Assessment of Heavy Metals and Organic Pollutants in Soil and Plants from Aba-Eku Municipal Dumpsite in Ibadan, Oyo State

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Certification

This is to certify that **Makinde, Ifeoluwa Mayowa** with the matriculation number **LCU/PG/002352**, carried out this research work tittled "Assessment of Heavy Metals and Organic Pollutants in Soil and Plants from Aba-Eku Municipal Dumpsite in Ibadan, Oyo State" in the Department of Biological Sciences, Faculty of Natural and Applied Sciences, Lead City University Ibadan, Oyo State, for the award of Master of Science Degree (MSc) in Environmental Management and Toxicology and this has not been previously submitted.

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Dedication

This thesis is dedicated to Almighty God and to my wonderful family.

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I want to acknowledge Leadcity University and members of A-library for their support and knowledgeable impact.

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Even though the above-mentioned institutions and persons have assisted in the process of this research work, I alone stand responsible for the errors, if any, found in the work.

Abstract

Indiscriminate dumping of waste releases toxic pollutants which generate significant environmental pollution and hazard. This research work investigated the levels of heavy metals, polycyclic aromatic hydrocarbons (PAHs) and phthalate esters (PAEs) in soil and plants from Aba-Eku Municipal Dumpsite in Ibadan, Oyo State. Soil samples were collected at four locations around the dumpsite and three edible vegetables namely water leaf (*Talinum triangulare*), jute leaf (*Corchorus olitorius*) and scent leaf (*Ocimum gratissimum*) were randomly collected on the dumpsite. Five selected heavy metals namely Copper (Cu), Cadmium (Cd), Lead (Pb), Manganese (Mn), Iron (Fe), were determined using Atomic Absorption Spectrophotometer (AAS). Extraction and determination of PAHs and PAEs was done using USEPA 8270c and 8061A standard methods. Data obtained were subjected to descriptive statistics and correlation coefficients. Results showed that the average concentration of heavy metals observed in soil samples were 1.01, 0.03, 0.12, 0.48 and 4.31 mg/kg, for Cu, Cd, Pb, Mn and Fe respectively; while the contamination factor in decreasing order ranked iron>copper>manganese> cadmium>lead. Highest accumulation of heavy metals was observed in water leaf followed by jute mallow and then scent leaf. The average concentration of PAHs in the soil samples were naphthalene 36.15 mg/kg, acenaphthylene 33.18 mg/kg, acenaphthene 8.02 mg/kg, phenanthrene 3.94 mg/kg, fluorene 3.48mg/kg, and anthracene 1.14 mg/kg. The vegetable samples in order of total accumulated PAHs ranked scent leaf > water leaf > jute mallow. The PAHs showed strong positive correlation and are significantly different from one another ($p<0.05$). Only dipropyl phthalate and diethyl phthalate were observed in the soil samples with average concentration of 3.80 and 3.74 mg/kg respectively. Scent leaf accumulated more PAEs than jute mallow while water leaf showed no tolerance to the phthalate esters. Improper waste management at the dumpsite obviously poses a pollution risk to scavengers and local population's health.

Keywords: Heavy metal, polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PAEs), Soil, Plant

Word Count: 298

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List of Acronyms

Abbreviation	Meaning
AAS	Atomic absorption spectroscopy
ANOVA	Analysis of Variance
DBP	Di-n-butyl phthalate
DEHP	Di-2 ethylhexyl phthalate
DEP	Diethyl phthalate
EDCs	Endocrine Disruptor Chemicals
GC-FID	Gas chromatography Flame Ionization Detector
HMW	High Molecular Weight
HPLC	High Performance Liquid Chromatography
LC	Liquid Chromatography
LMW	Low Molecular Weight
LOD	Limits of Detection
MFO	Mixed-function Oxidase
PAEs	Phthalate Esters
PAHs	Polycyclic Aromatic Hydrocarbon
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PLI	Pollution Load Index
PPCPs	Pharmaceutical and Personal Care Products

PVC	Polyvinyl chloride
RfD	Reference Dose
RSD	Relative Standard Deviation
SON	Standard Organization of Nigeria
Tf	Transfer factor
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

Chapter One

Introduction

1.1 Background to the Study

Wastes generation have become an inevitable part of human life. Notwithstanding the proper management of waste stream is an integral part of ecosystem sustainability in most developing countries like Nigeria[1]. Global municipal waste generation is currently at an estimated 1.3 billion tonnes per year and is expected to increase to 2.2 billion by 2025 and to 13.1 billion by 2050[2]. The increased generation of solid waste is a particular challenge for the developing nations due to its rapid urbanization caused by rural-urban migration, industrialization, political changes and technological transformation[3].

It is noteworthy that wastes generation have become part of all sectors, depending on the types of activities waste generated includes hospitals, agriculture, market, workshops, food processing and so on. These wastes include hazardous chemicals, radioactive material, pharmaceutical, pressurized containers, batteries, plastics materials etc[4]. Due to the poor and inefficient management of waste streams in most developing countries, piles of waste defacing the aesthetics of cities have become a mainstay. The poor management of waste stream poses a great threat to the environmental and public health of inhabitants and scavengers around waste dumpsites[5]. The end-point of various disused household products otherwise regarded as municipal solid waste in many urban centres in Nigeria is the closest dumpsites to the depositor[6]. The contents of municipal solid waste are usually food waste, paper, metal scraps, plastics, ceramics, glass, hospital wastes, petrochemical products and

ashes. The decomposition or oxidation and incomplete combustion of these materials discharges the harmful heavy metals[5].

Organic pollutants are chemical substances that contain carbon atoms and originate from natural or human-made sources. The air, water, soil, and biota are only a few of the environmental compartments where these contaminants may be found[7]. Because they are poisonous, persistent, and bioaccumulative, organic pollutants can affect both the environment and living things. Organic pollutants come in a vast variety, and depending on where they come from and certain chemical characteristics, they can be divided into many classes. Among common examples include the Polycyclic Aromatic Hydrocarbons (PAHs) and Phthalate esters (PAEs)[8]. Organic pollutants such as Polybrominated diphenyl ethers (PBDEs) Polychlorinated biphenyl (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs), Phthalates Esters (PAEs) etc are also present in these wastes into the soil of the dumpsite and hence pollute the soil[7].

Polycyclic Aromatic Hydrocarbons are a class of organic compounds made up of several fused benzene rings. They are created when organic materials, like wood, tobacco, and fossil fuels, burn partially. Smoke from cigarettes, industrial pollutants, and exhaust fumes all include PAHs[7]. Phthalate esters on the other hand, sometimes known as phthalates, are a class of chemical substances used largely as plasticizers in a variety of commercial and consumer goods. These esters, which generally have carbon chains spanning from C4 to C13, are made from phthalic acid and alcohols. Phthalates are versatile chemicals that are added to plastics and other materials to increase their flexibility, toughness, and transparency. Phthalates are frequently utilized in the production of items made of polyvinyl chloride (PVC), personal care items, and packaging materials[8].

Several heavy metals like Copper (Cu), Cadmium (Cd), Chromium (Cr), Nickel (Ni), Zinc (Zn) and Lead (Pb) are normally discovered in dumpsites owing to remains deposited into soil from metallic wastes and other products[8]. These heavy metals are not only associated with pollution and toxicity but also include some elements which are essential for living organisms at low concentrations. Studies of heavy metals in ecosystems has shown that many areas near urban complexes where waste is dumped contain high levels of these heavy metals[9].

As the heavy metals accumulates above the threshold value in the soil or environment, it can lead to toxicity and this can be very dangerous to plants, animals including humans[10]. The harmful impacts of these heavy metals may include: destruction of ecosystem, destruction of marine biota, hindering of fisheries and other aquacultural operations, poisoning of sea food, contamination of surface and underground water, disturbances of soil function, reduction of plants productivity and chance of survival[11]. These heavy metals unlike organic contaminants, do not ordinarily experience chemical or microbial degradation through changes in their chemical forms[12]. Also, in developing countries, it is common to see crops grown around dumpsites due to the belief that these wastes are high in organic matter and thus can be used as manure and plants also tend to grow in these dumpsites and there is a high tendency for heavy metals to accumulate in the soil which is taken up by plants[13]. Soils therefore are the major sink for heavy metals released in to the environment by dumping of refuse on land[14].

The dumpsite soil across south-western and other part of Nigeria have been reported to aid plants development and biodiversity and as such they have been broadly utilized for growing

assortments of consumable vegetables and plant based foodstuff[15]. The practice of this recommendation has posed critical environmental and health challenges as a result of anthropogenic pollution of these dumpsite soils with unbearable level of toxic chemical materials[16]. The concentration of heavy metals soils is a basic requirement to estimate the risk associated with refuse dumpsites[17]. Be that as it may, the mobility, bioavailability and fate of these heavy metal pollutants are predicted using the chemical fractions/species/ of heavy metals present[18]. Hence, there is necessity to assess the species and chemical forms of these metals since the soil mineral mobility and bioavailability are controlled by the chemical species/ fraction which eventually control the soil-plant transfer of heavy metals[19].

The soil is known as the repository for pollutants, whether polycyclic aromatic hydrocarbons, heavy metals or and Phthalates Esters[20]. When pollutants such as polycyclic aromatic hydrocarbons and Phthalates Esters are constantly discharged into the soil, they subsequently accumulate to level that can constitute risk to the environment[21]. The accumulation of these compounds in the soil can lead to contamination of food chain, since plants derive their nutrients from the soil and are eaten by man and animals[22]. Beside the intake by plants within the immediate vicinity, there is the issue of redistribution by leaching and runoffs and transformation by microbes[23]. The presence of PAHs in the environment is currently a matter of concern, because they are considered as responsible or as precursors of some diseased conditions such as carcinogenicity, mutagenicity, teratogenicity and other toxic effects[24]. Polycyclic aromatic hydrocarbons (PAHs) are possible atmospheric toxins which comprises of fused aromatic rings without considering those that have substituents[25]. PAHs are among the most prevalent pollutants in the ecosystem that are normally released to the environment through leachate infiltration from the unlined dumpsite[26]. The soil located within these

dumpsites is contaminated by leachates that contain PAHs and may cause serious health risks to the neighborhood[27]. The soil is an important indicator that serves as a reservoir for the retention of these PAHs in the environment[28]. PAHs are persistent and hydrophobic, which makes them enrich deeply in the soil matrix after being adsorbed in the soil[29]. PAHs are hazardous organic compounds mainly comprised 2–6 rings in their molecules. PAHs are grouped as lower mass PAHs or higher mass PAHs as a result of their chemical structures[30]. PAHs with lower mass contain 2 or 3 benzene, while the ones with higher mass are made of 4–6 aromatic rings[31]. The PAHs with lower mass which have of 2–3 rings are easily dissolved in water compared to the PAHs with higher mass of 4–6 rings. PAHs with higher mass are also less volatile in nature and are tend to be adsorbed easily by particulate matter [31]. The soil retains the PAHs in the ecosystem due to its ability to adsorb to the soil.[32] In the last few decades, Environmental contamination by PAHs over the past few decades has remained a great concern to researchers[32]. Many PAHs are perceived as environmentally problematic, based on their toxic nature and tend to bio-accumulate in humans[33]. They can also cause reproductive deformity and repression of the immune system[34].

Phthalates are another industrial chemical that is widely used. A recent study found that the annual production of PAEs is over 300 million tons[35]. As emissions from the continuous product life cycles (i.e., production, use, and disposal) increase, the concern over PAEs contamination on a worldwide scale has grown[36]. Phthalates are utilized as additives and solvents in paints, dyes, and insect repellents in addition to being used to increase the flexibility and durability of plastic products[37]. Phthalate esters (PAEs), which are classified as Endocrine Disruptor Chemicals (EDCs), accumulate in the terrestrial ecosystem along with other chemical pollutants, such as PAEs[38]. Di-2 ethylhexyl phthalate (DEHP) and di-n-

butyl phthalate (DBP) are the two most frequently utilized phthalate esters across all categories. As a plasticizer, DEP is utilized in medical tubing, food packaging films, and lubricants for food products[37]. Phthalate esters are among the many enduring and hazardous chemicals that naturally accumulate in soil. While crops are growing, PAEs leach from the plastic and go into the soil, potentially raising the danger to human health through the food chain[39].

Phthalates are endocrine disruptors because they have the potential to interfere with the endocrine system, which controls the synthesis and signalling of hormones. Hormonal imbalances can result from these substances' ability to imitate or impede the function of hormones[37]. Exposure to phthalates has been related to detrimental effects on reproductive health and development, especially during important developmental times (such as pregnancy and infancy)[36].

There have been reports of certain phthalates having harmful effects on both the male and female reproductive systems. Male testicular shrinkage and lower sperm quality and quantity have both been linked to exposure to certain phthalates in males[38]. Phthalates have been connected to changed hormone levels and irregular menstrual cycles in females[38]. Studies have shown that there is a connection between inhaling specific phthalates and respiratory issues including allergies and asthma[36]. These substances may aggravate respiratory problems and lead to airway irritation. Certain phthalates, particularly those with longer carbon chains, have been linked to liver and kidney damage. some phthalates have also been linked to a higher risk of developing certain malignancies, such as breast and liver cancer[39].

Using dumpsites as farmlands is also commonly done in sub-urban and urban areas across Asia since composted and rotted waste improve soil fertility[40]. These wastes frequently contain potentially toxic metals and organic pollutants in different states and varying concentrations[41]. Human beings are exposed to these pollutants majorly through three basic routes, i.e. skin adsorption, ingestion and inhalation[42].

Some of the metals like Lead (Pb) could be especially an unsafe metal that has no biological importance and adversely affects children in noteworthy ways[43]. The issue with these metals is that they are unaffected in the process of breakdown of organic waste and have harmful impacts on living organisms especially when they surpass a particular level. Therefore, the concentrations of metals in human bodies animals, water and plants is a reflection of high concentration of heavy metals in soils[44].

Thus, when toxic pollutants from solid waste gain entrance into encompassing water bodies by flood or rain, the nutrient concentration and toxic pollutants concentration of the water bodies will be altered[45]. Even at low concentration, pollution of the environment with heavy metals and organic pollutants have long-term aggregate health impacts and remain a leading health challenge worldwide[46]. For instance, when Pb bio-accumulates in the human body, it impedes with the working of mitochondria, subsequently disabling breath, conjointly causes digestive obstruction, paralysis, swelling of the brain, and inevitable death[47]. The circumstance is indeed more troubling within the third world nations where researches endeavours towards observing the environment have not been given the specified consideration by the stakeholders[48].

The heavy metal concentrations in the soil around waste dumpsites are affected by types of wastes, topography, runoff, and level of scavenging[41]. Once heavy metals are deposited in the soil, they are not degraded and they persist in the environment for a long time causing serious environmental pollution. There is an increasing concern about the likelihood of soil contamination resulting in the introduction of elements in food chains through uptake by plants and thereby affecting food safety[46]. They accumulate in soil and plants having a negative influence on physiological activities of plants such as photosynthesis, gaseous exchange, and nutrient absorption which result in plant growth reduction and dry matter accumulation. Although the rate of metal uptake by plants could be influenced by factors such as metal species, plant species, etc[49]. As it is in most cases, soils in municipal waste dumpsites commonly serve as fertile ground for the cultivation of a variety of crops, with little regard to the probable health hazards the heavy metal content of such soils may pose. Most dumpsite soils in developing nations are being utilized for planting different kinds of crops without proper scheduled evaluation of the related ecological and health effect[50].

Therefore, indiscriminate dumping and combustion of wastes at dumpsites result in severe health and environmental consequences[49]. Dumping leads to air and water pollution, soil degradation, habitat destruction, health consequences on both human health and animals. It also poses health risks for waste workers and causes aesthetic issues[48]. Burning of waste releases heavy metals and several toxic organic pollutants which generate significant environmental hazard, and pollution of soil, groundwater and the atmosphere[50].

1.2 Statement of the Problem

Heavy metals such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb) and Manganese (Mn). are contained in municipal waste, majority of which end up being dumped on soil that serve as the sink when they are leached out from the dumpsites. The soil remains a crucial asset for supporting two human needs of quality food supply and quality environment[47]. When plants are cultivated on polluted land contaminated with metropolitan, industrial or household wastes, they have ability to absorb heavy metals present in the soil in form of mobile ions using their roots or foliar absorption. The metals absorbed gradually bio-accumulate in the stems, roots, fruits, leaves, and grains of plants there by finding their way in to the food chain and are consumed by human beings and animals[48]. Heavy metals are known for their toxicity potential, tendency to bioaccumulation, high mobility and environmental persistence. Owing to their extreme toxicity, negative consequences on both human and environmental health, Nickel (Ni), Selenium (Se), Silver (Ag), Thallium (Ti), Cadmium (Cd), Copper (Cu), Lead (Pb), Mercury (Hg), Antimony (Sb), Arsenic (As), Beryllium (Be), Cadmium (Cd), Chromium (Cr), and Zinc (Zn) are listed by the EPA as the 13 Priority Pollutant Metals that have a significant impact on public health[46].

The effects of heavy metals on the health of living organisms can be felt even when in small amounts[46]. Some of the reported health effect of heavy metals in human include kidney damage, respiratory problems, bone density loss, with an increased risk of lung cancer, Skin lesions, cardiovascular issues, and an elevated risk of various cancers, including skin, lung, bladder, and liver cancer among others[48].

In the same vain, organic pollutants such as Polycyclic Aromatic Hydrocarbons and Phthalates Esters are critical environmental pollutants that have been studied in many places. Their harmful tendencies in the environment especially in humans have also been issues of

discussion in many reviews and they have been included in WHO priority list as harmful environmental pollutants[47]. The issues with environmental contamination and the risks associated with PAHs and PAEs are receiving more and more attention, and they are becoming a focus of environmental study.

1.3 Justification of the Study

The areas around dumpsites get undesirable enrichment with PAHs and heavy metals resulting from continuous accumulation of solid wastes from various sources. These toxic pollutants find their way the groundwater and soil, and consequently, constitute serious environmental threat[6].

Besides, the accumulation of these environmental pollutants (heavy metals and PAHs) under some biogeochemical instances are passed into the soil solution and thereby become bioavailable and absorbed by plants[48]. Plant development is influenced by high concentration of pollutions from the dumps by changing the biodiversity of vegetation because the delicate plants are stretched are not able to survive[49]. Too, long periods of exposure of plants to contaminated soils might result in plants taking up and getting to be tolerant to tall sum of heavy metals by numerous pathways and mechanisms such as: detoxification adsorption, accumulation and immobilization[50].

Heavy metal in human body may cause bone, blood disorders, decreased mental capacity, kidney damage and neurological damage[51]. Heavy metal poisoning can result in lower energy levels, harmed or decreased mental and central nervous function, and harm to lungs, blood composition, liver, kidneys and other crucial organs. One particular danger coming about from improper disposal of wastes transfer is the defilement by heavy metals that have critical

toxic potential for the environment (air, water and soil), human beings and the uncovered biodiversity[52].

Heavy metal or PAHs contamination of water and soil has attract attention because of their severe threats to the soil ecosystems, human health and food chain. It is therefore essential to carryout necessary investigation on soils/ farmland located in the immediate vicinity of open dumping sites, of possible presence of pollutants[49].

The indiscriminate refuse dump in Ibadan, Oyo State posed a great health risk to the environment and residents. This is more so because the heavy metals, PAHs and PAEs infiltrate the aquifer. However, little or nothing has been written about the heavy metal, PAHs and PAEs profile at Aba-Eku dumpsite Ibadan, this has led to a significant knowledge gap in the environmental impact and toxicology profile. Therefore, this study will provide baseline data for planning and executing proper waste management of the dumpsite. It will also serve as a veritable reference material in sensitizing the public on how to dispose waste materials.

