozor;

1985; Snowden and Ekweozor, 1987, Fodeke and Laden 1987) large areas of shallow tropical African seas, coral reefs, intertidal sand and mud flats and mangrove swamps are potentially at risk from oil industry influence, predicting the effect of these influences, is difficult however, because little is known of the basic biology of these tropical marine ecosystem (Baker 1981) and it is inappropriate to apply the valuable temperate information to tropical conditions because of the large number of ways shallow tropical marine ecosystem differ from the temperate ecosystem for example (Baker 1981) noted that some mangrove swamps, tropical sea grass beds and coral reefs have higher gross primary productivity than other marine or terrestrial communities.

Adverse environmental impacts from excessive heavy metals dispersed from mine and smelter sites include contamination of water and soil, phytotoxicity, soil erosion, are of potential risks to human health (McLaughlin et al. 1999; Adriano 2001; Pruvot et al. 2006). Heavy metal contamination of agricultural soils and crops in the vicinity of mining areas has

been regarded as a great environmental concern (Wcislo et al. 2002; Liu et al. 2005a; Kachenko and Singh 2006).

Several studies in China, South Korea, and the USA have shown that water (Lin et al. 2007), vegetables (Chang et al. 2005; Zheng et al. 2007), rice (Yang et al. 2006), and even fish (Schmitt et al. 2007) are often contaminated by heavy metals dispersed from mining and smelting operations. Li et al. (2006h) found that Chinese cabbage growing in the vicinity of nonferrous metals mining and smelting sites in Baiyin, China, contain high concentration of Cd exceeding the maximum permitted levels (0.05 mg kg^{-1}) by 4.5 times. In the vicinity of a Pb/Zn mine in Shaoxing, eastern China, it was reported that the respective Pb and Cd concentrations of some vegetables were 20 and 30 times higher than the permitted standards (Li et al. 2006a). Clearly, not only the ingestion or inhalation of contaminated particles, but also the ingestion of plants produced in the contaminated area is another principal factor contributing to heavy metal of exposure for population. It has been recognized that food crops can be an important source of heavy metals for humans and animals (Dudka and Miller 1999).

Both heavy metal uptake via roots from contaminated soils and surface water, and direct deposition of contaminants from the atmosphere onto plant surfaces can lead to plant contamination by heavy metals. Lead and Cd are considered potential carcinogens and are associated with etiology of a number of diseases, especially cardiovascular, kidney, blood, nervous, and bone diseases (Jarup 2003). Although Zn and Cu are essential elements, their excessive concentration in food and feed plants are of great concern because of their toxicity to humans and animals (Kabata-Pendias and Mukherjee 2007). Cultivation of crops for human or livestock consumption can potentially lead to the uptake and accumulation of these metals in edible plant parts with a resulting risk to human and animal health (Gupta and Gupta 1998; Lim et al. 2008). Serious systemic health problems can develop as a result of excessive dietary accumulation of heavy metals such as Cd and Pb in the human body (Oliver 1997). L et al. (1996) reported that soil and vegetables polluted with Pb and Cd in Copsa Mica and Baja Mare, Romania, significantly contributed to decreased human life expectancy within the affected areas, reducing average at

death by 9–10 years. In France (Pruvot et al. 2006) and Brazil (Bosso and Enzweiler 2008), it was reported that children living around a former smelter had high blood Pb levels. Turkdogan et al. (2002) suggested that the high prevalence of upper gastrointestinal cancer rates in the Van region of Turkey was related to the high concentration of heavy metals in the soil, fruit, and vegetables. Dietary intake is the main route of exposure for most people, although inhalation can play an important role in highly contaminated sites (Tripathi et al. 1997). Thus information about heavy metal concentrations in food products and their dietary intake is very important for assessing the risk to human health.

In China, there are over 9,000 state-owned and 30,000 private mining companies, and large amounts of hazardous wastes are released from base-metal mining and smelting operations annually. Cumulative use of land by mining was approximately 1,500,000 ha by 2006, with 60% of this area impacted by mine tailings (MEPPRC 2006). Metal ore processing usually leads to multimetal contamination of the environment, and topsoil in the vicinity of mines and smelters

contains elevated concentrations of heavy metal (Dudka and Adriano 1997). Dabaoshan mine area (Guangdong, southern China) has been confirmed to have soils and waters severely pollution by heavy metals (Zhou et al. 2007; Lin et al. 2007). Mining activities during the past four decades have generated large quantities of mine waste materials without any proper treatment. It has been reported that mining activities polluted approximately 83 to 85 ha of paddy fields, and 21 ha of ponds around this mine. In the vicinity of Dabaoshan mine area, the number of cases (esophageal cancer, liver cancer, etc.) is about nine times above the normal incidence of cancer, and the mortality rate approaches 56% (Liu et al. 2005b). Environmental surveys conducted by the Ministry of Health have shown that children living around the mine area had higher blood lead levels than those living in noncontaminated sites. This exposure has been probably attributed to the consumption of drinking water and crops contaminated by mining activities.

The present distribution of heavy metals in soils and tuber crops can serve as an indication of the time, history and extent of pollutants release or discharge into the area.

1.1 STATEMENT OF PROBLEM

The ever increasing global industrial growth has led to greater concern for the cleaner environment. This gave rise for the establishment of various environmental protection agencies by various government. Despite the effort, the problem of environmental pollution especially in water, air and land remain unabated.

The presence of trace metal in crude oil and other bituminous substances world wide had been recognized for some time. Osibanjo and Kakulu(1984), Milner and Kichmer (1952) karchmer and gunn(1952). Metal running the gamut of the period table had been determined in petroleum ball et al(1956), have reported determining v, Ni, Cu, and U in some 23 oil samples. Oderinde(1984) determined V and Ti in nine Nigeria oils and Whisman et al(1987) determined 20 elements, including Pb, B, Mg, Co, Ag, Ti in oil fraction. Milner et al,

(1952) and Nwadinigwe and Achilike (1987) have also reported a wide range of metal in petroleum.

The importance of determining trace metal in petroleum and its derivatives cannot be emphasized. Metallic compound in catalytic process, deposit and consequently accumulate on catalyst. In so doing poisoning this catalyst, it has been reported that when vanadium is deposited on cracking catalyst their activity is markedly reduced mills(1950) resulting in poor gasoline yield. Reforming catalyst are also not spared. Vanadium is especially harmful, these metal are possibly environmental harmful due to their toxicity. Also trace elemental analysis may be useful for the oil.

It has been shown, for example that a wide range of pollutants are increasingly toxic to test animals with increasing temperatures. (Carns et al, 1975).

This observation predict major expected differences in the impacts of pollutions on temperature and tropical ecosystems. Biodegradation of chemical unstable pollutants would be faster in warmer waters. Baker(1981), indicated that were a complex

biological accommodated community is destroyed or affected within an area, recovery may take long time. It is clear that acute and local effect pollutant will be more severe in the tropics while accumulation of pollutants may be less of a problem. The problem of this research will address is that of determining the concentration of heavy metal in soil and selected food crops in relation to heavy metal pollution in Etelebou flow station environment,

1.2 AIM AND OBJECTIVES

The aim of the study is to assess the level of some heavy metals in soil and tuber crops resulting from oil and gas activities around Etelebou flow station.

The present study has been undertaken presently to:

- i. Determine the concentration level of heavy metal in soil and food crops grown around the flow station
- ii. To evaluate the potential health risk of humans via consumption of food crops harvested around the gas flow station.

- iii. Assess the concentration of the bio-accumulated heavy metals in food crops in the study area.
- iv. Determine the relationship between trace metals in soil and food crops.
- v. Determination of variation in concentrations of heavy metals in food crops.
- vi. Determinations of spatial variation in concentration of heavy metals in soils

1.3 JUSTIFICATION OF STUDY

In considering the significance of the research, it is obvious that the sources of the soil and tuber crop pollution is known and their heavy metal content analyzed, the result will provide an insight into the quality and extent of heavy metal pollution that has resulted from the oil and gas activities in the study area. Suspicion falls on any heavy metal which accumulate in human tissues and plant with age among the trace metals essential to life health and optimal exposure situations.

The purpose of the study therefore is to survey the level of some heavy metals (Fe, Zn, Cr, Cu and Pb) resulting from the discharge of effluent of petroleum production in soil and food crops in Etelebou flow station with limitation to Etelebou flow station.

The study will save millions of people most especially those living within Etelebou communities who are losing their lives every year for lack of heavy metal health impact awareness.

It would alert the various communities within Etelebou flow station environment on the risk of growing crops within the flow station environment.

It will alert the government on degradable state of the production environment and the need to guide her in policy making especially increasing a safe and cleaner environment.

It could serve as a baseline data, text and resource to students/readers who might want to further research on this topic.

1.4 SCOPE OF STUDY

Etelebou Flow Station is an onshore flow station, operated by Shell SPDC sited less than 2km from Ogboloma, Nedugo-Agbia community also bounded by Akenfa and Igbogene communities all in Yenegua local government area of Bayelsa state. The flow station environment is characterize with a lot of exploration and industrial activities, such as, pipeline, well heads, discharge of crude and petroleum products into the environment, effluents discharge into water bodies. There is therefore the need for heavy metals concentration in soil and food crops to be study in this area. The targeted area is Etelebou flow station environment. To completely assess the effect of these heavy metals from the flow station activities, the following scope of investigation have to be followed during the study.

- i. A systematic collection of soil and tuber crops samples from study area.
- ii. Preparation and analysis of sample for heavy metals like Pb, Cr, Fe, Cu, and Zn.

- iii. To carry out analysis on results to determine the correlation and equality of mean variance using SPSS and ANOVA.

CHAPTER TWO: LITERATURE REVIEW

2.0 POLLUTION

Pollution is derived from the Latin word "pollute" which means defile, foul, make dirty or unclean and can be define as an undesirable change in or contamination of the environment (air, water and land) by the activities of man's industries which will be harmful to human and other life; that is the physical and biological system in which man and other organism live- is a whole albeit of complicated one with many interacting components (Tolba 1980) with respect to the above definition, many substance may be referred to as pollutants depending on where, how and in what quality they are present in the area of interest.

2.1 TYPES OF POLLUTION

There are different types of pollution among which are water, air, land, vegetation, and noise pollution. But for the purpose of this study, pollutant can be classified under air, land and water.

2.2 LAND POLLUTION

The indiscriminate dumping of garbage into the surrounding land around factories, shops, markets, residences etc leads to land pollution. Garbage may be define as household, agricultural and industrial wastes. The soil thus polluted with the agents above can in turn pollute surface water, ground water, which ultimately can be ingested by man and animals. Materials from industrial solid waste may contain poisonous chemicals, in solutions; these may become concentrated in nature by various organisms in the human food chain.

Soil surrounding industrial areas become contaminated from the fumes emitted by the smoke, flame and dust stakes of the industrial complexes, while those near roads or high ways tend to be high in lead from vehicle exhaust, the heavy metals may be present in the soil as a result of long term effect of road usage, agricultural operation, soil erosion, aerial deposition and some other climatic factors. These elements enrich at the top may be depleted by rains and exist in ionic form.

Many substances are strongly persistence in soil. For example pollutants that exist as Pb^{2+} , Mg^{2+} , Ni^{2+} DDT, may be associated or strongly bonded to negative charge site of organic matter and clay

2.3 AIR POLLUTION

Air pollution occurs as a result of the combustion of fossil fuels (i.e petroleum gasoline and natural gas) and the discharging of gaseous chemical, from industry and transport into the surrounding atmosphere. In heavily industrialized area, there is a high incidence of lung cancer and chronic bronchitis due to the inhaling of dust and smoke particles. In coal mining areas, "black Lung" is a common occurrence in miners due to the 'breathing in of coal dust. In the plastic industry, asbestos's dust a carcinogen causes pulmonary cancer. Various hydrocarbon that are released into the atmosphere from car exhaust include Carbon monoxide, Ozone, Lead particles and soot. Carbon monoxide, a poisonous gas produced because of incomplete combustion, combines with haemoglobin. This substance impedes the transport of oxygen in the blood. Breathing in lead particles found in anti-knock additives from

faulty automobile engines will lead to Lead poisoning and liver impairment. Ozone discharge will irritate the eyes and attack living tissues. It also destroys plant foliage, thereby reducing crop yield.

The extra ozone released may upset the protective blanket against cosmic radiation from the sun sulphur dioxide from the burning of petroleum is a lachrymatory irritant and if dissolved in rain, forms Sulphurous acid. The acid raises the PH of the soil and water making them unsuitable for biological life (Onafowokan, (1992). In recent years, the use of energy released in the fission or fusion of atomic nuclear has added a new dimension to the problem of air pollution. Radioactive contaminates like carbon 14 from nuclear reactors and fall-out nuclear weapon test's pose new threats to human lives. Scientist has found that radioactive exposure to even minimal dosage damage the genetic constitution of our sex cells, for example Japanese survivors of the first atomic Explosion produces siblings, a high percentages of when developed Leukemia or cancer of the blood.

The problems of air pollution are both immense and varied.

2.4 WATER POLLUTION

Water pollution refers to degradation of water quality as measured by biological, chemical or physical criteria. Degradation of water is generally judged in terms of the intended use of the water, departure from norm, effect on public health, or ecological impacts. Water pollution is caused by the indiscriminate dumping of refuse materials, sewage and industrial wastes (i.e pesticides, heavy metals and detergents) into any bodies of water. These pollutants not only destroy many aquatic communities but also have other far reaching effects. For example, in Japan, the Unwanton discharge of Mercury compounds into the sea not only caused millions of fishes to die but also affected the unsuspecting population who ate these fishes. These people contracted mercury poisoning and many died as a result. (Tolba; 1980; Hodges, 1977 and Mombeshara et al, 1981).

Crude oil spills from super tankers and oil rigs have fouled up beaches and threatened the rich coastal marine life, for example, in 1978 in a disastrous accident, the tanker Amoco Cadiz Sank off the coast of France and over night, the aquatic

life off the Western European coastline from Spain to Sweden was affected.

Insecticides and detergent pollutants are basically toxic to marine flora and fauna. Detergents, which are surface -active agents, affect the respiratory mechanism of aquatic organisms. Insecticides, which are non-biodegradable (i.e cannot be decomposed by bacteria, fungi etc) poison, are harmful to fish.

Chemical fertilizers increase crops yield but when these are concentrated in ponds and lakes, they make them unfit for living. Sewage contaminate waters causes water algae to grow profusely, clogging up water ways and rivers, turning them into foul, odorous and oxygen deprived aquatic environments.

