ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS AND HEAVY METALS CONCENTRATION IN CASSAVA TUBERS WITHIN OKIGWE MECHANIC VILLAGE, IMO STATE.

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CERTIFICATION

This is to certify that this research thesis/dissertation **ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) AND HEAVY METALS CONCENTRATION IN CASSAVA TUBERS IN OKIGWE MECHANIC VILLAGE OF IMO STATE** was carried out by Udoh, Utipmfon Christopher with Registration No: 20134872158 in partial fulfillment for the award of the degree of M.Sc. in Environmental Technology from the Department of Environmental Technology, Federal University of Technology, Owerri.

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DEDICATION

I humbly dedicate this work to HIM from whom all wisdom, all knowledge, all
Inspiration flows. To HIM that knows the end from the beginning
GOD the Omnipotent

And to my dearest mother
Mrs. Theresa Sandy Umoh and Late Sis. Imaobong Imoh-abasi

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First and foremost, my greatest thanks goes to my senior partner, my director and my all in all THE HOLYSPIRIT and to HIM that dwells between the cherubim , my rock, my provider, my deliverer, my sun and my shield, my God in whom I trust and with HIM I can do all things through Christ that strengthens me.

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ABSTRACT

Soils and cassava tubers in Okigwe auto-mechanic village of Imo state were investigated for presence of Polycyclic Aromatic Hydrocarbons (PAHs) and heavy metals. Six soil samples of 0 - 15 cm and 15 - 30 cm in depth were collected each, at 3 sites, in close proximity to selected automobile workshops. A distant location was used as the control site. Physicochemical properties of soils from this study area were investigated using standard methods, PAHs in the soil and cassava tubers were determined using Gas chromatography (GC) system equipped with flame ionization detector (GC/FID), Agilent Technologies 7890B, while heavy metals were analysed by Atomic Absorption Spectrophotometer (AAS). The results showed that, of the sixteen USEPA target PAHs (EPA-16) examined, PAHs showed in varying concentrations in mg kg^{-1} except naphthalene that was not detected in all the soil samples. There were significant variations in the concentration of the eight (8) heavy metals (Fe, Ni, Pb, Cu, Cr, Cd, Mn and Zn) and PAHs between the experimental and control sites at 0.05 confidence level. Correlation analysis was done on physiochemical parameters with heavy metals and PAHs to establish the relationship of the data with one another. Fe had the highest mean concentration of 5278.74 mg kg^{-1} and the least concentration was Cr and Cd with the mean concentration of 0.01. The concentration of total PAH components detected in the samples ranged from 122.2 mg kg^{-1} to 17.1 mg kg^{-1}. Implications of PAHs on health were discussed. It is recommended that mechanic villages should be sited far from residential areas, and such places should not be used as farmlands for the cultivation of edible crops. Also continuous education and trainings should be provided for automobile workers, emphasizing on the environmental implications of poor occupational waste management.

Keywords: Polycyclic; Aromatic; Hydrocarbons; Heavy Metals; Concentration; Cassava Tubers; Okigwe Mechanic Village

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Soil is the unconsolidated mineral or organic material on the immediate surface of the Earth that serves as a natural medium for the growth of land plants (Alloway, 1994). It is a basic component of ecosystems and one of the most vulnerable to contamination and degradation through accidental or deliberate mismanagement (Herbert et al., 1995). Soil constitutes a crucial component of rural and urban environments (USDA, 2001). Soil can become contaminated due to natural and anthropogenic activities, and also by the accumulation of heavy metals and metalloids through the emission from the rapidly expanding industrial areas, disposal of high metal wastes, leaded gasoline and paints (Wuana and Okieimen, 2011). Auto-mechanic activity as one of the anthropogenic activities is one of the major sources of soil contamination in Nigeria (Adewole and Uchegbu, 2010). The activity releases hydrocarbon pollutants, which may dispersed through the soil leading to serious pollution problems (Thouand et al., 1999).

Pollution effects of auto-mechanic village activities in Nigeria have received limited attention even though these activities produce petroleum based wastes (Nwachukwu et al., 2010). Excessive accumulation of heavy metals from petroleum and other related human activities have been documented in soils (Kabata and Pendias, 1989) and constitute major environmental and human health problems (EeLuiAng and

Jeffery, 2004). Heavy metals have been found in food crops and as a potential health hazards to man through the dietary pathway in Nigeria (Obiajunwa et al., 2001). Uptake of heavy metals increases in plants grown in polluted areas (LeCoultre, 2001) and high levels of accumulation in common garden vegetables have been reported (Boon and Soltanpour, 1992; Cobb et al., 2000; LeCoultre, 2001).

In Nigeria, automobile mechanic workshops are located or concentrated in areas known as mechanic villages, officially designated for repairs and servicing of automobiles. They are also used for recreational, residential and agricultural purposes (Nwoko et al., 2007). The vicinity of a mechanic village is characterized with heavy vehicular activities and high production of auto-mobile waste. The waste generated may include gasoline (petrol), diesel, spent engine oil and paints among others (Nwachukwu et al., 2010). These wastes are indiscriminately discarded in nearby bushes or surrounding areas. Spent lubricant or waste engine oil obtained after servicing auto-mobile and generator engines contains large amounts of hydrocarbons, highly toxic polycyclic aromatic hydrocarbons (Wang et al., 2000). As engine oil is used in automobile, it picks up a number of additional compounds from engine wear, including iron, steel, copper, zinc, lead, barium, cadmium, sulfur, dirt and ash. Used motor oil disposal can be more environmentally damaging than crude oil pollution because of the additives and contaminants, (Abioye et al., 2012).

The environmental effect of oil on growth and performance of plants have been reported by many researchers (Mackay, 1991; Gelowitz, 1995; Siddiqui and Adams, 2002; Lundstedt, 2003). Heavy metals present in spent lubricants can accumulate in plants and affect metabolic processes (Prasad and Prassad, 1987). The presence of spent lubricant oil in soil increases bulk density, decreases water holding capacity, aeration propensity and reduces nitrogen, phosphorus, potassium, magnesium, calcium and sodium content. Increased levels of heavy metals in soils contaminated with spent oil have been reported (Kayode et al., 2009). Crops cultivated on soil contaminated with spent engine oil takes up metals that bio-accummulates in the plant tissues (Amusan et al., 2005) and lubricating oils have toxic effects on germination, growth and yield of crops (Esenowo and Umoh, 1996). However, plant species respond differently to pollutants for instance, growth retardation was two times higher in tomato (*Lycopersicom esculentum*) than pepper (*Capsicum annum L.*) (Anoliefo and Vwioko, 1995).

In mechanic workshops, there are accidental or deliberate releases or discharge of petrol, diesel, solvents, grease and lubricants on the land. Many of these petroleum products are organic chemicals that can be highly toxic and hazardous to soil fauna and man. The indiscriminate disposal of spent engine oil increases trace elements and heavy metals concentrations in soils with adverse effect on the physicochemical and microbiological properties of the soil (Gupta and Gupta, 1998). Heavy metals found in auto-mechanic wastes can enter into the food chain if disposed on agricultural soils and around residential areas (Ademoroiti, 1996). Heavy metals such as copper, lead cadmium, zinc, manganese, and nickel have been detected in okro planted around and within mechanic villages (Adewole, 2006 and Ademoroti, 1996).

Heavy metals in the soil can bioaccumulate in plant and biomagnify along the food chain causing serious health risk to humans and animals when consumed (Singh et al., 2010; Anoliefo and Edegbai, 2000; Odjegba and Sadiq, 2002; Tulonen et al., 2006). Although some heavy metals such as copper, zinc, manganese and iron are essential in plant nutrition, the metallophytes are resistant to these toxins and even a smaller group actually thrives (Zhu et al., 1999).

Some plants have phytoremediating potentials and can extract hazardous substances such as arsenic, lead, and uranium from the soil and water (Cunningham and Lee 1995). In Nigeria, the use of cassava plant in phytoremediation have also been reported (Akonye and Onwudiwe, 2004; Habila et al., 2012). Thriving plants show particular potential for remediation because of their ability to transport and accumulate extremely high levels of soil pollutant. They are called hyper-accumulators (Akhionbare et al., 2010). Heavy metals such as lead, nickel, chromium, cadmium and arsenic accumulated in roots, stems and leaves of cocoyam (*colocesia esculenta*) and cassava (*mannihot esculenta*) from abandoned waste dump soils in Nigeria (Okoronkwo et al., 2005). However, the concentration of lead, nickel and cadmium were significantly higher than chromium and arsenic in the leaves and roots of the plants.

The levels of heavy metals in farm soil are generally not analyzed before planting and therefore consumption of contaminated fruits, seeds or tubers is common (LeCoultre, 2001). In Nigeria, most farmers or residents grow vegetables, maize and other crops around the mechanic villages or sink borehole without considering the health risks involved. It is in the interest of the public to know whether vegetables, fruits and crops cultivated in polluted soils are safe for human consumption, especially now that the environmental quality of food products are of major concern (Chiroma et al., 2003). High concentration of heavy metals (Cu, Cd and Pb) in fruits and vegetables has been related to high prevalence of upper gastrointestinal cancer (Turdogan et al., 2002). Absorption of heavy metals in low doses by humans over a long period of time through food resulted in serious health consequences (Jarup, 2003). Some common health implications of heavy metals in humans include kidney disease, damage to the nervous system, diminished intellectual capacity, heart disease, gastrointestinal disease, bone fracture, cancer and death (Jarup, 2003).

Cassava is a perennial shrub of the family *Euphorbiaceae,* an important starchy staple crop in Nigeria. High exposure to trace metals in cassava could result in an array of diseases to both human and animals. Apart from cassava, other vegetables can take up and accumulate heavy metals in quantities high enough to cause clinical problems in humans (Alam et al., 2003). Cassava (*mannihot esculenta*) was selected for this study because it is one of the major crops in the study area.

1.2 STATEMENT OF THE PROBLEM

The automobile mechanic activities have been a serious environmental and public health concern all over the world. Provision of environmental review that covers servicing, mechanical repairs in premises, sound environmental management repairs in premises, sound environmental management system of waste generated are lacking in Nigeria. The hazardous wastes such as brake fluid, greases, spent oil, radiator coolant, soot, fuel, metal scraps, chemicals and other volatile compounds are indiscriminately disposed into the soil and surrounding environment. These chemicals are not biodegradable and persistent with a potential to bioaccumulate in plants (Adewole, 2006). The pollution effects of mechanic village activities in Nigeria have received limited attention and also not well documented except for few works, even though these activities produces petroleum based waste (Nwachukwu et al., 2010 and Omokhodiori 1999). It is therefore important to express concerns and questions on the state of the soils and quality of food crops, fruits and vegetables cultivated in areas where auto mechanic workshops are located. Iwegbue (2007), observed that metals present around automobile mechanic waste dump in Port Harcourt found on the surface soil were relatively mobile, which could easily be carried away by rain water into the surrounding environment such as gardens where they are absorbed by cultivated crops or vegetables. The ingestion of metal accumulated in these food crops can result in serious health consequences (Jarup, 2003).

Residents around mechanic village sites still cultivate edible crops for consumption in any available plot of land even when these lands are being contaminated by the activity that goes on within that area. Given the scenario, it is suspected that activities and by-products of the technicians contaminate the soil and crops. The focus of this study is to investigate the extent of the contamination of the soil and cassava tubers around the mechanic village in Okigwe. This study will create awareness, provide insights on the implications of cultivating edible crops within the vicinity of an auto-mechanic village and also enlighten auto-mechanics on the environmental hazards and risk of indiscriminate dumping of automobile wastes on the soil ecosystem.

1.3 AIMS AND OBJECTIVES

The aim of this study is to assess the level of contamination of soils and cassava tubers around Okigwe mechanic village of Imo State.

To achieve this aim, the following objectives were followed:

i. Determine the physiochemical properties of the soil in the vicinity of Okigwe mechanic village
ii. Determine the level of PAH and heavy metals accumulated in cassava tubers in the area
iii. To correspond the results with permissible limits of heavy metals and PAHs

1.4 RESEARCH QUESTIONS

1. Can the cultivation of cassava crops within a mechanic village be of public health concern?
2. Can cassava crops cultivated within a mechanic village accumulate heavy metals and PAH in its tubers?
3. Can heavy metals found in the soil of a mechanic village also be present in cassava tubers cultivated within its vicinity?
4. What are the potential health implications of the accumulated pollutants in the cassava tubers?

1.5 SIGNIFICANCE OF STUDY

The indiscriminate dumping of waste by mechanics is on the increase because auto-mechanic villages and workshops are springing up every day and everywhere. These activities have caused soil degradation and crops contamination. These crops are essential for the upkeep and growth of living things especially humans. When these crops are contaminated with heavy metals, these metals accumulate and lead to the malfunctioning of some human organs when consumed. Therefore, it is necessary to know if these crops planted in these places are safe for human consumption. This study will enlighten the general public on the public health risk of cultivating edible crops within the vicinity of auto-mechanic village. This study will document the exposure risk of the population to PAHs and heavy metals by determining those recalcitrant pollutants that occur in soil in mechanic villages and how they impact on food crops.

Though few studies have been conducted on the effect of spent engine oil and other auto-mobile waste on food crops cultivated within mechanic village vicinity, but no study has been conducted on food crops cultivated in Okigwe mechanic village of Imo State, Nigeria. This study will add to the available information on the effect of cultivating edible crops within auto-mechanic village and also provide insights on the uptake of waste components from automobile workshops by cassava crops.

CHAPTER TWO

LITERATURE REVIEW

2.1 DEFINITION OF SOIL

Soil is the unconsolidated mineral or organic material on the immediate surface of the Earth that serves as a natural medium for the growth of land plants (Alloway, 1994). It is a basic component of ecosystems and is one of the most vulnerable to contamination and degradation through accidental or deliberate mismanagement (Herbert et al., 1995). Dmitriev (1996) defined the soil as a natural ‘‘exon,’’ which has properties developed as a result of the influence of autotrophic and heterotrophic organisms on soil constituents resulting from exogenic transformations. Nikitin (2001) considered the soil as an abiotic system with numerous biospheric functions and emphasized that a soil acts as a habitat, accumulator, and source of substances for all terrestrial organisms, as a link between the biological and geological cycles of matter, and as a planetary membrane (protective barrier and buffer system) that maintains suitable conditions for normal development of the biosphere.

2.1.1 Soil as a non-renewable natural resource

Soil is a natural resource with crucial ecological, economic and social functions. It is the upper part of the earth crust that exists of mineral and organic solids, and pores filled with air and water. Soil is the essential component of the terrestrial environment and forms the interface between geosphere, atmosphere, hydrosphere and biosphere (Doran and Parkin, 1994). The proportions of different components, especially sand, loam and clay, organic matter, mineral components, water and air (especially in the pore space) and the way they form a stable structure, determine the soil characteristics. Every soil exists of different horizons, with different physical, chemical and biological properties. Chemical properties are mostly related to the clay fraction and soil organic carbon, while physical properties are determined by the size distribution of the mineral particles (Wild, 2003).

This non-renewable resource has several important functions, including: biomass production; storing, filtering and transforming nutrients and water; hosting the biodiversity pool; acting as a platform for most anthropogenic activities; providing raw materials; acting as a carbon pool and storing geological and archeological heritages. These functions are determined by the soil characteristics and make it important to understand the physical, chemical and biological processes and their interactions (Hassett and Banwart, 1992 and Tóth et al., 2007).

2.2 SOIL FORMATION: FACTORS AND PROCESSES

Jenny (1980) uses five factors to define the state of the soil system. He presented the equation $S = \int (c, o, r, p, t \ldots.)$ where (S) the soil that is formed is a function of the variable factors of climate (c), organisms (o), topography/relief (r), parent material (p), time (t) and any other factors (….) that may affect soil formation. Soil forming processes has been described as “an assemblage of reactions occurring simultaneously or in sequence that create soil components and morphology features”

(Buol et al., 1997). For a given soil property to be present or measurable it must be able to co-exist with the current soil environment. Soil formation has been described as two overlapping steps, the accumulation of parent material and horizon differentiation. Each pedon results from combinations of processes, which have endured for a period of time.

2.3 SOIL STRUCTURE

Soil structure is the arrangement of soil particles into units of different sizes and shapes. These units are called peds or aggregates and the processes of formation of peds are collectively called aggregation. According to Lal (1991), soil structure refers to the size, shape, and arrangement of solids and voids, continuity of pores and voids, their capacity to retain and to transmit fluids and organic and inorganic substances, and ability to support vigorous root growth and development. Peds differ from "clods" and "concretions"; clods or chunks are artificially formed (such as by plowing) hard soil mass. Concretions are hard lumps produced by the precipitation of dissolved substances (usually iron and manganese oxides). In some soils and sediments, the particles are not aggregated but remain separated; such soils are called single grained, such as some sandy soils. Most soils are structured soils. In some soils such as heavy clays, all the particles adhere together. Structure of these soils is called massive.

Aggregates influence microbial community structure, limit oxygen diffusion, regulate water flow, determine nutrient adsorption and desorption (Linquist et al. 1997; Wang et al. 2001), and reduce run-off and erosion (Barthes and Roose 2002). All of these processes have profound effects on soil organic matter dynamics and nutrient cycling (Six et al. 2004).

Soil structure is classified based on shapes of peds into types, on size of peds into classes, and on distinctness and stability of aggregates into grades. There are four types of soil structure—spheroidal (granular and crumb), block like (angular blocky and sub-angular blocky), plate-like, and prism-like (prismatic and columnar). On the basis of size of aggregates, soil structure is divided into five classes: very fine, fine, medium, coarse, and very coarse. Grades of soil structure are identified on the basis of the visibility in a horizon and stability of aggregates. Stability of aggregates refers to their resistance to destruction by water.

2.4 PROPERTIES OF SOIL

Soil is essential to life on Earth and forms the interface between the atmosphere and lithosphere as well as the lithosphere and the hydrosphere (White 1997). Soil is a natural body, having both mineral and organic components, as well as physical, chemical and biological properties (Kabata-Pendias and Pendias 2001). Soils therefore have elements representative of the material from which they are formed and include essential plant nutrients such as nitrogen, sulphur, calcium, iron, magnesium, manganese, zinc, and chlorine (Miller and Donahue 1990). Although the parent material from which a soil is derived has important implications for soil processes by virtue of its properties, soil texture is equally important.

2.5 PHYSICAL PROPERTIES OF SOIL

The physical characteristics of a soil can significantly influence its engineering behavior and the attenuation of contaminants. Physical properties can also be used to evaluate the availability of contaminants and the potential effect of remediation on their attenuation.

2.5.1 Soil Texture

Soil texture is determined by the distribution of the particles sizes within the soil (White 1997) and is defined by the relative proportions of sand, silt and clay (Miller and Donahue 1990; White 1997). Minerals with different compositions will have different properties and soil texture is one of the most stable of these properties (White 1997). The distribution of sand, silt and clay fractions within the soil profile in influenced by a number of factors, including topography. Clays in the surface soil layers are carried downward by water and are deposited in soil layers at depths ranging from 15 to 60 cm (Miller and Donahue 1990).

2.5.2 Particle size

Particle size is defined as the percentages of various grain sizes present in a material as determined by sieving and sedimentation (British Standard BS, 1990).

2.5.3 Moisture content

The moisture content of a soil is the ratio of the mass of water to the mass of solids in the soil (Craig, 1992). The moisture content is determined as the mass of free water that can be removed from a material, usually by heating at 105°C, expressed as a percentage of the dry mass. If a soil or waste contains too much water then the porosity and permeability are likely to increase. If the amount of moisture present in a soil is above optimum then the density of the compacted product is reduced.

2.5.4 Permeability

The term permeability is used to express the coefficient of permeability or hydraulic conductivity, describing the rate (ms^{-1}) at which water can flow through a permeable medium. Permeability is related to the distribution of particle sizes, particle shape and soil structure. In general, the smaller the particles, the smaller are the average size of the pores and the lower is the coefficient of permeability. The transport of water through a soil will be faster if the soil has a higher coefficient of permeability than if it has a lower value (Craig, 1992). However, it should be noted that the rate of transport of contaminants depends upon a number of factors including solubility and the rate at which contaminants are attenuated in a soil.

2.5.5 Strength

The strength of a soil measures its capacity to withstand stresses without collapsing or becoming deformed (Brady and Weil, 1996). Soil strength can be considered in terms of the ability of a soil to withstand normal and/or shear stresses. Shear stress can be resisted only by the skeleton of solid particles, by means of the forces developed at the inter-particle contacts. Normal stress may be resisted by the soil skeleton due to an increase in the inter-particulate forces. If the soil is fully saturated, the water filling the voids can also withstand normal stress by an increase in pressure (Craig, 1992)

A soil's ability to withstand normal stresses can be influenced by a number of related soil characteristics, amongst which are: Soil compressibility, Soil compactability, and Bearing resistance. These factors in turn are determined by parameters such as soil moisture content, particle size distribution and the mineralogy of the soil particles.

2.6 CHEMICAL CHARACTERISTICS OF SOIL

2.6.1 Soil pH

Soil pH is probably the single most important chemical characteristic of the soil (Bloom 2000) and is used as the benchmark for the interpretation of soil chemical processes (Slattery *et al.* 1999). Soil pH exerts a major influence on many other soil properties and affects the mobility of trace metals within the soil. With increasing pH, the solubility of most trace cations will decrease (Kabata-Pendias and Pendias 2001).

2.6.2 Soil organic matter (SOM)

Soils contain a large variety of organic matter, usually at concentrations of 0.5-5% by mass in typical soils (Yong *et al.,* 1996). It is a key component in soil particularly in association with attenuation processes, even at such low proportions. Organic-rich soils, such as peat, also occur naturally and can contain more than 80% organic matter (Brady and Weil, 1996). Soils with an organic content up to 30% and water/solids ratio up to 2.5 will behave largely as mineral soils.

2.6.2.1 The Influence of Organic Matter on Contaminant

The influence of organic matter on contaminant (e.g. heavy metal) mobility depends on whether the material is in a solid or dissolved state. Solid organic matter generally has a retarding effect on heavy metals, but the contaminants can be more mobile due to complexing with dissolved phases (e.g. Cu). Alkaline conditions, as developed when using hydraulic binders, can lead to dissociation of organics that can affect the mobility of contaminants. For example, at $pH > 9$, carboxylic and phenolic-OH groups can protonate (release a H^+) and the humic molecule attain a high negative charge (Tan, 1993), making it available for complexation with metal cations.

2.6.3 Mineralogy

With the exception of some highly organic soils, the majority of soil material is mineral in character, having been derived from solid geological deposits. Minerals can be conceptually divided into primary and secondary materials.

Primary minerals are those derived in unaltered form from parent rock, generally through physical weathering processes (Yong *et al.,* 1996). They make up most of the sand and silt portion of soils and are usually only a minor constituent in the clay-sized portion. The most common primary minerals in soils are quartz and feldspar. These particles have a relatively low specific surface area, and therefore their role in contaminant interaction and attenuation processes is minimal (Yong *et al.,* 1996).

Secondary minerals are derived as altered products of physical, chemical and/or biological weathering processes. They are layer silicates and account for the majority of the clay-sized portion. Because of their small particle size, they exhibit a large specific surface area. The combination of their large surface area and the fact that they frequently exhibit a surface charge makes the secondary minerals important in the development of contaminant attenuation processes. Clays are also able to react with lime to form cementitious compounds. The most common layer silicates in soils include kaolinite, chlorite, mica, montmorillonite and illite.

2.6.3.1 Clay minerals

Clay minerals are made up of basic silica tetrahedra and alumina octahedra units, combined to form sheet-like, or platy, structures. Si and Al may be partially replaced by other elements, such as Al for Si and Fe, Mg for Al. The basic units are one tetrahedron to one octahedron (1:1 layer silicate) and one octahedron between two tetrahedra (2:1 layer silicate). These units are stacked and linked laterally to form the structural building blocks of clay minerals and characterize the nature and properties of the minerals. The clay minerals are commonly amorphous and usually carry a residual negative charge, mainly due to isomorphous substitution of Si and Al or disassociation of hydroxyl ions. The negative charge results in cations from solution being attracted to the particle surfaces, forming a double layer of particle surface and dispersed layer of cations. Such cations are weakly bonded and can be replaced by other cations (cation exchange).

Forces of repulsion and attraction act between clay particles, due to the like charges of the double layers and the characteristics of the layers respectively. An increase in cation valency or concentration can result in a decrease in repulsive forces. The forces of attraction are responsible for the cohesive nature of fine-grained soils. The properties of clay minerals, in particular the reactivity of the particle surfaces, have a significant influence on geochemical processes in soil that affect the attenuation of contaminants (Yong and Mulligan, 2003).

2.6.3.2 Carbonates

A number of carbonate minerals may be present in soil including calcite, magnesite, siderite and dolomite. Calcite is the most common form and has a significant influence on the pH of the soil and pore water. Carbonate minerals may be effective in adsorbing heavy metals and phosphates (Yong and Mulligan, 2003).

2.6.3.3 Oxides and (oxy) hydroxides

Oxides and (oxy) hydroxides are abundant weathering products of parent rock, most commonly iron oxides. The iron forms are amorphous or cryptocrystalline, with the amorphous form having a pH-dependent surface charge. Because of this surface charge, the amorphous forms readily coat solid particles and significantly alter the surface reactivity of the particles.

2.6.3.4 Sulfates

The presence of sulfates in soil can arise from a number of sources. Sulfur is present in proteins and amino acids bound within the humus and clay fractions. Oxidation of SOM frequently results in the transformation of these sulfur-containing compounds to sulfates. The second source of sulfates in soils comes from the oxidation of: Sulfides, Sulfur retained by soils high in Fe-Al oxides and kaolinite and Atmospheric sulfur deposited onto soils. The Building Research Establishment (BRE, 2001) identifies that the presence of naturally occurring sulfates depends on the geological strata, the weathering history of those strata and the groundwater flow patterns.

2.7 SOIL DEGRADATION

Soil degradation can be defined as the loss of soil or soil quality for a number of soil functions. Loss of organic matter, erosion, floods, salinisation, compaction, landslides, contamination and sealing are the eight most important degradation processes and are closely related to agriculture. Most of the degradation processes are strongly correlated. Risk of soil degradation can also be caused by extreme natural condition, but are rather rare in comparison with human influence (Blum, 1998). Degradation of soil has a direct impact on water and soil quality, influences food chains, climate change and hinders biosphere functioning (Tóth et al., 2007). This makes it important to maintain a good soil condition to guarantee good environmental conditions and high productivity.

2.7.1 Soil degradation by contamination

Soil contamination is defined as the occurrence of certain products in such a concentration that it causes deterioration or loss of soil functions. The most common contaminations are heavy metals and high levels of nitrogen. High nitrate and phosphor concentrations introduced by fertilizers and manure are the most common diffuse contaminants in agricultural soils (Gay et al., 2009). These contaminations reduce the capability to serve nutrients to crops, to buffer and filter. Consequently, this leads to yield reduction, leaching of nutrients to groundwater and eutrophication (Maréchal et al., 2008).

In agriculture, soil contamination remediation is rarely used because the cost is too high. Crop rotation contributes to reduction of the use of chemicals and thus reduces contamination. Some plants absorb contaminants and thus improve water and soil quality. Biological activity also has a positive influence on the grade of contamination because it stimulates the breakdown of chemical components (Gay et al., 2009).

2.8 SOIL POLLUTION

Soil is a very important natural resource to man as it is a source of his life on this planet. Without soil the earth would be as barren as the moon hence lifeless (Misra and Mani, 2009). Despite its importance, soil is often contaminated by human activities and this is reflected in the high horizontal and vertical variability brought about by the anthropogenic influence on soil formation and development (Fong et al., 2008). A variety of human activities including municipal waste disposal, industrial emissions, military testing and agricultural practices have left their impacts on soils in the form of elevated and high level of toxicants (Van and Krivolutsky, 1996).

Materials that enter the soil system persist and accumulate in toxic concentrations becoming sources of pollution in the soil (Misra and Mani, 2009). The soil is thus becoming increasingly polluted with chemicals and other pollutants which can reach the food chain, surface water or ground water and ultimately be ingested by man (Misra and Mani, 2009). These pollutants concentrates in soil and their impact on ecosystems can be influenced by many factors such as the parent rock, climate and anthropogenic activities (Jia et al., 2010). Among the pollutants that persist and accumulate in the soils include; inorganic toxic compounds for example fertilizers, organic wastes, organic pesticides and radionuclides (Misra and Mani, 2009; Jia et al., 2010).

2.8.1 Natural Sources of Soil Pollution

Natural sources of soil pollution could occur as a result of:

Natural accumulation of compounds in soil due to imbalances in atmospheric deposition and leaching away with precipitation water (e.g. concentration and accumulation of perchlorate in soils in the environment), Natural production in soil under certain environmental conditions, natural formation of perchlorate in soil in the presence of chlorine source, metallic object and using the energy generated by a thunderstorm and Leaks from sewer lines into subsurface (e.g. adding chlorine water could generate trihalomethanes such as chloroform).

2.8.2 Anthropogenic Sources of Soil Pollution

Soil pollution caused by the presence of man-made chemicals or other alteration in the natural soil environment. This type of contamination typically arises from the rupture of underground storage links, application of pesticides, and percolation of contaminated surface water to subsurface strata, oil and fuel dumping, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals. A soil pollutant is any factor which deteriorates the quality, texture and mineral content of the soil or which disturbs the biological balance of the organisms in the soil. Pollution of the soil has adverse effect on plant growth.

Soil pollution is associated with indiscriminate use of fertilizers, indiscriminate use of pesticides, insecticides and herbicides, dumping of large quantities of solid waste and deforestation and soil erosion.

a. Indiscriminate use of fertilizers: Fertilizers contaminate the soil with impurities, which come from the raw materials used for their manufacture. Mixed fertilizers often contain ammonium nitrate (NH_4NO_3), phosphorus as P_2O_5, and potassium as K_2O. Since the metals are not degradable, their accumulation in the soil is always above their toxic levels due to excessive use of phosphate fertilizers and therefore becomes an indestructible poison for crops. The over use of NPK fertilizers reduce quantity of vegetables and crops grown on soil over the years (Provost et al., 2008).

b. Indiscriminate use of pesticides, insecticides and herbicides: DDT (dichlorodiphenyltrichloroethane) and gammaxene pesticides persist in the environment, and biomagnified up the food chain while causing harm to bird who feeds on them. DDT has been now been banned in most western countries.

Ironically many of them including USA still produce DDT for export to other developing nations whose needs outweigh the problems caused by it (Toccalino et al., 2006).

c. Dumping of solid wastes: Solid waste includes garbage, domestic refuse and discarded solid materials such as those from commercial, industrial and agricultural operations. The portion of solid waste that is hazardous such as oils, battery metals, heavy metals from smelting industries and organic solvents are the ones to be paid a particular attention to. These can in the long term, get deposited to the soils of the surrounding area and pollute them by altering their chemical and biological properties (Patterson et al., 2007).

d. Deforestation: Deforestation, agricultural development, temperature extremes, precipitation including acid rain, and human activities contribute to soil erosion.

Humans speed up this process by construction, mining, cutting of timber, over cropping and overgrazing. It results in floods and cause soil erosion. Forests and grasslands are an excellent binding material that keeps the soil intact and healthy. They support many habitats and ecosystems, which provide innumerable feeding pathways or food chains to all species. Their loss would threaten food chains and the survival of many species. Deforestation is slowly destroying the most productive flora and fauna areas in the world, which also form vast tracts of a very valuable sink for CO_2 (Paumen et al., 2008).

e. Pollution due to urbanization: Pollution of surface soils materials (like vegetables, animal wastes, papers, wooden pieces, carcasses, plant twigs, leaves, cloth wastes as well as sweepings) and many non-biodegradable materials (such as plastic bags, plastic bottles, plastic wastes, glass bottles, glass pieces, stone /cement pieces) (Nawrot et al., 2006).

2.9 HEAVY METALS POLLUTION

Heavy metals are elements having a density greater than 5 g/cm^3 in their elemental form (Bose and Hemantaranjan, 2005; Misra and Mani, 2009). Heavy metal pollution has received the attention of researchers all over the world, mainly due to their harmful effects on living beings (Misra and Mani, 2009). Human biology is full of instances where heavy metal toxicity has led to mass deaths (Shrivastav, 2001). All heavy metals are toxic to living organisms at excessive concentrations, but some are essential for normal healthy growth and reproduction by plants at low but critical concentrations (Bose and Hemantaranjan, 2005). The heavy metals essential in trace elements to plants include Co, Cu, Fe, Mo and Zn and for animals are Cr, Ni and Sn. The heavy metals Cd, Hg and Pb have not been shown to be essential for either plants or animals (Misra and Mani, 2009).