1.4 Aim and Objectives of the Study

The aim of this study was to determine the level of heavy metals and organic pollutants PAHs and PAEs in soil and edible plants present in Aba Eku municipal dump site Ibadan.

The specific objectives of this study ware to determine;

i. the concentrations of cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb) and manganese (Mn). in soil samples around Aba Eku municipal dump site Ibadan;

ii. the concentrations of cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb) and Manganese (Mn). in edible plants around Aba Eku municipal dump site Ibadan;

iii. the PAHs in edible plants and soil samples around Aba Eku municipal dumpsite Ibadan;

iv. the PAEs in edible plants and soil samples around Aba Eku municipal dumpsite Ibadan.

1.5 Research Questions

1. What are the levels of heavy meatal in the soils of Aba-Eku dumpsite?
2. What are the levels of heavy metals in edible vegetables growing around Aba-Eku dumpsite?
3. What are the levels of PAHs in the soils and edible vegetables of Aba-Eku dumpsite?
4. What are the levels of PAEs in the soils and edible vegetables of Aba-Eku dumpsite?
5. What are the environmental impacts of these heavy metals, PAHs and PAEs?

1.6 Significance of the Study

It is crucial to investigate heavy metals, PAHs and PAEs since even small increases in their concentrations above safe thresholds, whether as a result of anthropogenic or natural processes, can have major adverse effects on the environment and human health. This study's findings were anticipated to increase our understanding of the environmental concerns connected with solid waste dumps, crops planted close to dumpsites, and the suitability of such areas for plant cultivation.

1.7 Scope of the Study

This study considered six metals namely Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb) and Manganese (Mn) only. The soil samples collected were only top soil at a depth of 0-5 cm and only three edible vegetables were sampled at Aba-Eku dumpsite., Ibadan.

1.8 Limitations of the Study

Getting access permit to the dumpsite was difficult, eventually an existing permit of a PhD student also working on the dumpsite was used. The scavengers at the dumpsite were scared of being exposed to social platforms so they were reluctant leading us to some part of the dumpsite. There are security challenges at the dumpsite, some workers have to be paid to ensure security coverage while working on the dumpsite.

1.9 Operational Definition of Terms

Dumpsite: An area of land where large amount of waste materials are disposed or buried under the earth

Waste: Unwanted or unusable materials, substances or by-products.

Solid Waste: The unwanted or useless solid materials generated from human activities in residential, industrial or commercial areas.

Municipal: Relating to a town or a district or its governing body.

Environment: "The natural world in which people, animals and plants live, as a whole or in a particular geographical area especially as affected by human activity".

Pollution: "The presence or introduction into the environment of a substance which have harmful or poisonous effects".

Soil: "The upper layer of earth in which plant grow, consisting a mixture of organic remains, clay and rock particles"

Plant: A living thing that grows in the earth and usually has leaf stem and root.

Soil Pollution: "The presence of toxic chemicals (contaminants) in soil, in high enough concentration to pose a risk to human health and/or the ecosystem".

Hazardous: "Risky or dangerous, has potential to cause danger"

Anthropogenic: "Originating from human activity"

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Chapter Two

Literature Review

2.1 Municipal Solid Waste Management

In the highly populated towns and cities of most underdeveloped and developing nations, facilities to handle municipal wastes are not available due to its high cost and inability to enforce relevant enactment. Lack of organised landfill sites, Poor urban and regional planning, lack of enforcement of relevant laws and edicts on waste disposal have immensely contributed to the presence of dumpsites around residential areas in the third world countries. This has led to the dumping of domestic refuse and sewage untreated into the environment; leachates and surface run-off from dumpsites are sources of fresh water contamination[1].

Domestic production of industrial and municipal wastes has increased with recent population and industrial growth, and these waste are indiscriminately dumped in landfills, drainages and water bodies without treatment[2]. Municipal solid waste disposal constitutes one of the most environmental and health problems confronting governments of African cities. This can be since indeed in spite of the fact that these cities are utilizing 20-50 percent of their budget in management of solid waste, as it were 20-80 percent of the waste is collected. The uncollected or illicitly disposed wastes constitute a calamity for human health and the natural degradation[3].

In developing nations, there are thousands of abandoned landfills and dumpsites that, unless adequate action is taken, pose a hazard to human health over the ensuing decades. The practice of open dumping of solid wastes poses threats to the environment and human health in the majority of developing nations[4]. Unplanned urbanization, population growth, and

industrialization have partially or completely transformed our environment into landfills for waste[5].

To minimize the environmental issues created by landfills and to improve waste management, a number of techniques have been put forth. In Sweden, different types of waste were first disposed of in distinct cells in the 1980s. The main goal at the time was to maximize landfill gas production by developing so-called "biocells"[6]. The trash that has a lower potential for gas generation would subsequently be sent to other cells. However, only a few locations in Sweden continued to use this sort of independent landfilling by the end of the 1990s. Political objectives, rather than technological advancements or market demands, were the main drivers of recent decades' big changes. As a result, legislation must be examined with technological considerations when considering landfilling[7]. Sustainability is the overarching objective of landfill laws and regulations. However, landfilling might be seen as the antithesis of sustainability, and the idea of "sustainable landfilling" has generated significant discussion. Therefore, it could be more suitable to talk about the idea of acceptable risk[8]. When the waste mass, post-closure, does not represent a threat to human health or the environment and the landfill no longer requires considerable management or monitoring, final storage quality, or functional stability, has been achieved[9]. Since inert waste landfills do not require any leaching control measures, it has been suggested that in most countries the acceptance criteria for inert waste might be utilized as the leaching limit value[10]. A situation of indiscriminate waste disposal is shown in Figure 2.1.

Figure 2.1: An image showing the Indiscriminate disposal of waste in Nigeria

Source[13]

2.2 Leaching in Dumpsites

Leachate generation is one of the landfills' most major environmental effects, hence environmental monitoring programs for landfills frequently concentrate on looking into the effects of leachate, particularly any contamination of ground and surface water[11]. Leachate is the contaminated liquid produced by the waste breakdown and percolation of rain water, through wastes contained in the landfill or dump site that have entered the landfill from outside sources[12]. Groundwater and the flow of surface water may also play a role. Pollutants from the dumped waste may "leach" into deeper soil layers as water flows through the landfill[13].

After burial, solid waste starts to decompose, and this involves a number of intricate simultaneous physical, chemical, and biological processes[14]. While the chemical processes include the oxidation of metals and the reactions involving organic acid and dissolved carbon dioxide, the physical processes involve compression, dissolution, absorption, and adsorption. The primary mechanisms directly responsible for the creation of landfill gas (mostly methane and carbon dioxide) and leachate are biological activities, which involve both aerobic and anaerobic organisms[15]. It is crucial to comprehend the mechanisms involved in leachate generation and composition because leachate may contain high quantities of metals that are hazardous to both human health and the environment[16].

The biological breakdown of organic matter depends on the activity of microorganisms, which in turn is influenced by factors such as pH, oxygen levels, moisture, temperature, depth, compaction, and the concentration of hazardous components[17]. The degradation of

trash has been found to be mainly influenced by moisture, and the microbiological processes taking place inside the landfill utilize water[18].

There are four main phases that the primary biological processes in the landfill may be divided into;

Phase 1: Aerobic organisms quickly degrade degradable waste in the presence of oxygen after it is initially disposed of, producing carbon dioxide, organic compounds, heat, and water in the process. In this stage, the pH is typically neutral[17]. Because oxygen is no longer available once the garbage is covered, organisms typically survive under these circumstances for only a few days. Both the Biochemical Oxygen Demand (BOD) and the Chemical Oxygen Demand (COD) levels rise as well[18].

Phase 2: The breakdown process is then taken over by bacteria that can survive in the absence of oxygen once aerobic organisms have died off[17]. The pH drops as a result of the production of volatile fatty acids (50–90% of the gas created) and carbon dioxide. Metal species become mobilized and may form metal complexes as a result of leachate's chemical aggression[18].

Phase 3: The growing population of methanogenic bacteria uses the acids created in Phase 2 to make methane and carbon dioxide during this initial methanogenic phase. As the pH of the leachate rises, its organic content falls. As volatile fatty acids are eaten, the amounts of BOD and COD decline[18].

Phase 4: After the carboxylic acids are used, methane production in this stable phase of the methanogenic phase reaches its maximum but subsequently declines[17]. The concentrations of

metals, inorganics, fatty acids, COD, and BOD all decrease as the methanogenic phase removes soluble organic components, and the pH rises until the leachate is stable[18].

Due to the high pH's enhancement of metal sorption and precipitation, metal concentrations in the methanogenic phase typically tend to be low[18]. Because of this, metals are more easily adsorbed onto particles and concentrate in the sludge and waste residue, where they are then immobilized[17].

Metals are not always attenuated in landfills, though; certain methods may be able to mobilize them for use in solutions. A crucial part of these activities is played by organic matter[17]. In order to efficiently mobilize metals, their concentration in the leachate must be increased by the formation of metal complexes to organic ligands and sorption to colloids by humic material[17]. All four of the aforementioned stabilization phases—which occur at various points in municipal waste landfills—have a distinct leachate composition[18]. Young and old leachates differ from one another, as shown by monitoring data from the Horotiu (Hamilton) and Rosedale Rd. (Auckland) landfills[17]. It's also crucial to keep in mind that the amount of leachate produced at a specific location greatly depends on whether the landfill under investigation is open or closed[17]. These periods typically overlap since landfills are filled gradually, which is the norm. It is safe to argue that no landfill actually has a single "age," but rather a family of ages, each of which is linked to a specific cell within the landfill complex that is moving closer to final stabilization[18].

2.3 Effect of Poor Waste Management on the Environment

Due to the possibility of the trash polluting water, food sources, land, air, and vegetation, poor waste management poses a significant threat to the health of city people, especially

those who live close to dumpsites. Thus, improper garbage treatment and disposal results in ecosystem collapse, environmental deterioration, and serious threats to public health. The garbage that results from this accumulation endangers the health of city dwellers and the environment[19].

Solid waste can cause environmental issues such as health risks, water and soil contamination, unpleasant look, and objectionable odour. Deterioration of our environment's quality is the end outcome of these[20]. The majority of dumps are situated close to populated areas and wetlands. The disposal sites frequently lack basement preparation for the selective adsorption of harmful compounds as well as lining. As a result, it is likely to emit pollutants through leachates and dumpsite gases, respectively, into the neighbouring water and the air[21]. Due to the uncontrolled disposal of waste, many water sources have become unclean and dangerous to people and other living things[22].

The majority of uncontrolled dumps have been around for many years, evolving from modest dumps into enormous, uncontrolled trash sites. Dump sites that are not monitored significantly harm the ecosystem. The biggest hazard to life comes from solid waste since it has the ability to pollute the terrestrial, aquatic, and airborne environments[23]. To monitor heavy metal pollution brought on by anthropogenic activity, soil samples are a great monitoring medium. By leaking into groundwater or being absorbed by plants and animals, heavy metals in polluted soil have an impact on the ecosystem and pose serious dangers owing to bioaccumulation[24].

Because of the potential harm they could do to both people and the environment, heavy metals and persistent organic pollutants are of concern. According to a report, when polluted

soils are used for crop production, heavy metals have the potential to be hazardous to plants, animals, and people. Heavy metal contamination of the biosphere brought on by industrial, agricultural, and home activities presents significant challenges for the safe use of agricultural lands[25]. The majority of studies on the leaching of metals from soil columns or field research come to the conclusion that trace metals are tightly bonded to topsoil[26].

Some dumpsites burn trash outdoors and leave the ashes where they fall, with little thought given to the effects on the ecosystem. The potential for an explosion makes this directly unsafe. Burning trash eliminates organic components and oxidizes metals, resulting in ash that is higher in metal content. Following the oxidation and corrosion processes, these metals dissolve in rainwater and are subsequently leached into the soil, where they are subsequently ingested by developing plants and enter the food chain[27].

Heavy metals concentration in the soil is influenced by anthropogenic activities such agricultural practices, industrial operations, and waste disposal systems, as well as biological and geochemical cycles[25]. Significant amounts of harmful and persistent metals can be released into the soil environment by waste dump sites. These metals are absorbed by plants, which then enter the food chain[28]. These metals are absorbed by cultivated plants either as mobile ions in the soil solution through their roots or through their leaves, rendering them unfit for consumption[29]. Therefore, higher soil heavy metal concentrations may cause higher plant absorption levels. A plant's rate of metal uptake may be affected by variables such the type of metal, the type of plant, the age of the plant, and the type of plant part[30].

2.4 Heavy Metals

When a metal has a density greater than 5–6 g cm3, it is referred to as a "heavy metal" [31]. Some heavy metals, which naturally occur in small amounts in organisms, are frequently referred to as "trace metals," even if the word "trace metal" may indicate that an organism has an absolute need for that particular metal[32].

Two-thirds of all elements are made up of metals, which also make up around 24% of the Earth's mass. On Earth, the majority of metals are either found in their pure form or combined with other elements (e.g. as sulphides, oxides, silicates and carbonates). A subset of the elements that are distinguished by their metallic characteristics is known as heavy metals (such as; high density, malleability, ductility and conductivity). A range of criteria, including as chemical characteristics, toxicity, density, atomic weight, or atomic number, have been used to define heavy metals[33].

Examples of heavy metals are aluminium, antimony, arsenic, barium, cadmium, cobalt, chromium, copper, iron, nickel, lead, manganese, molybdenum, selenium, zinc, titanium, vanadium amongst others. Heavy metals can be divided into two groups namely; (i) metals essential to at least some organisms (micronutrients) such as Fe, Cu, Co etc. and (ii) nonessential heavy metals with no known biological function which include Hg, Pb and Cd. Even though micronutrients are essential to some forms of life, they become toxic at high concentrations[33].

In addition to others, heavy metals include antimony, aluminium, arsenic, cadmium, barium, cobalt, copper, chromium, iron, lead, nickel, manganese, selenium, molybdenum, vanadium and titanium. Heavy metals can be categorized into two categories:

(I) Essential Metals (micronutrients) that are necessary for at least some organisms, such as Cu, Co and Fe; and

(II) Non-Essential Heavy Metals, such as Cd, Pb and Hg, that have no recognized biological role. Despite the fact that some forms of life require micronutrients, excessive amounts of them can be toxic[33].

2.4.1 Cadmium (Cd)

Cadmium (Cd) is a naturally occurring metal. Its chemical behaviour is comparable to zinc's, and it is located between zinc (Zn) and mercury (Hg) on the Periodic Table of the Elements. Typically, it exists as a combination of two additional elements called a divalent cation (e.g., CdCl2). Cd is present in the earth's crust at a rate of around 0.1 parts per million[37]. It is typically found as an impurity in deposits of zinc (Zn) or lead (Pb), and is thus predominantly created as a by-product of the smelting of these metals. Since it is water-insoluble and inflammable, Cd is employed as a protective plate that resists corrosion. Cadmium burns in air to produce cadmium oxide. Cadmium is dissolved by nitric, sulfuric, and hydrochloric acids by producing, respectively, cadmium nitrate, cadmium sulfate, and cadmium chloride. Additionally, cadmium is utilized in nuclear reactor control rods, where it functions as a neutron poison to regulate the neutron flux during nuclear fission[38].

Consumption of contaminated food or water, such as that from old Zn-Cd sealed water pipes or industrial pollution, can expose a person to cadmium and cause long-term health effects. Examples of contaminated food include crustaceans, organ meats, leafy vegetables, and rice

from specific regions of Japan and China. Drug and dietary supplement contamination could also be a source of contamination[38]. Burning fossil fuels like coal or oil and incinerating municipal trash are the two biggest environmental sources of airborne cadmium. Additionally, smelters for copper, lead, or zinc may release cadmium into the atmosphere. Food is typically the biggest source of cadmium exposure for non-smokers. The use of phosphate fertilizers or the spreading of sewage sludge on farm fields can raise the levels of cadmium in various foods. Another significant way to be exposed to cadmium is through smoking. Smokers' bodies contain nearly twice as much cadmium than non-smokers'[39].

Humans who are exposed to high levels of cadmium via acute inhalation may experience effects on their lungs such as high quantities of cadmium inhaled suddenly by people may have negative consequences on the lungs, such as bronchial and pulmonary inflammation. Lung function can be permanently harmed by a single acute exposure to high amounts of cadmium. Based on short-term animal testing using rats, cadmium is believed to have a significant acute toxicity[38]. Humans who are exposed to cadmium over an extended period of time from inhalation and ingestion experience a build-up of the metal in their kidneys, which can result in kidney disease, proteinuria, a reduction in glomerular filtration rate, and an increased risk of kidney stone development[37]. Effects on the lungs, such as bronchiolitis and emphysema, have also been observed in industrial situations where humans are exposed to cadmium in air over time. The liver, kidney, lung, immune system, bone, blood, and neurological system are all affected when animals are exposed to cadmium over an extended period of time through inhalation or oral intake[38]. The Reference Dose (RfD) for cadmium in drinking water is 0.0005 milligrams per kilogram per day (mg/kg/d), and the RfD for cadmium exposure through food is 0.001 mg/kg/d. Both are based on severe proteinuria in

humans. The RfD is an estimation (with uncertainty spanning possibly an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is anticipated to be without considerable risk of adverse non-cancer effects over the course of a lifetime[40]. It serves as a benchmark to evaluate the potential consequences rather than serving as a straight risk estimator. The likelihood of negative health impacts rises as exposure levels above the RfD. Lifetime exposure over the RfD does not guarantee the occurrence of a negative health effect[39].

There is an increased risk of lung cancer in people who are exposed to breathed cadmium, according to several occupational studies. Confounding factors39, however, make the findings insufficient rather than decisive. Inhalation exposure to various types of cadmium has been linked to cancer in animal studies, although cadmium compound exposure through food consumption has not been linked to cancer[40].

2.4.2 Chromium (Cr)

In nature, chromium (Cr), a grey, hard metal that is most frequently found in the trivalent state in rocks, animals, plants, and soil, is also present in combination with other elements to produce a variety of compounds. Chromium(III) and chromium are the two primary types of chromium (VI). There are a few hexavalent (chromium(VI)) compounds as well. The only mineral that contains a considerable proportion of chromium is chromite (FeOCr2O3). In its highest grade, the ore contains around 55% chromic oxide; the ore has not been discovered in its pure form[41]. After being released from chromium-using businesses, such as those engaged in electroplating, leather tanning, textile manufacturing, and the creation of chromium-based

products, chromium can also be found in air, soil, and water. Burning coal, oil, or natural gas can potentially emit chromium into the environment[42].

For both acute and long-term exposures, chromium (VI) is significantly more hazardous than chromium (III). When chromium (VI) is exposed to humans through inhalation, the respiratory tract is the main organ that is affected. When someone inhaled exceptionally high doses of chromium trioxide, symptoms such shortness of breath, coughing, and wheezing were noted[41].

Other effects noted from acute inhalation exposure to very high concentrations of chromium (VI) include gastrointestinal and neurological effects, while dermal exposure causes skin burns in humans[42]. Ingestion of high amounts of chromium (VI) causes gastrointestinal effects in humans and animals, including abdominal pain, vomiting, and hemorrhage[41].

Chronic inhalation exposure to chromium (VI) in humans results in effects on the respiratory tract, with perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, asthma, and nasal itching and soreness reported[43]. Chronic human exposure to high levels of chromium (VI) by inhalation or oral exposure may produce effects on the liver, kidney, gastrointestinal and immune systems, and possibly the blood. Rat studies have shown that, following inhalation exposure, the lung and kidney have the highest tissue levels of chromium. Dermal exposure to chromium (VI) may cause contact dermatitis, sensitivity, and ulceration of the skin[44].