The growth of industries in Nigeria has increased the problem of water pollution. Untreated liquid waste from many industries in Lagos are discharge into the Lagos creeks. This is also true of many industrial towns in Nigeria, in Benin City, Lkpoba River which is the major source of drinking water is highly polluted by dumping and washing from the factories,

industrial complexes such as the breweries and from the abattoir sited very close to the river bank.

The resultant effect of the indiscriminate pollution of water sources are that heavy metals, pesticides, residues and small concentrations of hundreds of industrial chemicals, many of which are associated with dangerous diseases such as cancer are found in Nigeria drinking water. Studies have shown that most of the rivers passing through heavily urbanised and industrial areas contain strongly elevated concentration of some heavy metals (Egborge, 1986) and (Fufeyin, 1988) and (Ndiokewe and Guin, 1983).

2.5 TRANSPORT OF ENVIRONMENTAL CONTAMINANTS IN ONSHORE FLOW STATIONS.

The nature of the geo-ecology of a particular environment generally influences the dispersion and containment of petroleum in the ocean and its impact on the coastal system, Inland waters and terrestrial ecosystem.

The landform in Nigeria as those of other western and low land Africa countries consist essentially of sedimentary basin and basement complex rocks (Ifeadi and Awa, 1987).

It has been recorded that the northern countries of the west regions are part of African basement complex with outcropping of igneous and metamorphic rocks in most areas (UNEP; 1982). This complex is also found in more than half of Nigeria. (Ifeadi and Awa, 1987). Also noted that sedimentary rocks which consist mostly of sand stones, shale, different kinds of clays and limestone's are located in the Niger Delta. Implication of these differences in Nigerian is that the overlying layers have been sufficiently weathered to allow permeability of fluids. The permeability coefficient however varies with permeability being lower in region, where the overlying layers contain a lot of clay as in basins rock region, and higher in the regions of the sedimentary basins with smaller clay formations.

There are two primary types of subsurface transport for onshore release that can impact the environment. The transport of fluids at or above the water table from the surface

spills and the transport of fluids from one geological formation to another through improperly plugged and abandoned wells.

When petroleum industry materials are discharged into the ground the liquid fraction including any dissolved chemicals, begin to enter the pore network. These materials can travel through soil pore network in four ways first, a separate non aqueous phase liquid (NAPL) can flow through the pores.

Secondly, contaminants can dissolve into ground water and be transported by it. Third, very small solids (colloids) can also be transported as a vapour through the Vadose (Air saturated zones).

The transport of waste through ground water depends on a number of factors including the permeability of soil, capillary pressure between phases in the soil, solubility of the waste partitioning coefficient, adsorption properties and volatility. Adsorption partitioning and volatilization decrease the concentration of chemicals in water, while leaching de-

absorption and runoff increase the concentration (Hunt et al, 1988a; 1988b).

Metals tend to form insoluble complexes in high pH environment, minimizing their ability to leach away from a site (American Petroleum Institute, 1983b). The primary mechanism for the fixation of metals by soils are adsorption, iron exchange and chemical precipitation. Iron exchange and adsorption are surface phenomena that are highly depended on soil type and composition, particularly the amount of clays present. Factors that effect adsorption are the structural characteristics, the chemical, the organic content of the soil, the pH of the fluid medium, the soil grain size, the iron exchange capacity of the soil (clay content) and the temperature. Migration of heavy metals away from drilling sites generally does not occur. Another important pathway for the transport of petroleum waste is improperly plugged and abandon wells. Those wells allow fluids from geological formation having high hydrocarbon, salt and/or heavy metals concentrations to flow into formation containing fresh water. Wells that are properly plugged and abandoned do not provide

a permeable flow channel for fluids. Fluid flow, however, is not possible between layers if they are in hydrostatic pressure equilibrium; regard less of whether channels exist between the layers.

Numerical modeling of fluid flow in improperly abandoned wells can indicate the likelihood of fresh water contamination at a particular site (Warner and MC Connel, 1993).

The relative contamination potential of abandoned wells ranges, from highly likely to impossible, depending on the age of the well, the depth of the well, the types of well, how the wells was constructed, how it was plugged, the history of well activity, and the hydro-geologic conditions at the site.

Another important pathways for the transport of petroleum waste is the atmosphere. Many petroleum industry waste are gaseous and will be dispersed into the air, where they are transported with the wind, upon release, air born pollutants undergo transport by wind (advection), dispersion from atmospheric turbulence vegetation and building. Chemical

transformation may also take place that alter the chemical or physical state of the emitted pollutants.

2.6 HEAVY METALS

Heavy metals are inorganic elements required or that are essential for plant growth in very minute quantities and with densities greater than $5g/cm^3$. Most heavy metals are important to life even though they occur only in trace amount in the body tissues, but can become toxic, if it injures the growth or metabolism of cells, when present above a given concentration. Heavy metals are toxic at high concentration (Tolba, 1980) for instance nickel is a micro-nutrient for most organism but it become highly poisonous if taken above the normal concentration for a prolonged period of time in an unusual biochemical form or when the metal is presented in an organism by a way of an unusual route of in take (Tolba, 1980), (OKPOKWARI and Njoku, 1989).

Environmental protection of United States in the book titles Environmental Toxicology written by John etal, 1980. Noted that excessive level of trace metals may occur naturally

as a result of normal geological phenomena such as ore formation, weathering of rocks, leaching or in case of mercury degreasing may form the metal, by burning fuels, mining, smelting, discharging industrial and domestic waste etc. Heavy metals made available are not readily removed or detoxified by metabolic activities from the environment, but rather cause environmental nuisance to the inhabitants in the surrounding.

The EEC Directives in the discharge of dangerous substances into the aquatic environment have been implicated in the death of millions of organisms resulting from accidental chemical discharge into the aquatic environment.

In Japan in 1975, Mercury leaked into the Minamata Bay and was absorbed by fish over 100 persons who consumed the contaminated fish died while many others were paralyzed or had visual and acoustic problems Tolba, 1980; Hodges, 1977 and Mombeshara et al, 1981. Mercury also caused the death of tons of eels in River Rhine in Europe in 1986. Although other heavy metals such as Arsenic (As), Chromium (Cr), Copper (Cu), Lead (Pb), Nickel (Ni), Zinc (Zn), etc are placed on the grey list (or potentially hazardous contaminants) in the EEC

Directive. They have also been implicated in a number of human disorder. Chromium and Copper can cause Chromosomal abnormalities and brain damage respectively in man. Lead is known to accumulate in the Liver, Kidney, bone and teeth of human beings who eat contaminated fish, crabs and crayfishes. Lead interferes with the synthesis of haemoglobin and so cause ANAEMIA.

The Toxicity of TEL (Tetraethyl Lead) is mainly due to its effect on our upper respiratory, tracts, central nervous system digestive system and the haemopoietic system (blood system). Mild intoxication is characterized by headache, irritation, restlessness, anxiety, fatigues and insomnia with bad dream. In more severe cases, there is toxic psychosis, delusions and complete disorientation.

Also heavy metals associated with mining industries, oil spillage's are known to have toxic properties if present in the body above certain levels (Bowen, 1986; Dulka and Risby, 1979; Underwood 1971). The greatest danger to the quality of our environment is posed by human activities such as, poorly organized and unregulated disposal of industrial, domestic

waste and crude oil spillage are the major causes of the environmental deterioration (Mombeshara et al 1981).

2.7 SOURCES OF HEAVY METALS

Heavy metals which are not biodegradable are released into the soil, water and air by various sources- potential sources and causes of oil pollution which include heavy metals in oil industry operational areas in Nigeria have been reviewed (Irrechukwu, 1981; Nwankwo, 1987). Ndiokwere and Ezehe, (1990). Also report high levels of heavy metals in soils and plants near the Warri Refinery. Emoyan *et al.*, (2006a; 2006b) have also confirmed high levels of heavy metal contamination of River Ijana – an effluent receiving stream that flows by the same refinery. Braide *et al.*, (2004) observed high concentrations of heavy metals in the Miniweja stream in the eastern Niger Delta. Furthermore, Spiff and Horsfall, (2004) reported trace metal contamination of the intertidal flats of the Upper New Calabar River in the Niger Delta.

These include industrial effluents mining effluents, domestic, effluents, geological weathering and petroleum

industry. All these sources can be classified into Natural and anthropogenic sources.

2.8 INDUSTRIAL EFFLUENT

Industrial effluents from the chemical and processing industries contains poisonous heavy toxic metals such as cadmium, lead and mercury etc. and the diversion of urban effluent into sewage treatment plants also contribute to the amount of heavy metals in the environment, for instance lead in the effluent of metal lead load (Garland, 1975). The use of heavy metal in industrial manufacturing process lead to the manufacture of contaminated waste. For example the Minamata and Taitai Castrotrophes resulted from the contamination of Japanese water by mercury and cadmium from industrial waste (Tolba, 1980; Hodges, 1977. and Mambeshora et al, 1981).

2.9 GEOLOGICAL WEATHERING

Very high level of heavy metals in soil reaches water body and sediment in areas that are characterized by metal bearing formation. The smelting operation of ores and the discharge of affluent as well as natural geological weathering of such area

result in air and water pollution. Thereby increasing the amount of heavy metals in the environment, the differences between heavy metal of natural and anthropogenic source has been widely inferred from the departure of metal concentration usually with the upper most 20-30cm of sediment from those at depth and an increase is usually assume to be anthropogenic being confined to limited number of metals like cadium, mercury lead (Chow et al, 1973; Kakulu 1985).

2.10 DOMESTIC EFFLUENT

Meckenzie and Purves (1975) reported that domestic sewage contain heavy metals, preliminary studies of the leaching of some trace metals from kitchen faucets indicates that in some cases concentration of metals could lead to intake of excess of the maximum permissible limit of these metals.

2.11 ATMOSPHERIC SOURCE

Many trace metal" brought about by air borne particulate derived from high temperature and combustion sources. Example blast furnaces, metallurgical smelters, fossils fuelled

power plants, vehicles and municipal incineration (Regaini et al 1977).

2.12 MINING EFFLUENTS

Onotowokan (1992) confirmed that damage is done by effluent made up mainly of metal discharge from a mine in central wale into water body. In South Africa gold mine, pyrite is the predominant ore mineral. Large quantities of metals which occur as sulphide ore are produce and this has a number of side effects. Example the release of heavy metal (Garland, 1975), when these ore roasted is smelters large quantities of sulphur (iv) oxide gas was formed. When the gas was expose to air and moisture, it is oxidized to tetraoxosulphate (vi) acid solution which is harmful to plant and animal tissues and this is very irritating to human and raise the acid level of water body thereby affecting the metabolism of aquatic organism.

2.13 PETROLEUM INDUSTRY

The rapidly increasing rate of exploration, processing of crude oil and their transportation and marketing are very important in the consideration of the environmental quality, sustenance of the region, because it exposes the environment where crude oil is obtained to constant threat of oil pollution crude oil contain heavy metals such as Lead, Iron, Zinc, Mercury etc. Chemical used in crude oil industry for drilling mud's and pipes contain heavy metals which also pollute the environment. Most oil field explored area beneath the land mass and are capable of polluting the sea, vegetation, when oil spill occurs since oil and the chemical contain heavy metals, hence they in turn contribute to an increase or source of heavy metal in the environment (Omgbu, 1992).

2.14 TOXICITY OF HEAVY METALS

The heavy metals encountered in drilling and production, activities are related to a variety of environmental concerns, depending on the metal and its concentration. At very low concentrations, some metals are essential to healthy cellular

activity. Essential metals include, chromium, cobalt, iron, nickel, zinc, copper, iodine, vanadium, manganese, selenium, molybdenum (Valkonic, 1987).

At high concentrations, however metals can be toxic. Because most concentration encountered during drilling and production are relatively low. The environmental impact is generally observed only after chronic exposure.

The environmental impact of heavy metals is manifested primarily through their interaction with enzymes in animal cells.

Enzymes are complex proteins that catalyse specific biochemical reactions. Heavy metals affect the action of enzymes. Excess concentrations of metals inhibit normal biochemical processes. In cells, this inhibition can result in damage to the liver, kidney, or reproductive blood forming or nervous systems. These effects may also include mutations, or tumors. Many metals can impact embryo and larval stages of fishes and benthic invertebrates.

The toxicity of trace metals found in the upstream petroleum industry have been summarized by the American conference of Governmental industrial Hygienist (ACGIH Proctor et al, 1989). This table lists the threshold limit values (TLV) for air borne exposures.

The toxicity of trace metals in agricultural soil is summarized by Logan and Traina (1993). It can be seen that many metals are essential in low concentration, but toxic in high concentration.

2.15 EFFECT OF METAL ON ECOSYSTEM

The effects are inadequately known (Tolba, 1980) some appear to affect the rate of basic life processes, there are also wide variation of the up take of metal from the soil by different plants. Some tolerate high lead level and absorb little of the metal, whereas, the presence of mercury cadmium are poisonous to most organism irrespective of the type of pollution the undesirable effect of pollution may cause change in the plant ecosystem which effect on one species may lead to effect on the other plants or animals. Example, some crops like

wheat and rice take up much cadmium from the soil and they became hazardous when eaten by consumers.

2.16 EFFECT OF METAL ON MAN

The effect is focused first on the acute poisoning following industrial exposure or through diet. Many metals have been known to be toxic over the years, for example, inhalation of mercury vapour both in mining and felt hot industries has reported many cases of damage of central nervous system, lead, cadmium, nickel, tin are known hazard to those working with them.

2.17 EFFECT OF METAL ON ANIMALS

Water pollutants endanger aquatic life. Fish are killed in millions. Toxic chemicals and diseased organism also make water unfit for use by farm animal. Excess heating of water in rivers and lakes kill fishes. Also pesticide level in many species of birds have reduced reproductive rate. Air pollutants produces eyes and respiratory irritation (Hodges, 1977).

Pollution of combine effect of two or more pollutant is called "Synergism effect" when it is more severe or more

quantitative different from individual effect or the separate pollutant. For instance peanut Texas, United States was adversely affected due to synergism action of Ozone (O_3) and sulphur iv oxide (SO_2) gas (Applegate and Durrant 1976). But when combine effect of two or more pollutant is less, it is called antagonisms. Example cyanide in industrial effluents are quite poisonous and when Nickel is present, a Nickel, Cyanide complex that is not toxic is formed (antagonistic effect) (Will 1969).

However, the study of the synergism effect may be different as different pollutant may be present in the environment.