It is important to note however that the concentrations of individual metals in living tissues must be kept very low and should be maintained within narrow limits to permit the optimum biological performance of most organisms (Misra and Mani, 2009). Heavy metals are serious pollutants because of their toxicity, persistence and non-biodegradable conditions in the environment, thereby constituting a threat to human beings and other forms of biological life (Adeleken and Abegunde, 2011; Voet et al., 2008).

Heavy metals have low environmental mobility as a result of this, a single contamination could set a stage for a long term exposure of human, microbial, fauna, flora and other edaphic communities to heavy metals (Adeleken and Abegumde 2011). The compilation of past and present catalogues of atmospheric heavy metal concentration is an activity of great importance (Shrivastav, 2001).

2.9.1 Soil pollution by heavy metals

Heavy metal pollution in soils refers to cases where the quantities of the elements in soils are higher than maximum allowable concentrations and this is potentially harmful to biological life at such locations. Heavy metals occur at typical background in all ecosystems, however, anthropogenic releases can result in higher concentrations of these metals relative to their normal background values hence the pollution (Adeleken and Abegunde, 2011). Heavy metals released from vehicular emission can accumulate in surface soils and their deposition over time can lead to abnormal enrichment, thus causing metal contamination of the surface soils (Fong et al., 2008). Studies have shown that both long term and short term contamination of soils have effects on microbial activity and enzyme activities of the soil (Adeleken and Abegunde, 2011).

The toxicity and mobility of heavy metals in soils depend not only on the total concentration but also on their specific chemical form, bonding state, metal properties, environmental factors, soil properties and organic matter content (Osu and Okoro, 2011). Exposure of children, generally accepted as the highest risk group who have a higher adsorption rate of heavy metals because of their active digestion system and sensitivity of haemoglobin, to heavy metals, can greatly increase ingestion of metal laden soil particles via hand - to - mouth activities. In addition, adults may be exposed to threat since inhalation is easier pathway for toxic metals to enter their body (Fong et al., 2008).

2.10 Effects of heavy metal pollution

2.10.1 Lead (Pb)

Lead has a negative influence on both children and adults. For children, Pb reduces the physical growth and mental growth (Simeonov et al., 2010). The intelligent quotient of children is diminished and symptoms of irritability and fatigue could be observed. Pregnant women exposed to Pb have higher rates of infertility, miscarriage and still births (Ediin et al., 2000). Chronic exposure to Pb can affect physical growth and can cause anaemia, kidney damage, headache, hearing problems, speaking problems, fatigue or irritable mood (Simeonov et al., 2010). The toxicity of Pb is multiple biochemical effects. It has the ability to inactivate enzymes, compete with calcium for incorporation into bones and interfere with nerve transmission and brain development (Ediin et al., 2000).

The main sources of Pb in the environment include, dust from leaded paints from older houses, leaded gasoline and tap water from soldered pipes (Ediin et al., 2000). Indoor chemicals and indoor smoking is also a source (Simeonov et al., 2010). In the soils, the maximum allowable limits of lead in UK and USA is 200 mg kg^{-1} (Mamtaz and Chowdhury, 2006). Soils contaminated with Pb have been reported to decrease the growth and yield of plants (Balba et al., 1991). A study carried out by Mico et al. (2006) on heavy metal content of agricultural soils in a Mediterranean Semiarid Segura River Valley in Spain recorded 19.6 mg kg of Pb in the soil with a range of

8.9 to 34.5 mg kg^{-1}. A study by Ijeoma et al. (2011), on heavy metal content in high traffic area soils of Pakistan, recorded a minimum lead concentration of 10.06 mg kg^{-1} and a maximum Pb concentration of 29.71 mg kg^{-1}. A study by Atiemo et al. (2011) recorded levels of Pb in road soils ranging from 33.640 to 117.45 mg kg^{-1}. Similarly Jaradat and Momani (1999) recorded levels of Pb in roadside soils at different distances from the road ranging from 3.700 to 272.200 mg kg^{-1}.

2.10.2 Cadmium (Cd)

Cd is a heavy metal characterized by high mobility in biological systems. It is emitted to the atmosphere in combustion processes, mainly in the form of oxides. Cd uptake by plants is partly limited by presence of calcium, phosphorus and chelating compounds in the soil (Wieczorek et al., 2004). The exposure of Cd and especially chronic exposure can cause renal dysfunction, calcium metabolism disorders and also increased incidence of some forms of cancer (Selinus and Alloway, 2005).

In plants, Cd induces oxidative stress in plant cells and inactivates some enzymes. Cd taken up by plants from the soil accumulates first of all in the roots, and then transported in smaller quantities to stems and seeds (Wieczorek et al., 2004). Among the sources of Cd in the environment include; mining and smelting of metal ores, fossil fuel combustion and also phosphate fertilizers. Cd is also used in the production of nickel-Cd rechargeable batteries that become deposited in sewage sludge, thus raising environmental levels of Cd (Challa and kumar, 2009). Farming practices such as tobacco growing also increases the level of Cd in the environment as tobacco is known to accumulate it in its tissues (Selinus and Alloway, 2005). The sources of Cd in the urban areas are much less well defined than those of Pb, but metal plating and tire rubber were considered the likely sources of Cd within Kirisia Commercial area which houses Maralal town (Jaradat and Momani, 1999).

Cd is also found in lubricating oils as part of many additives and car tyres as a result of the vulcanization process. In the absence of any major industry in the sampling sites, the levels of Cd could be due to lubricating oils and/or old tires, that are frequently used, and the rough surfaces of the roads which increase the wearing of tires (Jaradat and Momani, 1999). At higher concentrations, it is known to have a toxic potential. The other sources of Cd are industrial activities; the metal is widely used in electroplating, pigments, plastics, stabilizers and battery industries (Mehbrahtu and Zerabruk, 2011). Cd is highly toxic and responsible for several cases of poisoning through food.

Small quantities of Cd cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures and kidney damage (Mehbrahtu and Zerabruk, 2011). The recommended concentration in the soils is 3 mg L^{-1} (Adeleken and Abegunde, 2011). A study by Kisamo (2003) on the environmental hazards associated with heavy metals in Lake Victoria Basin reported levels of Cd in soils ranging from 0.16 to 0.55 mg L^{-1}. The range recorded in the above study was below the WHO maximum permissible limit of Cd set at 3 mg L^{-1}. A study by Delbari and Kulkarni (2011) recorded Cd values in agricultural soils ranging from 0.000 to 0.004 mg L^{-1} with a mean value of 0.002 mg kg^{-1} in summer season and 0,001 to 0.004 mg kg^{-1} with the mean value of 0.002 mg kg^{-1} in winter season. Similarly, Jaradat and Momani (1999) recorded Cd levels in roadside soils ranging from 0.21 to 0.75 mg kg^{-1}.

2.10.3 Chromium (Cr)

Chromium is one of those heavy metals in the environment whose concentration is steadily increasing due to industrial growth, especially the development of metals, chemicals and tanning industries (Adeleken and Abegunde, 2011). The most common forms of chromium are chromium VI and chromium III (Hilgenkamp, 2006). Chromium III is an important component of a balanced human and animal diet and its deficiency causes disturbance to the glucose and lipid metabolism in humans while chromium VI is carcinogenic (Chernoff, 2005). Although chromium toxicity in the environment is rare, it still presents some risks to human health since chromium can be accumulated on skin, lungs, muscle fat, liver, dorsal spin, hair, nails and placenta where it is traceable to various health conditions (Adeleken and Abegunde, 2011).

Among the health effects brought about by the exposure to chromium VI include lung cancer, malignant neoplasia, chromium dermatitis and skin ulcers (Sarkar, 2005). Perforations and ulcerations of the nasal septum and bronchial asthma have also been reported. The sources of chromium in the environment include, cement, leather, plastics, dyes, textiles, paints, printing ink, cutting oils, photographic materials, detergents, wood preservatives among others (Hilgenkamp, 2006). Other sources of chromium are water erosion of rocks, power plants, liquid fuels, brown and hard coal and industrial and municipal wastes. Non biodegradability of chromium is responsible for its persistence in the environment (Adeleken and Abegunde, 2011).

The maximum allowable limit of chromium in the soil set by the United Kingdom is 300 mg/kg. A study by Adeleken and Abegunde (2011) on the levels of heavy metals contamination at automobile mechanic villages in Ibadan, Nigeria reported levels of chromium in soil ranging from 2.0 to 29.75 mg kg^{-1} and were within the maximum allowable limit of chromium in the soils set by United Kingdom. Similarly, a study by Delbari and Kulkarni (2011), recorded chromium in the agricultural soils around Tehran ranging from 0.234 to 1.577 mg kg^{-1} with a mean value of 0.58 mg/kg.

2.10.4 Manganese (Mn)

Manganese is essential for normal physiological functioning of humans and animals and exposure to low levels of manganese in the diet is considered nutritionally essential in humans. However chronic exposure to higher doses is detrimental to human health (Calkins, 2009). In higher doses manganese is toxic and its toxicity varies with route of exposure, chemical species, age, sex and animal species (EPA, 2004; Kohl and Medlar, 2007). Generally, the nervous system is the primary target organ with neurological effects and syndrome called manganism may result from chronic exposure to higher levels of manganese (EPA, 2004; Calkins, 2009). Manganism is characterized among other symptoms, weakness, tremors, a masklike face and psychological disturbance. Sources of manganese due to human activities in the environment include; combustion of coal, residential combustion of wood, iron and steel production plants and power plants (Calkins, 2009).

2.10.5 Zinc (Zn)

Zinc is an essential trace element for plants, animals and humans found in virtually all food and potable water in the form of salts or organic complexes (Swaminathan et al., 2011). Although drinking water seldom contains zinc above 0.1 mg L^{-1}, levels in tap water can be considerably higher because of the zinc used in plumbing material (Swaminathan et al., 2011). The average adult body contains between 2-3 g of zinc (Miculescu et al., 2011). Zinc is used to form connective tissues like ligaments and tendons (Miculescu et al., 2011).

Zinc toxicity is rare but at concentrations of up to 40 mg L^{-1}, it may induce toxicity characterized by symptoms of irritability, muscular stiffness and pain (Al-Weher, 2008). Some of the anthropogenic sources of zinc in soil and water include, discharges of smelter slag and wastes and the use of commercial products such as fertilizers, paints and wood preservatives containing zinc (Lew, 2008). In a study by Jia et al. (2010) on levels of heavy metals in soils of Yucheng city in China, it recorded levels of zinc ranging from 48.49 - 124.30 mg L^{-1} with a mean level of 71.94 mg L. Okonola et al. (2007) recorded values of zinc in soils ranging from 41.66 to 237.96 mg kg^{-1}. Similarly, a study by Yahoya et al. (2010) recorded zinc values in roadside soils ranging from 30.2 to 131.06 mg kg^{-1} during wet season and 73.3 to 202.4 mg kg^{-1} during dry season.

2.10.6 Copper (Cu)

Copper occurs naturally in ores. It is mined as a primary ore product from copper sulfide and oxide ores. It is released into the environment through mining, agriculture and industrial activities. Copper is used extensively in the manufacture of textiles, antifouling paints, electrical conductors, plumbing fixtures, pipes, coins, cooking utensils, wood preservatives, pesticides and fungicides, and copper sulfate fertilizers. The mobility of copper in soil depends on the soil pH and the content of organic compounds and other minerals with which copper might interact. In general, copper has low mobility in plants relative to other elements (Heidary-Monfared, 2011).

Sensitivity to the toxic effects of excess dietary copper is influenced by its chemical form, species, and interaction with other dietary minerals. High levels can cause symptoms of acute toxicity, including nausea, abdominal discomfort, diarrhoea, haemoglobinuria and/or haematuria, jaundice, oliguria/anuria, hypotension, coma and death. Histopathological effects have been observed in the gastrointestinal tract, liver and kidney. There is limited information on chronic copper toxicity. However, copper does not appear to be a cumulative toxic hazard for man, except for individuals suffering from Wilson's disease. Copper is not considered to be mutagenic, carcinogenic or affect reproduction (Codex, 2011).

2.10.7 Iron (Fe)

Iron occurs as a natural constituent of all foods of plant and animal origin, and may also be present in drinking water. In food it occurs as iron oxides, inorganic and organic salts or organic complexes such as haeme iron. Processing may affect the chemical form of iron. Levels of iron range from low for many fruits, vegetables and fats, to medium for red meats, chicken, eggs, whole wheat flower, to high for organ tissues, fish, green vegetables and tomatoes. Meat and grain contribute to a great part of diet-derived iron. Other important dietary sources include water, beverages and iron medication. Iron fortification of food, and also contamination of food during its preparation could increase the intake of iron. The rate of absorption of iron is affected by the chemical form of the dietary iron, the source of iron (plant or animal), its interaction with other food components and the body's need for iron (mucosal regulation) (Codex, 2011).

The effects of toxic doses of iron in animal studies are characterized by initial depression, coma, convulsion, respiratory failure and cardiac arrest. Post-mortem examination reveals adverse effects on the gastrointestinal tract. No long-term feeding studies are available, however, injection-site tumours have been observed in several animals' studies after injection with iron preparations. Some iron-forms were found positive in mutagenicity tests. No teratogenic effects were observed (Codex, 2011).

In human, acute toxicity of iron ingested from normal dietary sources has not been reported; the amount of iron absorbed in normal subjects is subject to mucosal regulation so that excessive iron is not stored in the body. However, subjects with impaired ability to regulate iron absorption (that is suffering from idiopathic haemochromatosis), will be at risk from excessive exposure to iron. Excess iron intake may result in siderosis (deposition of iron in tissue) in liver, pancreas, adrenals, thyroid, pituitary and heart depending on the chemical form (Codex, 2011).

2.10.8 Nickel (Ni)

Nickel occurs in the environment only at very low levels. Humans use nickel for many applications like the use of nickel as an ingredient of steel and other metal products (Lenntech, 2013), in the metallurgical, chemical and food processing industries, especially as catalysts and pigments (Cempel et al., 2006). Foodstuffs have low natural content of nickel but high amounts can occur in food crops growing in polluted soils. Humans may also be exposed to nickel by inhalation, drinking water, smoking and eating contaminated food (Lenntech, 2013). Uptake of high quantities of nickel can cause death, systemic effects, respiratory effects, cardiovascular effects, gastrointestinal, haematological musculoskeletal, hepatic, renal, endocrine, metabolic, immunological and lymphoreticular, neurological, reproductive, developmental effects and cancer (ATSDR, 2005).

2.11 HEAVY METALS IN CROPS CULTIVATED IN POLLUTED SOILS

Idodo-Umeh and Ogbeibu (2010) investigated the bioaccumulation of heavy metals in cassava tubers and plantain fruits grown in soils impacted with petroleum and non-petroleum activities in Isoko South LGA of Delta State, Nigeria. The results showed that all heavy metals revealed higher values in petroleum impacted soil than non-impacted soil. The values of heavy metals were higher both in epicarp and mesocarp of plantain fruits harvested from petroleum impacted soils than from non-petroleum impacted soil. In cassava tubers, the values of heavy metals in the cortex were all higher in the petroleum impacted soil than in non-impacted soil.

The concentration of heavy metals has been of great concern to many researchers in the Niger Delta Region. According to Hart et al (2005), the concentration of trace metals Pb, Fe, Cu and Zn were estimated in crops (cassava, cocoyam, okra, pumpkin and water leaf) harvested in some oil prospecting location in Rivers State, Nigeria. The study revealed higher concentration of heavy metal of Pb with corresponding high level of Fe, Cu and Zn in various food crops harvested at areas of high industrial activities in river state in Nigeria compared to the non-industrialized area.

2.12 BIOAVAILABILITY AND BIOACCUMULATION OF HEAVY METALS IN PLANTS

2.12.1 Bioavailability and Bioaccumulation

Bioavailability is the proportions of total metals that are available for incorporation into biota (bioaccumulation). Total metal concentrations do not necessarily correspond with metal bioavailability (Davis et al., 2001). Some living species have the capacity to accumulate in their organism heavy metals in concentrations much higher than these metal concentrations usually are in the environment. This process can be defined by using two basic notions: bio-concentration and bioaccumulation. Bio-concentration is the direct uptake of a pollutant concentration while it passes from the environment to an organism. In the case of terrestrial organism, this process takes place by the pollutant passage from soil into the plant through the radicular system or from air into the animal organism by direct inhaling (Smical et al., 2008).

Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment (Ismail, 2009). These processes can be expressed by using the concentration factor (BCF). The concentration factor expresses the ratio between the pollutant concentration in an organism and its concentration in the biotope (Smical et al., 2008). BCF = metal concentration in organism / metal concentration in biotope.

2.12.2 Factors Affecting Heavy Metals Mobility and Bioavailability in Plants

Plant uptake of trace elements is generally the first step of their entry into the agricultural food chain. Plant uptake is dependent on: movement of elements from the soil to the plant root, elements crossing the membrane of epidermal cells of the root, transport of elements from the epidermal cells to the xylem, in which a solution of elements is transported from roots to shoots, and possible mobilization, from leaves to storage tissues used as food (seeds, tubers, and fruit) in the phloem transport system. After plant uptake, metals are available to herbivores and humans both directly and through the food chain. The limiting step for elemental entry to the food chain is usually from the soil to the root (Amare, 2007).

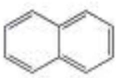
Plant species, relative abundance and availability of necessary elements also control metal uptake rates. Abundant bio available amounts of essential nutrients can decrease plant uptake of non-essential but chemically similar elements. Bioavailability may also be related to the availability of other elements. For example, copper toxicity is related to low abundances of zinc, iron, molybdenum and (or) sulphate (Amare, 2007).

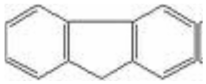
2.13 Polycyclic Aromatic Hydrocarbons, PAHs

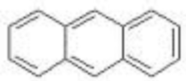
Generally, PAHs are hydrocarbon compounds which can be found in coal and all oil types, such as crude oil, petroleum, benzene, and diesel. The PAHs structure consists of carbon and hydrogen atoms in the form of two or more fused aromatic (benzene) rings. A benzene ring shares a pair of carbon atoms with another ring (Gary and

Petrocelli, 1985). In the purest form, PAHs are flat, solid, and range in appearance from colorless to white or pale yellow-green. In general, PAHs in the environment are produced from incomplete combustion of substances with carbon molecules such as oil, wood, or coal. Other anthropogenic sources include motor vehicles, cooking ovens, and cigarettes. Furthermore, PAHs can come from natural sources which are forest fires and volcanic eruptions. Additionally, PAHs are also found naturally in the environment especially in some plant species.

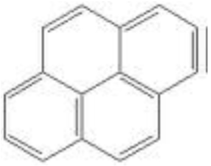
The basic structure of PAHs includes carbon and hydrogen atoms which are arranged in the form of two or more fused aromatic rings. Two aromatic rings are fused together by sharing a pair of carbon atoms. Their structures are in a single plane. Generally, their molecular weight is in the range of 166 to 328. The molecular weight of each molecule depends on its number and position of fused rings and other components. PAHs are crystalline solid with high melting and boiling points but with low vapor pressure and water solubility. Furthermore, they have a high affinity for solid particles, especially with high organic content. Thus, when they reach to the aquatic environment, they tend to rapidly adsorb on solid surfaces such as suspended particles and sediments. Generally, PAHs in linear form are less soluble than angular or condensed form (NRCC, 1983). Some PAHs structures are shown in Fig 2.1



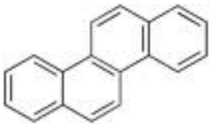




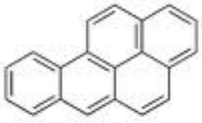
Naphthalene (Naph) Fluorene (Fl) Anthracene (Ant)



Pyrene (Pyr)



Chrysene (Chr)



Benzo[a]pyrene (BaP)

Fig 1 showing some PAHs structures (Witt, 1995).

PAHs are classified as highly toxic pollutants; they can cause both acute and chronic effects in the organisms (Narro, et al., 1992). PAHs can cause mutation and cancer and also affect endocrine systems. Low molecular weight PAHs tend to cause more acute effects, while the high molecular weight PAHs tend to have chronic effects (Ashok and Saxena, 1995).

2.14 PROPERTIES OF PAHs

The polycyclic aromatic hydrocarbons belong to the group of organic compounds consisting of 2 to 13 aromatic rings (Bojakowska, 1995). PAHs are weakly volatile and dissolve weakly in water, the solubility decreases with an increase in the number of aromatic rings. PAHs dissolve well in organic solvents and are lipophilic. All PAHs are solid and have high melting and boiling points. PAHs are highly chemically inactive but bond to particulate matter. When absorbed at the surface of dust. PAHs are highly thermo and photosensitive. They can be cracked at high temperature (50°C) and when exposed to light, especially ultraviolet light, but also visible light. Photo-oxidation is one of the most important ways of removing PAHs from the atmosphere. It was found that even a short time of dust irradiation (about 6 hours) results in decomposition of 15-20 % absorbed PAHs (Maslowski, 1992; Zakrzewski, 1995).

In 1976 over 100 different PAHs found in atmosphere were identified, and in 1981 more than 200 PAHs were found in cigarette smoke (Lee et al., 1976 and 1981). Many PAHs contains the same amount of rings but the differences in configuration of rings may lead to differences in the compound's properties. In the environment one can also find substituted PAHs with functional groups such as $–OH_2$ $–NO_{2,}$ =O and $–CH_{3.}$

2.15 SOURCES OF PAHS IN THE ENVIRONMENT

PAHs are ubiquitous environmental contaminants. Sources of PAHs can be broadly classified as pyrogenic (combustion origin) and petrogenic (petroleum origin). The presence of higher molecular weight (HMW) PAHs indicates likely pyrogenic source, while the presence of lower molecular weight (LMW) PAHs implies likely petrogenic origin of the PAHs (Boehm and Farrington, 1984). Naphthalene, fluorene, anthracene, phenanthrene are examples of LMW PAHs, while benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(*cd*)pyrene and benzo(*ghi*)perylene are some HMW PAHs. Pitt, *et al.*1995 has summarized from literature major sources of commonly found PAHs in the environment. High molecular weight PAHs, which are assumed to be pyrogenic in origin, were noted to be of original petroleum sources. PAH released into the environment undergo chemical, physical and biological changes (Countyway, *et al.* 2003). Physical changes, such as evaporation, or physical transport of PAH by air or water from one location to other; chemical changes such as photo transformation of PAH to metabolic products; and biological changes such as biotransformation of the PAHs, changes their profile in the environment. Differentiating the sources of PAHs based on observed PAHs molecular weights may be a useful tool if the samples analyzed for PAHs are assumed not to be affected by any of these changes.

2.16 PAHS IN SOILS

Accumulation of PAHs in soils without direct industrial contamination is believed to result mainly from atmospheric deposition after long-range transport (Greenberg et al., 1985). Forest fires and airborne pollution deposition are the main source of soil PAHs in remote areas. Soil levels of PAHs resulting from natural processes are estimated to be in the range of 1 - 10 μg kg^{-1} (Edwards, 1983). Jones et al. (1989a) reported a total PAH concentration of 0.1 - 55 mg kg^{-1} in Welsh soils that resulted strictly from atmospheric deposition with no direct industrial pollution. Levels of PAHs in soils have increased in the past 100 - 150 years because of growing industrial activities. Polycyclic aromatic hydrocarbon concentrations in urban industrial soils can be 10 - 100 times higher than in remote soils (Wild and Jones, 1995). In soils at industrial sites, PAH concentrations and type of PAH found vary depending on the type of industry. For instance, Juhasz and Naidu (2000) in a review of the literature, reported total PAH concentrations of 5863 mgkg^{-1} at a creosote production site, 18,704 mg kg^{-1} at a wood preserving site, 821 mg kg^{-1} at a petrochemical site, and 451 mg kg^{-1} at a gas manufacturing plant site.

The major pathway of PAH loss in soil is degradation by microbial metabolism. The physical and chemical properties of the particular PAH compound being degraded will affect this process, as well as environmental factors such as soil temperature, moisture, pH, and oxygen concentration (Manilal and Alexander, 1991; Weissenfels et al., 1992). Sims and Overcash (1983) concluded that photolysis, hydrolysis and chemical oxidation processes did not contribute measurably to loss of PAHs from soil, but Wild and Jones (1993) reported some abiotic loss of LMW PAHs from soil by volatilization.

2.17 PAHS IN PLANTS

Polycyclic aromatic hydrocarbons accumulate in vegetation mainly through atmospheric deposition on and uptake by above-ground parts of the plant. Concentrations of PAHs in plant tissue in non-industrialized regions range from 50-80 μg kg^{-1} (Edwards, 1986), although specific plant tissue concentrations will depend on plant species, type of PAH, and environmental conditions (Salanitro et al., 1997). Vegetation in urban areas can have up to 10 times higher PAH levels than rural vegetation (Juhasz and Naidu, 2000). Sims and Overcash (1983) and Edwards (1986) found that PAHs can be adsorbed onto plant roots, but translocation to the above-ground parts was negligible because plants are unable to transport hydrophobic compounds such as PAHs in xylem.

2.18 CHARACTERISTICS OF PAHs

2.18.1 Molecular weight

Polycyclic aromatic hydrocarbons are classified as low molecular weight (LMW) if they have two or three fused rings or high molecular weight (HMW) if they have four or more fused rings. LMW PAHs are degraded and volatilized more rapidly than HMW PAHs (Harvey, 1997). As molecular weight increases, hydrophobicity/lipophilicity increases, water solubility decreases, vapor pressure decreases, and the compound will have a more *recalcitrant* (difficult to degrade) structure. High molecular weight PAHs persist in the environment because of low volatility, resistance to leaching, and recalcitrant nature (Jones et al., 1996; Wild and Jones, 1995).

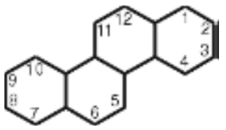
2.18.2 Structure

Polycyclic aromatic hydrocarbons are also classified into two groups based on ring structure: alternant and non-alternant. Alternant PAHs such as anthracene, phenanthrene, and chrysene are derived from benzene by fusion of additional six-membered benzoid rings, and contain fewer than eight benzoid rings (Harvey, 1998). Non-alternant PAHs may contain rings with fewer than six carbon atoms in addition to six membered rings. This group is extremely broad in structure and greatly increases PAH diversity (Harvey, 1998). Examples of four-, five-, and six membered rings are fluorine and fluoranthene (Harvey, 1997; Dabestani and Ivanov, 1999).

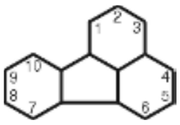
Notice the difference in the two structures of alternate and non-alternate PAHs in the below diagrams. Chrysene consists of four fused, six carbon benzene rings. Fluoranthene, on the other hand, contains naphthalene and a benzene unit connected by a five-membered ring (in the center of the structure) and is indicative of lower temperature and less efficient combustion. Information on number of rings for select PAH compounds are provided in Table 1.

Fig. 2.2

Alternate (Chrysene)



Nonalternate (Fluoranthene)



2.18.3 Solubility

Solubility of PAH compounds in water is dependent upon temperature, pH, ionic strength (concentration of soluble salts), and other organic chemicals (i.e. dissolved organic carbon) (Pierzynski et al., 2000). Solubility is estimated by chemical structure and octonol-water partition coefficients

Table 1: US EPA's 16 priority pollutant PAHs and selected properties

PAH name	Number of rings (g mole-1)	Molecular weight (mg L-1)	Solubility in water	Vapor pressure (Pa)	Log K_{ow}
Naphthalene	2	128.17	31	11.866	3.37
Acenaphthene	3	154.21	3.8	0.500	3.92
Acenaphthylene	3	152.2	16.1	3.866	4.00
Anthracene	3	178.23	0.045	3.40×10^{-3}	4.54
Phenanthrene	3	178.23	1.1	9.07×10^{-2}	4.57
Fluorene	3	166.22	1.9	0.432	4.18
Fluoranthene	4	202.26	0.26	1.08×10^{-3}	5.22
*Benz[a]anthracene**	4	228.29	0.011	2.05×10^{-5}	5.91
*Chrysene**	4	228.29	0.0015	1.04×10^{-6}	5.91
Pyrene	4	202.26	0.132	5.67×10^{-4}	5.18
*Benzo[a]pyrene**	5	252.32	0.0038	6.52×10^{-7}	5.91
*Benzo[b]fluoranthene**	5	252.32	0.0015	1.07×10^{-5}	5.80
*Benzo[k]fluoranthene**	5	252.32	0.0008	1.28×10^{-8}	6.00
*Dibenz[a,h]anthracene**	6	278.35	0.0005	2.80×10^{-9}	6.75
*Benzo[g,h,i]perylene**	6	276.34	0.00026	1.33×10^{-8}	6.50
*Indeno[1,2,3-cd]pyrene**	6	276.34	0.062	1.87×10^{-8}	6.50

*The U.S. EPA has classified PAH in italics as possible human carcinogens (adapted from Lundstedt, 2003; Bojes and Pope, 2007).

Chemical structure: In general, as the number of benzene rings in a PAH compound increases, solubility decreases (Wilson and Jones, 1993). There are, of course, exceptions to the rule. Symmetry, planarity, and the presence of substituents affect PAH solubility in organic solvents. Solubility has been found to increase in linearly-fused PAH as the number of rings increase because the bonds become weaker (olifinic) in character, but has not observed in angularly fused PAH (Harvey, 1997). Planar PAHs are less reactive (i.e. less soluble) and biologically less toxic (Dabestani and Ivanov, 1999). Substituted PAHs are those in which a functional group in the compound has been replaced with another functional group. For example, in a methyl-substituted PAH, one of the functional groups has been replaced by a univalent compound with the general formula CH_3^-.

Alternant PAH compounds that are planar and symmetrical require a relatively high energy of solubilization because of their ability to fit closely in a lattice. Thus, they tend to be less soluble (Harvey, 1997). As the compounds deviate from planarity or symmetry they tend to be more soluble in organic solvents. Methyl and polar substitution may also increase the solubility of PAHs in certain solvents (Harvey, 1997).

Octanol-water partition coefficients*:* There are substantial amounts of data on the relationship between aqueous solubility and octonol-water partition coefficients (K_{ow}) for the partitioning of PAH between water and organic matter in soils (Mackay and Callcott, 1998). There is an inverse relationship between K_{ow} and solubility which is determined with the following equation:

$$K_{ow} = \frac{\text{amount of organic chemical in octanol (mg L}^{-1}\text{)}}{\text{amount of organic chemical in water (mgL}^{-1}\text{)}}$$

The octanol-water coefficient is often expressed as the log K_{ow}. Naphthalene has a log K_{ow} of 3.37, while Indeno[1,2,3-cd]pyrene K_{ow} is 6.50. In this case, naphthalene is more soluble than Indeno[1,2,3-cd]pyrene. This is also in agreement with the influence of chemical structure on solubility. Solubility and K_{ow} of select PAH are provided in Table 1.

2.18.4 Vapor pressure

Vapor pressure defines the point at which PAHs in the solid state either evaporate into a gaseous form or condense back to a solid state. The higher the vapor pressure (at normal temperatures), the more volatile the compound is. Naphthalene has (11.866 Pa) and is more volatile and would readily evaporate more rapidly than dibenz[a,h]anthracene (2.80 x 10^{-9} Pa) at normal temperatures (Mackay and Callcott, 1998). Polycyclic aromatic hydrocarbon vapor pressures are important for determining risk associated with dredge sediments, transfer between two resources (soil and air) as well as field sampling and lab safety. Vapor pressures of selected PAHs are presented in Table 1.

2.19 HEALTH AND ENVIRONMENTAL EFFECTS OF PAHS

Because of combustion of fossil fuels and organic waste, PAHs are ubiquitous in the environment. Studies show that certain PAHs metabolites interact with DNA and are genetoxic, causing malignancies and heritable genetic damage in humans. Many of these compounds have carcinogenic and mutagenic activities and present a hazard for human health (Tsibart and Gennadiev, 2013). In humans, heavy occupational exposure to mixtures of PAHs entails a substantial risk of lung, skin, or bladder cancer. PAHs generally have a low degree of acute toxicity in humans. The most significant endpoint of PAHs toxicity is cancer. Increased incidence of lungs, skin and bladder cancers are associated with occupational exposure to PAHs. Animal studies show that certain PAHs affect the hematopoietic immune, reproductive and neurologic system and cause developmental effects (ATSDR, 2009).