2.4.3 Copper (Cu)

Copper (Cu) is a chemical element and essential trace mineral that is a reddish metal which occurs naturally in rock, soil, sediment, water, and at low levels, air. The Earth's crust is the

primary natural source of copper with an average copper concentration of 50 ppm[51]. Copper also occurs naturally in all plants and animals, and hence is found in foods and food supplements[51].

Copper can enter the environment through releases from the mining of copper and other metals, and from factories that make or use copper metal or copper compounds. Copper can also enter the environment through waste dumps, domestic waste water, combustion of fossil fuels and wastes, wood production, phosphate fertilizer production, and natural sources (for example, windblown dust, from native soils, volcanoes, decaying vegetation, forest fires, and sea spray). Therefore, copper is widespread in the environment. About 1,400,000,000 pounds (640,000,000,000 grams) of copper were released into the environment by industries in 2000. Copper is often found near mines, smelters, industrial settings, landfills, and waste disposal sites[52].

Depending on the quantity consumed, the mineral copper can be harmful while also being vital for human health. Healthful bones, immunological function, an increased risk of infection, cardiovascular risk, and changes in cholesterol metabolism are all linked to copper. Its metabolism is intricately linked to that of other microminerals, and a lack of it has been shown to hinder the mobilization of iron, leading to secondary iron deficiency[53]. "Gastrointestinal distress can be brought on by brief exposure to copper levels in drinking water that are higher than the action limit. Long-term exposure may harm the kidneys or liver. If the level of copper in their water is higher than the action threshold, people with Wilson's illness should speak with their personal physician. Wilson's illness is a hereditary ailment that results in excessive copper retention in the body. Wilson's disease patients may be more susceptible to negative health impacts than the general public[54].

2.4.4 Iron (Fe)

Iron is the second most prevalent metal element on Earth, it has the atomic number 26 and the chemical symbol Fe. Iron is a transition metal element that can exist in a number of various oxidation states, the most prevalent of which are +2 and +3[55]. Iron has a shiny silver-gray surface in its basic state, but when it comes into contact with oxygen in the air, it produces iron oxides, which are more popularly known as rust. Iron and nickel are assumed to make up the majority of the Earth's core, and meteorites' high iron concentration is thought to be proof that iron is a common element in our solar system. Magnetite (Fe_2O_3) and hematite (Fe_2O_3) are two prevalent forms of iron (Fe_3O_4). Iron is frequently found as impurities in other minerals due to its abundance on the globe. The sapphire gem is famous for its brilliant colour, which is caused by an iron impurity[56]. Because of its exceptional structural strength, iron and its alloys (also known as steel) are the most often utilized metals in building the world in which we live. Additionally, iron is crucial to both human and animal daily life. Haemoglobin, an iron-containing porphyrin protein molecule, transports oxygen in plasma, while myoglobin, a similar substance, stores oxygen in muscle[55].

Because intestinal absorption of iron is regulated by iron stores, iron toxicity is rare. Consuming large quantities of alcohol may increase the absorption of iron. Hemochromatosis, a genetic disorder, also increases iron absorption. Once iron is absorbed it is only excreted through blood loss. Excess iron will build up in tissues and organs, may increase the risk for certain cancers and may eventually lead to death. The main concern with iron toxicity is overdoses in children[57]. An overdose of iron supplements can cause toxicity in adults and children. However, in children as little as 20 to 60 mg of iron/kg body weight can cause toxicity and death. It is important to keep iron supplements away from children and tightly

closed. The tolerable upper limits for iron as set by the Institute for medicine and the National Academy of Sciences is 40 mg/day for children under the age of 14 and 45 mg/day for anyone 14 years of age or older. This limit is set as the largest amount of iron a person can consume without risk of negative side effects[58].

2.4.5 Lead (Pb)

Lead (Pb) is ubiquitous and one of the earliest metals discovered by the human race. Unique properties of lead, like softness, high malleability, ductility, low melting point and resistance to corrosion, have resulted in its widespread usage in different industries like automobiles, paint, ceramics, plastics, etc. This in turn has led to a manifold rise in the occurrence of free lead in biological systems and the inert environment[59].

Lead (Pb) is a potentially dangerous element that builds up in the blood and bones as well as in organs like the liver, kidneys, brain, and skin after being absorbed by the body. Because Pb is poorly excreted by the human body, its harmful health consequences can be both immediate and chronic. The reproductive, hepatic, endocrine, immunological, and gastrointestinal systems in humans have all been proven to be impacted by lead exposure. Lead and its inorganic compounds may cause cancer in humans, however there is only weak evidence for this[60].

Lead exposure can occur from lead-contaminated paint, dust, water, or soil. Lead poisoning is most frequently brought on by contaminated paint chips and dust. Up to 1978, residential paint contained lead, which contaminated nearby soils and homes. The usage of leaded gasoline up to the middle of the 1980s has also raised the amount of lead in soil. In some

places of Michigan, lead was used in drinking water service lines up until 1947, and lead-based solder was used on copper pipes constructed in home plumbing up until 1986[61].

There are numerous methods for humans to be exposed to lead, all of which include environmental pollution. Lead can enter the body by ingestion or inhalation when it comes from sources like soil, food, lead dust, and contact with lead in common household items and at the office. Although lead is also absorbed through the digestive system, the respiratory system is the predominant pathway for Pb and its derivatives to enter the body in the workplace[62].

Nearly every organ and function in your body is susceptible to lead damage. The effects of lead are particularly dangerous to children under the age of six. "Even low amounts of lead in children's blood can result in behaviour and learning issues, reduced IQ, hyperactivity, slower growth, hearing impairments, and anaemia," according to the United States Environmental Protection Agency (USEPA)[63]. Lead exposure poses a specific concern to expectant mothers and can impair fetal growth, cause stillbirths, and premature birth. Adults may experience reproductive issues, kidney function decline, and cardiovascular effects[6].

2.4.6 Manganese (Mn)

Manganese (Mn) is an element widely distributed in the earth's crust. It is ranked as the fifth most common metal and the twelfth most common element. The most significant manganese-containing minerals are oxides, carbonates, and silicates because manganese does not normally occur in a pure condition. Pyrolusite (MnO_2), the most prevalent manganese mineral, is typically extracted using open-cast methods in sedimentary deposits. Most iron

ores contain manganese. It is present in crude oil, although at much lower concentrations. Its amount in coal ranges from 6 g/g to 100 g/g[65].

Depending on the plant type and the surrounding environment, various plants have variable levels of manganese toxicity. Due to the toxicity of manganese, excessive quantities of manganese in the leaves in acidic soils impair photosynthesis, which in turn inhibits growth[66]. Manganese toxicity manifests as brown patches on adult leaves and chlorotic dots at the tips of juvenile leaves. When compared to lower light intensities, these symptoms are less noticeable in uplighting[67]. Chlorotic leaves were the first to develop manganese poisoning, and then immature leaves[66]. The edge of the leaf is where the first signs of manganese toxicity appear, and they move outward into the spaces between the leaves as the toxicity increases. extended leaf necrosis with higher toxicity Manganese poisoning has a greater impact on cell size than on cell density. Manganese poisoning has two impacts on chloroplasts: an uneven distribution of chlorophyll and a build-up of granules of starch. Using a lot of magnesium helps get rid of manganese toxicity[68].

In mammals, manganese's necessity has been proven beyond a shadow of a doubt. However, no nutritional deficits in humans have been found, and no amount has been suggested for the necessary daily intake of manganese[69].

2.5 Heavy Metals in Soil

Soil (terrestrial ecosystem) is a major sink for heavy metal contaminants arising from natural and anthropogenic sources. Due to long history of industry, approximately three million sites are estimated to have been contaminated in Europe[70]. The presence of soil contamination in various parts of the world has also been established. From both natural and manmade

processes, heavy metals are released into the environment. Natural sources of heavy metals include volcanic emissions, rock weathering, mineral dusts, and forest fires[71]. Through the exploitation of mines and smelters, sewage sludge, fossil fuel combustion, metallurgical industries, intensive agricultural practices and pesticides, military operations, paints, gas works, battery manufacturers, and electronics, industrialization and urbanization have increased the anthropogenic sources of heavy metals to the environment[72]. Due to the fact that most metals do not degrade through microbial or chemical processes, each source of contamination has its own negative consequences on the entire ecosystem. Instead, they are changing from one oxidation state to another, resulting in a long-lasting persistence of the total metal concentration in soil following metal release into the environment[73]. Heavy metal build-up in soil has been noted to have the potential to endanger the entire ecosystem[74]. As a result, some nations such as the United Kingdom have specified the maximum permissible heavy metal concentration in soils and established standards to restrict heavy metal concentrations in soil amendments[75].

2.6 Heavy Metals in Vegetables

Human's diet should include vegetables because they are a source of nutrients. By providing protein, vitamins, iron, calcium, and other elements that have noticeable benefits on health, vegetables contribute to vital functional dietary components[76]. Plants have a natural inclination to absorb hazardous chemicals, including heavy metals, which are then passed through the food chain[77]. Because food products play a significant role in human diet, the presence of heavy metal pollution in vegetables cannot be understated. One of the most significant components of ensuring food quality is heavy metal contamination of the food items[78]. For both manufacturers and consumers, heavy metal contamination of food has

become a problem. Vegetable crops primarily absorb heavy metals from their growth media (soil, air, nutrient solutions) through their roots or foliage[79]. Only when heavy metals are consumed over an extended period of time through contaminated plants can their poisonous and harmful effects become apparent. To prevent an excessive build-up of these heavy metals in the human food chain, regular monitoring of heavy metals in vegetables and other food items should be carried out[80]. Heavy metals in high enough concentrations in vegetables can absorb them and build up to the point where they start to harm humans clinically. Estimates of daily metal intake can simply predict the potential ingestion rate of a certain metal while ignoring the possibility of metals being expelled through metabolism. Food consumption causes a long-term, low level build-up of heavy metals in the body, and it takes several years of exposure before the negative effects are felt[81]. Because they absorb these metals through their roots, leafy vegetables produced on heavy metal-contaminated soils collect greater levels of metals than those grown on uncontaminated soils[82]. Because they remain in the environment, heavy metals can bioaccumulate in food chains. In contrast to grain or fruit crops, they are more readily collected in the edible sections of green vegetables[83].

2.7 Health Risks due to Heavy Metal Intake

There are numerous ways that metals can poison the environment at large. Due to their stability, they may occasionally permeate the soil and water systems many years after the initial deposition. This pollution can also result from the weathering of discarded products[84]. The build-up of heavy metals in plants and soil from both natural and man-made sources, as well as the repercussions, represent significant environmental contamination issues. This is one of the most serious environmental concerns because to potential health risks and food safety concerns[85].

Through the intake of polluted food, drink, or inhalation of dust, heavy metals can enter the body[86]. Long-term exposure to heavy metals raises the possibility of organ and nervous system damage, including renal, heart, liver, and kidney damage[87]. Malnutrition results from the vital nutrients being depleted as a result of high levels. In turn, this impairs the immune system and results in growth retardation, psychosocial behavioural issues, and immune system weakness. Additionally, eating foods polluted with heavy metals has been linked to an increased risk of gastrointestinal cancer[88].

When present in trace amounts, some heavy metals, including copper, zinc, manganese, cobalt, and molybdenum, work as micronutrients for the growth of both animals and people, but others, like cadmium, arsenic, and chromium, operate as carcinogens[89]. Lead and mercury have been linked to the development of anomalies in children, while cadmium has been linked to cancers of the prostate, ovary, and renal tissues when consumed over an extended period of time[90]. The harmful effects of excessive amounts of heavy metals on biochemical levels typically involve competition for sites with necessary metabolites, replacement of essential ions, reactions with -SH groups, damage to cell membranes, and reactions with the phosphate groups[91].

2.8 Review of studies on Heavy Metals

In an appraisal of "Heavy Metal Concentration in Soil and Selected Subterranean Animals in Olusosun Landfill, Ojota, Lagos State in 2022", four composite soil samples weighing one kilogram each were taken using an auger from a depth of 0 to 15 centimetres below the soil surface. Determined were the levels of variables such soil pH, soil temperature, and soil moisture content. To get rid of soil particles, earthworms, maggots, and spiders from each analyzed soil were washed in distill water. Atomic absorption spectroscopy (AAS) was then

used to evaluate the heavy metals (Zn, Cd, Cr, Cu, and Pb). According to the study's findings, the landfill soil sample had greater mean concentrations of Pb and Cd than the control soil sample and underground animals (0.75 mg/kg and 0.1 mg/kg, respectively). Additionally, compared to soil samples from landfill and control areas as well as spider, maggot and earthworm had greater mean Zn concentrations (0.31 mg/kg and 0.14 mg/kg, respectively). According to the data, there is a significant anthropogenic influence on Zn, Cd, Cr, Cu, and Pb. The disposal of waste, particularly toxic waste, on this landfill should be strictly regulated, and it may be necessary to fortify the landfill immediately or to evacuate it. To prevent health issues from eating nearby plants, it is critically necessary to raise awareness of the soil contamination levels in the area surrounding the waste, especially among the local residents. The three subterranean creatures that were used in the study have shown that they can also be used as entomoremediators of heavy metal-polluted locations. However, when comparing the mean concentration of heavy metals on landfill soil and underground creatures, the result was not statistically significant. In the study, there was no evidence of chromium (Cr). The study concluded that there is a significant anthropogenic influence with regard to Zn, Cd, Cr, Cu, and Pb, as well as high anthropogenic influence and persistence of the heavy metals that have accumulated in the ecosystem and represent substantial ecological and health concerns[92].

In another report on “Assessment of Heavy Metals Concentration in the Soil and Crops Grown around Dumpsites Surakarta a city in Central Java, Indonesia”, taken into account some specific soil characteristics and the metal content of crops and soil samples from disposal sites. Standard methods were used for the metal concentration analysis using an atomic absorption spectrophotometer (Buck Scientific model 210) and assessment. Each

metal was discovered at low levels in the control site compared to the dumpsites, demonstrating that heavy metals were contributed by humans through the disposal of wastes made of or containing heavy metals. Cr, Cd, and Pb were present in the crops at the two sites and in the control at levels below detection limit. All of the metal concentrations in soil and crops that were examined were found to be within the World Health Organization's (WHO) maximum allowed level for heavy metals in soil and crops, suggesting that the crops are now safe for consumption by humans. A need to avoid consuming crops grown on these sites and to discourage the use of the sites for any type of farming activity is implied by the increased concentration of metals in the crops at the dumpsite and their crops compared to the control site. The report showed that there is heavy metal pollution on dumpsites soil which is the resulting effect of heavy metal-containing wastes that are improperly disposed of there. Build ups of heavy metal on these dumpsites have leached to the nearest place of uptake by crops around them. Even while the soil and crops under study were deemed to be safe for the time being, there are worries about the gradual and ongoing build-up that has already begun and is seen in the clear difference in the metal content between the dumpsites and the control site. The report concluded that continuous cultivation of consumable crops in or around dumpsites is highly risky to humans and also it is necessary to take measures both to stop cultivating crops and to conduct a public talk on the risks associated with dumpsite[93].

In 2020, an investigation was done to asses “some heavy metals concentrations in soil and groundwater around refuse dumpsite in Ibadan Metropolis, Nigeria”. In five locations around the Ibadan Metropolis, Nigeria (Arapaja, Moniya Garage, Iyana Apapa, Aleshinloye, and Alarafa), the study reported the level of various heavy metals in the soil and groundwater around garbage dumpsites. Atomic absorption spectroscopy was used to determine the

presence of the heavy metals Cd, Co, Pb, Cr, Zn, Mn, and Ni in five samples taken from each soil and ground water location. while the water samples, which were taken from hand-dug wells that were no deeper than 10 meters, the soil samples were collected in triplicates at intervals of 25 cm. The range of heavy metal concentrations found in water is Pb (0.01-0.02), Co (0.01-0.04), Cr (0.02-0.05), Ni (0.02-0.05), Mn (0.02-0.05), and Zn (0.40-0.70); cadmium, however, was not found. The limitations set by the Standard Organization of Nigeria (SON) and the World Health Organization (WHO) were exceeded by the Pb and Ni concentrations in ground water from Arapaja, Aleshinloye, and Alafara. A conclusion that can be drawn from the findings within the study region is that greater concentrations of heavy metals in soils and ground water near refuse dumpsites may be due to incorrect waste disposal, human activity, or runoff or leaching that occurred on the soil there. People's consumption of the groundwater near the dumpsites constitutes a health danger. As a result, it is advised that there is an urgent need to build a typical environmental sanitary dumpsite and promote recycling of trash nearby. Additionally, Ministries of the Environment should place a high priority on groundwater monitoring, treatment, and protection issues[94].

In 2019, similar study was conducted to determine heavy metals in waste dumpsites in Lafia town and environs[95]. Ten (10) topsoil samples (0–12 cm) were collected from each of the five zones in Lafia town and its surroundings (Lafia South, Lafia west, Lafia North, Lafia East and Lafia Central). Atomic absorption spectrometer was used to determine the amounts and concentrations of these metals (AAS). The results showed that the mean amounts of Cd (7.2813mg/kg), Pb (138.456mg/kg), Se (0.515mg/kg), and Zn (432.296mg/Kg) at the waste dumpsites detected surpassed respective WHO/FAO standards and reported geological backgrounds. Zn and Pb were found at every location, however only 3 to 4 of the 10 sites

under analysis included Cd and Se. Their high concentrations may be linked to rising human activity, such as garbage disposal, the burning of electronic waste, and heavy traffic. The concentrations of Cr, As, Fe, Mn, Cu, Co, Ba, and Ni, however, were within acceptable ranges and don't pose a threat. These metals come from both anthropogenic and natural sources, including the progressive accumulation of harmful metals in landfills. The study suggests taking the necessary precautions and raising awareness in order to monitor and lessen any negative impacts resulting from improper garbage disposal in order to protect the environment, safeguard human health, and maintain the balance of nature. The results of the study demonstrate the need for ongoing heavy metal monitoring in order to prevent excessive accumulation of these metals in humans through the food chain. The study has additionally demonstrated how we run the risk of destroying our environment, endangering our health, disturbing the natural order, and contaminating the air, water, and soil that are so vital to life. This knowledge will serve as a baseline for future research[95].

Also in 2018, the "Assessment of Some Heavy Metals in Soils and Plants Growth in Dumpsites was carried out in Benin City". This study examined the presence of heavy metals (lead, zinc, chromium, nickel and cadmium) in the soil and plants of three dumpsites in Benin City, Edo State: Ikhueniro, Iguomo, and Oluku. The dumpsite and the control regions had soil samples taken at random from two depths (0-15 cm and 15-30 cm). Additionally, random plant samples (Talinium triangulare) were gathered from the dumpsite and control locations. Analysis of the soil and plant samples revealed substantial differences ($P<0.05$) between the control sites and the dumpsites in the amounts of heavy metals, particularly zinc. It was found that the dumpsite soils had a low pollution index (1 in both the control and

dumpsite areas, while the other metals stayed at 1 in the Iguomo dumpsite area. The plant composition of a site is considerably altered by the presence of heavy metals in the soil. The fact that there are plant species on their sites indicates that such species can tolerate high amounts of metals and support them. Plant heavy metal mean contents range from 110 mg/kg (Oluku) to 176 mg/kg (Iguomo) to 155 mg/kg (Ikhueniro) for Zn, from 1.07 mg/kg (Oluku) to 0.07 mg/kg (Iguomo) to 0.09 mg/kg (Ikhueniro) for Cr, from 0.1 mg/kg (Oluku) to 0.3 mg/kg (Iguomo) to 0.1 mg/kg (Ikhueniro) for Pb, from 0.08 mg/kg (Oluku) to 0.18 mg/kg (Iguomo) to 0.05 mg/kg (Ikhueniro) for Cd and from 0.17 mg/kg (Oluku) to 0.16 mg/kg (Iguomo) to 0.15 mg/kg (Ikhueniro) for Ni. For the control and dumpsite locations, the transfer factor for metal accumulation in the plant was computed. Plant species, soil characteristics, and the effectiveness of various plants in absorbing metals—assessed by plant absorption or soil to plant transfer factors of the metals—determine the accumulation of heavy metals in plants. This study demonstrated the presence of heavy metals in the dumpsite locations under investigation, which are harmful to humans, animals, and plants in high concentrations and can cause a variety of illnesses. Also, according to the findings of this study, the concentration of heavy metals is typically higher at 0–15 cm depth than at 15–30 cm deep. Therefore, it is advised that garbage collectors and town refuse control personnel exercise caution when operating at waste dump sites. Additionally, areas near reclaimed waste dumps should not be considered for use as markets or other enterprises where people might come into direct touch with the soil during their activities[96].