2.18 EFFECT OF IRON

Iron is the fourth most abundant element in the earth crust. Its greatest use is for structural iron and steel. But it is also used for making dyes and abrasives, it is an essential micro-nutrient in trace quantities for most organism, but ingestion in an excessive amount may result in the inhibition of activity of many enzymes.

Inhalation of iron dust cause benign pneumoconiosis and can enhance harmful effect of sulphurdioxide and various carcinogens. Many streams are poisoned by high level of iron in acid mine drainage-pyrite (iron ore),iron sulphide found in close association with coal deposits, when exposed to moisture and atmosphere oxygen, the ferrous iron is oxidized to the ferric state, a relation which is frequently accelerated by bacteria the Thiobacillus-ferrobacillus group. The ferric iron can then react with sulphide in the presence of water to produce sulphuric acid or react directly with water to produce a yellow flocculent mass of ferric hydroxide consumption of excessive doses of absorbable iron over long periods can cause disturbances of the blood stream and liver cirrhosis (Roe 1966; Jacobs, 1977; Tolba, 1980).

Accidental ingestion of large amount of iron has caused severe poisoning in children, report show that iron oxide play some part in the development of lung cancer in occupationally exposed workers. (International Agency for Research on cancer 1976; Tolba, 1980).

2.19 EFFECT OF LEAD

Lead occurs naturally on the earth's crust in the concentration of about 13mg/kg. The greatest risk arises from the emission to the environment, associated with human use of the metal and its derivatives. When lead is smelted, fumes arises from it, also during the manufacture of insecticides, paints, storage batteries and from gasoline containing lead additives.

Lead affects micro-organisms by retarding the heterotrophic breakdown of organic matter. Little is known about the toxic effect of lead to plant. It tend to affect the root system while animal take in lead by inhalation or ingestion. Most of the lead taken up by the red blood cells are distributed over the whole body which may be concentrated in the liver and kidney and this may be redistributed to the bones, teeth and brain.

Anaemia is the first symptom 'of chronic lead poisoning in animals because lead interferes with the synthesis of heam which is associated with abnormal symptoms which include

nausea, vomiting and abnormal pain. Concentration of lead in soil are raised by deposition near industries using the metal. There is some evidence that some soluble lead salts, are carcinogenic in some animals, but there is little evidence of their carcinogenicity in humans. Organo metallic derivatives may be concentrated in lipid tissue and cause chromosome damage. Some plants show retarded growth at 10ppm sub toxic effect have been observed in microflora at 0.1pmm.(Tolba 1980), U.S. Environmental protection Agency 1977.

There is least effect of lead on birds and mammals, but near land smelters. The presence of lead in the air poses increasing hazard to the health of urban dwellers. The metal effect include damage to the liver, kidneys, brain and central nervous and reproductive system. Effect of lead on children include mental retardation and other central nervous system damage.

2.20 EFFECT OF ZINC

Zinc is present in plants, vegetables, mammalian muscle, bones, marine, algae and fish. It has an atomic weight of 65g

and most diet provide 10 to 15mg/day of zinc. It is one of the most abundant of the essential trace metals in humans and it is non-carcinogenic. Zinc exists in the form of zinc blende (ZnS), which is insoluble in water, but it is easily oxidised to soluble zinc tetraoxosulphate ($ZnSO_4$), during weathering.

Zinc is a common fresh water pollutant, often in association with lead. The human adult body contains about 2.30g of zinc, 65 percent of which is found in muscles; 20 percent in bones, 6 percent in the plasma, 3 percent in the liver and 2.8 percent in the erythrocyte, 60 to 400mg per litre of zinc is found to be toxic in plants, 150 to 600mg per day is also toxic to man. It functions as a catalyst in peptidase and amylases. It also stabilizes coiled ribosomes.

Zinc acts on fish gills, hindering normal breathing and if in large concentration it kills. The upper limits tolerable to fish is found to be 0.70mg (SPRAGUE, 1962). Zinc is essential to human health in very small quantities just like all other essential trace metals. Zinc salts are relatively non-toxic owing to an efficient zinc homeostatic mechanism (Vanugopal and Lucky, 1978; Volume II). However, it is toxic when in high

dose. A single dose of 750mg is lethal to human, vomiting, cramps, renal damage and haemorrhage, pancreatitis preceded the death of a woman who takes up to 6gm of zinc in the form of zinc tetrasulphate (vi) (COWAN,) (1947). Inhalation of zinc (II) oxide at 1 to 34mg/m³ causes metal fume fever in human. Also, evidence of zinc carcinogenesis is increasing (ADDINK, 1960; and VIKBLANDH, (1950). Most animals have high tolerance of zinc, however in rats acute zinc intoxication caused anaemia, decreased erythrocyte production and encourage production of immature thocyte and increased leucocyte production (SUTTON and NELSON 1937).

2.21 EFFECT OF COPPER

Copper is a metal with a wide distribution in nature, it has an atomic weight of 64g and is also an essential nutrient for plants and animals. In nature, it exist as copper (II) oxides, copper (I) sulphide and chalcopyrite (CuFeS₂). The environmental levels of the element has been influenced by man since they began to explore it. Today, copper pollution arises from many sources such as effluent from copper ore smelting and copper plating, mining of copper ore and

application of copper contained pesticides. Copper is used extensively in the manufacture of electrical equipment and coinage. Copper salt are used as insecticides, rodenticides, algaecides and fungicides while copper-chrome arsenite is used in wood preservation. Copper is highly toxic to aquatic organism, especially the highly water soluble copper salts. Excessive ingestion of copper by mammals leads to its accumulation in the tissue.

The adult human body contain about 100mg of copper and one-third of it is in the muscle tissues. Also the liver and brain are rich in copper. Acute copper poisoning in humans occur typically in 10-90 minutes following ingestion of acidic beverages stored or drawn through copper containers. Copper is more toxic in drinks than foods. Abdominal cramps, vomiting and diarrhea caused by copper last less than 24hours SHRIER, and HAWSON, (1969).

Copper accumulate in the liver, kidney, cornea and brain. This accumulation causes trauma in the brain which leads to death. A high incidence of cancer among copper-smiths and abdominal cancer in humans living in regions with high

zinc/copper ratio in the soil are suggestive of a carcinogenic capacity of copper STOKINGER, AND COFFIN, (1978).

In plant, low level copper are essential for normal activity of a number of enzyme and for chlorophyll synthesis. However at a slightly higher concentration copper is the most toxic element after mercury. Inhibition of growth occurs at a concentration less than 0.1ppm in majority of plant species. Intake of copper in plant is accelerated by presence of calcium and magnesium ions but this metals tends to suppress nitrogen fixation.

2.22 EFFECT OF CHROMIUM

Chromium is present in all organic matter and is an essential trace element, however' Only trivalent and hexavalent form of chromium are of biological significance. Trivalent chromium is the most common form of the metal in nature and it is in this state the metal almost always occurs in a living system. Hexavalent chromium is capable of crossing the cell membrane and is rapidly reduced to its trivalent state inside a living cell.

Small quantity of trivalent chromium are essential to carbohydrate metabolism in mammals while is also a co-factor

for action insulin. A little amount of chromium is helpful in improving glucose tolerance in diabetic patients, weak and old individuals. No conclusive evidence of harmful effect of trivalent chromium is available. Most of the mammals can tolerate almost a hundred times more chromium in trivalent state than their usual body burden without apparent toxic effects.

Acute chromium toxicity serious renal tubular necrosis. Exposure to hexavalent chromium has been found to cause dermatitis, allergic skin reactions, chronic ulceration and injury to nasal septum, gastrointestinal ulcers, etc. (Langard and Norseth 1979) chronic chromium toxicity has been associated with incidences of cancers of respiratory tracks in occupationally involved workers. Tetratogenic properties has also been attributed to this metals. It is not certain as to which form of chromium is a more potent carcinogenic agent. As, it is the trivalent form which is metabolically more active, it is probable that the trivalent chromium bond to nucleic acid should be responsible to the tetratogenic and carcinogenic

action. At present, however both forms are considered equally potent carcinogenic agents.(Norseth 1981).

2.23 ATOMIC ABSORPTION SPECTROPHOTOMETER IN HEAVY METALS POLLUTION STUDIES.

In environmental research studies, three major sources of pollutants can be distinguished. These are halogenated hydrocarbons such as pesticides, fungicides, herbicides, etc and trace elements which mainly consists of heavy metals. Atomic absorption spectroscopic method has been proved to be suitable for the investigation of level of micro, trace of ultra quantities of solid sample, especially heavy metals as pollutants of these enumerated forms in near human environment (Vorwald and Urban 1966).

This method of instrumental analysis provide a sensitive means for the determination of numerous elements, at least over sixty elements (Vorwald and Urban 1966). Except for radio activation method, this method exceed all' known method of instrumental analysis in sensitivity and detection limits (Ishikama 1960). Due to this high selectivity the use of atomic

absorption spectrophotometer in the determination of isotopic ratios of single element is quite possible (Ishikama 1960). This high selectivity and freedom from interference also made atomic absorption spectroscopy better compared to flame emission spectroscopy.

The usage of atomic absorption spectroscopy has the inability however to recognized single oxidation steps of the element being analyzed; also one cannot draw conclusion about the chemical environment of the element being investigated. The relative experimental error has an average value of 1%, so that analysis involving a high percentage content are sometimes determined better by conventional means rather than using this method. Also, majority of element which have their resonance wavelengths less than 190nm cannot be determined using this method at present (Ishikama 1960).

Today, this method has made it possible to determine heavy metals contamination of various sample in the environment. Atomic absorption spectroscopic technique has been used in various ways such as in metal determination in

soil, leaves, water urine, blood, food, biological materials, pesticides etc. It has been applied to the determination of magnesium in biological extracts.

CHAPTER THREE: RESEARCH METHODOLOGY

3.1 STUDY AREA

The study was conducted in June 2010, at two sites of cultivated land in Etelebou, Yenagoa Local Government Area of Bayelsa State. (Fig 1). The area marks the geological boundary of the formation and the meader belts of the upper deltaic plains of the Niger Delta. Summary descriptions of the physiography and geology of the study area has been brought to focus by Allen, (1965); Short and Stable (1967), ERML (1997) and UNDP (2006). As older sands of the Niger Delta comprising massive, generally fine to medium grained and fairly sorted but consolidated sand.



Fig. 3.1: Map of Study Area Showing the Impacted Flow Station Sites and Boundary
Source: Shell Petroleum Development Company (SPDC) 2000 bulletin

3.1.1 LOCATION AND SITE

The two sites fall within the tropical climate characterized by rainy and dry seasons. (Ofune, 1979; Here and Carter 1984).

Site1: is a farm land by the side of petroleum activities. It lies between latitude $5^{\circ} 29' 37''$ N and longitude $6^{\circ} 08' 7''$ N. It is a farm land in which cassava, cocoyam and plantain are cultivated. There is one flow station, gas compressor and many oil wells nearby. The site lies by a tarred road and traffic is relatively low. Cultivated plants included plantain cocoyam and cassava.

Site 2: lies between latitude $5^{\circ} 25' 31.1''$ and longitude $6^{\circ} 08' 4''$ N. It is a farm land in which cassava, cocoyam and plantain are cultivated. It lies by a tarred road. There are few in-habited houses. The site is close to a stream and is about 2km away from site 1. Traffic is relatively low and petroleum activities are completely absent.

3.1.2 CLIMATE AND VEGETATION

Etelebou which is in Bayelsa State in the Niger Delta region is situated in the gulf of guinea between longitude 5° E to 8° E and latitudes 4° N to 6° N as shown in (Opafunson, 2007), ERML

(1997) defines the original Niger Delta region (about 29,900 square kilometers) as comprising the area covered by the natural delta of the River Niger and the areas to the east and west, which also produce oil. Its approximate northern boundaries are close to the bifurcation of the River Niger at Aboh, while the Western and Eastern boundaries are around the River Benue and River Imo respectively. Summary descriptions of its physiography and geology may be found in Allen (1965), Short and Stauble (1967), ERML (1997) and UNDP (2006). It is the largest wetland in Africa and the third largest in the world consisting of an overlying swampy terrain that is criss-crossed by meandering and anastomosing streams, rivers and creeks. The well-endowed Niger Delta ecosystem, which contains one of the highest concentrations of biodiversity on the planet, in addition to supporting the abundant flora and fauna, arable terrain that can sustain a wide variety of crops and economic trees, has more species of fresh water fish than any ecosystem in West Africa (Wikipedia, 2007).

3.1.3 POPULATION AND ACTIVITIES

The targeted population was of Ogboloma, Nedugo-Agbia, Akenfa, and Igbogene all of Yenegoa local government area which are boundary communities to the flow station. The major activities carried out by the citizens are peasant farming, such as fishing, hunting, planting of food crops. They also engage in commercial activities.

3.1.4 INFRASTRUCTURES

The infrastructural amenities present in the area include;

Road, electricity, schools and health centres.

3.2 RESEARCH DESIGN

Although there are many types of research design, the one adopted in this study is experimental design. Twenty (20) soil samples were collected, 50m apart (10 top soil, 0 ,to 15cm and 10 bottom soil 15 – 30cm) at each sampling point and three (3) edible plant samples –cocoyam tuber (*Xanthosoma mataffa*), cassava tuber (*Manihot esculeuta*), plantain fruit (*Musca sapientum*) grown within the vicinity of the flow station were collected.

This research study tries to carry out analysis on the impact of oil and gas activities (heavy metal concentration) on the soil and food crops in Etelebuo flow station environment. The heavy metals analyse for in the samples are Fe, Pb, Cr, Zn and Cu.

3.3 SOURCES OF DATA

The types of data used for this study are primary and secondary.

3.3.1 Primary data: The primary data consist of valid informations that are illuminating and truth manifesting because of the presence of the researcher. In this study primary data were obtained from the result of the analysis of the twenty (20) soil samples, 10 top and 10 bottom of heavy metals Pb, Cr, Zn, Fe and Cu and the three (3) edible plants Pb, Cr, Zn, Fe and Cu, heavy metal concentration result. Also a control samples result from site (2) unpolluted farm land were used.

3.3.2 Secondary Data: The secondary data consist of data that has been existing before the need for this research.

Research materials include; text books, newspapers, journal, hand books, unpublished papers, research project work etc. A description of some heavy metals data are given below.

