# ACCUMULATION OF HEAVY METALS AND POLYCYCLIC AROMATIC HYDROCARBONS IN TOPOSEQUENCE AROUND THE INDUSTRIAL AREA OF ABA, NIGERIA.

**BY**
**FRANKLIN, IFEOMA ROSE**
**20184142818**

**A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI, NIGERIA.**

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE (M.Sc) DEGREE IN ENVIRONMENTAL MANAGEMENT (POLLUTION CONTROL)**

**DECEMBER, 2022**

## CERTIFICATION

This is to certify that this study **"Accumulation of Heavy Metals and Polycyclic Aromatic Hydrocarbons in Toposequence around Industrial Area of Aba, Abia State, Nigeria"** was carried out by me **Franklin, Ifeoma Rose** (**Reg. No: 20184142818**) in partial fufilment for the award of the Degree of Master of Science (M.Sc) in Environmental Management in the Department of Environmental Management of the Federal University of Technology, Owerri.

.....
**Prof. P. N. Okeke**
(Supervisor)

13/12/2022
Date

.....
**Dr. (Mrs) N. E. Verla**
(Co-Supervisor)

13/12/2022.
Date

.....
**Dr. C. C. Ejiogu**
(Head of Department)

17/01/23
Date

.....
**Prof. J. D. Njoku**
(Dean, SOES)

17/01/23
Date

.....
**Prof. B. O. Esonu**
(Dean, PG School)

.....
Date

.....
**Prof. S. Y. Mohammed**
(External Examiner)

15/12/2022
Date

## DEDICATION

This work is dedicated to God Almighty for His love and infinite mercy towards me throughout the programme.

## ACKNOWLEDGEMENTS

I would like to thank God Almighty for His infinite grace, love, wisdom, and strength throughout my M.Sc. programme. Without God, this would have been impossible.

I am very grateful to my supervisors, Prof. Okeke Peter N. for his constant academic guidance, encouragement, and support. I am also appreciative of my second supervisor, Dr. (Mrs) Verla E. N. for her thoughtful supports and contributions towards the completion of this programme.

I will use this singular opportunity to acknowledge the Dean SOES Prof. Njoku J.D., the HOD Dr. C.C. Ejiogu., the P.G. coordinators Dr. Emeribeole and Dr. Mgbeahuruike L. U.

I appreciate my lecturers; Prof. Owuama C.O., Prof. Nkwocha E. E., Prof. (Mrs) Akhionbare S.M.O., Prof. Nwoke C.O., Dr. Njoku P.C., Prof. Nwachukwu M.A., Dr Ebe T.E., Dr. Ihejirika C.E., Dr. Ejiogu C.C., DR Amangabara G.T., Dr (Mrs.) Diagi B.E., Dr. Anyanwu J.C., Mr Uzoka C.N., Mr Edo F.A. Mr Iwuji K.M. and other lecturers for their assistance throughout this programme.

I acknowledge the Departmental Secretary and all non-Academic Staff of the Department.

Thanks to my friends and colleagues, who have shown love, support, kindness in various ways. Baridakara Sordum, Anna, Chijioke Uyo (My able course rep.), Chioma, Chinenye, Nlemolisa Oluchi, Ejide Chinwe, ljeoma, Uche, Chinyere, Felicia and others.

To my loving, caring, and ever understanding husband, Engr. Nnamdi Franklin words cannot express my sincere gratitude for the spiritual, moral, and financial supports that you have always provided for me.

To My Lovely children, Chimdinma, Chizaram, Chikamso and King David. You kids are so special to me. I am very grateful to my parents, Sir & Lady A.E Kalu for their prayers and moral supports.

To my wonder siblings, Prince, Bros Gab, Bros Patrick and Joe and my wonderful cousins and in-laws. Thank you all for your supports.

I will not fail to acknowledge My Colleagues, especially Mr. Chukwuemeka F. Nnadozie, Dr. Anyika for their contribution towards this programme.

Specially, I want to thank Mrs. Ogechi Anyanwu for her sincere academic support, prayers and encouragements.

Finally, thanks to everyone who in one way or the other have contributed to the success of this programme.

## TABLE OF CONTENT

## LIST OF TABLES

## LIST OF FIGURES

## ABSTRACT

The simultaneous accumulations of heavy metals and polycyclic hydrocarbons (PAHs) have gained considerable attention since soils contaminated with PAHs were frequently reported to contain high amounts of heavy metal. The present study was carried out to assess heavy metals and polycyclic aromatic hydrocarbons in soils around the industrial area of Aba. Samples were collected from Ogbor hill, Ndi Egoro and Umuobo village. Umuobo village, served as the control. Heavy metals analyzed were lead, cadmium, iron, argon, manganese, mercury, zinc and copper using atomic absorption spectrophotometer method. Polycyclic aromatic hydrocarbon analyzed were naphthalene, acenaphthylene, acenaphthene,fluorine, phenanthrene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (e) pryene, dibeno (a,h) anthracene, Indeno (1,2,3-cd) pyrene, benzo (b) triphenylene and benxo (ghi) perylene using Gas Chromatography-Flame Ionization Detection (GC-FID) method. The statistical methods used were standard error of mean, two way analysis of variance and multiple unpaired T-test of variance. Iron recorded the highest concentration in all the sampling points with the mid slope having the highest concentration of 295.83±1.15 mg/kg and 291.77±5.94 kg/mg (0-15 cm) for Ogbor hill and Ndi Egoro, respectively. While cadmium has the lowest concentration in all the points, with the valley bottom having the lowest with 0.01±0.02 mg/kg and 0.25±0.08 kg/mg in Ogbor hill and Ndi Egoro, respectively. The control recorded a very low concentration of the heavy metals in both sampling sites. The highest was at the crest with the concentration of 0.7±0.00 mg/kg (15-30 cm) in Iron. Mercury and argon were not detected in crest, mid slope and valley bottom of both Ogbor hill and Ndi Egoro. In Ogbor hill, indeno (1, 2, 3-cd) pyrene recorded the highest concentration at both the crest and mid slope, with 2.53±0.43 and 1.02±0.03 respectively. While Benzo (e) pryene recorded the highest concentration at the valley bottom with 0.68±0.28. The control also recorded the lowest concentrations of the entire polycyclic aromatic hydrocarbon. The highest concentration was recorded at the crest with 1.86±1.64 ppm (15-30 cm) of Indeno (1, 2, 3-cd) pyrene. It is recommended that the industry owners/operators should ensure that effluent treatment plants are installed in their facilities, and should be operated at optimum conditions and manned by qualified personnel

**KEYWORDS: Heavy metals, Polycyclic Aromatic Hydrocarbons, Toposequence, Industrial area and Control.**

# CHAPTER ONE

# INTRODUCTION

## 1.1 Background to the study

In the process of industrialization and urbanization, industrial contamination has long been recognized as priority environmental concern. The simultaneous accumulation of heavy metals and Polycyclic Aromatic Hydrocarbons (PAHs) have gained considerable attention since soils contaminated with PAHs were frequently reported to contain high amounts of heavy metals. Several studies carried out have demonstrated that the combination of these two types of contaminants could potentiate great environmental risk to vegetation, soil microbes, and human health (Maier,Schumann, Chang, Talaska and Puga, 2002; Achten and Hofmann 2009; Abarikwu, S., Iserhienrhien, B. and Badejo, T. (2013).

Polycyclic Aromatic Hydrocarbons (PAHs) can be adsorbed not only by the soil, but also by leaves and roots of plants. Direct pollution of the urban environment can be as a result of the washing of these harmful substances such as heavy metals and PAHs by rainfall into the soil (Al-Maliki, 2005; Adriano, D. C (2003).

They are non-biodegradable, hence are not readily detoxified and removed by metabolic activities once they are available in the environment. This may subsequently lead to their buildup to toxic levels or bioaccumulation in the ecosystem. The sources of heavy metals in soil and plants are mainly natural, including geologic sources such as rock formation, soils, and transported sediments by winds, while the artificial sources include industrial sources that supply the heavy metals to the air and soil causing contamination of the environment. It is expected that the heavy metal concentration varied considerably with the polluted, industrial, and contaminated areas, depending on the wind speed and

directions (Ahrens, 2005). The high concentration of heavy metals in soils is reflected by higher concentrations of metals in plants. The polycyclic aromatic hydrocarbons (PAHs) in the environment largely are a product of the incomplete combustion of petroleum, oil, and coal (Adeniyi, A.A. and Afolabi, J.A.2002). Sources in the urban environment include industrial emissions and wastes, power plants, vehicles, mineral/crude oil extraction, and petroleum refining processes. It is conceivable that faster deposition of exhaust aerosol droplets occurs close to the highway, while further spreading mediated by their adsorbed form on the dust particles that are distributed with wind affects other media (example, air, water, soil, and plants). The spatial heterogeneity of concentrations of PAHs in soil and plants is also affected by heterogeneity of soil property. Once PAHs are released into the atmosphere, they attach to particles, and via dry and wet deposition, they tend to accumulate in soils (Agency for Toxic Substances and Disease Registry (ATSDR) (2011).The implication of heavy metals, as well as polycyclic aromatic hydrocarbons (PAHs) and PHs in the environment, is increasingly becoming an issue of global concern especially as the soil makes up an important aspect of the rural and urban environment. Oil increases the levels of heavy metals in the soil, and as a result of its hydrophobic nature, oil reduces water infiltration into the soil. Several earlier reports revealed that human exposure to elevated concentration of heavy metals particularly children may result in several illnesses such as kidney and liver damage, paralysis, convulsion, depression, and pneumonia. Other effects of heavy metals on human health have been reported in several key publications (Ibe, Opara, Ibe and Amaobi, 2019; Ibe, Opara, Ibe, Adindu and Ichu, 2018).

Polycyclic aromatic hydrocarbons, another class of toxic chemicals, are released by low-temperature combustion of environmental waste. Although limited data exist on the distribution and transport of polycyclic aromatic hydrocarbons (PAHs) from environmental waste dumpsites in Nigeria, PAHs are known to be lipophilic and accumulate in the food chain near contaminated sites. (Buszewski, B.,

Jastrzębska, A., Kowalkowski, T. and Górna-Binkul, A. (2000). Their lipophilicity also makes dermal absorption possible. Epidemiological studies on occupational exposure to PAHs indicate that they can contribute to induction of skin and lung cancers. It has been reported that certain PAH metabolites interact with deoxyribonucleic acid (DNA) and are genotoxic, causing malignancies and heritable genetic damage in humans (Tsibart and Gennadiev, 2013).The lower molecular weight PAHs (example, 2-3 rings) such as naphthalene, fluorene, phenanthrene and anthracene have significant acute toxicity to aquatic organisms, while higher molecular weight PAHs (4-7 rings) such as chrysene and coronene do not, but are carcinogenic.

### 1.2 Statement of the research problem

Aba industrial area is characterized with increased human population and urbanization due to high level of industrialization. These activities going on within this vicinity have been recognized as causal factors influencing the generation and accumulation of chemical contaminants in the soils in the environments. However, if particles of soil are ingested or the chemicals are absorbed by plant roots, the toxicants enter the food web and bioaccumulate thereby threatening larger consumers including human.

### 1.3 Aim and Objectives of the study:

This research work is aimed at assessing the heavy metal and polycyclic aromatic hydrocarbon accumulation in toposequence around industrial area of Aba, Nigeria.

The objectives of this research work are;

1. To determine the concentration level of heavy metals and polycyclic aromatic hydrocarbon in the crest, midslope and valley bottom of the study area.

2. To compare the level of heavy metals concentration polycyclic aromatic hydrocarbon in the polluted area with control.
3. To compare the results (heavy metal and polycyclic aromatic hydrocarbons) with that of regulatory bodies (e.g. NESERA).

### 1.4 Justification of the study

The need for this study became necessary owning to the paucity of PAH data in the study area. There are few documented studies on soil of this area, and these studies reported heavy metals and PAH on the surface soil and in groundwater sources (Muze *et al.*, 2020; Eze and Ogbuehi, 2015). Often times, heavy metals and polycyclic aromatic hydrocarbons are the main constituents of effluents and solid waste released from production industries, mining, smelting and metallurgical activities. Also through some agricultural practices such as the use of pesticides and fertilizers, these heavy metals are introduced into the environment; rainfall also washes these pollutants into the soil. The soil is also polluted by the dismantled components if burnt, could lead to severe contamination of the surrounding air, soil, and river sediments by organic contaminants, such as PAHs, polychlorinated biphenyls (PCBs), and polybrominated diphenyls ethers (PBDEs).Long-term exposure to these pollutants could lead to severe problems such as brain dysfunction, cancer, tumors, nervous system, and reproductive disorders in humans and animals. The ecological as well as human health risks of PAHs are attracting serious concern due to their carcinogenic, mutagenic, as well as its persistent characteristics. The importance of this study arises from the urgency to regularly monitor PAH levels and heavy metal in the environment.

## 1.5 Scope and limitations of the study

The research work entails collection of samples from soil in Ogbor hill (Ikot Ekpene road) and Ndi Egoro. Samples were collected from the crest, mid slope, valley bottom and Umuobo village which will serve as the control. Heavy metals and polycyclic aromatic hydrocarbons were determined by atomic absorption spectrophotometry and gas chromatography coupled and mass spectrophotometer (GC-FID). The heavy metals determined were: iron, zinc, copper, manganese, lead, cadmium, argon and mercury. The polycyclic aromatic hydrocarbons investigated included: Naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (e) pryene, dibeno (a,h) anthracene, Indeno (1,2,3-cd) pyrene, benzo (b) triphenylene and benxo (ghi) perylene.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Heavy Metals

Metals in general are class of chemical element that forms lustrous solid that are good conductors of heat and electricity. Heavy metals are defined in a number of ways based on cationic hydroxide formation, hard soft acid and bases, and more recently, association with eutrophication and environmental toxicity (Njoku, P., Ibe, F.C., Alinnor, J. and Opara, A. (2016).Heavy metals also known as trace elements had been reported to come from weathering of rock (natural) minerals which may be increased substantially by anthropogenic activities such as industrial and agricultural activities and enter our environment (Kabata-Pendias, 2000).

Heavy metals are metallic chemical elements that have relatively high density, toxic or poisonous at low concentration. They are natural components of the earth crust that cannot be degraded or destroyed. These contaminants which mostly occur as trace metals adsorb onto the soil matrix (Umar and Opaluwa, 2010). Heavy metals constitute an ill-defined group of inorganic chemical hazards, and those most commonly found at contaminated sites include lead (Pb), chromium (Cr), arsenic (As), zinc (Zn),cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni), and so on.

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. They may enter the human body through food, water, air or absorption through the skin when they come in contact with humans in agriculture, manufacturing, pharmaceutical, industrial or residential settings. If the soil particles containing heavy metals are ingested, they enter the food web,

shellfish, fish, and other organisms which tend to bioaccumulate these toxicants thereby threatening human existence (Madu, Tagwoi and Babalola, 2008).

### 2.1.1 Sources of metals in the environment

Heavy metals occur naturally in the environment from pedogenetic processes of weathering of parent materials and also through anthropogenic sources (Figure 2.3). The most significant natural sources are weathering of minerals, erosion and volcanic activity, while the anthropogenic sources depend upon human activities such as mining, smelting, electroplating, use of pesticides and phosphate fertilizer discharge, as well biosolids (for example, livestock manures, composts, and municipal sewage sludge), atmospheric deposition, (Nwachukwu, E., Newman, Y. and Janefrances, I. (2017). The heavy metals essentially become contaminants in the soil and water environment because of their excess generation by natural and man-made activities, transfer from mines to other locations where higher exposure to humans occurs, discharge of high concentration of metal waste through industries, and greater bioavailability (Wasiullah, Malaviya, Pandiyan, Singh, Sahu, Shukla, Singh, Rai, Sharma, Lade and Paul, 2015).

### 2.1.2 Potential Risks of Heavy Metals.

The most common heavy metals found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Cu, and Hg (Kabata-Pendias, and Pendias, 2001). These metals are important since they are capable of decreasing crop production due to the risk of bioaccumulation in the food chain (Sumner, 2000). There is also the risk of superficial and groundwater contamination. The knowledge of the basic chemistry and associated health consequences of these heavy metals is important in understanding their behaviour and remedial options. The fate and transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal (Bolan, Ko, Anderson and Vogeler, 2008).

Once in the soil, heavy metals are absorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying mobility, and toxicity. This distribution is believed to be controlled by reactions of heavy metals in soils such as; mineral precipitation and dissolution, ion exchange, adsorption, and desorption, aqueous complexation, biological immobilization and mobilization, and plant uptake (Zhao and Kaluarachchi, 2002).

### 2.1.2 Lead

Lead is not an essential element. It is a naturally occurring, bluish gray metal usually found as a mineral combined with other elements, such as sulphur (PbS, $PbSO_4$), or oxygen ($PbCO_3$). Other uses include solders, bearings, cable covers, ammunition, plumbing, pigments, and caulking. Inhalation and ingestion of lead are the two routes of exposure, and the effects from both are the same. The most serious source of exposure to soil lead is through direct ingestion (eating) of contaminated soil or dust (Baldwin and Marshall, 1999). In soils testing high in lead, it is possible for some lead to be taken up. It is well known to be toxic and its effects have been more extensively reviewed than the effects of other trace metals. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys.

Lead poisoning, which is so severe as to cause evident illness, is now very rare. Lead performs no known essential function in the human body, it can merely do harm after uptake from food, air, or water. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys. Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing young and infants being more sensitive than adults. Lead accumulates in the body organs (brain),

which may lead to poisoning or even death. The gastrointestinal tract, kidneys, and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration (Rosen, 2002).

### 2.1.3 Chromium

Chromium is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$. Major sources of Cr contamination include releases from electroplating processes and the disposal of Cr containing wastes (Smith and Means, 1995). Chromium (VI) is the form of Cr commonly found at contaminated sites. Also, chromium (VI) is the dominant form of Cr in shallow aquifers where aerobic conditions exist. Chromium (VI) is the more toxic form of chromium and is also more mobile. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater. Chromium is associated with allergic dermatitis in humans (Scragg, 2006)

### 2.1.5 Cadmium

Cadmium is one of the *big three* heavy metal poisons and is not known for any essential biological function. In its compounds, Cd occurs as the divalent Cd(II) ion. Cadmium has a chemical similarity to that of Zn, an essential micronutrient for plants and animals. This may account in part for Cd's toxicity because Zn being an essential trace element, its substitution by Cd may cause the malfunctioning of metabolic processes (Manahan, 2003). The most significant use of Cd is in Ni/Cd batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance, and high tolerance to physical and electrical stress. Other uses of cadmium are as pigments, stabilizers for polyvinyl chloride (PVC), in alloys and electronic compounds. Cadmium is

also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products. In addition, acid rain and the resulting acidification of soils and surface waters have increased the geochemical mobility of Cd, and as a result its surface-water concentrations tend to increase as lake water pH decreases. Cadmium is produced as an inevitable by-product of Zn (Manahan, 2003). The application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils.

Exposures of humans to Cd through their food chain are through the consumption of certain species of shellfish or vegetables. Cadmium in the body can affect several enzymes. It is believed that the renal damage that results in proteinuria is the result of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules (Manahan, 2003).

### 2.1.6 Copper

Copper is the third most used metal in the world. Copper is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. Copper normally occurs in drinking water from Cu pipes, as well as from additives designed to control algal growth. Research shows that most Cu introduced into the environment rapidly becomes stable and results in a form which does not pose a risk to the environment (Eriksson and Anderson, 1997). In fact, unlike some man-made materials, Cu is not magnified in the body or bioaccumulated in the food chain. In plants, Cu is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage (Davies and Jones, 1988).

The connection between soil and water contamination and Cu uptake by plants is determined by many chemical and physical soil factors as well as the physiological properties of the crops. Soils

contaminated with Cu may pose negative effects of metals on crop growth and yield by entering the human food chain with a potentially negative impact on human health. Furthermore, reduction of crop yield by a few percent could lead to a significant long-term loss in production and income.

### 2.1.7 Zinc

Zinc occurs naturally in soil, but Zn concentrations are rising unnaturally, due to anthropogenic additions. Most Zn is added during industrial activities, such as mining, coal, and waste combustion and steel processing (Lasat, 2000). Many foodstuffs contain certain concentrations of Zn. Drinking water also contains certain amounts of Zn, which may be higher when it is stored in metal tanks. Industrial sources or toxic waste sites may cause the concentrations of Zn in drinking water to reach levels that can cause health problems. Zinc is a trace element that is essential for human health. Zinc shortages can cause birth defects. The world's Zn production is still on the rise which means that more and more Zn ends up in the environment. Water is polluted with Zn, due to the presence of large quantities present in the wastewater of industrial plants.

A consequence is that Zn polluted sludge is continually being deposited by rivers on their watershed. Some fish can accumulate Zn in their bodies, when they live in Zn-contaminated waterways. When Zn enters the bodies of these fish, it is able to biomagnify up the food chain (Eriksson and Anderson, 1997). Water-soluble zinc that is located in soils can contaminate groundwater. Plants often have a Zn uptake that their systems cannot handle, due to the accumulation of Zn in soils. Finally, Zn can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter (Manahan, 2003).

## 2.2 Polycyclic Aromatic Hydrocarbon

A polycyclic aromatic hydrocarbon (PAH) is a hydrocarbon, a chemical compound containing only carbon and hydrogen, this compound is composed of multiple aromatic rings. The group is a major subset of the aromatic hydrocarbons. The simplest of such chemicals are naphthalene, having two aromatic rings, and the three-ring compounds anthracene and phenanthrene. The terms polyaromatic hydrocarbon or polynuclear aromatic hydrocarbon are also used for this concept (Agency for Toxic Substances and Disease Registry, 2011).