In a case of "Determination Heavy Metal Contents in Soil and Plants at Dumpsites: A Case Study of Awotan and Ajakanga Dumpsite Ibadan, Oyo State, Nigeria"[97]. The study focused on the physiochemical and heavy metal levels of the underlying soils at Ibadan's Awotan and

Ajakanga dumpsites, the relationship between the soil metal content at the dumpsites and the rate of bio-accumulation by plants, and the heavy metal contents in soils and plants at those sites. A total of twelve soil samples (four samples from each site) at an interval of 20m away and forty-eight dominant vegetable/plant species were collected by uprooting them from the two dumpsites. Samples were also collected from Idi-Ose farm land area which serve as control site. At each plot, soil samples were taken from 0 to 30 cm deep using a clean stainless steel shovel. Using nitric acid digestion and the Atomic Absorption Spectrophotometer method, the concentration of heavy metals (Cd, As, Co, Fe, Cu, Zn, Pb, and Ni) in the soils, plants, and vegetables from dumpsites and the control site was determined (AAS). The transfer factor (Tf) showed that plants grown on dumpsite soils collected more metal than plants cultivated on typical agricultural soil (control site). In general, the results suggest that there was a higher concentration of heavy metals in the two dumpsite soils than in the soils at the control sites. While the concentrations of Pb and Cd in the plants were greater at the dumpsite than the control site, the heavy metal (Fe and Zn) contents in the plants were higher at the two (2) dumpsites than the control sites. The order of the transport of heavy metals was Cu > Cd > As > Fe > Co > Pb > Zn > Ni for site A and Cd > Cu > Fe > Co > As > Pb > Ni > Zn for site B. As a result, solid waste dumpsites had significant amounts of heavy metals, which the plants growing there later absorbed and accumulated. Through the release of pollutants like heavy metals, which in high concentrations in the soil can be harmful to humans if consumed directly or indirectly, as well as plants, which depend on the nutrients from the soil for their growth and development, the indiscriminate disposal of these solid wastes in the environment has greatly harmed our ecosystem. Environmental concerns arise when heavy metals in soil and plants are

contaminated, particularly when the chemical makeup of the metals is affected. Heavy metal concentration levels were found to be influenced by seasonal variations, sampling distance, soil depth, and plant component. The findings of this study also showed that plants grown on dumpsite soils are more likely to collect hazardous metals than plants cultivated on typical agricultural soils. As a result, plants cultivated on Awotan garbage dumpsites contain more metal than their Ajakanga counterparts. High quantities of heavy metals in vegetables may result in health problems if consumed. It will be wise to regularly monitor the health of the soil and the plants in order to detect changes in the environment's chemistry and possibly apply corrective actions. The concentration of heavy metals found in soil samples from Awotan and Ajakanga dump sites is in the following order: Cu>As>Fe>Co>Pb>Cd>Zn>Ni>, while that from Idi-Ose (control site) is in the following order: Cu>Co>Zn>Fe>As>Ni>Pb. In plants cultivated on dumpsites, copper was shown to have the greatest concentration level, while nickel had the lowest. Despite the fact that these metals were discovered in the soil and vegetation near the dumps, it is important to emphasize that they were below WHO allowed levels. Lead levels were found to be higher than the WHO guideline maximum permitted of 0.01 mg/kg and lower than the tolerable values. However, if these are present in plants in large quantities, it may be harmful to human health. Using dumpsites to produce plants and crops on a regular basis could cause toxic metals to bio-accumulate and have a negative impact on human health[97].

2.9 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic Aromatic Hydrocarbons (PAHs) are a “family of organic compounds of the six carbon benzene ring origin; the benzene ring is the one responsible for their aromatic behaviour and they are made up of a few to several fused rings of benzene hydrocarbon

compounds"[98]. Organic pollutants such as PAHs are created both naturally and by anthropogenic activities such as industrialisation and urbanization. Over 400 different types of PAHs have been identified thus far, along with their effects[99]. A class of dangerous chemical compounds known as PAHs is made up of two or more benzene rings bound together in clusters, lines, or angles. Most PAHs are solids that are colourless, white, or pale yellow.[100].

Based on their potential for human exposure, toxicity, frequency of occurrence at hazardous waste sites, and the amount of information currently available, the USEPA has classified 16 of the PAHs as priority contaminants[101]. There are 16 PAHs in all namely, Acenaphthene, Benzo[ghi]perylene, Chrysene, Acenaphthylene, Benz[a]anthracene, Benzo[b]fluoranthene, Anthracene, Benzo[k]fluoranthene, Benzo[a]pyrene, Fluoranthene, Indeno[1,2,3- cd]pyrene, Naphthalene, Phenanthrene, Dibenz[a,h]anthracene, Fluorene, and Pyrene. The structure of these 16 PAHs are shown in Figure 2.2.

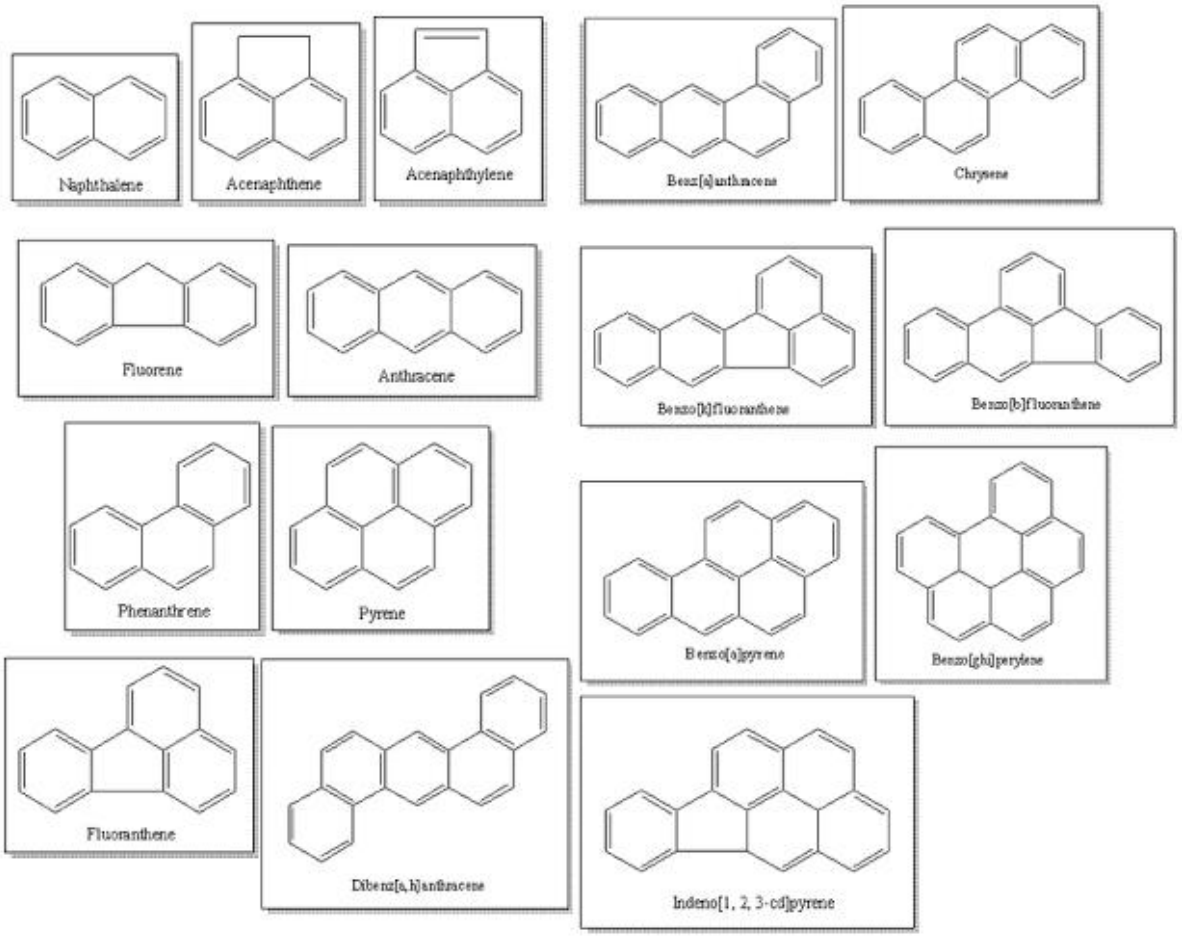

Figure 2.2: Structures of the 16 PAHs on the USEPA priority pollutant list

Source[98]

The majority of PAHs found in the environment have pyrogenic, petrogenic, and biologic origins[102]. The combustion of petroleum products and plant materials, as well as volcanic eruptions, are thought to be the primary pyrogenic origins of the majority of PAHs. For example, phytoplankton, algae, bacteria, and plants can all produce PAHs, as can gradual modifications to organic matter[103]. The incomplete combustion of organic matter, such as that found in vehicle fuel, power plant emissions, oil spills, coal mining, and other anthropogenic sources, results in the formation of PAHs. The majority of PAHs are lipophilic and hydrophobic, making biodegradation extremely challenging[104]. Although there are many PAHs, the majority of laws, studies, and research often concentrate on only 14 to 20 specific PAHs. Due to the former's comparatively higher volatility and solubility, low molecular weight PAHs (two or three rings) are more degradable as compared to high molecular weight PAHs (four or more rings)[105].

2.10 PAHs Formation and Sources

Polycyclic aromatic hydrocarbons (PAHs), commonly referred to as polyarenes, are pervasive environmental pollutants that can be either man-made or naturally occurring. Fuel oil or gasoline spills, natural seeps, the combustion of fossil fuels (coal, oil, natural gas), wood, and creosote emissions are all examples of anthropogenic sources of PAHs (Figure 2.3). The primary sources of PAHs include incomplete combustion of coal, oil, and gasoline, wood preservation facilities, or petrochemical industry processes[106].

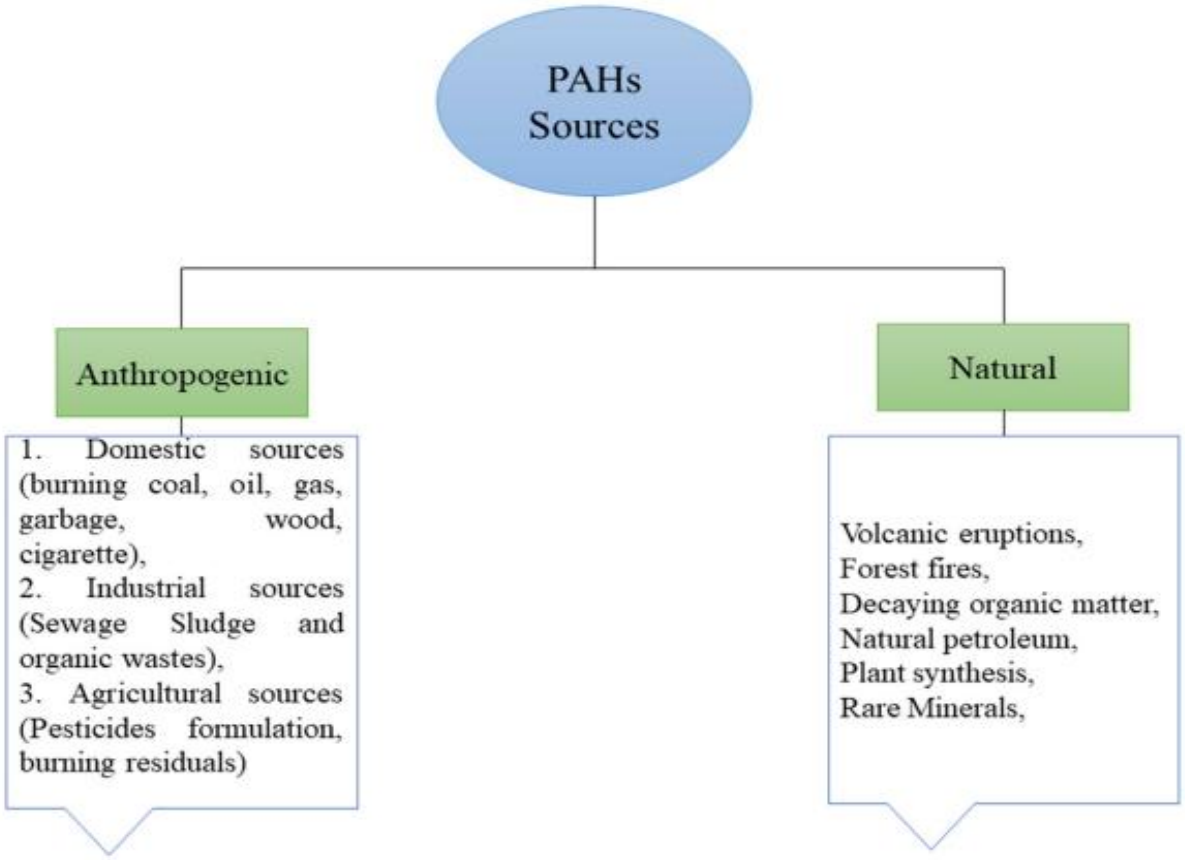

Figure 2.3: Sources of PAHs

Source[106]

They happen in the environment on their own, during things like thermal geological reactions and spontaneous fires. Additionally, peat, lignite, coal, and crude oil all naturally contain PAHs. Volcanoes and forest fires are biogenic sources of PAH[107]. Since PAHs are created throughout all processes requiring incomplete combustion (insufficient oxygen supply) of organic molecules, human activities represent important sources in the environment. The durability, hydrophobicity, bioaccumulation, and carcinogenicity of various polyarenes in these substances all contribute to the dangers they pose. Analytical chemist continues to be interested in PAHs because to their widespread dispersion and detection in soils and sediments[108].

2.11 PAHs Exposure Route

The PAHs can enter your body through your lungs when you breathe air that contains them (usually stuck to air particles or dust). Cigarette smoke, wood smoke, coal smoke, and smoke from many industrial sites may contain PAHs[108]. People living near hazardous waste sites can also be exposed by breathing air containing PAHs[109]. However, it is not known how rapidly or completely your lungs absorb PAHs. Drinking water and swallowing food, soil, or dust particles that contain PAHs are other routes for these chemicals to enter your body, but absorption is generally slow when PAHs are swallowed. If your skin comes into touch with dirt that contains high amounts of PAHs (which could happen close to a hazardous waste site), used crankcase oil, or other materials (like creosote) that include PAHs, PAHs may enter your body under typical environmental exposure conditions[110]. The rate at which PAHs enter your body by eating, drinking, or through the skin can be influenced by the presence of other compounds that you may be exposed to at the same time with PAHs. Figure 2.4 shows the human exposure pathways of PAHs.

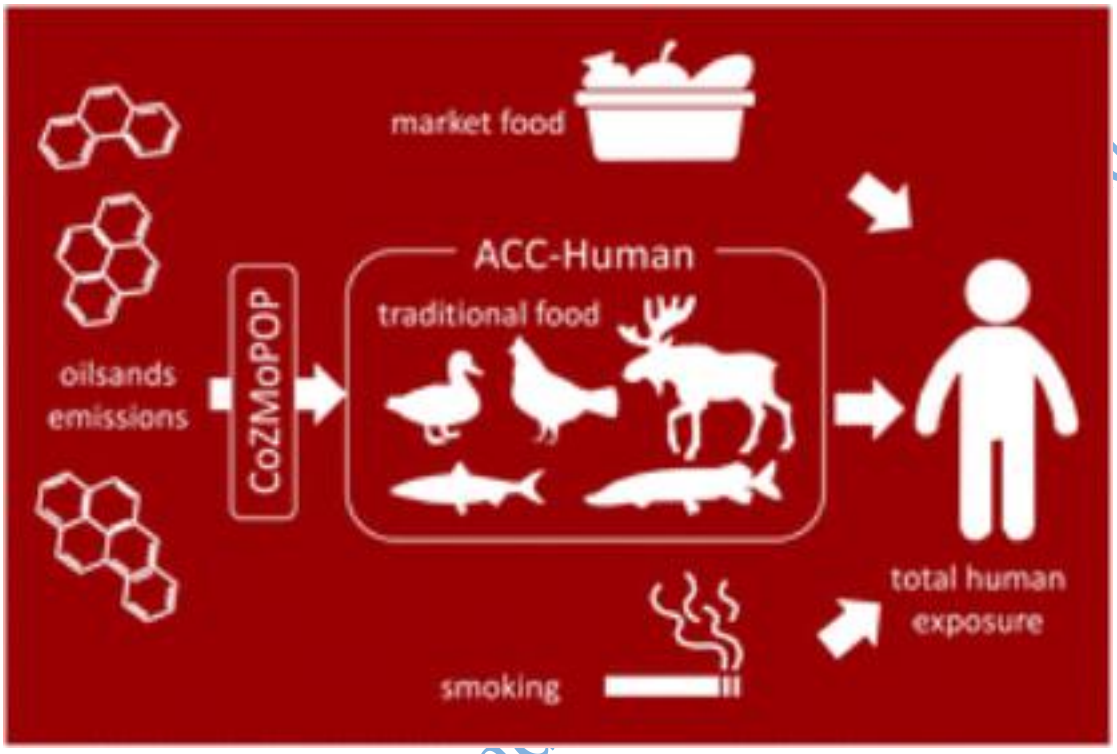

Figure 2.4: PAHs Exposure Pathways in Human

Source[110]

The PAHs can also enter all the body tissues that contain fat. They tend to be stored mostly in kidneys, liver, and fat. Smaller amounts are stored in spleen, adrenal glands, and ovaries. PAHs are changed by all tissues in the body into many different substances. Some of these substances are more harmful and some are less harmful than the original PAHs. Results from animal studies show that PAHs do not tend to be stored in the body for a long time. Most PAHs that enter the body leave within a few days, primarily in the faeces and urine[111].

2.12 Toxicology of PAHs

Polycyclic aromatic hydrocarbons are metabolized to a wide variety of compounds principally by enzymes of the cytochrome P-450 mixed-function oxidase (MFO) system and epoxide hydrolase[112]. The most important step of primary metabolism is epoxidation. A small proportion of all PAHs will, after epoxidation and subsequent diol formation, be further epoxidized by the microsomal monooxygenases to diol epoxides. Benzoring diol epoxides, in which the epoxide forms part of the bay region of the hydrocarbon molecule, are likely highly reactive and are implicated as the ultimate biologically reactive intermediates involved in the binding of PAHs to macromolecules and resulting toxicity[113]. They may also be detoxified and excreted as metabolites in bile, feces, and urine by conjugation with glutathione or glucuronic acid, or by further metabolism to tetrahydrotetrols[114]. The cytochrome P-450 activities of the lung are less than those in the liver and intestinal tract (i.e., metabolism to the active species is slow); moreover, the activity of the conjugating enzyme systems and epoxide hydrase in the lung is very low (i.e., detoxification is slow). These differences may account for possible variations in potency of PAHs following inhalation and ingestion[115]. The bay region diol epoxide intermediates of PAHs are currently considered to be the ultimate carcinogen for most PAHs, although for some, other reactive intermediates

may also be important[116]. Though examined principally in animal models in vitro and in vivo, results of studies on the metabolism of benzo[a]pyrene in primary cultures of human hepatocytes and a human hepatoma cell line indicate that these mechanisms are likely relevant to humans[117].