Table 3.1: CONCENTRATION LIMITS FOR HEAVY METALS IN (mg/m³)

Metals	TLV (mg/m³)
Aluminium	2.0
Arsenic	0.2
Barium (soluble compounds)	0.5
Barium (barium sulphate)	10
Cadmium	0.05
Chromim (trivalent)	0.5
Chromium (hexavalent)	0.05
Lead	0.15
Mercury	0.05
Nickel (soluble inorganic compounds)	0.1
Vanadium (as vanadium pentoxide)	0.05
Zn (as zinc oxide)	5

Source: Proctor et al, (1989)

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TABLE 3.2: MAXIMUM RECOMMENDED HEAVY METAL CONCENTRATION IN SOIL IN mg/kg

ELEMENT	Soil concentration (mg/kg)
Arsenic	300
Boron	3.*
Barium	**
Beryllium	50
Cadmium	3
Cobalt	200
Chromium	1,000
Copper	250
Mercury	10
Manganese	1,000
Molydenum	5

Nickel	100
Lead	1,000
Selenium	5
Vanadium	500
Zinc	500

* Concentration in soil-paste extract

** Depending on site conditions, can be as high as 100,000
mg/kg

Source Anderson et al, (1983)

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permission

TABLE 3.3 ROLES OF TRACE METALS IN PLANTS AND ANIMALS

METAL	Essential to plant	Beneficial to animals	Toxic to plants	Toxic to animals	Typical concentration mg/kg
Antimony	No	No	?	Yes	1.5
Arsenic	No	Yes	Yes	Yes	7
Barium	No	Possible	Low	Low	500
Beryllium	No	No	Yes	Yes	2
Bismuth	No	No	Yes	Yes	0.2
Boron	Yes	No	Yes	-	20
Cadmium	No	No	Yes	Yes	0.35
Chromium	No	Yes	Yes	Yes(Cr ⁶⁺)	75
Cobalt	Yes	Yes	Low	Low	9
Copper	Yes	Yes	Yes	Yes	22
Lead	No	No	Yes	Yes	25
Manganese	Yes	Yes	Yes	Low	700

Mercury	No	No	No	Yes	0.07
Molybdenum	Yes	Yes	Yes	Yes	1.5
Nickel	Possible	Yes	Yes	Yes	30
Selenium	Yes	Yes	Yes	Yes	0.3
Silver	No	No	No	Yes	0.05
Tin	No	Yes	3	Yes	4
Tungsten	No	No	?	?	1.5
Vanadium	Yes	Yes	Yes	Yes	75
Zinc	Yes	Yes	Yes	Yes	60

Source: Adapted from Logan and Trains 1993.

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3.4 DATA COLLECTION TECHNIQUE

3.4.1 Sampling

The purpose of sampling is to collect a portion of material small enough in volume to be transported conveniently and handled in the laboratory and still have the accuracy of the presented material being sampled.

This means that the relative proportions or concentrations of all pertinent components will be the same in the sample as in the materials being sampled and that the sample will be handled in such a way that no infinitesimal changes in composition will occur before the tests are made.

3.4.2 Sampling Period

The research was conducted in June 14, 2010 in Etelebuo flow station in Yenagoa Local Government Area Bayelsa State.

Soil and edible plant samples cocoyam, cassava and plantain fruits were collected on the 14th of June between 9am and 11.am.

3.4.3 Sampling Site Locations

Two sampling site locations were chosen for sample collection. Site 1 is the impacted farmlands within the gas flow station. Site 2 is 2km away from gas flow station which is unpolluted farm lands. All in Etelebou environment.

3.5 SAMPLE COLLECTION TECHNIQUES

3.5.1 Soil Samples

Ten (10) sampling point were judiciously selected 50m apart along the farm land within the flow station environment. Twenty (20) soil samples were collected (10 top soil 0 to 15cm and 10 bottom soil 15 to 30cm) at each sampling point. Soil samples were collected with Auger and put into polyethene bags which were carefully labeled for easy identification so as to avoid the incidence of mixing or contamination.

3.5.2 Edible plant samples:

Three (3) edible plant samples – cocoyam tuber (*Xanthosoma mataffaa*), cassava tuber (*manihot esculeuta*), plantain (*musa sapientum*), 3 samples each grown within the farmlands of the flow station site were randomly collected with

a stainless steel knife. Plant samples of the same species were also collected from the unpolluted site 2 chosen as control.

3.6 SAMPLE HANDLING AND TREATMENT

Sample handling and treatment is an important step in pollution studies. Samples that are not handled and treated properly are liable to introduce some errors during analysis. Storage is another important factor that can limit or promote such errors depending on the type of containers contact time and the concentration of the parameter in question.

Care was taken to ensure that samples meant for elemental analysis did not come in contact with materials made up of these metals.

3.7 SAMPLE PRESERVATION AND TREATMENT

The soil samples were taken in a cooler to the laboratory. On reaching the laboratory they were preserved in a refrigerator to prevent or retard the chemicals, biological or physical changes that could occur once the samples are removed from their source.

The food crops were also washed in water to remove soil

and dirt, then peeled and sliced thinly before drying. All samples were dried in an air oven at 60°C for about 72 hours, then cooled to ambient temperature, milled by means of a hammer mill and served through a mesh of 1mm diameter. The milled samples were stored in air tight plastic container until required for analysis.

3.8 PREPARATION OF SAMPLES

The main aim of sample preparation is to convert the analyt of interest to a measurable form.

3.8.1 Determination of metals in soil samples

Samples were air dried, ground, and sieved through a 2-mm nylon sieve. Dried soil samples that fell below the sieve were used for solution preparation. Then 3g of sieve air-dried soil samples were weighted in a 100-cm³ Kjeidahl flask. They were treated with 1cm³ H₂SO₄, 15cm³, HNO₃, and 2cm³ HClO₄. The contents were digested slowly in an electro thermal heater until white fumes were formed. The contents were allowed to cool for 15min after the appearance of white fumes into a

100cm³ volumetric flask, and diluted to volume with distilled water (Allen et al, 1974).

Standards were prepared from metal compounds manufactured by May and Baker Limited, Dagenham, England. Metal stock solutions were prepared and diluted as described by Allen et al. (1974).

Sample solutions were analyzed with a Varian Spectre AA10 Atomic Absorption Spectrophotometer with an air/acetylene flame equipped with an autoprint-out system and metal hollow cathode lamps. Wavelengths used were 213.9nm zinc, 283.3nm lead, 324.7nm copper, 257.9nm chromium, 248.3nm iron.

3.8.2 Determination of metals in Edible Plant Samples

Collected tubers were washed with water, sliced and dried to a constant weight in an oven also to a temperature of 70⁰C. The dry sample was pulverized using an agate pestle and mortar and kept in polyethene bags.

Concentrated HNO_3 (3ml) and 0.5ml H_2SO_4 were added to a 50ml flask containing 1g ground oven-dried plant sample and 1ml of 60% HClO_4 and 0.5ml concentrated H_2SO_4 . The flask was swirled gently and the contents digested slowly on an electrothermal heater to 250°C for 15 minutes. The increase in temperature was gradual until it reached 250°C . The digest was then cooled and filtered through 541 Whatman filter paper into a volumetric flask and diluted to 50ml with distilled water. The residual acid concentration of the digested sample was brought to 1% v/v after digestion. The digested samples were analyzed for trace metals, using the Atomic Absorption Spectrophotometer, Model 451. The instrument was calibrated using standard solutions of lead, iron, copper, chromium and Zinc. The absorbances obtained were used in calculating the concentration of the metals in the different samples.

3.9 PREPARATION OF STANDARD SOLUTION

Standard solutions of the various metals to be analyzed were prepared by dissolving 1.00g of each metal in 10.00cm³ of 4M hydrochloric acid. This was then made up to 1000cm³ with

deionised water. This is regarded as the stock solution and it contain $1000\text{mg}/\text{cm}^3$ of the metal.

10.00cm^3 of the stock solution was measured into a 1000.00cm^3 standard volumetric flask and diluted to mark with deionised water the resulting solution contains $100\text{mg}/\text{cm}^3$ of the metal. Dilution of 1.00cm^3 of this solution to 100.00cm^3 with deionised water using standard volumetric flask, will give $100\text{mg}/\text{cm}^3$ (1.00ppm) concentration of the metal.

3.10 INSTRUMENTATION

3.10.1 Principal Of Atomic Absorption Spectroscopy

If a solution containing metallic species is aspirated in a flame such as air acetylene or Air-nitrous oxide systems, an atomic vapour will usually be formed with some of the metal atoms being excited to higher energy level. The proportion excited is usually small but the ground state atoms have a highly specific and very sharp absorption spectrum. If light of one of those wavelengths is generated outside and passed through the flame, then absorbance to the BEER LAMBERT'S LAW. It is proportional to the path length and concentration (in

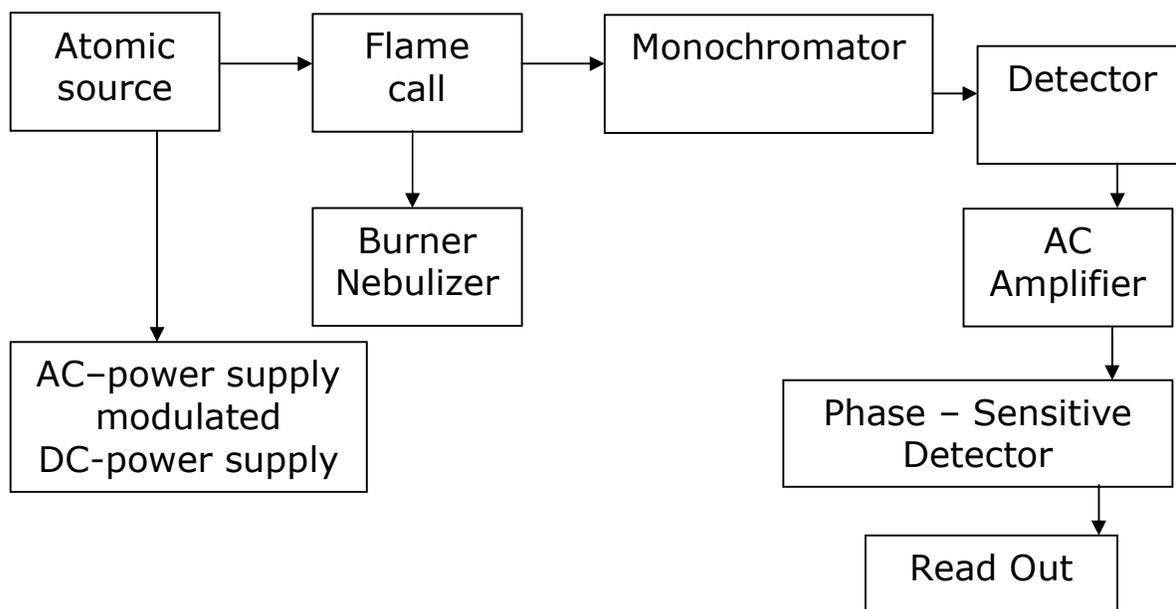
a flame). Evaluation is usually by calibration curve method or by direct reading of concentration of the sample from the instrument.

3.10.2 Atomic Absorption Spectroscopy Component

Atomic absorption spectrophotometric set up consist of the following essential components.

- a) A nebulizer - burner system which produce gaseous metal atoms by using suitable combustion flame involving a full gas- oxidant gas mixture (STEROBEL H.A (1973).
- b) A spectrophotometric system which include a suitable optical train a photo sensitive detection and an appropriate display device for the output from the detector.
- c) A resonance line source, which is required for each element to be determined. The line source used is the Hollow cathode lamp. There are hollow cathode lamps for more than seventy elements (STROBEL H.A (1973).

Figure 3.2: schematic diagram showing the disposition of essential components of a single- beam atomic absorption spectroscopic system. {sterobel h.a (1973)}



3.11 LABORATORY EQUIPMENT AND EXPERIMENTAL MATERIALS

3.11.1 Apparatus and Equipments

Through the research period, the following apparatus were used in determination of various parameters at different times

- i. Various size of Pyrex beakers
- ii. Various size of standard volumetric flask
- iii. Various sizes of measuring cylinder
- iv. 5cm³ micro-pipette

- v. 1.00mm and 64.0mm mesh sieve
- vi. Porcelain mater and pestle
- vii. Carbolite electric furnaces
- viii. Naber electric oven
- ix. Fitter papers wharman 42 and 40
- x. Thistle funnels
- xi. Porcelain crucibles
- xii. Subtechnic grinding machine
- xiii. Mettler PC 800 Digital Weighing Balance
- xiv. Sartorius AR700 Digital Weighing Balance
- xv. Sartorius 2462 weighing balance
- xvi. Sample bottles
- xvii. Sample bags
- xviii. Magnetic stirrer
- xix. International laboratory service atomic absorption spectrophotometer model S₁₂.

3.11.2 Reagents and Chemicals

- i. **4M Hydrochloric Acid:** Analytical grade hydrochloric acid (HCl), mw =36.46, SG=1.18, and percentage purity 36% from MAY and BAKER was used in the preparation of 4m

HCl, this reagent was used in conjunction with deionised water at varied volumes for the final digestion of the various samples for A.A.S analysis.

- ii. **Tetraoxochlorate (vii) Acid:** Analytical grade tetraoxochlorate (vii) acid (HClO_4) MW= 100.50, S.G = 1.66 and percentage purity 60% from British Drug House (BDH) was used for soil and water effluent digestion.
- iii. **Trioxonitrate (v) acid:** Analytical grade trioxonitrate (v) acid (HNO_3), MW= 63.01, SG = 1.50 and percentage purity 96% from E. Merck Darmstadt GMBH was also used for water effluent and soil digestion.
- iv. **Tetraoxosulphate (vi) acid:** Analytical grade tetraoxosulphate (vi) acid M.W= *98.08g/mols*, SG= 1.84 and percentage purify 95-96%. From E.Merk Darmstadt GMB was used for soil and water influent digestion.
- v. Pure metallic sample of (a) Iron (b) lead (c)Zinc (d) Copper (e) Chromium were used for the preparation of metal standard solutions. They were obtained from B.D.H

3.12 ANALYTICAL METHOD AND TECHNIQUES

3.12.1 Analytical Method

The metal concentrations were determined in all standard solutions, samples and blank by atomic. Absorption spectrometer model S₁₂ having digital readout. Air Acetylene flame was used for all determination using the recommended instrumental conditions for each element.

The absorbance by a method from the working standard, blank and the sample solution were determined in that under the conditions as indicated below in table (3.4) using the flame absorption data for common elements which is also tabulated in table (5) as guide.