Polycyclic aromatic hydrocarbons are organic pollutants and composed of two or more fused aromatic rings of carbon and hydrogen atoms, which are primarily colorless, white, or pale yellow solid compounds (Maslin, P. and Maier, R.M (2000); Suman, Sinha and Tarafdar, 2016). The molecular arrangements of aromatic rings in space can be linear, angular, or in clusters (Abdel-Shafy and Mansour, 2016).Polycyclic aromatic hydrocarbons (PAHs) are compounds consisting of two or more fused rings that have raised more concerns due to their persistent property and toxicity featured by considerably high direct-acting mutagenicity and carcinogenicity (Yang, Zhang and Korenaga 2002).PAHs are characterized through their low water solubility, low vapor pressure, and high melting and boiling points, depending on their structures (Lee and Vu, 2010).PAHs with increased molecular weight are tending to decrease water solubility and increase lipophilicity, making them more recalcitrant compounds (Okere and Semple, 2012).

### 2.2.1 Classification of Polycyclic aromatic hydrocarbon

With the number of rings present in the compounds, PAHs are classified into light-molecular weight PAHs (LMW PAHs; having two or three aromatic rings) and High-molecular weight PAHs (HMW PAHs; having four or morearomatic rings). Depending upon their molecular weight, they

are emitted either as gaseous phase (LMW PAHs) or in the particulate form (HMW PAHs) (Lee and Vu, 2010).

PAHs with two or three rings (naphthalene, acenaphthene, anthracene, fluorene, phenanthrene), are present in the air mainly in the gas phase, whereas those with four rings (fluoranthene, pyrene, chrysene) are present in both the gas phase and the aerosol, and those having five or more rings (benzo[a]pyrene, benzo[g,h,j]pyrene) are mainly condensed on suspended particulate matters. These compounds never occur individually; the presence of one of the compounds from this group indicates the presence of the others (Abdel-Shafy and Mansourb, 2016).

Based on the structure of rings, PAHs are also classified as: alternant PAHs, which contain only fusion of six carbon benzene rings, whereas the non-alternant PAHs like fluorene contain fusion of six carbon benzene rings along with an additional ring of less than six carbon (Gupte, Tripathi, Patel, Rudakiya and Gupte, 2016).

### 2.2.2 Properties of Polycyclic aromatic hydrocarbon

#### 2.2.2.1 Physiochemical

PAHs are nonpolar and lipophilic. Larger PAHs are generally insoluble in water, although some smaller PAHs are soluble (Feng, Pisula and Müllen, 2009). The larger members are also poorly soluble in organic solvents and in lipids. The larger members, example, perylene, are strongly colored (Ivan and Sven, 2012)

#### 2.2.2.2 Redox

Polycyclic aromatic compounds characteristically yield radical anions upon treatment with alkali metals. The large PAH form dianions as well (Castillo,Metta-Magaña and Fortier2016). The redox potential correlates with the size of the PAH.

### 2.2.3 Sources of polycyclic aromatic hydrocarbon

PAHs find their way into the environment through natural sources such as volcanoes, forest fire, and biosynthetic process. It could also be emitted from diverse anthropogenic sources such as vehicle exhausts; power plants; chemical, coke, and oil-shale industries; and urban sewage (Yunker, Macdonald, Vingarzan, Mitchell, Goyette and Sylvestre, 2002).

The sources of PAH pollution are categorized mainly into two, such as anthropogenic emission sources and natural emission sources (Mojiri, Zhou, Ohashi, Ozaki and Kindaichi, 2019).

#### 2.2.3.1 Natural emission

PAHs can be formed naturally and many of them are recalcitrant and have toxic properties (Kamal, Cincinelli, Martellini and Malik, 2015; Li, Huijbregts and Jolliet, 2015; Wang, Dao, Zhang and Teng, 2015).

Natural emission sources such asvolcanic eruptions, natural forest fire, and moorland fire causedby lightning flashes are negligible or less important (Srogi,2007; Ravindra, Sokhi and Van Grieken, 2008; Abdel-Shafy and Mansour, 2016).

#### 2.2.3.2 Anthropogenic emission

Anthropogenic emission sources are the main determinants of PAH pollution, which can be divided into four types, i.e., industrial, mobile, domestic, and agricultural emission sources (Ravindra, Sokhi and Van Grieken, 2008). Incomplete combustion is the prime source of PAH emissions by various industrial activities such as waste incineration, iron and steel production, aluminum production, cement manufacturing, coal-tar pitch production, dye manufacturing, asphalt industries, rubber tire manufacturing, fungicide and insecticide production, exhaust from refineries, and power production (Srogi, 2007; Ravindra, Sokhi and Van Grieken, 2008; Abdel-Shafy and Mansour, 2016; Gupte, Tripathi, Patel, Rudakiya and Gupte, 2016; Mojiri, Zhou, Ohashi, Ozaki and Kindaichi, 2019).

##### 2.2.3.2.1 Industrial emission

Other industrial emission sources are coal gasification, electric arc furnace, oxygen furnace, diesel engine, and gasoline-powered engines of large machineries (Srogi, 2007; Ravindra, Sokhi and Van Grieken, 2008).

##### 2.2.3.2.2 Mobile emission

Mobile emission sources include exhaust from many vehicles like aircrafts, ships, trains, and off-road heavyweight and lightweight vehicles (Srogi, 2007;Ravindra, Sokhi and Van Grieken, 2008).

##### 2.2.3.2.3 Domestic emission

Domestic emission sources involve household activities suchas garbage burning, coal coking, wood burning, cooking on oil/gas burners and kerosene/wood stoves, and other residential heating (Johnsen

and Karlson, 2007; Ravindra, Sokhi and Van Grieken, 2008;Gupte, Tripathi, Patel, Rudakiya and Gupte, 2016).

#### 2.2.3.2.4 Agricultural emission

Agricultural emission sources are open biomass burning and agricultural waste burning when burning is performed under suboptimum combustion conditions (Ravindra, Sokhi and Van Grieken, 2008).

High PAH pollution in a rural area is mainly due to domestic and agricultural sources, whereas in an urban area due to industrial, mobile, and domestic sources.

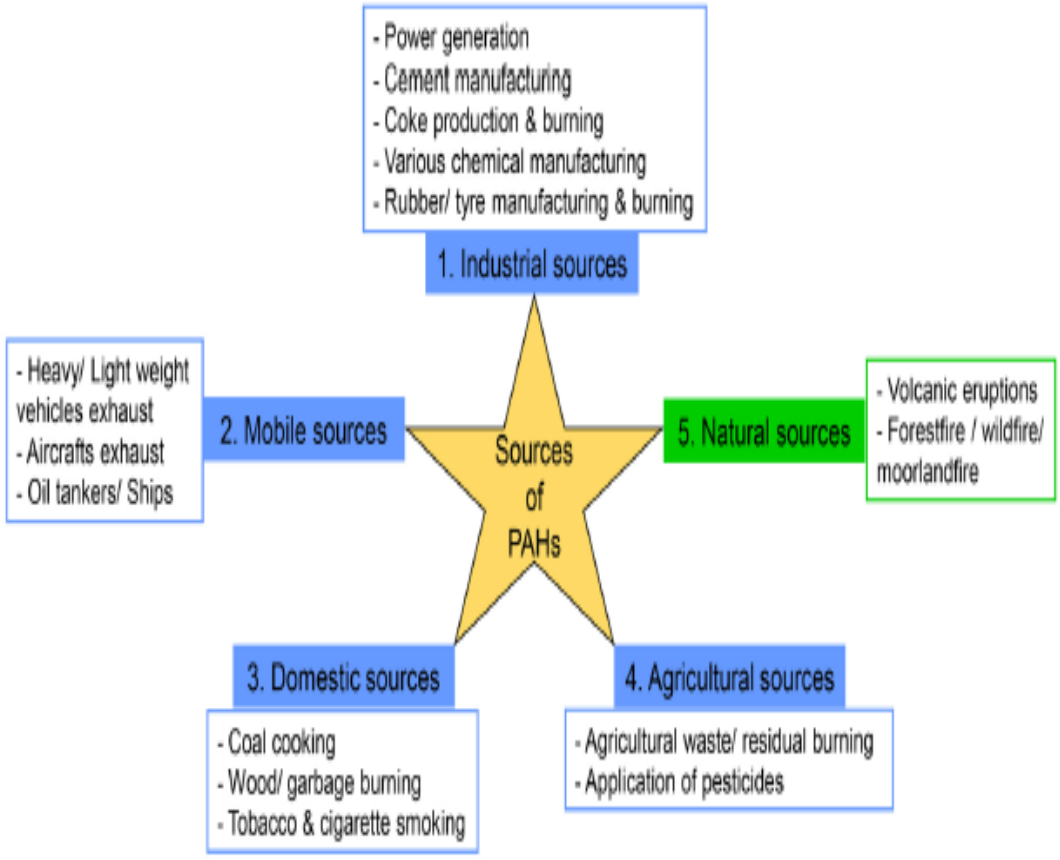


**Figure 2.1 Sources of Polycyclic aromatic hydrocarbon. (Patel, Shaikh, Jain, Desai and Madamwar,2020).**

The PAH sources are also categorized based on their origin of production into three types, that is, pyrogenic, petrogenic, and biogenic (Mojiri, Zhou, Ohashi, Ozaki and Kindaichi, 2019).

**Pyrogenic PAHs** are formed through unintentionally incomplete combustion of organic materials at very high temperatures (350–1,200_C) under no or low oxygen conditions (Abdel-Shafy and Mansour, 2016).Some intentional pyrolytic processes such as thermal breaking of petroleum complex compounds into lighter hydrocarbons and distillation of coal into coal tar and coke also produce pyrogenic PAHs. The concentrations of pyrogenic PAHs are generally higher in urban areas (Abdel-Shafy andMansour, 2016;Mojiri, Zhou, Ohashi, Ozaki and Kindaichi, 2019). **Petrogenic PAHs** are present in petroleumand its by-products that are widespread due to storage, transport, use, and leakage of crude oil and its products (Abdel-Shafy and Mansour, 2016). Pyrogenic sources are predominated byHMW PAHs, and petrogenic sources consist majorly of LMWPAHs (Marris, Kompella, Miller, Incardona, Brette and Hancox, 2020).

**Biogenic PAHs** are synthesized by biological entities like microorganisms, phytoplankton, algae,and plants and during slow biological conversion of organic materials (Mojiri, Zhou, Ohashi, Ozaki and Kindaichi, 2019).

Atmospheric PAHs (gaseous phase as aerosols) are deposited in water, soil, and plants in the particulate phase through dry/wet deposition processes (Abdel-Shafy and Mansour, 2016).

### 2.2.4 Polycyclic hydrocarbon exposure

Accumulation of PAHs in soil/sediment is responsible for further transport of pollution to the groundwater, plants, and food, example, plant roots absorb PAHs from polluted soil and translocate to the farther plant parts. Exposure to PAHs is unavoidable in the current situation. PAH exposure

occurs mainly via three routes, i.e., inhalation, ingestion, and dermal contact (Burchiel and Luster, 2001). Itis also possible that exposure can occur via more than one route, simultaneously, e.g., dermal and inhalation exposures from contaminated soil (Rengarajan, Rajendran, Nandakumar, Lokeshkumar, Rajendran and Nishigaki, 2015; Abdel-Shafy and Mansour, 2016). For many people, the primary exposure occursat the workplace, e.g., workers in coke manufacturing factoriesand food processing industries, traffic police through inhalation of vehicle exhaust and road dust containing PAHs (Lee and Vu,2010). All are not workplace-based exposure, such as consuming polluted water, grilled and smoked food items, smoking, and so on(Lee and Vu, 2010; Suman, Sinh and Tarafdar2016). For smoking people, one cigarette causes an intake of 20–40ng of benzo(a)pyrene(Skupinska, Misiewicz and Kasprzycka-Guttman, 2004). Up to 70% of PAH exposure can berelated to diet for non-smoking persons (Skupinska, Misiewicz and Kasprzycka-

Guttman, 2004).In drinking water, PAH concentration varies between 1mg/Land 11mg/L, and the highest acceptance by WHO forbenzo(a)pyrene is 0.7mg/L (Skupinska, Misiewicz and Kasprzycka-Guttman, 2004). PAHs are formed during domestic and industrial food processing like roasting, toasting, drying, grilling, frying, baking, and barbecuing (Rose, Holland, Dowding, Petch, White and Fernandes,2015). Vegetables and fruits may be contaminated by their growth in PAH-polluted soil and atmospheric deposition (Zelinkova and Wenzl, 2015).

Duedahl-Olesen, Aaslyng, Meinert, Christensen, Jensen and Binderup (2015). Polycyclicinvestigated the presence of PAH [chrysene, benzo(a)pyrene,benzo(a)anthracene, benzo(b)fluoranthene] in 18 brands of tea and 13 brands of coffee. The highest PAH4 was detected in black tea (25–115 mg/kg) and in instant coffee (2.2–5.1 mg/kg).As per report of the German Environment Agency, PAHs are found in using products, e.g., toys, bathing shoes, mouse pads, bicycle handles, many sports items, etc., daily (Brandtand Einhenkel-Arle, 2016). Paschke, Hutzler, Brinkmann, Henkler and Luch, (2015)

detected benzo(a)pyrene, pyrene, phenanthrene, and naphthalene in newspaper's ink at levels up to 52, 553, 778, and 283 mg/kg, respectively.

#### 2.2.4.1 Effects of PAHs exposure

Exposures from various occupations and high levels of pollutant mixtures containing PAHs are known to result in symptoms such as eye irritation, nausea, vomiting and diaorrhea. Mixtures of PAHs are also known to cause skin irritation and inflammation. Anthracene, benzo(a)pyrene, and naphthaleneare direct skin irritants while anthracene and benzo(a)pyrene are reported to be skin sensitizers, i.e. as cause of an allergic skin response in animals and humans (Unwin, Cocker, Scobbie and Chambers,2006).

A series of health problems (an increased risk of skin, lung, bladder, and gastrointestinal cancers) for workers exposed to mixtures of PAHs and other work place exposure of PAH chemicals have been reported (Armstrong, Hutchinson, Unwin and Fletcher, 2004) (Smith, A.H., Lingas, E.O. and Rahman, M. (2000), Diggs, Huderson, Harris, Myers, Banks and Rekhadevi,2011), PAH example, BaP and Pyrene has been identified as the cause of cancer in laboratory animals. Repeated skin contact to the PAH naphthalene can result in redness and inflammation of the skin (Kem, 2007). DNA damage induced by PAH exposure has been demonstrated by numerous authors (Gunter, Divi, Kulldorff, Vermeulen, Haverkos and Kuo, 2003; John, Ragavan, Pratt, Singh, Al-Buheissi and Matanhelia, 2009; Garcia-Suastegui, Rose, M., Holland, J., Dowding, A., Petch, S. R., White, S. and Fernandes, A. (2015). Long term exposure to PAHs is suspected to raise the risks of cell damage via gene mutation and cardio pulmonary mortality.

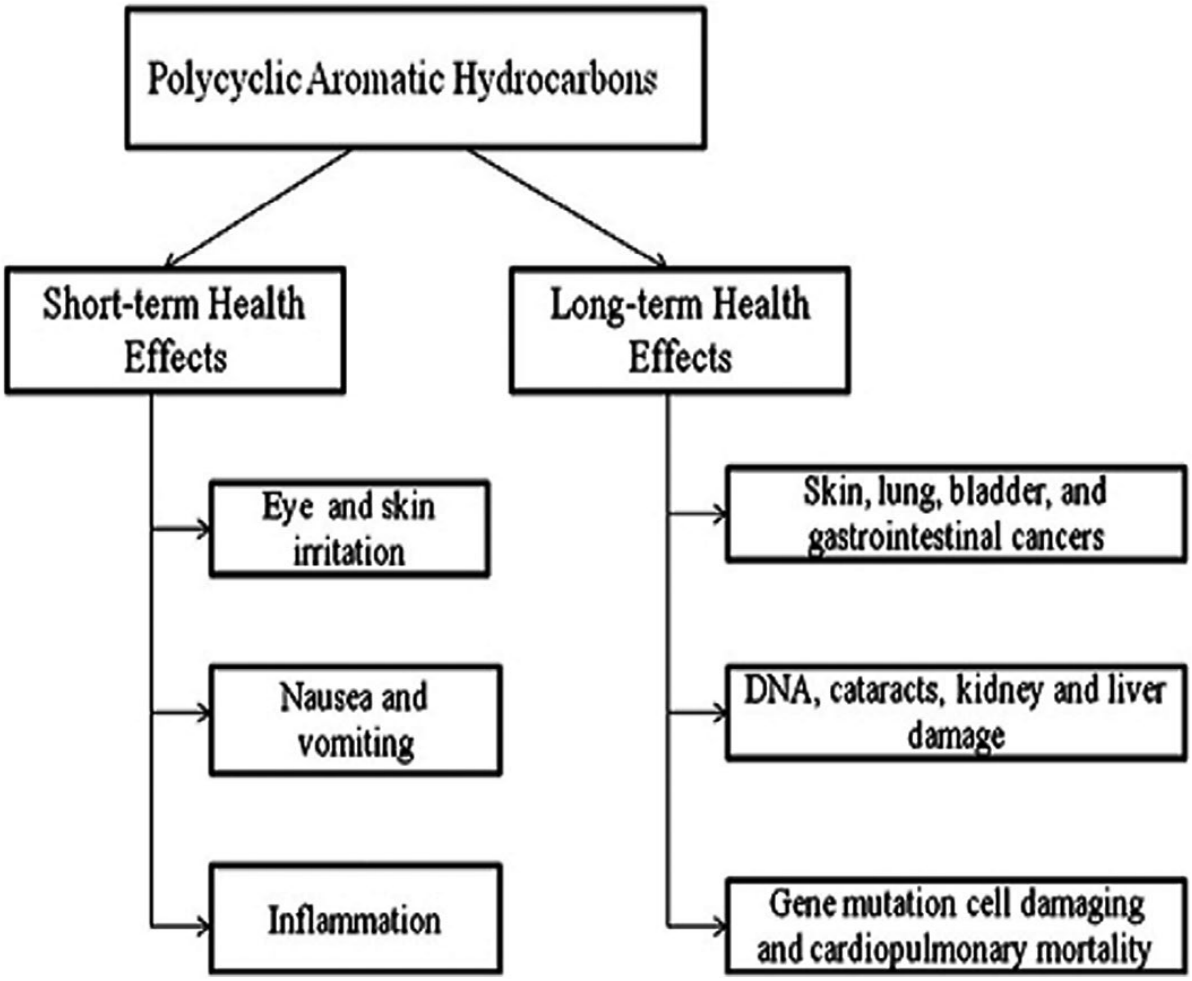


**Figure 2.2. Flow chart showing short and long term health effects of exposure to PAHs (Kim *et al.*, 2013).**

### 2.2.5 PAHs in surface soils

PAHs in the Atmosphere are continuously deposited to the soil by dry or wet deposition processes. Automotive exhaust from adjacent roadways is one of the sources these PAHs. Other PAHs are from more distant sources and have been carried various distances through the air. In the meantime, PAHs can be added to soils if fill materials contain PAHs. These PAHs can become mobile when they are deposited onto the earth's surface. Since the majority of PAHs in the soil will be bound to soil particles (Masih and Taneja, 2006; Cachada, Pato, Rocha-Santos, Duedahl-Olesen, L., Aaslyng, M., Meinert, L., Christensen, T., Jensen, A.H. and Binderup, M.L. (2015). In the subsurface, the most important factor influencing the PAH mobility of particulates is the sorbet particulate size and the pore throat size of the soil. The pore throat is defined as the smallest opening found between individual grains of soli (Huang, j., Huang, Y., Pontius, R.G. and Zhang, Z. (2015).

The tendency of PAHs to be sorbet to soil depend on both the properties of the PAH and the soil. Therefore, PAH sorption is one of the processes that govern the soil mobility of individual PAHs. Numerous studies of the correlation of the partition coefficient with soil properties have found that the organic carbon content (f) usually yields the most significant correlation (Electric Power Research Institute, 2000). In determining the sorption of PAHs to soils, octanol-water partitioning coefficient of PAHs is important. The solubility of an organic compound in water is related to the octanol-water partitioning coefficient (Kow) (Schwarzenbach, Gschwend and Imboden, 1993).As the Kow increases, the aqueous solubility decreases and the tendency for sorption to a particular soil increases. Nevertheless, the Kow and solubility can affect PAH mobility in soil. Other factors such as soil conductivity also have a significant influence on PAH movement (Shang, Kim and Haberl,2014).

### 2.2.6PAHs in sediments

PAHs are deposited to the sedimentary environment by similar processes that govern the deposition to surface soils. The PAHs sorbet to atmospheric particles can settle on the surface of lakes, streams, and oceans by dry or wet deposition in the rural areas. There they are dispersed by currents and eventually become integrated with the sediment. On the other hand, sediments near urban centers are influenced by atmospheric deposition of PAHs. PAHs from storm and sanitary sewer effluents as well as roadway runoff are also part inputs in the sediments near urban centers. Eventually, some of the PAHs will be sorbet to particles, settle, and become part of the sedimentary record. This record has been used by several authors by examining the depositional history in sediment cores to identify trends of PAH input into the environment.

These cores are usually taken in anoxic sediment, where there is no oxygen in the water (Electric Power Research Institute, 2000; Tehrani, Hshim, Sulaiman, Tavakoly and Salleh, 2012). Because their non-polar structures inhibit them from dissolving in water, PAHs are incorporated into sediments and are immobile. Nevertheless, PAHs are not completely insoluble, particularly the lower molecular weight PAHs. Thus, small amounts of PAHs do dissolve and become included in the pore water where they are bio available. The presence of pore water organic colloids can increase the concentrations of PAHs beyond their aqueous solubility because PAHs will be sorbet onto these organic colloids. These in turn are easily transported through the pore spaces of the sediment. Thus, the sorption to colloids can increase the mobility and bioavailability of PAHs in sediments (Dong, Chen and Chen, 2012).