2.13 Carcinogenicity of PAHs

Multiple PAHs have been shown to cause tumors in laboratory animals in numerous investigations, primarily as a result of cutaneous exposure. However, information on the induction of tumors after exposure through the primary exposure pathways for the general population is rather scarce (i.e., inhalation and ingestion)[118]. Only a small number of research have looked at the carcinogenic effects of PAH exposure through inhalation, and they were all limited to benzo[a]pyrene. In addition, two of the studies concurrently exposed animals to additional substances[119]. It has been noted that female Wistar rats exposed to the combustion fumes of a coal furnace for a maximum of 22 months showed an elevated incidence of lung tumors. This exposure occurred on average for 16 hours per day, five days per week. Rats exposed to sulphur dioxide ($S0_2$) and benzo[a]pyrene at 10 ppm (103 mg/m^3) also had an increased incidence of respiratory tract tumors[120].

Another study exposed groups of 24 male Syrian golden hamsters to concentrations of 0, 2.2, 9.5, and 45.6 mg/m^3 B[a]P by inhalation (nose only) during the first 10 weeks, and for the remaining exposure time (up to 96 weeks), for 3 hours per day[121]. The body weights of all surviving exposed animals were comparable to those of the controls from the tenth to the sixty-first week of the trial, despite the fact that body weight gain in exposed animals decreased during the first ten weeks of the experiment (with the exception of the high

exposure group). Additionally, mean survival fell in the group receiving 46.5 mg/m^3 exposure. There were no cases of unidentified tumors in the nasal cavity, larynx, or trachea in any of the 27 controls, 0 cases in the low-dose group, 9 cases (34.6%), in the mid-dose group, and 13 cases (52%) in the high-dose group. In the pharynx (0, 0, 23, and 56% for control, low-, mid-, and high dose, respectively), oesophagus (0, 0, 0, and 8% for control, low-, mid-, and high dose, respectively), and forestomach (0, 0, 4, and 4% for control, low-, mid-, and high-dose, respectively), exposure-related neoplasms (unspecified) were present. No lung tumors were found[121].

A relationship between the ingestion of benzo[a]pyrene and the development of benign and malignant tumours has been documented in several limited studies in experimental animals[118]. In the most extensive, though limited, early study in which mice were fed a diet containing benzo[a]pyrene at concentrations of 40 to 45 ppm {equivalent to 5.2 to 5.9 mg/[kg (b.w.)·d]} for 110 days, the incidence of stomach tumours was increased 10% or less, whereas in mice fed a diet containing 50 to 250 ppm B[a]P {equivalent to 6.5 to 32.5 mg/[kg (b.w.)·d]} for 70 to 197 days, it exceeded 70%. In a second experiment in which a diet containing 250 ppm B[a]P {equivalent to 32.5 mg/[kg (b.w.)·d]} was fed to mice for different periods of time, incidences of tumours of the fore stomach (the only tissue examined) were as follows: 2 to 4 days of feeding, 10%; 5 to 7 days of feeding, 30 to 40%, 30 days of feeding, 100%. However, after administering a lower dose of benzo[a]pyrene in the diet for up to 7 days [100 ppm or equivalent to 13 mg/kg (b.w.)d] increases in the incidence of forestomach tumours were not seen[122].

2.14 Review of Studies on PAHs

In 2020, the “Contamination Levels of Polycyclic Aromatic Hydrocarbons in Soil at Uncontrolled Solid Waste Dumpsites in Port Harcourt City, Nigeria” was investigated[123]. The dumpsites considered in the study were those of close proximity to residential areas where household solid wastes are dumped, those around market areas and those around semi-industrial areas. At each of the dumpsites, different soil samples were taken with an auger at a depth of 0–15 cm, and they were then analyzed using gas chromatography. To identify and ascertain the origins and degree of PAHs contamination in comparison to the control sites, the data acquired were subjected to several statistical analyses, some of which were Standard Deviation, 2 sample T=test, Hierarchical cluster analysis, and main components analysis. Each of the dumpsites was categorized as "Heavily contaminated" because it had a total PAHs value more than 1(>1). According to the T-test results, the degree of significance of the data ranged from 0.008 to 0.047 with respect to the control sites. Four PAHs at the Diobu location exceeded 2.8 and 4.2 mg/kg, while variations between 0.7 and 2.8 mg/kg are seen at other locations. The presence of polycyclic aromatic hydrocarbons (PAHs) found in the study clearly demonstrated that PAHs can be produced via the pyrogenic approach whenever organic waste materials are exposed to high temperatures under low or no oxygen conditions. High molecular weight (HMW PAHs) of 4 to 6 rings were prevalent and significantly greater than low molecular weight (LMW PAHs) of 2 to 3 rings at all the dumpsites in the extremely polluted Diobu area. The study concluded that Diobu area was contaminated and has higher levels of PAHs than other garbage dump sites. Solid trash must be quickly removed from all dumpsites in the Port Harcourt city regions with in-situ waste segregation[123].

In another study in the year 2017 titled the "distribution of PAHs in soils within the vicinity of an electronic waste open burning workshop in Aba, south east Nigeria" [124]. E-waste processing facilities scattered throughout the city of Aba were investigated. The e-waste facilities used open burning to disassemble electronics, remove valuable components and subassemblies, and minimize the volume of e-waste before disposal. Open burning of e-waste pollutes the area around the site with dust and smells. In the study, soil samples were taken at a depth of 0 to 5 cm from the vicinity of various e-waste open burning workshops. Hexane was employed for PAH extraction, and Agilent GC-FID was used to analyze the extracted material. According to the findings, Aba's open burning of e-waste significantly contaminated the soils near the open-burning e-waste workshop, especially with cancer-causing HMW PAHs. In the Aba metropolis, soils close to an open-burning e-waste workshop were contaminated with PAHs, with HMW predominating over LMW. A pyrogenic source for PAHs was indicated by the abundance of Benzo (α) anthracene (BaA), Benzo(b)fluoranthene (BbF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IP), Dibenzo(a,h)anthracene (DA), and Benzo(g,h,i)perylene (BP) in the soils. The abundance of Naphthalene and Chrysene suggested that unburned petroleum was introduced into the soils from the open burning site. Therefore, soils near the workshop in the city of Aba were primarily contaminated with PAHs by the open burning of e-waste[124].

The same year, heavy metals and PAHs in soil from e-waste dumpsites in Lagos and Ibadan, Nigeria, were examined in order to assess the potential contaminant contribution from e-waste activities, composite soil samples were collected at depths of 0-15 cm, 15-30 cm, and 30-45 cm from major e-waste dumpsites in Lagos and Ibadan. These samples were then analyzed for lead (Pb), cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), and PAHs. At the

University of Ibadan's Botanical Garden, control samples were gathered. After acid digestion, samples were examined for heavy metals using atomic absorption spectrophotometry, and for PAHs, cold solvent extraction was used, and were quantified using gas chromatography-mass spectrometry. The study showed that dumpsite soils contained moderate to extremely high levels of contamination from various metals, which could pose risks to both human and ecological health. PAHs were detected in dumpsite soils at amounts more than 1,000 g/kg, indicating anthropogenic pollution from both petrogenic and pyrogenic sources. The overall PAH concentrations at the 0–15 cm level were 1,756–2,224 g/kg, at the 15–30 cm level they were 1,664–2,152 g/kg, and at the control site they were 278 g/kg. In comparison to the control soil, the total PAHs in the soil of e-waste dumpsites were substantially greater. The findings corroborate earlier findings at e-waste dumpsites in other nations and show that open burning, stockpiling, and other poor e-waste management techniques may have caused harmful metal accumulation in the soil of e-waste dumpsites in Lagos and Ibadan. The research also demonstrated the importance of routine soil monitoring at significant dumpsites in Nigeria and suggested that inappropriate e-waste disposal at these locations may contribute to increased metal and PAH contamination. The study concluded that open burning and careless disposal of e-waste are possible sources of harmful metal and PAH emissions, which can have detrimental effects on the environment and human health[125].

Also, in a research carried out to determination of polycyclic aromatic hydrocarbons (PAHs) on selected dumpsites in Abeokuta Metropolis, SW, Nigeria. Using a stainless soil auger, undisturbed surface soil was removed from the chosen dumpsites at depths of 0–15 cm (top soil) and 15–30 cm (subsoil). The five sub-samples that made up the composite of the soil samples were each taken at two different depths from the four corners and the center of a 10

m by 10 m square in the dumpsites. Gas chromatography Flame Ionization Detector (GC-FID) was used to measure the concentrations of specific PAHs. According to the findings, the Saje dumpsite had the highest concentration of a single PAH chemical, (fluoranthene, with values of 33.75 mg/kg and 22.74 mg/kg at depths of 0–15 and 15–30 cm, respectively). At the Alogi dumpsite, the fluoranthene/pyrene isomer ratio was 2.69, which indicated that the PAHs were likely derived from pyrogenic sources. The study revealed that the three separate dumpsites at Saje, Alogi, and Igbore in the Abeokuta metropolis had measurable, varied, and non-detectable levels of the 16 PAHs profile in their soils. The Saje dumpsite and Igbore had the greatest concentrations of PAHs, respectively. In contrast to the Alogi and Igbore dumpsites, which are unlawful dumpsites, the cumulative amount for 10 PAHs compounds at the Saje dumpsite was 35.49 mg/kg, making it the highest and only legal dumpsite in the Abeokuta city. Concerns regarding possible human exposure through the food chain were raised by the presence of carcinogenic PAHs, which made up roughly 1.29–15.69% of all PAHs found in the dumpsite. Due to trash combustion, the study found that the dumpsites are the main sources of PAHs in the study region. The growing volume of traffic in vehicles and other nearby human activity could be another factor. Improvements in waste management systems, restrictions on the types of waste that can be handled, and environmental legislation designed to minimize pollution should all work together to ensure that there is no significant risk to the local population's health. Uncoordinated and inadequate management of waste material on the dumpsites studied can undoubtedly present a pollution risk and a potential health hazard. It was advised that the authorities take into account treating dumpsites in basements before using them. As a result, pollutant sorption surfaces will be provided, and groundwater contamination will be avoided[126].

2.15 Phthalate Esters

Phthalate esters (PAEs) are man-made plastic additives that are added to a variety of plastic products, including toys, beverage containers, polyvinyl chloride (PVC) pipes, pharmaceutical and personal care products (PPCPs), medical equipment, and agricultural films, to improve the strength and plasticity of the target product[127]. Due to the weak covalent connection that exists between PAEs and plastic products, PAEs exhibit hydrophobic qualities and are quickly dissociated from plastic products into various environmental matrices[128]. The environment is full of PAEs, which are alleged to be endocrine disruptors and pose a serious harm to creatures, including people. The mammalian endocrine system, hormone secretion, and protein expression may be impacted by PAEs, despite their modest acute toxicity, which they demonstrate estrogenic toxicity potential for[129].

2.15.1 Phthalate Esters in the Environment

It is simple to release PAEs into the environment, and they can be found in a variety of matrices, including air, water, soils, and sewage sludge, to name a few. Fortunately, they are not persistent because they disintegrate quickly. These chemicals are more prevalent in urban air than in rural air because, as has been suggested, more waste/garbage is often generated in metropolitan areas[128]. Their widespread pollution of the air, soil, and rivers, especially in China, is the result of their extensive use in daily life and industrial activity. There is also a high likelihood that PAE chemicals may build up in agricultural soils and be absorbed by

crops and vegetables, contaminating the human food supply and directly harming plants[130]. Some PAE substances have also been identified as environmental carcinogens, teratogens, and mutagens as well as endocrine disruptors. Three of the six PAE compounds, namely dimethyl phthalate (DMP), diethyl phthalate (DEP), and di-n-octyl phthalate (DnOP), have now been added to China's priority pollutants list. The USEPA nominated six PAE compounds as priority pollutants in 1999[131]. Different land utilization methods played a significant effect in all the parameters that influenced the overall content of target PAE pollutants in soil samples, which could also be regarded as the pollution status of all the analyzed plots. For instance, the majority of PAE compounds were found to degrade much more quickly under aerobic environmental conditions than they did under anaerobiosis created by flooding. As a result, the total concentration of the target pollutants in long-term flooding plots may be higher than in non-flooded plots[132].

2.15.2 Health effect of Phthalate Ester Pollution

Phthalate esters (PAEs), which are thought to have some endocrine activity, are among the several chemical substances analyzed from landfills. Endocrine activity is broadly described as any type of hormonal system interference[133]. The World Health Organization has regulated these compounds in water bodies below 8 g/L, and the EU has prohibited the use of PAEs in children's toys due to the potential health risks[134]. Apparently, PAEs have been found in medical tubings, which is concerning because it raises the possibility that they will contaminate whatever is injected through the tubes[132]. According to one study, respiratory illnesses are more common in environments with greater concentrations of phthalate esters than in environments with lower concentrations[135].

In another study, the occurrence of early breast development in Puerto Rican girls was linked to PAE exposure[136]. Unfortunately, exposure to PAEs cannot be avoided due to their widespread use as additives in virtually all plastic household items, including toys, cosmetics, vinyl flooring, bags, food packaging, and vinyl flooring, to name a few. They are also reportedly used to soften hard plastics[137].

2.16 Atomic Absorption Spectrometry (AAS)

Atomic absorption depends on the phenomenon whereby atoms of an element are able to absorb electromagnetic radiation which occurs when the toms are unionized and are not bound to similar or other atoms. The sample is initially in solution then sprayed into a flame. At the temperature of flame only a very small fraction of all atoms is excited to emission, 99% remain unexcited[138]. Therefore, the absorption due to a transition from the ground electronic state to a higher energy level is virtually an absolute measure of the number of the atoms in the flame, and hence the concentration of element in a sample[139]. The atoms absorb light at discrete resonant wavelengths which are identical to the light the atom would emit when falling from a higher energy level back to the ground state. The number of atoms capable of absorbing any transmitted light of appropriate wavelength is proportional to the product of the concentration of these atoms in the flame and the length of the light path through the flame[140]. Atomic absorption follows Beer's law namely:

$$\log I/Ic = A.B.C$$

where I and Ic are the intensities of the light before and after passing through the flame, A is the absorption coefficient, B is the path length of the flame and C is the concentration.

An important advantage of MS is that it allows measurements of the ratio of two intensities: the intensity of monochromatic light source in the presence and absence of absorbing atoms. The usual procedure for determining the relationship between absorption and atom concentrations in solution is by measuring the absorbance of a number of standard solutions containing a known concentration of the analyte, then drawing a calibration graph by plotting absorbance against concentration[141]. The schematic representation of AAS is shown in Figure 2.5.

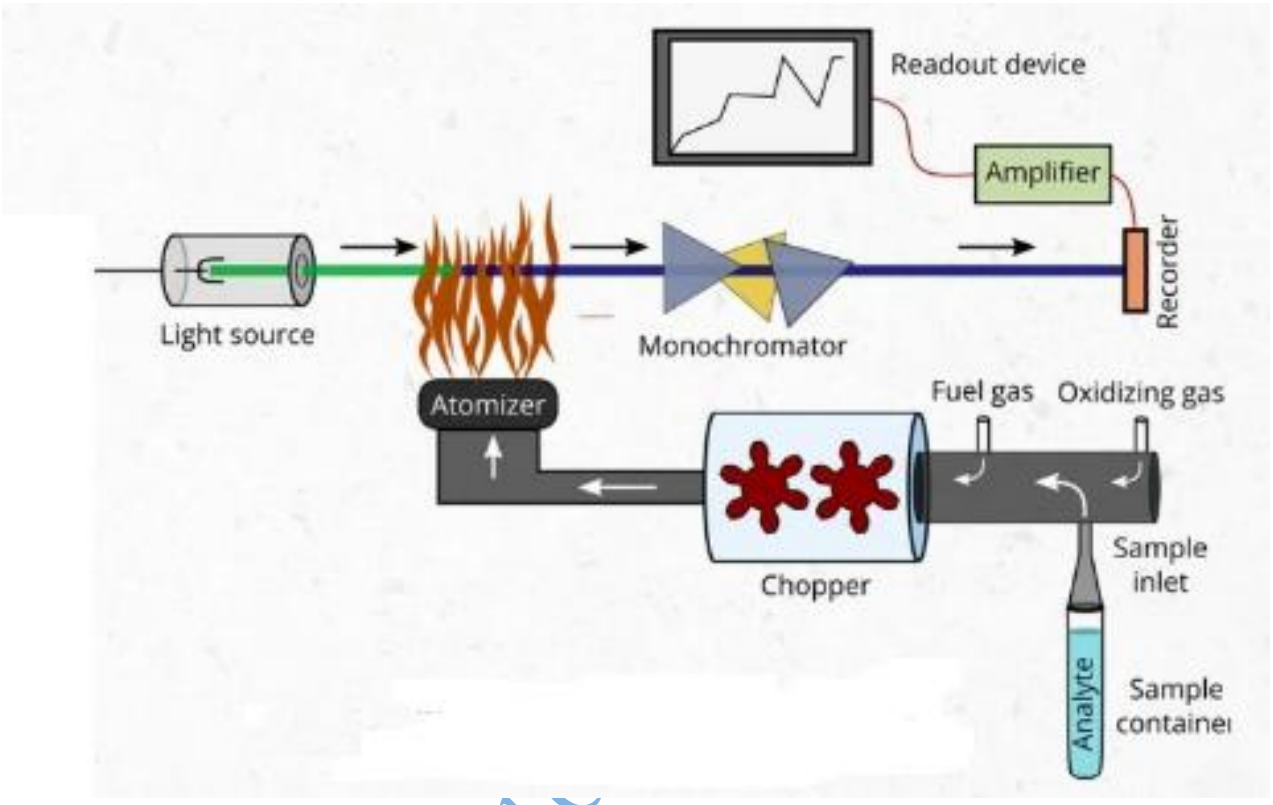

Figure 2.5: Schematic representation of AAS system

Source[141]

Care should be taken to analyze the unknown solutions within the concentration range of the prepared standards and to ensure the graph is linear at these concentrations. Nearly all metallic elements of the periodic table can be analyzed by this technique or variation of the procedure. Therefore, the applications are almost unlimited. The only criterion for sample preparation is that the metal should be in solution. The most common solutions are usually of very low pH (<1.0) retaining the metals in solution and also prevent loss due to adsorption on the vessel walls. The technique has been used widely in geochemistry, environmental pollution analysis and water & waste water analysis. Pre-concentration techniques for dilute samples are quite easy to use, they include ion-exchange and solvent extraction[142].

2.17 Gas Chromatography

Gas Chromatography requires injecting a sample that has been vaporized into a stream of inert gas (helium). The sample is transported into a chromatography column by the gas. A liquid stationary phase that interacts with the sample lines the interior of the column. The separation of the compounds is caused by varying degrees of adsorptive contact between the sample compounds in the gas stream and the stationary phase. The heating of the column aids in the separating process as shown in Figure 2.6. The various chemicals are subsequently transported to the detector through the column[143].