PAHs are not produced for commercial purposes. They are naturally formed during volcanic eruptions and forest fires. Most PAHs originate from anthropogenic sources such as the incomplete combustion of fossil fuels, wood and waste, automobile exhaust and petroleum derivative spills. PAHs are compounds consisting of two or more aromatic rings and two adjacent benzene rings that share two carbon atoms. These compounds have been widely studied (Mc Elroy et al., 1989) because of their carcinogenic and mutagenic character. The main environmental significance of PAHs is their carcinogenic potential as established by several workers (Marvin et al., 1995).

PAHs are classified as highly toxic pollutants; they can cause both acute and chronic effects in the organisms (Narro et al., 1992). Low molecular weight PAHs tend to cause more acute effects, while the high molecular weight PAHs tend to have chronic effects (Ashok and Saxena, 1995).

2.20 UPTAKE AND MOVEMENT OF CHEMICAL ELEMENTS FROM SOIL BY PLANTS

Plants differ in their capacity to absorb nutrients from the soil. Some of these differences are genetic in nature and are associated with physical distribution and chemical characteristics (Isirimah 2001). Almost any element in soil solution is taken up by the plant to some extent, whether needed or not. The process of material uptake by plants is complex and knowledge of it is incomplete although the following key points are worthy of note.

i. The process is not the same for all plants concerning one or more minerals/contaminants.

ii. The complete process occurs in a healthy root system.

iii. The necessary mineral/contaminant must be available in the rhizhosphere in Suitable amounts.

iv. Uptake varies from one mineral/contaminant to another

Although effluents and sludge have been applied on many kinds of grasses, vegetables, legumes, field crops and woody plants, grasses seem to be the most effective in neutralizing wastes. Grasses have superior biological pumps (Isirimah, 2001). The most important factor affecting contamination of plants is bioavailability and that, as bioavailability increased, the concentrations in the root and shoot compartments of the plants were predicted to increase; and also that microbial activities and contamination of plants are closely related, suggesting that both can have complementary roles in phytoremediation (Sung et al., 2004).

In a related study using *Vigna unguiculata*, Isikhuemhen et al., (2001) stated that significant improvements were achieved in the percentage germination, plants height and root elongation of the experimental plants, as well as decreased hydrocarbon degradation in soil. In the work of Ogbo et al., (2009), S. *rhombifolia and M. alternifolius* successfully extracted over 60% of total petroleum hydrocarbons from respective sites, and were therefore considered suitable for use in phytoremediation of oil contaminated soil. However, for all the plants species used in this study, reduction in shoot length, leaf area, root length and total chlorophyll content, were observed.

The effectiveness of phytoremediation crop – *Vigna unguiculata* in the remediation of crude oil-polluted soil for cassava cultivation was investigated and the effects of petroleum hydrocarbon contamination on plants included retarded seed germination, reduction in height, stem density; photosynthetic rate and biomass or in complete mortality (Pezeshki et al., 2000). Tanee and Anyanwu (2007) reported that cassava cannot tolerate post- planting crude oil pollution at concentration as low as 500ml/m^2 probably due to the reduction in available nutrients for plants in the soil as observed by (Akonye and Onwudiwe, 2004), or phytotoxicity of the oil. Consequently, results from their efforts concluded that the use of *Vigna unguiculata* as a phytoremediation plant is a good remedial option in crude oil-polluted soil for cassava cultivation as phytoremediation caused increased "fresh weight yield" and above/below ground weights respectively, of the cassava varieties used (Tanee and Akonye, 2009).

2.21 THE CASSAVA PLANT

Cassava (*manihot esculenta crantz*) is a staple food for more than 500 million people who rely on it as a major energy source (Cock, 1985). Cassava was first cultivated in Brazil. It is often described as a famine killer as it can be harvested anytime from nine months after planting and can be left growing up to two years. Cassava plant is a perennial that grows under cultivation to a height of 2.4m.

2.21.1 Nutritional Value and Application of Cassava

Cassava tubers consist mainly of carbohydrates (90% on a dry weight basis) 3% protein and lack cysteine and methionine (Gomez et al., 1985). The Cassava leaves however are rich in protein, vitamin A and B and are commonly eaten as a vegetable in Africa (Kirnanet al., 2000). Industrially, cassava is used as a raw material for starch extraction, alcohol production and incorporation in bread making and as a sun dried chips for animal feed (Kimaryo, 2000). Cassava starch has an advantage over other types of starch because of its low level of impurities, giving it subtle flavor release. It is used in the production of beer, baby foods and other dried foods, also in meat production (hunt, 1999). In Africa, 70% of total production of cassava is processed into a wide range of products including pastes, chips, flour, granules, starch and alcohol beverages (Nweke, 1994). Some of these products such as garri and flour can be stored for a relatively long time under ambient conditions (Danhiya, 1994).

2.22 EFFECTS OF AUTO-MECHANIC WASTES ON SOIL AND PLANTS

Auto mechanic activity is one of the major sources of heavy metals concentration in Nigeria (Odjegba and Sadiq, 2000). During these activities reasonable amount of spent engine oil and metal fillings are deposited on topsoil (Adewole and Uchegbu, 2010). Soils polluted with spent engine oil had reduced soil microbial activities and reduced soil fertility status (McGrathet al., 1995). Anoliefo and Vwioko (1995) suggested that heavy metals toxicity and insufficient soil aeration to growing plants are associated problems to soil polluted with spent engine oil. Horsfall (2001) reported that environmental pollution with petroleum products (complex mixture of hydrocarbon) has been recognized as a serious environmental problem especially as it is being spilled on large scale.

According to the study conducted by Ogbonna and Okeke (2010) on heavy metal concentration increased by auto mechanic activities, the mean concentration of Hg in soils close to mechanic workshops ranged between 0.50 and 6.00mg kg^{-1} with the mean value of 3.07mg kg^{-1}, while the Hg ranged between 0.01 and 0.20mg kg^{-1} in the control sites with a mean of 0.03mg kg^{-1}. The mean value of Pb was 91.03mg kg^{-1} ranging between 4.90 and 205.20mg kg^{-1} at the experimental site, while the mean concentration was 60.25mg kg^{-1} ranging from 2.90 to 98.30 mg kg^{-1}. The mean value of Cd was 5.63mg kg^{-1} in soils in control site was 1.79mg kg^{-1} with a range of 0.10 - 6.40mg kg^{-1}. The heavy metals concentrations were higher in the soils close to the mechanic workshops than the control sites.

Renault et al (2000) reported that PAHs are found in spent oil and has shown to have indirect secondary effects including disruption on plant-water-air relationship. Udom et al (2012) reported that soil contamination by oil hinders germination, reduces crop yield and also leads to premature deaths of plants. Ekundayo et al (2001) studied the effect of spent lubricating oil pollution from an auto mechanic workshop and concluded that the presence of spent lubricating oil in soil results in delay seed emergence and inhibits germination of seeds at higher concentrations.

Research has shown that many of the anthropogenic activities have some potential to compromise soil quality and distort plant growth and functions, thereby being a threat to human health and the environment. Therefore further research is necessary to determine important management and risk analysis decision.

From this review it is evident that no data is available on the pollution that occurs from the activity from Okigwe auto-mechanic Village of Imo State, Nigeria. Therefore the current investigations are aimed to fill the lacuna in information of heavy metal levels and PAHs levels in the soils and crops of this mechanic village.

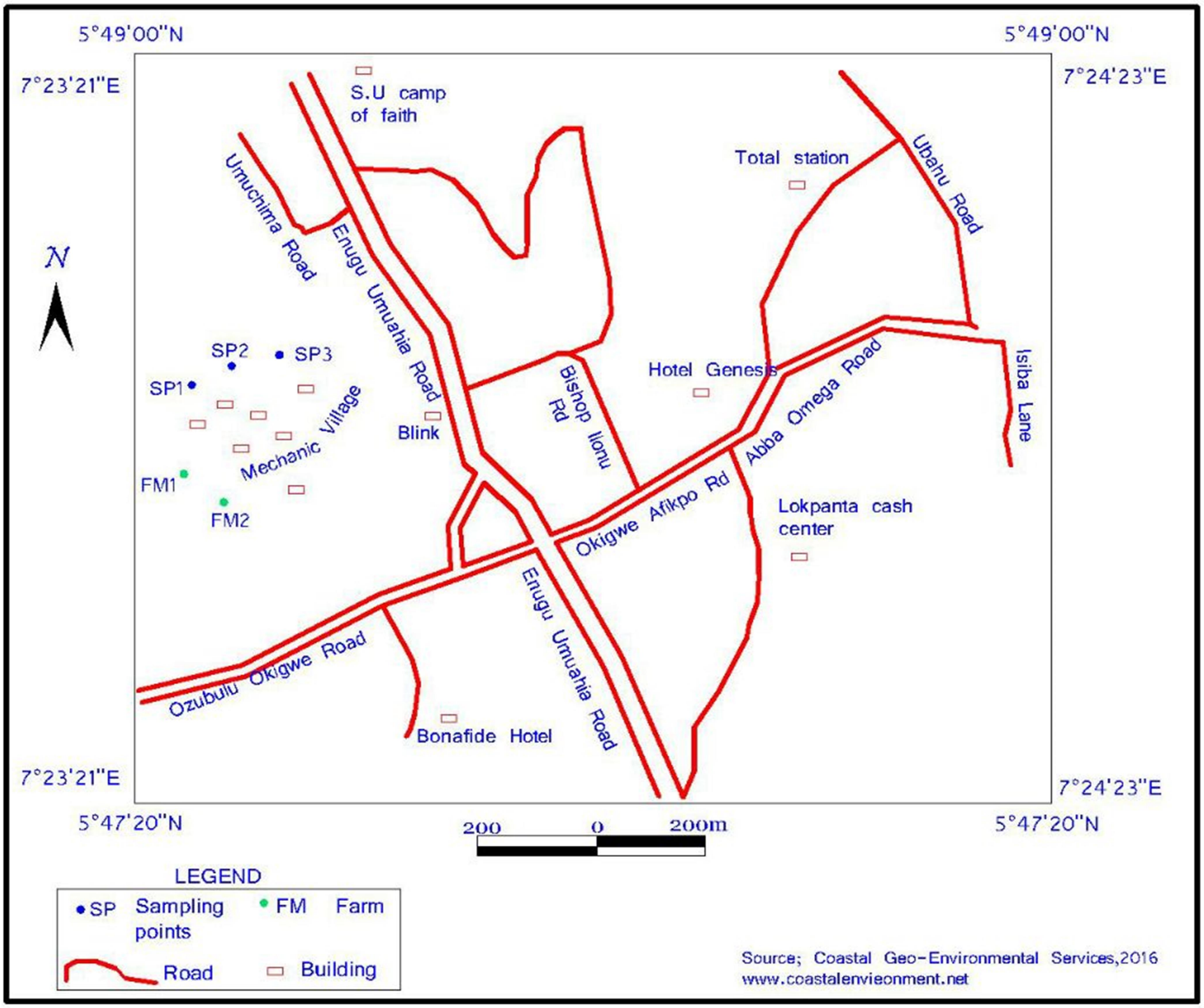
CHAPTER THREE
RESEARCH METHODOLOGY

3.1 Study area

The study area is the Okigwe mechanic village located in Okigwe LGA of Imo State, Nigeria. Okigwe mechanic village lies within longitude 7^0 19' E and 7^0 64'E and latitude 5^0 49'N and 5^0 46'N. It is an area of flat agricultural land converted to mechanic workshops, shops and homes. Okigwe LGA has humid tropical climate, having a mean annual temperature of 27^0 - 28^0C (FEDALR, 1985).

3.2 Types and sources of data

The data used include cassava tubers and soil samples. A variety of sweet cassava (*Manihot esculenta*) tubers were obtained from two different farms of 500m away from each other as well as 300m away from the mechanic village and soil samples were obtained from five (5) different locations within the Okigwe mechanic village and also at a control distance where there is no auto-mechanic activity. The farms are owned by the inhabitant of the community.



Source; Coastal Geo-Environmental Services,2016
www.coastalenvieonment.net

Fig. 3.1: Map of Imo State Showing the Study Area

3.3 Sample collection

The cassava (*Manihot esculenta*) and soil samples were collected during the dry season in October. Tools used for the collection of data include soil auger, GPS, polyethene bags and machete. Surface soil samples (0 – 15 and 15 - 30 cm) were used because they are the first locus of input of metals where they tend to accumulate on a relatively long term basis (Abenchi et al., 2010) and that pollutants normally contaminate the upper layer of the soil at a depth of 0 – 40 cm (Krishna and Grovel, 2007).

3.3.1 Methods of cassava sample collection

The cassava plants were uprooted from two different farms and the tubers were cut with the use of a machete. The cassava tubers were wrapped in polyethene bags and properly labeled.

3.3.2 Methods of soil sample collection

Soil samples were randomly collected from the mechanic village and stored in a polyethene bags and were labeled accordingly. Three (3) sampling locations of 250 m apart were identified within the mechanic village. At each location, soil samples were collected at two points and at a depth of 0 – 15 cm and 15 – 30 cm using a soil auger. Two (2) soil samples at a depth of 0 -15 cm and 15 – 30 cm were also collected in the two farms identified. Two samples from each depth of each location were separately homogenized to make a composite sample of each depth. Control samples were similarly collected at a distance of one kilometer away from the auto-mechanic village. All the samples were appropriately labeled, stored in polyethene bags and transported to the laboratory for analysis.

3.4 Physicochemical analysis of soil samples

3.4.1 pH of soil

The hydrogen ion concentration of soils from the study area was measured using a pH meter as reported by Mclean (1982). 20 grams air-dried soil was passed through 2mm sieve and dissolved in a 50 mL beaker with 20 mL of distilled water was allowed to stand for 30 minutes and properly stirred with a glass rod. The pH of the sample was then taken using pH meter by inserting the pH electrode into the beaker.

3.4.2 Conductivity of soil

The conductivity of the soil was measured by using a conductivity meter as reported by AOAC (1984). Five gram of the soil was dissolved in a 250 mL beaker with 25 mL of distilled water and stirred with a stirring rod. The electrode of the conductivity meter was rinsed with distilled water before inserting it into the beaker and the reading was taken.

3.4.3 Organic matter of soil

Organic matter was determined by ashing using the AOAC method (1984). Two grams of soil samples was weighed into a well- washed and dried crucible. The sample was ashed in a muffle furnace at 540 ^{0}C for 3 hours after which it was removed and reweighed. The sample was then taken back and further ashed until a constant weight was attained. The percentage organic matter was calculated relative to fresh soil sample.

Calculation of % organic matter = $\frac{x-y}{z} \times 100$

Where z = weight of fresh soil to be determined (g)

y = weight of crucible (g)

x = weight of ash+ crucible (g)

3.4.4 Determination of percentage (%) moisture content

Moisture content was determined by AOAC method (1984). This involved drying to a constant weight at 102 ^{0}C and calculating moisture as the loss in weight of the dried samples. An empty crucible was dried in the oven for 15 min and it was allowed to cool in a desiccator containing calcium chloride for about 20 min and weighed. Five grams of soil was weighed into the crucible and placed in the oven at a temperature of 102 ^{0}C for 24 hrs. It was then brought out cooled in a desiccator and reweighed. This process was repeated until a constant weight was obtained. The percentage moisture content was obtained as loss in weight of the original sample.

Calculation of percentage moisture = $\frac{(X-B) - (Y-B)}{A} \times 100$

Where A = weight of sample to be determined (g)

X = weight of crucible + sample before oven drying (g)

Y = weight of crucible + dry sample after oven drying (g)

B = weight of crucible (g)

3.4.5 Determination of nitrate

Nitrate was determined using colorimetric method as adapted from AOAC (1984): Nitrate ion reacts in the presence of sodium salicylate to give yellow sodium para - nitrosalicylate which is then determined colorimetrically. Two grams of crushed soil sample was weighed into a 250 mL conical flask and 5.0 mL of sodium salicylate added to the flask and made up to 50 mL with distilled water. 1 millilitre of sample supernatant was transferred into a test tube and 10 mL of distilled water added into the test tube and allowed to stand for 20 min. The absorbance of the sample was then read at 415 nm using distilled water as blank. Working nitrate standard were prepared from 0.001 mg/l to 0.006 mg/l and treated as test sample. The absorbance were measured at 415 nm using water as reagent blank and the calibration curve for nitrate standard drawn. The value of the test sample was read off from the nitrate standard calibration curve.

3.4.6 Determination of phosphate

Phosphate ion was determined colorimetrically according to AOAC (1984). Phosphate ions react with molybdate and sulphuric acid to give a blue colour which is measured spectrophotometrically at 420 nm. Two grams of soil sample was weighed into a dried crucible and was ashed in muffle furnace at 540 ^{0}C for 3 hours and then was allowed to cool. The sample was digested with 5 mL of $HN0_3$ and the volume made up to 50 mL with distilled water. Five millilitre of the filtrate was transferred into a test tube with pipette and 2.0 mL of ammonium molybdate and 10 mL sulphuric acid solution added into the test tube. The mixture was swirled and allowed to settle for 10 min. The absorbance was read at 420 nm using distilled water as blank. The standard solution was treated as the test sample. The calibration graph for the phosphate standard was used to read off the concentration of the phosphate.

3.4.7 Determination of sulfate

5 grams of air-dried, crushed and grind soil sample was weighed into a 50 mL Erlenmeyer flasks, 25 mL of potassium dihydrogen phosphate (KH_2PO_4) solution was added and placed on a mechanical shaker for 30 minutes, the suspension was filtered into a Buchner funnels by using a filter papers Whatman no. 42. 10 mL of the sample aliquot was pipette into a 25 mL volumetric flask and distilled water was then added to bring the volume to approximately 20 mL. 1 mL of gelatin- $BaCl_2$ reagent was added to make up to the volume with distilled water, the content was mixed thoroughly and allowed to stand for 30 minutes. The content in the flask was shaken and poured into a photo-test tube. The absorbance was read at 420 nm using distilled

water as blank. The standard solution was treated as the test sample. The calibration graph for the sulfate standard was used to read off the concentration of phosphate.

3.4.8 Determination of total organic carbon

Total organic carbon was determined by titremetric method of AOAC (1984). 0.1 gram of soil sample was weighed into a 250 millilitre conical flask and 10 mL of potassium dichloromate and 10 mL of sulphuric acid introduced into the conical flask and swirled to mix the sample with the extracting solvent. The content of the flask was heated at 150^{o}C using a hot plate for 20 min and was allowed to cool. 10 milliltres of distilled water was added into the flask and shaked to ensure even mixing. A drop of orthophenanthroline ferrous sulphate indicator was added and the solution was titrated with ferrous ammonium sulphate till the colour changed to red wine indicating the end point and the percentage total organic carbon was calculated from the titre value using the formular below.

$$\% \text{ TOC} = \frac{\text{BL-ST } (0.2\text{x}0.3) \text{ x}100}{\text{Wt}}$$

BL= blank titre value

ST= sample titre value

Wt= weight of sample

3.5 Determination of heavy metal concentration in soil samples

The soil composite samples were conned and quartered several times before the required samples for analysis were obtained. Following the method of Kakulu (1993), the samples were then air dried to constant weight to avoid microbial degradation, crushed in a mortar and sieved through a 2mm sieve. Three (3) replicate samples of 2.0 g of the air dried, ground and sieve samples were accurately weighed and digested with aqua-regia (i.e in a 3:1 mixture of concentrated hydrochloric and nitric acid), the mixture was heated to dryness using heating mantle. The residue was filtered with 20 mL of deionized distilled water into 50mL universal bottle. The digested samples were then subjected to analysis of the eight (8) heavy metals using Atomic Absorption Spectrophometer (AAS model 210/211 VGP).

3.6 Determination of heavy metal concentration in cassava tubers

The cassava tubers were gently dipped in a bucket of water and rinsed twice with distilled water to remove attached soil particles. They were peeled and the edible parts washed with deionized distilled water, cut into smaller pieces, the pieces were ground using an electric powered blender (mill) to powder state and the ground pieces were air dried for 5 days. 2 grams of the each air dried, ground sample were accurately weighed into a beaker and digested with aqua-regia (i.e in a 3:1 mixture of concentrated hydrochloric and nitric acid), the mixture was heated to dryness using heating mantle. The residue was filtered with 20 mL of deionized distilled water into

50mL universal bottle. The digested samples were then subjected to analysis of the eight (8) heavy metals using Atomic Absorption Spectrophotometer (AAS model 210/211 VGP).

3.7 DETERMINATION OF PAHs IN THE SOIL SAMPLES

3.7.1 Sample extraction

A thin layer of the composite samples were screened on a filter paper to remove fragments of plants debris and stone. The screened samples were thereafter air-dried in the dark. The dry soil samples were then ground into powder in a ceramic mortar. 2 g of each of the soil samples was weighed into a clean 100 mL conical flask, 20 mL of extraction solvent (hexane) was added to the 2 g of soil sample, stirred with a stirring rod and placed in a mechanical shaker for 10 min and allowed to settle. The mixtures were carefully filtered into a clean 50 mL beaker using filter paper filtered into Buchner funnels.

3.7.2 Sample clean-up/ Separation

The filtered extract was passed through a 10 mm chromatographic column after the column was conditioned by clamping the separating column in a retort stand. Activated glass wool, sodium sulphate and silica gel were stored in the oven for about 24 hrs. 1 cm of activated glass wool was inserted at the base of the 10 mm ID × 250 mm long chromatographic column with the aid of a glass rod. Slurry of 2 g activated silica gel in 10 mL DCM was prepared and placed into the column. 0.5 g of sodium sulphate was added to the top of the column, 10 mL of DCM was introduced to the column with a 25 mL measuring cylinder and allowed to pre-elute into a 50 mL beaker and the eluate discarded. 10 mL of hexane was introduced to the column and was allowed to flow through the column at a rate of about two minutes until the liquid in the column was just above the sulphate layer. Immediately 20 mL of the extracted sample was introduced into the column. The extraction bottle was rinsed with 1 mL of hexane and added to the column as well. The stop clock of the column was opened and allowed to elute into a beaker. The fraction in the beaker was transferred into a labeled round bottom flask and concentrated using fume cupboard to 1.5 mL and the concentrate transferred into a well- labeled 2 mL sample vials (with Teflon rubber crimp caps) for gas chromatograph flame ionization detector (GC/FID) analysis.

3.7.3 GC/FID analysis

The EPA-16 PAHs determination was conducted using Gas Chromatographic System (Agilent technologies 7890B) equipped with a single detector (FID), single column and a single AS auto-sampler and a quadrupole Mass Spectrometer (Agilent 7890B MSD). A 1.00 µL of the concentrated extracts were injected by means of hypodermic syringe through a rubber septum into the GC port set at column conditions: HP-5 cross linked PH-ME siloxane, Length of 30 m, I.D: 0.25 mm, thickness of 1 µm with helium carrier gas set in the spitless, constant flow mode with 1.2 mL min^{-1} flow rate. Other GC and FID operating set-up were done according to the instrument's method development as specified in the operating instruction manual Identification and quantification of individual PAHs was based on internal calibration standard containing known concentrations of the 16 PAHs (EPA-16). Separation occurs at the vapour constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column (at a constant flow rate) by the FID detector whose response is dependent upon the composition of the vapour. The specificity of the 16 PAHs sought for in the samples was confirmed by the presence of transition ions (quantifier and qualifier) as shown by their retention times which corresponded to those of their respective standards. The measured peak area ratios of precursor to quantifier ion were in close agreement with those of the standards. Results obtained were presented as mg kg^{-1} concentration per analyte.

3.8 Determination of PAHs in cassava tubers

3.8.1 Sample extraction

The harvested cassava tubers were washed, rinsed with distilled water and then peeled using knife to remove the coat. The peeled samples were sliced and 20 grams of each of the samples were blended to slurry form before analysis. 2 grams of the processed cassava sample was weighed into a 100 mL conical flask, 20 mL of extraction solvent (hexane) was added to the 2 g of soil sample, stirred with a stirring rod and placed in a mechanical shaker for 10 min and allowed to settle. The mixtures were carefully filtered into a clean 50 mL beaker using filter paper filtered into Buchner funnels.

3.8.2 Sample clean-up/ Separation

The filtered extract was passed through a 10 mm chromatographic column after the column was conditioned by clamping the separating column in a retort stand. Activated glass wool, sodium sulphate and silica gel were stored in the oven for about 24 hrs. 1 cm of activated glass wool was inserted at the base of the 10 mm ID × 250 mm long chromatographic column with the aid of a glass rod. Slurry of 2 g activated silica gel in 10 mL DCM was prepared and placed into the column. 0.5 g of sodium sulphate was added to the top of the column, 10 mL of DCM was introduced to the column with a 25 mL measuring cylinder and allowed to pre-elute into a 50 mL beaker and the eluate discarded. 10 mL of hexane was introduced to the column and was allowed to flow through the column at a rate of about two minutes until the liquid in the column was just above the sulphate layer. Immediately 20 mL of the extracted sample was introduced into the column. The extraction bottle was rinsed with 1 mL of hexane and added to the column as well. The stop clock of the column was opened and allowed to elute into a beaker. The fraction in the beaker was transferred into a labeled round bottom flask and concentrated using fume cupboard to 1.5 mL and the concentrate transferred into a well- labeled 2 mL sample vials (with Teflon rubber crimp caps) for gas chromatograph flame ionization detector (GC/FID) analysis.

3.8.3 GC/FID analysis

The EPA-16 PAHs determination was conducted using Gas Chromatographic System (Agilent technologies 7890B) equipped with a single detector (FID), single column and a single AS auto-sampler and a quadrupole Mass Spectrometer (Agilent 7890B MSD). A 1.00 µL of the concentrated extracts were injected by means of hypodermic syringe through a rubber septum into the GC port set at column conditions: HP-5 cross linked PH-ME siloxane, Length of 30 m, I.D: 0.25 mm, thickness of 1 µm with helium carrier gas set in the spitless, constant flow mode with 1.2 mL min^{-1} flow rate. Other GC and FID operating set-up were done according to the instrument's method development as specified in the operating instruction manual Identification and quantification of individual PAHs was based on internal calibration standard containing known concentrations of the 16 PAHs (EPA-16). Separation occurs at the vapour constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column (at a constant flow rate) by the FID detector whose response is dependent upon the composition of the vapour. The specificity of the 16 PAHs sought for in the samples was confirmed by the presence of transition ions (quantifier and qualifier) as shown by their retention times which corresponded to those of their respective standards. The measured peak area ratios of precursor to quantifier ion were in close agreement with those of the standards. Results obtained were presented as mg kg^{-1} concentration per analyte.

3.9 Statistical analysis

Mean ± standard deviation (Mean ± SD) of the concentrations of polycyclic aromatic hydrocarbon (PAH) and heavy metals for the various samples were calculated with

Microsoft office excel (2007) spreadsheet. Concentrations of heavy metals were subjected to analysis of variance (ANOVA) using SPSS version 16 to compare differences in mean result of different sample groups. Correlation analysis was done on physiochemical parameters with heavy metals and PAHs to establish the relationship of the data between them. Interpretation was done based on Hinkle et al., (1994) rule of thumb for interpreting the size of a correlation coefficient.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 Physiochemical properties of the soil

The physicochemical properties of soil samples from the study area are presented in figure 4.1 to figure 4.8 as well as table 1 with error bars representing standard deviation of the mean.

4.1.1.1 pH of the soil

pH measured for all soil samples within the study area shows that the mean concentration for all the different samples from mechanic workshops and farm soil ranged between 8.11 to 9.29 and 7.5±0.1 to 7.45±0.1 respectively with L3 (location 3) recording the highest concentration (Fig. 4.1). The analysis between the farm soils showed no significant difference with the control but the response in the pH analysis for all soil samples was 2.8 times lower in the control and the differences were not statistically significant at ($P \geq 0.05$) (Appendix 3).

4.1.1.2 Conductivity of the soil

Conductivity analysis for all soil samples from the study area indicates that the mean concentration for all the different samples from the mechanic workshops ranged from 138.2 to 195.7 times higher than the control (Figure 4.2a) but the difference in the mean concentrations were not significant at ($P \geq 0.05$) when compared with the control. The soil samples from the farmlands were 35.5 and 43.9 times higher than the control (Figure 4.2b) and the mean concentrations were also not significant at (P≥0.05) when compared with the control (Appendix 3).

4.1.1.3 Moisture content of the soil

Moisture content analysis for all the soil samples were carried out and the result shows that the samples from L1, L2 and L3 (location 1, 2 and 3) of the mechanic workshops were not significantly different at ($p \geq 0.05$) compared to that of control (Appendix 3). L3 was 1.4 times higher than the control. The samples from the farmlands ranged between 1.1 and 1.7 times higher than the control (Figure 4.3a and 4.3b) and were not significantly different at (P≥0.05) when compared with the control.

4.1.1.4 Percentage organic matter of the soil

Organic matter analysis conducted indicated that the mean concentration from the mechanic workshops soil ranged from 0.42 to 1.8 times higher than the control (Figure 4.4a). The soil samples from the farmlands was between 1.2 and 1.3 times higher than the control (Figure 4.3b) and were not significantly different at (P≥0.05) when compared to the control (Appendix 3).

4.1.1.5 Percentage organic carbon of the soil

Organic carbon result from the different soil samples of the mechanic workshops ranged from 0.22 to 1.07 times higher than the control (Figure 4.4a) and the samples from the farmlands ranged between 0.7 and 0.8 times higher than the control

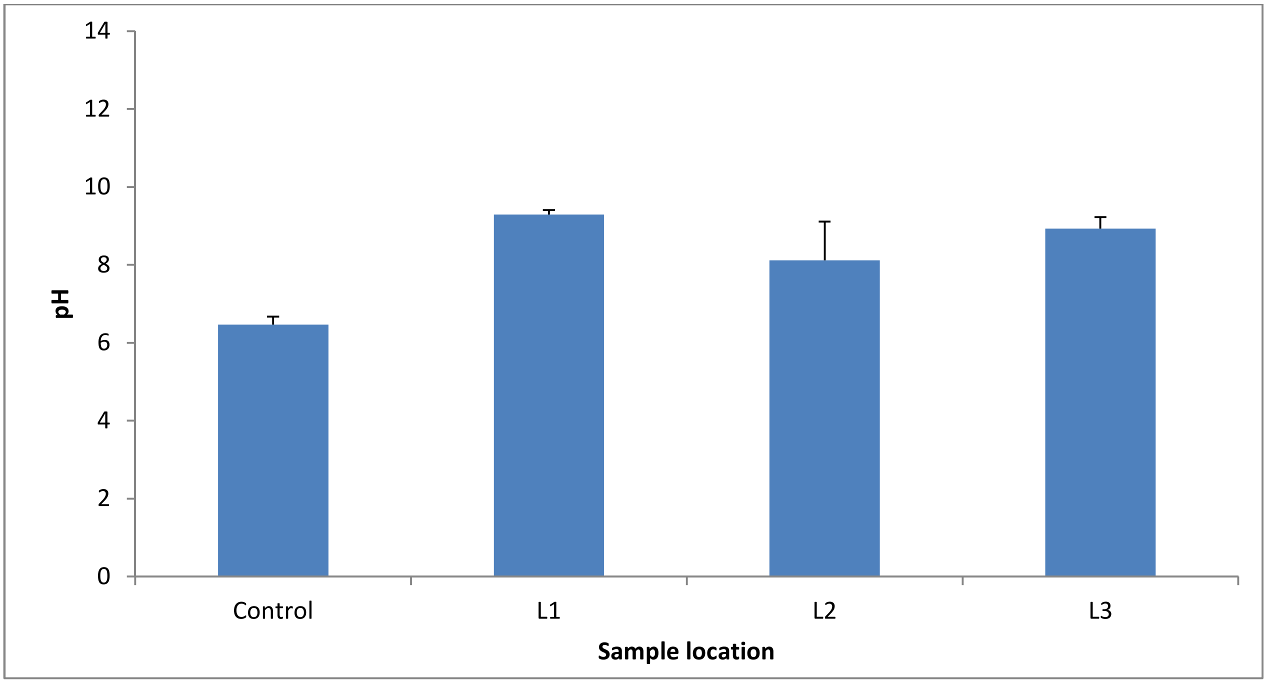


Figure 4.1a: pH of soils from mechanic workshops and control

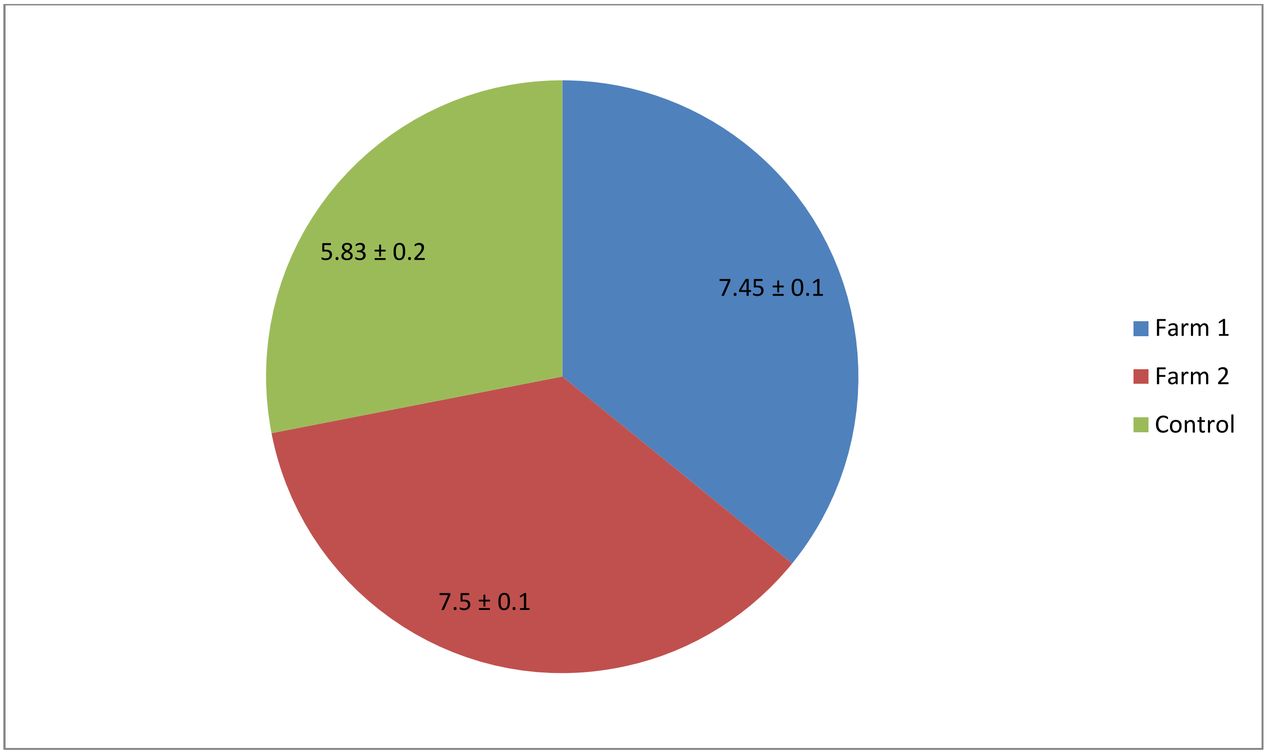


Figure 4.1b: pH of soils from farmlands and control.