TABLE 3.4. FLAME ABSORPTION DATA FOR HEAVY METAL**UNDER STUDY**

S/No	Element	Wave Length (nm)	Optimum Working Range For Beer's Law (Ug/Cm³)	Fuel	Oxidant	Slit Setting
1	Pb	217.0	5.0-20.00	Acetylene	Air	1.0
2	Zn	213.9	0.4-1.6	"	"	1.0
3	Cu	324.7	2.0-8.0	"	"	0.5
4	Fe	248.3	2.5-10.0	"	"	0.2
5	Cr	357.9	2.0-8.0	"	"	0.2

1. Except for chromium (Cr) in which Air/Acetylene rich flame is employed, Air/Acetylene lean flame is employed for others.
2. Nitrous oxide (N₂O) can also be used as oxidant (or support) for all the elements except iron (Fe). Source: Analytical methods for flame spectroscopy by Varian Techtron ply, Ltd spring vate Australia (1979).

**TABLE 3.5: FLAME ATOMIC ABSORPTION DATA FOR THE
COMMON ELEMENTS BASSET (1978).**

ELEMENTS	WAVELENGTH OF MAIN RESONANCE	FLAME	WORKING RANGE ($\mu\text{g}/\text{CM}^3$)
Ag	328-1	AA(L)	1-5
Al	309.3	NA(R)	40-200
AS	193.7	AH(R) ¹	50-200
B.	249.8	NA(R)	400-600
Ba	553.6	NA(R)	10-40
Be	234.9	AA(L)	1-5
Bi	223.1	AA(L)	10-40
Ca	422.7	NA(R)	1-4

Cd	228.8	AA(L)	0.5-2
Co	240.7	AA(L)	3-12
Cr	357.9	AA(R)	2-8
Cs	825.1	AP(L)	2-20
Cu	324.7	AA(L)	2-8
Fe	248.3	AA(L)	2.5-10
Ga	294.4	AA(L)	50-200
Ge	265.2	NA(R)	70-280
Hg	253.7	AA(L)	100-400
In	303.9	AA(L)	15-60
Ir	208.9	AA(R)	40-160
K	766.5	AP(L)	0.5-2

Li	670.8	AP(L)	1-4
Mg	285.2	AA(L)	0.1-0.4
Mn	279.5	AA(L)	1-4
Mo	313.3	NA(R)	15-60
Na	589.0	AP(L)	0.15-0.60
Ni	232.0	AA(L)	3-12
Os	290.9	NA(R)	50-200
Pb	217.0	AA(L)	1-5
Pd	244.8	AA(L)	4-16
Pt	265.9	AA(L)	50-120
Rb	780.0	AP(L)	2-10
Rh	343.0	AA(L)	5-25

Ru	349.9	AA(L)	30-120
Sb	217.6	AA(L)	10-40
Sc	391.2	NA(R)	15-60
Se	196.0	AH(R)	20-90
Si	251.6	NA(R)	70-280
Sn	224.6	AH(R)'	15-60
Sr	460.7	NA(L)	2-10
Te	214.3	NA(R)	10-40
Ti	276.8	AA(L)	60-240
TI	276.8	AA(L)	10-50
V	318.5	NA(R)	40-120
W	255.1	NA(R)	250-1000

Y	410.2	NA(R)	200-800
Zn	213.9	AA(L)	1-5

KEY

L = Fuel Lean

R = Fuel/Rich

AA = Air/ Acetylene

AP = Air/Propane

NA = Nitrous oxide/Acetylene

AH = Air/Hydrogen

Source: Flame Atomic Absorption Data for common Elements by Basset et al, (1978).

3.12.2. Analytical Techniques

In atomic absorption spectrophotometric techniques the intensity of the atomic line radiation is attenuated by resonance absorption in the atomic reservoir. The results are recorded as absorbencies for each element. To convert the

measured absorption values into concentrations of the substance being determined it is necessary either to make use of a calibration curve or to carry out the standard addition procedure. Incidentally, the calibration curve is the most frequently used technique.

A calibration curve for use in atomic absorption measurement is obtained by aspirating into the flame samples of solutions containing known concentrations of the elements to be determined, measuring the absorption of each solution and then constructing a graph in which the measured absorption is plotted against the concentration of the solution. By using the calibration curve, it is simple to interpolate from the measured absorbance of the test solution the concentration of the relevant elements in the solution STEROBEL (1973).

Furthermore, in the preparation of the sample solution when using flame methods like atomic absorption spectrophotometry, it is necessary that the sample under investigation is dissolved in a suitable solvent. The complete instrumentation in the flame method is geared towards aerosol formation and atomisation. Inorganic solids such as metallic

alloys, minerals, cement, soil etc must be brought into solution by the usual standard techniques. The aim is to ensure that a clear solution with no loss of the element to be determined is produced. Organic solids which contain trace elements can sometimes be dissolved in a suitable solvent, or the organic material may be oxidised and the residues treated to give an aqueous solution of the elements to be determined.

Apart from water, the burner and mixing chamber are constructed so that nearly all mineral acids and alkalis as well as virtually all organic solvents may be used.

In atomic absorption spectrophotometry, the test solution, are usually of very low concentrations. It therefore implies that the standard solution which will be required for the analysis must contain very small concentrations of the relevant element, and it is rarely practicable to prepare the standard solutions by weighing out directly the required substance. The usual practise therefore is to prepare stock solution which contain about $1000\mu\text{g}/\text{cm}^3$ of the required elements; .and then the working standard solutions are prepared by suitable dilution of the stock solution STROBEL (1973).

The stock solutions are ideally prepared from pure metal or the pure metal oxide by dissolution in a suitable acid solution. The solid used must be of the high purity range of reagents. In most cases, however, it is prepared by dissolution of a suitable metallic salt in deionised water provided the salt satisfied the normal requirement of a primary standard. Analytical method for flame spectroscopy (1979) MANNING (1972), STEROBEL (1973), STROUTS (1962).

3.12.3 Choice Of Analytical Techniques

There is a variety of instrumental techniques available for the analysis of environmental pollutants, and the choice of an analytical technique depends on various factors - suitability, availability, sensitivity, and cost effectiveness. The AAS, ICP-AES and ICP-MS are the primary choices for metal speciation. By contrast, non-metals such as H, C, N, O, P and S and the halogens cannot be determined at their typical concentration levels in airborne particles. NAA is an extremely sensitive and versatile method for determination of trace elements. However, since it requires access to a nuclear research reactor, it is less widely applied for elemental analysis than techniques like AAS,

ICP, ICP-MS and XRF. NAA is preferred for rare earth and some other elements. However, limits of detection offered by NAA, AAS and ICP-AES exhibit large fluctuations among the elements. By contrast, limits of detection vary very little from element to element in XRF and PIXE methods. Once sample is prepared XRF is more rapid than NAA. Non techniques are not sensitive enough to detect Cd and Mo. Comparison of detection characteristics of trace elements and detection limits of analytical techniques are given.

CHAPTER FOUR

RESULTS

4.0 RESULTS

Statistical analysis of the data obtained was done using the statistical package SPSS 11.0 for windows (SPSS Inc, USA), Difference in heavy metals concentrations among different food crops was detected using one-way analysis of variance (ANOVA), followed by multiple comparison using the least significant difference test. Results are as follows.

Table 4.1: Concentration of Zn, Pb, Cu, Fe And Cr In mg/kg In Soil Samples, Where T represent Topsoil and B represent Bottom soil.

Station	Station	Zn	Pb	Cu	Fe	Cr
1	T	8.19	0.98	1.81	18.50	0.81
	B	9.00	1.67	3.01	19.30	0.91
2	T	8.30	2.33	2.30	27.10	0.51
	B	9.90	3.33	4.20	27.10	0.60
3	T	7.40	0.64	2.20	20.00	0.10
	B	8.60	0.91	4.10	22.01	0.40
4	T	8.14	1.32	2.44	20.90	0.47
	B	9.37	1.97	3.77	21.80	0.64
5	T	7.96	1.10	2.10	23.40	0.61
	B	6.30	1.43	3.43	24.70	0.78
6	T	6.89	2.22	3.30	17.10	0.21
	B	7.32	3.10	4.41	19.20	0.81
7	T	6.93	1.42	2.10	19.10	0.30
	B	9.22	2.38	3.92	20.10	1.02
8	T	7.33	2.08	2.23	16.02	0.42
	B	8.24	2.42	3.10	18.50	0.52
9	T	6.82	2.10	2.54	17.80	0.31
	B	7.12	2.70	3.81	19.20	0.77
10	T	7.10	1.85	2.46	19.60	0.48
	B	8.34	2.90	3.27	20.40	0.93
CONTROL SITE 2	T	1.40	0.03	1.20	14.40	0.002
	B	1.60	0.04	2.34	15.10	0.003

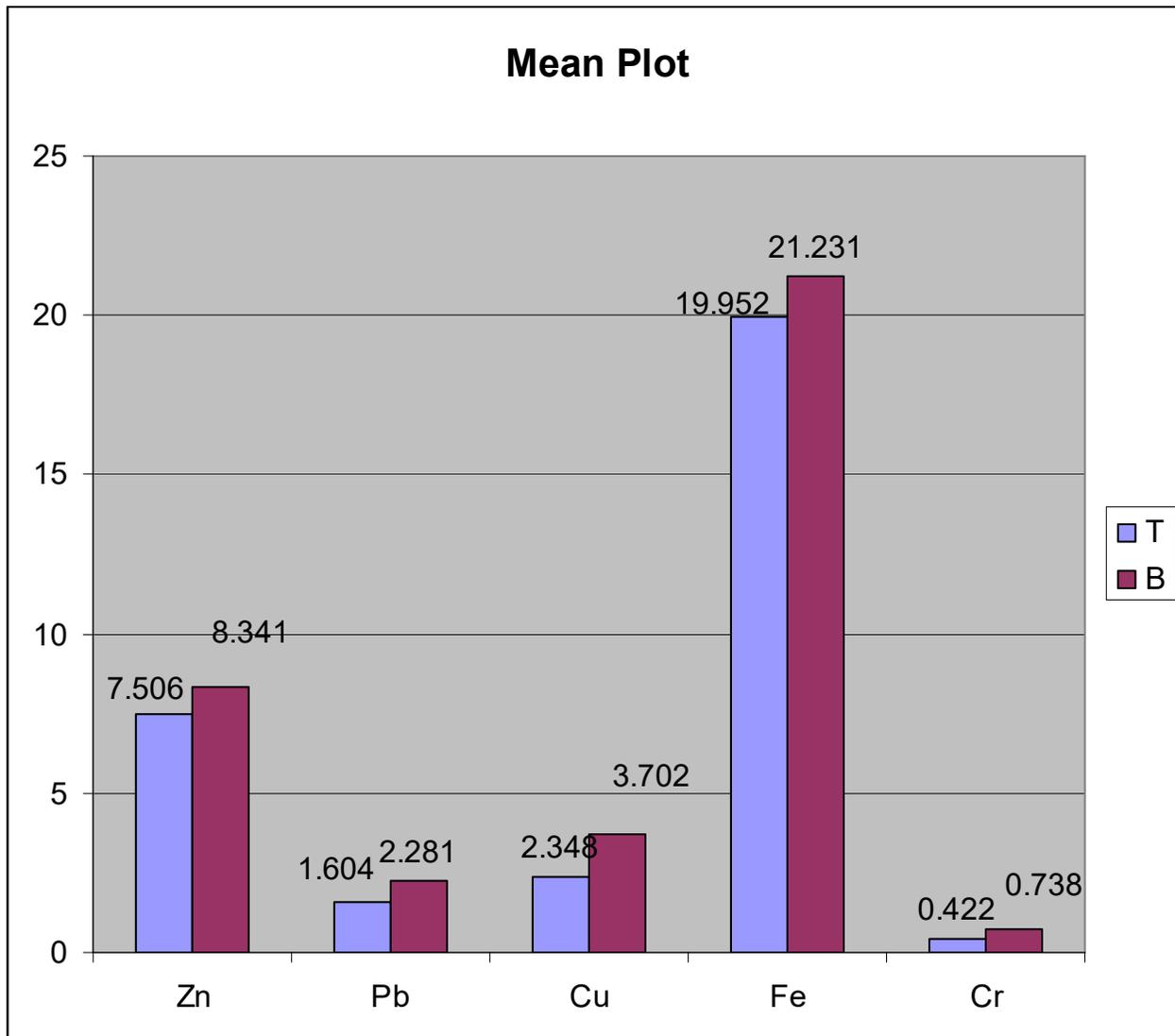


Fig. 4.1: Mean concentration (mg/kg) of Zn, Pb, Cu, Fe, and Cr in soil samples, where T represent Top soil and B Bottom soil.