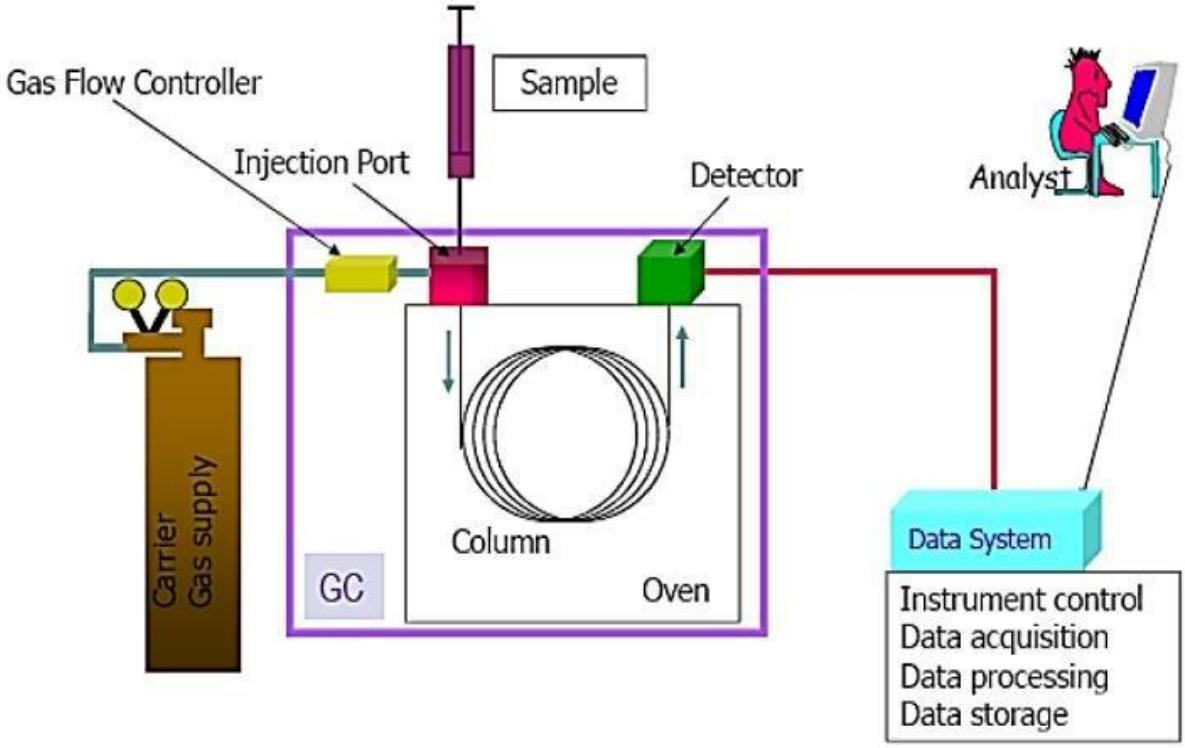

Figure 2.6: Schematic representation of Gas Chromatography System

Source[142]

An electron impact ionizer graphic shows how the molecule entering the MS is bombarded by a high energy electron beam, which can cause the compound to fragment and become ionized. The electron trap opposite the filament focuses the electron beam, and an array of lenses focuses the fragmented ions when they are ejected from the ionization unit by the ion repeller. In a quadrapole, the fragmented ions are subsequently processed (an arrangement of four electromagnets)[144].

The mass charge ratio (m/z) of the fragmented ion, measured in Daltons (Da), and the quadrupole settings determine which m/z range the quadrupole will permit an ion to pass through. The mass spectrum software can be used to regulate which m/z range the quadrupole will allow an ion to pass through. The detection of any fragments outside the defined m/z range is not possible. This has the advantage of increasing sensitivity to the target chemicals[145].

The mixture is divided into its constituent elements by the GC. By dividing the component into charged ions, the MS can identify a unique "fingerprint" of the substance. A segment of the chromatograph created by running a sample containing a combination of chemicals. At minutes 13.08, 14.00, and 15.78, respectively, three chemical molecules can be spotted eluting from the GC column: acenaphthene, dibenzofiiran, and fluorene. The different chemicals elute from the GC at different times due to the molecular weight, atomic arrangement, and contact with the stationary phase in the GC column[146]. This displays the compound's mass spectrum as it leaves the GC column at 13.08 minutes. The fragmented ions (that made it to the detector) that make up the entire compound can be seen as a succession of red lines of varied diameters in the mass spectrum. Each component will have a

distinct mass spectrum, allowing for comparison and identification of unidentified molecules. The characteristic mass/charge ion is the largest of the red lines[147].

By utilizing the information produced by the mass spectrum, qualitative analysis is feasible. The software included with the GC MS instrument allows comparison of the obtained spectrum with a library of mass spectra of several recognized substances[148].

2.18 High Performance Liquid Chromatography (HPLC)

High performance liquid chromatography (HPLC) uses a similar separation concept to traditional liquid or column chromatography (LC), albeit there are some differences in the sample size and column size[149]. With regard to speed, automation, elution duration, and individual manual assays of collected fractions, it differs from LC. When using HPLC, a liquid mobile phase is pumped under pressure through a column that contains stationary solid inert phase coated with nonvolatile liquid phase, allowing microgram quantities of the sample to pass through. Components migrate through the liquid mobile phase at varying speeds depending on their relative affinities[150]. Several operational factors, including as retention time, pressure, and plate number, must be tuned for HPLC to obtain the required separation. Short analysis times or the number of plates required to complete a challenging separation are of particular interest. A suitable HPLC system must first be chosen, such as one that uses adsorption, bonded-phase, reverse phase, ion-exchange, exclusion, affinity, or any other type of chromatography[151].

The following are the general components of HPLC equipment: i) A reservoir for a solvent for the mobile phase. ii) A pump that can supply the mobile phase at a variety of pressures up to several hundred atmospheres in order to obtain manageable flow rates. iii) Sampling loops

or valves that allow the sample to be injected into the moving mobile phase or dissolved in it. iv) A guard column or online filter to keep the primary column clean. vi) A packing-containing separation column that carries out the intended separation. These could be gel, ion-exchange resin, modified silica gel, or some other special packing. vii) A detector powerful enough to gauge the levels of solutes. viii) A recording and display system for displaying time versus peak intensity[152]. Additionally, extra electronic devices are needed for data manipulations. Figure 2.7 provides a schematic representation of them.

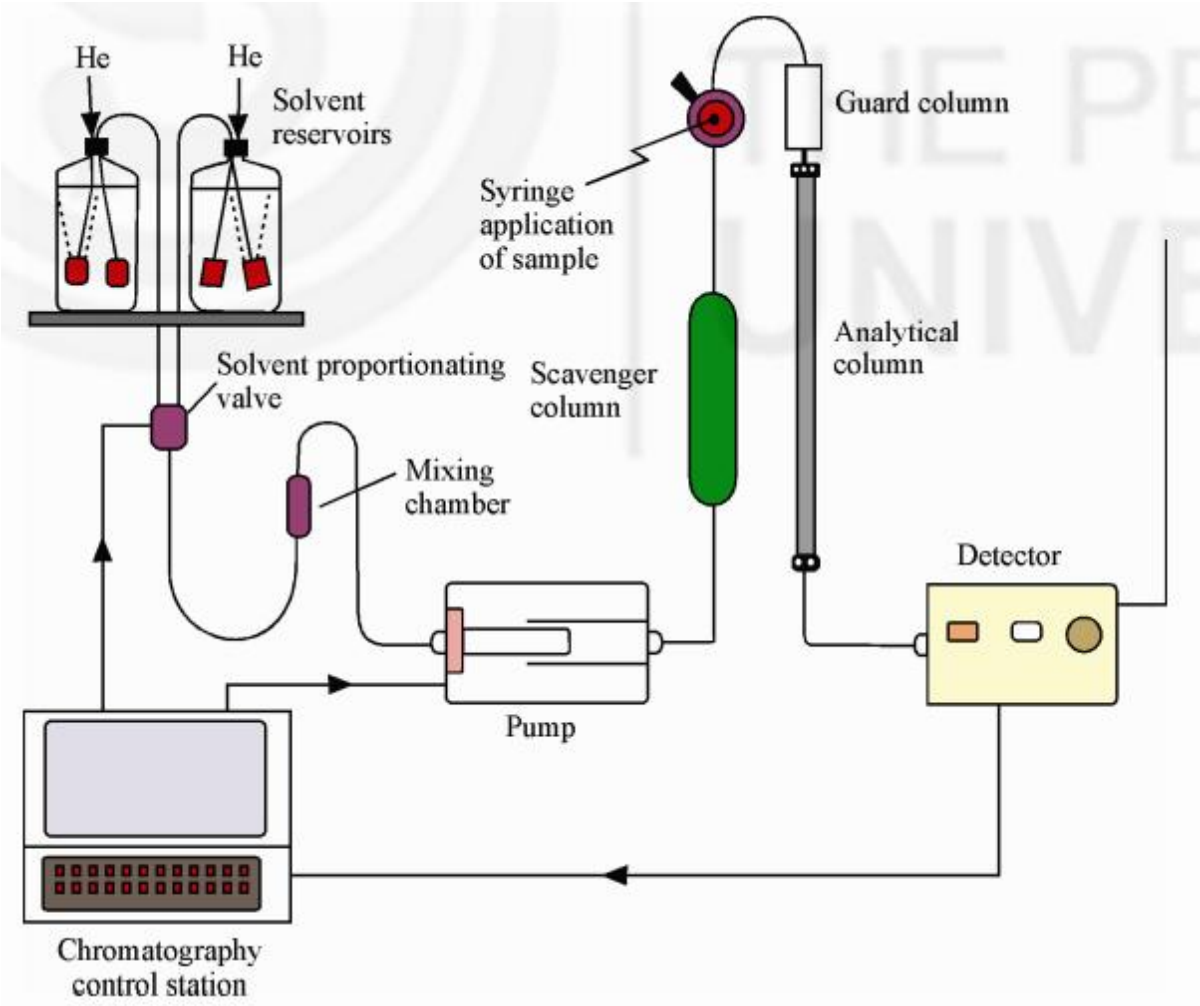

Figure. 2.7: **Schematic Illustration of various Components of HPLC**

Source[150]

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Chapter Three

Methodology

3.1 Study Area

Ibadan, which was established in 1829, is located between latitudes 3°35'N and 4°10'N and longitudes 7°2'E and 7°40'E. Immigrants moved into the city at first and took up residence there in quest of safety from intertribal conflicts. It is the capital of Oyo state, one of Nigeria's 36 states, and is currently the biggest indigenous city in tropical Africa. It lies 530 kilometres southwest of Abuja, the federal capital, and 128 km northeast of Lagos[1]. The Ibadan metropolitan area, often known as "Ibadan land," is made up of eleven Local Government Areas, five of which are located in the inner city and six in the outside (semi-urban) areas. Due to Ibadan's administrative and commercial importance, land has become a valuable investment and status symbol for the locals[2]. The city has had tremendous population and area growth since its founding. From just 100 acres in 1830 to 12.5 km^2 in 1931, 30 km^2 in 1963, 112 km^2 in 1973, 136 km^2 in 1981, and 214 km^2 in 1988, more land was developed. Similar to now, the population of Ibadan metropolitan area according to the National Population Commission was projected to be 60 000 in 1856, 200 000 in 1890, 625 000 in 1963, and 586 people per km^3 as of 2006[2].

Some major dumpsites in Ibadan metropolis include Awotan, Ajakanga, Lapite and Aba-Eku. The study site, Aba Eku dumpsite is located at KM 13 along Akanran road, Olunloyo, Ona Ara Local Government Area of Oyo State. It is about 600m away from the Aba-Eku community and is bordered by two other neighbouring residential areas namely Aba Epa and Amuloko communities. The dumpsite was established in the year 1985 and covered about

9.419 hectares of land. It is characterized majorly by domestic wastes some of which include plastics, papers, nylons, kitchen waste, beverage cans among others[4]. The map and a cross-section of Aba-Eku dumpsite are shown in Figure 3.1 and 3.2

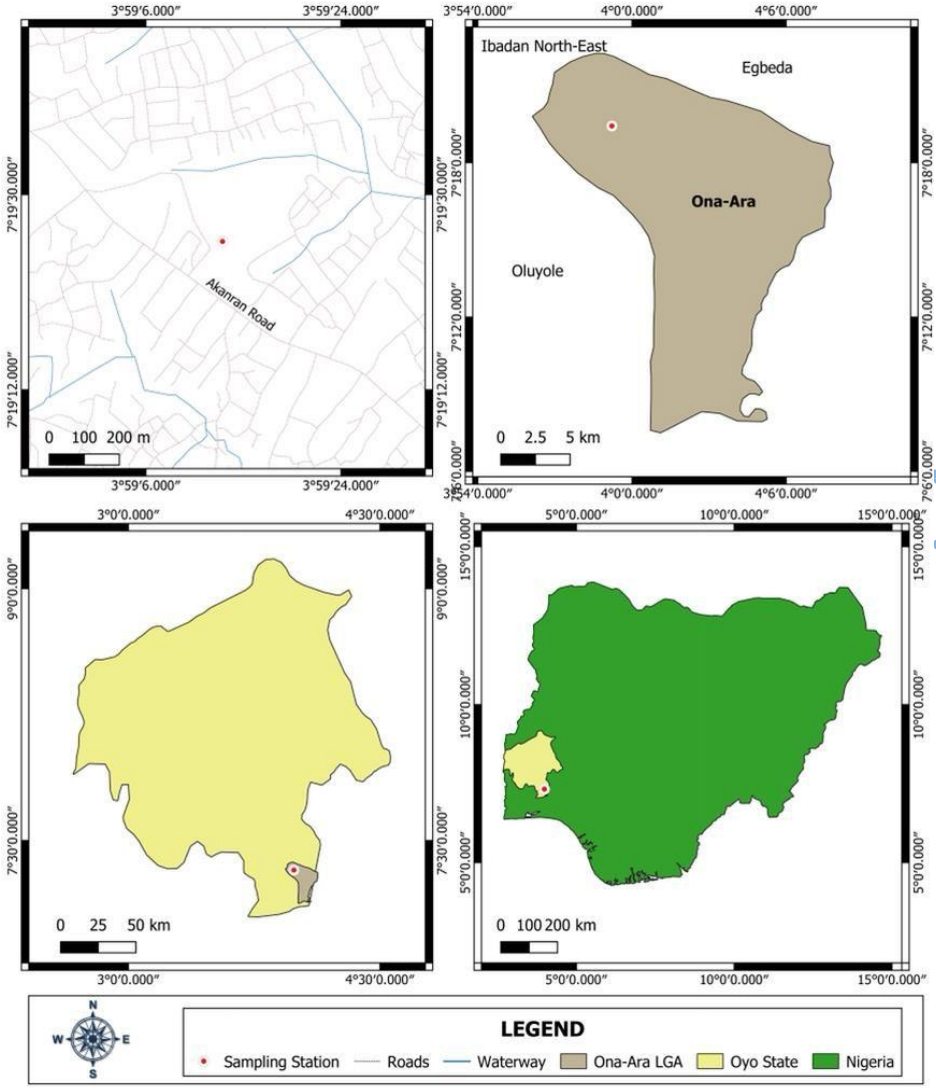

Figure 3.1: The map of Aba-Eku municipal dumpsite Ibadan

Source: Author's Field Work, 2023

Figure 3.2: A cross-section of Aba-Eku dumpsite

Source: Author's Field Work, 2023

3.2 Research Design

This research work was conducted in two stages, and it is directed to identify two groups of environmental pollutants: heavy metals and organic pollutants such polycyclic aromatic hydrocarbons (PAHs) and phthalates esters (PAEs). The first stage involved site inspection, location profile determination, and sample collection. The analytical stage, which took place in the second stage, entails sample preparation, laboratory bench work, and instrument analysis.

3.3 Sample Collection

3.3.1 Soil Sample Collection

Soil samples were collected in four specific areas in and around the dumpsite. These top soil samples were collected in six grab samples from each of the designated areas to create a composite sample. In order to reflect the plough layer and the average root zone for nutrient uptake and heavy metals burden by plants, soil samples were taken at a depth of 0 to 15 cm at each of the four sites[5]. After being air dried, the soil samples were pulverized, put through a screen, placed in clean polythene bags, and kept at room temperature for laboratory analysis[5].

3.3.2 Vegetable Sample Collection

Samples of three leafy edible vegetables growing within the dumpsite were collected. The vegetables collected are *Talinum triangulare* also known as water leaf, *Corchorus olitorius* also known as Jute mallow and *Ocimum gratissimum* also known as scent leaf (Figure 3.3, 3.4 and 3.5). For laboratory processing, the samples were then placed in pristine polythene

bags. The vegetables were rinsed with distilled water after being ran under running tap water to remove soil and other debris. After being divided into small pieces, the samples were air dried in sealed chambers at room temperature for roughly two weeks before being ground into a fine powder with a stainless grinder. Following that, samples of ground vegetables were gathered in labelled polythene bags and stored in a desiccator while being analysed in the laboratory[6].

Figure 3.3: Water leaf *(Talinum triangulare*) growing on Aba-Eku dumpsite

Source: Author's Field Work, 2023

Figure 3.4: Jute Mallow (*Corchorus olitorius*) growing on Aba-Eku dumpsite

Source: Author's Field Work, 2023

Figure 3.5: Scent leaf (*Ocimum gratissimum*) growing on Aba-Eku dumpsite

Source: Author's Field Work, 2023

3.4 Chemicals and Reagent Used

All chemicals used were of Analar grade and of highest purity. Reagents used include; dichloromethane, n-Hexane, alumina (HPLC/GC grade) as desiccant, perchloric acid ($HClO_4$), concentrated nitric acid (HNO_3), sulphuric acid (H_2SO_4), activated copper powder, anhydrous sodium sulphate, acetone and organic free reagent water. Sigma Aldrich Stock standard solutions 1000 µg/ml of Arsenic, Cadmium, Chromium, Lead and Zinc for AAS, Accu standard mixture of all the 16 priority pollutant PAHs and Accu Standard mixed solution (1 mg/mL) composing PAE compounds and the internal standard benzyl benzoate (BB, 5 mg/mL).

3.5 Determination of Heavy Metals

3.5.1 Digestion of Soil Samples

The soil samples were digested using United States Environmental Protection Agency (USEPA) method 3050b[7]. Two grammes (2.0g) each dried and sieved soil sample was measured using the Boeco scale and placed in a glass beaker. A volume of 5 ml aqua regia was added (1:3 HNO_3: HCl) and the samples was placed in a hot air oven for 30-60 minutes until completely digested. The oven did not have a thermometer and the temperature was adjusted by switching on and off the oven trying to keep the temperature at approximately 90-110 °C. To make sure the samples did not get burned they were frequently checked and when completely digested the samples were left to cool. 15 ml of distilled water was added to each beaker and the samples were left to rest for about an hour. Thereafter each sample was filtered into a plastic beaker and the glass beaker was rinsed with 5 ml distilled water which

was also added to the filtration. The samples were placed in refrigerator until AAS analysis was carried out.

3.5.2 Digestion of Vegetable Samples

Similarly, the vegetable samples were digested using United States Environmental Protection Agency (USEPA) method 3050b[7]. Two grammes (2.0g) each dried and grinded vegetable sample was measured using the Boeco scale and placed in a glass beaker. A volume of 5 mL aqua regia was added (1:3 HNO_3: HCl) and the samples was placed in a hot air oven for 30-60 minutes until completely digested. The oven did not have a thermometer and the temperature was adjusted by switching on and off the oven trying to keep the temperature at approximately 90-110 °C. To make sure the samples did not get burned they were frequently checked and when completely digested the samples were left to cool. 15 mL of distilled water was added to each beaker and the samples were left to rest for about an hour. Thereafter each sample was filtered into a plastic beaker and the glass beaker was rinsed with 5 mL distilled water which was also added to the filtration. The samples were placed in refrigerator until AAS analysis was carried out.