## 2.3 Chemistry of Soil

Soil is a mixture of organic matter, minerals, gases, liquids, and organisms that together support life. Earth's body of soil, called the pedosphere, has four important functions: as a medium for plant growth, as a means of water storage, supply and purification, as a modifier of Earth's atmosphere and as a habitat for organisms. All of these functions, in their turn, modify the soil and its properties. Soil is also commonly referred to as earth or dirt; some scientific definitions distinguish *dirt* from *soil* by restricting the former term specifically to displaced soil. The pedosphere interfaces with the lithosphere, the hydrosphere, the atmosphere, and the biosphere (Chesworth, 2008). Soil, the biologically active, porous medium that has developed in the uppermost layer of the earth's crust. It is one of the principal substrate of life on earth, serving as a reservoir of water and nutrient, as a medium for the filtration and breakdown of injurious waste, and as a participant in the cycling of carbon and other elements through the global ecosystem. It has evolved through weathering processes driven by biological, climatic, geologic and topographic influences (Sposito, 2021).

Soils have a unique structural characteristic that distinguishes them from mere earth materials and serves as a basis for their classification: a vertical sequence of layers produced by the combined actions of percolating waters and living organisms. These layers are called horizons, and the full vertical sequence of horizons constitutes the soil profile. Soil horizons are defined by features that reflect soil-forming processes. For instance, the uppermost soil layer (not including surface litter) is termed the A horizon. This is a weathered layer that contains an accumulation of humus (decomposed, dark-coloured, carbon-rich matter) and microbial biomass that is mixed with small-grained minerals to form aggregate structures. The soil profile, showing the major layers from the O horizon (organic material) to the R horizon (consolidated rock).

Below the A and B horizons is the C horizon, a zone of little or no humus accumulation or soil structure development. The C horizon often is composed of unconsolidated parent material from which the A and B horizons have formed. It lacks the characteristic features of the A and B horizons and may be either relatively unweathered or deeply weathered. At some depth below the A, B, and C horizons lies consolidated rock, which makes up the R horizon (Sposito, 2021).

# CHAPTER THREE

# MATERIALS AND METHODS

## 3.1 Study Area

### 3.1.1 Location

Aba lies along the west bank of the Aba River, and is at the intersection of roads leading to Port Harcourt, Owerri, Umuahia, Ikot Ekpene, and Ikot Abasi. The city became a collecting point for agricultural products following the British made railway running through it to Port Harcourt. Aba is a major urban settlement and commercial center in a region that is surrounded by small villages and towns. The indigenous people of Aba are the Ngwa. Aba is well known for its craftsmen. The coordinate of the study area lies within latitudes 5° 06' 60.00" N and Longitude 7° 21' 59.99" E.

### 3.1.2 Climate

The study area falls within the humid tropical rainforest climate. The average rainfall for the area is about 2285 mm and falls from March to November with a relative humidity of 80% and mean temperature of 27 $^{o}$C. Most parts of the area are flooded during the rainy season due to poor drainage system and construction. The dry season in the area is from November to March and is characterized by dry, cold and windy weather, with little or no rainfall. The temperature is highest in December and lowest in February due to the harmattan (Ijeh and Onu, 2013).

### 3.1.3 Soil and geology

The rock system and geological history of this area are due to events that took place during the Mesozoic and Cenozoic eras respectively. Her geological structure is divided into three namely; upper coal measure, false-bedded sand stones, and lower coal measure. The upper coal measure formation is the largest geological formation in this region. It comprises mainly of coarse grains, alternating sediments of the grey sand, dark shale which contains sands of impure coal in place of vertical horizon (Jimoh, 2005).

Soil around these areas are compressible, friable, very loose and are suitable as an embankment material for road pavement. They are however unsuited for use in construction of water reservoirs like earth dams and leaves due to their moderate permeability characteristics.

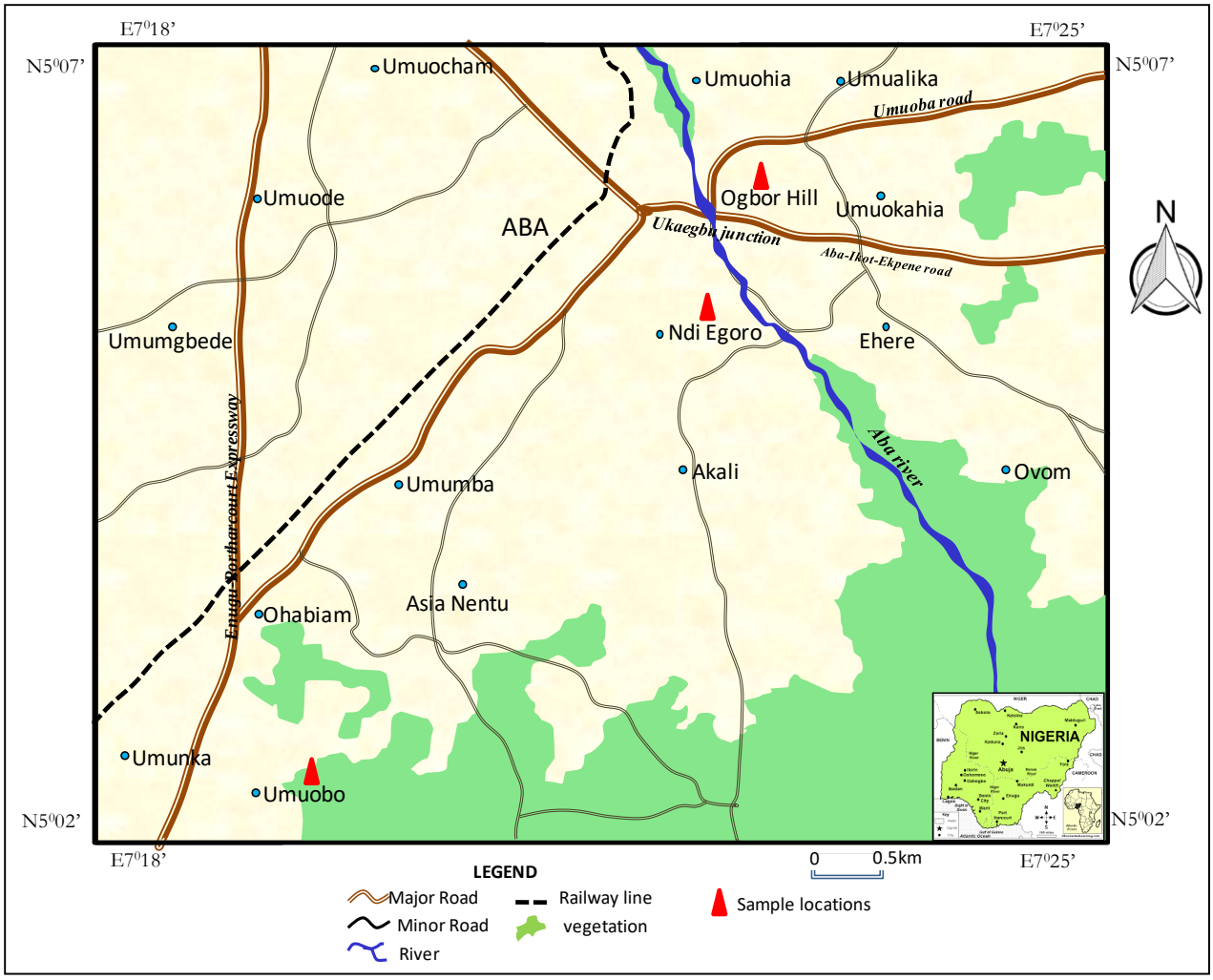


**Figure 3.1: Location map of the study area (Source: Nigeria Geological Survey Agency, 2004)**

### 3.2Soil Sampling and Preparation

The samples were collected from Industrial area in Aba which include; Ogbor hill (Ikot Ekpene road) and Ndi Egoro while Umuobo village serves as the control. Samples were collected randomlyat 5m distance from three different points and combined to form a composite sample, with this process repeated at three different depths (0-15 cm and 15-30 cm) for heavy metal determination and two depths (0-15 cm and 15-30 cm) for PAH determination (modification from Adeyi and Oyeleke, 2017).

Samples for PAH determination were collected with a stainless steel hand trowel, while plastic was used for collection of samples for heavy metal determination. The stainless hand trowel and plastic were cleaned thoroughly to prevent cross contamination. Samples for PAHs were packed in pre-cleaned aluminum foil, which was previously solvent rinsed and dried at $80^{\circ}$C. Polyethylene bags were used for packing soils for heavy metal determination. Samples for metals were air-dried in the laboratory after manual removal of stones, twigs and other large materials then ground in a porcelain mortar and passed through a 2-mm sieve. PAH samples were preserved on ice and kept in the refrigerator prior to extraction and analyses. This method was a modification from Adeyi and Oyeleke (2017).

### 3.3 Laboratory analyses

#### 3.3.1Heavy metal determination

Five grams (5 g) of the sieved samples were weighed into digestion tubes and 10 ml aqua regia (concentrated nitric acid, hydrogen chloride and hydrogen fluoride ($HNO_3$, HCl,HF) ratio 5:3:2 v/v) added (modification from Ibe, Opara, Ibe, Adindu and Ichu,2018). The tubes were covered, heated in a water bath to $100^0$C for 2 hours with intermittent shaking, cooled to room temperature, and then

filtered using filter papers (pore size 110 mm). The filtrate was diluted with distilled water to 25 mL and analyzed for total lead (Pb), cadmium (Cd), iron (Fe), argon (Ar), manganese (Mn), mercury (Hg), zinc (Zn) and copper (Cu) using atomic absorption spectrophotometer.

### 3.3.2Analysis of Polycyclic Aromatic Hydrocarbons in the Samples

The extraction and analysis of soil samples for PAH characterization followed the method in Nor and Suhaimi (2013). In this method, 500 mg of the soil samples were dissolved using a mixture of 25 ml n-hexane and acetone (7:3, v/v). A microwave extraction arrangement was used with its pressure carefully controlled for 45 minutes. After cooling, the extract was filtered with a Whatman glass fiber filter in a glass bottle, followed by a concentration of the extract to 1.5 ml using a rotatory evaporator. PAH was determined by the GC quadrupole Mass Spectrometer (GC-FID) (Agilent 5975 MSD). The samples were separated into its components by chromatographic separation using a capillary column of an internal diameter of 30 m×0.25 mm and film thickness of 0.25 μm, HP- 5MS and a helium carrier gas of high purity (99.5%), having a flow rate of 1 mL/min from a steel cylindrical pipe. The chromatographic separation conditions include an injector temperature of 250˚C and an initial 70˚C temperature of the chromatographic column which was held for 1 minute. The temperature increase by 30˚C/min to 200˚C, by 35˚C/min to 250˚C, and by 10˚C/min to 300˚C and this was maintained for 25 minutes. The PAH content of the soil samples was quantified from the resulting chromatogram as earlier reported (Rauckyte, Zak, Pawlak and Oloyede, 2010).

### 3.4 Statistical analysis

The statistical methods used were standard error of mean, two way analysis of variance and Multiple Unpired T-test of variance.

# CHAPTER FOUR

# RESULTS AND DISCUSSION

## 4.1 Results

### 4.1.1 Heavy Metals concentration from Ogbor Hill

The results for the concentrations of heavy metals in soil sample from Ogbor hill and Comparison of mean values with the control, and standard deviation are shown in Table 4.1, Figure 4.1A, Figure 4.1B and Table 4.2, respectively. Iron (Fe) has the highest concentration in all the sampling points with mid slope having the highest concentration of 295.83±1.15 mg/kg (0-15cm), while cadmium had the lowest concentration in all the points, with the valley bottom having the lowest with 0.01±0.02 mg/kg (15-30 cm). Argon (Ar) and mercury (Hg) were not detected in all the sites. The control had very low concentrations of some of the metals. All the metals with the exception of argon (Ar), mercury (Hg) and the control exceeded NESREA standard.

For the 0-15cm, depth the mean Pb value (29.57±0.21) from mid slope recorded was significantly (p=0.001369) higher than other Pb values from other sites of collection and control, respectively. The mean Zn value (165.17±0.35) from mid slope recorded was significantly (p=0.000015) higher than other Zn values from other sites of collection and control. There was no significant difference (P=0.346746) as compared to test and control in Cd-(mg/kg) test. The mean Samples collected from mid slope (58.43±2.05) recorded a significant (p=0.000093) highest Cu- (mg/kg) as compared to other sites of collection and control, respectively.

The mean Samples collected from mid slope (295.83±1.15) recorded a significant (p=0.000007) highest Fe- (mg/kg) as compared to other sites of collection and control. The mean Samples

collected from mid slope (30.1±0.61) recorded a significant (p=0.000475) highest Mn- (mg/kg) as compared to other sites of collection and control. The mean Samples collected from crest (5.4±0.20) recorded a significant (p=0.000475) highest PAH- (mg/kg) as compared to other sites of collection and control, respectively. Two way analysis of variance showed that the test samples recorded a significant greater number of heavy metals as against the control samples. [(F=8.36, 8.36, 1.36); (p=<0.0001, <0.0001, <0.0001)].

For 15-30 cm, the result of heavy metals determined from soil samples from Ogbor hill showed no significant difference (p>0.05) among the samples collected from different points. Although there was a numerical different between the test samples and control samples, but Two way analysis of variance showed that; there were no significant different between control and test samples in the area sampled. [(F=0.7870, 2.32); (p=0.6033, 0.1019)]

**Table 4.1: Concentrations of heavy metals in soil sample from Ogbor hill.**

| SN | PARAMETERS (mg/kg) | Depth (cm) | Crest | | | | Mid slope | | | | Valley Bottom | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Site 1 | Site 2 | Site 3 | Control | Site 1 | Site 2 | Site 3 | Control | Site 1 | Site 2 | Site 3 | Control |
| 1 | Pb - mg/kg | 0-15 | 22.6 | 22.8 | 20.4 | 0.06 | 29.5 | 29.4 | 29.8 | 0.05 | 19.5 | 20.4 | 19.2 | 0.00 |
| | | 15-30 | 20.3 | 19.8 | 19.7 | 0.04 | 25.3 | 25.2 | 25.7 | 0.03 | 15.8 | 16.3 | 15.8 | 0.00 |
| 2 | Zn - mg/kg | 0-15 | 150.6 | 148.2 | 151.2 | 0.03 | 165.5 | 164.8 | 165.2 | 0.02 | 144.4 | 143.5 | 146.5 | 0.01 |
| | | 15-30 | 135.8 | 122.5 | 139.0 | 0.01 | 155.5 | 153.9 | 159.0 | 0.00 | 128.7 | 126.4 | 134.0 | 0.00 |
| 3 | Cd - mg/kg | 0-15 | 0.48 | 0.50 | 0.51 | 0.00 | 0.65 | 062 | 0.64 | 0.00 | 0.38 | 0.42 | 0.44 | 0.00 |
| | | 15-30 | 0.29 | 0.30 | 0.39 | 0.00 | 0.45 | 0.43 | 0.48 | 0.00 | 0.20 | 0.23 | 0.25 | 0.00 |
| 4 | Cu - mg/kg | 0-15 | 54.6 | 52.8 | 52.3 | 0.00 | 58.4 | 60.5 | 56.4 | 0.00 | 48.5 | 45.6 | 46.5 | 0.01 |
| | | 15-30 | 47.1 | 49.7 | 45.4 | 0.00 | 40.2 | 45.9 | 43.9 | 0.00 | 39.7 | 35.6 | 37.5 | 0.00 |
| 5 | Fe - mg/kg | 0-15 | 286.4 | 286.4 | 286.5 | 1.0 | 296.5 | 296.5 | 294.5 | 0.01 | 265.8 | 266.4 | 260.5 | 0.01 |
| | | 15-30 | 236.2 | 235.0 | 239.3 | 0.7 | 250.3 | 250.7 | 248.5 | 0.00 | 218.7 | 220.0 | 225.5 | 0.00 |
| 6 | Ar - mg/kg | 0-15 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | | 15-30 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 7 | Mn - mg/kg | 0-15 | 25.6 | 24.6 | 25.4 | 0.5 | 30.5 | 30.4 | 29.4 | 0.01 | 21.6 | 22.4 | 21.0 | 0.00 |
| | | 15-30 | 19.5 | 16.0 | 19.7 | 0.3 | 20.5 | 20.2 | 18.7 | 0.00 | 15.8 | 17.3 | 15.6 | 0.00 |
| 8 | Hg - mg/kg | 0-15 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | | 15-30 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |

**Table 4.2: Comparison of mean values with the control and standard deviation of soil sample from Ogbor hill**

| | | Ogbor hill TEST | | | Control | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Heavy Metals (mg/kg)** | **Depth (cm)** | **Crest (Mean±SEM)** | **Mid slope (Mean±SEM)** | **Valley BOTTOM (Mean±SEM)** | **Crest (Mean±SEM)** | **Mid slope (Mean±SEM)** | **Valley BOTTOM (Mean±SEM)** | **P value** | **NESREA Standard** |
| Pb | 0-15 | 21.93±1.33 | 29.57±0.21 | 19.7±0.62 | 0.06±0.01 | 0.05±0.00 | 0±0.00 | 0.001369 | 0.1 |
| | 15-30 | 19.93±0.32 | 29.6±0.21 | 0.07±0.08 | 0.0±0.00 | 0.03±0.03 | 0.0±0.0 | 0.368952 | |
| Zn | 0-15 | 150±1.59 | 165.17±0.35 | 144.8±1.54 | 0.03±0.00 | 0.02±0.00 | 0.01±0.00 | 0.000015 | 0.2 |
| | 15-30 | 132.43±8.75 | 0.13±0.16 | 1.68±2.91 | 0.0±0.00 | 0.00±0.00 | 0.0±0.0 | 0.351781 | |
| Cd | 0-15 | 0.5±0.02 | 21.1±35.42 | 0.4±0.03 | 0±0.00 | 0±0.00 | 0±0.00 | 0.346746 | 0.01 |
| | 15-30 | 0.33±0.06 | 2.92±5.05 | 0.01±0.02 | 0.0±0.00 | 0.00±0.00 | 0.0±0.0 | 0.317015 | |
| Cu | 0-15 | 53.23±1.21 | 58.43±2.05 | 46.9±1.48 | 0±0.00 | 0±0.00 | 0.01±0.00 | 0.000093 | 0.01 |
| | 15-30 | 47.40±2.17 | 0.02±0.03 | 0.42±0.72 | 0.0±0.00 | 0.00±0.00 | 0.0±0.0 | 0.358516 | |
| Fe | 0-15 | 286.43±0.06 | 295.83±1.15 | 264.2±3.25 | 1±0.00 | 0.01±0.00 | 0.01±0.00 | 0.000007 | - |
| | 15-30 | 236.83±2.22 | 0.72±1.25 | 0.29±0.51 | 0.7±0.00 | 0.00±0.00 | 0.0±0.0 | 0.371096 | |
| Ar | 0-15 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | | 0.01 |
| | 15-30 | 0.00±0.00 | 1.21±0.88 | 0.00±0.00 | 0.0±0.00 | 0.00±0.00 | 0.0±0.0 | | |
| Mn | 0-15 | 25.2±0.53 | 30.1±0.61 | 21.7±0.70 | 0.5±0.00 | 0.01±0.00 | 0±0.00 | 0.000475 | - |
| | 15-30 | 18.40±2.08 | 0.00±0.00 | 0.34±0.59 | 0.3±0.00 | 0.00±0.00 | 0.0±0.0 | 0.338418 | |
| Hg | 0-15 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | | 0.01 |
| | 15-30 | 0.00±0.00 | 0.89±1.03 | 0.00±0.00 | 0.0±0.00 | 0.00±0.00 | 0.0±0.0 | | |

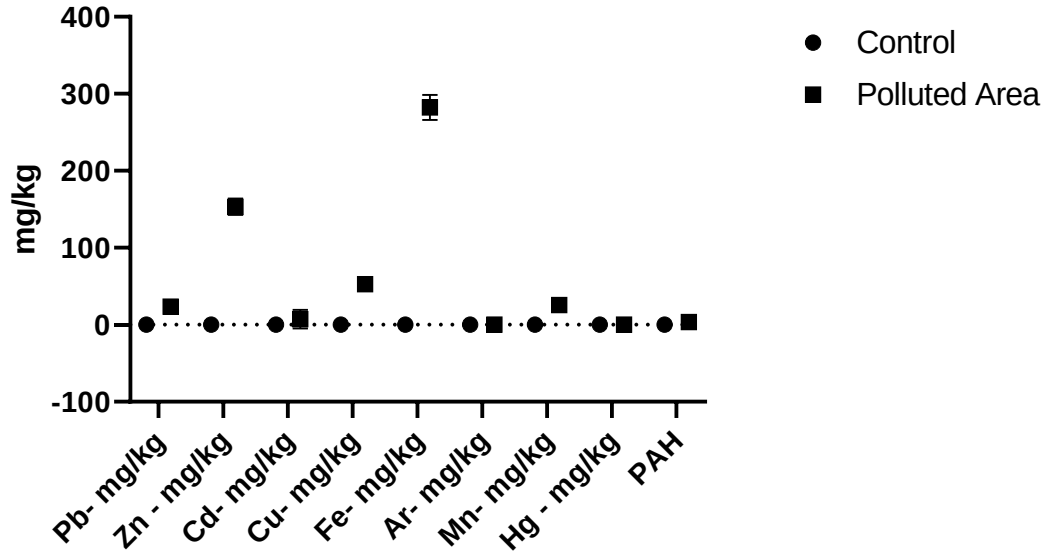


**Figure 4.1A: Concentration of heavy metals in polluted area (Ogbor hill) and control for 0-15 cm.**

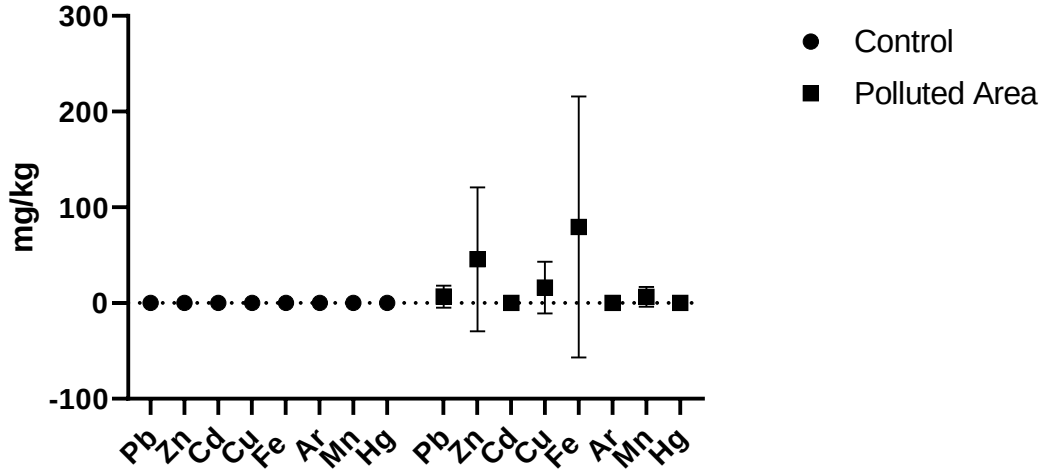


**Figure 4.1B: Concentration of heavy metals in polluted area (Ogbor hill) and control for 15-30 cm.**

### 4.1.3 Heavy Metal concentration of soils from Ndi Egoro

Table 4.3, Figure 4.2A, Figure 4.2B and Table 4.4, shows the results for the concentrations of heavy metals in soil sample from Ndi Egoro and Comparison of mean values with the control and standard deviation of soil from Ndi Egoro. Iron (Fe) has the highest concentration in all the sampling sites, with the mid slope having the highest concentration of 291.77±5.94 kg/mg (0-15 cm). Cadmium (Cd) has the lowest concentration in all the sites, with the crest having the lowest concentration of 0.25±0.08kg/mg (15-30 cm). Argon (Ar) and mercury (Hg) has concentration 0.00 in all the sites. The control has very low concentrations of lead (Pb), zinc (Zn), copper (Cu), iron and manganese (Mn). With the exception of argon, mercury and the control, all the metal exceeded the concentration NESREA.