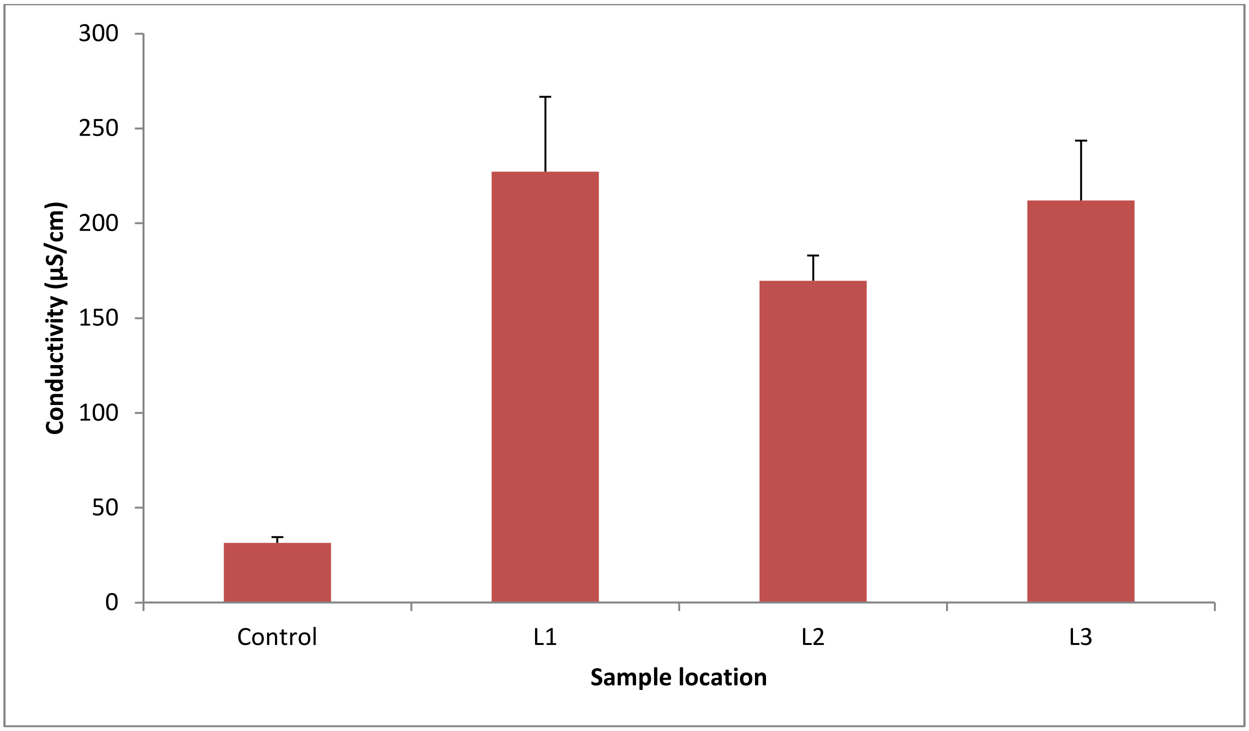


Figure 4.2a: Electrical conductivity of soils from mechanic workshops and control.

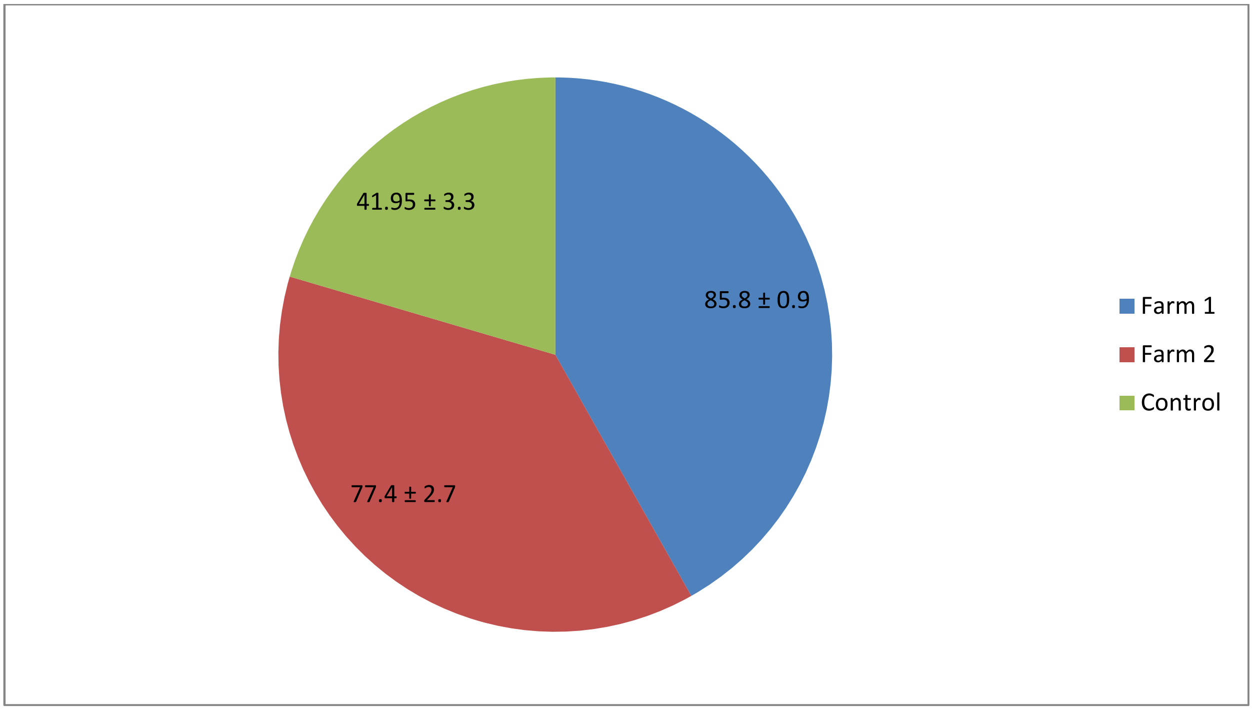


Figure 4.2b: Electrical conductivity of soils from farmlands and control.

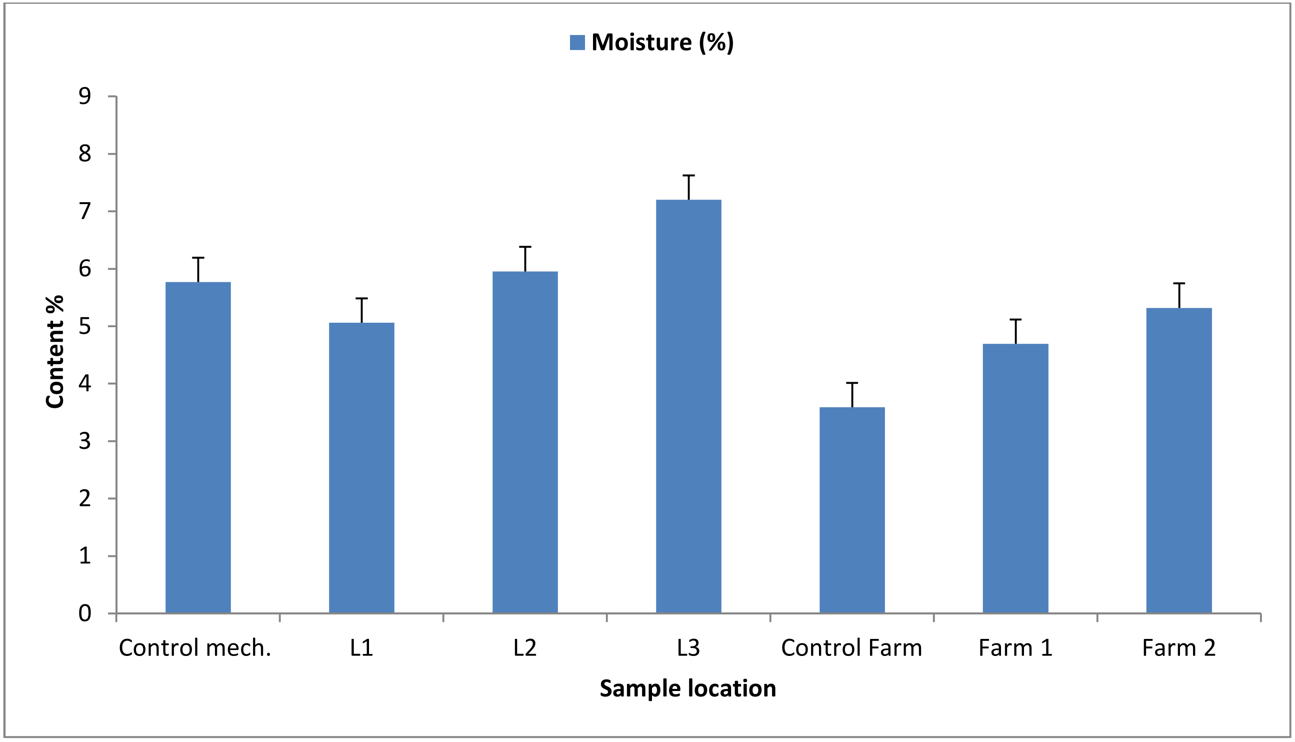


Figure 4.3a: Moisture content of soils from mechanic workshops, farmlands and controls

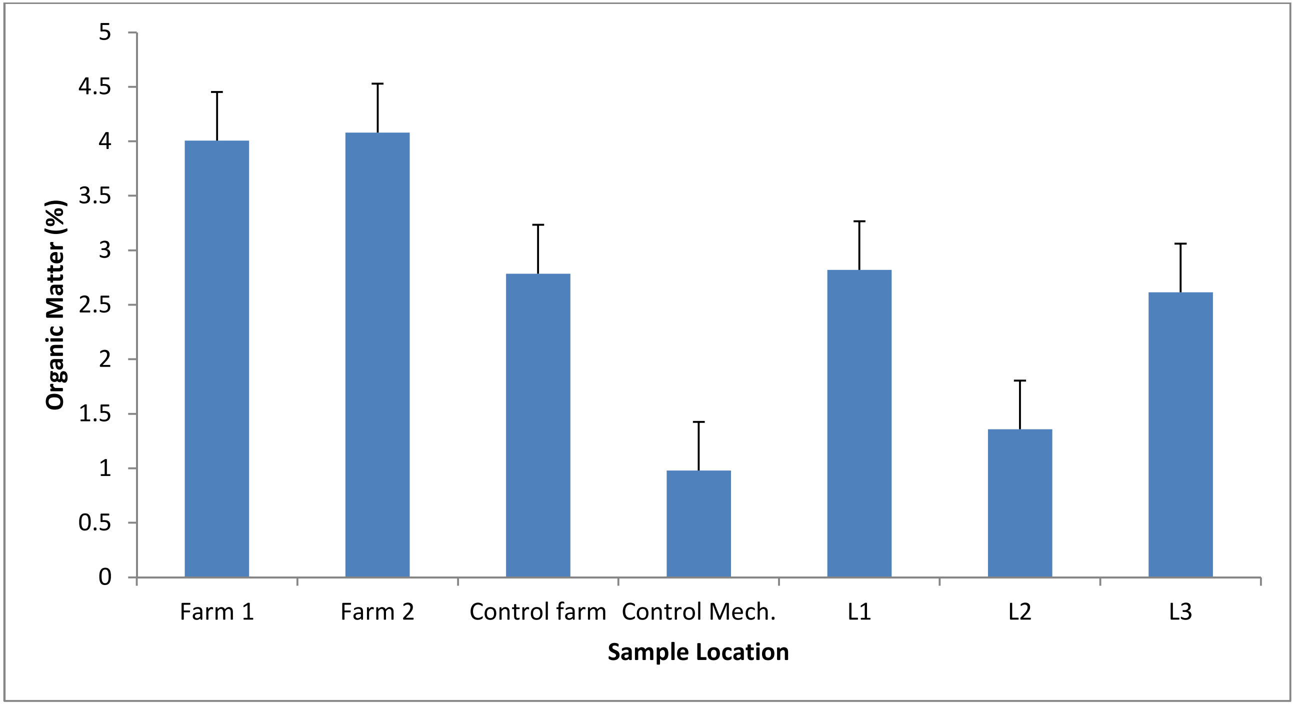


Figure 4.3b: Percentage organic matter of soils from farmlands, mechanic workshops and controls.

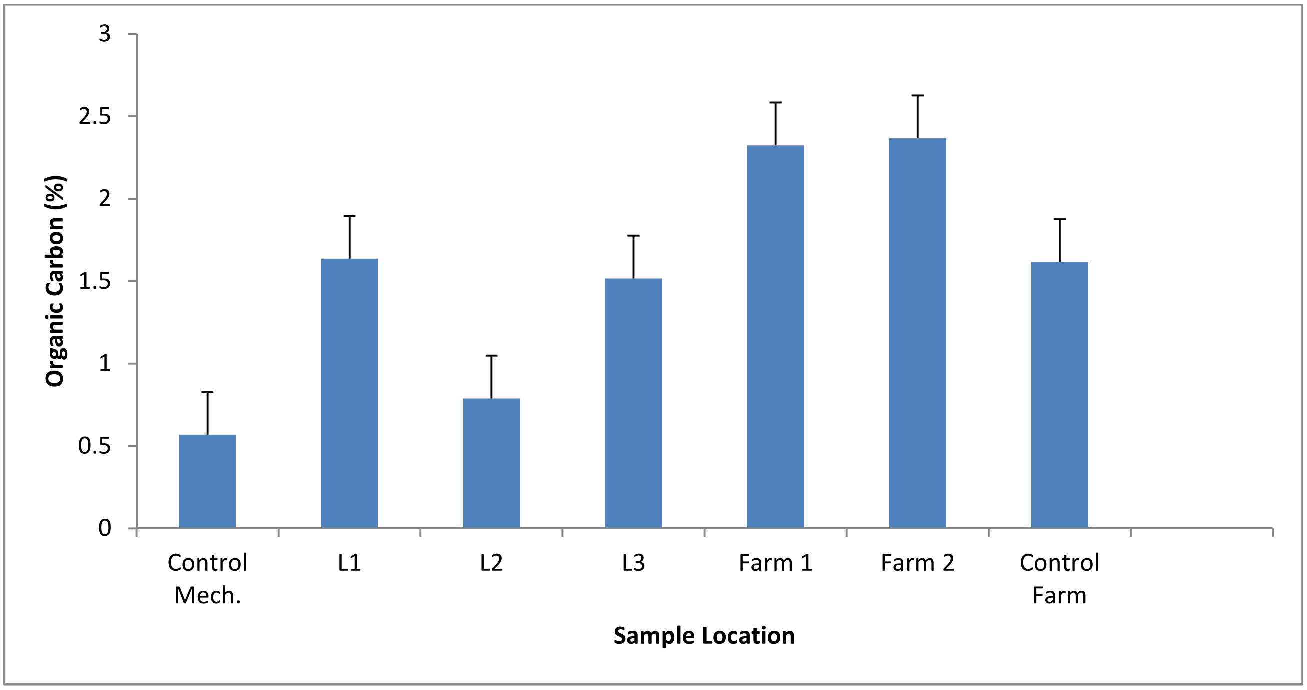


Figure 4.4a: Percentage organic carbon of soils from mechanic workshops, farmlands and controls

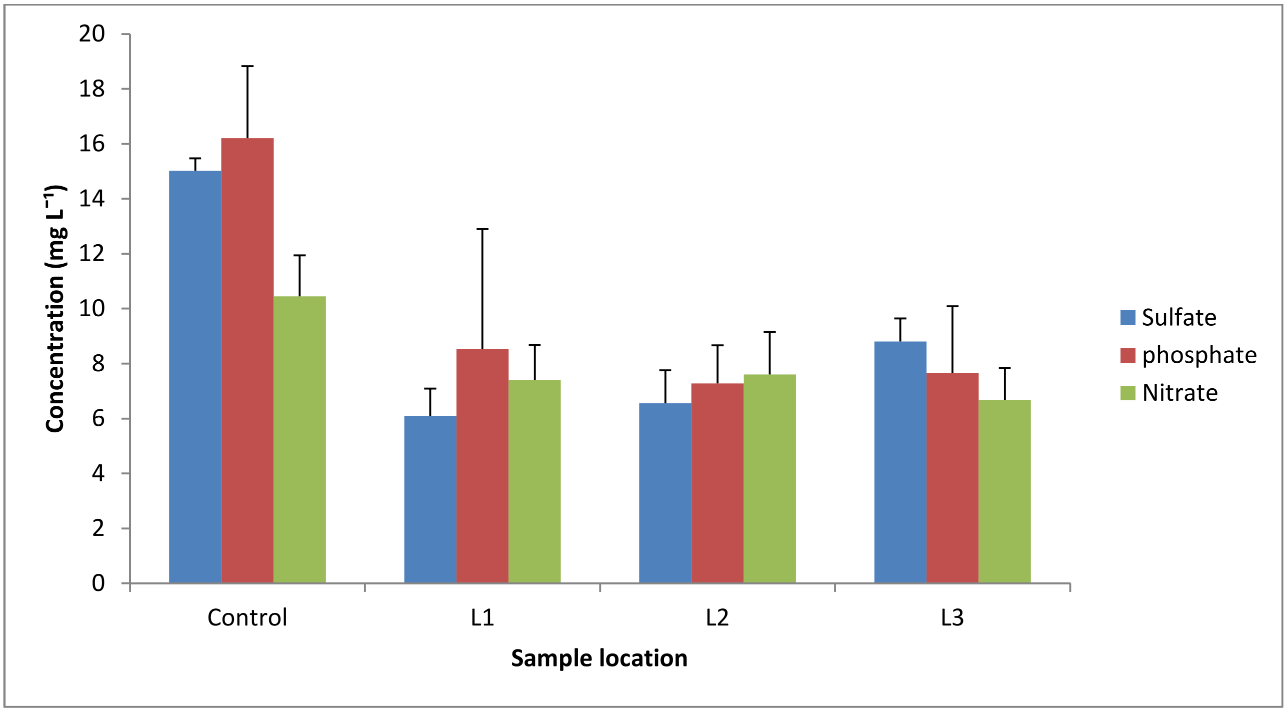


Figure 4.5a: Sulfate, phosphate and nitrate concentrations of soils from mechanic workshops and control.

(Figure 4.3b) but were not significantly different at ($p \geq 0.05$) when compared to the control (Appendix 3).

4.1.1.6 Phosphate content of the soil

Phosphate analysis result for all the soil samples from the mechanic workshops shows a range that is 7.7 to 8.9 times lower than the control (Fig. 4.5a). The result of the analysis from the farmlands ranged between 7.3 and 8.4 times higher than the control (Fig. 4.5b) but the difference was not significant at ($P \geq 0.05$) when compared with the control (Appendix 3).

4.1.1.7 Sulfate content of the soil

The result gotten from the analysis of the different soil samples of the mechanic workshops shows a range that is 6.2 to 8.9 times lower than the control (Figure 4.5a). Result also gotten from analysis of the soil samples from the farmlands ranged between 3.6 to 5.4 times lower than the control (Figure 4.5b) and were not significantly different at ($P \geq 0.05$) when compared with the control.

4.1.1.8 Nitrate content of the soil

Nitrate result from the different soil samples of the mechanic workshops ranged from 2.8 to 3.8 times lower than the control. (Figure 4.5a) The samples from the farmlands ranged from 2.2 to 2.9 times lower than the control (Figure 4.5b) and were not significantly different at ($P \geq 0.05$) when compared with the control

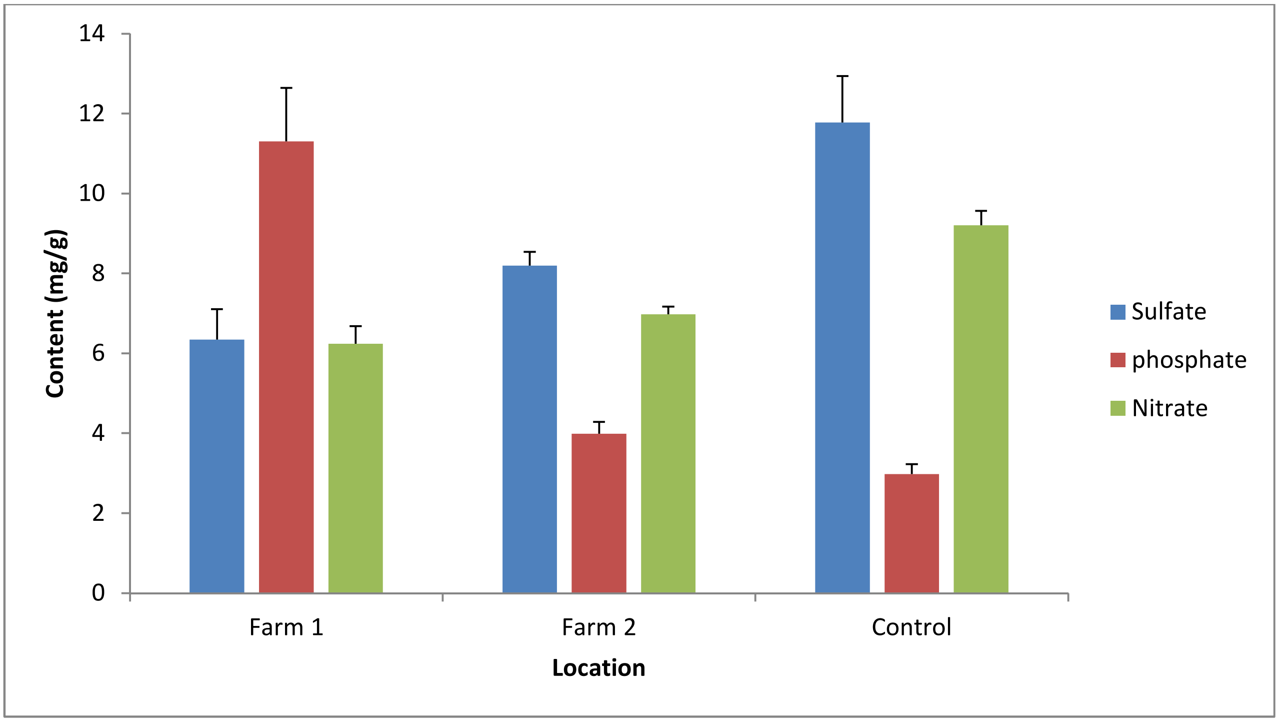


Figure 4.5b: Sulfate, phosphate and nitrate concentrations of soils from farmlands and control

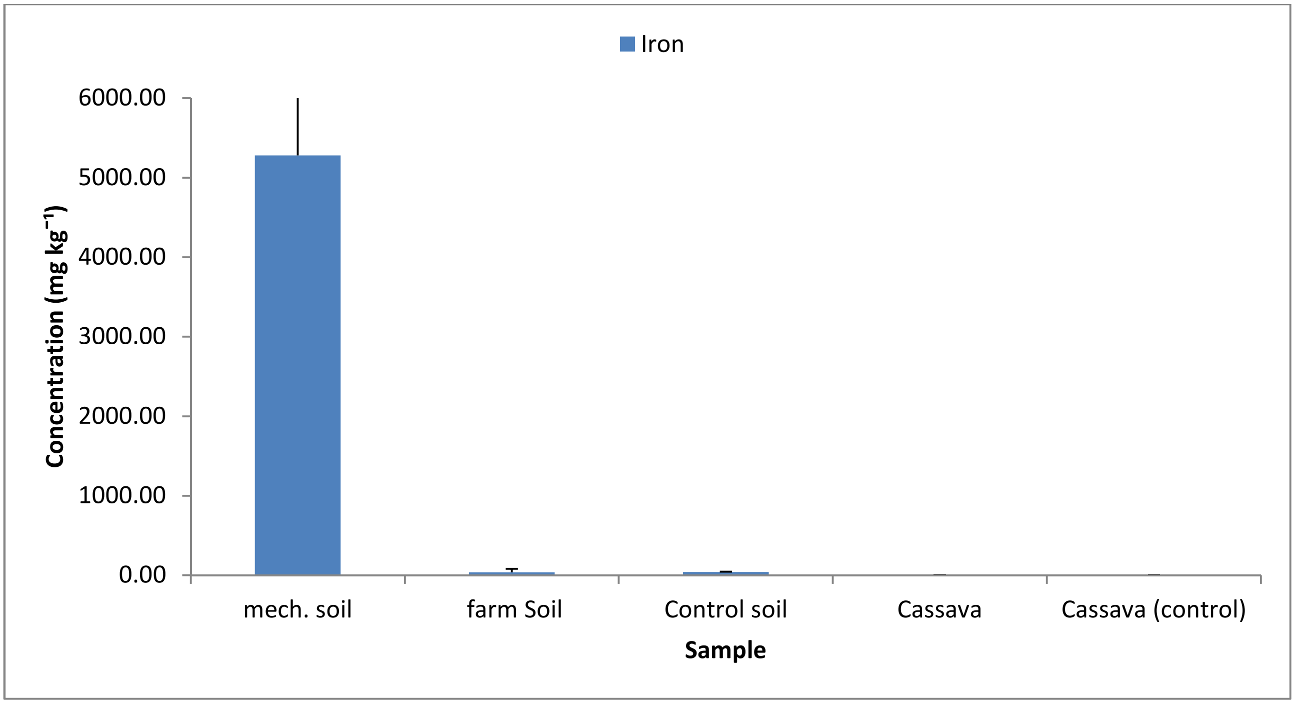


Figure 4.6: Concentration of Fe in soils, cassava tubers and controls

4.1.2 Heavy metal concentration in soils and cassava tubers

The results of heavy metal (Fe, Ni, Mg, Cu, Zn, Pb, Cr, and Cd) concentration in soils and cassava tubers are presented in Figures 4.6 to figure 4.10.

4.1.2.1 Iron (Fe) Concentration.

A high Fe concentration in all the different soil samples was recorded from the mechanic workshops and it was 124.6 times higher when compared to that of control (Figure 4.6). The Fe concentration of soil samples from both farm 1 and farm 2 were 1.2 times lower than the control and also the cassava tubers from the farmlands (farm 1 and 2) indicates that Fe concentration was 0.46 times higher than the control (Figure 4.6). In general, the mean concentration for all the samples were not significantly different at ($P \geq 0.05$) from the control area (Appendix 2).

4.1.2.2 Nickel (Ni) Concentration

The result of the analysis carried out on all the different soil samples from the mechanic workshops and farmlands shows that the concentration of Ni ranged between 6.5 and 1.5 times higher than that of control (Figure 4.7) and the mean concentration was not significantly different at ($P \geq 0.05$). Also the cassava tubers from the 2 farmlands indicate mean concentrations of 0.01 and were not significantly different at ($p \geq 0.05$) when compared with the control (Appendix 2).

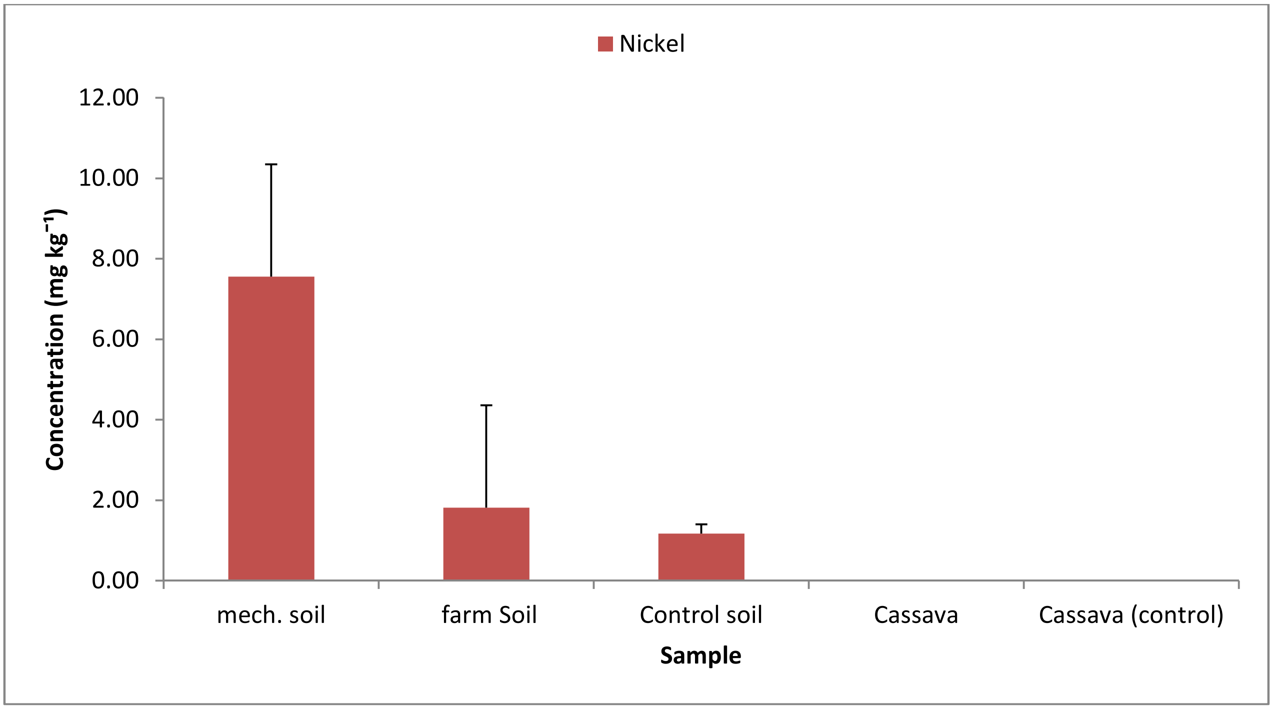


Figure 4.7: Concentration of Ni in soils, cassava tubers and controls.