Table 4.2: Concentration of Zn, Pb, Cu, Fe And Cr In Cocoyam, Cassava And Plantain Fruit In Mg/Kg

Elements	Cocoyam	Cassava	Plantain
Zn	7.70	8.25	6.410
	6.24	7.28	5.320
	5.30	6.94	4.810
Fe	7.60	9.80	10.55
	8.40	8.40	9.70
	6.30	8.30	9.42
Cu	3.10	3.22	2.93
	2.40	3.21	2.76
	2.60	2.81	2.10
Pb	2.00	2.41	1.92
	1.73	2.00	1.20
	1.81	1.94	1.74
Cr	0.54	0.71	0.62
	0.33	0.63	0.42
	0.41	0.41	0.58
Control	0.001	0.003	0.006

TABLE 4.3: MINIMUM AND MAXIMUM CONCENTRATION OF HEAVY METAL IN FOOD CROPS In Mg/Kg

		Minimum	Maximum
Zn	Cocoyam	5.30	7.70
	Cassava	6.94	8.25
	Plantain Fruit	4.81	6.41
	Total	4.81	8.25
Fe	Cocoyam	6.30	8.40
	Cassava	8.30	9.80
	Plantain Fruit	9.42	10.55
	Total	6.30	10.55
Cu	Cocoyam	2.40	3.10
	Cassava	2.81	3.22
	Plantain Fruit	2.10	2.93
	Total	2.10	3.22
Pb	Cocoyam	1.73	2.00
	Cassava	1.94	2.41
	Plantain Fruit	1.20	1.92
	Total	1.20	2.41
Cr	Cocoyam	.33	.54
	Cassava	.41	.71
	Plantain Fruit	.42	.62
	Total	.33	.71

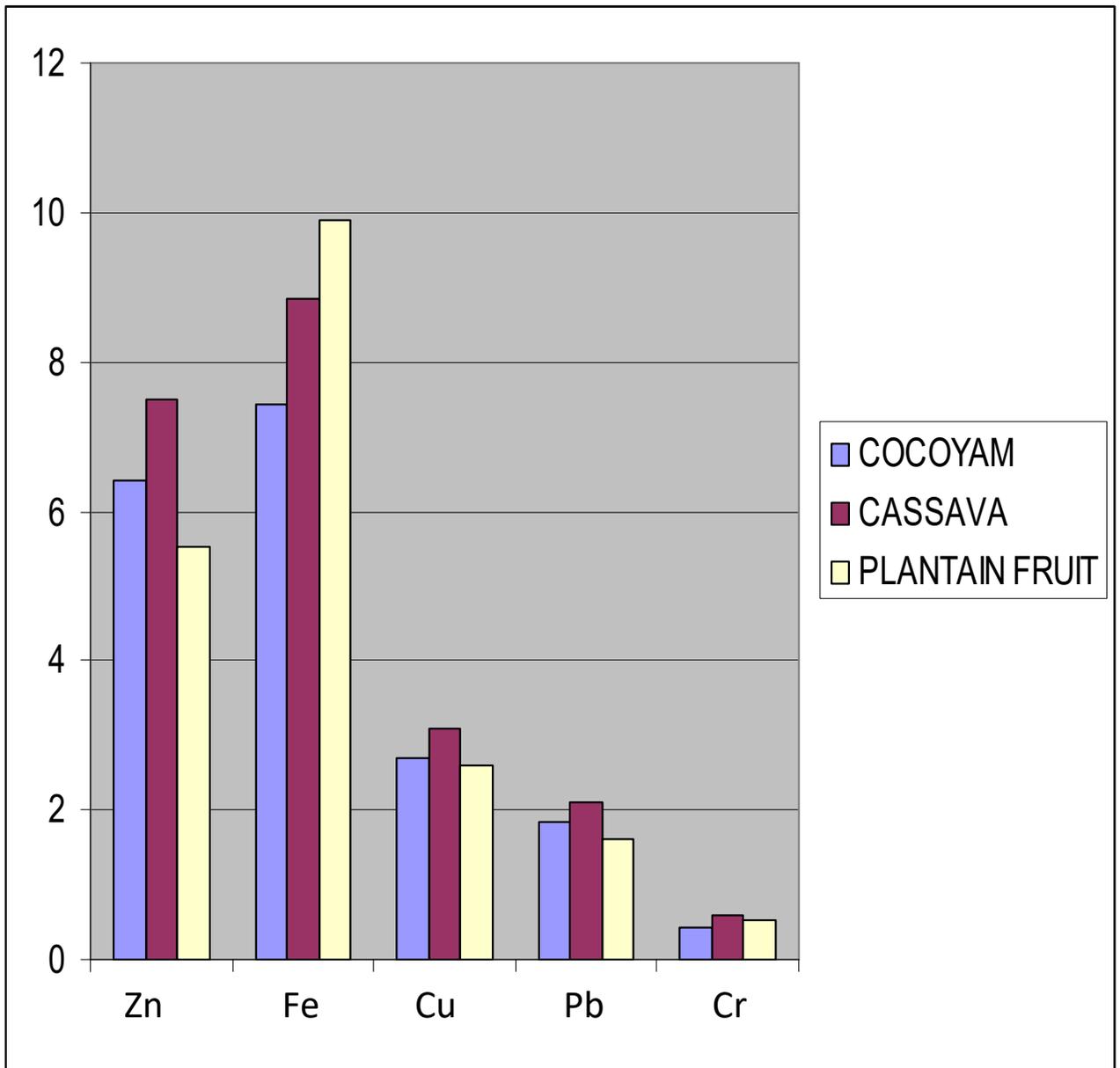


Fig. 4.2 CONCENTRATION OF HEAVY METALS IN FOOD CROPS IN mg/kg

4.1 RESULTS ANALYSIS

4.1.1 Zinc: The result in figure 4.1 shows the mean concentration of zinc in top and bottom soil samples and table 4.2 shows concentration of lead in various crops viz: cassava, cocoyam and plantain fruit.

In figure 4.1 shows the mean concentration of Zinc in top and bottom soils ranges from 7.506mg/kg in top soil to 8.34mg/kg¹ for bottom soil.

Table 4.2 shows minimum and maximum concentration of zinc in food crops, with cocoyam having 5.30mg/kg⁻¹ to 7.70mg/kg⁻¹, 6.94mg/kg to 8.25mg/kg in cassava and plantain fruit 4.81mg/kg to 6.410mg/kg respectively all in site 1. But zinc in site 2 has 1.10mg/kg in soils and below detectable limit for food crops in site 2.

4.1.2 Lead

Figure 4.1 shows mean lead concentration in top soils and bottom soils ranging from 1.604mg/kg in top soil to 2.281mg/kg in bottom soil. Table 4.2 shows lead concentration in food crops ranging from 1.73mg/kg to 2.0mg/kg in cocoyam, 1.94mg/kg to 1.92mg/kg in plantain fruit. Result from site 2 shows 1.20mg/kg to 2.34mg/kg for top and bottom

soil respectively, while food crops below detectable limit for lead. 0.002mg/kg, 0.004mg/kg and 0.12mg/kg respectively for cocoyam, cassava and plantain fruit.

4.1.3 Chromium

Figure 4.1 show mean concentration of chromium in top and bottom soil ranging from 0.422mg/kg to 0.738mg/kg respectively.

Table 4.2 shows concentration of chromium in crops ranging from 0.33mg/kg to 0.54mg/kg in cocoyam, 0.41mg/kg to 0.71mg/kg in cassava and 0.42mg/kg to 0.62mg/kg in plantain fruit. The results from site 2 shows chromium is below detectable limits in soil and crop samples.

4.1.4 Iron

Figure 4.1 and table 4.2 show iron concentration in soils and of various crops in fig 4.1 shows mean iron concentration ranging from 19.952mg/kg in top soil to 21.231mg/kg in bottom soil, while in table 4.2 the minimum and maximum concentration of iron in crops ranges between 6.3mg/kg to 8.4mg/kg in cocoyam, 8.3mg/kg to 9.8mg/kg in cassava and 9.42mg/kg to 10.55mg/kg in plantain fruits, iron concentration in site 2 ranges from 10.4mg/kg to 14.0mg/kg in top and

bottom soil respectively while in food crops apart from Zn and Fe, the other metals were below detectable limits.

4.1.5 Copper

In figure 4.1 means concentration of Cu in top soil and bottom soil ranges from 2.348mg/kg to 3.702mg/kg respectively, while in table 4.2 Cu concentration in crops ranged between 2.40mg/kg to 3.1mg/kg in cocoyam, 2.81mg/kg to 3.22mg/kg in cassava and 2.1mg/kg to 2.93mg/kg in plantain fruit. Result of site 2 shows 0.94mg/kg to 1.1mg/kg for top and bottom soil respectively and 0.001mg/kg, in cocoyam, 0.001.0mg/kg in cassava and 0.01mg/kg for plantain fruits. The level of heavy metals reported on soil samples had an abundance ratio in the order of Fe>Zn>Cu>Pb>Cr.

Table 4.4: T-test and F₉₅ confidence interval of Zn, Pb, Cu, Fe, and Cr in mg/kg of top soil and bottom soil samples, where T represent topsoil B represent bottom soil, and * is significant at 95% confidence limit

Heavy Metals		Zn	Pb	Cu	Fe	Cr
Mean	T	7.5060	1.6040	2.3480	19.9520	0.4220
	B	8.3410	2.2810	3.7020	21.2310	0.7380
SD	T	0.5864	0.5894	0.3965	3.2501	0.2042
	B	1.1290	0.7770	0.4800	2.7652	0.1956
T-value		-2.075*	-2.195*	-6.878	-0.948	-3.534
95% confidence Interval	T	7.5060±0.4195	1.6040±0.4217	2.3480±0.2836	19.9520±2.325	0.4220±0.1461
	B	8.3410±0.8077	2.2810±0.555	3.7020±0.3434	21.2310±1.9781	0.7380±0.1399

**Table 4.5: Calculation of standard deviation for lead Pb
in Top and bottom soil**

Top Soil

X	$X - \bar{X}$	$(X - \bar{X})^2$
0.98	-0.624	0.3894
2.33	+0.726	0.5271
0.64	-0.964	0.9293
1.32	-0.284	0.0807
1.10	-0.504	0.2540
2.22	0.616	0.3795
1.42	-0.184	0.0339
2.08	0.476	0.2266
2.10	0.496	0.2460
1.85	0.246	0.0605
TOTAL 16.04	0	3.127
\bar{X} 1.604		

$$\delta^2 = \frac{3.127}{10} = 0.3127$$

$$= \sqrt{0.3127}$$

$$S_D = 0.5894$$

**Table 4.6: Calculation of standard deviation for lead Pb
bottom soil**

Bottom soil

X	$X - \bar{X}$	$(X - \bar{X})^2$
1.67	-0.611	0.3733
3.33	1.049	1.1004
0.91	-1.371	1.8796
1.97	-0.311	0.0967
1.43	-0.851	0.7242
3.10	0.819	0.6708
2.38	0.099	0.0098
2.42	0.139	0.0193
2.70	0.419	0.1756
2.90	0.619	0.3832
TOTAL 22.81	0	5.4329
\bar{X} 2.281		

$$\delta^2 = \frac{5.4329}{10} = 0.54329$$

$$= \sqrt{0.54329}$$

$$S_D = 0.7770$$

Calculation for T-value

Formular connecting t – value for lead (Pb)

$$t = \frac{(\bar{X}_1 - \bar{X}_2)}{S} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$\text{Where } S^2 = \frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2}$$

$$t = \frac{1.604 - 2.281}{S} \sqrt{\frac{10 \times 10}{10 + 10}}$$

Where S

$$= \sqrt{\frac{9(0.5894)^2 + 9(0.7770)^2}{18}} = \sqrt{0.47556068}$$

$$S = 0.6896090777$$

Substituting for t =

$$t = \frac{-0.6677}{0.6896090777} \times 2.236067977$$

$$t = -2.165$$

Calculate of confidence interval for Pb at F_{95} for top soil and bottom soil

Top soil t-table value at F_{95} at a degree of freedom of 9

$$F_{95} = \bar{X} \pm Z \times \frac{S}{\sqrt{n}}$$

$$= \frac{2.262 \times 0.5894}{10} = 0.4217$$

Bottom soil

$$\frac{2.262 \times 0.7770}{10}$$

$$= 0.555$$

Table 4.7: Descriptives

				Statistic	Std. Error	
Zn	Top Soil	Mean		7.5060	.1854	
		95% Confidence Interval for Mean	Lower Bound	7.0865		
			Upper Bound	7.9255		
		5% Trimmed Mean		7.5000		
		Median		7.3650		
		Variance		.344		
		Std. Deviation		.5864		
		Minimum		6.82		
		Maximum		8.30		
		Range		1.48		
		Interquartile Range		1.2325		
		Skewness		.239		.687
		Kurtosis		-1.896		1.334
			Bottom Soil	Mean		
95% Confidence Interval for Mean	Lower Bound			7.5333		
	Upper Bound			9.1487		
5% Trimmed Mean				8.3678		
Median				8.4700		
Variance				1.275		
Std. Deviation				1.1290		
Minimum				6.30		
Maximum				9.90		
Range				3.60		
Interquartile Range				1.9875		
Skewness				-.533		
Kurtosis				-.514		
Pb	Top Soil			Mean		1.6040
		95% Confidence Interval for Mean	Lower Bound	1.1823		

		for Mean	Upper Bound	2.0257	
		5% Trimmed Mean		1.6172	
		Median		1.6350	
		Variance		.347	
		Std. Deviation		.5894	
		Minimum		.64	
		Maximum		2.33	
		Range		1.69	
		Interquartile Range		1.0600	
		Skewness		-.295	.687
		Kurtosis		-1.402	1.334
	Bottom Soil	Mean		2.2810	.2457
		95% Confidence Interval	Lower Bound	1.7252	
		for Mean	Upper Bound	2.8368	
		5% Trimmed Mean		2.2989	
		Median		2.4000	
		Variance		.604	
		Std. Deviation		.7770	
		Minimum		.91	
		Maximum		3.33	
		Range		2.42	
		Interquartile Range		1.3400	
		Skewness		-.424	.687
		Kurtosis		-.719	1.334
Cu	Top Soil	Mean		2.3480	.2457
		95% Confidence Interval	Lower Bound	2.0644	
		for Mean	Upper Bound	2.6316	
		5% Trimmed Mean		2.3250	
		Median		2.2650	
		Variance		.157	

		Std. Deviation		.3965	
		Minimum		1.81	
		Maximum		3.30	
		Range		1.49	
		Interquartile Range		.3800	
		Skewness		1.517	
		Kurtosis		3.742	.687
					1.334
	Bottom Soil	Mean		3.7020	.1518
		95% Confidence Interval for Mean	Lower Bound	3.3586	
			Upper Bound	4.0454	
		5% Trimmed Mean		3.7011	
		Median		3.7900	
		Variance		.230	
		Std. Deviation		.4800	
		Minimum		3.01	
		Maximum		4.41	
		Range		1.40	
		Interquartile Range		.8975	
		Skewness		-.122	.687
		Kurtosis		-1.291	1.334
Fe	Top Soil	Mean		19.9520	1.0278
		95% Confidence Interval for Mean	Lower Bound	17.6270	
			Upper Bound	22.2770	
		5% Trimmed Mean		19.7733	
		Median		19.3500	
		Variance		10.563	
		Std. Deviation		3.2501	
		Minimum		16.02	
		Maximum		27.10	
		Range		11.08	

		Interquartile Range		3.9000	
		Skewness		1.252	
		Kurtosis		1.694	.687
					1.334
	Bottom Soil	Mean		21.2310	.8744
		95% Confidence Interval	Lower Bound	19.2529	
		for Mean	Upper Bound	23.2091	
		5% Trimmed Mean		21.0567	
		Median		20.2500	
		Variance		7.646	
		Std. Deviation		2.7652	
		Minimum		18.50	
		Maximum		27.10	
		Range		8.60	
		Interquartile Range		3.4825	
		Skewness		1.302	.687
		Kurtosis		1.027	1.334
Cr	Top Soil	Mean		.4220	6.458E-02
		95% Confidence Interval	Lower Bound	.2759	
		for Mean	Upper Bound	.5681	
		5% Trimmed Mean		.4183	
		Median		.4450	
		Variance		4.171E-02	
		Std. Deviation		.2042	
		Minimum		.10	
		Maximum		.81	
		Range		.71	
		Interquartile Range		.2575	
		Skewness		.325	.687
		Kurtosis		.321	1.334