For 0-15 cm, the mean samples collected from mid slope (29.03±0.55) recorded a significant (p=0.002015) highest Pb- (mg/kg) as compared to other sites of collection and control. The mean Samples collected from mid slope (155.5±10.37) recorded a significant (p=0.000004) highest Zn-(mg/kg) as compared to other sites of collection and control, respectively. There was no significant difference (P=0.339836) as compared to test and control in Cd-(mg/kg) test. The mean Samples collected from mid slope (57.03±1.27) recorded a significant (p=0.000194) highest Cu- (mg/kg) as compared to other sites of collection and control, respectively. The mean Samples collected from mid slope (291.77±5.94) recorded a significant (p=0.000004) highest Fe- (mg/kg) as compared to other sites of collection and control. The mean Samples collected from crest (23.2±4.93) recorded a significant (p=0.000002) highest Mn- (mg/kg) as compared to other sites of collection and control, respectively.Two way analysis of variance showed that the test samples recorded a significant greater number of heavy metals as against the control samples. [(F=7.14, P=<0.0001); (F=1.2, P=0.0021); F=7.14, P= <0.0001)].

For 15-30 cm, the mean samples collected from mid slope (25.70±1.14) recorded a significant (p=0.008931) highest Pb- (mg/kg) as compared to other sites of collection and control. The mean Samples collected from mid slope (134.00±3.32) recorded a significant (p=0.000003) highest Zn- (mg/kg) as compared to other sites of collection and control, respectively. The mean Samples collected from mid slope (0.34.±0.00) recorded a significant (p=0.000338) highest Cd- (mg/kg) as compared to other sites of collection and control, respectively. The mean Samples collected from mid slope (41.43±0.94) recorded a significant (p=0.002331) highest Cu- (mg/kg) as compared to other sites of collection and control, respectively. The mean Samples collected from mid slope (256.57±0.91) recorded a significant (p=0.000007) highest Fe- (mg/kg) as compared to other sites of collection and control, respectively. The mean Samples collected from Crest (15.80±5.27) recorded a significant (p=<0.000001) highest Mn- (mg/kg) as compared to other sites of collection and control, respectively. Two way analysis of variance showed that the test samples recorded a significant greater number of heavy metals as against the control samples.[(F=876.0, 560.4); (p=<0.0001, P=0.0018)].

**Table 4.3: Concentrations of heavy metals in soil sample from Ndi Egoro.**

| SN | PARAMETERS (mg/kg) | Depth (cm) | Crest | | | | Mid slope | | | | Valley bottom | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Site 1 | Site 2 | Site 3 | Control | Site 1 | Site 2 | Site 3 | Control | Site 1 | Site 2 | Site 3 | Control |
| 1 | Pb | 0-15 | 22.8 | 21.4 | 20.0 | 0.04 | 28.5 | 29.0 | 29.6 | 0.03 | 17.5 | 19.2 | 18.1 | 0.00 |
| | | 15-30 | 18.9 | 17.5 | 15.0 | 0.01 | 25.3 | 25.9 | 25.9 | 0.01 | 10.8 | 13.7 | 12.9 | 0.00 |
| 2 | Zn | 0-15 | 148.6 | 147.2 | 131.2 | 0.02 | 145.5 | 154.8 | 166.2 | 0.08 | 140.8 | 145.5 | 146.0 | 0.01 |
| | | 15-30 | 129.7 | 128.5 | 119.2 | 0.00 | 125.5 | 131.8 | 144.7 | 0.03 | 119.6 | 123.6 | 124.5 | 0.00 |
| 3 | Cd | 0-15 | 0.50 | 0.50 | 0.50 | 0.00 | 0.55 | 052 | 0.54 | 0.00 | 0.48 | 0.42 | 0.46 | 0.00 |
| | | 15-30 | 0.30 | 0.29 | 0.30 | 0.00 | 0.35 | 0.32 | 0.34 | 0.00 | 0.28 | 0.22 | 0.26 | 0.00 |
| 4 | Cu | 0-15 | 54.8 | 53.8 | 50.4 | 0.01 | 56.4 | 58.5 | 56.2 | 0.00 | 44.5 | 42.6 | 44.4 | 0.01 |
| | | 15-30 | 38.1 | 37.7 | 35.1 | 0.00 | 40.3 | 43.9 | 40.1 | 0.00 | 25.5 | 23.4 | 25.3 | 0.00 |
| 5 | Fe | 0-15 | 288.0 | 276.2 | 275.4 | 1.0 | 286.5 | 298.2 | 290.6 | 0.01 | 265.6 | 266.8 | 260.8 | 0.01 |
| | | 15-30 | 254.1 | 250.7 | 253.4 | 0.6 | 251.1 | 260.3 | 258.3 | 0.00 | 233.7 | 234.5 | 230.4 | 0.00 |
| 6 | Ar | 0-15 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | | 15-30 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 7 | Mn | 0-15 | 18.6 | 22.6 | 28.4 | 0.5 | 18.5 | 22.5 | 28.4 | 0.01 | 21.6 | 22.4 | 21.0 | 0.00 |
| | | 15-30 | 11.5 | 15.4 | 19.5 | 0.2 | 10.9 | 14.9 | 19.4 | 0.00 | 13.7 | 14.9 | 18.8 | 0.00 |
| 8 | Hg | 0-15 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | | 15-30 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |

**Table 4.4: Comparison of mean values with the control and standard deviation of soil sample from Ndi Egoro**

| | | Ndi Egoro | | | Control | | | |
|---|---|---|---|---|---|---|---|---|
| **HEAVY METALS (mg/kg)** | **Depth (cm)** | **Crest (Mean±SEM)** | **Mid slope (Mean±SEM)** | **Valley BOTTOM (Mean±SEM)** | **Crest (Mean±SEM)** | **Mid slope (Mean±SEM)** | **Valley Bottom (Mean±SEM)** | **NESREA standard** |
| Pb | 0-15 | 21.4±1.40 | 29.03±0.55 | 18.27±0.86 | 0.04±0.0 | 0.03±0.0 | 0±0.0 | 0.1 |
| | 15-30 | 17.13±1.98 | 25.70±1.14 | 12.47±4.16 | 0.01±0.00 | 0.01±0.00 | 0.0±0.00 | 0.008931 |
| Zn | 0-15 | 142.33±9.67 | 155.5±10.37 | 144.1±2.87 | 0.02±0.0 | 0.08±0.0 | 0.01±0.0 | 0.2 |
| | 15-30 | 125.80±5.75 | 134.00±3.32 | 122.57±40.87 | 0.00±0.00 | 0.03±0.00 | 0.0±0.00 | 0.000003 |
| Cd | 0-15 | 0.5±0.00 | 17.7±29.71 | 0.45±0.03 | 0±0.0 | 0±0.0 | 0±0.0 | 0.01 |
| | 15-30 | 0.30±0.01 | 0.34±0.00 | 0.25±0.08 | 0.00±0.00 | 0.00±0.00 | 0.0±0.00 | 0.000338 |
| Cu | 0-15 | 53±2.31 | 57.03±1.27 | 43.83±1.07 | 0.01±0.0 | 0±0.0 | 0.01±0.0 | 0.01 |
| | 15-30 | 36.97±1.63 | 41.43±0.94 | 24.73±8.24 | 0.00±0.00 | 0.00±0.00 | 0.0±0.00 | 0.002331 |
| Fe | 0-15 | 279.87±7.06 | 291.77±5.94 | 264.4±3.17 | 1±0.0 | 0.01±0.0 | 0.01±0.0 | - |
| | 15-30 | 252.73±1.80 | 256.57±0.91 | 232.87±77.62 | 0.60±0.00 | 0.00±0.00 | 0.0±0.00 | 0.000005 |
| Ar | 0-15 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.0 | 0±0.0 | 0±0.0 | 0.01 |
| | 15-30 | 0.00± | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.0±0.00 | |
| Mn | 0-15 | 23.2±4.93 | 23.13±4.98 | 21.67±0.70 | 0.5±0.0 | 0.01±0.0 | 0±0.0 | - |
| | 15-30 | 15.47± | 15.07±2.25 | 0.00±0.00 | 0.20±0.00 | 0.00±0.00 | 0.0±0.00 | <0.000001 |
| Hg | 0-15 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.0 | 0±0.0 | 0±0.0 | 0.01 |
| | 15-30 | 0.00± | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.0±0.00 | |

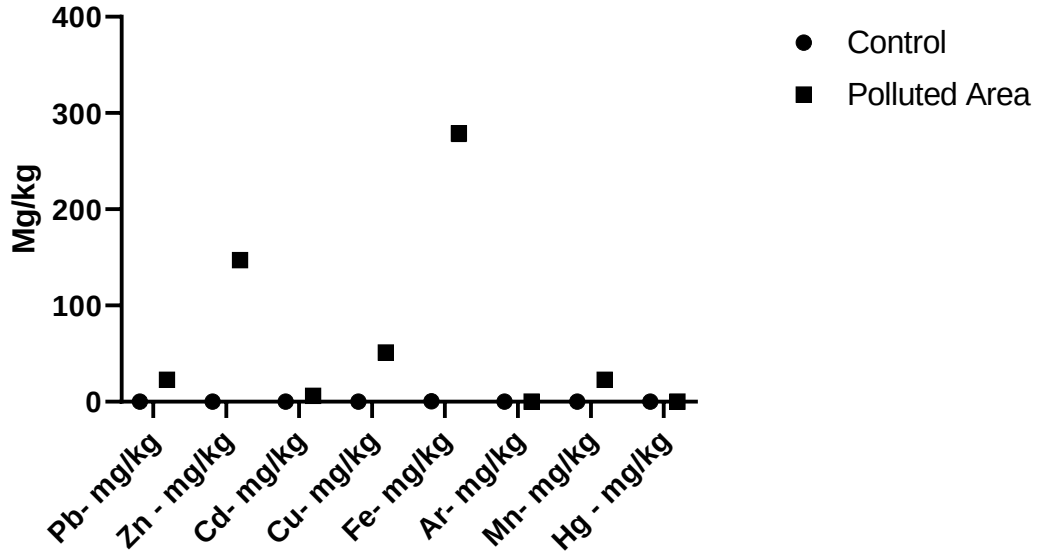


**Figure 4.2A: Concentration of heavy metals in polluted area (Ndi Egoro) and control for 0-15 cm.**

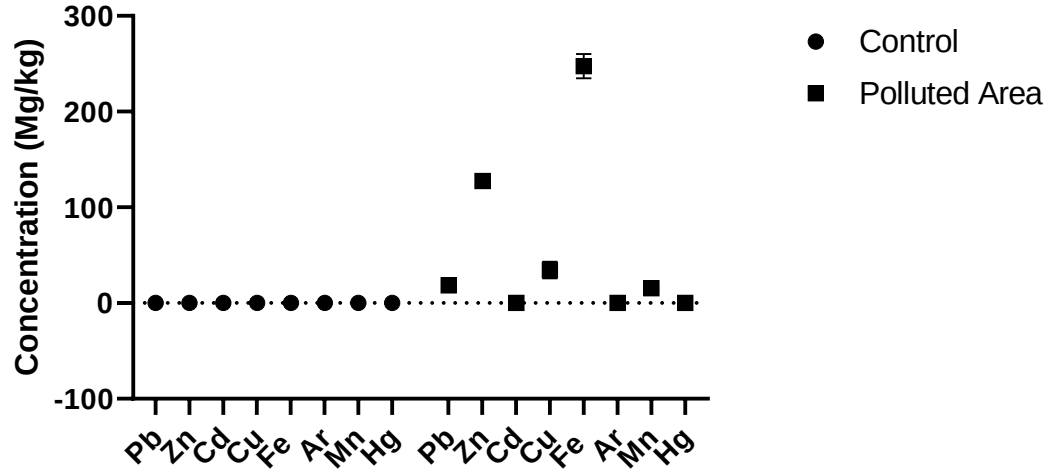


**Figure 4.2B: Concentration of heavy metals in polluted area (Ndi Egoro) and control for 15-30 cm**

### 4.1.3 Polycyclic Aromatic Hydrocarbons in Ogbor Hill

The results for the concentrations of polycyclic aromatic hydrocarbon in soil sample from Ogbor hill and Comparison of mean values with the control and standard deviation were shown in table 4.5, figure 4.3A, figure 4.3B and figure 4.6. Indeno (1, 2, 3-cd)pyrene recorded the highest concentration at both the crest and mid slope, with 2.53±0.43 ppm and 1.02±0.03 ppm in 0-15 cm respectively, while Benzo (e) pryene recorded the highest concentration at the valley bottom with 0.68±0.28 ppm (0-15 cm). Acenaphthylene, Fluorene, Dibeno (a,h) anthracene and Benzo (b)triphenylene recorded the lowest concentration at the crest, with the concentration of 0.01. The control recorded 0.00 in all the site, with the exception of Benzo (e) pryene, which recorded 0.01 in both crest and mid slope.

Multiple Unpired T-test of variance for 0-15cm showed that, there was no significant difference in the PAHS parameters among samples collected from crest, mid slope and valley bottom. Although, there was no difference among the test samples, two ways analysis of variance showed that, the test samples recorded significant high concentration of PAHS as compared to the control samples. [(F 11.48, P=0.0104); (F=11.48, P=0.0098) (F= 14.93, P=0.0003)].

Multiple Unpired T-test of variance for 15-30ch showed that, there was no significant difference in the PAHS parameters among samples collected from Crest, Mid slope and Valley BOTTOM. Although, there was no difference among the test samples, two ways analysis of variance showed that, the test samples recorded significant high concentration of PAHS as compared to the control samples. [(F=2.867, P=0.0057)].

**Table 4.5: Concentrations of polycyclic aromatic hydrocarbon in soil sample from Ogbor hill**

| SN | PARAMETERS | Depth (cm) | Crest | | | | Mid slope | | | | Valley Bottom | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ( PPM) | | Site 1 | Site 2 | Site 3 | Control | Site 1 | Site 2 | Site 3 | Control | Site 1 | Site 2 | Site 3 | Control |
| 1 | Naphthalene | 0-15 | 0.13 | 0.02 | ND | ND | 0.13 | 0.02 | ND | ND | 0.02 | 0.02 | ND | ND |
| | | 15-30 | 0.11 | 0.00 | ND | ND | 0.1 | 0.00 | ND | ND | 0.00 | 0.01 | ND | ND |
| 2 | Acenaphthylene | 0-15 | 0.02 | 0.01 | 0.01 | ND | 0.01 | 0.00 | ND | ND | 0.00 | ND | ND | ND |
| | | 15-30 | 0.00 | 0.00 | 0.00 | ND | 0.00 | 0.00 | ND | ND | 0.00 | ND | ND | ND |
| 3 | Acenaphthene | 0-15 | 0.02 | 0.01 | 0.06 | ND | 0.01 | 0.01 | 0.04 | ND | 0.02 | 0.01 | 0.02 | ND |
| | | 15-30 | 0.01 | 0.00 | 0.03 | ND | 0.00 | 0.00 | 0.02 | ND | 0.00 | 0.00 | 0.02 | ND |
| 4 | Fluorene | 0-15 | 0.01 | ND | ND | ND | 0.01 | ND | ND | ND | ND | ND | ND | ND |
| | | 15-30 | 0.00 | ND | ND | ND | 0.01 | ND | ND | ND | ND | ND | ND | ND |
| 5 | Phenanthrene | 0-15 | 0.00 | ND | 0.05 | 0.00 | 1.0 | 0.00 | 0.06 | ND | 0.00 | 0.04 | 0.00 | ND |
| | | 15-30 | 0.00 | ND | 0.03 | 0.00 | 1.0 | 0.00 | 0.06 | ND | 0.00 | 0.02 | 0.00 | ND |
| 6 | Benzo (b) fluoranthene | 0-15 | 0.89 | 0.67 | 1.01 | 0.00 | 1.0 | 1.00 | 1.00 | 0.00 | 0.00 | 0.00 | 0.20 | ND |
| | | 15-30 | 0.59 | 0.39 | 0.56 | 0.00 | 1.0 | 1.00 | 1.00 | 0.00 | 0.00 | 0.00 | 0.20 | ND |
| 7 | Benzo (k) fluoranthene | 0-15 | 0.02 | 0.01 | 0.10 | 0.00 | 1.00 | 1.00 | 1.00 | 0.00 | 0.20 | 0.35 | 0.22 | ND |
| | | 15-30 | 0.02 | 0.00 | 0.10 | 0.00 | 1.00 | 1.00 | 1.00 | 0.00 | 0.14 | 0.29 | 0.15 | ND |
| 8 | Benzo (e) pryene | 0-15 | 2.01 | 2.00 | 1.01 | 0.01 | 0.02 | 1.05 | 1.00 | 0.01 | 1.0 | 0.54 | 0.50 | ND |
| | | 15-30 | 1.00 | 0.59 | 0.69 | 0.01 | 0.02 | 1.05 | 1.00 | 0.01 | 0.7 | 0.30 | 0.29 | ND |
| 9 | Dibeno (a,h) anthracene | 0-15 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | ND |
| | | 15-30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | ND |
| 10 | Indeno (1,2,3-cd)pyrene | 0-15 | 2.06 | 2.89 | 2.65 | ND | 1.00 | 1.05 | 1.00 | 0.00 | 0.00 | 0.00 | ND | ND |
| | | 15-30 | 1.09 | 1.96 | 1.86 | ND | 1.00 | 1.05 | 1.00 | 0.00 | 0.00 | 0.00 | ND | ND |
| 11 | Benzo (b)triphenylene | 0-15 | ND | ND | 0.01 | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | | 15-30 | ND | ND | 0.00 | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 12 | Benxo (ghi) perylene | 0-15 | 0.46 | ND | 0.01 | 0.00 | ND | ND | ND | ND | ND | ND | ND | ND |
| | | 0.46 | ND | 0.00 | 0.00 | ND | ND | ND | ND | ND | ND | ND | ND | 0.46 |