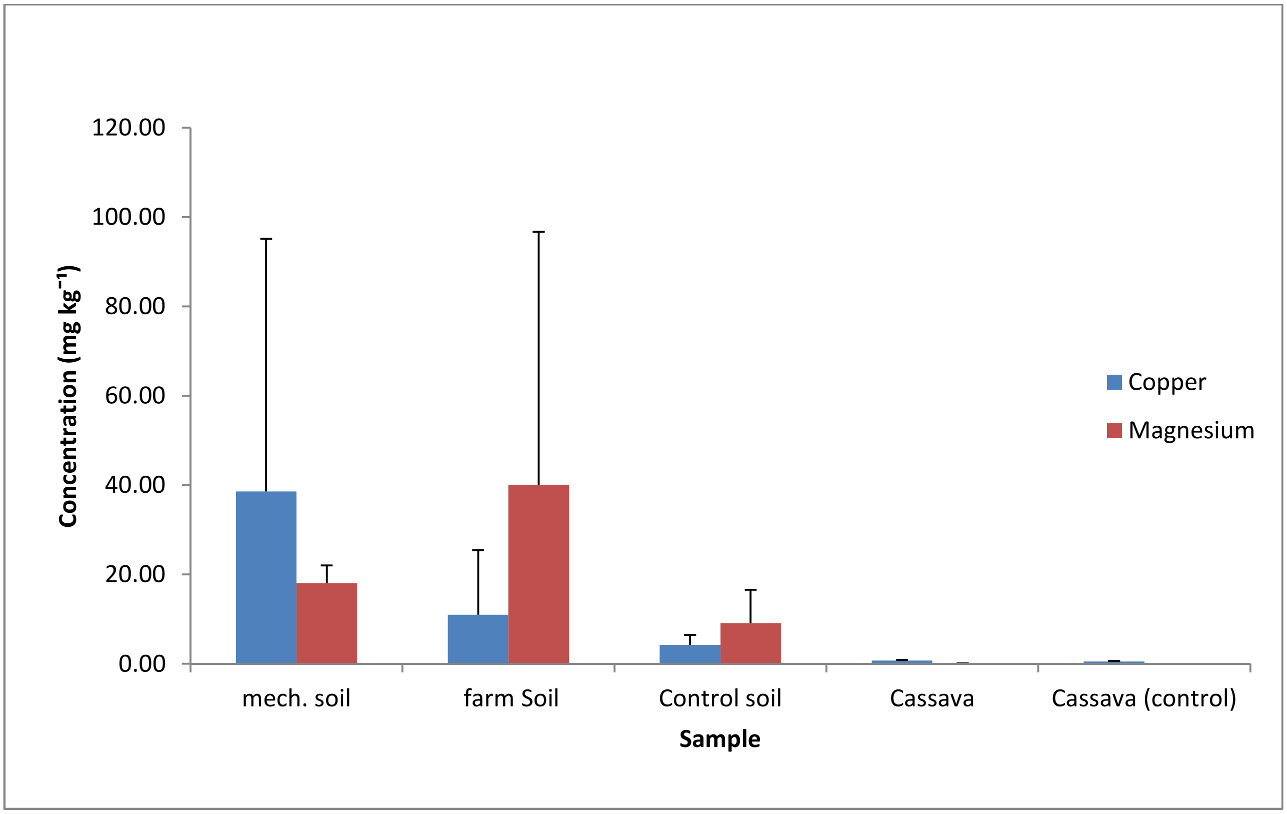


Figure 4.8: Concentration of Cu and Mn in soils, cassava tubers and control.

4.1.2.3 Manganese (Mn) Concentration

The result of the analysis carried out on all the different soil samples from the mechanic workshops and farmlands shows that the concentration of Mn ranged between 4.4 and 1.9 times higher than that of control (Figure 4.8). Also the cassava tubers concentration from the 2 farmlands was 0.01 times higher than the control (Figure 4.8) but there was no significant difference at ($p \geq 0.05$) between the farmlands and the control (Appendix 2).

4.1.2.4 Copper (Cu) Concentration

The result of the analysis carried out on all the different soil samples from the mechanic workshops and farmlands shows that the concentration of Cu ranged between 9.1 and 2.6 times higher than that of control (Figure 4.8). Also the cassava tubers concentration from the 2 farmlands was 0.25 times higher than the control (Figure 4.8) but there were no significant difference at ($p \geq 0.05$) from the control (Appendix 2).

4.1.2.5 Zinc (Zn) Concentration

The result of the analysis carried out on all the different soil samples from the mechanic workshops and farmlands shows that the concentration of Zn ranged between 46.6 and 6.7 times higher than that of control (Figure 4.9). The cassava tubers concentration from the 2 farmlands was 0.7 times lower than the control (Figure 4.9) and there were no significant difference at ($p \geq 0.05$) from the control (Appendix 2).

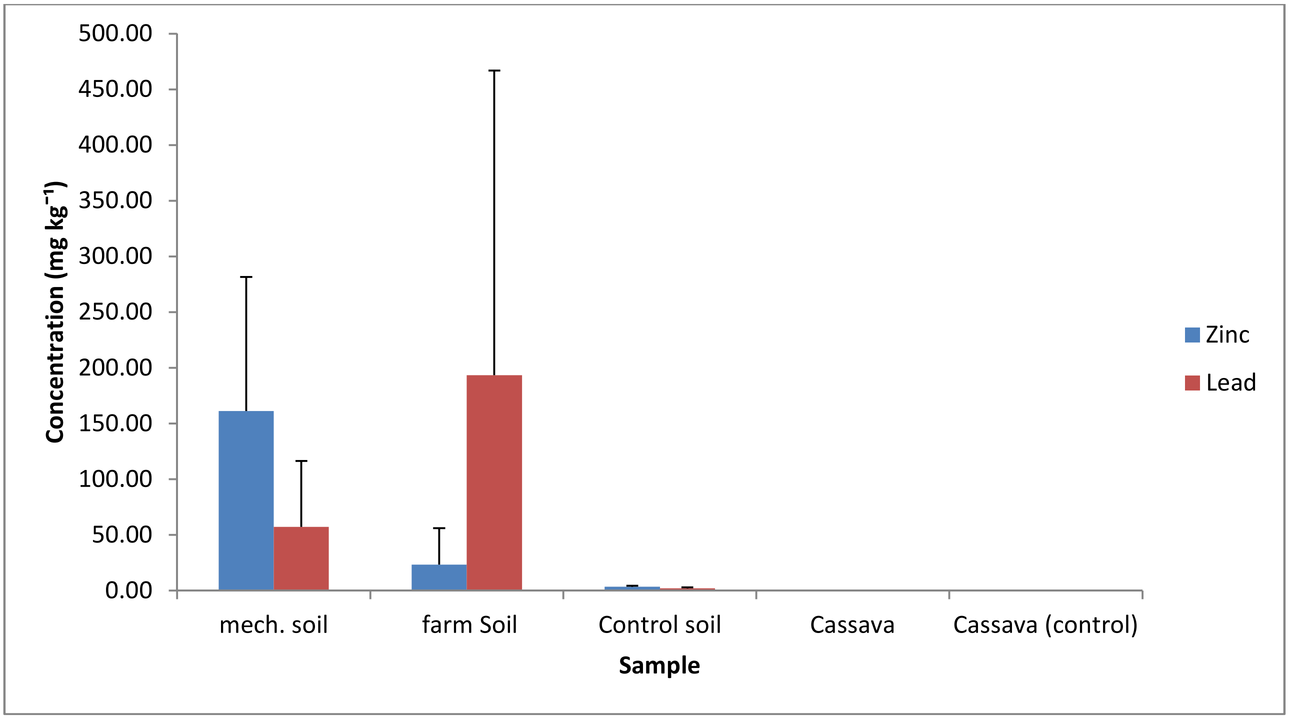


Figure 4.9: Concentration of Zn and Pb in soils, cassava tubers and control

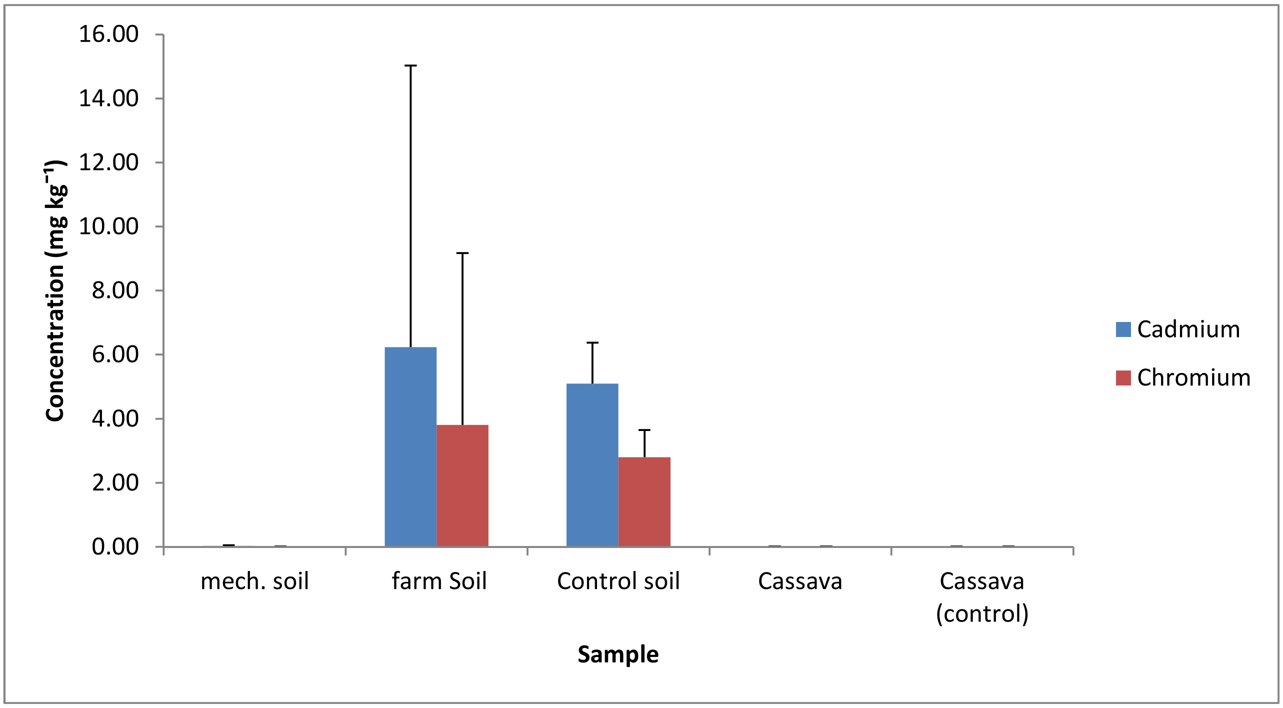


Figure 4.10: Concentration of Cd and Cr in soils, cassava tubers and controls

4.1.2.6 Lead (Pb) Concentration

The result of the analysis carried out on all the different soil samples from the mechanic workshops and farmlands shows that the mean concentration of Pb ranged between 93.4 and 27.6 times higher than that of control (Figure 4.9). The cassava tubers concentration from the 2 farmlands were not significantly different at ($p \geq 0.05$) from the control (Appendix 2).

4.1.2.7 Cadmium (Cd) Concentration

The result of the analysis carried out on all the different soil samples from the mechanic workshops and farmlands shows that the mean concentration of Cd ranged between 5.1 times lower and 1.2 times higher than that of control respectively (Figure 4.5). At varying concentration they were not significantly different at ($p \geq 0.05$) when compared with the control (Appendix 2).

4.1.2.8 Chromium (Cr) Concentration

The result of the analysis carried out on all the different soil samples from the mechanic workshops and farmlands shows that the mean concentration of Cr ranged between 2.8 times lower and 1.4 times higher than that of control respectively (Figure 4.10). The mean concentrations of the samples were not significantly different at ($p \geq 0.05$) when compared with the control.

4.1.2.9 Summary of heavy metals result

Taking all heavy metals into consideration for soil samples from the mechanic workshops and farmlands, the decreasing order of the mean concentration of heavy metals in the workshops was as follows Cr<Cd<Ni<Mg<Cu<Pb<Zn<Fe and that of farmlands was as follows Ni<Cr<Cd<Cu<Zn<Fe<Mg<Pb. The mean concentration of Fe from workshop soil ranged between 92.3 and 32.8 times higher than the other metals such as Zn and Pb respectively and were not significantly different at ($p \geq 0.05$) from one another, and also the mean concentration of Fe from workshop soil ranged from 698.2 to 136.8 times higher than heavy metals such as Cu, Mg and Ni and was not significantly different at ($p \geq 0.05$) when compared to one another (Appendix 2).

The mean concentration of Pb from farmlands soil ranged between 5.4 and 4.8 times higher than the other metals such as Mg and Fe respectively. Furthermore, the mean concentration of Pb from farmlands soil also ranged from 31.0 to 8.3 times higher than heavy metals such as Zn, Cu and Cd. There were no significant differences at ($p \geq 0.05$) between the mean concentrations of all the heavy metals in the soil from the mechanic workshops and farmlands when compared to the control.

4.2.2.9 Pearson Correlation between Physiochemical Parameters and Heavy Metals

Variations in metal concentration and physiochemical parameters recorded during present investigation were subjected to Pearson correlation coefficient (Appendix 6).

Cd, Ni and Cr showed negative correlation with all recorded physiochemical parameters except for nitrate that showed a moderate positive correlation ($r = 0.67$), Fe showed a high positive correlation with all the physiochemical parameters except for sulfate and moisture that had a negative relation with Fe. Cu showed a high positive correlation with sulfate and moisture and a negative correlation with all the other physiochemical parameters. Zn and Mn showed a low to high positive correlation of ($r = 0.32 – 0.93$) and ($r = 0.17 – 0.99$) respectively with all the physiochemical parameters except for nitrate and moisture that showed a negative correlation. Pb showed a positive correlation with all the physiochemical parameters except for phosphate and nitrate (Appendix 6)

4.1.3 POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS AND CASSAVA TUBERS

The result of the total PAHs concentrations from the study area is presented in Fig. 4.11. The result shows that the sum mean of PAHs in soils from mechanic workshops ranged between 2.61 and 7.13 times higher than that of farm soil and cassava tubers respectively but the differences was only significant at ($p<0.05$) (Appendix 4). The result also indicated the presence of Low molecular weight (LMW) PAHs (Acenaphthylene, Acenaphthene, Fluorine, Phenanthrene, Anthracene) and high molecular weight (HMW) PAHs (Benzo(a)anthracene, Chrysene, Benzo(k)fluoranthene, Benzo(b)fluoranthene, Benzo(a)pyrene, Benzo(g,h,i)perylene, Dibenzo(a,h)anthracene, Indeno(1,2,3-cd)pyrene in all the investigated samples,

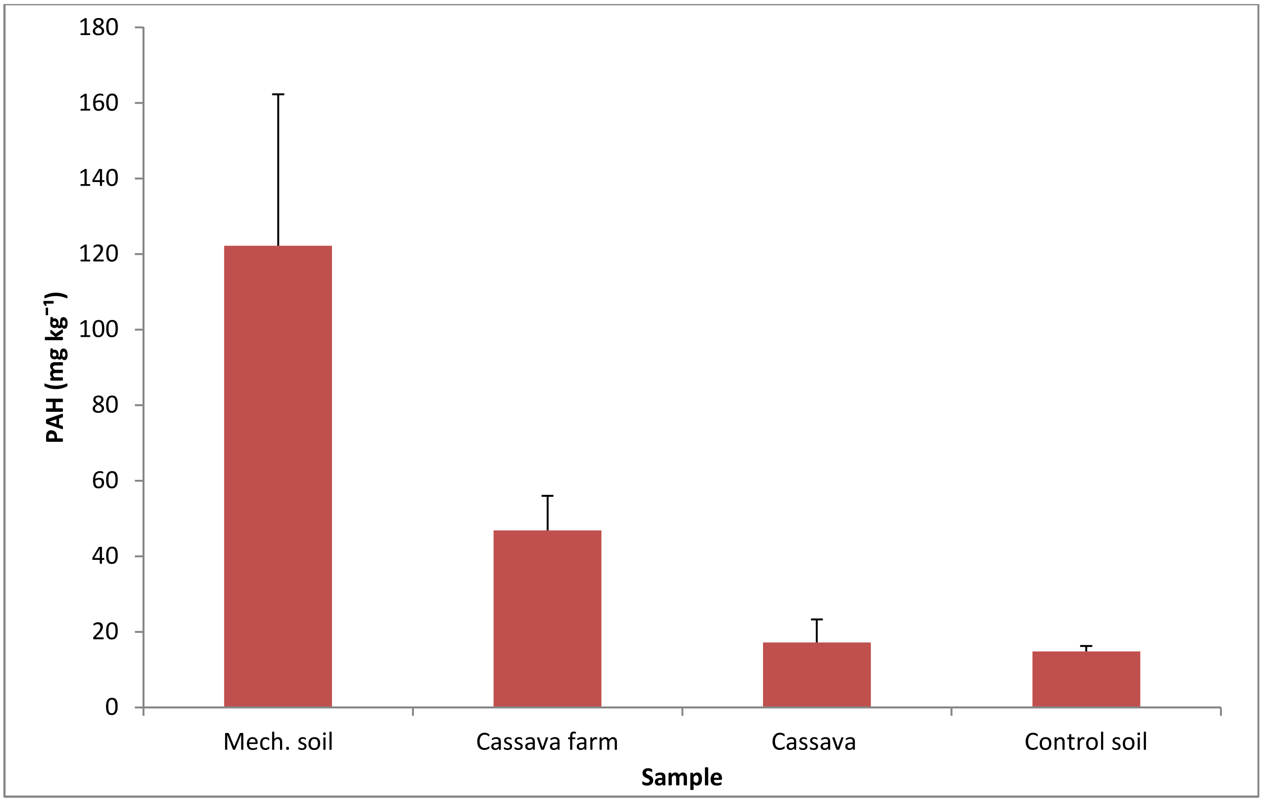


Figure 4.11: Total PAHs concentration in soils, cassava tubers and control

Except for Naphthalene which was not detected in all the soil samples. The medium molecular weight (MMW) PAHs (fluoranthene and pyrene) were present in all the soil samples and cassava tubers.

4.1.3.1 Polycyclic aromatic hydrocarbons concentrations in soils (farm 1) and cassava tubers (farm 1)

LMW PAHs naphthalene was not detected in both the soil and cassava tubers. The mean concentration of Pyrene in the soil and cassava tubers ranged from 4.8 to 1.4 and between 4.9 and 1.3 times higher than the other PAHs present respectively. HMW PAHs were not detected in cassava tubers from farm 1 except for chrysene (2.31 mg/kg) and benzo(b)flouranthene (0.58 mg/kg) (Fig. 4.12). PAHs in soil (farm1) and cassava tubers (farm 1) were at varying concentrations significantly different at ($p<0.05$). However, the concentration of 1, 2-benzoanthracene in soil ranged from 2.3 to 1.1 times higher than the other HMW PAHs. HMW PAHs in cassava tubers were not detected except for chrysene and benzo(b)flouranthene. The result indicates that PAHs in soils shows significant differences among means at $p<0.05$ (Appendix 4).

4.1.3.2 Polycyclic aromatic hydrocarbons concentrations in soils from mechanic workshops

The presence of 1,2-benzoanthracene in the soil samples from location 1 (L1) indicates a concentration that ranged from 1.7 to 2.2 times higher than the other PAHs namely pyrene and indeno(1,2,3 cd)pyrene respectively, acenaphthene and

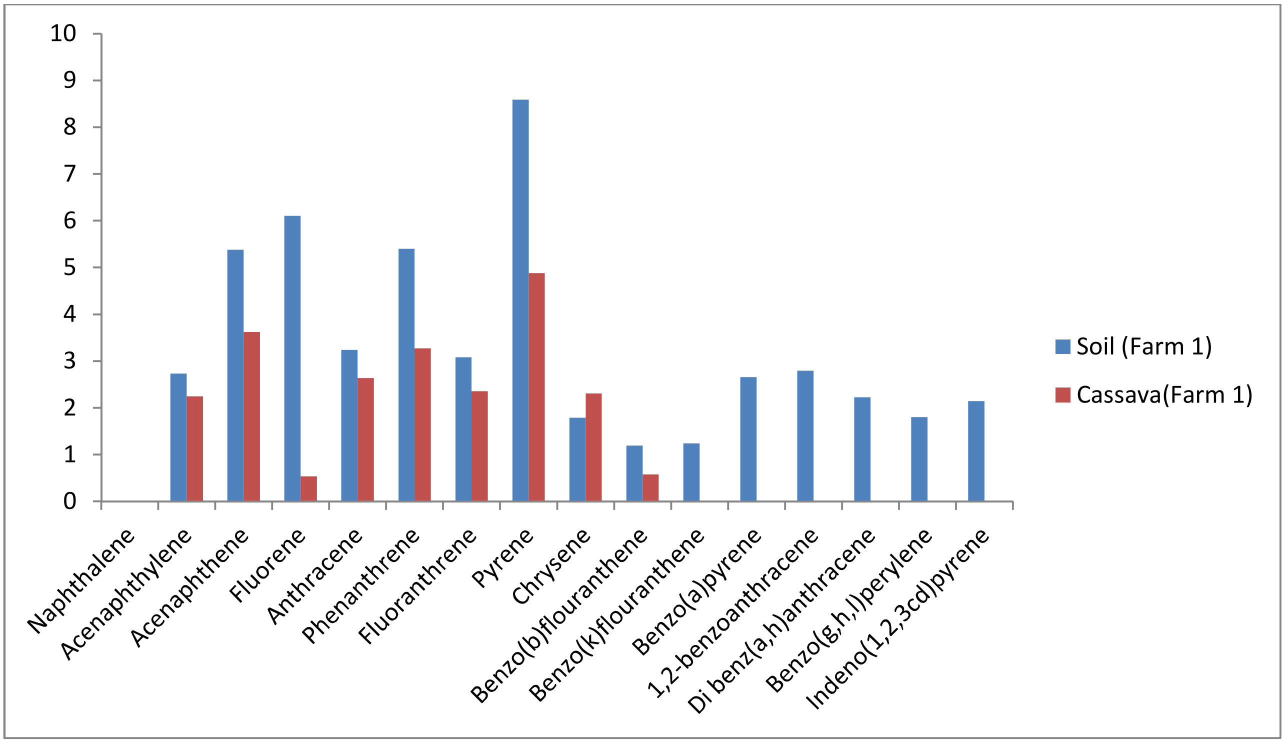


Figure 4.12: PAHs concentration in soil (farm 1) and cassava tubers (farm 1)

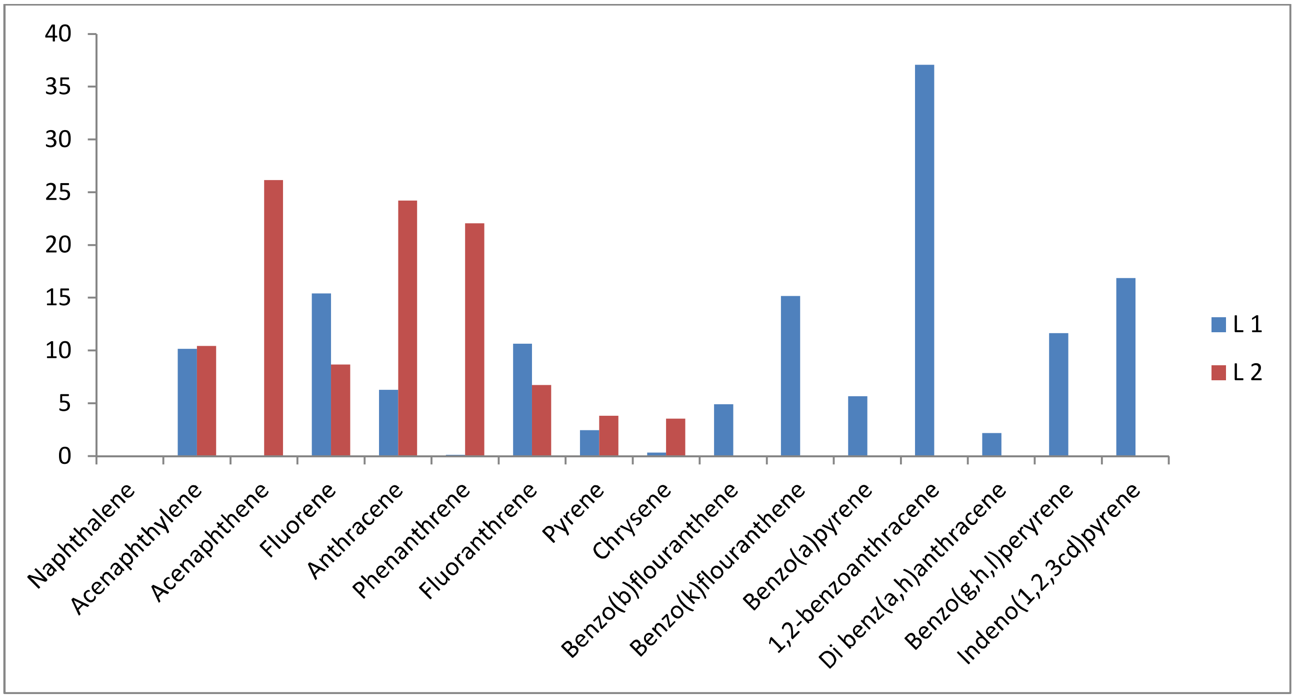


Figure 4.13: PAHs concentration in soil (location 1 and 2)

phenanthrene were not present in L1 and also naphthalene was not detected in the samples.

In location 2 (L2), HMW PAHs were not detected except for chrysene but all the LMW PAHs were detected at varying concentrations (Fig. 4.13). In L2, acenaphthene ranged from 1.94 to 22.63 times higher than the other PAHs present namely chrysene and anthracene respectively. In L2, 1,2-benzoanthracene ranged from 20.2 to 34.9 times higher than the other PAHs present namely dibenz(a,h)anthracene and indeno(1,2,3cd)pyrene respectively. PAHs in location 1 and 2 where at varying concentrations not significantly different at ($p<0.05$) (Appendix 4). In location 3 (L3) no PAHs were detected.

4.1.3.3 Polycyclic aromatic hydrocarbons levels in soil (farm 1), cassava tubers (farm 1) and control

LMW and MMW PAHs were detected in the soil and cassava tubers from farm 1 except for naphthalene which was not detected in the samples. The presence of pyrene in the soil samples (farm 1) indicates a concentration that ranged from 7.4 to 1.9 times higher than the other PAHs namely flourene and benzo(k)flouranthene respectively. In cassava tubers (farm 1), HMW PAHs were not detected except for chrysene and benzo(b)flouranthrene. Pyrene ranged from 4.34 to 1.26 times higher than the other PAHs present, namely acenaphthene and flourene respectively (Figure 4.14). In the control only anthracene and fluoranthrene were detected for LMW and

MMW respectively and for HMW PAHs benzo(g,h,i)perylene, benzo(a)pyrene and dibenz(a,h)anthracene were detected. The concentration of anthracene in the soil and cassava tubers (farm 1) ranged between 2.3 to 1.2 times higher than the control and that of flouranthene ranged between 2.4 to 1.9 times lower than the control, but they were only significantly different at $p \leq 0.05$ (Appendix 4).

4.1.3.4 Polycyclic aromatic hydrocarbons concentration in soil (farm 2), cassava tubers (farm2) and control

LMW and MMW PAHs were detected in both the soil and cassava tubers except for naphthalene which was not detected in the samples. The presence of acenapthylene in the soil samples (farm 2) indicates a concentration that ranged from 5.1 to 1.0 times higher than the other PAHs namely acenaphthene and benzo(b)flouranthene respectively (Fig. 4.15). In cassava tubers (farm 2), HMW PAHs were not detected except for chrysene and benzo(b)flouranthene and for soil samples benzo(k)flouranthene, 1.2-benzoanthracene and indeno(1,2,3 cd)pyrene were not detected. In the control only anthracene and fluoranthrene were detected for LMW and MMW PAHs respectively and Benzo(g,h,i)perylene, benzo(a)pyrene and dibenz(a,h)anthracene were detected for HMW PAHs. Flouranthrene in soil (farm 2) and cassava tubers (farm 2) ranged between 4.34 and 1.14 times lower than the control farm soil. In the control only anthracene and fluoranthrene were detected for LMW and MMW PAHs.

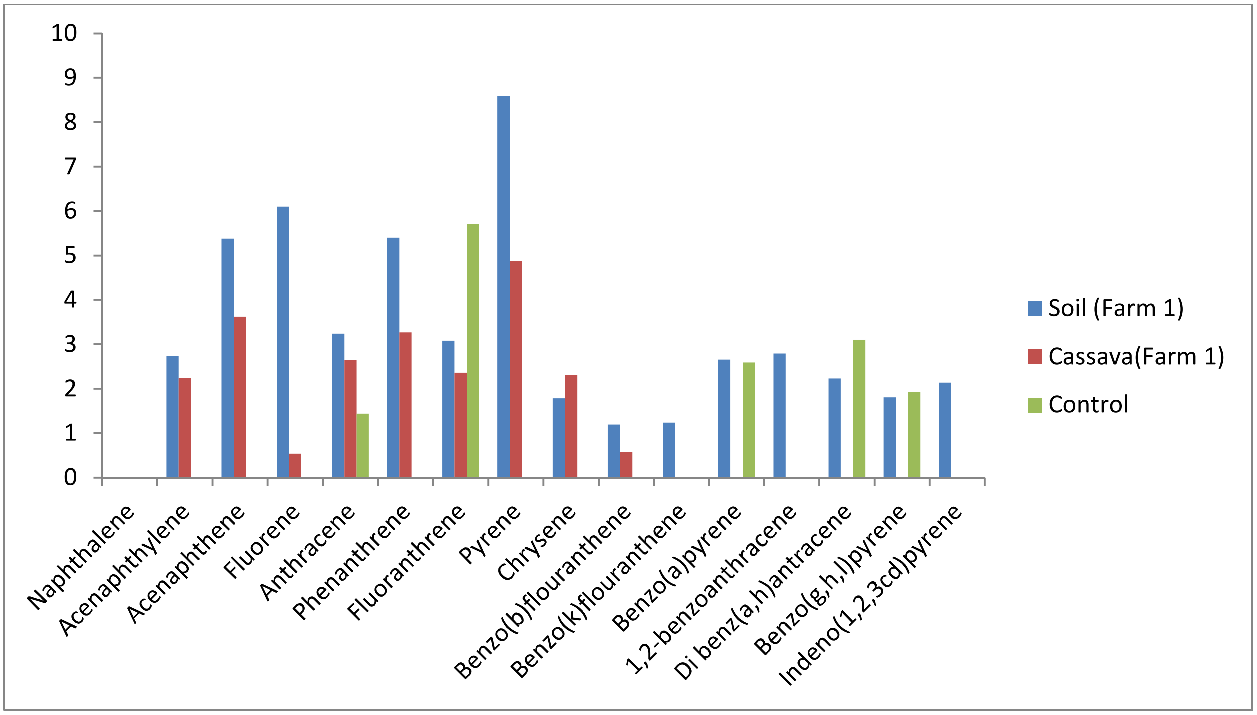


Figure 4.14: PAHs concentration in soil (farm 1), cassava tubers (farm 1) and control

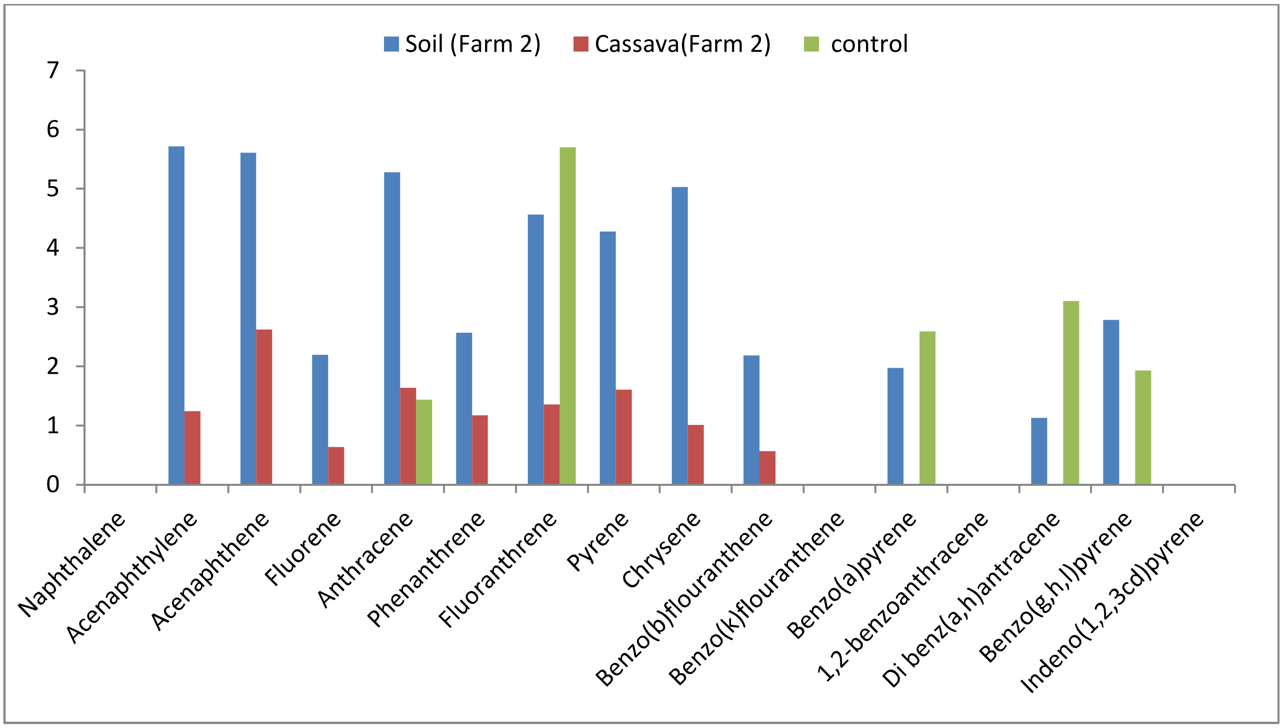


Figure 4.15: PAHs concentration in soil (farm 2), cassava tubers (farm 2) and control

Benzo(g,h,i)perylene, benzo(a)pyrene and dibenz(a,h)anthracene were detected for HMW PAHs. At varying concentration, all the PAHs were significantly different at ($p \leq 0.05$) (Appendix 4).