Bottom Soil	Mean		.7380	6.186E-02	
	95% Confidence Interval for Mean	Lower Bound	.5981		
		Upper Bound	.8779		
	5% Trimmed Mean		.7411		
	Median		.7750		
	Variance		3.826E-02		
	Std. Deviation		.1956		
	Minimum		.40		
	Maximum		1.02		
	Range		.62		
	Interquartile Range		.3350		
	Skewness		-.324		.687
	Kurtosis		-.709		1.334

TABLE 4.8: F-95 CONFIDENCE INTERVAL FOR MEAN OF HEAVY METAL CONCENTRATION IN FOOD CROPS

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		
					Lower Bound	Upper Bound	
Zn	Cocoyam	3	6.4133	1.2094	.6982	3.4091	9.4175
	Cassava	3	7.4900	.6798	.3925	5.8013	9.1787
	Plantain Fruit	3	5.5133	.8173	.4719	3.4830	7.5437
	Total	9	6.4722	1.1759	.3920	5.5684	7.3761
Fe	Cocoyam	3	7.4333	1.0599	.6119	4.8005	10.0662
	Cassava	3	8.8333	.8386	.4842	6.7500	10.9167
	Plantain Fruit	3	9.8900	.5885	.3398	8.4282	11.3518
	Total	9	8.7189	1.2970	.4323	7.7219	9.7159
Cu	Cocoyam	3	2.7000	.3606	.2082	1.8043	3.5957
	Cassava	3	3.0800	.2339	.1350	2.4909	3.6610
	Plantain Fruit	3	2.5967	.4384	.2531	1.5075	3.6858
	Total	9	2.7922	03779	.1260	2.5017	3.0827
Pb	Cocoyam	3	1.8467	.1387	8.007E-02	1.5022	2.1912
	Cassava	3	2.1167	.2558	.1477	1.4812	2.7521
	Plantain Fruit	3	1.6200	.3747	.2163	.6892	2.5508
	Total	9	1.8611	.3204	.1068	1.6149	2.1074
Cr	Cocoyam	3	.4267	.1060	6.119E-02	.1634	.6900
	Cassava	3	.5833	.1553	8.969E-02	.1974	.9692
	Plantain Fruit	3	.5400	.1058	6.110E-02	.2771	.8029
	Total	9	.5167	.1286	4.288E-02	.4178	.6156

Table 4.9: Discriptives

			Statistic	Std. Error	
Zn	Cocoyam	Mean	6.4133	1.225	
		Median	6.2400		
		Variance	1.463		
		Std. Deviation	1.2094		
		Minimum	5.30		
		Maximum	7.70		
		Range	2.40		
		Interquartile Range			
		Skewness	.632		
		Kurtosis			
Cassava		Mean	7.4900	.3925	
		95% Confidence Interval for Mean	Lower Bound Upper Bound		5.8013 9.1787
		5% Trimmed Mean			
		Median	7.2800		
		Variance	.462		
		Std. Deviation	.6798		
		Minimum	6.94		
		Maximum	8.25		
		Range	1.31		
		Interquartile Range			
		Skewness	1.257		1.225
		Kurtosis			
		Plantain Fruit			Mean
95% Confidence Interval for Mean	Lower Bound Upper Bound			3.4830 7.5437	
5% Trimmed Mean					
Median	5.3200				
Variance	.668				
Std. Deviation	.8173				
Minimum	4.81				
Maximum	6.41				
Range	1.60				
Interquartile Range					
Skewness	1.005			1.225	
Kurtosis					
Fe	Cocoyam			Mean	7.4333

		95% Confidence Interval for Mean	Lower Bound Upper Bound	4.8005 100662	
		5% Trimmed Mean			
		Median		7.6000	
		Variance		1.123	
		Std. Deviation		1.0589	
		Minimum		6.30	
		Maximum		8.40	
		Range		2.10	
		Interquartile Range			
		Skewness		-.690	1.225
		Kurtosis			
	Cassava	Mean		8.8333	.4842
		95% Confidence Interval for Mean	Lower Bound Upper Bound	6.7500 10.9167	
		5% Trimmed Mean			
		Median		8.4000	
		Variance		.703	
		Std. Deviation		.8386	
		Minimum		8.30	
		Maximum		9.80	
		Range		1.50	
		Interquartile Range		.	
		Skewness		1.704	1.225
		Kurtosis		.	.
	Plantain Fruit	Mean		9.8900	.3398
		95% Confidence Interval for Mean	Lower Bound Upper Bound	8.4282 11.3518	
		5% Trimmed Mean			
		Median		9.7000	
		Variance		.346	
		Std. Deviation		.5885	
		Minimum		9.42	
		Maximum		10.55	
		Range		1.13	
		Interquartile Range		.	
		Skewness		1.301	1.225
		Kurtosis		.	.
Cu	Cocoyam	Mean		2.7000	.2082

		95% Confidence Interval for Mean	Lower Bound Upper Bound	1.8043 3.5957	
		5% Trimmed Mean			
		Median		2.6000	
		Variance		.130	
		Std. Deviation		.3606	
		Minimum		2.40	
		Maximum		3.10	
		Range		.70	
		Interquartile Range		.	
		Skewness		1.152	1.225
		Kurtosis		.	.
	Cassava	Mean		3.0800	.1350
		95% Confidence Interval for Mean	Lower Bound Upper Bound	2.4990 3.6610	
		5% Trimmed Mean			
		Median		3.2100	
		Variance		5.470E-02	
		Std. Deviation		.2339	
		Minimum		2.81	
		Maximum		3.22	
		Range		.41	
		Interquartile Range		.	
		Skewness		-1.728	1.225
		Kurtosis		.	.
	Plantain Fruit	Mean		2.5967	.2531
		95% Confidence Interval for Mean	Lower Bound Upper Bound	1.5075 3.6858	
		5% Trimmed Mean			
		Median		2.7600	
		Variance		.192	
		Std. Deviation		.4384	
		Minimum		2.10	
		Maximum		2.93	
		Range		.83	
		Interquartile Range		.	1.225
		Skewness		-1.444	.
		Kurtosis		.	.
Pb	Cocoyam	Mean		1.8467	8.007E-02

		95% Confidence Interval for Mean	Lower Bound Upper Bound	1.5022 2.1912	
		5% Trimmed Mean			
		Median		1.8100	
		Variance		1.923E-02	
		Std. Deviation		.1387	
		Minimum		1.73	
		Maximum		2.00	
		Range		.27	
		Interquartile Range		.	
		Skewness		1.107	1.225
		Kurtosis		.	.
	Cassava	Mean		2.1167	.1477
		95% Confidence Interval for Mean	Lower Bound Upper Bound	1.4812 2.7521	
		5% Trimmed Mean		.	
		Median		2.0000	
		Variance		6.543E-02	
		Std. Deviation		.2558	
		Minimum		1.94	
		Maximum		2.41	
		Range		.47	
		Interquartile Range		.	1.225
		Skewness		1.625	.
		Kurtosis		.	.
	Plantain Fruit	Mean		1.6200	.2163
		95% Confidence Interval for Mean	Lower Bound Upper Bound	.6892 2.5508	
		5% Trimmed Mean		.	
		Median		1.7400	
		Variance		.140	
		Std. Deviation		.3747	
		Minimum		1.20	
		Maximum		1.92	
		Range		.72	
		Interquartile Range		.	
		Skewness		-1.293	1.225
		Kurtosis		.	.
Cr	Cocoyam	Mean		.4267	6.119E-02

	95% Confidence Interval for Mean	Lower Bound Upper Bound	.1634 .6900	
	5% Trimmed Mean		.	
	Median		.4100	
	Variance		1.12E-02	
	Std. Deviation		.1060	
	Minimum		.33	
	Maximum		.54	
	Range		.21	
	Interquartile Range		.	
	Skewness		.690	1.225
	Kurtosis		.	.
Cassava	Mean		.5833	8.969E-02
	95% Confidence Interval for Mean	Lower Bound Upper Bound	.1974 .9692	
	5% Trimmed Mean		.	
	Median		.6300	
	Variance		2.413E-02	
	Std. Deviation		.1553	
	Minimum		.41	
	Maximum		.71	
	Range		.30	
	Interquartile Range		.	
	Skewness		-1.230	1.225
	Kurtosis		.	.
Plantain Fruit	Mean		.5400	6.110E-02
	95% Confidence Interval for Mean	Lower Bound Upper Bound	.2771 .8029	
	5% Trimmed Mean		.	
	Median		.5800	
	Variance		1.120E-02	
	Std. Deviation		.1058	
	Minimum		.42	
	Maximum		.62	
	Range		.20	
	Interquartile Range		.	
	Skewness		-1.458	1.225
	Kurtosis		.	.

CHAPTER FIVE DISCUSSION

5.0 DISCUSSION

Heavy metals have been found in soil, and food crops and have a potential health hazards to man through the dietary pathway in Nigeria (Obiajunwa et al, 2001). Heavy metals concentrations in site 1 around Etelebou flow station was high while, below detection level was recorded for site 2 (an area of non-oil and gas activities). This high value could be attributed to the operation of the flow station activities, such as gas flaring, gas compressor, giant electric generators and well head repairs.

Flaring of gas and numerous oil wells are associated with site 1; An abandoned dry burrow pit probably receiving waste arising from petroleum activities, Rain water runoff could also have carried spilled crude oil and petroleum effluents to the burrow pit during the raining season. The absence of heavy metals or lower values in site 2, which is 2km away from site 1 is a confirmation of petroleum activities being responsible for the value recorded in site 1. Pollution of the groundwater with petroleum hydrocarbons and heavy metals is a possibility since the soil of Etelebuo is mainly composed of sand (Allen, 1965).

The soils also lacks clay layer above the aquifer (Egwebe, 2003).

Petroleum renders the soil infertile, burns vegetable and kills useful organisms (Idodo-Umeh, 2004). The bioaccumulation of heavy metals in cassava, plantain fruits and cocoyam were generally higher at site 1 than at site 2. This is expected since the area near petroleum activities has higher level of pollutants including heavy metals (Woodward and Riley, 1983). Uptake of heavy metals is increased in plants that are grown in areas with increased soil concentration of heavy metals (Lecoultre, 2001).

The atmosphere is a major source of metal pollution (Forstner and Wittman, 1981, National water and soil consevation 1985). Cr were below detectable levels in both plantain fruits, cassava tuber and cocoyam, indicating non absorption and contamination from anthropogenic source.

In the cassava, cocoyam and plantain fruits, the values of heavy metal bioaccumulated were higher in site 1 than site 2 suggesting that absorption and bioaccumulation depend upon availability of metals.

Metals tend to bioaccumulate in animals and plants. (Melville and Burchett, 2002). Anthropogenic origin of petroleum wastes, crude oil and continuous gas flaring in site 1 could have possibly enriched the soil with heavy metals than site 2.

Anthropogenic sources of heavy contaminant such as burning of fossil fuels oil spills and use of fertilizers are likely the cause of higher metals contaminants in soils (Woolson, 1973, Boon and Soltanpor, 1992, Manathan, 1994, Ademoroti, 1996, Cobb et al, 2000, Lecoultre, 2001). Many investigators have reported that some common garden vegetables accumulate high level of heavy metals from soils (Gacia et al, 1979, Xlong, Cob et al, 2000, Lecoultre, 2001). Species of some Brassica ((Cabbage) are hyperaccumulators of heavy metals in the edible tissues of the plant (Xiong, 1998) and this creating a pathway for heavy metal accumulation for people who consume the vegetables and fruits grown in heavy metal contaminated soil (Lecoultre, 2001).

The values of Pb, 2.41mg/kg, in cassava 1.92mg/kg, in plantain and Zn (8.25mg/kg) in cassava and Zn (6.41) in plantain were higher than the values recorded in soils,

indicating hyperaccumulation. Therefore plantain fruits and cassava tubers can be used as bioindicators of soil pollutions.

The levels of heavy metals in farm soils are generally not analysed before planting and therefore consumption of contaminated fruits, seeds or tubers is common (Lecoultre, 2001). Heavy metals concentrations in tree fruits are very low even when grown in contaminated soils (ISHS, 2005). However, the level of metals with mean concentration in soils of Etelebou, which ranges for Fe (19.95mg/kg to 1.23mg/kg), Zn, 7.50mg/kg to 8.34mg/kg, Pb, 1.60mg/kg to 2.28mg/kg, Cu, 2.34mg/kg to 3.70mg/kg and Cr, 0.4220mg/kg to 0.7380mg/kg in petroleum impacted site 1 call for serious concern though the values do not exceed the maximum recommended heavy metals concentration in soil but continuous petroleum wastes and production activities will increase level of heavy metal concentration.

However the levels of Zn (7.70mg/kg) in cocoyam, 8.25mg/kg in cassava and 6.41mg/kg in plantain fruit and Fe, 8.4mg/kg in cocoyam, 9.8mg/kg in cassava, and 10.55mg/kg in plantain fruit.

Also Pb, (2.0mg/kg, 2.4mg/kg and 1.72mg/kg call for serious concern as the heavy metals exceed WHO (1984) maximum acceptable limits for foods, although Pb value (1.92mg/kg) in cassava in site 1 (petroleum impacted soil) was below WHO limit (2mg/kg) for food, threat to Pb poison is likely.

Garri which is a product of cassava is consumed daily by Nigerians in large quantity. Therefore, Pb concentration could be cumulative, Pb can easily cross the placenta and damage the foetal brain and may also cause development of autoimmunity in which a person's immune system attacks its own cells leading to disease such as the rheumatoid arthritis, diseases of kidneys, nervous system and circulatory system (Casarett and Doull, 1996). The populations most affected by consumption of contaminated farm products are pregnant women and young children (Boon and Soltanpour, 1992; LeCoultre, 2001). Neurological disorders, central nervous system destruction and cancers of various body organs are some of the reported effects of heavy metal disorders (Luckey and Venugopal, 1978; Forstner and Wittman, 1981; Manahann, 1994; Casarett and Doull, 1996; Van Vuren and Nussey, 1999).

Low birth weight and severe mental retardation of newborn children have been reported in some cases where pregnant mothers ingested toxic amounts of heavy metals (Mahaffey et al, 1981). Soils contaminated with Pb have been reported to decrease the growth and yield of plants (Balba et al., 1991).