**Table 4.6: Comparison of mean values with the control and standard deviation of soil sample from Ogbor hill**

| PARAMETERS (ppm) | Depth (cm) | PAHS @ Ogbor hill TEST | | | Control | | | |
|---|---|---|---|---|---|---|---|---|
| | | Crest (Mean±SEM) | Mid (Mean±SEM) | Valley BOTTOM (Mean±SEM) | Crest (Mean±SEM) | Mid slope (Mean±SEM) | Valley BOTTOM (Mean±SEM) | P value |
| Naphthalene (ppm) | 0-15 | 0.05±0.07 | 0.05±0.07 | 0.01±0.01 | 0± | 0±0.0 | 0±0.0 | 0.051374 |
| | 15-30 | 0.04±0.06 | 0.03±0.06 | 0.00±0.01 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.124170 |
| Acenaphthylene | 0-15 | 0.01±0.01 | 0±0.01 | 0±0.00 | 0± | 0±0.0 | 0±0.0 | 0.373901 |
| | 15-30 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | |
| Acenaphthene | 0-15 | 0.03±0.03 | 0.02±0.02 | 0.02±0.01 | 0± | 0±0.0 | 0±0.0 | 0.002192 |
| | 15-30 | 0.01±0.02 | 0.01±0.01 | 0.01± | 0.03±0.00 | 0.00±0.00 | 0.00±0.00 | >0.999999 |
| Fluorene | 0-15 | 0.01±0.01 | 0±0.01 | 0±0.00 | 0± | 0±0.0 | 0±0.0 | 0.373901 |
| | 15-30 | 0.00±0.00 | 0.00±0.01 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | |
| Phenanthrene | 0-15 | 0.02±0.03 | 0.35±0.56 | 0.01±0.02 | 0± | 0±0.0 | 0±0.0 | 0.320167 |
| | 15-30 | 0.01±0.02 | 0.35±0.56 | 0.01±0.01 | 0.03±0.00 | 0.00±0.00 | 0.00±0.00 | 0.375566 |
| Benzo (b) fluoranthene | 0-15 | 0.86±0.17 | 1±0.00 | 0.07±0.12 | 0± | 0±0.0 | 0±0.0 | 0.090390 |
| | 15-30 | 0.51±0.11 | 1.00±0.00 | 0.07±0.12 | 0.56±0.00 | 0.00±0.00 | 0.00±0.00 | 0.357290 |
| Benzo (k) fluoranthene | 0-15 | 0.04±0.05 | 1±0.00 | 0.26±0.08 | 0± | 0±0.0 | 0±0.0 | 0.209881 |
| | 15-30 | 0.04±0.05 | 1.00±0.00 | 0.19±0.08 | 0.1±0.00 | 0.00±0.00 | 0.00±0.00 | 0.277644 |
| Benzo (e) pryene | 0-15 | 1.67±0.57 | 0.69±0.58 | 0.68±0.28 | 0.01± | 0.01±0.0 | 0±0.0 | 0.037449 |
| | 15-30 | 0.76±0.21 | 0.69±0.58 | 0.43±0.23 | 0.69±0.01 | 0.01±0.00 | 0.00±0.00 | 0.189964 |
| Dibeno (a,h) anthracene | 0-15 | 0.01±0.01 | 0±0.01 | 0.01±0.02 | 0± | 0±0.0 | 0±0.0 | 0.116117 |
| | 15-30 | 0.0±0.0 | 0.00±0.01 | 0.01±0.01 | 0.0±0.00 | 0.00±0.00 | 0.00±0.00 | 0.373901 |
| Indeno (1,2,3-cd)pyrene | 0-15 | 2.53±0.43 | 1.02±0.03 | 0±0.00 | 0± | 0±0.0 | 0±0.0 | 0.182643 |
| | 15-30 | 1.09±1.96 | 1.02±0.03 | 0.00±0.00 | 1.86±1.64 | 0.00±0.00 | 0.00±0.00 | 0.912600 |
| Benzo (b)triphenylene | 0-15 | 0.01±0.01 | 0±0.00 | 0±0.00 | 0± | 0±0.0 | 0±0.0 | 0.373901 |
| | 15-30 | 0±0 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | |
| Benxo (ghi) perylene | 0-15 | 0.16±0.26 | 0±0.00 | 0±0.00 | 0± | 0±0.0 | 0±0.0 | 0.373901 |
| | 15-30 | 0.46± | 0.00±0.00 | 0.00±0.00 | 0±0.15 | 0.00±0.00 | 0.00±0.00 | 0.373901 |

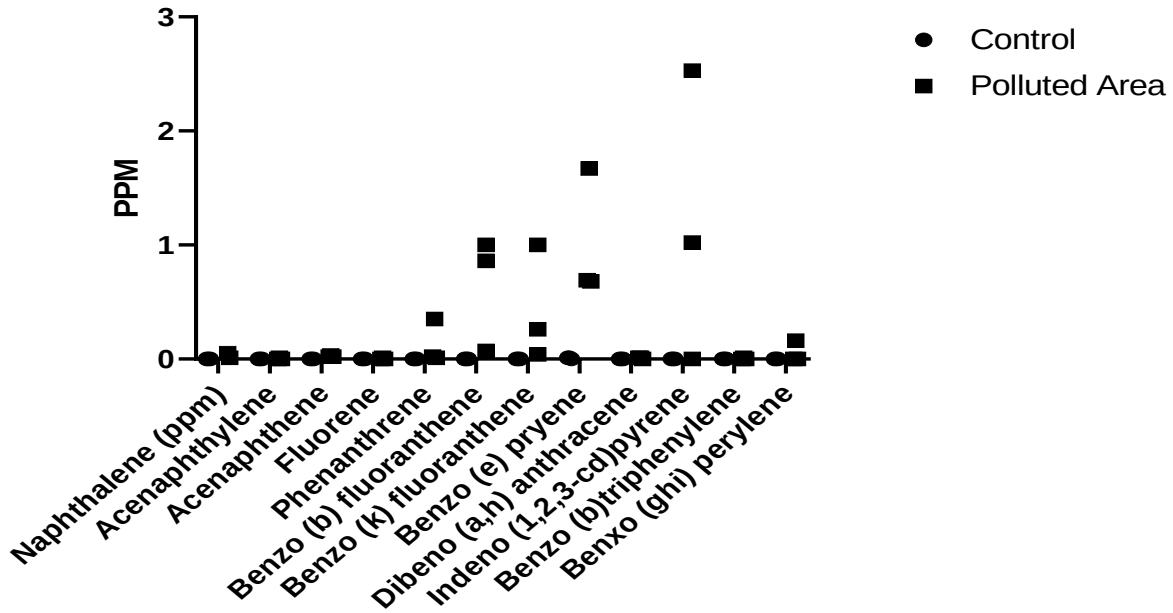


**Figure 4.3A: Concentration of PAH in polluted area (Ogbor hill) and the control for 0-15 cm.**

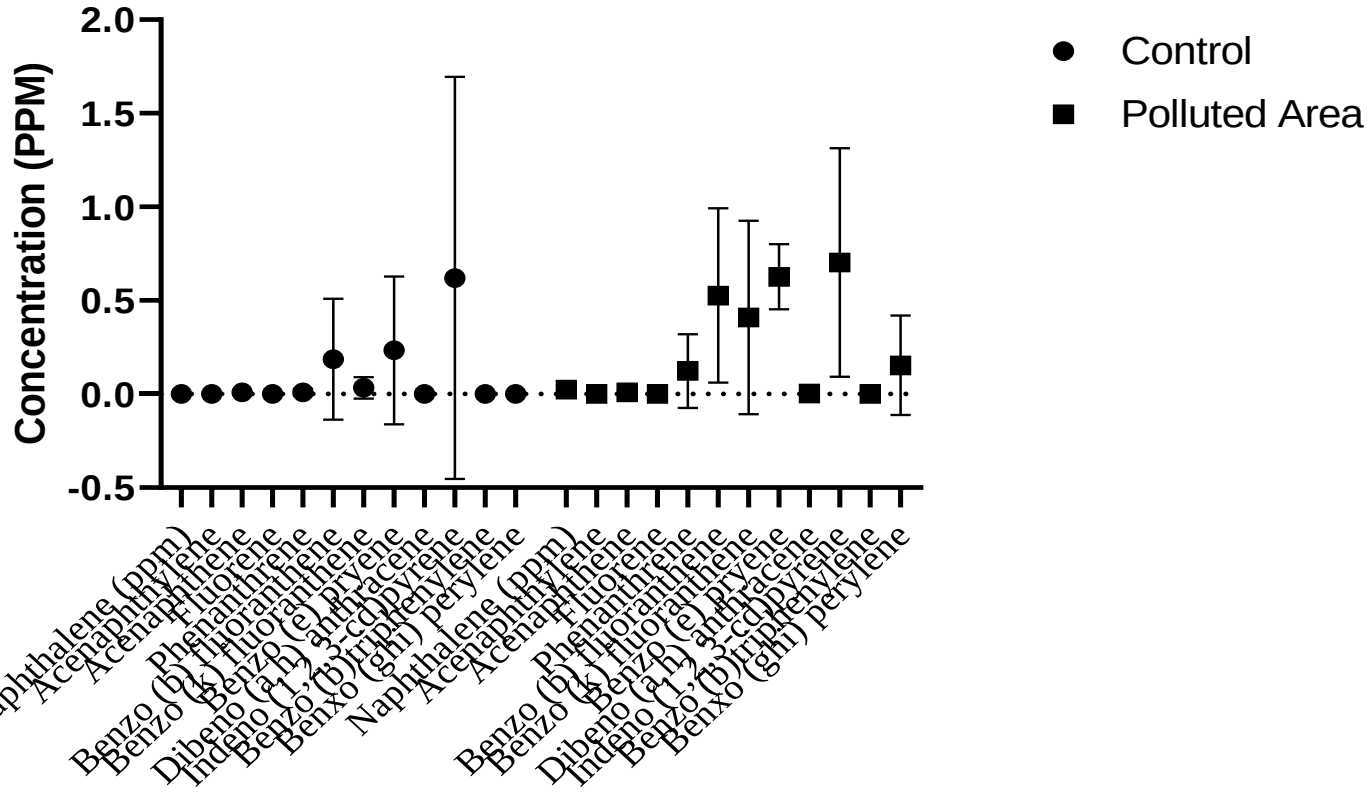


**Figure 4.3B: Concentration of PAH in polluted area (Ogbor hill) and the control for 15-30 cm.**

### 4.1.4 Polycyclic Aromatic Hydrocarbon from Ndi Egoro

Table 4.7, Figure 4.4A, Figure 4.4B and Table 4.8 s shows the results for the concentrations of heavy metals in soil sample and Comparison of mean values with the control and standard deviation of soil from Ndi Egoro.Indeno (1, 2, 3-cd)pyrene recorded the highest concentration in two sites; crest and mid slope with 2.53±0.44 and 1.02±0.03 for 0-15 cm respectively, while Benzo (e) pryene recorded 0.68±0.28 (0-15cm) as the highest concentration in valley bottom. Benzo (b)triphenylene and Benxo (ghi) perylene recorded 0.00 concentration in both mid slope and valley bottom. The control recorded 0.00 in the concentrations of the PAHs, with the exception of Benzo (e) pryene, which recorded 0.00 in both crest and mid slope, respectively. Benzo (b)triphenylene recorded the lowest concentration in all the sites.

Multiple Unpired T-test of variance for 0-15 cm showed that, there was no significant difference in the PAHS parameters among samples collected from crest, mid slope and valley bottom. Although, there was no difference among the test samples, two way analysis of variance showed that, test samples recorded significant high concentration of PAHS as compared to the control samples. [(F=11.48, P=0.0072); (F=11.48, P=0.0067); (F=1.48, P=0.0002).

For 15-30 cm, result shows that only Acenaphthene determination showed a significant discrepancy as against the other PPM parameters. Analysis showed that soil samples collected from crest (0.02±0.01) had the highest significant Acenaphthene as against other samples collection areas. Two way analysis of variance showed that the test samples recorded a significant greater number of PPM parameters as against the control samples.[(F= 2.805, F=16.07); (p=P=0.0168, p=0.0005)].

**Table 4.7: Concentrations of polycyclic aromatic hydrocarbon in soil sample from Ndi Egoro**

| SN | PARAMETERS ( PPM) | Depth (cm) | Crest | | | | Mid slope | | | | Valley BOTTOM | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Site 1 | Site 2 | Site 3 | Control | Site 1 | Site 2 | Site 3 | Control | Site 1 | Site 2 | Site 3 | Control |
| 1 | Naphthalene (ppm) | 0-15 | 0.12 | 0.02 | ND | ND | 0.10 | 0.02 | ND | ND | 0.02 | 0.02 | ND | ND |
| | | 15-30 | 0.08 | 0.01 | ND | ND | 0.00 | 0.01 | ND | ND | 0.00 | 0.02 | ND | ND |
| 2 | Acenaphthylene | 0-15 | 0.02 | 0.01 | 0.01 | ND | 0.01 | 0.00 | ND | ND | 0.00 | ND | ND | ND |
| | | 15-30 | 0.00 | 0.00 | 0.01 | ND | 0.00 | 0.00 | ND | ND | 0.00 | ND | ND | ND |
| 3 | Acenaphthene | 0-15 | 0.01 | 0.01 | 0.06 | ND | 0.01 | 0.01 | 0.04 | ND | 0.02 | 0.01 | 0.02 | ND |
| | | 15-30 | 0.01 | 0.0 | 0.03 | ND | 0.01 | 0.00 | 0.02 | ND | 0.01 | 0.01 | 0.00 | ND |
| 4 | Fluorene | 0-15 | 0.01 | ND | ND | ND | 0.01 | ND | ND | ND | ND | ND | ND | ND |
| | | 15-30 | 0.00 | ND | ND | ND | 0.00 | ND | ND | ND | ND | ND | ND | ND |
| 5 | Phenanthrene | 0-15 | 0.00 | ND | 0.04 | 0.00 | 1.0 | 0.00 | 0.06 | ND | 0.00 | 0.04 | 0.00 | ND |
| | | 15-30 | 0.00 | ND | 0.02 | 0.00 | 0.6 | 0.00 | 0.03 | ND | 0.00 | 0.02 | 0.00 | ND |
| 6 | Benzo (b) fluoranthene | 0-15 | 0.88 | 0.67 | 1.00 | 0.00 | 1.0 | 1.00 | 1.00 | 0.00 | 0.00 | 0.00 | 0.20 | ND |
| | | 15-30 | 0.50 | 0.39 | 0.60 | 0.00 | 0.6 | 0.50 | 0.50 | 0.00 | 0.00 | 0.00 | 0.20 | ND |
| 7 | Benzo (k) fluoranthene | 0-15 | 0.00 | 0.01 | 0.08 | 0.00 | 1.00 | 0.88 | 0.90 | 0.00 | 0.20 | 0.35 | 0.22 | ND |
| | | 15-30 | 0.00 | 0.01 | 0.05 | 0.00 | 0.80 | 0.54 | 0.60 | 0.00 | 0.09 | 0.15 | 0.14 | ND |
| 8 | Benzo (e) pryene | 0-15 | 2.00 | 2.00 | 1.01 | 0.00 | 0.02 | 1.05 | 1.00 | 0.00 | 1.0 | 0.54 | 0.50 | ND |
| | | 15-30 | 1.30 | 1.30 | 0.67 | 0.00 | 0.00 | 0.70 | 0.50 | 0.00 | 0.50 | 0.32 | 0.39 | ND |
| 9 | Dibeno (a,h) anthracene | 0-15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | ND |
| | | 15-30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | ND |
| 10 | Indeno (1,2,3-cd)pyrene | 0-15 | 2.04 | 2.89 | 2.65 | ND | 1.00 | 1.05 | 1.00 | 0.00 | 0.00 | 0.00 | ND | ND |
| | | 15-30 | 1.02 | 1.30 | 1.28 | ND | 0.50 | 0.53 | 0.50 | 0.00 | 0.00 | 0.00 | ND | ND |
| 11 | Benzo (b)triphenylene | 0-15 | ND | ND | 0.01 | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | | 15-30 | ND | ND | 0.00 | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 12 | Benxo (ghi) perylene | 0-15 | 0.44 | ND | 0.00 | 0.00 | ND | ND | ND | ND | ND | ND | ND | ND |
| | | 15-30 | 0.24 | ND | 0.00 | 0.00 | ND | ND | ND | ND | ND | ND | ND | ND |

**Table 4.8: Comparison of mean values with the control and standard deviation of soil sample from Ndi Egoro**

| PARAMETER (ppm) | **Depth (cm)** | **PAHS@ Ndi Egoro** | | | **Control** | | | |
|---|---|---|---|---|---|---|---|---|
| | | **Crest (Mean±SEM)** | **Mid slope (Mean±SEM)** | **Valley BOTTOM (Mean±SEM)** | **Crest (Mean±SEM)** | **Mid slope (Mean±SEM)** | **Valley BOTTOM (Mean±SEM)** | **P value** |
| Naphthalene (ppm) | 0-15 | 0.05±0.06 | 0.04±0.05 | 0.02±0.01 | 0±0.00 | 0±0.00 | 0±0.00 | 0.014173 |
| | 15-30 | 0.03±0.04 | 0.003±0.01 | 0.007±0.01 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | 0.188177 |
| Acenaphthylene | 0-15 | 0.01±0.01 | 0±0.01 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | 0.373901 |
| | 15-30 | 0.02±0.01 | 0.00±0.00 | 0.000±0.00 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | |
| Acenaphthene | 0-15 | 0.03±0.03 | 0.02±0.02 | 0.02±0.01 | 0±0.00 | 0±0.00 | 0±0.00 | 0.002192 |
| | 15-30 | 0.01±0.02 | 0.010±0.01 | 0.007±0.01 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | 0.000844 |
| Fluorene | 0-15 | 0±0.01 | 0±0.01 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | |
| | 15-30 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | |
| Phenanthrene | 0-15 | 0.01±0.02 | 0.35±0.56 | 0.04±0.02 | 0±0.00 | 0±0.00 | 0±0.00 | 0.287151 |
| | 15-30 | 0.01±0.01 | 0.21±0.34 | 0.01±0.01 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | 0.322978 |
| Benzo (b) fluoranthene | 0-15 | 0.85±0.17 | 1±0.00 | 0.2±0.12 | 0±0.00 | 0±0.00 | 0±0.00 | 0.049653 |
| | 15-30 | 0.50±0.11 | 0.53±0.06 | 0.07±0.12 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | 0.071037 |
| Benzo (k) fluoranthene | 0-15 | 0.03±0.04 | 0.93±0.06 | 0.26±0.08 | 0±0.00 | 0±0.00 | 0±0.00 | 0.206433 |
| | 15-30 | 0.02±0.03 | 0.64±0.14 | 0.13±0.03 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | 0.243483 |
| Benzo (e) pryene | 0-15 | 1.67±0.57 | 0.69±0.58 | 0.68±0.28 | 0.01±0.00 | 0.01±0.00 | 0±0.00 | 0.037449 |
| | 15-30 | 1.09±0.36 | 0.40±0.36 | 0.40±0.09 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | 0.051404 |
| Dibeno (a,h) anthracene | 0-15 | 0±0.00 | 0±0.01 | 0.04±0.02 | 0±0.00 | 0±0.00 | 0±0.00 | 0.373901 |
| | 15-30 | 0.00±0.00 | 0.00±0.00 | 0.01±0.01 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | 0.373901 |
| Indeno (1,2,3-cd)pyrene | 0-15 | 2.53±0.44 | 1.02±0.03 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | 0.182643 |
| | 15-30 | 1.20±0.16 | 0.51±0.02 | 0.00±0.00 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | 0.176491 |
| Benzo (b)triphenylene | 0-15 | 0±0.01 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | |
| | 15-30 | 0.00±0.00 | 0.00±0.00 | 0.00±0.00 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | |
| Benxo (ghi) perylene | 0-15 | 0.15±0.25 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | 0±0.00 | 0.373901 |
| | 15-30 | 0.08± | 0.00±0.00 | 0.00±0.00 | 0.0±0.0 | 0.0±0.0 | 0.0±0.0 | |

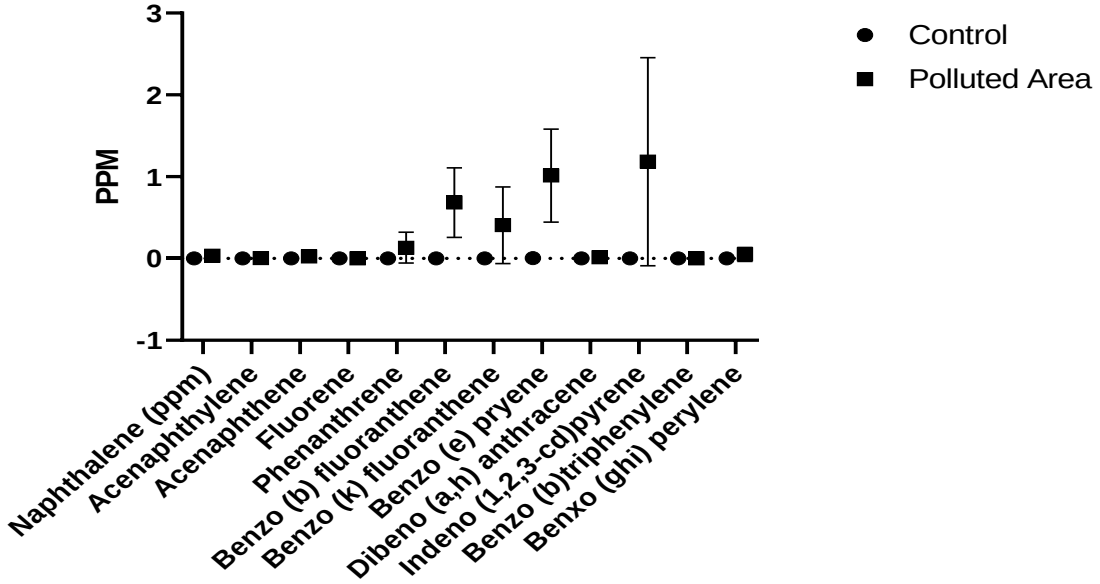


**Figure 4.4B: Concentration of PAH in polluted area (Ndi Egoro) and the control for 0-15 cm.**

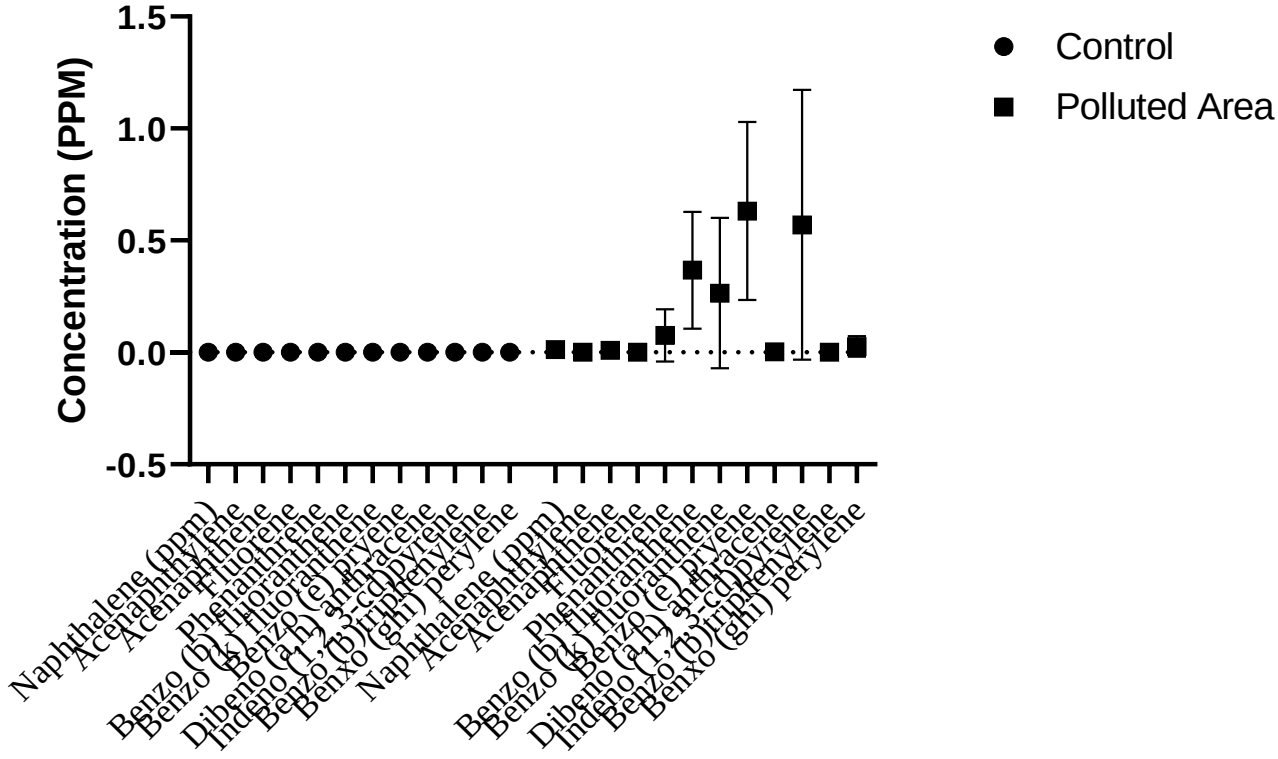


**Figure 4.4B: Concentration of PAH in polluted area (Ndi Egoro) and the control for 15-30 cm.**

## 4.2 Discussion of Results

### 4.2.1 Heavy Metals

The metals that were analyzed in this study included; lead (Pb), cadmium (Cd), iron (Fe), argon (Ar), manganese (Mn), mercury (Hg), zinc (Zn) and copper (Cu). The results obtained showed that Iron (Fe) recorded the highest concentration in both Ogbor hill and Ndi Egoro, while cadmium recorded the lowest concentrations in both sampling sites. This is in line with Nwachukwu, Newman, and Janefrances (2017), where their results showed that the sediment samples were heavily polluted with Fe and moderately polluted with Cd.Cadmium had the lowest concentration of 0.4±0.03 mg/kg in Ogbor hill, while Ndi Egoro also recorded the lowest cadmium of 0.4±0.03 mg/kg; this is in line with Ziola and Slaby, (2020), in their study, cadmium recorded the lowest concentration of 0.62 ±0.41 mg/kg.