4.1.3.5 Polycyclic aromatic hydrocarbons concentrations in soils from mechanic workshops and control

The presence of 1,2-benzoanthracene in the soil samples from location 1 (L1) indicates a concentration that ranged from 1.7 to 2.2 times higher than the other PAHs namely pyrene and indone(1,2,3 cd)pyrene respectively. 1,2-benzoanthracene, pyrene and indone(1,2,3 cd)pyrene were not detected in the control samples. For LMW PAHs, acenaphthene and phenanthrene were not present in L1 and also naphthalene was not detected in the samples. In location 2 (L2), HMW PAHs were not detected except for chrysene but all the LMW PAHs were detected at varying concentrations. In the control only anthracene and fluoranthrene were detected for LMW and MMW PAHs respectively, benzo(g,h,i)pyrelene, benzo(a)pyrene and dibenz(a,h)anthracene were also detected for HMW PAHs. For LMW PAHs, anthracene in L2 ranged between 17.95 and 22.48 times higher than L1 and control respectively. For MMW PAHs, flouranthene in L1 ranged between 3.92 and 4.92 times higher than the L2 and control respectively. For HMW PAHs in L1, benzo(a)pyrene was 3.08 times higher than the control, dibenz(a,h)anthracene was 0.93 times lower than the control and benzo(g,h,i)perylene was 9.7 times higher than the control (Figure 4.16). In location 3 (L3) no PAHs were detected. At varying concentration, all the PAHs were significantly different at $(p \leq 0.05)$ (Appendix 4).

4.1.3.6 Polycyclic aromatic hydrocarbons concentrations in soils from mechanic workshops (L2), cassava (farm 2) and control.

In all the samples, naphthalene was not detected; LMW and MMW PAHs were detected for L2 and cassava (farm 2). In control, anthracene and flouranthene were detected for LMW and MMW PAHs respectively. for HMW, chrysene was detected in L2 and cassava (farm 2), benzo(b)flouranthene for cassava (farm 2), benzo(a)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene for control. Anthracene in L2 ranged between 22.58 and 22.78 times higher than cassava (farm 2) and control respectively. flouranthrene in L2 also ranged between 1.01 and 5.35 times higher than the control and cassava (farm 2) respectively (Figure 4.17). Acenaphthene concentration was higher than all the samples detected. At varying concentration, all the PAHs were significantly different at $(p \leq 0.05)$ (Appendix 4).

4.1.3.7 Pearson Correlation between Physiochemical Parameters and PAHs

Variations in PAHs concentration and physiochemical parameters recorded during present investigation were subjected to Pearson correlation coefficient (Appendix 4). Acenaphthene, Anthracene, Phenanthrene and Chrysene show positive correlation to pH, conductivity, organic matter and organic carbon but negative correlation to sulfate, phosphate and nitrate. However, Acenaphthylene shows positive correlation to organic matter and organic carbon as well as Dibenz(a,h)anthracene showing a negative correlation with sulfate, phosphate and nitrate. Moisture content shows a positive correlation with flouranthene, pyrene, chrysene, benzo(b)flouranthene, benzo(a)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene. (Appendix 4).

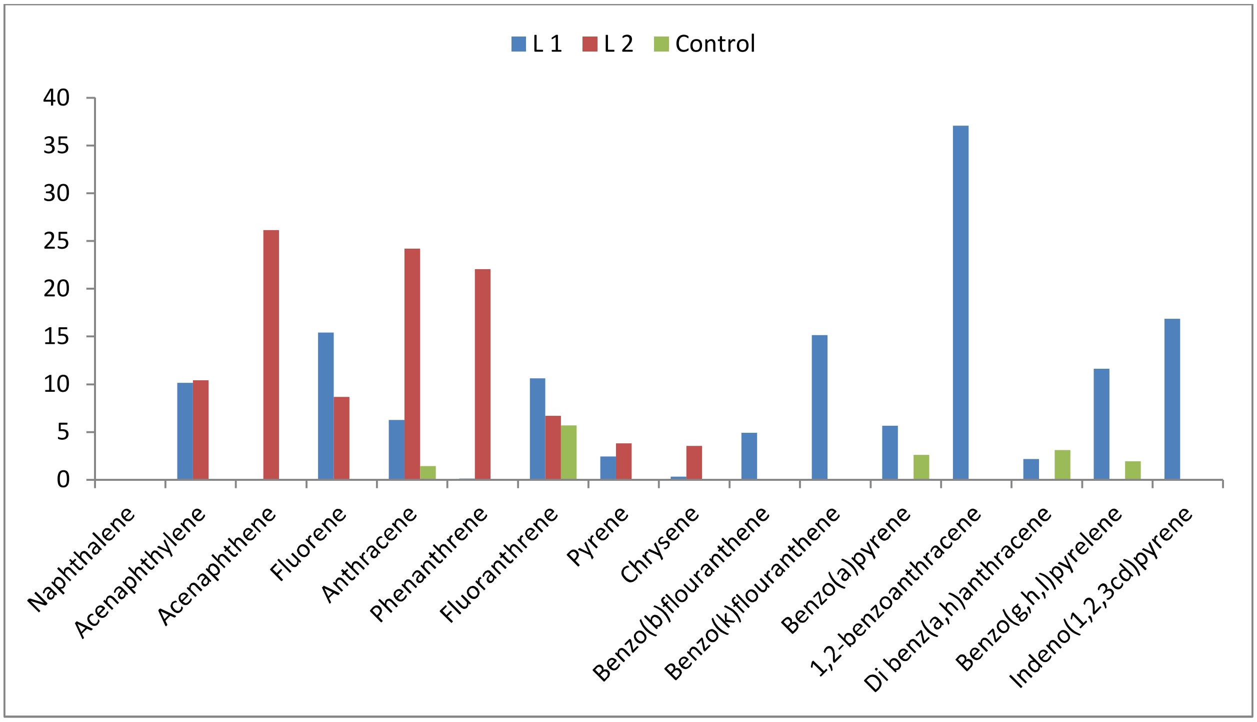


Figure 4.16: PAHs concentration in soil (location 1 and 2) and control

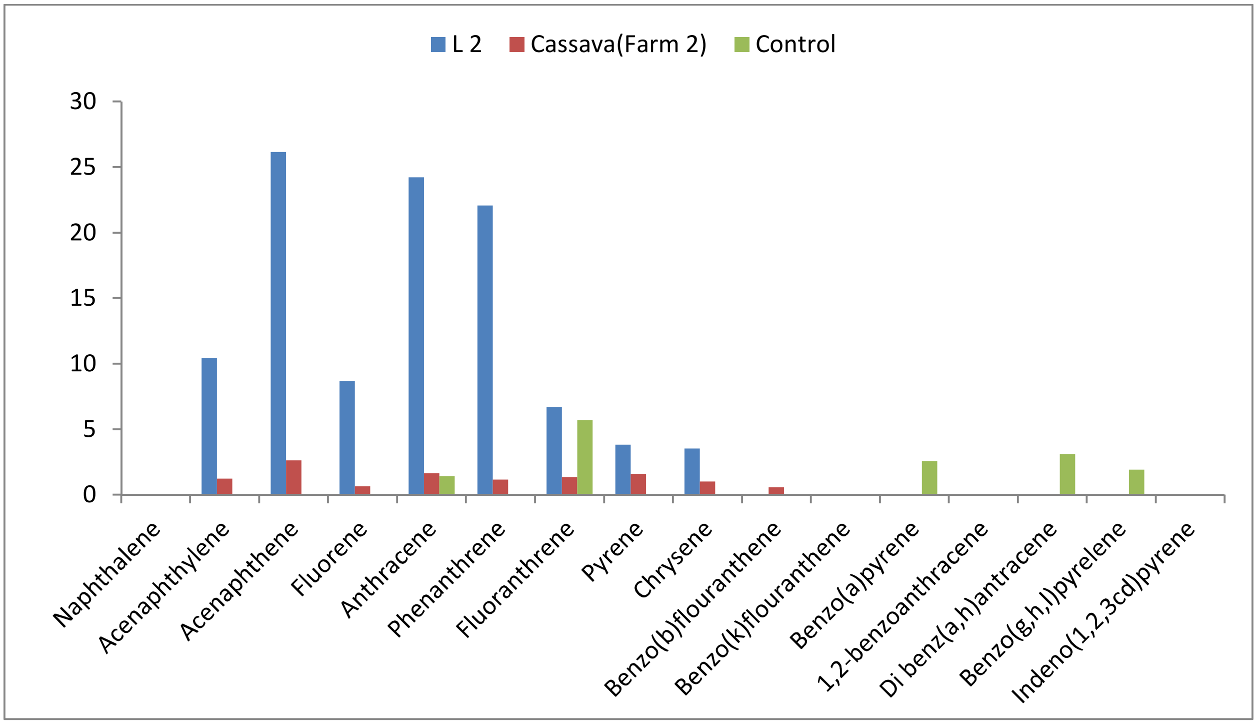


Figure 4.17: PAHs concentration in soil location 1, cassava tubers (farm 2) and control

4.2 DISCUSSION

4.2.1 Physiochemical properties of the soil

4.2.1.1 pH of the soil

pH is an important parameter as it helps in ensuring availability of plants nutrients (Deshmukh , 2012). Williams (1990) had studied effect of pH on nutrient balance and observed that high pH of soil can affect the micronutrients content present in soil. This observation supports the findings in the study area due to the fact that heavy metals concentrations present in the soil were low. At low pH values solubility of micronutrients is high while at high pH solubility and availability of micronutrient to plant is declined (Brady and Weil, 2002). This observation can also be attributed to the low concentration of heavy metals in the study area and most especially in the farmlands, high pH led to the low heavy metals availability in the farmlands when compared to the corresponding workshops. This is because heavy metal availability in soil and plant is pH dependent. High pH value ranging from 7.5 to 8.9 (slightly and moderately alkaline) was recorded for the soils from the auto-mechanic village in comparison to control which was between 5.8 and 6.5 indicating an acidic soil.

Auto-mechanic village soil was above the neutral level indicating that the soils were alkaline (Fig. 4.1). The result is in agreement with the study by Stephen et al., (2010) who reported pH range from 6.97 to 8.27 in a waste lubricating oil contaminated soil. These observed pH values however, do not fall completely within the acceptable standards of 5.5 to 6.5 (DPR, 2002). The rise in the pH favours oil degradation by microorganisms as observed in similar studies that higher pH range (6 to 9) provides better conditions for mineralization of hydrocarbons since most bacteria capable of metabolizing hydrocarbons develop best at pH conditions close to neutrality (Tanee and Kinako, 2008; Manuel et al., 1993; Atlas and Bartha, 1992). The sodium content of the soil may have given rise to the high pH concentration in soils; this is in line with the report of Elango et al., (1992) who reported that high sodium content gives rise to high pH in the soil.

4.2.1.2 Conductivity of the soil

Electrical Conductivity (EC) is a measure of ionic concentration in the soils and is therefore related to dissolve solutes. As salt content increases, so does Electrical Conductivity. The conductivity at the auto-mechanic village was higher than the control ranging from 77.4 to 227.2µS/cm; this could be as a result of the high concentration of charged ions (cations and anions) in the study area. Anions, metallic ions and carbonic acids contribute to Electrical Conductivity of tropical soils.

There was a corresponding relationship between the pH and the conductivity in the samples because the higher pH in each case corresponds to higher conductivity (Fig. 4.1 and 4.2) and Deko and Sarma, (2012) reported that the solubility of heavy metal ions in soil is mainly influenced by pH and conductivity. These factors (pH and conductivity) are part of the soil chemistry which influences the general mobility of metal ions in soil (Adelekan and Abegunde, 2011). This finding was observed in the study area, this is due to the fact that the mobility of metals from the workshops to the farmlands was low. Soil electric conductivity can also serve as a proxy for soil physical properties such as organic matter and cation exchange capacity (Khattak and Page, 1992). Therefore, there is a relationship between conductivity and organic matter because as conductivity increased, organic matter content increased and as conductivity decreased, organic matter content also decreased (Fig. 4.2 and 4.4). The conductivity values observed in this study are in consonants with some of the values observed by Edori and Edori (2012) which ranged from 1.18×10^2 to 6.60×10^2 in two mechanic villages in Port Harcourt, Rivers State.

4.2.1.3 Moisture content of the soil

The moisture content of L1, L2 and control was not significantly different, meaning that the auto-mechanic activities did not have any effect on the soil moisture content of L1 and L2. It was also observed that L3, farm 1 and farm 2 have the capacity to retained more water than the control soil (Fig. 4.4). This result is in agreement with the study by Aloysius et al., (2013) who reported % moisture content range from 1.90 to 9.60 in an automobile mechanic sites. The high moisture content can be attributed to insufficient aeration of the soil that might have arisen from the displacement of air in the auto-mechanic village soils, this probably encouraged water logging and reduced rate of evaporation. High moisture content may reduce microbial activities (therefore promote the availability of heavy metals and PAHs in the soil) not as a result of the water itself but rather by the indirect hindrance to the movement of air which would reduce oxygen supply to plants.

4.2.1.4 Soil organic matter

Soil organic matter (SOM) enhances the usefulness of soils for agricultural purposes. It supplies essential nutrients and has unexcelled capacity to hold water and absorb cations. It also functions as a source of food for soil microbes and thereby helps enhance and control their activities (Brady, 1996). The auto-mechanic village soils contain high amount of organic matter, about 4.0% which may be responsible for increase in the soil pH as compared to that of the control soil. This observation was supported by Oyedele et al. (2008) who reported that dump sites have significantly higher pH regime and soil organic matter as compared to the control soil. The result is in agreement with the study by Amos-Tautua et al., (2014) who reported an organic matter content of 1.03±0.64 to 4.71±0.85% in a waste dumpsite. Ayolagha and Onwugbuta (2001) also demonstrated that high OM (>2.0%) in soils is conducive for heavy metal chelation formation. There is a relationship between moisture content and organic matter because decomposition of organic matter is mainly dependent on the soil moisture and if water becomes too low, a plant becomes stressed.

4.2.1.5 Organic carbon of the soil

Organic carbon is the index for nitrogen content in the soil, the high % total organic carbon (TOC) in the soils of the auto-mechanic village indicated the possible presence of organic matter content, and it was observed that as organic carbon increases, organic matter content also increases. Organic matter normally increases due to the presence of used oil and other carbonaceous substances in the auto-mechanic villages and according to Osuji et al., (2006) this might cause an increase in the presence of soil microorganisms which are always breaking down organic compounds in soils. Total organic carbon in the soils under investigation in this study was low to moderate ranging from 0.8 to 2.4 % (Fig. 4.3b and 4.4a). The result is in agreement with the study by Amos-Tautua et al., (2014) who reported an organic carbon content of 0.6±1.07 to 2.73±1.25% in a waste dumpsite. Organic carbon plays a central role in ecosystem chemistry because it complexes metals and nutrients, affects pH and alkalinity, and acts as a substrate for microbial production (Dillon and Molot 1997). Organic carbon increase in L1 and L3 also resulted in organic matter and pH increase in L1 and L3 respectively. Organic carbon depletes the soil nutrient during microbial metabolism by reducing nutrient uptake by plants (Amadi et al., 2005).

4.2.1.6 Phosphate content of the soil

Phosphorus is a part of every living cell in plant. It is one of the most important micronutrient essential for plant growth. The high content of phosphate in farm 1 could be attributed to the presence of high amount of organic matter and plants decomposition (Ideriah et al., 2006). In the result, L1 had a higher phosphate content and also a higher organic matter content compared to L2 and L1 and this agrees with Miller and Donahuer (2001) who reported that the soil with high organic matter content have better supplies of organic phosphate for plant uptake than the soils with low organic matter content. The result alters the study by Amos-Tautua et al., (2013) who reported a phosphate content of 68.22±1.07 to 0.89±1.25% in a waste dumpsite and control 35.00±1.01 to 37.12±0.85%.

4.2.1.7 Sulfate content of the soil

The sulfate content was lower in the mechanic village soil than the control area, indicating the presence of microorganisms which could be as a result of oil degradable substances. The availability of microorganisms is also because of the high pH concentration in the mechanic village soil and this is supported by Tanee and Kinako (2008), who reported that the rise in the pH may favour oil degradation by microorganisms since most bacteria are capable of metabolizing hydrocarbons develop best at pH conditions close to neutrality.

4.2.1.8 Nitrate content of the soil

Nitrates are essential for normal plant growth. Crops grown in soils with low nitrogen content can exhibit necrosis, wilting and chlorosis (Nwaogu et al. 2012). It was observed that as organic carbon increases, nitrate content decreases and as organic content decreases, nitrate content increases. This observation is in line with the findings of Singh and Negi (2013), who said that soil nitrogen is directly related with soil organic carbon. The concentration of nitrate from the soil of the mechanic village was lower than the control area, indicating the presence of microorganisms that might have used up the nitrogen due to their breaking down of degradable substances in the soil. This is supported by Defoer et al., (2000), who reported that the lower value of total nitrogen in the farm soil could be as a result of crop uptake, immobilization by microorganism and it loss through volatilization. And according to Ideriah et al. (2006), the low values of N ratio shows high decomposition and efficient mineralization process in the mechanic village soil.

4.2.1.9 Correlation of Physiochemical Properties of Soil

The correlation of physicochemical properties of soil indicates that relationship exist among the physicochemical parameters (Appendix 41)

The pH showed a significant (-0.87 to -0.93) negative correlation with sulfate, phosphate and nitrate and a significant (0.92 to 0.99) positive correlation with organic matter, organic carbon, conductivity and no correlation with moisture content indicating that increase in pH decreases nitrate, sulfate and phosphate content and increases organic matter, total organic carbon, conductivity. The trend also followed that moisture content, nitrate and phosphate negatively correlated with organic matter, and total organic carbon. High negative correlation (- 0.87 to - 0.93) of sulfate, phosphate and nitrate with pH in the mechanic village soil indicate that farm 1&2 are polluted and may be unsuitable for agricultural purposes (Appendix Table 41)

4.2.2 Heavy metal concentration in soils and cassava tubers from Okigwe Mechanic village

4.2.2.1 Iron (Fe) Concentration.

The high concentration of iron (5278.74 mg kg^{-1}) in the mechanic village confirms that most soils contain a maximum concentration of iron. According to Nwachukwu et al., (2010), engine oil and other transmission fluids collect heavy metals such as lead, cadmium, zinc, iron and copper when an automobile engine is running and they remain in the used oil. When it is discharged, it increases the concentration of heavy metals in soils and this is responsible for the higher concentration of Fe in the auto-mechanic village soils than the control which is not exposed to high volume of waste engine oil. Though Iron is a plant micronutrient, which is needed in small amount for plant growth but the concentration of iron in the mechanic village was high compared to the control (42.35 mg kg^{-1}), indicating that there is another source of iron input in the area. This observation is supported by Ayeni, 2010 and Abidemi (2011), who said that the increase in iron content of the soil in the mechanic village is due to dumping of (Fe) scrap, unused body parts of vehicles, tin cans, solvents, hydraulic fluid, spent lubricants most of which are dumped into the soil directly.

Left over corroding vehicles also contributed to Fe increased in the study area, this is because Fe is a major component of steel alloy which is the material used in manufacturing of the body of vehicles. This result is in agreement with the study by Olayiwola (2011) who reported a high ranged of 38125±30 - 4500±10 mg kg^{-1} concentration of iron in automobile workshop in Osun State. Although iron is not generally considered as soil pollutant because of its high background concentrations (Huamain et al., 1999), but excess iron intake may result in siderosis in liver, pancreas, adrenals, thyroid, pituitary and heart depending on the chemical form (Codex, 2011). The relatively high concentration of Fe in the soil from this study area is a cause of concern.

The accumulation of iron in the cassava tuber was 0.46 times higher than that of the control and this shows that Fe in the cassava tubers was higher than the corresponding soil. The absorption of Fe in the cassava tubers was higher suggesting that bioaccumulation and absorption depends on heavy metals availability. The Fe concentration in the cassava tubers was below the WHO permissible limit for iron in plants which is 20 mg kg^{-1} (Afzal Shah et al., 2011).

4.2.2.2 Nickel (Ni) Concentration

Nickel has been considered to be an essential trace element for human and animal health (Zigham Hassan et al., 2012). The concentration of nickel in the study area was within the natural range of nickel in soil, which according to (Vecera et al., 1999) is 10 - 1000 mg kg^{-1}. Small amounts of nickel are needed by the human body to produce red blood cells, however, in excessive amounts, nickel can become mildly toxic. Ingestion of nickel may cause hyperglycemia, depression of the central nervous system and kidney damage (Vincoli, 1995). The presence of nickel in this study area may be due to the activities such as dewaxing, cleaning of vehicles, the use and disposal of polluting liquids such as oil, paints, solvents, antifreeze and other coolant additives.

Exposures by inhalation, ingestion or skin contact occur in nickel and nickel alloy production plants as well as in welding, electroplating, grinding and cutting operations which are done in auto-mechanic workshops. The concentrations of Ni in cassava tubers was the same as the control and also lower than the corresponding soil indicating that there was no accumulation of Ni in the cassava tubers. The result is in agreement with the study of Wodaje (2015) who reported a non-detectable to 0.43 mg kg^{-1} in cereal samples collected from Ambo market. The concentration of Ni in the cassava tubers was below the permissible limit of 10mg/kg in plants recommended by WHO (Zigham Hassan et al., 2012).

4.2.2.3 Manganese (Mn) Concentration

The concentration of manganese in the soil of the mechanic village was higher than the control and it was within the permissible limit of 100 - 4,000 mg kg^{-1} (Vecera et al., 1999). The presence of Mn in the soils of the automobile village may be as a result of vehicular exhaust and also from waste engine oil. Chronic exposure to higher levels of manganese may cause manganism. Manganism is characterized among other symptoms, weakness, tremors, a masklike face and psychological disturbance. The concentration of Mn in cassava tubers was lower than the corresponding soil and the difference in the concentration of Mn in cassava tubers from the automobile farmlands and the control indicates a non-bioaccumulation of the Mn in the plant.

4.2.2.4 Copper (Cu) Concentration

The concentration of Cu from the automobile village soil was high compare to the control and this indicates that there is a release of Cu from anthropogenic activities within the vicinity. The concentration of Cu in the cassava tubers was below the permissible limit of Cu for plants recommended by WHO (Zigham Hassan et al., 2012). The high concentration of copper (Cu) determined in the mechanic workshop soil was higher than the farmlands soil close to it, this was as a result of the fact that Cu does not travel very far after being released. This limited mobility explains why copper (Cu) accumulate in soils (Adelekan and Abegunde, 2011). High levels of Cu can cause symptoms of acute toxicity, including nausea, abdominal discomfort, diarrhoea, haemoglobinuria and/or haematuria, jaundice, oliguria/anuria, hypotension, coma and death. Cu accumulates in liver and brain. Cu toxicity is fundamental cause of Wilson's disease (Samuel Zerabruk et al., 2011). The concentration of Cu in the cassava tuber is in agreement with the study of Wodaje (2015) who reported a ranged of 0.13 to 1.72 mg kg^{-1} Cu concentration in cereal samples collected from Ambo market.

4.2.2.5 Zinc (Zn) Concentration

Zn is one of the important trace elements that play a vital role in the physiological and metabolic process of many organisms. The natural range for the concentration of zinc in soil is 10 - 300 mg kg^{-1} (Vecera et al., 1999). The value of Zn in the automobile soil was within the range of 23.2 and 161.1 mg kg^{-1} and this concentration is still higher than the control which implies that there is an anthropogenic input of Zn in the mechanic village. The high level of Zn observed in this environment than in the control site might be due to exhaust from vehicle and gasoline combustion.

Zinc used as an additive in lubricating oil (Ayodele and Gaya, 1998) may also be responsible for the observed concentration of Zn in this environment. Although Zn is an essential trace element in low concentration, it is toxic in high concentration (Oborn et al., 2005); high concentration of Zn can also influence the activity of microorganisms and earthworms thereby retarding the breakdown of organic matter (Wuana and Okieimen, 2011). Ingestion of Zinc in excess of 12 mg per day may cause lung disturbance (Eka and Udotong, 2003).

The concentration of Zn in cassava tubers was very low compare to the corresponding soil, the difference in the concentration of Zn in cassava tubers from the automobile farmlands and the control indicates a non-bioaccumulation of the Zn in the tubers. The concentration of Zn in the cassava tubers was below the recommended limit of 50 mg kg^{-1} in plants by WHO (Afzal Shah et al., 2011)

4.2.2.6 Lead (Pb) Concentration

Lead (Pb) occurs naturally in all soils in concentrations ranging from 1 to 200 mg kg^{-1} with a mean value of 15 mg kg^{-1} (Chirenje *et al.,* 2004). Lead concentrations in the soil of the automobile village exceeded the National Environmental Standards and Regulations Enforcement Agency (NESREA) limit for lead in soil for the auto-mechanic village. The lead concentrations in this study were in agreement with the study by Adekunle and Abegunde (2011), who reported Pb range from 11.75 to 15100.00 mg kg^{-1} from soil in some mechanic villages in Ibadan. The high concentration of Pb may be due to higher amount of used automobile batteries - which are a ready source of lead. Pb in the soil of the automobile when compared to those measured at the control site provides further evidence that Pb is accumulating in the soil of this automobile village.

Lead as a soil contaminant is a widespread issue; it accumulates with age in bones aorta, and kidney, liver and spleen. It can enter the human body through uptake of food (65%), water (20%) and air (15%). Exposure to Pb can lead to Pb poisoning, which will result in memory loss and restlessness. Lead has been found to inhibit enzymatic activity (Vincoli, 1995). The concentration of Pb in cassava tubers was very low compare to the corresponding soil indicating a non-bioaccumulation of the Pb in the tubers. The concentration of Pb in the cassava tubers was below the permissible limit of 2 mg kg^{-1} recommended in plants by WHO.

4.2.2.7 Cadmium (Cd) Concentration

Cd is a highly toxin Non-essential heavy metal and it does not have a role in biological process in living organism. Thus even in low concentration, Cd could be harmful to living organisms (Ambedkar and Muniyan, 2012). Cd poisoning in man could lead to aneamia, renal damage, bone disorder and cancer of the lungs (Ademoroti, 2013). Generally, the low concentration of Cd obtained from the workshop soils compared to the other heavy metals in the same soils could be attributed to the high mobility of Cd through the soil layers. Cd is likely to be more mobile in soil systems than many other heavy metals (Adelekan and Abegunde, 2011). This result is in agreement with the study of Baodu (2014), who also obtained a low Cd concentration in soil than the other heavy metals studied from Agbogbo oshie scrap market, Accra. High levels of cadmium (Cd) exposure may lead to severe pains in the joints, bone diseases, kidney and lung problems and anaemia (Hardy et al., 2008). It may affect sperm, reduces birth weight and a causal factor in cardiovascular diseases and hypertension (Adelekan and Abegunde, 2011; Asio, 2009).

Cd concentrations in the farm soil (farm 1 & 2) were found to be higher than the natural limits of 0.01-3.0 mg kg^{-1} in soil as given by MAFF (1992). According to Jarup, (2003) and Ebong et al., (2008) the presence of Cadmium is due to the dumping of PVC plastics, nickel-cadmium batteries, motor oil in the auto-mechanic village. The presence of cadmium in automobile waste dump soils have also been reported by Uba et al (2008) and Myung (2008). The concentration of Cd obtained from the workshops soil and cassava tubers from both farms are in agreement with the findings of Asawalam and Eke (2006) and Njoku and Ayoka (2007) who investigated the trace metal concentration and heavy metal pollutants from dump soils in Owerri, Nigeria.

The concentration of Cd in the farm soil was higher than that of the cassava tubers indicating that there was no uptake of the metal by the plant. The permissible limit of Cd in the cassava tubers was lower than 0.02 mg kg^{-1} recommended by WHO. The concentration of Cd in the control can be as a result of natural occurrence of Cd and probably due to bush burning and other processes.

4.2.2.8 Chromium (Cr) Concentration

The concentration of Cr in the cassava tubers from farm 1& 2 was lower than its corresponding soil and it was below the permissible limit of 1.3mg/kg in plants recommended by WHO. The result was lower than the study of Reqia Nazir et al., (2015) who reported a chromium concentration of 0.263±0.00 – 2.466±0.235 mg kg^{-1} in plants collected from Tanda dam Kohat. Although Cr toxicity in the environment is relatively rare, it still presents some risks to human health since chromium can be accumulated on skin, lungs, muscles fat, and it accumulates in liver, dorsal spine, hair, nails and placenta with various health implications (Reyes-Gutiérrez et al., 2007).

The Chromium concentration obtained from the workshop and farm (farm 1&2) soils are lower than the critical permissible level of 50 mg kg^{-1} below the maximum tolerable levels proposed for soil recommended for agriculture by MAFF (1992). This result is in agreement with the study by Adekunle and Abegunde (2011), who reported Cr concentration of 3.50 mg kg^{-1} from soil in some mechanic villages in Ibadan. Sources of chromium in the mechanic village soil could be due to waste consisting of lead-chromium batteries, coloured polythene bags, discarded plastic materials and empty paint containers (Jung et al., 2006).

4.2.3 POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS AND CASSAVA TUBERS

Naphthalene was the only low molecular weight PAH not detected in all the soil and cassava samples analyzed probably due to the high volatilization or dissolution which may have occurred during the process of extraction. It may also be due to the length of time of exposure of the soil samples prior to this study. It is well known that light PAHs compound occur in soil in lower proportions than heavier ones due to their physicochemical properties such as high solubility, volatility, biodegradability and lower sorption ability to soil organic portion (Weiss et al., 2000, Jensen et al., 2007). This also corroborates the report of Reid et al., (2000), Semple et al., (2003) and Dick et al., (2005) who stated that the fate of PAHs in the soil is affected by factors such as weather and climate, biological diversity and abundance, the amount and the nature of the soil minerals and organic matter and pollutant properties such as solubility, polarity, hydrophobicity, lipophilicity and molecular structure. This explains the difference in PAHs concentrations between soil samples that are not in close proximity as well as variation in PAHs concentration of the same site.

Low molecular weight PAHs such as naphthalene, acenaphthalene, acenaphthene, fluorene, anthracene and phenanthrene are transformed rapidly by many bacteria and fungi while high molecular weight PAHs however are more recalcitrant in the environment and resist both chemical and microbial degradation (Carl and John

2009). It is evident from the results that the soil samples of Okigwe auto-mechanic village were contaminated with PAHs at varying concentrations. The total PAHs concentration were very high when compared with the maximum background limits of 15 mg/kg and 50 mg/kg in polluted soils set by Dutch and polish Environmental Ministries respectively, (Polish Environmental Ministries, 2002).

High molecular weight PAHs are known to be carcinogenic and these were detected in the soil from the study area. Consequently, it is perceived that the population of people living in and around the Okigwe auto-mechanic village may be predisposed to risk of cancer due to long-term exposure to PAHs and most especially among the artisans, even at low levels PAHs pose a major threat in terms of its carcinogenic effects. These effects depend mainly on the extent of exposure, dose, innate toxicity and exposure routes. The accumulation of these PAHs in cassava tubers, suggests that food from cassava tubers remain a major endogenous source of PAHs among the artisans and close residents of the mechanic village. However consumption of cassava with high PAHs level from the mechanic village may lead to adverse health effect which includes mental retardation, cancer, asthma, DNA mutation, reproductive defect and heart disease (Fetzer, 2000).