3.5.3 Heavy Metals Determination

The heavy metals of both the soil and vegetable samples were analyzed. The digested samples were analyzed for heavy metals (Cd, Cr, Cu, Fe, Pb and Mn) using atomic absorption spectrophotometer (AAs VGB 210 System)[8].

3.6 Extraction, Clean-up and Quantification of PAHs

Polycyclic aromatic hydrocarbons (PAHs) were analyzed using gas chromatography-mass spectrometry (GS/MS) following modified USEPA method 8270 C[9].

3.6.1 Solvent Extraction of PAHs

Approximately 5 g of each sample and 5 g of anhydrous sodium sulphate were weighed and homogenized to a complete mixture. The mixtures were transferred to pre-cleaned extraction tubes, and 25 mL dichloromethane added. The tubes were tightly capped, allowed to stand for 30 minutes, and then shaken vigorously for 30 minutes. The solids were allowed to settle and solvent layers were filtered using filter papers. The procedure was repeated with 25 mL dichloromethane. The two extracts were combined, concentrated on a rotary evaporator (Büchi Rotavapor R-114), exchanged with 5 mL of n-hexane and re-concentrated to 1 mL for clean-up. The extracts were then eluted with 25 mL dichloromethane/ hexane (20:80 v/v) on a silica gel column. The extracts were evaporated and re-dissolved in 1 mL n-hexane[9].

3.6.2 Sample Clean-up Procedure for PAHs

Sample clean-up was done on a silica gel-aluminium oxide glass column (10cm x6 mm ID), and elution was conducted by successively loading 5mL n-hexane and 20ml n-hexanedichloromethane (3:7, v/v) and the elution was collected for PAH determination. The elution was concentrated and solvent exchange to 1ml of hexane containing 200ug/L hexamethyl benzene and perylene-d12 as internal standards. The final extract was sealed and kept at -4°C until further analysis[10].

3.6.3 Quantification of PAHs

The cleaned extracts were analyzed for the 16 representative PAHs using a Shimadzu GS/MS QP 2010 model. Helium gas was used as the carrier gas with a constant flow rate of 1 mL/ min, HP-1 ms column (30 m x 0.25 µm 0.25 mm ID), injection mode was pulsed splitless, volume of extract injected was 1 µL, injection port temperature was 2900 C, pulse pressure and flow were 35 psi (0.5 min) and 20 mL/min (2 min), respectively; solvent delay was 5 min, initial oven temperature and hold time was 500 C (1 min), ramped at 300 C/min to 2800 C and 150 C/min to 3100 C with final hold time of 4 min. External calibration using PAHs standard was used for analytes quantification, while identification was based on retention time. The quantification limit of the PAHs in the standard and the samples was 0.001 ppm. The average response factor for the weight ranges were calculated and used for sample quantification. The concentration of each analyte was determined by calculating the amount of analyte injected from the peak response in area ratio as shown below[10]:

3.7 Analysis of Phthalate Esters

Phthalate esters in soil and vegetable samples were determined using USEPA 3546 and 8061A standard methods.

3.7.1 Phthalate Esters Extraction Method

Microwave Assisted Extraction (MAE) was used for the extraction of phthalates from soil samples. Microwaves can easily penetrate into the sample, heating the solvent trapped in pores evenly. Compared to Soxhlet and ultrasonic extraction methods. MAE was preferable, due to consumption of small amount of solvents, possibility of stirring of sample and about 20-30mins per batch of as many as 12 samples can be performed. Acetonitrile was used as an

extraction solvent for phthalates. It has better extraction efficiency over other solvents because of dipole moment and an ability to dissolve wide range of ionic and non-polar compounds. Also, it is further used as a mobile phase in HPLC[11].

3.7.2 HPLC Analysis

HPLC technique was used to separate out, identify and quantify the components in a mixture. PerkinElmer Series 200 HPLC coupled with UV/VIS Detector transmitting at 254 nm and C-18 Column was used for analysis. Flow rate used was 1.0ml/min and the column was operated using a mixture (mobile phase) of 70% Acetonitrile and 30% Water. HPLC was used for both Qualitative and Quantitative analysis of Phthalates in the samples[12].

3.8 Quality Control/Quality Assurance

All quality assurance/quality control protocol was observed throughout the experiment. Safety was generally carefully handled by using appropriate sampling equipment, containers and preservation method to avoid contamination of samples. All glass wares for metal analysis were previously soaked in 14% HNO_3 for 24 hours. All reagents used were of analytical grade and reagent blank determinations were used to correct errors. Multiplicity of samples for each determination ensured reproducibility of data to minimise background contamination, all potential sources of instrumental and procedural contamination were eliminated. Spiked blank, reagent blank, and appropriate standard reference materials were included with each set of samples to ascertain the integrity of the analytical method and corresponding analytical results. The average recoveries for the PAH congeners, varying between 83 and 110% were determined by adding known amounts of PAHs standards to samples, before extraction and recovery, and relative standard deviation (RSD) values

obtained were within the U.S. Environmental Protection Agency (EPA) standard for recovery (70–130%). The limits of detection (LOD) were calculated as three times the signal-to-noise ratio and varied between 0.2 ng/g to 2.0 ng/g. To confirm the accuracy of the analysis for the PAEs, soil matrix and blanks mixing material were spiked. With an RSD of 3.78–8.81, the recovery rates of the soil matrix spiked at 100 mg/kg (DW) ranged from 74.78 to 106.71%. The PAE compounds had instrument detection limits (IDLs) of 0.12–0.36 mg/kg and method detection limits (MDLs) of 69–136 mg/kg[8].

3.9 Data Analysis

3.9.1 Statistical Analysis of Results

The raw data were subjected to Descriptive statistics, one-way Analysis of variance (ANOVA) and Pearson Product Moment Correlation which is a parametric statistical tools used to test significant difference in mean levels of pollutants/variables.

3.9.2 Contamination Factor

It is used to assess soil contamination by comparing the contaminant concentration in the surface layer to a background value. Here, a modified contamination factor formula (Equation 3.1) is employed using metals concentrations in the control samples instead of background values, which are currently lacking for Nigeria.

CF =Cm/Bm …….Equation 3.1

Where CF= contamination factor of the element of interest;

Cm= mean concentration of each metal in the soil,

Bm = background or baseline value (concentration of each metal in the control sample was used).

Contamination factor has four categories which include:

<1= low contamination;

1-3= moderate contamination;

3 – 6= considerable contamination;

>6= very high contamination factor[11].

3.9.3 Degree of Contamination

The degree of contamination of the sampling site soils and the control site soils was evaluated using two indices, Contamination factor and Pollution Load index.

This is the sum of all the contamination factors of all the elements in the soil sample[11]. It is indicated in Equation 3.2:

Cdeg =Σ CF ……Equation 3.2

Where

CF= Contamination factor of each element of interest;

Four categories have been defined for the degree of contamination which includes:

<8=low degree of contamination;

8-16=moderate degree of contamination;

16- 32=considerable degree of contamination;

>32=very high degree of contamination[11].

3.9.4 Pollution Load Index

Pollution load index (PLI) was also used to assess the metal accumulation and multi-element contamination resulting in increased overall metal toxicity[12]. Heavy metal contamination is associated with a mixture of contaminants rather than one metal contaminant. The higher the pollution load index, the more serious the heavy metal accumulation in the soil. We used the PLI to characterize the aggregate contamination of the five target metals using Equation 3.3 as shown below"[12].

$$PLI = (Cf\ Cd \times Cf\ Cr \times Cf\ Cu \times Cf\ Fe \times Cf\ Pb \times Cf\ Mn)^{1/6} \quad \text{Equation 3.3}$$

Where;

PLI < 1 → No Pollution

PLI 1 and above → Pollution has occurred

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Chapter Four

Results and Discussion of Findings

4.1. Results of Analyses

The results obtained from the determination of heavy metals, polycyclic aromatic hydrocarbons (PAHs) and Phthalate esters (PAEs) in various soil and edible vegetable samples collected from in and around Aba-Eku dumpsite, Ibadan are presented in the following subsections.

4.1.1 Results of Analysis of Heavy Metals

The concentrations of heavy metals in soil and vegetable samples collected from in and around Aba-Eku dumpsite are presented in Table 4.1 and Table 4.2

Table 4.1: Concentration of Heavy Metals in Soil in and around Aba-Eku MSW Dumpsite

Metals	Dumpsite	300 meters	600 meters	River soil	Control
Cu (mg/kg)	0.08±0.01	2.21±0.01	1.62±0.03	0.12±0.02	0.27±0.06
Cr (mg/kg)	ND	ND	ND	ND	0.01±0.01
Cd (mg/kg)	0.07±0.01	ND	0.01±0.01	0.02±0.02	0.01±0.01
Pb (mg/kg)	ND	0.37±0.02	0.11±0.02	ND	0.08±0.01
Mn (mg/kg)	0.93±0.02	0.05±0.01	0.33±0.02	0.62±0.01	0.14±0.02
Fe (mg/kg)	7.63±0.01	1.33±0.02	2.81±0.02	2.48±0.02	0.96±0.10

Mean±SD ND= Not Detected

Source: Author's Field Work, 2023

Table 4.2: Concentration of Heavy Metals in Vegetables at Aba-Eku MSW Dumpsite

Metals	Water leaf (Talinum trangulare)	Jute mallow (Corchorus olitorious)	Scent leaf Ocimum gratissimum)	Control
Cu (mg/kg)	0.99±0.01	1.22±0.03	0.86±0.01	0.01±0.01
Cr (mg/kg)	ND	ND	ND	ND
Cd (mg/kg)	ND	0.01±0.01	ND	ND
Pb (mg/kg)	ND	ND	0.02±0.01	ND
Mn (mg/kg)	12.85±0.02	4.31±0.02	1.44±0.03	0.02±0.01
Fe (mg/kg)	15.71±0.02	11±0.17	8.06±0.06	0.12±0.01

Mean±SD ND= Not Detected

Source: Author's Field Work, 2023

Table 4.3: Contamination factor, Degree of Contamination and Pollution Load Index of Heavy Metals in the Dumpsite Sampling Location

Metal	Average Concentration (mg/Kg)	Contamination Factor	Remark
Cu	0.08	0.30	Low Contamination
Cr	0.00	0.00	No Contamination
Cd	0.07	7.00	Very High Contamination
Pb	0.00	0.00	No Contamination
Mn	0.93	6.64	Very High Contamination
Fe	7.63	7.95	Very High Contamination
Degree of Contamination	**-**	**21.89**	**Considerable degree of contamination**
Pollution Load Index	**-**	**2.01**	**Polluted**

Source: Author's Field Work, 2023

Table 4.4: Contamination factor, Degree of Contamination and Pollution Load Index of Heavy Metals in the 300m Location

Metal	Average Concentration (mg/Kg)	Contamination Factor	Remark
Cu	2.21	8.19	Very High Contamination
Cr	0.00	0.00	No Contamination
Cd	0.00	0.00	No Contamination
Pb	0.37	4.63	High Contamination
Mn	0.05	0.36	Low Contamination
Fe	1.33	1.39	Moderate Contamination
Degree of Contamination	**-**	**14.55**	**Moderate**
Pollution Load Index	**-**	**2.08**	**Polluted**

Source: Author's Field Work, 2023

Table 4.5: Contamination Factor, Degree of Contamination and Pollution Load Index of Heavy Metals in the 600m Location

Metal	Average Concentration (mg/Kg)	Contamination Factor	Remark
Cu	1.62	6.00	Very High Contamination
Cr	0.00	0.00	Low Contamination
Cd	0.01	1.00	Moderate Contamination
Pb	0.11	1.38	Moderate Contamination
Mn	0.33	2.36	Moderate Contamination
Fe	2.81	2.93	Moderate Contamination
Degree of Contamination	**-**	**13.66**	**Moderate**
Pollution Load Index	**-**	**2.24**	**Polluted**

Source: Author's Field Work, 2023

Table 4.6: Contamination factor, Degree of Contamination and Pollution Load Index of Heavy Metals in Soil Samples at the River Side Location

Metal	Average Concentration (mg/Kg)	Contamination Factor	Remark
Cu	0.12	0.44	Low Contamination
Cr	0.00	0.00	NoContamination
Cd	0.02	2.00	Moderate Contamination
Pb	0.00	0.00	No Contamination
Mn	0.62	4.43	High Contamination
Fe	2.48	5.71	High Contamination
Degree of Contamination	**-**	**12.58**	**Moderate**
Pollution Load Index	**-**	**2.18**	**Polluted**

Source: Author's Field Work, 2023

Table 4.7: Pollution Rating of Heavy Metals in the Overall Aba-Eku MSW Dumpsite

Metal	Concentration (mg/Kg)	Contamination Factor	Remark
Cu	1.01	3.73	High Contamination
Cr	0.00	0.00	No Contamination
Cd	0.03	2.50	Moderate Contamination
Pb	0.12	1.50	Moderate Contamination
Mn	0.48	3.45	High Contamination
Fe	4.31	4.49	High Contamination
Degree of Contamination	**-**	**15.67**	**Moderate**
Pollution Load Index	**-**	**1.86**	**Polluted**

Source: Author's Field Work, 2023

Table 4.8: Correlation Matrix of Heavy Metals in Soil

	Cu (mg/kg)	*Cd (mg/kg)*	*Pb (mg/kg)*	*Mn (mg/kg)*	*Fe (mg/kg)*
Cu (mg/kg)	1				
Cd (mg/kg)	-0.7632	1			
Pb (mg/kg)	0.9098	-0.6695	1		
Mn (mg/kg)	-0.9426	0.9223	-0.8924	1	
Fe (mg/kg)	-0.9543	0.9210	-0.8653	0.9955	1

Source: Author's Field Work, 2023

Table 4.9: Pollution Rating of Each Sampling Location in the Study Area

Sites	Degree of Contamination	Pollution Load Index	Remark
Dumpsite	21.89	2.01	Polluted with high Degree of Contamination
300 meters	14.55	2.08	Polluted with moderate Degree of Contamination
600 meters	13.66	2.24	Polluted with moderate Degree of Contamination
river soil	12.58	2.18	Polluted with moderate Degree of Contamination
Study Average	15.67	1.86	Polluted with moderate Degree of Contamination

Source: Author's Field Work, 2023

Table 4.10: Correlation Matrix Between the Sampling Locations

	Dumpsite	*300 meters*	*600 meters*	*river soil*
Dumpsite	1			
300 meters	0.2741	1		
600 meters	0.8325	0.7571	1	
River soil	0.9998	0.2904	0.8414	1

Source: Author's Field Work, 2023

Table 4.11: Comparison of Heavy Metal Concentrations with Literatures

Metals	Aba-Eku, Ibadan [This Study]	Olusosun, Lagos [13]	Mojosongo, Indonesia [7]	Lafia Metropolis [5]	Awotan, Ibadan [14]
Cu (mg/kg)	1.01	0.14	NA	25.32	0.91
Cd (mg/kg)	0.03	0.10	0.94	7.28	0.48
Pb (mg/kg)	0.12	0.75	14.55	138.46	0.49
Mn (mg/kg)	0.48	NA	341.36	175.16	NA
Fe (mg/kg)	4.31	NA	8403	2550.11	0.63

NA=Not Analysed

Source: Author's Field Work, 2023

Table 4:12: Comparison of Heavy metals in soils around Aba-Eku MSW Dumpsite with International Standards

	Dumpsite area	300 meters	600 meters	River soil	Aba-Eku, Ibadan [This Study]	NESREA	WHO	USEPA
Cu (mg/kg)	0.08	2.21	1.62	0.12	1.01	0.10	2.00	0.10
Cr (mg/kg)	ND	ND	ND	ND	ND	0.01	0.05	0.01
Cd (mg/kg)	0.07	ND	0.01	0.02	0.03	-	0.02	-
Pb (mg/kg)	ND	0.37	0.11	ND	0.12	0.05	0.01	0.05
Mn (mg/kg)	0.93	0.05	0.33	0.62	0.48	-	-	-
Fe (mg/kg)	7.63	1.33	2.81	2.48	4.31	3	0	3

ND=Not Detected

Source: Author's Field Work, 2023

Table 4.13: Correlation Matrix of Heavy Metal Accumulation Between the Vegetables

	Water leaf	*Jute mallow*	*Scent leaf*
Water leaf	1		
Jute mallow	0.9178	1	
Scent leaf	0.8064	0.9746	1

Source: Author's Field Work, 2023

Table 4.14: Correlation Matrix Between Heavy Metals in Vegetable

	Cu (mg/kg)	*Cd (mg/kg)*	*Pb (mg/kg)*	*Mn (mg/kg)*	*Fe (mg/kg)*
Cu (mg/kg)	1				
Cd (mg/kg)	0.9343	1			
Pb (mg/kg)	-0.7759	-0.5000	1		
Mn (mg/kg)	0.0851	-0.2758	-0.6946	1	
Fe (mg/kg)	0.2297	-0.1324	-0.7922	0.9892	1

Source: Author's Field Work, 2023

Table 4.15: Comparison of the Mean Concentration of Heavy Metals in Plants Around Aba-Eku MSW Dumpsite with International Standards

	Water leaf	Jute mallow	Scent leaf	EU	WHO	USEPA
Copper	0.99±0.01	1.22±0.03	0.86±0.01	40	73.3	0.1
Chromium	ND	ND	ND	-	0.05	0.01
Cadmium	ND	0.01±0.01	ND	0.2	0.02	
Lead	ND	ND	0.02±0.01	0.3	0.03	0.05
Manganese	12.85±0.02	4.31±0.02	1.44±0.03	-	-	-
Iron	15.71±0.02	11±0.17	8.06±0.06	-	425.5	3

Source: Author's Field Work, 2023

4.1.2 Results of Analysis of PAHs

The concentrations of polycyclic aromatic hydrocarbons in soil and vegetable samples collected from in and around Aba-Eku dumpsite are presented below.