In most cases, Cu, Zn and Pb concentrations were highest in topsoil, which was evidence of recent/ anthropogenic contamination (Gowd, Reddy, and Govila,2010), this is also in agreement with this present study where Cu, Zn and Pb recorded concentrations that exceeded National Environmental Standards and Regulations Enforcement Agency National (2011) and United States Environmental Protection Agency (2009) standards. Cu, Zn and Pb recorded concentration of 29.57±0.21 mg/kg, 165.17±0.35 mg/kg and 58.43±2.05 mg/kg respectively. Heavy metal levels obtained showed that (Pb), cadmium (Cd), iron (Fe), argon (Ar), manganese (Mn), mercury (Hg), zinc (Zn) and copper (Cu) had concentrations higher than the maximum permissible limit stipulated by both National Environmental Standards and Regulations Enforcement Agency National (2011) and United States Environmental Protection Agency (2009).

The high concentration of these metals may be attributed to anthropogenic activities. Metals such as Zn, Cr, Cu, As and Pb were measured in Krakow (Nowa Huta) in earlier years (Samek, Stegowski, Furman, and Fiedor, 2016). This is in line with this study were (Pb), cadmium (Cd), iron (Fe), argon (Ar), manganese (Mn), mercury (Hg), zinc (Zn) and copper (Cu) were also measured. Cd concentration levels were less than 1 mg/kg to 8.5 mg/kg for the study area in the study carried out by (Muze, Opara, Ibe, and Njoku2020).The observed values were higher than the control values of less than 1mg/kg and also higher than the allowed value of 1 mg/kg by USEPA (Muze, Opara, Ibe, and Njoku 2020). This is in agreement with this study where observed values are also higher than the control.

The high-level of Pb observed in the soil from the study area could be from the indiscriminate disposal of waste from lead-acid batteries, lead-based solder; metallic alloy, lead-based paints, used oil, waste incineration, scrap and junk part of automobile (Nkansah, Christy, and Barth, 2011). These parts may be coated with oil or grease, which may contain lead residues that may in the long run harmfully affect storm water runoff that may further endanger aquatic life and public drinking water supplies. Also, leachates from these wastes via storm water run-off could infiltrate in the groundwater system. Aquifers are known to be vulnerable to various contaminants and sediment loads including microscopic bacteria, viruses, and protozoa (Nouri, Poorhashemi, Monavari, Dabiri, and Hassani,2011). Seepage and infiltrations of pollutants from surface water could also affect the quality of groundwater. Pb has no known biological benefit to humans as it can damage various systems of the body including the nervous system, reproductive system, and the kidney, and can further cause high blood pressure and anaemia (World Health Organization, 2011). The Cd concentrations in the study area may be a result of the disposal of waste containing

Cd such as waste batteries and paints (Muze, Opara, Ibe, and Njoku, 2020). The metals in both Ogbor hill and Ndi Egoroshowed the following trend:

The concentration of iron is the highest followed by zinc, copper, manganese, lead, cadmium and mercury and argon has the lowest concentration, thus this;

Ogbor hill (Ikot Ekpene road): Fe > Zn > Cu > Mn > Pb > Cd > Ar and Hg;

Ndi Egoro: Fe > Zn > Cu > Mn > Pb > Cd > Ar and Hg.

The source of the PAH may be products of incomplete combustion of fossil fuel while other important sources may include automobile and truck emissions. The observed differences in the concentration of the pollutants in both Ogbor hill and Ndi Egoro may be attributed to the mode of wastes disposal and type of soil (Ololade, 2014). Chemical composition analyzes have shown the presence of polycyclic aromatic hydrocarbons from incomplete combustion of fossil fuels and other substances in municipal and industrial processes (Rengarajan, Rajendran, Nandakumar, Lokeshkumar, Rajendran, and Nishigaki, 2015). Relatively high concentrations of benzo[a]pyrene, considered a carcinogen, have been reported. High concentrations of polycyclic aromatic hydrocarbon in the environment is of public health concern, since several of the measured PAHs are considered probable human carcinogens (benz(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene and indeno(1,2,3-c,d)pyrene) or possibly (benzo(a)fluoranthene, benzo(k) fluoranthene and indeno(1,2,3-c,d) pyrene) (Toxicological profile for polycyclic aromatic hydrocarbons, 1995).

The USEPA identified 16 priority PAHs, which can be classified as being of low or high molecular weight. Low molecular weight (LMW) PAHs (i.e., acenaphthylene, naphthalene, acenaphthene,

fluorene, phenanthrene and anthracene), also referred to as petrogenic (formed during the emission of non-combustion-derived matter, including inadvertent oil spills), have molecular weights ranging from 128.2 to 178.2 g/mol. High molecular weight (HMW), pyrolytic PAHs, are fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(a) fluoranthene, benzo(k)pyrene, dibenzo(a, h)anthracene, benzo(g, h, i) perylene and indeno(1,2,3-cd) pyrene and have molecular weights ranging from 202.3 to 278.4 g/mol (Oketola and Akpotu, 2015; Duke, 2008).Pyrogenic PAHs are formed during the incomplete combustion of coal, oil, gas wood and garbage. Petrogenic and pyrogenic PAHs in this study are of emission from both non-combustion derived matter and incomplete combustion of coal, oil, gas wood and garbage.

PAHs are among the pollutants that are considered ubiquitous in the environment (Tobiszewski and Namiesnik, 2012). Atmospheric deposition could contribute to high PAH concentrations in areas considered unpolluted by virtue of the economic and other anthropogenic activities in such areas (Marr, Dzepina, Jimenez, Reisen, Bethel, Arey, Gaffney, Marley, Molina, and Molina,2006; Tian, Chen, Qiao, Wang, Yang, Wang, and Ge,2009; Opara, Ibe, Njoku, Alinnor, and Enenebeaku,2016; Njoku, Ibe, Alinnor, and Opara,2016; Ibe, Opara, Duru, Isiuku, and Enedoh,2020).Benzo (b) fluoranthene recorded concentration of 0.85±0.17 in the crest; this is in agreement with Ibe, Duru and Akalazu, (2021), where benzo (b) fluoranthene recorded a concentration of 0.870.In Ibe, Duru and Akalazu,2021, benzo (k) fluoranthene recorded 0.956, which is also in agreement with this study where,benzo (k) fluoranthene recorded concentration of 0.93±0.06.

The mean PAH concentrations of the present study compared to related studies in Nigeria revealed that higher PAH values were reported by Muze, Opara, Ibe, and Njoku, 2020, except for phenanthrene, benzo(b)fluoranthene, benzo (k) fluoranthene and benzo (e) pryene which recorded

a lower concentration than the present study.Obini, Okafor and Afiukwa (2013),Ogoko (2014), and Ekanem, Osabor and Ekpo (2019) recorded higher concentration of PHAs than the present study. In Ibe, Duru and Akalazu, 2021, the concentrations of the PAHs recorded almost the same concentrations with the records in this present study. The mean PAH levels observed in the study are in the order;

Ogbor hill (Ikot Ekpene road)

Crest; Indp>Bep> Bbf> Bgp>Nap> Bkf>Ant>Phe> Apt, Flu, Dbh and Bbt;

Mid slope; Indp> Bbf and Bkf > Bep> Phe > Nap > Ant>Apt, Flu, Dbh, Bbt and Bgp;

Valley bottom; Bep> Bkf> Bbf> Ant> Nap, Phe and Dbh> Ant, Flu, Indp,Bbt and Bgt

Ndi Egoro

Crest; Indp>Bep> Bbf> Bgp> Nap> Bkf and Ant> Phe and Apt > Flu, Dbh and Bbt;

Mid slope; Indp>Bbf >Bkf > Bep> Phe > Nap and Ant>Apt, Flu, Dbh, Bbt and Bgp;

Valley bottom; Bep> Bkf> Bbf>Phe and Dbh> Nap, Ant and Bbf >Flu, Indp,Bbt and Bgt.

# CHAPTER FIVE

# SUMMARY, CONCLUSION AND RECOMMENDATIONS

## 5.1 Summary

This study was carried out to determine the accumulation of heavy metals and polycyclic aromatic hydrocarbons in the toposequence around the industrial area of Aba. The results revealed that Iron (Fe) has the highest concentrations in all the sampling sites, while cadmium showed the lowest concentrations in all the sampling sites and also in both sampling sites. Mercury and argon were not detected in all the sampling sites and also both sampling sites. The control recorded very low concentrations of the metals. The Polycyclic aromatic hydrocarbon revealed that indeno (1,2,3-cd) pyrene recorded the highest in all the sampling sites except for the valley bottom in both Ogbor hill (Ikot Ekpene road) and Ndi Egoro, while benzo (e) pryene recorded the highest in the valley bottom of both Ogbor hill (Ikot Ekpene road) and Ndi Egoro. Ogbor hill (Ikot Ekpene road)

Crest; Indp>Bep> Bbf> Bgp> Nap> Bkf > Ant> Phe> Apt, Flu, Dbh and Bbt;

Mid slope; Indp> Bbf and Bkf > Bep> Phe > Nap > Ant>Apt, Flu, Dbh, Bbt and Bgp;

Valley bottom; Bep> Bkf> Bbf> Ant> Nap, Phe and Dbh> Ant, Flu, Indp,Bbt and Bgt

**Ndi Egoro**

Crest; Indp>Bep> Bbf> Bgp> Nap> Bkf and Ant > Phe and Apt > Flu, Dbh and Bbt;

Mid slope ; Indp> Bbf >Bkf > Bep> Phe > Nap and Ant>Apt, Flu, Dbh, Bbt and Bgp;

Valley bottom; Bep> Bkf> Bbf> Phe and Dbh> Nap, Ant and Bbf > Flu, Indp, Bbt and Bgt.

## 5.2 Conclusion

The degree of contamination posed by heavy metals and polycyclic aromatic hydrocarbon in the toposequence around the industrial area in Aba, Nigeria were evaluated in the present study. The results provide evidence that open burning, stockpiling, and other improper waste management practices may have resulted in toxic heavy metal and polycyclic aromatic hydrocarbon accumulation in soils of industrial area in Aba. Various heavy metals contamination indices showed moderate to very high levels of contamination in soils around the industrial areas soils, indicating potential threats to human and ecological health. We found PAHs at levels exceeding National Environmental Standards and Regulations Enforcement Agency National (2011) and United States Environmental Protection Agency (2009) standards, suggesting anthropogenic contamination from both petrogenic and pyrogenic sources.

This work shows that improper industrial waste handling at these sites may contribute additional heavy metals and PAH contamination.

## 5.3 Recommendations

1. The result of this study is of serious health concern. There could be a buildup of these heavy metal and polycyclic aromatic contaminants in the study area, which may eventually contaminate the groundwater as well as nearby surface water resources in the area. Therefore, there is a serious need to frequently monitor activities in the study area to avert possible health challenges that may arise from increased levels of the heavy metals and PAHs resulting from the mechanics during automobile maintenance or servicing in the area.

2. Also, serious regulations should be enacted to assist in the control of activities of automobile mechanics in the automobile repair workshops.
3. There is need for effective monitoring of industrial wastewater discharges by the regulatory bodies to ensure good quality effluent and compliance with set standards.
4. NESREA, the regulating body in Nigeria and other stakeholders should map out holistic measures to tackle this continuous menace to our receiving water bodies and environment.
5. Lastly, industry owners/operators should as a matter of urgency obey the laws governing their operations and should perform their corporate and social responsibilities and ensure that effluent treatment plants are installed in their facilities, and should be operated at optimum conditions and manned by qualified personnel

**Contribution to knowledge**

The result from this study shows that there are high concentrations of the polycyclic aromatic hydrocarbon and heavy metals in the study areas; this is because of the industrial activities that take place in the area (Ogbor hill and Ndi Egoro). Several works has been done on these areas but on level of topography though, there is a depth of information on accumulation of these heavy metals and polycyclic aromatic hydrocarbon on various segment of toposequence namely, the crest, midslope and valley bottom. This is the gap that the study helped to close.

It will serve as useful reference tool to give guidance for future research.

.

## REFERENCES


Abarikwu, S., Iserhienrhien, B. and Badejo, T. (2013). Rutin-and selenium attenuated cadmium-induced testicular pathophysiology in rats. *Human and Experimental Toxicology, 32*(4):395-406.

Abdel-Shafy, H.I. and Mansour, M.S.M. (2016). A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum,25*:107–123.

Achten, C. and Hofmann, T. (2009). Native polycyclic aromatic hydrocarbons (PAH) in coals— a hardly recognized source of environmental contamination. *Science of the Total Environment, 407*:2461–2473.

Adeniyi, A.A. and Afolabi, J.A. (2002). Determination of total petroleum hydrocarbons and heavy metals in soils within the vicinity of facilities handling refined petroleum products in Lagos Metropolis. *Environmental International, 28*(1-2):79-82.

Adeyi, A.A. and Oyeleke, P. (2017). Heavy Metals and Polycyclic Aromatic Hydrocarbons in Soil from E-waste Dumpsites in Lagos and Ibadan, Nigeria. *Journal of Health and Pollution, 15: 71–84.*

Adriano, D. C (2003). Trace Elements in Terrestrial Environments: *Biogeochemistry, Bioavailability and Risks of Metals*, *Springer*, New York, NY, USA, 2nd edition.

Agency for Toxic Substances and Disease Registry (ATSDR) (2011).Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs): Health Effects Associated With PAH Exposure. *Environmental Medicine; Environmental Health Education.*

Ahrens, C.D. (2005). Essentials of meteorology: an invitation to the atmosphere.3th Edition, Cambridge University Press, *463.*

Akonye, L.A. and Onwudiwe, I.O. (2007). Effects of certain soil amendment agents on lead (Pb) uptake by plants grown on oil-polluted soil. *Scientia Africana, 6*(1):85-93.

Al-Maliki, M.A.S. (2005). Evaluation of air pollutants, water and soil in the city of Baghdad, using geographic information system (GIS), *PhD thesis*, Faculty of Science, Baghdad University, (171).

Armstrong, B. G., Hutchinson, E., Unwin, J. and Fletcher, T. (2004). Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: A review and meta-analysis.*Environmental HealthPerspect, 112*:970–978.

Baldwin, D.R., W. J. Marshall (1999). Heavy metal poisoning and its laboratory investigation. *Annals of Clinical Biochemistry*, 36(3):267–300.

Bolan, N. S., Ko, B.G., Anderson, C.W.N., Vogeler, I. (2008). Solute interactions in soils in relation to bioavailability and remediation of the environment," in *Proceedings of the 5th International Symposium of Interactions of Soil Minerals with Organic Components and Microorganisms*, Pucon,´ Chile, November.

Brandt, M., and Einhenkel-Arle, D. (2016). Polycyclic Aromatic Hydrocarbons Harmful tothe Environment! Toxic! Inevitable? *German Environment Agency*, 1–24.

Burchiel, S. W. and Luster, M. I. (2001). Signaling by environmental polycyclic aromatic hydrocarbons in human lymphocytes. *Clinical Immunology, 98*: 2–10.

Buszewski, B., Jastrzębska, A., Kowalkowski, T. and Górna-Binkul, A. (2000). Monitoring of selected heavy metals uptake by plants and soils in the area of Torun, Poland. *Pollution Journal of Environmental Studies, 9*(6):511–515.

Cachada, A., Pato, P., Rocha-Santos, T., Ferreira da Silva, E. and Duarte, A.C. (2012). Level, sources and potential human risks of organic pollutants in urban soils. *Science of the Total Environment, 430:*184-192.

Cao, W., Yin. L., Zhang, D., Wang, Y., Yuan. J., Zhu, Y. and Dou, J. (2019). Contamination, Sources, and Health Risks Associated with Soil PAHs in Rebuilt Land from a Coking Plant, Beijing, China. *International Journal of Environmental Research and Public Health*, *16*(670):1–16.

Castillo, M., Metta-Magaña, A. J. and Fortier, S. (2016). Isolation of gravimetrically quantifiable alkali metal arenides using 18-crown-6. *New Journal of Chemistry, 40* (3): 1923–1926.

Chesworth, W. (2008). Dordrecht, the Netherlands: *Springer*.

Davies, B.E., Jones, L.H.P (1988). Micronutrients and toxic elements in *Russell's* Soil Conditions and Plant Growth, A. Wild, Ed.,781–814, JohnWiley and Sons;Interscience, New York, NY, USA, 11th edition.

Diggs, D.L., Huderson, A.C., harris, K.L., Myers, J.N., Banks, L.D. and Rekhadevi, P.V. (2011). Polycyclic aromatic hydrocarbons digestive tract cancers: a prespective. *Journal of Environmental Science Health Part C Environmental Carcinogenesis and Ecotoxicology Reviews*, 29: 324-357

Dong, C., Chen, C. and Chen, C. (2012). Determination of polycyclic aromatic hydrocarbons in industrial hard or sediments by GC-MS. *International Journal of Environmental Research and Public Health 9*: 2175–2188.

Duedahl-Olesen, L., Aaslyng, M., Meinert, L., Christensen, T., Jensen, A.H. and Binderup, M.L. (2015). Polycyclic aromatic hydrocarbons (PAH) in Danish barbecued meat. *Food Control,* 57:169-176.

Duke, O. (2008). Source determination of polynuclear aromatic hydrocarbons in water and sediment of a creek in the Niger Delta region**.** *Afr J Biotechnol* 7(3):282-5.

Eriksson, J., Andersson, A., Andersson, R. (1997). The state of Swedish farmlands,Tech. Rep. 4778, *Swedish Environmental Protection Agency*, Stockholm, Sweden.

Eze, S.O. and Ogbuehi, G.I. (2015). Assessment of heavy metals and polycyclic aromatic hydrocarbon concentration in some stockfish species sold in five major markets of Aba South, Abia State, Nigeria. *European Journal of Pure and Applied Chemistry*, *2*(1):1-7.

Feng, X., Pisula, W. and Müllen, K. (2009). Large polycyclic aromatic hydrocarbons: Synthesis and discotic organization. *Pure and Applied Chemistry, 81* (2): 2203–2224.

Garcia-Suastegui, W. A., Huerta-Chagoya, A., Carrasco-Colın, K. L., Pratt, M. M., John, K. and Petrosyan, P. (2011). Seasonal variations in the levels of PAH-DNA adducts in young adults living inMexico City. *Mutagenesis, 26*:385–391.

Gowd, S.S., Reddy, M.R. and Govila, P.K. (2010). Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India. *Journal of Hazard Mater, 174*(1-3):113-21.

Gu, Y.G., Li, Q.S., Fang, J.H., He, B.Y., Fu, H.B. and Tong, Z.J. (2014). Tong Identification of heavy metal sources in the reclaimed farmland soils of the Pearl River estuary in China using a multivariate geostatistical approach. *Ecotoxicology and Environmental Safety, 105*:7-12.

Gunter, M. J., Divi, R. L., Kulldorff, M., Vermeulen, R., Haverkos, K. J. and Kuo, M. M. (2003). Leukocyte polycyclic aromatic hydrocarbon-DNA adduct formation and colorectal adenoma. *Carcinogenesis, 28*:1426–1429.