Though acenaphthylene, acenaphthene, anthracene, benzo(g.h.i.)perylene, fluoranthene, fluorene, phenanthrene and pyrene are not classified as human carcinogen by DHH, IARC or EPA (Emily, 2010) but they are present in the soil and cassava tubers of the study area and may react with other pollutants to form more toxic derivatives. This is supported by Tang et al., (2005) who reported that the carcinogenicity of PAHs mixtures may be influenced by the synergistic, additive or antagonistic effects of other components emitted together with PAHs during incomplete combustion.

Generally, high molecular weight PAHs (recalcitrant PAHs) were lower in cassava tubers than the low molecular weight PAHs. Recalcitrant PAHs have lower water solubility, higher water octanol partition coefficient and low potential for root uptake from the soil suggesting reasons for low levels of high molecular weight PAHs in cassava tubers. This is in line with ASTDR (1994) report that compounds with high water octanol partition coefficient (log k_{ow}) are tightly bound to organic factor in the soil which renders it less available for degradation, leaching and volatilization and plant uptake. Wood combustion, petroleum hydrocarbon, pollution through oil spillage and unregulated fires has been considered as sources of higher molecular weight PAHs (Kim et al., 2003; Tuteja et al., 2011). This explains the concentration of PAHs in the control soil which is available due to previous bush burnings for farming processes.

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 SUMMARY OF RESEARCH FINDINGS

The study reveals that auto-mechanic village activity is responsible for the preponderance of PAHs and heavy metals in the soils of Okigwe mechanic village.

The result showed that of the 16 USEPA target PAHs (EPA-16) examined, only Naphthalene was not detected in all samples and the rest of the PAHs detected showed varying concentrations in mg kg^{-1}. The total PAH concentration ranged from 122.2 mg kg^{-1} to 17 mg kg^{-1}. Soil pH was alkaline ranging from 7.5 to 9.29. Correlation analysis was conducted and it revealed that pH had a high negative correlation with sulfate, phosphate and nitrate and a high positive correlation with organic matter, organic carbon and conductivity.

Eight (8) heavy metals were analyzed from samples in the study area; all the 8 heavy metals were present in various concentrations. Fe had the highest mean concentration of 5278.74 mg kg^{-1} and the least concentration was Cr and Cd with the mean concentration of 0.01 mg kg^{-1}

5.2 CONCLUSIONS

Cassava crop was chosen for this study after observing that it is the most common food crop planted within the auto-mechanic village and also it is widely consumed by the inhabitants surrounding the auto-mechanic village. The data gathered during this study shows that for heavy metals, Fe had the highest concentration amongst all the parameters measured. Heavy metals from the mechanic village soil and cassava tubers were higher than the control showing a high concentration of heavy metal contamination in the study area. PAHs were present in the soil and cassava tubers at varying concentrations except for naphthalene which was not detected in the samples analyzed, although in L3 of the mechanic workshop soil, no PAHs was detected also. It is evident from this study that Okigwe auto-mechanic site is gradually being contaminated with PAHs and heavy metals arising from activities like indiscriminate disposal of spent crankcase engine oils, panel beating, metal scraps, spray paints etc. The presence of heavy metals that are above the natural levels in the soil can also be attributed to other sources apart from the above mentioned like the different chemicals and substances used at the study area and also scraps and used engine oil are not usually properly disposed of which has added greatly to the increase concentration of pollution in mechanic village,. These activities are potentially dangerous to the environment and the human health. Evidence of contamination of this soil from the mechanic workshops and farmlands (1&2) by Pb, Cu, Zn, Mn, Ni, Fe and PAHs were obvious when compared to the control site, except for Fe that the control was higher than that of the farmlands which explains the natural occurrence of Fe in soil. Pb in soil from the mechanic workshops exceeded the Pb concentration limit set by NESREA. Cd concentrations in the farm soil (farm 1 & 2) were found to be higher than the natural limits of 0.01-3.0 mg/kg in soil as given by MAFF (1992).

It has been observed that some of the heavy metals (Pb and Mn) and PAHs build up to very high concentrations in the farms soil, thereby being available for uptake by the cultivated cassava crop within the area, posing great hazards to the soil and the crop consumers.

This study shows that soil within the Okigwe auto-mechanic village is highly polluted with heavy metals and PAHs and the frequent ingestion of the cassava crops will lead to accumulation in the body with time and may pose a threat to the consumers. Hence it is not advisable to farm in such areas because these pollutants are hazardous to human health and animals.

5.3 RECOMMENDATIONS

Only cassava as a food crop was assessed for health risk under the current investigation, and the contamination of this soil from the mechanic workshops and farmlands (1&2) by Pb, Cu, Zn, Mn, Ni, Fe and PAHs were obvious when compared to the control site. Therefore it is evident that the soil of the study area is contaminated by these pollutants. Maize and mango are important crops grown in the area too which could also encounter similar food contamination from these pollutants.

Therefore, the following recommendations are made

1. Further studies are recommended to bring the potential health risk from cultivated crops consumption in the area to a full disclosure.

2. Due to the improper disposal of wastes by auto-mechanics on the surface soil which render farmlands unfit for agriculture as well as pollute the ground and surface water systems. It is therefore recommended that, mechanic villages should be sited far from residential and farmland areas to avoid the transfer of these pollutants into the food chain, ground and surface water systems.
3. In addition, as the city is expanding with more business outlay emerging, recycling and re-use advocacy is being recommended to track the spread of waste oils in the environment.
4. Continuous education and training should be provided for the automobile workers, emphasizing on the environmental implications of their poor occupational waste management.
5. Government should enforce a law to curb the cultivation of edible crops around or within any vicinity of a mechanic village as well as other environments where their activities bring about soil pollution.

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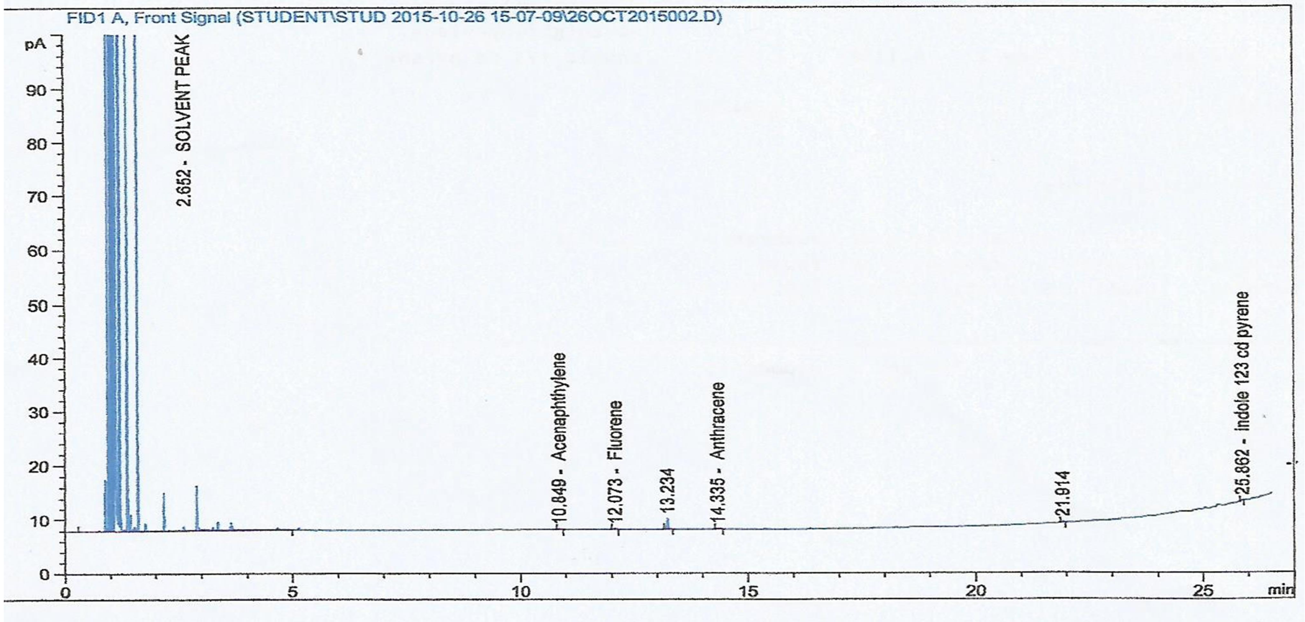
APPENDIX 1: CHROMATOGRAM OF PAHS

LOCATION 1 (0-15CM)



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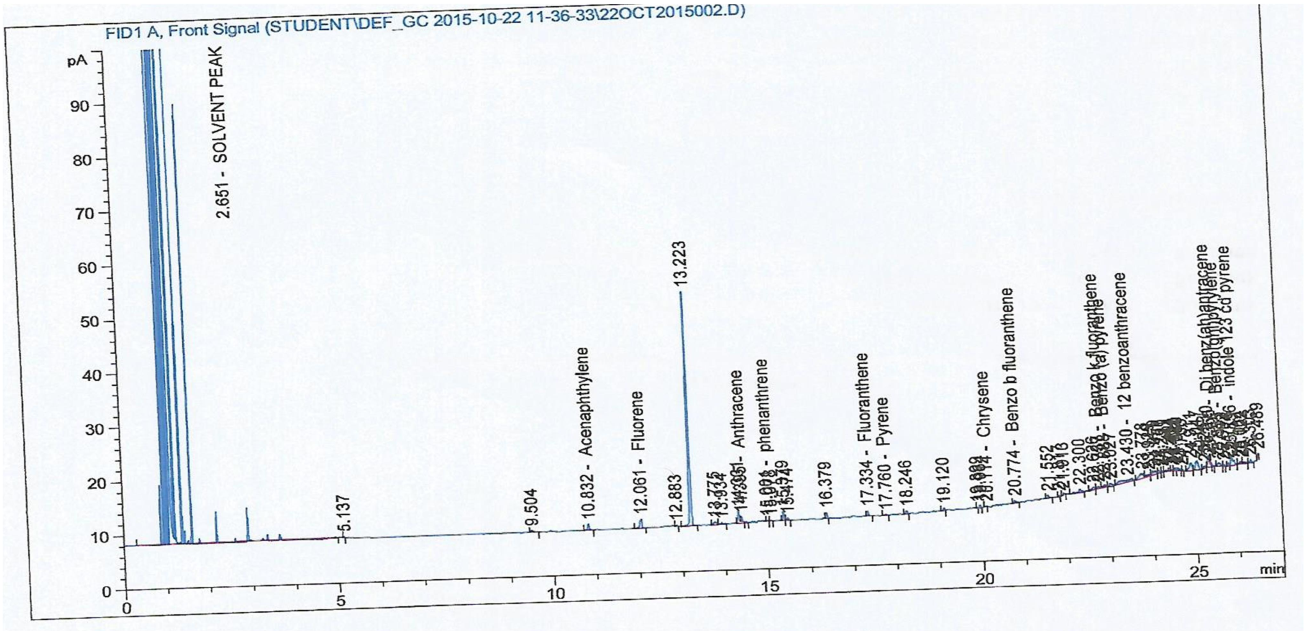

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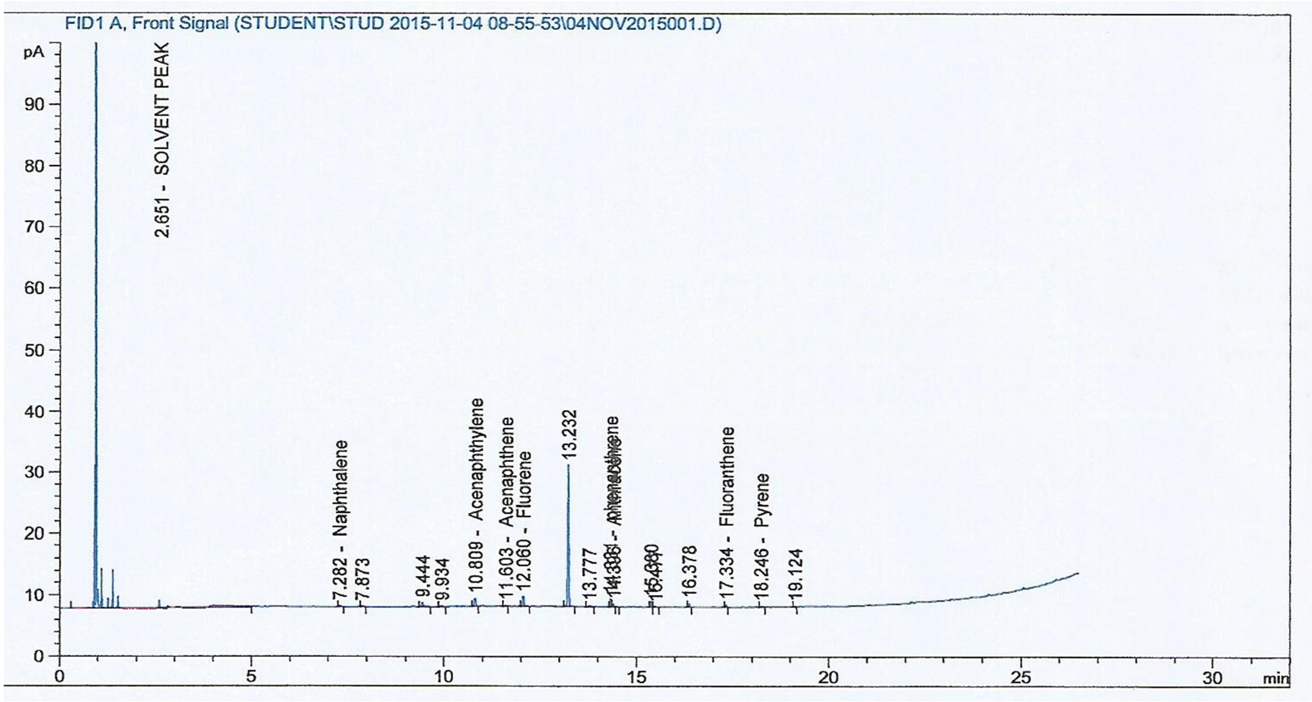

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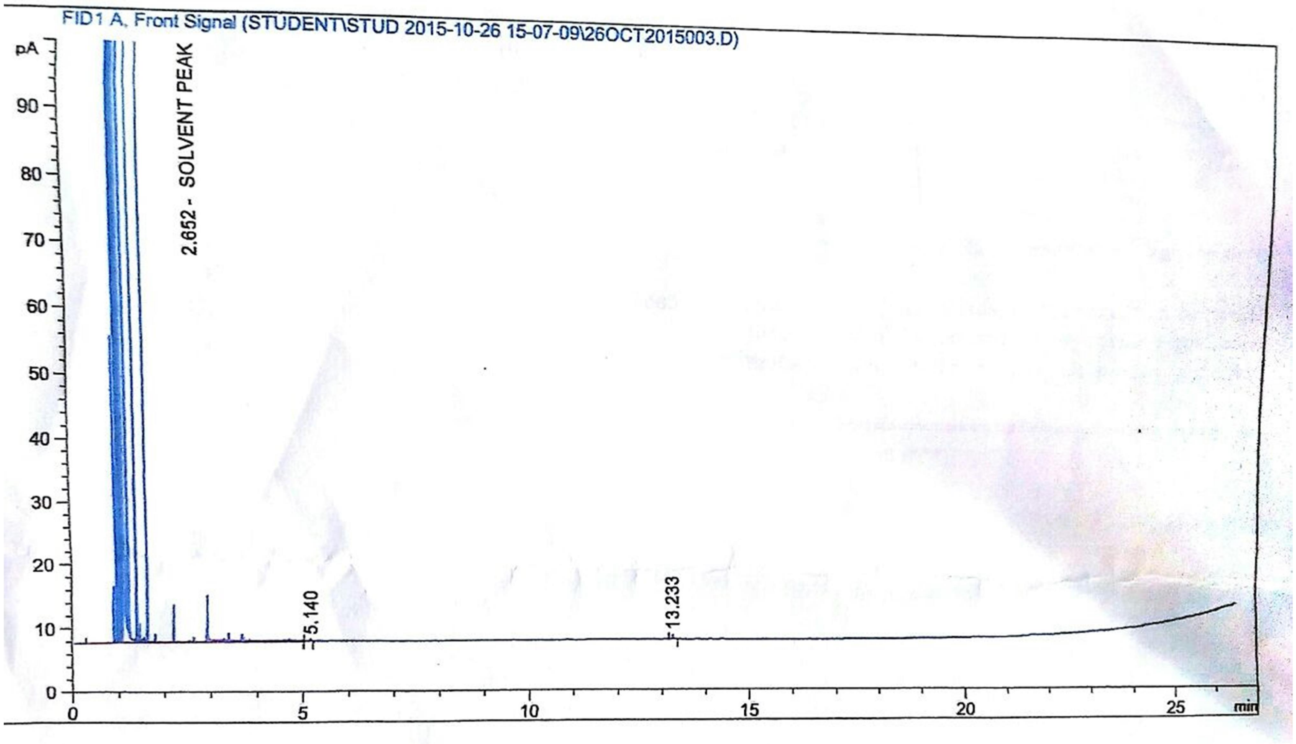

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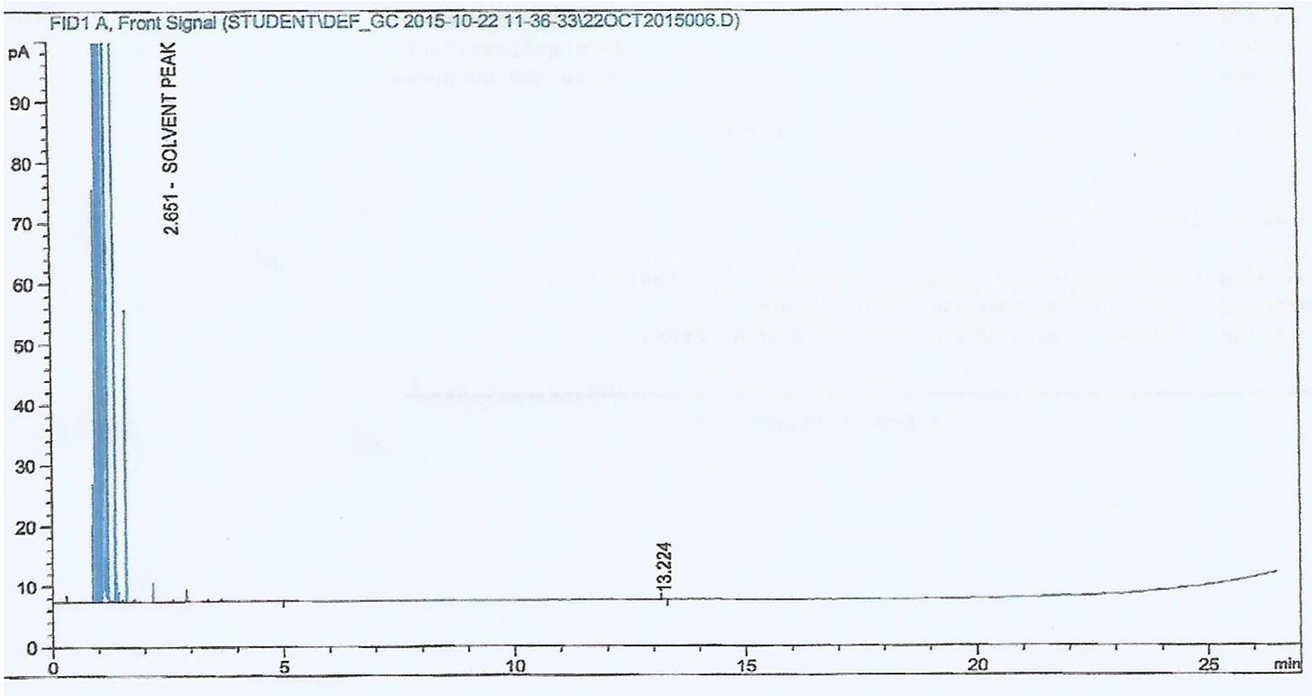

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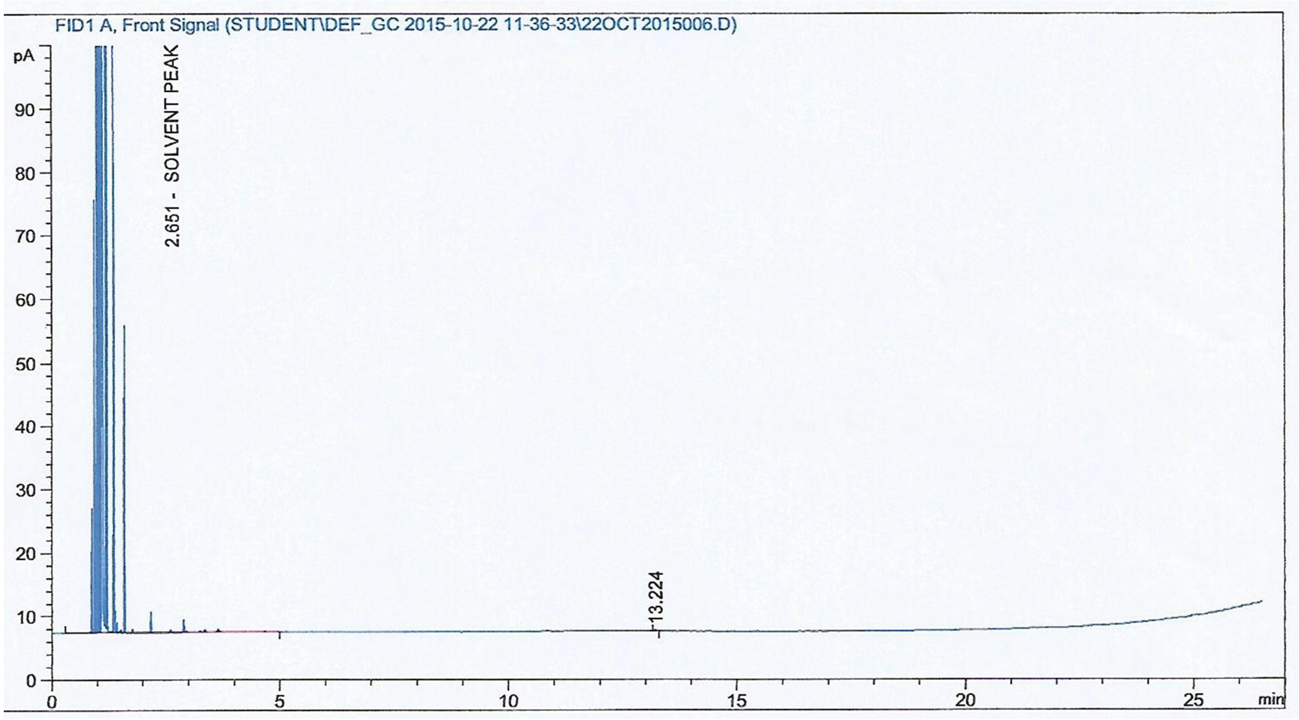
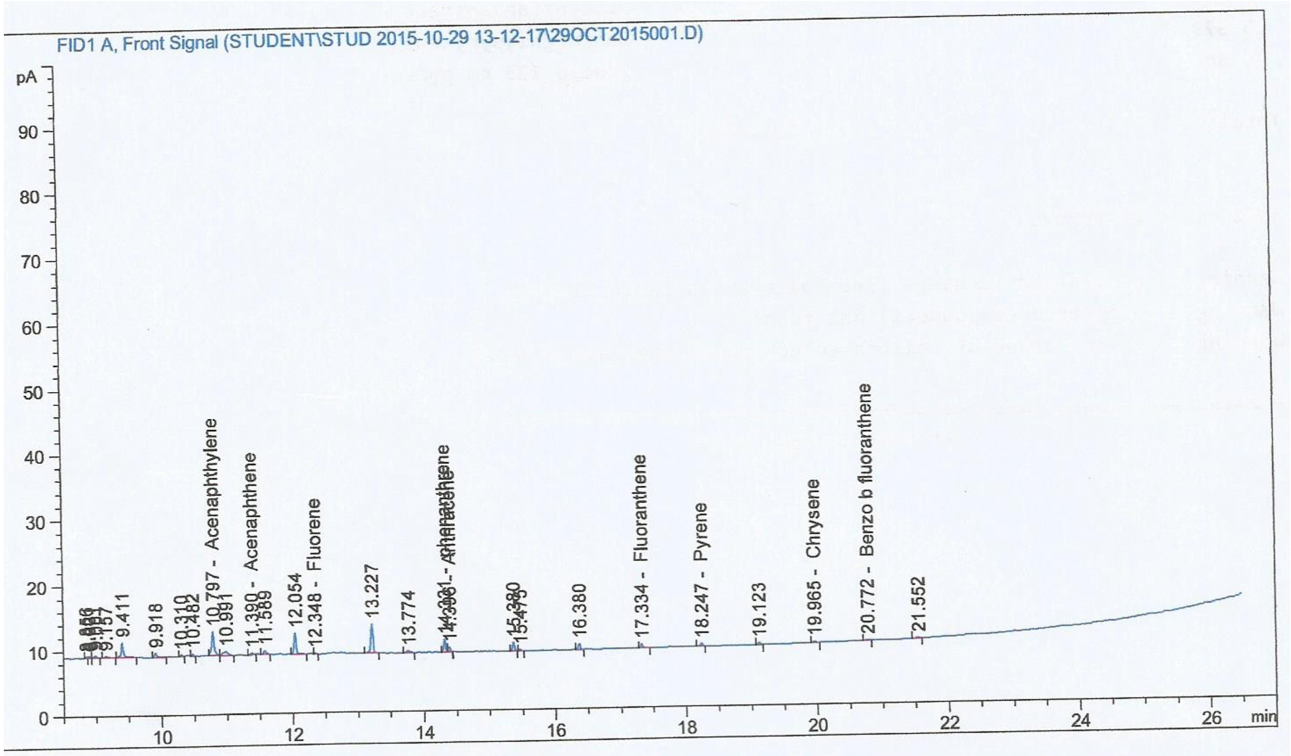


CASSAVA FARM 1



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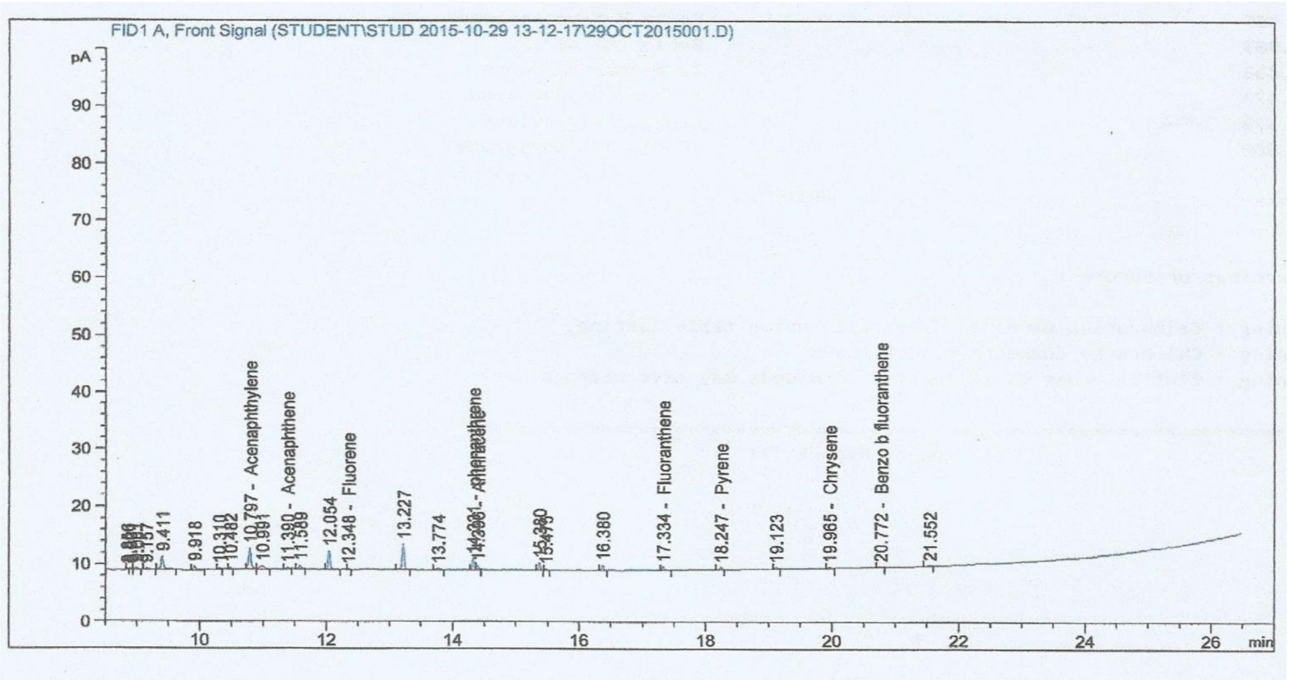
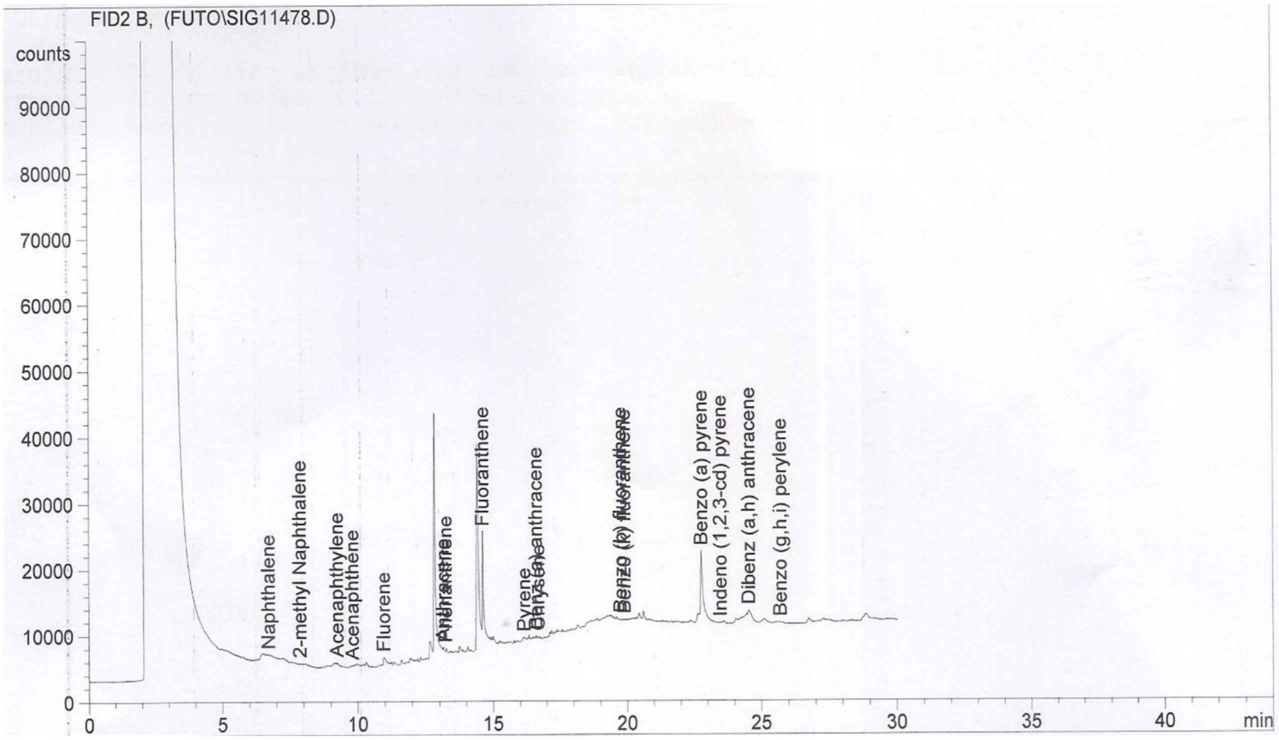


SOIL FARM 1 (0-15CM)