CHAPTER SIX

CONCLUSION AND RECOMMENDATION

6.1 CONCLUSION

This study is a pioneer work on heavy metal accumulation in soil and edible food crops in this part of the country (ETELEBOU) ravaged by oil pollution activities. All heavy metals showed higher values in petroleum impacted soil than non-impacted soil. The heavy metal concentrations in cassava tubers and plantain fruits grown in petroleum impacted soil were significantly higher than the levels recorded in the same crops grown in non-impacted soils. These findings are indicative of oil and gas activities pollution. Although the essential elements are beneficial to man and plant, when found in excessive amounts well above the levels normally found in food and agricultural soil, can prove detrimental to health, this is more so when they exist in commonly consumed food crops particularly cassava, cocoyam and plantain which are generously consumed by all households.

Although well regulated in some countries gas flaring activities has been the source of many contaminants and chemicals in food. Flow station activities have the potential for

generating air emissions, waste water effluents and solid wastes, all of which enter the food chain and cause danger to man, animals and plants. In view of these findings, there is need to monitor closely the environment under review and put in place appropriate checks and balances to preserve the health of communities within the vicinity of the flow station environment, particularly as the effect of heavy metals are bioaccumulative and pose great danger to the health of humans, animals and plants.

6.2 RECOMMENDATION

The contamination of the environment by the flow station effluents discharge in relation to heavy metals may not generate any public discontent or concern at present among the populace due to the level of pollutants presently in the environment. But for the fact that there may be accumulation of some of these pollutants, especially heavy metals in the animals that live in these areas, for instance fishes in the ponds and lakes, birds and human beings in the air and land respectively, effort should be made to reduce the overall quantity of pollutants in the environment. Therefore, various

recommendations which would reduce pollution of the environment are necessary.

The Federal Environmental Protection Agency (FEPA) decree 58 of 1978 enjoins Federal Ministry of Environment to establish such environmental criteria, issue emission guideline for each category of industry and standards for the protection of the nations atmosphere and surface waters as may be necessary to protect the health, ensure safety and welfare of the populace from environmental degradation, enforce environmental impact assessment implementation in all industrial projects, and to fund, monitor and co-ordinate environmental quality studies. With this wide powers, it is therefore high time the authority reappraise its priority and put things in its right position so as to rectify this environmental deterioration. The gas flow stations (SPDC) must from time to time carry out routine treatment on their fume, dust and aqueous effluent discharged, this is to ensure minimum discharge of trace elements into the environment. Effort should be made by SPDC to minimize generation of pollutants into the flow station environment through continuous monitoring of production processes, strict compliance with production

procedure and on the spot repair of equipment's whenever faults are detected, as a means of minimizing pollutant, generation, SPDC and those company operating within the researched vicinity should take necessary action to control their wastes, especially water effluent. Although the flow station posses modern water treatment plants, more effort should be made towards research and monitoring techniques relevant to environmental problems. More emphasis should be placed on manpower development, efficient usage and maintenance of these pollution control equipment. Also environmental impact assessment (EIA) should form an integral part of the planning process.

Most communities in the area depends on the gas flow station environment as a means of livelihood such as fishing and agricultural practices, transportation, etc. All these result in health complication in man since these production activities release pollutant into the immediate environment it is therefore necessary that parameters should be made to meet World Health Organization (WHO) standards for water, soil, air and food crops

There is abundant reasons to make one believe that Nigerians are increasingly becoming aware of the need to maintain and preserve the quality of the nations environment. Competent man- power should be developed for the purpose of undertaking environmental impacts assessment on every aspect of pollution in the country. This can be used in the future as a baseline data for monitoring the industrial environment as a form of check and balances.

REFERENCES

- Ademoroti C.M.A. (1996) Environmental Chemistry and Toxicology 1st ed, Foludex Press Ltd. Ibadan 215pp.
- Akhionbare S.M.O. (2009) The environmental Concepts, Issues and Control of Pollution 1st ed, M.C. Computer Press, Owerri 430pp.
- Allen, S.E; Grinshaw, H.M; Parkinson, J.A; Quarmby (1974) Chemical methods of Analyzing Ecological Materials. London: Oxfords Blackwell Scientific Publication 565pp.
- American Petroleum Institute, (1986) Review of Ground-water Models, A.P.I Publication 434, Washington D.C.
- American Petroleum Institute, (1988) Phase Separated Hydrocarbon Contaminant; Modeling for Corrective Action A.P.I Publication 4474, Washington D.C, O.C.
- Applelegate H.G. Durrant L.C. (1969) Synergistic Action of Ozone SO₂ in Peanut, International Journal. Environmental Studies.
- Atuma S. and Egborge AMM (1986) Insecticides and metals in Nigeria Surface Water in River. International - Journal. Environmental Studies 101.27pp, 139-142pp.
- Basset J. Denney, R.C. Jeffery, G.H and Mendham J. (1978). Vogels Testbook of Quantitative Inorganic Analysis Including Elemental Instrumental Analysis, Forth Edition, pg 810-844. Longman Group Limited London.
- Bhatia S.C. (2003) Environmental Chemistry 1st ed. CBS Publishers and Distribution, New Delhi, 549pp
- Boon DY and PN Soltan Pour (1992) Lead, Cadmium and Zinc Contamination of Aspen Garden Soils and Vegetation .Journal. Environ. Qual. 21: 1, 82 – 86pp.
- Chow T.J et al (1973) Lead Pollution Record in Southern California Coastal Sediments. Science 181: 551 – 552.
- Duffus, J.H (1980); Environmental Toxicology, Edward Arnol Publisher Limited, London pp 69 – 77

- Dulka, J.J and Risby T. H (1976) Ultra-Trace Metal in Some Environment and Biological System. Anal Chem. 48, 640A-653A.
- Garland J.K (1975 Chemistry of Our World Macmillan Publisher C. Inc. New York. 645pp
- Hart, A.D, Oboh C.A, Barimalea I.S and T.G. Sokari (2005) Concentrations of TRACE METALS (LEAD, IRON, COPPER AND ZINC) in Crops Harvested in Some Oil Prospecting Locations in Rivers State. African Journal of Food and Nutrients Sciences, Volume 5 No 2
- Hostader, R.A et al (1976) "Analysis of Petroleum for Trace "Metal" America Chemical Society, 643pp.
- Hunt J.R, Sitar N and Udelli K.S. (1988a). Non-Aqueous Phase Liquid Transport and Clean up 1. Analysis of mechanism, Water Resources Research, Vol. 24, No8. pp 1247 – 1258.
- Hunt J.R, Sitar N and Udelsi K.S. (1988b). Non-Aqueous Phase Liquid Transport and Clean up: 2 Experimental Studies "Water Resources Research, vol. 24 No.8 pp 1259 – 1265.
- Idodo – Umeh, G, and A.E, Ogbeibu 2010. Bioaccumulation of the Heavy Metals in Cassava Tubers and Plantain Fruits Grown in Soil, Impacted with Petroleum and non Petroleum Activities Research. Journal. Environmental. Sciences, 4: 33 – 41.
- J.A. Omgbu and M.A. Kokogho June (1993) Determination of Zn, Pb, Cu and Hg in Soils of Ekpan, Nigeria. Environmental International.
- J.H. Karchmer and E.L. Gunn (1952) Anal chem 24: 1733pp,.
- Kakulu S.E (1985), Heavy Metal in the Niger Delta, Impact of Petroleum Industry on the Baseline Levels. PHD thesis Department of Chemistry, University of Ibadan 320pp
- Liv, H.Y, Probst, A. & Liad B.H. (2005a) Metal Contamination of Soils and Crops Affected by the Cherizhou Lead/zinc Mine Spill (Human, China) The Science of the Total Environment, 39, 153 – 166pp.

- M.A. Balogun. 1994. A Survey of Some Heavy Metal Pollution in Some Industrial Cities in Nigeria Using Warri as a Case Study; Its M.Sc thesis Department of Chemistry University of Benin, Benin City.
- Memibe Shara, C. Ajayi S.O and Osibanji O. (1981) Pollution Studies on Nigeria Rivers. Toxic Heavy Metals Status on Surface Water in Ibadan City, Environmental International 4958pp.
- Ndiokwere, C.L, Ezehe (1990). The Occurrence of Heavy Metals in the Vicinity of Industrial Complexes in Nigeria "Environmental International. 16: 291 – 295pp.
- Okpokowasili G.C. and Njoku H. (1989) Eco-toxicological Evaluation of Chemical Use in the Nigeria Oil Industry Proceeding Seminar on the Petroleum Training Institute, Warri Nigeria.
- Omgbu. J.A. (1992). The distribution of Fe, Hg, Cd, Cu and Pb in Soil of Farcados Terminal and its Environment. Its M.Sc. thesis Department of Chemistry University of Port Harcourt, Nigeria.
- Opafunson Z.O (2007) 3D Formation Evolution of an Oil Field in the Niger Delta Area of Nigeria using Schlumberger Petrol Workflow Tool. Journal of Engineering and Applied Science 2(11) 1651 – 1660pp.
- Pruvot, C., Douay, F., Herve, F., abd Waterlot, C. (2006). Heavy Metals in Soil, Crops and Grass as a Source of human Exposure in the Former Mining Areas. Journal of Soils and Sediments, 6, 215 – 220pp.
- Purves, D. (1985) Trace Element Contamination of the Environment. Amsterdam: Elsevier.
- Regain et al (1977) Environmental Science and Technology 11:8pp.
- Sprague J.B (1962) "Effect of Sublethal Concentration of Zinc and Copper on Migration of Atlantic Salmon" Biological Problems in Water Pollution.
- Stokinger H.E and Coffin, D.L. (1978) Biological Effect of Air Pollutants. Air Pollution Academic Press. New York USA
- Stokinger, H.E (1963), "Metal Excluding lead" Industrial Hygiene and Technology, Volume II D.W Fasset and D.O Irish Edition.

- Strobel H.A (1973) Chemical Instrumentation A Systematic Approach to Instrumental Analysis Second Edition Addison – Wesley Publishing Company (Massachusetts USA).
- Strouts C.R.N, Wilson H.N and Parry Jonnes R.T (1962) Chemical Analysis, The Working Tools, Charenden Press – Oxford.
- Sullivan R.J. (1969). Air pollution Aspects of Manganese and its Compounds. Litton System Inc. US Department of Commerce Publication number PB 1880.99.
- U.S. Environmental Protection Agency (1977) Air Quality Criteria For Lead Report. ERA – 6001877 – 017 US EPA Washington D.C.
- Underwood, E.J (1971) Water Criteria and Standards Water Pollution Control 77: 25 – 30pp.
- Vanugopal B. and Lucky T.D (1973) Metal Toxicology in Mammals, Chemical Toxicology of Metals and Metalloids (volume II).
- Warner D.L and MC Connel C.L Sept. (1993) Assessment of Environmental Implication of Abandoned Oil and Gas Well Journal Petroleum Technology 8: 74 – 88pp
- WHO (World Health Organization) (1993) Evaluation of Certain Food Additives and Contaminants (forty-first Report of the joint FAO/WHO Expert committee on Food Additives). WHO Tech. Report Series No.837
- Willbur C.G (1969) The Biological Aspect of Water Pollution, Springfield M; GC Momes Publisher.
- World Health Organization (1977) Lead in the Environment. Health Criteria 3 WHO Geneva.
- Zheng, N., Wang, Q. C., and Zheng, D.M (2007) Health Risk of Hg, Pb, Cd, Zn and Cu to the Inhabitants Around Huludao Zinc Plant in China via Consumption of Vegetables. The Science of the Total Environment, 383: 81 – 89.

APPENDIX



Cassava farm land grown around Etelebou flow station



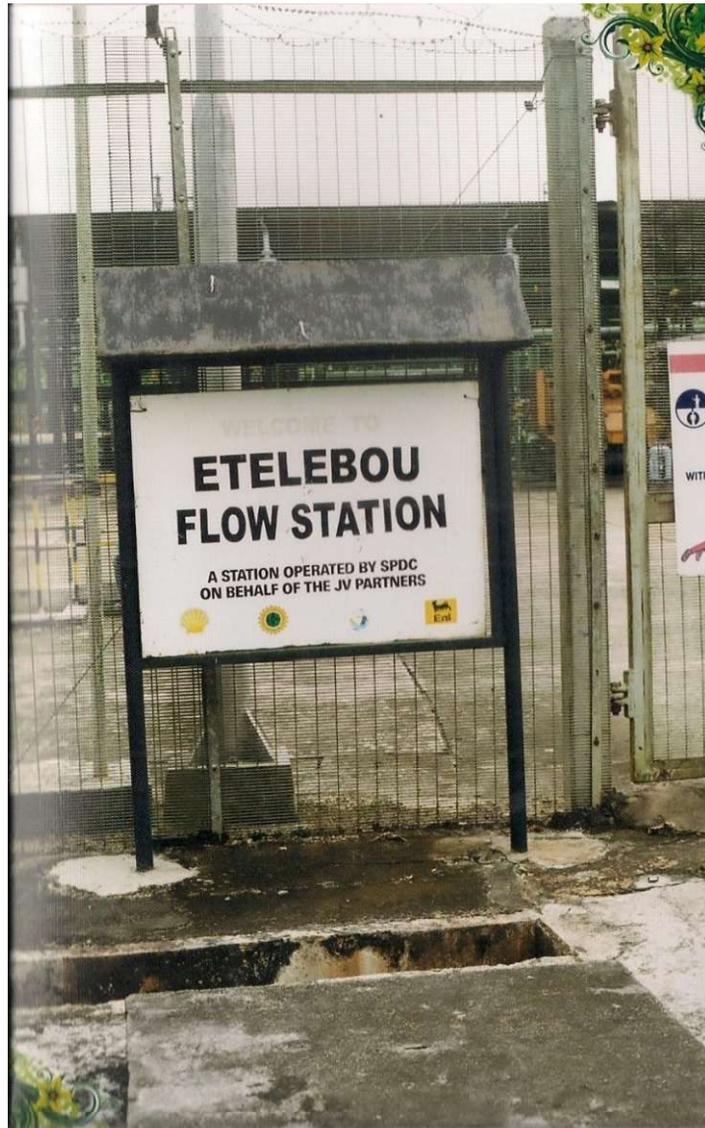
Oil well head in Etelebou flow station



Effluent discharge site in Etelebou flow station



Plantain plantation around Etelebou flow station



Etelebou Flow Station main gate



Gas and Oil Pipe Line around the flow station



Ground Gas flare stack in Etelebou flow station



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