Gupte, A., Tripathi, A., Patel, H., Rudakiya, D. and Gupte, S. (2016). Bioremediation of polycyclic aromatic hydrocarbon (PAHs): a perspective. *Open Biotechnology Journal*, 10:363–378.

Hashim, B.M. (2009). Measurement and study concentrations some air pollutants in Baghdad city. *M. Sc. thesis College of Science*, Al - Mustansiriyah University, *95*.

Huang, j., Huang, Y., Pontius, R.G. and Zhang, Z. (2015). Geographically weighted regression to measure spatial variations in correlations between water pollution versus land use in a coastal watershed. *Ocean and Coastal Management, 103*:14-24.

Ibe, F.C., Opara, A.I., Duru, C.E., Isiuku, B.O. and Enedoh, M.C. (2020). Statistical analysis of atmospheric pollutant concentrations in parts of Imo State, Southeastern Nigeria. *Scientific African, 7*(e00237):1–27

Ibe, F.C., Opara, A.I., Ibe, B.O., Adindu, B.C. and Ichu, B.C. (2018). Environmental and health implications of trace metal concentrations in street dust around some electronic repair workshops in Owerri, Southeastern Nigeria. *Environmental Monitoring and Assessment, 190*(696):1-2.

Ijeh, B.I. and Onu, N.N. (2013). Assessment of pollution levels of groundwater in parts of Imo River Basin, South Eastern Nigeria. *International Journal of Water Resources andEnvironmental Engineering, 5*(4): 194-202.

Institute of Environmental Protection—National Research Institute. (IEP). (2019). National Emissions of SO2, NOx, CO, NH3, NMVOC, Dust, Heavy Metals, POP for 2015–2017; Institute of Environmental Protection—National Research Institute: Warszawa, Poland.

Ivan, G. and Sven, J. C. (2012): *Introduction to the Theory of Benzenoid Hydrocarbons*. 152.

Jimoh, H.I. (2005). Tropical Rainfall Events on Erosion Rate in Rapidly Developing Urban Areas in Nigeria. *Singapore Journal of Tropical Geography*, 26(1):77-80.

John, K., Ragavan, N., Pratt, M. M., Singh, P. B., Al-Buheissi, S. and Matanhelia, S. S. (2009). Quantification of phase I/II metabolizing enzyme gene expression and polycyclicaromatichydrocarbon-DNA adduct levels in human prostate. *Prostate, 69*:505–519.

Kabata-Pendias, A. (2000). Trace Elements in Soils and Plants. *CRC Press*, Boca Raton, USA.

Kabata-Pendias, A and Pendias, H (2001).*Trace Metals in Soils and Plants*, CRC Press, Boca Raton, Fla, USA, 2nd edition, 2001.

Kamal, A., Cincinelli, A., Martellini, T. and Malik, R. N. (2015). A review of PAH exposure from the combustion of biomass fuel and their less surveyed effect on the blood parameters. *Environmental Science and PollutionResearch, 22*:4076–4098.

Kim, K.H., S.A. Jahan, S.A. Kabir, E. and Brown, R.J.C. (2013). A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human effects. *Environment International, 60:*71–80.

Kem, S. (2007). Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. *Environmental Chemistry Letters, 5*:169–195.

Khan, S. and Cao, Q. (2012). Human health risk due to consumption of vegetables contaminated with carcinogenic polycyclic aromatic hydrocarbons. *Journal of Soils Sediment, 12*(2):178-84.

Köppen-Geiger. (2017). Koppen climate classification climatology *Encyclopedia Britannica*.

Kostrz, M. and Satora, P. (2017). Compounds responsible for air pollution. *Ecological Engineering, 18*:89–95.

Lasota, J. and Błońska, E. (2018). Polycyclic aromatic hydrocarbons content in contaminated forest soils with different humus types. *Water Air and Soil Pollution*, 229:204.

Lasat, M.M (2000). Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues, *Journal of Hazardous Substances Research*, 2:1–25.

Lawal, A.O., Batagarawa,S.M., Oyeyinka,O.D. and Lawal,M.O. (2011). Estimation of heavy metals in Neem tree leaves along Katsina–Dutsinma– Funtua Highway in Katsina State of Nigeria. *Journal of Applied Science and Environmental Manag*ement, *15*(2):327–330.

Lee, B. K. and Vu, V. T. (2010). Sources, distribution and toxicity of polyaromatic hydrocarbons (PAHs) in particulate matter, in Air Pollution, London: *Intech Open*, 99-122.

Li, Y., Liu, Z., Zhao, X., Li, H. and Li, H. (2010). Evaluation on potential ecological risk of heavy metal pollution in sediment of urban sewage river, *National Basic Research Program and National Natural Science Foundation of China.*

Madu, P.C., Tagwoi J.T., Babalola, F (2008). A study of heavy metal pollution of River Antau, Keffi, Nasarawa State, Nigeria, *Indian Journal of Multilingual Research and Development, 4*(1): *8-18.*

Maier, A., Schumann, B.L., Chang, X.Q., Talaska, G. and Puga, A. (2002). Arsenic co-exposure potentiates benzo[a]pyrene genotoxicity. *Mutation Research, 517*:101–111.

Manahan, S.E (2003). *Toxicological Chemistry and Biochemistry*, CRC Press, Limited Liability Company (LLC), 3rd edition.

Marr, L.C., Dzepin,a K., Jimenez, J.L., Reisen, F., Bethel, H.L., Arey, J., Gaffney, J.S., Marley, N.A., Molina, L.T. and Molina, M.J. (2006). Sources and transformations of particle bound polycyclic aromatic hydrocarbons in Mexico City. *Atmospheric Chemistry and Physics, 6*:1733–1745.

Martin, S. and Griswold, W. (2009). Human health effects of heavy metals. *Environmental science and technology brief for citizens center for hazardous substance research, 15*:1-6.

Masih, A. and Taneja, A. (2006). Polycyclic aromatic hydrocarbon (PAHs) concentrations and related carcinogenic potencies in soil at a semi-arid region of India. *Chemosphere, 65*:449–456.

Masitah, A., Zaini, H. and Lee, S.K. (2007). PM10 and total suspended particulates (TSP) measurements in various power stations. *Malays Journal Analytical Science*, *11*(1):255–261.

Maslin, P. and Maier, R.M (2000). Rhamnolipid-enhanced mineralization of phenanthrene in organic-metal co-contaminated soils, Bioremediation *Journal*, *4*(4): 295–308.

McClellan, T. (2021). Soil composition. University of Hawai‘i at Mānoa, College of Tropical Agriculture and Human Resources.

Mojiri, A., Zhou, J. L., Ohashi, A., Ozaki, N. and Kindaichi, T. (2019). Comprehensive review of polycyclic aromatic hydrocarbons in water sources, their effects and treatments. *Science of the Total Environment*, 13:39-71.

Maurya, .N. (2014). *Assistant Professor Dept. of Civil EngineeringFaculty of Engineering and TechnologyMadhav University*

Muze, N.E., Opara, A.I., Ibe, F.C. and Njoku, O.C. (2020). Assessment of the geo-environmental effects of activities of auto-mechanic workshops at Alaoji Aba and

Elekahia Port Harcourt, Niger Delta, Nigeria. *Environmental Analysis Health and Toxicology, 35*(2):2671-9225.

National Environmental Standards and Regulations Enforcement Agency National (NESREA) (2011). Environmental (Surface and Ground water Quality Control) Regulations- Effluent discharges, irrigation and reuse standards.

Njoku, P., Ibe, F.C., Alinnor, J. and Opara, A. (2016) Seasonal variability of carbon monoxide (CO) in the ambient environment of Imo State, Nigeria. *International Letter of Natural Science,5*:40–52.

Nkansah, M.A., Christy, A.A. and Barth, T. (2011). The use of anthracene as a model compound in a comparative study of hydrous pyrolysis methods for industrial waste remediation. *Chemosphere, 84*(4):403-408.

Nwachukwu, E., Newman, Y. and Janefrances, I. (2017). Ecological risk assessment of heavy metals and polycyclicaromatic hydrocarbons in sediments of rivers Niger and Benueconfluence, Lokoja, Central Nigeria. *Environmental Science and Pollution Research,* 17-9511-6

Nor, A.F. and Suhaimi, A. (2013). Hazards due to polycyclic aromatic hydrocarbons (PAHs) and heavy metals at the closed Kubang Badak landfill, Selangor. *International Journal of Environmental Monitoring and Analysis, 1*(2):71-77.

Nouri, N., Poorhashemi, S.A., Monavari, S.M., Dabiri, F. and Hassani, A.H. (2011). Legal criteria and executive standards of solid waste disposal subjected to solid waste management act. *International Journal of Environmental Research, 5*(4):971-980.

Occupational Safety and Health Administration (OSHA). (2004). Safety and health topics: Heavy metals.

Okere, U. and Semple, K. (2012). Biodegradation of PAHs in 'pristine'soils from different climatic regions. *Journal Bioremediation Biodegradation,* S1:006.

Oketola, A.A. and Akpotu, S.O. (2015). Assessment of solid waste and dumpsite leachate and topsoil. *Chemical Ecological, 31*(2):134–46.

Ololade, I.A. (2014). An assessment of heavy-metal contamination in soils within auto-mechanic workshops using enrichment and contamination factors with geoaccumulation indexes. *Journal of Environmental Protection, 5*:970-982.

Olsson, A. C., Fevotte, J., Fletcher, T., Cassidy, A., Mannetje, A. and Brennan, P. (2010). Occupational exposure to polycyclic aromatic hydrocarbons and lung cancer risk: amulticenter studyin Europe. *Occupational and Environmental Medicine,67*:98–103.

Paschke, M., Hutzler, C., Brinkmann, J., Henkler, F., and Luch, A. (2015). Polycyclic aromatic hydrocarbons in newspaper inks: migration, metabolism, and genotoxicity in human skin. *Polycyclic Aromatic Compounds, 35*:32–40.

Patel, A.B., Shaikh, S., Jain, K, R., Desai, C. and Madamwar, D. (2020). Polycyclic Aromatic Hydrocarbons: Sources, Toxicity, and Remediation Approaches. *Frontiers in Microbiology, 11*:562813

Rauckyte, T., Zak, S., Pawlak, Z. and Oloyede, A. (2010). Determination of oil and grease, total petroleum hydrocarbons and volatile aromatic compounds in soil and sediment samples. *Journal of Environmental Engineering Landscape Managing, 18*(3):163-169.

Ravindra, K., Sokhi, R. and Van Grieken, R. (2008). Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmospheric Environment, 42:*2895–2921.

Rengarajan, T., Rajendran, P., Nandakumar, N., Lokeshkumar, B., Rajendran, P. and Nishigaki, I. (2015). Exposure to polycyclic aromatic hydrocarbons with special focus on cancer. *Asian Pacific Journal of Tropical Biomedicine, 5*:182–189.

Riccardi, C., Filippo, P.Di., Pomata, D., Basilio, M.Di. and Spicaglia, S. (2013). Identification of hydrocarbon sources in contaminated soils of three industrial areas. *Science of the Total Environment, 450*:13-21.

Rose, M., Holland, J., Dowding, A., Petch, S. R., White, S. and Fernandes, A. (2015). Investigation into the formation of PAHs in foods prepared in the home to determine the effects of frying, grilling, barbecuing, toasting and roasting. *Food and Chemical Toxicology, 78:*1–9.

Rosen, C.J. (2002).Lead in the home garden and urban soil environment, *CommunicationandEducational Technology Services*, University of Minnesota Extension.

Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M. (1993). Environmental organic chemistry, John Wiley and Sons, Inc.

Scragg, A (2006).*Environmental Biotechnology*, Oxford University Press, Oxford, UK, 2nd edition.

Shang, D., Kim, M. and Haberl, M. (2014). Development of a rapid liquid chromatography tandem mass spectrometry method for screening of trace naphthenic acids in aqueous environment. *Journal of Chromatography A,1334*:118–125.

Samek, L., Stegowski, Z., Furman, L. and Fiedor, J. (2016). Chemical content and estimated sources of fine fraction of particulate matter collected in Krakow. *Air Quality Atmosphere and Health.*

Smith, A.H., Lingas, E.O. and Rahman, M. (2000). Contamination of drinking water byarsenic in Bangladesh: a public health emergency. *Bull WHO, 78*(9):1093-1103.

Smith, L.A., Means, J.L. (1995). *Remedial Options for Metals-Contaminated Sites*, Lewis Publishers, Boca Raton, Fla, USA.

Sposito, G. (2021). Soil. *Pedology.*

Srogi, K. (2007). Monitoring of environmental exposure to polycyclic aromatichydrocarbons: a review. *Environmental Chemistry Letters, 5*:169–195.

Sumner, M.E (2000). Beneficial use of effluents, wastes, and biosolids,*Communications in Soil Science and Plant Analysis*, 31(11–14):1701–1715.

Suman, S., Sinha, A. and Tarafdar, A. (2016). Polycyclic aromatic hydrocarbons (PAHs) concentration levels, pattern, source identification and soil toxicity assessment in urban traffic soil of Dhanbad. India. *Science of the Total Environment*, 545: 353–360.

Tang, X., Shen, C., Shi, D., Cheema, S.A., Khan, M.I., Zhang, C. and Chen, Y. (2010). Heavy metal and persistent organic compound contamination in soil from Wenling: an emerging e-waste recycling city in Taizhou area, China. *Journal of Hazardous Materials,173*(1-3):653-60.

Tehrani, G.M., Hshim, R., Sulaiman, A.H., Tavakoly, S.S.B. and Salleh, A. (2012). Histopathological and bacteriological study on hepatic abscesses of herrik sheep. *Environment Protection Engineering, 15* (2012) 115–128.

Tian, F., Chen, W., Qiao, X., Wang, Z., Yang, P., Wang, D. and Ge, L. (2009). Sources and seasonal variation of atmospheric polycyclic aromatic hydrocarbons in Dalian, China: factor analysis with non-negative constraints combined with local source fingerprints. *Atmospheric Environment, 43*:2747–2753

Tobiszewski, M. and Namiesnik, J. (2012). PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution, 162*:110–119.

Toxicological profile for polycyclic aromatic hydrocarbons(TPPAHs) (1995). Atlanta, Georgia: Agency for Toxic Substances and Disease Registry, 487.

Tsibart, A.S. and Gennadiev, A.N. (2013). Polycyclic aromatic hydrocarbons in soils: sources, behavior, and indication significance (a review). *Eurasian Soil Science, 46*(7):728-41.

Umar, M.A and Opaluwa, O.D (2010). Evaluation of heavy metals in sediments of Rafin Mallam stream in Keffi, Nasarawa State, *International Journal of Chemical Science, 20***(**2**)**: 99-103

Unwin, J., Cocker, J., Scobbie, E. and Chambers, H. (2006). An assessment of occupational exposure to polycyclic aromatic hydrocarbons in the UK. *Annals of Occupational Hygiene, 50*:395–403.

United States Environmental Protection Agency (US EPA). (2009). Drinking water contaminants. Washington, DC, USA.

Wani, S. and Kaushal, G. (2009). Watershed management concept and principles. *International Crops Research Institute for the Semi-Aridn Tropics (ICRISAT)*, Andhras Pradesh, India.

Wasiullah, R.D., Malaviya, D., Pandiyan, K., Singh, U.B., Sahu , A., Shukla, R., Singh, B.P., Rai, J.P., Sharma, P.K., Lade, H. and Paul, D. (2015). Bioremediation of Heavy Metals from Soil and Aquatic Environment: An Overview of Principles and Criteria of Fundamental Processes. *Sustainability*, **(7)**: 2189-2212

Wei, L. and Liu, Y. (2012). Present Status of e-waste Disposal and Recycling in China. *Procedia Environmental Sciences, 16*:506–14.

World Health Organization (WHO) (2011). Drinking-water quality standard, world health organization guidelines (WHO) for drinking-water quality fourth edition.

Yang, Y., Zhang, X.X. and Korenaga, T. (2002). Distribution of polynuclear aromatic hydrocarbons (PAHs) in the soil of Tokushima, Japan, *Water, Air, and Soil Pollution*, *138*(1–4):51–60.

Yongzhen, L., Guoxiang, C., Hairuo, Q., Tagen, D. and Qianhong, W. (2011). Sources of polycyclic aromatic hydrocarbons in street dust from the Chang-Zhu- Tan region, Hunan, China. *Journal of Environmental Protection*, *2*:1331–1340.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D. and Sylvestre, S. (2002). PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry, 33* (4):489–515.

Zelinkova, Z. and Wenzl, T. (2015). The occurrence of 16 EPA PAHs in fooda review. *Polycyclic Aromatic Compound*, 35, 248–284.

Zhao, Q. and Kaluarachchi, J.J. (2002). Risk assessment at hazardous waste-contaminated sites with variability of population characteristics,*Environment International*, 28(1-2): 41–53,

Ziola, N. and Slaby, K. (2020). The Content of Selected Heavy Metals and Polycyclic Aromatic Hydrocarbons (PAHs) in PM10 in Urban-Industrial Area. *Sustainability, 12*(5284): 1-16.

# APPENDIX

**Ogbor hill(Multiple Unpired T-test) for 0-15 cm**

| Parameter (mg/kg) | Discovery? | P value | Mean of Control | Mean of Ogbor hill | Difference | SE of difference | t ratio | df | q value |
|---|---|---|---|---|---|---|---|---|---|
| Pb | Yes | 0.001369 | 0.03667 | 23.73 | -23.70 | 2.989 | 7.929 | 4.000 | 0.000553 |
| Zn | Yes | 0.000015 | 0.02000 | 153.3 | -153.3 | 6.111 | 25.09 | 4.000 | 0.000015 |
| Cd | No | 0.346746 | 0.000 | 7.333 | -7.333 | 6.883 | 1.065 | 4.000 | 0.100061 |
| Cu | Yes | 0.000093 | 0.003333 | 52.85 | -52.85 | 3.334 | 15.85 | 4.000 | 0.000062 |
| Fe | Yes | 0.000007 | 0.3400 | 282.2 | -281.8 | 9.384 | 30.03 | 4.000 | 0.000015 |
| Ar | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Mn | Yes | 0.000475 | 0.1700 | 25.67 | -25.50 | 2.442 | 10.44 | 4.000 | 0.000240 |
| Hg | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |

**2way Anova) for Ogbor hill (0-15 cm)**

| **Table Analyzed** | **Grouped: Entering replicate data** | | | | |
|---|---|---|---|---|---|
| Two-way ANOVA | Ordinary | | | | |
| Alpha | 0.05 | | | | |
| Source of Variation | % of total variation | P value | P value summary | Significant? | |
| Interaction | 40.52 | <0.0001 | **** | Yes | |
| Row Factor | 40.67 | <0.0001 | **** | Yes | |
| Column Factor | 18.37 | <0.0001 | **** | Yes | |
| ANOVA table | SS | DF | MS | F (DFn, DFd) | P value |
| Interaction | 110431 | 8 | 13804 | F (8, 36) = 413.3 | P<0.0001 |
| Row Factor | 110847 | 8 | 13856 | F (8, 36) = 414.8 | P<0.0001 |
| Column Factor | 50056 | 1 | 50056 | F (1, 36) = 1499 | P<0.0001 |
| Residual | 1202 | 36 | 33.40 | | |
| Difference between column means | | | | | |
| Mean of Control | 0.06407 | | | | |
| Mean of Ogbor hill | 60.96 | | | | |
| Difference between means | -60.89 | | | | |
| SE of difference | 1.573 | | | | |
| 95% CI of difference | -64.08 to -57.70 | | | | |
| Data summary | | | | | |
| Number of columns (Column Factor) | 2 | | | | |
| Number of rows (Row Factor) | 9 | | | | |
| Number of values | 54 | | | | |

**Ndi Egoro (Multiple Unpired T-test) for 0-15 cm**

| Parameter (mg/kg) | Discovery? | P value | Mean of Control | Mean of River Bank Side A | Difference | SE of difference | t ratio | df | q value |
|---|---|---|---|---|---|---|---|---|---|
| Pb | Yes | 0.002015 | 0.02333 | 22.90 | -22.88 | 3.195 | 7.159 | 4.000 | 0.000407 |
| Zn | Yes | 0.000004 | 0.03667 | 147.3 | -147.3 | 4.127 | 35.69 | 4.000 | 0.000001 |
| Cd | No | 0.339836 | 0.000 | 6.217 | -6.217 | 5.742 | 1.083 | 4.000 | 0.057206 |
| Cu | Yes | 0.000194 | 0.006667 | 51.29 | -51.28 | 3.906 | 13.13 | 4.000 | 0.000049 |
| Fe | Yes | 0.000004 | 0.3400 | 278.7 | -278.3 | 7.930 | 35.10 | 4.000 | 0.000001 |
| Ar | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Mn | Yes | 0.000002 | 0.1700 | 22.67 | -22.50 | 0.5253 | 42.82 | 4.000 | 0.000001 |
| Hg | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |

**Ndi Egoro (2way Anova) for 0-15 cm**

| **Table Analyzed** | **Grouped: Entering replicate data** | | | | |
|---|---|---|---|---|---|
| | | | | | |
| Two-way RM ANOVA | Matching: Both factors | | | | |
| Assume sphericity? | Yes | | | | |
| Alpha | 0.05 | | | | |
| | | | | | |
| Source of Variation | % of total variation | P value | P value summary | Significant? | |
| Row Factor | 39.75 | <0.0001 | **** | Yes | |
| Column Factor | 20.34 | 0.0021 | ** | Yes | |
| Row Factor x Column Factor | 39.59 | <0.0001 | **** | Yes | |
| Subject x Row Factor | 0.07943 | | | | |
| Subject x Column Factor | 0.08377 | | | | |
| Subject | 0.08290 | | | | |
| | | | | | |
| ANOVA table | SS | DF | MS | F (DFn, DFd) | P value |
| Row Factor | 102323 | 7 | 14618 | F (7, 14) = 1001 | P<0.0001 |
| Column Factor | 52368 | 1 | 52368 | F (1, 2) = 485.6 | P=0.0021 |
| Row Factor x Column Factor | 101923 | 7 | 14560 | F (7, 14) = 1029 | P<0.0001 |
| Subject x Row Factor | 204.5 | 14 | 14.61 | | |
| Subject x Column Factor | 215.7 | 2 | 107.8 | | |
| Subject | 213.4 | 2 | 106.7 | | |
| Residual | 198.2 | 14 | 14.15 | | |
| | | | | | |
| Difference between column means | | | | | |
| Mean of Control | 0.07208 | | | | |
| Mean of Ndi Egoro | 66.13 | | | | |
| Difference between means | -66.06 | | | | |
| SE of difference | 2.998 | | | | |
| 95% CI of difference | -78.96 to -53.16 | | | | |
| | | | | | |
| Data summary | | | | | |
| Number of columns (Column Factor) | 2 | | | | |
| Number of rows (Row Factor) | 8 | | | | |
| Number of subjects (Subject) | 3 | | | | |
| Number of missing values | 0 | | | | |

**PAHS @ Ogbor hill (Multiple Unpired T-test) for 0-15 cm**

| Parameter (ppm) | Discovery? | P value | Mean of Control | Mean of Ogbor hill | Difference | SE of difference | t ratio | df | q value |
|---|---|---|---|---|---|---|---|---|---|
| Naphthalene | No | 0.051374 | 0.000 | 0.03667 | -0.03667 | 0.01333 | 2.750 | 4.000 | 0.207553 |
| Acenaphthylene | No | 0.373901 | 0.000 | 0.003333 | -0.003333 | 0.003333 | 1.000 | 4.000 | 0.377640 |
| Acenaphthene | No | 0.002192 | 0.000 | 0.02333 | -0.02333 | 0.003333 | 7.000 | 4.000 | 0.026569 |
| Fluorene | No | 0.373901 | 0.000 | 0.003333 | -0.003333 | 0.003333 | 1.000 | 4.000 | 0.377640 |
| Phenanthrene | No | 0.320167 | 0.000 | 0.1267 | -0.1267 | 0.1117 | 1.134 | 4.000 | 0.377640 |
| Benzo (b) fluoranthene | No | 0.090390 | 0.000 | 0.6433 | -0.6433 | 0.2895 | 2.222 | 4.000 | 0.273881 |
| Benzo (k) fluoranthene | No | 0.209881 | 0.000 | 0.4333 | -0.4333 | 0.2904 | 1.492 | 4.000 | 0.363394 |
| Benzo (e) pryene | No | 0.037449 | 0.006667 | 1.013 | -1.007 | 0.3284 | 3.066 | 4.000 | 0.207553 |
| Dibeno (a,h) anthracene | No | 0.116117 | 0.000 | 0.006667 | -0.006667 | 0.003333 | 2.000 | 4.000 | 0.281466 |
| Indeno (1,2,3-cd)pyrene | No | 0.182643 | 0.000 | 1.183 | -1.183 | 0.7349 | 1.610 | 4.000 | 0.363394 |
| Benzo (b)triphenylene | No | 0.373901 | 0.000 | 0.003333 | -0.003333 | 0.003333 | 1.000 | 4.000 | 0.377640 |
| Benxo (ghi) perylene | No | 0.373901 | 0.000 | 0.05333 | -0.05333 | 0.05333 | 1.000 | 4.000 | 0.377640 |

**PAHS @ Ogbor hill (TWO Way ANOVA) for 0-15 cm**

| **Table Analyzed** | **Grouped: Entering replicate data** | | | | |
|---|---|---|---|---|---|
| | | | | | |
| Two-way ANOVA | Ordinary | | | | |
| Alpha | 0.05 | | | | |
| | | | | | |
| Source of Variation | % of total variation | P value | P value summary | Significant? | |
| Interaction | 23.88 | 0.0104 | * | Yes | |
| Row Factor | 24.11 | 0.0098 | ** | Yes | |
| Column Factor | 12.34 | 0.0003 | *** | Yes | |
| | | | | | |
| ANOVA table | SS | DF | MS | F (DFn, DFd) | P value |
| Interaction | 3.003 | 11 | 0.2730 | F (11, 48) = 2.626 | P=0.0104 |
| Row Factor | 3.031 | 11 | 0.2756 | F (11, 48) = 2.651 | P=0.0098 |
| Column Factor | 1.552 | 1 | 1.552 | F (1, 48) = 14.93 | P=0.0003 |
| Residual | 4.989 | 48 | 0.1039 | | |
| | | | | | |
| Difference between column means | | | | | |
| Mean of Control | 0.0005556 | | | | |
| Mean of Ogbor hill | 0.2942 | | | | |
| Difference between means | -0.2936 | | | | |
| SE of difference | 0.07599 | | | | |
| 95% CI of difference | -0.4464 to -0.1408 | | | | |
| | | | | | |
| Data summary | | | | | |
| Number of columns (Column Factor) | 2 | | | | |
| Number of rows (Row Factor) | 12 | | | | |
| Number of values | 72 | | | | |

**PAHS@ Ndi Egoro (Multiple Unpired T-test) 0-15 cm**

| Parameter (ppm) | Discovery? | P value | Mean of Control | Mean Ndi Egoro | Difference | SE of difference | t ratio | df | q value |
|---|---|---|---|---|---|---|---|---|---|
| Naphthalene | No | 0.014173 | 0.000 | 0.03667 | -0.03667 | 0.008819 | 4.158 | 4.000 | 0.071572 |
| Acenaphthylene | No | 0.373901 | 0.000 | 0.003333 | -0.003333 | 0.003333 | 1.000 | 4.000 | 0.377640 |
| Acenaphthene | No | 0.002192 | 0.000 | 0.02333 | -0.02333 | 0.003333 | 7.000 | 4.000 | 0.022141 |
| Fluorene | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Phenanthrene | No | 0.287151 | 0.000 | 0.1333 | -0.1333 | 0.1087 | 1.227 | 4.000 | 0.377640 |
| Benzo (b) fluoranthene | No | 0.049653 | 0.000 | 0.6833 | -0.6833 | 0.2455 | 2.783 | 4.000 | 0.125373 |
| Benzo (k) fluoranthene | No | 0.206433 | 0.000 | 0.4067 | -0.4067 | 0.2700 | 1.506 | 4.000 | 0.347495 |
| Benzo (e) pryene | No | 0.037449 | 0.006667 | 1.013 | -1.007 | 0.3284 | 3.066 | 4.000 | 0.125373 |
| Dibeno (a,h) anthracene | No | 0.373901 | 0.000 | 0.01333 | -0.01333 | 0.01333 | 1.000 | 4.000 | 0.377640 |
| Indeno (1,2,3-cd)pyrene | No | 0.182643 | 0.000 | 1.183 | -1.183 | 0.7349 | 1.610 | 4.000 | 0.347495 |
| Benzo (b)triphenylene | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Benxo (ghi) perylene | No | 0.373901 | 0.000 | 0.05000 | -0.05000 | 0.05000 | 1.000 | 4.000 | 0.377640 |

**PAHS@ Ndi Egoro (2way Anova) for 0-15 cm**

| **Table Analyzed** | **Grouped: Entering replicate data** | | | | |
|---|---|---|---|---|---|
| Two-way ANOVA | Ordinary | | | | |
| Alpha | 0.05 | | | | |
| Source of Variation | % of total variation | P value | P value summary | Significant? | |
| Interaction | 24.40 | 0.0072 | ** | Yes | |
| Row Factor | 24.63 | 0.0067 | ** | Yes | |
| Column Factor | 12.59 | 0.0002 | *** | Yes | |
| ANOVA table | SS | DF | MS | F (DFn, DFd) | P value |
| Interaction | 3.036 | 11 | 0.2760 | F (11, 48) = 2.775 | P=0.0072 |
| Row Factor | 3.065 | 11 | 0.2786 | F (11, 48) = 2.801 | P=0.0067 |
| Column Factor | 1.566 | 1 | 1.566 | F (1, 48) = 15.75 | P=0.0002 |
| Residual | 4.774 | 48 | 0.09946 | | |
| Difference between column means | | | | | |
| Mean of Control | 0.0005556 | | | | |
| Mean of Ndi Egoro | 0.2956 | | | | |
| Difference between means | -0.2950 | | | | |
| SE of difference | 0.07433 | | | | |
| 95% CI of difference | -0.4445 to -0.1455 | | | | |
| Data summary | | | | | |
| Number of columns (Column Factor) | 2 | | | | |
| Number of rows (Row Factor) | 12 | | | | |
| Number of values | 72 | | | | |

**Ogbor hill(Multiple Unpired T-test) for 15-30 cm**

| Parameter (kg/mg) | Below threshold? | P value | Mean of control | Mean of Ogbor hill | Difference | SE of difference | t ratio | df | Adjusted P Value |
|---|---|---|---|---|---|---|---|---|---|
| Pb | No | 0.368952 | 0.02333 | 6.710 | -6.687 | 6.610 | 1.012 | 4.000 | 0.898499 |
| Zn | No | 0.351781 | 0.003333 | 45.68 | -45.67 | 43.38 | 1.053 | 4.000 | 0.898499 |
| Cd | No | 0.317015 | 0.000 | 0.1200 | -0.1200 | 0.1050 | 1.142 | 4.000 | 0.898499 |
| Cu | No | 0.358516 | 0.000 | 16.18 | -16.18 | 15.61 | 1.036 | 4.000 | 0.898499 |
| Fe | No | 0.371096 | 0.2333 | 79.44 | -79.21 | 78.69 | 1.007 | 4.000 | 0.898499 |
| Ar | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Mn | No | 0.338418 | 0.1000 | 6.543 | -6.443 | 5.931 | 1.086 | 4.000 | 0.898499 |
| Hg | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |

**ANOVA forOgbor hill (15-30 cm)**

| **Table Analyzed** | **Grouped: Entering replicate data** | | | | |
|---|---|---|---|---|---|
| Two-way ANOVA | Ordinary | | | | |
| Alpha | 0.05 | | | | |
| Source of Variation | % of total variation | P value | P value summary | Significant? | |
| Interaction | 11.92 | 0.6086 | ns | No | |
| Row Factor | 12.03 | 0.6033 | ns | No | |
| Column Factor | 6.192 | 0.1019 | ns | No | |
| ANOVA table | SS | DF | MS | F (DFn, DFd) | P value |
| Interaction | 8597 | 7 | 1228 | F (7, 32) = 0.7801 | P=0.6086 |
| Row Factor | 8673 | 7 | 1239 | F (7, 32) = 0.7870 | P=0.6033 |
| Column Factor | 4466 | 1 | 4466 | F (1, 32) = 2.836 | P=0.1019 |
| Residual | 50382 | 32 | 1574 | | |
| Difference between column means | | | | | |
| Mean of Group A | 0.04292 | | | | |
| Mean of Group B | 19.33 | | | | |
| Difference between means | -19.29 | | | | |
| SE of difference | 11.45 | | | | |
| 95% CI of difference | -42.62 to 4.041 | | | | |
| Data summary | | | | | |
| Number of columns (Column Factor) | 2 | | | | |
| Number of rows (Row Factor) | 8 | | | | |

| | |
|---|---|
| Number of values | 48 |

**Ndi Egoro (Multiple Unpired T-test) for 15-30 cm**

| Parameter | Discovery? | P value | Mean control | Mean Ndi Egoro | Difference | SE of difference | t ratio | Df | q value |
|---|---|---|---|---|---|---|---|---|---|
| Pb | Yes | 0.008931 | 0.006667 | 18.43 | -18.43 | 3.874 | 4.756 | 4.000 | 0.009020 |
| Zn | Yes | 0.000003 | 0.01000 | 127.5 | -127.4 | 3.402 | 37.46 | 4.000 | 0.000009 |
| Cd | Yes | 0.000338 | 0.000 | 0.2967 | -0.2967 | 0.02603 | 11.40 | 4.000 | 0.000512 |
| Cu | Yes | 0.002331 | 0.000 | 34.38 | -34.38 | 4.992 | 6.886 | 4.000 | 0.002825 |
| Fe | Yes | 0.000005 | 0.2000 | 247.4 | -247.2 | 7.347 | 33.65 | 4.000 | 0.000009 |
| Ar | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Mn | Yes | <0.000001 | 0.06667 | 15.45 | -15.38 | 0.2213 | 69.49 | 4.000 | 0.000002 |
| Hg | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |

**Ndi Egoro ANOVA for 15-30 cm**

| **Table Analyzed** | **Grouped: Entering replicate data** | | | | |
|---|---|---|---|---|---|
| Two-way RM ANOVA | Matching: Both factors | | | | |
| Assume sphericity? | Yes | | | | |
| Alpha | 0.05 | | | | |
| Source of Variation | % of total variation | P value | P value summary | Significant? | |
| Row Factor | 40.75 | <0.0001 | **** | Yes | |
| Column Factor | 18.29 | 0.0018 | ** | Yes | |
| Row Factor x Column Factor | 40.65 | <0.0001 | **** | Yes | |
| Subject x Row Factor | 0.09305 | | | | |
| Subject x Column Factor | 0.06526 | | | | |
| Subject | 0.06591 | | | | |
| ANOVA table | SS | DF | MS | F (DFn, DFd) | P value |
| Row Factor | 82056 | 7 | 11722 | F (7, 14) = 876.0 | P<0.0001 |
| Column Factor | 36816 | 1 | 36816 | F (1, 2) = 560.4 | P=0.0018 |
| Row Factor x Column Factor | 81839 | 7 | 11691 | F (7, 14) = 900.7 | P<0.0001 |
| Subject x Row Factor | 187.4 | 14 | 13.38 | | |
| Subject x Column Factor | 131.4 | 2 | 65.70 | | |
| Subject | 132.7 | 2 | 66.36 | | |
| Residual | 181.7 | 14 | 12.98 | | |
| Difference between column means | | | | | |
| Mean of Group A | 0.03542 | | | | |
| Mean of Group B | 55.43 | | | | |
| Difference between means | -55.39 | | | | |
| SE of difference | 2.340 | | | | |
| 95% CI of difference | -65.46 to -45.32 | | | | |
| Data summary | | | | | |
| Number of columns (Column Factor) | 2 | | | | |
| Number of rows (Row Factor) | 8 | | | | |
| Number of subjects (Subject) | 3 | | | | |
| Number of missing values | 0 | | | | |

**PAH for Ogbor hill(Multiple Unpired T-test)for 15-30 cm**

| Parameter (ppm) | Discovery? | P value | Mean control | Mean Ogbor hill | Difference | SE of difference | t ratio | Df | q value |
|---|---|---|---|---|---|---|---|---|---|
| Naphthalene (ppm) | No | 0.124170 | 0.000 | 0.02333 | -0.02333 | 0.01202 | 1.941 | 4.000 | 0.487699 |
| Acenaphthylene | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Acenaphthene | No | >0.999999 | 0.01000 | 0.01000 | 0.000 | 0.01000 | 0.000 | 4.000 | >0.999999 |
| Fluorene | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Phenanthrene | No | 0.375566 | 0.01000 | 0.1233 | -0.1133 | 0.1138 | 0.9961 | 4.000 | 0.487699 |
| Benzo (b) fluoranthene | No | 0.357290 | 0.1867 | 0.5267 | -0.3400 | 0.3271 | 1.039 | 4.000 | 0.487699 |
| Benzo (k) fluoranthene | No | 0.277644 | 0.03333 | 0.4100 | -0.3767 | 0.3000 | 1.255 | 4.000 | 0.487699 |
| Benzo (e) pryene | No | 0.189964 | 0.2333 | 0.6267 | -0.3933 | 0.2494 | 1.577 | 4.000 | 0.487699 |
| Dibeno (a,h) anthracene | No | 0.373901 | 0.000 | 0.003333 | -0.003333 | 0.003333 | 1.000 | 4.000 | 0.487699 |
| Indeno (1,2,3-cd)pyrene | No | 0.912600 | 0.6200 | 0.7033 | -0.08333 | 0.7131 | 0.1169 | 4.000 | >0.999999 |
| Benzo (b)triphenylene | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Benxo (ghi) perylene | No | 0.373901 | 0.000 | 0.1533 | -0.1533 | 0.1533 | 1.000 | 4.000 | 0.487699 |

**PAH Anova for Ogbor hill (15-30 cm)**

| **Table Analyzed** | **Grouped: Entering replicate data** | | | | |
|---|---|---|---|---|---|
| | | | | | |
| Two-way ANOVA | Ordinary | | | | |
| Alpha | 0.05 | | | | |
| | | | | | |
| Source of Variation | % of total variation | P value | P value summary | Significant? | |
| Interaction | 4.697 | 0.9621 | ns | No | |
| Row Factor | 36.53 | 0.0057 | ** | Yes | |
| Column Factor | 3.182 | 0.1039 | ns | No | |
| | | | | | |
| ANOVA table | SS | DF | MS | F (DFn, DFd) | P value |
| Interaction | 0.4078 | 11 | 0.03707 | F (11, 48) = 0.3687 | P=0.9621 |
| Row Factor | 3.171 | 11 | 0.2883 | F (11, 48) = 2.867 | P=0.0057 |
| Column Factor | 0.2763 | 1 | 0.2763 | F (1, 48) = 2.748 | P=0.1039 |
| Residual | 4.826 | 48 | 0.1006 | | |
| | | | | | |
| Difference between column means | | | | | |
| Mean of Group A | 0.09111 | | | | |
| Mean of Group B | 0.2150 | | | | |
| Difference between means | -0.1239 | | | | |
| SE of difference | 0.07474 | | | | |
| 95% CI of difference | -0.2742 to 0.02639 | | | | |
| | | | | | |
| Data summary | | | | | |
| Number of columns (Column Factor) | 2 | | | | |
| Number of rows (Row Factor) | 12 | | | | |
| Number of values | 72 | | | | |

**PAH for Ndi Egoro (Multiple Unpired T-test) for 15-30 cm**

| Parameter (ppm) | Discovery? | P value | Mean control | Mean Ndi Egoro | Difference | SE of difference | t ratio | df | q value |
|---|---|---|---|---|---|---|---|---|---|
| Naphthalene | No | 0.188177 | 0.000 | 0.01333 | -0.01333 | 0.008413 | 1.585 | 4.000 | 0.304094 |
| Acenaphthylene | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Acenaphthene | Yes | 0.000844 | 0.000 | 0.009000 | -0.009000 | 0.001000 | 9.000 | 4.000 | 0.006818 |
| Fluorene | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Phenanthrene | No | 0.322978 | 0.000 | 0.07567 | -0.07567 | 0.06717 | 1.126 | 4.000 | 0.335680 |
| Benzo (b) fluoranthene | No | 0.071037 | 0.000 | 0.3667 | -0.3667 | 0.1501 | 2.442 | 4.000 | 0.191327 |
| Benzo (k) fluoranthene | No | 0.243483 | 0.000 | 0.2647 | -0.2647 | 0.1936 | 1.367 | 4.000 | 0.327890 |
| Benzo (e) pryene | No | 0.051404 | 0.000 | 0.6310 | -0.6310 | 0.2295 | 2.749 | 4.000 | 0.191327 |
| Dibeno (a,h) anthracene | No | 0.373901 | 0.000 | 0.002333 | -0.002333 | 0.002333 | 1.000 | 4.000 | 0.335680 |
| Indeno (1,2,3-cd)pyrene | No | 0.176491 | 0.000 | 0.5700 | -0.5700 | 0.3477 | 1.639 | 4.000 | 0.304094 |
| Benzo (b)triphenylene | | | 0.000 | 0.000 | 0.000 | 0.000 | | | |
| Benxo (ghi) perylene | No | 0.373901 | 0.000 | 0.02667 | -0.02667 | 0.02667 | 1.000 | 4.000 | 0.335680 |

**PAH Anova for Ogbor hill (15-30 cm)**

| **Table Analyzed** | **Grouped: Entering replicate data** | | | | |
|---|---|---|---|---|---|
| | | | | | |
| Two-way RM ANOVA | Matching: Across row | | | | |
| Assume sphericity? | Yes | | | | |
| Alpha | 0.05 | | | | |
| | | | | | |
| Source of Variation | % of total variation | P value | P value summary | Significant? | |
| Row Factor x Column Factor | 24.53 | 0.0168 | * | Yes | |
| Row Factor | 24.53 | 0.0168 | * | Yes | |
| Column Factor | 12.77 | 0.0005 | *** | Yes | |
| Subject | 19.08 | 0.5000 | ns | No | |
| | | | | | |
| ANOVA table | SS | DF | MS | F (DFn, DFd) | P value |
| Row Factor x Column Factor | 0.9215 | 11 | 0.08377 | F (11, 24) = 2.805 | P=0.0168 |
| Row Factor | 0.9215 | 11 | 0.08377 | F (11, 24) = 2.805 | P=0.0168 |
| Column Factor | 0.4799 | 1 | 0.4799 | F (1, 24) = 16.07 | P=0.0005 |
| Subject | 0.7167 | 24 | 0.02986 | F (24, 24) = 1.000 | P=0.5000 |
| Residual | 0.7167 | 24 | 0.02986 | | |
| | | | | | |
| Difference between column means | | | | | |
| Mean of Group A | 0.000 | | | | |
| Mean of Group B | 0.1633 | | | | |
| Difference between means | -0.1633 | | | | |
| SE of difference | 0.04073 | | | | |
| 95% CI of difference | -0.2473 to -0.07921 | | | | |
| | | | | | |
| Data summary | | | | | |
| Number of columns (Column Factor) | 2 | | | | |
| Number of rows (Row Factor) | 12 | | | | |
| Number of subjects (Subject) | 36 | | | | |
| Number of missing values | 0 | | | | |