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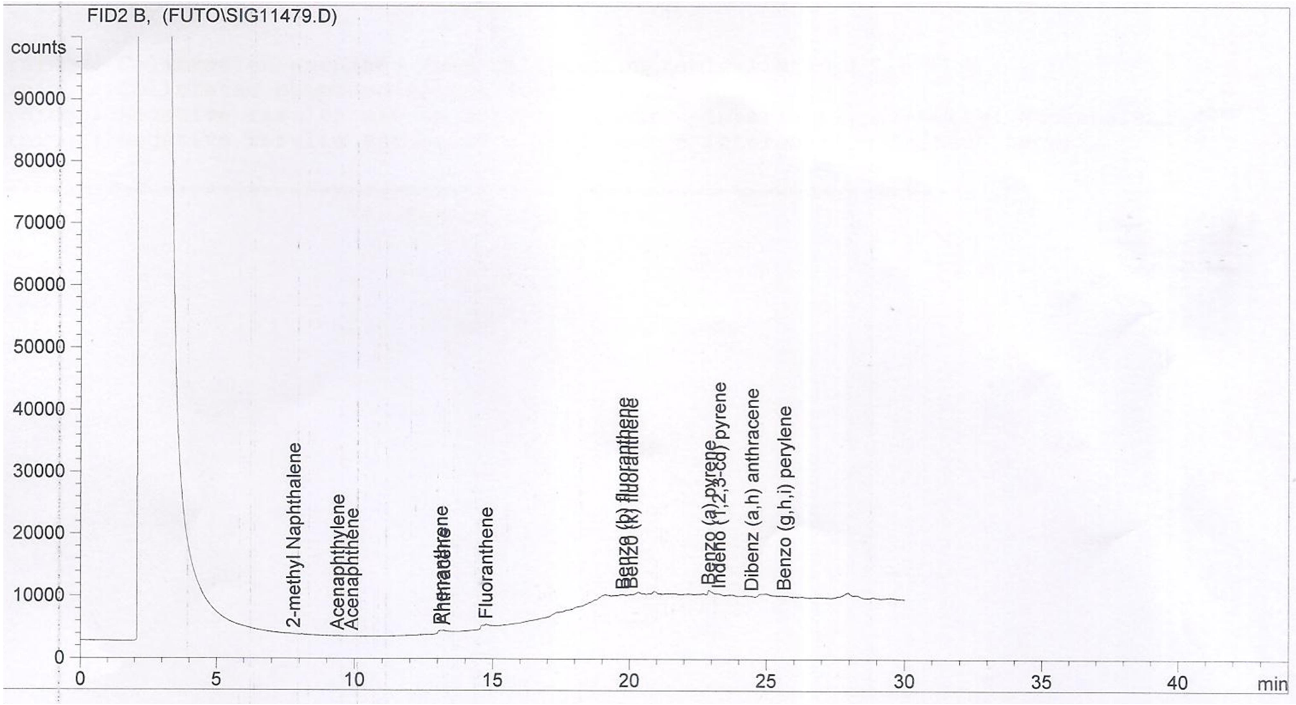

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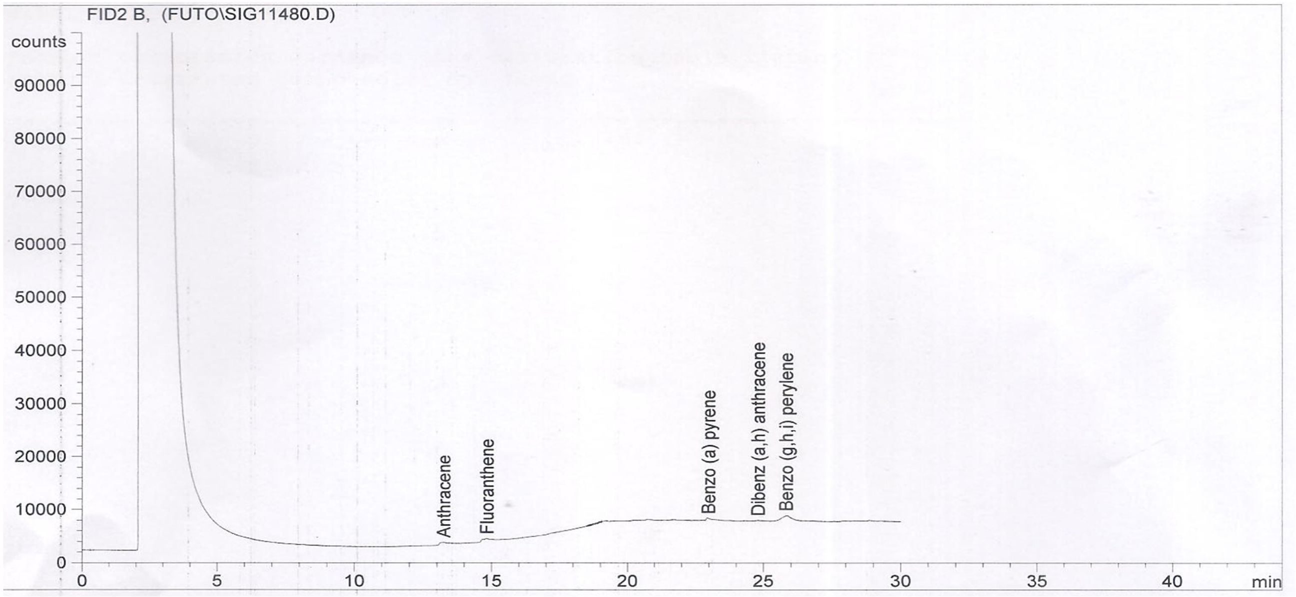

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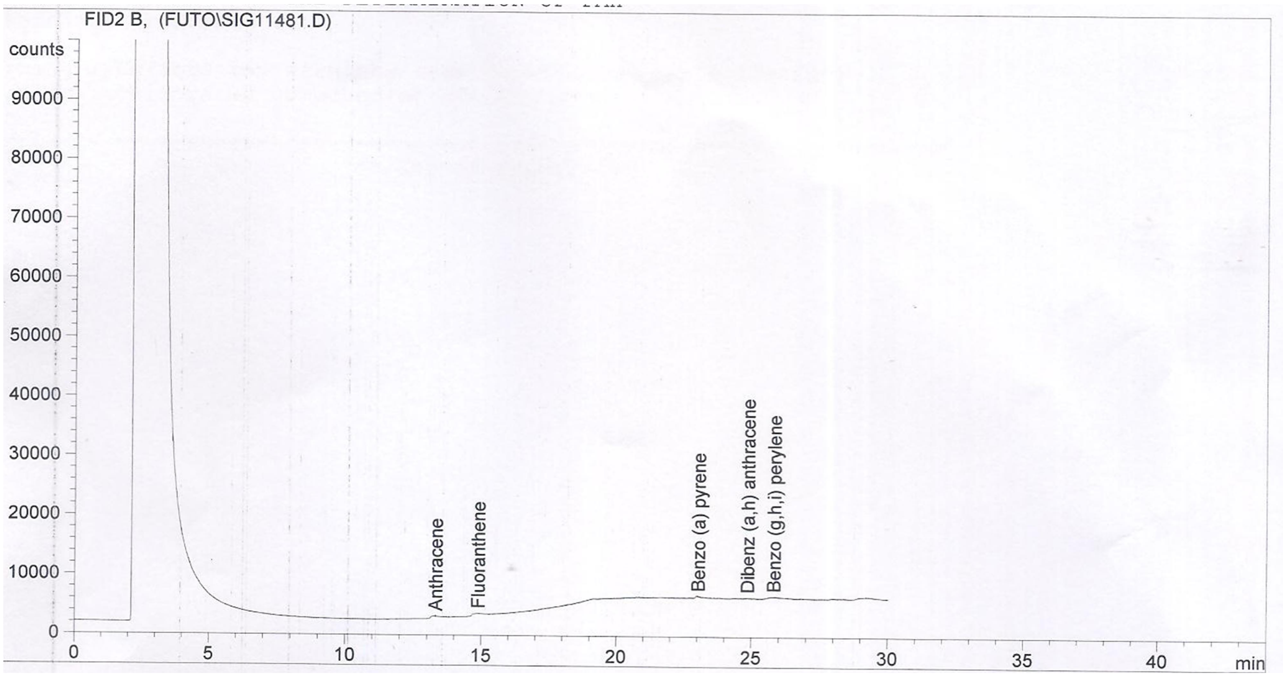
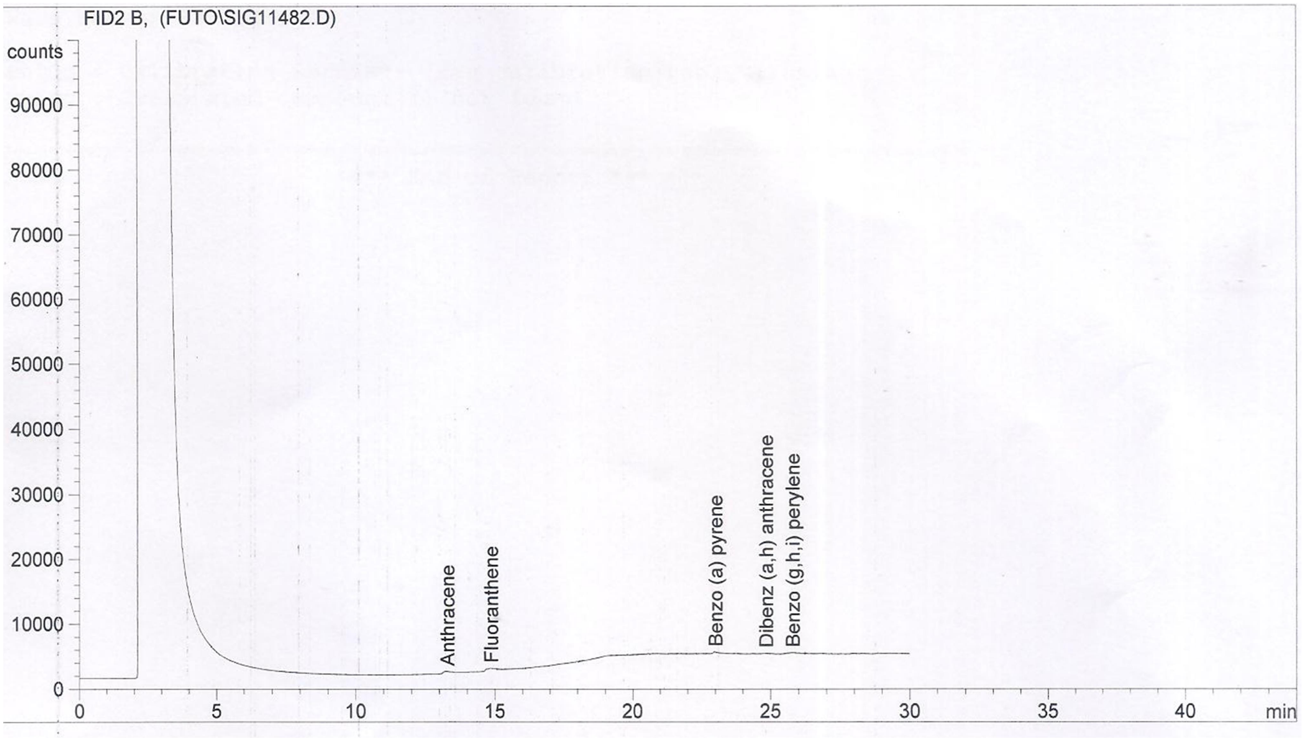


SOIL CONTROL (0-15CM)



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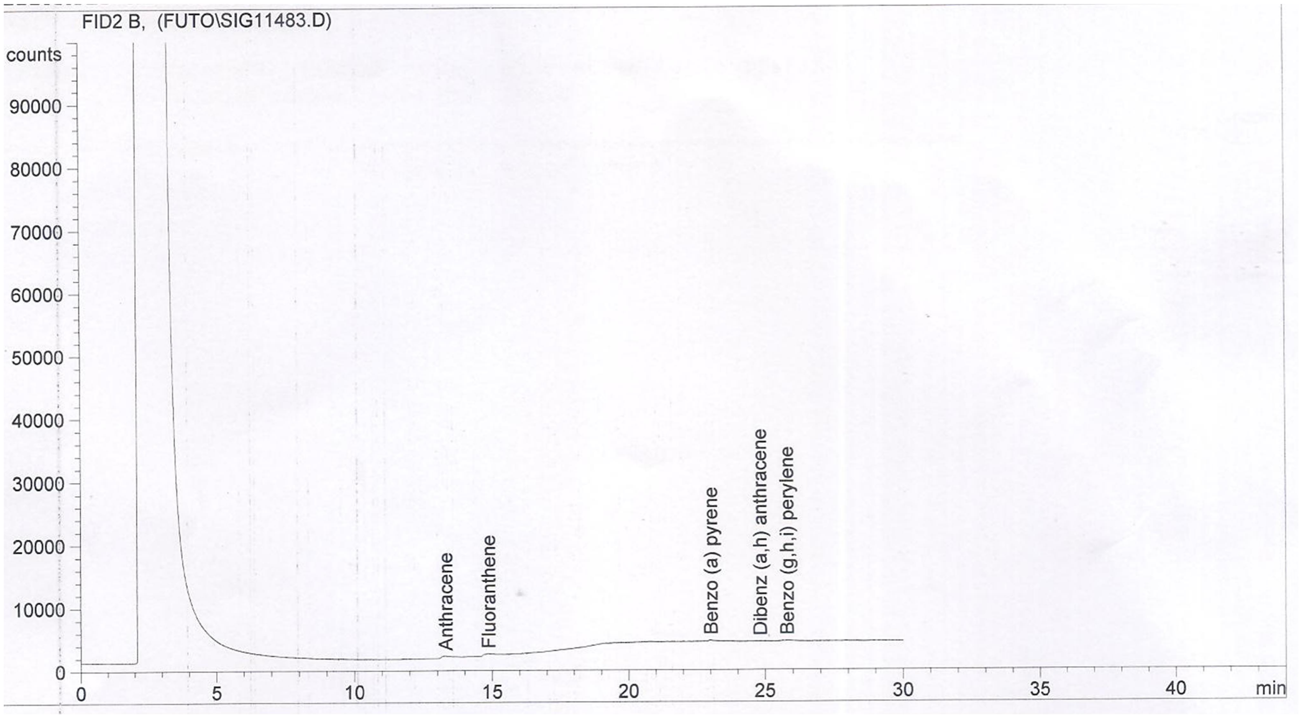
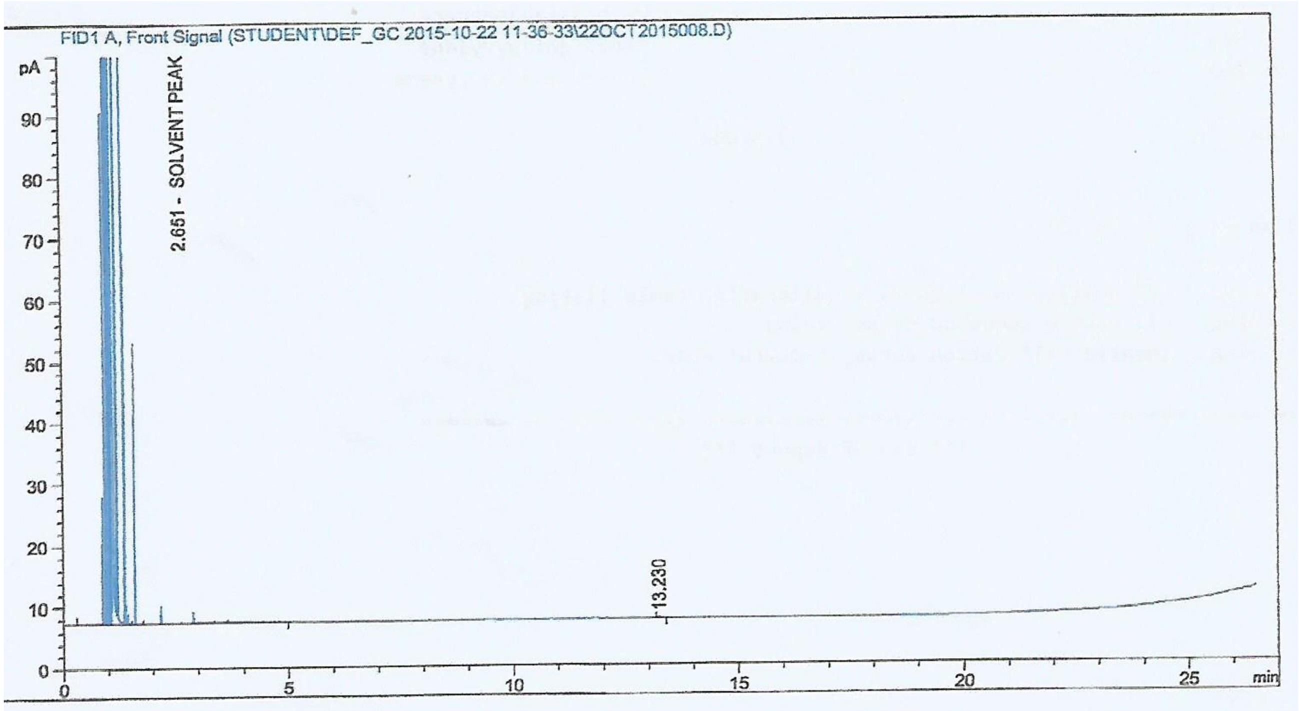
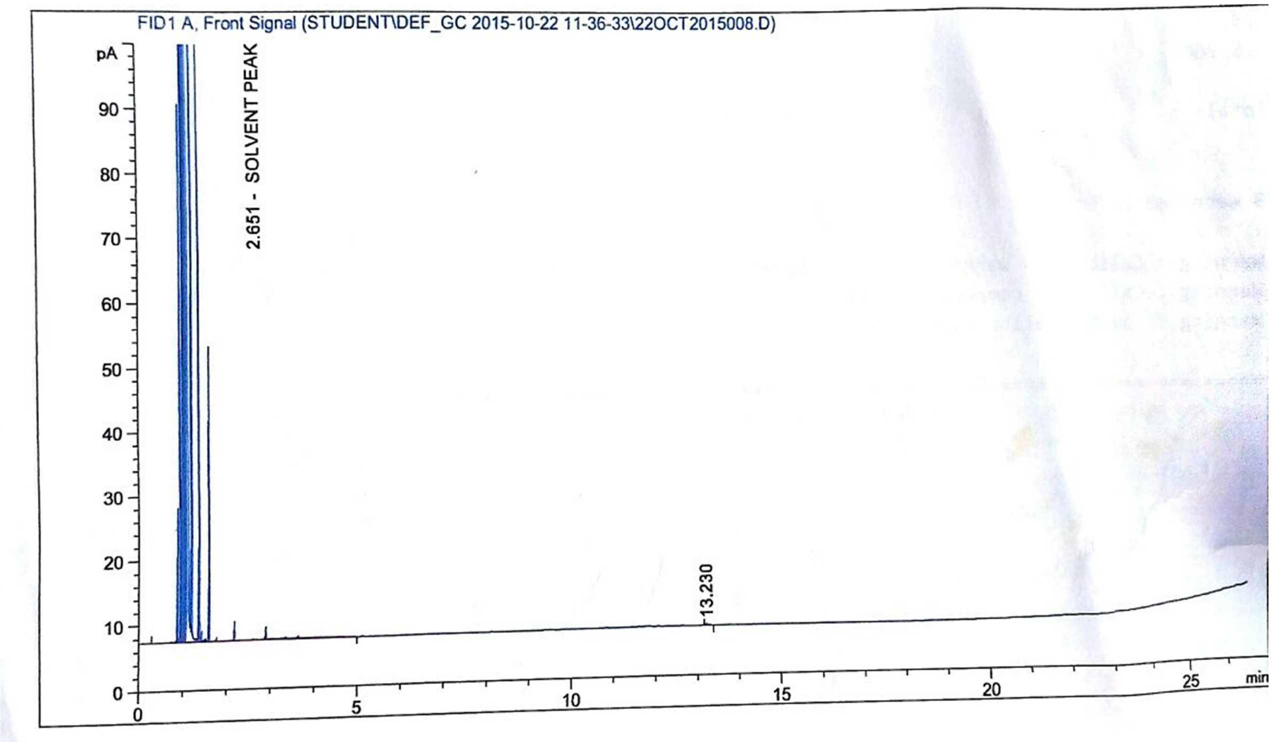


CONTROL (0-15CM)



CONTROL (15-30CM)



Appendix 2: ANOVA of Heavy Metals

Farm 1, farm 2 and control

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	29077.36	2	14538.68	2.635455	0.095239	3.4668
Within Groups	115848.1	21	5516.574			
Total	144925.4	23				

Farm 1 and farm 2

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	24071.91	1	24071.91	2.94278	0.108299	4.60011
Within Groups	114519.8	14	8179.989			
Total	138591.8	15				

Farm 2 and Control

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	19278.28	1	19278.28	2.330049	0.149169	4.60011
Within Groups	115832.7	14	8273.767			
Total	135111	15				

Farm 1 and Control

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	265.853	1	265.853	2.770274	0.118242	4.60011
Within Groups	1343.529	14	95.96633			
Total	1609.382	15				

LI and Control

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4840851	1	4840851	0.719526	0.410568	4.60011
Within Groups	94189643	14	6727832			
Total	99030494	15				

L2 and Control

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	439187.1	1	439187.1	0.301845	0.591384	4.60011
Within Groups	20370091	14	1455006			
Total	20809278	15				

L3 and Control

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	17590.24	1	17590.24	0.058534	0.812336	4.60011
Within Groups	4207188	14	300513.4			
Total	4224778	15				

Appendix 3: ANOVA of Physiochemistry

FARM 1 AND CONTROL

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	146.5794	1	146.5794	0.298838	0.593219	4.60011
Within Groups	6866.984	14	490.4988			
Total	7013.563	15				

FARM 1 AND FARM 2

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9.530341	1	9.530341	0.013131	0.910398	4.60011
Within Groups	10161.4	14	725.8145			
Total	10170.93	15				

LOCATION 1, 2 and 3

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	256.5941	2	128.2971	0.025986	0.97438	3.4668
Within Groups	103678.9	21	4937.092			

Total	103935.5	23				

LOCATION 1,2 3 AND CONTROL

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2555.306	3	851.7687	0.228443	0.875796	2.946685
Within Groups	104400.1	28	3728.575			
Total	106955.4	31				

FARM 1 and FARM 2

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	10106.63	7	1443.805	179.6337	3.7E-08	3.500464
Within Groups	64.29994	8	8.037492			
Total	10170.93	15				

Appendix 4: ANOVA of PAHs

FARM 1 and FARM 2

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.556986	1	1.556986	0.333326	0.568015	4.170877
Within Groups	140.1317	30	4.671057			
Total	141.6887	31				

CASSAVA FARM 1 and FARM 2

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3.497371	1	3.497371	2.119305	0.155839	4.170877
Within Groups	49.50733	30	1.650244			
Total	53.0047	31				

ALL SAMPLES

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	961.105	6	160.1842	5.853156	2.74E-05	2.186993
Within Groups	2846.183	104	27.36714			
Total	3807.288	110				

SOIL FARM 1, CASSAVA FARM 1 and CONTROL

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	43.89728	2	21.94864	6.476972	0.003372	3.204317
Within Groups	152.4924	45	3.388719			
Total	196.3896	47				

SOIL FARM 2, CASSAVA FARM 2 and CONTROL

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	37.7694	2	18.8847	7.131308	0.00204	3.204317
Within Groups	119.1663	45	2.64814			
Total	156.9357	47				

SOIL FARM 1, CASSAVA FARM 2 and CONTROL

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	44.42989	2	22.21494	5.518738	0.007186	3.204317
Within Groups	181.1415	45	4.025367			
Total	225.5714	47				

CASSAVA FARM 1, CASSAVA FARM 2 and CONTROL

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3.733654	2	1.866827	0.928081	0.402745	3.204317
Within Groups	90.51714	45	2.011492			
Total	94.25079	47				

FARM 1 and CASSAVA FARM 1

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	24.38756	1	24.38756	6.562703	0.015679	4.170877
Within Groups	111.4826	30	3.716085			
Total	135.8701	31				

FARM 2 and CASSAVA FARM 2

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	30.9215	1	30.9215	11.86907	0.001708	4.170877
Within Groups	78.15648	30	2.605216			
Total	109.078	31				

LOCATION 1 and LOCATION 2

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	54.57438	1	54.57438	0.605099	0.44294	4.182964
Within Groups	2615.534	29	90.19083			
Total	2670.108	30				

LOCATION 1, LOCATION 2 and CONTROL

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	566.0892	2	283.0446	4.688032	0.014267	3.209278
Within Groups	2656.544	44	60.376			
Total	3222.633	46				

LOCATION 1, CASSAVA FARM 2 and CONTROL

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	355.1718	2	177.5859	5.844919	0.005539	3.204317
Within Groups	1367.233	45	30.38296			
Total	1722.405	47				

APPENDIX 5: PEARSON CORRELATION BETWEEN PHYSICOCHEMICAL PARAMETERS

	Sulfate	Moisture (%)	Phosphate	organic carbon	organic matter	pH	Conductivity	Nitrate
Sulfate	1							
Moisture (%)	0.110566322	1						
Phosphate	0.937068993	-0.242590946	1					
organic carbon	-0.627790504	0.093581414	-0.627331663	1				
organic matter	-0.627431496	0.093762636	-0.627038546	0.99999989	1			
pH	-0.87464092	0.073318044	-0.868413052	0.922282574	0.922113296	1		
Conductivity	-0.912810412	0.118952461	-0.9242747	0.870531236	0.870326125	0.991928629	1	
Nitrate	0.866290018	-0.353070407	0.964016933	-0.780363215	-0.780173174	-0.931789652	-0.963958213	1

Interpretation:

0.00 to 0.30 (- 0.00 to - 0.30) Little if any correlation

0.30 to 0.50 (- 0.30 to - 0.50) Low positive (negative) correlation

0.50 to 0.70 (- 0.50 to - 0.70) Moderate positive (negative) correlation

0.70 to 0.90 (- 0.70 to - 0.90) High positive (negative) correlation

0.90 to 1.00 (- 0.90 to - 1.00) Very high positive (negative) correlation

APPENDIX 6: PEARSON CORRELATION BETWEEN PHYSICOCHEMICAL PARAMETERS AND HEAVY METALS

	Sulfate	*Moisture (%)*	*Phosphate*	*organic carbon*	*organic matter*	*pH*	*Conductivity*	*Nitrate*	*Cadmium*	*Iron*	*Copper*	*Zinc*	*Magnesium*	*Chromium*	*Nickel*	*Lead*
Sulfate	1															
Moisture (%)	0.962892	1														
Phosphate	-0.36817	-0.60544	1													
organic carbon	0.234024	-0.03705	0.81778	1												
organic matter	0.234357	-0.03671	0.817582	1	1											
pH	0.057913	-0.21367	0.906876	0.984152	0.984091	1										
Conductivity	0.10887	-0.16345	0.88415	0.99193	0.991887	0.998693	1									
Nitrate	-0.93436	-0.80352	0.012696	-0.5651	-0.56539	-0.40985	-0.45594	1								
Cadmium	-0.35695	-0.0916	-0.73709	-0.99172	-0.99176	-0.95323	-0.96743	0.666381	1							
Iron	-0.42232	-0.65129	0.998262	0.78244	0.782227	0.880466	0.855079	0.071603	-0.69598	1						
Copper	0.848043	0.959594	-0.80493	-0.31675	-0.31642	-0.47992	-0.43445	-0.60354	0.192307	-0.8385	1					
Zinc	0.564922	0.321265	0.559198	0.934436	0.934558	0.856476	0.881742	-0.82187	-0.97244	0.509368	0.041813	1				
Magnesium	0.16742	-0.10487	0.854997	0.997689	0.997665	0.993927	0.998253	-0.50774	-0.9807	0.822946	-0.38047	0.908077	1			
Chromium	-0.35921	-0.09401	-0.73545	-0.9914	-0.99145	-0.95249	-0.96682	0.668184	0.999997	-0.69424	0.189932	-0.973	-0.98022	1		
Nickel	-0.34	-0.07357	-0.74919	-0.99388	-0.99392	-0.95854	-0.97185	0.652785	0.999836	-0.70886	0.210027	-0.96806	-0.98408	0.99979	1	
Lead	0.97924	0.888197	-0.17206	0.426239	0.426549	0.259073	0.308107	-0.98719	-0.53889	-0.22982	0.723021	0.720453	0.363786	-0.54093	-0.52356	1

APPENDIX 7: PEARSON CORRELATION BETWEEN PHYSICOCHEMICAL PARAMETERS and HEAVY METALS

	Acnthp	*Acena*	*Fluorene*	*Anthra*	*Phena*	*Fluor*	*Pyrene*	*Chrysene*	*Benzo(b)fl*	*Benzo(k)fl*	*Benzo(a)pyr*	*1,2-benzo*	*Di benz(a,h)*	*Benzo(g,h,l)*	*ndeno(1,2,3cd)*	*Sulfate*	*Moisture (%)*	*Phosphate*	*rganic carbor*
Acenaphthylene	1																		
Acenaphthene	0.559976105	1																	
Fluorene	0.845382426	0.217795	1																
Anthracene	0.758596697	0.948606	0.457683	1															
Phenanthrene	0.549716843	0.99177	0.2571	0.944114	1														
Fluoranthrene	0.747089366	0.097037	0.820496	0.395746	0.115799	1													
Pyrene	0.094667326	0.222248	0.144339	0.076679	0.259231	-0.28156	1												
Chrysene	0.330749338	0.555287	-0.12549	0.438946	0.477504	-0.18878	0.432262	1											
Benzo(b)flouranthene	0.537604228	-0.38075	0.725123	-0.13763	-0.38582	0.657611	0.02827	-0.12127	1										
Benzo(k)flouranthene	0.563630006	-0.30711	0.83901	-0.02076	-0.2741	0.789415	-0.1309	-0.42068	0.9071843	1									
Benzo(a)pyrene	0.307326877	-0.47959	0.647877	-0.23832	-0.44795	0.735037	-0.05926	-0.4124	0.82330361	0.83276948	1								
1,2-benzoanthracene	0.564595453	-0.30668	0.83787	-0.01963	-0.27411	0.790631	-0.13595	-0.4201	0.90691528	0.99997915	0.831173572	1							
Di benz(a,h)antracene	-0.168345731	-0.50112	0.185853	-0.38358	-0.45665	0.427298	-0.10892	-0.49665	0.30834824	0.35314308	0.782442175	0.3507284	1						
Benzo(g,h,l)pyrene	0.519863136	-0.38573	0.772702	-0.09818	-0.36916	0.815916	-0.15423	-0.34321	0.9435295	0.96525021	0.922904866	0.9652386	0.500690755	1					
Indeno(1,2,3cd)pyrene	0.556151922	-0.30981	0.84606	-0.02869	-0.2737	0.779907	-0.0951	-0.42425	0.90800692	0.99896206	0.84304003	0.9986471	0.369757475	0.96418828	1				
Sulfate	0.265459898	-0.3708	0.343143	-0.2071	-0.34608	0.34571	0.033802	-0.1136	0.61673061	0.61238174	0.366031853	0.6138473	-0.05111116	0.56214138	0.601318059	1			
Moisture (%)	-0.074612368	-0.35125	-0.16933	-0.35568	-0.4079	0.040595	0.207318	0.454887	0.32252769	-0.02701729	0.34407504	-0.0275214	0.383314294	0.20644202	-0.023429577	0.110566	1		
Phosphate	0.298835592	-0.25871	0.395008	-0.093	-0.21949	0.33404	-0.03088	-0.23391	0.52559301	0.62061324	0.256279649	0.6223198	-0.18206146	0.50063121	0.607839731	0.937069	-0.24259095	1	
organic carbon	0.166145946	0.564028	-0.20619	0.45981	0.471591	-0.25897	-0.14012	0.549496	-0.3457387	-0.46890877	-0.553266511	-0.4670202	-0.54423736	-0.4561669	-0.481675049	-0.62779	0.093581414	-0.62733166	1
organic matter	0.166366246	0.564006	-0.20608	0.459844	0.471542	-0.25887	-0.14014	0.549681	-0.3454835	-0.46873097	-0.553243145	-0.4668408	-0.54445779	-0.4559971	-0.481508734	-0.62743	0.093762636	-0.62703855	0.99999989
pH	-0.047101349	0.502178	-0.31094	0.355127	0.431783	-0.33016	-0.08674	0.408222	-0.5057803	-0.59686182	-0.493838825	-0.5965609	-0.2670518	-0.5486717	-0.598277199	-0.87464	0.073318044	-0.86841305	0.922282574
Conductivity	-0.113039177	0.453214	-0.34108	0.297361	0.388876	-0.34014	-0.05882	0.374815	-0.5245108	-0.61924664	-0.446167361	-0.6194531	-0.158873	-0.5512071	-0.617056736	-0.91281	0.118952461	-0.9242747	0.870531236
Nitrate	0.187796078	-0.32807	0.388127	-0.16817	-0.26238	0.331139	-0.00668	-0.40592	0.4695064	0.62434104	0.323790412	0.6251342	-0.02060255	0.49890636	0.618006452	0.86629	-0.35307041	0.964016933	-0.78036321