Table 4.16: Distribution of PAHs in soil samples in and around Aba-Eku MSW Dumpsite

	Dumpsite	300m	600m	River side	Mean of Study Area	Control
Naphthalene (mg/kg)	61.65	33.69	30.23	19.03	36.15	5.22
Acenaphthylene (mg/kg)	45.67	20.69	ND	ND	33.18	0.12
Acenaphthene (mg/kg)	8.94	4.73	10.52	7.89	8.02	1.26
Fluorene (mg/kg)	ND	ND	ND	3.48	3.48	ND
Phenanthrene (mg/kg)	2.71	5.37	3.75	ND	3.94	1.75
Anthracene (mg/kg)	1.55	ND	0.67	1.19	1.14	ND
Minimum	**1.55**	**4.73**	**0.67**	**1.19**	**1.14**	**0.12**
Maximum	**61.65**	**33.69**	**30.23**	**19.03**	**36.15**	**5.22**
Mean per site	**24.10**	**16.12**	**11.29**	**7.90**	**14.32**	**2.09**
∑ Total PAH per site	**120.52**	**64.48**	**45.17**	**31.59**	**85.91**	**8.35**

ND= Not Detected

Source: Author's Field Work, 2023

Table 4.17: Distribution of PAHs in Vegetable samples in and around Aba-Eku MSW Dumpsite

	Water leaf	Jute mallow	Scent leaf	Mean of Study Area	Control
Naphthalene (mg/kg)	24.45	8.15	52.11	28.24	3.77
Acenaphthylene (mg/kg)	8.65	1.96	ND	5.31	0.12
Acenaphthene (mg/kg)	10.26	ND	3.08	6.67	1.26
Fluorene (mg/kg)	1.09	ND	1.25	1.17	ND
Phenanthrene (mg/kg)	ND	0.87	ND	0.87	ND
Anthracene (mg/kg)	ND	ND	0.95	0.95	ND
Minimum	**1.09**	**0.87**	**0.95**	**0.87**	**0.12**
Maximum	**24.45**	**8.15**	**52.11**	**28.24**	**3.77**
Mean per site	**11.11**	**3.66**	**14.35**	**7.20**	**1.72**
∑ Total PAH per site	**44.45**	**10.98**	**57.39**	**43.20**	**5.15**

ND= Not Detected

Source: Author's Field Work, 2023

Table 4.18: Comparison of PAHs Concentrations with Literatures

	Aba-Eku, Ibadan [This Study]	Okija, Rivers [123]	E-waste Dump, Aba [124]	Alaba, Lagos [125]	Ogunpa, Ibadan [125]	Saje, Abeokuta [126]
Naphthalene (mg/kg)	36.15	0.005	ND	10.0	ND	1.56
Acenaphthylene (mg/kg)	33.18	0.039	ND	37.0	38.0	0.80
Acenaphthene (mg/kg)	8.02	0.209	ND	9.0	9.0	3.62
Fluorene (mg/kg)	3.48	**0.120**	3.6	140.0	143.0	3.22
Phenanthrene (mg/kg)	3.94	**0.420**	1.4	323.0	392.0	ND
Anthracene (mg/kg)	1.14	0.015	2.0	ND	ND	0.64

ND= Not Detected

Source: Author's Field Work, 2023

Table 4.19: Correlation Matrix Between PAHs in Soil Samples

	Naphthalene (mg/kg)	Acenaphthylene (mg/kg)	Acenaphthene (mg/kg)	Fluorene (mg/kg)	Phenanthrene (mg/kg)	Anthracene (mg/kg)
Naphthalene (mg/kg)	1					
Acenaphthylene (mg/kg)	0.8947	1				
Acenaphthene (mg/kg)	0.1428	0.7802	1			
Fluorene (mg/kg)	0.0256	0.1526	0.4156	1		
Phenanthrene (mg/kg)	-0.7321	-0.8145	-0.7866	0.3582	1	
Anthracene (mg/kg)	0.6337	0.2214	-0.6771	0.4391	-0.7485	1

Source: Author's Field Work, 2023

4.1.3 Results of Analysis of PAEs

The concentrations of phthalate esters (PAEs) in soil and vegetable samples collected from in and around Aba-Eku dumpsite are presented below.

Table 4.20: Distribution of Phthalate Esters in Soil samples in and around Aba-Eku MSW Dumpsite

Phthalate	Dumpsite area	300m Away	600m Away	River soil
Dipropyl Phthalate (mg/kg)	0.94	5.75	3.15	5.34
Diethyl Phthalate (mg/kg)	ND	ND	3.74	ND
Benzylbutyl Phthalate (mg/kg)	ND	ND	ND	ND
Minimum	0.94	5.75	3.15	5.34
Maximum	0.94	5.75	3.74	5.34
Mean per site	0.94	5.75	3.445	5.34
∑ Total PAH per site	0.94	5.75	6.89	5.34

ND=Not Detected

Source: Author's Field Work, 2023

Table 4.21: Distribution of Phthalate Esters in Vegetable samples in and around Aba-Eku MSW Dumpsite

Phthalate	Water leaf	Jute mallow	Scent leaf
Dipropyl Phthalate (mg/kg)	ND	0.79	2.88
Diethyl Phthalate (mg/kg)	ND	ND	0.13
Benzylbutyl Phthalate (mg/kg)	ND	2.96	1.09
Minimum	ND	0.79	0.13
Maximum	ND	2.96	2.88
Mean per site	ND	1.88	1.37
∑ Total PAH per site	ND	3.75	4.10

ND=Not Detected

Source: Author's Field Work, 2023

4.2 Discussion of Findings

4.2.1 Discussion on Heavy Metals in Soil Samples

The concentration of heavy metals observed in soil samples varied in levels across all the sampling sites considered in this study as shown in Table 4.1. The concentration of Copper ranged from 0.08±0.01 – 2.21±0.01 mg/kg with an average value of 1.01 mg/kg. The highest level of Copper in the soil samples was observed at 300m location away from the dumpsite, with copper having an overall contamination factor of 3.73 (Table 4.7) which signifies moderate contamination. Burning of electrical devices and other copper-based trash, such as vehicle parts, may be the explanation for the concentration of copper observed. As a cofactor in redox enzymes and as a need for maintaining blood chemistry, copper is crucial to the organism[1]. However, in large concentrations, copper may be poisonous[2].

On the other hand, Chromium was not detected in all the four sampling locations, this could be that the concentration of Chromium was too low to be determined by the analytical method employed in this study. The highest concentration of Cadmium (0.07±0.01 mg/kg) in this study was recorded at the dumpsite area while lowest concentration (0.01±0.01 mg/kg) was recorded at 600m away from the dumpsite area. Even though Cadmium was not detected at 300m location away from the dumpsite area, Cadmium recorded an average concentration of 0.03mg/kg in the whole study area and this was the lowest concentration recorded among the heavy metals. The contamination factor of Cadmium (2.5) suggests that cadmium contamination in the study area was moderate. The level of cadmium observed in this study as shown in Table 4.1 was relatively lower than that of other metals. However, cadmium

poisoning can be acute or chronic, and it can have negative effects on the immune system, kidney, liver, vascular, and hepatic functions[3].

The average concentration of Lead observed in soil samples was 0.12 mg/kg. Although, Lead was not detected at the dumpsite and the river area, the highest and lowest lead concentration were 0.37±0.02kmg/kg (observed at 300m location away from the dumpsite) and 0.11±0.02 mg/kg (observed at 600m location away from the dumpsite) respectively. The contamination factor of lead in the study area ranked 1.50 (Table 4.7) which indicated that lead constituted moderate contamination to the study area. It is noteworthy lead had the lowest contamination factor among the metals considered in this study. This suggests that pipes, lead-based paint, plastics, and lead batteries were disposed of at the landfill. The lead concentration may be influenced by the burning of electrical garbage, including old computers, cables, printers, photocopiers, car tires, batteries, air conditioners, and other items[4]. Manganese concentration in the soil samples varied between 0.05±0.01 mg/kg and 0.93±0.02 mg/kg with an average value of 0.48 mg/kg and manganese highest concentration was observed at the dumpsite area sampling location. The levels of Manganese found at each location were significantly lower than those found in the Lafia metropolitan dumpsites[5]. However, Manganese in the body system is important for the metabolism of carbohydrates and the production of bones, and it is a cofactor in a number of enzymes[6].

Iron concentration was higher than other metals in most of the sampling sites, while the dumpsite area sampling location recorded highest iron concentration. The concentration of iron ranged from 7.63±0.01 mg/kg at the dumpsite area to 1.33±0.02mg/kg at 300m location away from the dumpsite. The average iron concentration observed in this study was 4.31 mg/kg and the contamination factor of Iron was 4.49

(Table 4.7) which signify high contamination. This contamination factor was highest among all the heavy metals considered in this study making iron the biggest metal pollutant in Aba-Eku MSW dumpsite. This trend was similar to what was reported for dumpsites in Lafia metropolis and Mojosongo Indonesia where iron also contributed highest heavy metal contamination to the dumpsites[5,7]. The high Fe concentration was due to the steel scrap being dumped at the dumpsite. As a result of the oxidation of ferrous to ferric form, the creation of ferric hydroxide colloids, and complexes with humic acid, hence the soil samples' dark brown colour[8].

Chromium and lead were not detected soil samples collected at the dumpsite area, Iron concentration was the highest while cadmium was the lowest. In order of decreasing concentration Iron > Manganese >Copper > Cadmium. Interestingly, at this sampling site cadmium ranked the second highest contamination factor after iron, followed Manganese and then Copper (Table 4.3). Cadmium has negative impact on numerous enzymes in the body and it is thought that these negatively impacted enzymes are what causes the renal damage that leads to proteinuria[9].

Similarly, at 300meters location away from the dumpsite, Chromium and Cadmium were not detected. Meanwhile Copper concentration was the highest followed by Iron, Lead and Manganese. Copper was also most contaminating metal at this site with a contamination factor of 8.19 (Table 4.4). The metals ranked in decreasing order of contamination as Copper > Iron > Lead > Manganese.

Chromium was not detected at 600meters location away from the dumpsite. At this site, most of the metal concentrations observed were relatively lower. Notwithstanding, iron

concentration was highest followed by copper, manganese, lead and cadmium. The contaminating factor of the metals at this site in decreasing order ranked Copper > Iron > Manganese > Lead > Cadmium (Table 4.5).

Finally at the river side, Chromium and Lead were not detected. Iron recorded the highest concentration followed by Manganese Copper and lead. The level of heavy metals observed at this site were low compared to other sites. In decreasing order of contamination, the metals ranked Iron > Manganese > Cadmium > Copper (Table 4.6).

In Table 4.7, the pollution load index of the study area (Aba-Eku MSW dumpsite) was rated 1.86 which implies the study area Aba-Eku MSW dumpsite was polluted with heavy metals and the overall degree of contamination was rated 15.67, this value further explained that the study site was moderately polluted. However, iron recorded the highest concentration in most of the sampling locations. In similar term, Iron, Copper and Manganese were of higher contamination contribution to Aba-Eku dumpsite than the remaining metals. The high level of iron was caused by the disposal of iron and steel waste, while the high level of copper was brought on by the dumping of paints, blades, bottle caps, pesticides, medications, and cosmetics[11]. The contribution of each individual metal to the pollution at the Aba-Eku MSW dumpsite was rated by their contamination factor in decreasing order as follow; Iron (4.49) > Copper (3.73) > Manganese (3.45) > Cadmium (2.50) > Lead (1.50). Analysis of variance between heavy metals revealed that the concentrations of heavy metals are significantly different from one another ($P<0.05$). This is an indication that there was anthropogenic impact on the soil through different types of waste and scrap materials disposed at the dumpsite which are responsible for each metal contamination. Correlation analysis (Table 4.8) showed that Copper-Cadmium, Copper-Manganese, Copper-Iron and Cadmium-Lead had

strong negative correlation while others combinations have positive correlation. The levels of lead and cadmium observed in this study were above the WHO limits for metals in soil (Table 4.12) thereby making the dumpsite not suitable for agricultural purposes except proper remediation is carried out. Heavy metals have long been known to attach to biological matter, and when organic matter decays, heavy metals may become less trapped in organic matter[12].

Considering all the four sampling locations around the dumpsite where samples were collected namely (i) dumpsite area (ii) 300meters away (iii) 600meters away and (iv) the river side. From Table 4.19, the dumpsite area sampling location had highest degree of contamination and highest accumulation of heavy metals and thus the most polluted out of all the sampling locations, the reason is obvious because the dumpsite area constituted where majority of refuse and waste items were being discharged or dumped. Other sampling locations were polluted with moderate degree of contamination with the river area being the lowest contaminated. In order of decreasing degree of contamination, the locations ranked; dgumpsite area > 300m > 600m > River area. This showed that the degree of pollution reduces as we move farther away from the dumpsite area.

One-way Analysis of variance (ANOVA) between these locations revealed that the pollution recorded across the locations were not significant (P>0.05), Similarly correlation analysis (Table 4.10) revealed that there was strong positive correlation between most of the sampling locations. All these indicated that other sampling locations aside the dumpsite area were not contaminated independently but as a result of run-off from the dumpsite area and are polluted due to overflow of contaminants from the dumpsite area.

From Table 4.11, the level of heavy metal contamination observed in this study was lower compared to what was observed in dumpsites from Lafia metropolis and Mojosongo, Indonesia but however followed a similar trend of Iron being the most dominant pollutant in the dumpsites[5,7]. The level of heavy metals reported at Olusosun and Awotan dumpsites of Lagos and Ibadan respectively were within similar range of with what was observed in this study and in these reports cadmium level was observed to be the lowest[13,14]. Heavy metal concentrations were higher than the control site in every sample location, indicating that the dumpsite likely received anthropogenic input.

4.2.2 Discussion of Heavy Metals in Vegetable Samples

In the edible vegetables, appreciable levels of heavy metals were observed. The concentration of heavy metals ranged from as low as 0.01mg/kg to as high as 15.71 mg/kg in the vegetables (Table 4.2). In the water leaf samples, heavy metals such as Chromium, Cadmium and Lead were not detected. This may be due to the fact that the levels of these heavy metals present in the water leaf samples were too low to be determined by the analytical technique employed in this study. The average concentration of copper observed in the water leaf samples was 0.99±0.01 mg/kg while that of Manganese was 12.85±0.02 mg/kg and that of iron was 15.71±0.02 mg/kg. In the water leaf samples, out of all the heavy metals considered, iron concentration was highest followed by manganese and then copper. Since many iron compounds, including a number of iron chelation complexes, are highly soluble in aqueous conditions, this helps to explain why iron is rapidly absorbed and stored by the vegetable samples[15].

In the Jute mallow samples, Chromium and Lead were not detected while cadmium was found at a very low level. The concentration of heavy metals in the jute mallow samples varied between 0.01±0.01 mg/kg and 11.00±0.17 mg/kg. Also in the Jute mallow, the concentration of iron remained highest among all the metals considered. The average concentration of copper in the jute mallow was 1.22±0.03 mg/kg, cadmium was 0.10±0.01 mg/kg, manganese was 4.31±0.02 mg/kg and Iron was 11.00±0.17 mg/kg. In decreasing order, the heavy metals ranked; Iron > Manganese > Copper > Cadmium. Although Cadmium had the lowest concentration, heavy metals' non-residual components are closely related to cadmium, which makes them more mobile and potentially bioavailable for plant absorption. Cadmium in significant concentrations may affect animal and human reproductivity and digestion[16].

In the Scent leaf samples, concentration of heavy metals ranged between 0.02±0.01 mg/kg and 8.06±0.06 mg/kg. similarly, chromium and cadmium were not detected while Lead was detected at low quantity. Lead is a harmful heavy metal that plants may absorb from the soil, thus disrupting the food chain[17]. It has been reported that the nervous system is where lead has its greatest impact[17]. Lead is commonly known to be harmful even at low concentrations, especially in young children, and lead intake has been linked to negative consequences including central nervous system disorders[18]. Due to the presence of fodder grasses on the dumpsite, livestock that graze there may be exposed to health hazards related to lead toxicity which can harm the liver in animals, particularly in cattle[19].

Concentration of iron was also the highest among all the metals considered. Even though iron toxicity is rare, consumption of vegetables with high iron content may result in build-up of excess iron in the tissues and organs and may increase the risk for certain cancers which may

eventually leads to death[20]. The average concentration of each metal was copper: 0.86±0.01 mg/kg, Lead: 0.02±0.01mg/kg, Manganese: 1.44±0.03 mg/kg and Iron 8.06±0.06 mg/kg. Among the three vegetables the concentration of iron observed was higher than the other metals. Also it can be seen that water leaf has higher heavy metal content than other vegetables signifying that water leaf is able to absorb more metals through it roots. In decreasing order of their heavy metal content the vegetables ranked as follow; Water leaf > Jute mallow > Scent leaf.

One-way analysis of variance revealed that the concentration of each metal differ significantly ($P<0.05$) from one another. The variation in the concentration of the heavy metal can be due to anthropogenic factors and possibly plants' affinity for the metals. There is a positive correlation between Copper-Cadmium and also Manganese-Iron, while a negative correlation existed in-between Copper-Lead and Lead-Manganese (Table 4.14). However, analysis of variance between these three edible vegetables revealed that there was no significant difference ($P>0.05$) in the heavy metals accumulated by the metals and similarly, there was a strong positive correlation between the edible vegetables (Table 4.13).

The level of heavy metals observed in the three edible vegetables were within the WHO allowable limits (Table 4.15). However, human consumption of such vegetables is not encouraged in order to prevent heavy metal accumulation in the human tissues and organs which may result to severe health challenges. Long-term exposure to heavy metals raises the possibility of organ and nervous system damage, including renal, heart, liver, and kidney damage[21]. Additionally, eating foods polluted with heavy metals has been linked to an increased risk of gastrointestinal cancer[21].

4.2.3 Discussion on PAHs in Soil Samples

The results of determination and quantification of polycyclic aromatic hydrocarbons (PAHs) in the soil samples were presented in Table 4.16. A total of six PAHs were identified and quantified in the soil samples collected from various locations in Aba-Eku MSW dumpsite. These PAHs include naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene.

The highest concentration of naphthalene, acenaphthylene and anthracene were observed at the dumpsite area, highest concentration of acenaphthene was at the 600m location, fluorine was detected only at the river area and phenanthrene was highest at the 300meters location. Phenantherene was mostly produced from petrogenic sources (from the emission of unburned petroleum products including gasoline, diesel fuel, and fuel oil from vehicle traffic), which are thermodynamically stable compounds[22].

At the dumpsite area, concentration of naphthalene (61.65kg/mg) was highest while anthracene had lowest concentration. Fluorene was not detected at this sampling location and the total accumulation of PAHs at this sampling location was 120.52mg/kg. Similarly, at the 300meters location, naphthalene's concentration was highest and accumulation of PAHs was 64.48mg/kg. The same trend was observed in the 600meters location and the river area. Also from the results naphthalene was the only 2-rings PAHs observed while others were 3-rings PAHs. It was also observed that naphthalene (PAHs with two-rings) exhibits higher concentration compared to other PAHs. It is clear from this that human activities at the dumpsite have contaminated the ecosystem with more two-ring PAHs. The ability of naphthalene to be converted into methylated derivatives like 1-methylnaphthalene and 2-

methylnaphthalene due to its high solubility and ease of disintegration in aqueous solution also contributes to this observation. In comparison to the original molecule, these methylated derivatives have been proven to be extremely toxic, yet they are also vulnerable to microbial decay[23].

The average concentration of acenaphthylene, which was observed, was the highest average concentration in the 3-rings series for the remaining three-rings PAHs, at 33.18 mg/kg. Also among the three-ringed PAHs in the research area, acenaphthene was found in higher concentration at the 600-meter and river area locations. Acenaphthylene is the PAH with the highest concentration among the three-ringed PAHs, followed by phenathrene, fluorene, and anthracene.

Among all the sampling locations, the dumpsite area had highest pollution due to PAHs, followed by the 300meters, 600meters and the river area. One-way analysis of variance showed that the concentration of the PAH are significantly different from one another ($P<0.05$) with only few exhibiting strong positive correlation (Table 4.19). This could be attributed to anthropogenic sources and majority of sources of PAH in soil are burning of fuels that causes atmospheric deposition, Petrogenic sources may also include petroleum or engine oil activities around the dumpsite. The lower molecular weight PAHs, which are hydrophilia chemicals and are soluble in water, tend to settle in dumpsite soils, and it has been discovered that PAHs pollution in dumpsites represent the history of fossil fuel combustion which is taking place in the environment[24]. Two-ring and three-ring PAHs predominate in the research area. The High Molecular Weight PAHs are very minor components, but they are dominant in organic waste and the combustion of waste materials at the dumpsite. The Lower Molecular Weight PAHs are typically caused by petroleum

products and derivatives dumped at the dumpsite, such as engine oil, plastics, polyethylene products, etc[25].

The levels of PAHs observed in this study as shown in Table 4.18 were higher than what was reported at Okija dumpsite in Rivers State and Saje dumpsite in Ogun State due to the huge quantities of waste plastics, polyethylene at Aba-Eku dumpsite. In another instance, e-waste dumpsite in Aba and Alaba dumpsite in Lagos reported higher levels of fluorene and phenenthrene compared to what was observed in this study. The e-waste dumpsite in Aba and Alaba dumpsite in Lagos are characterized by open burning of electronic materials and electronic wastes which is responsible for PAHs abundance in soils within these dumpsites.

4.2.4 Discussion on PAHs in Vegetables

The result PAHs in vegetable samples as presented in Table 4.17 showed that only six PAHs were detected across the three vegetable samples considered at Aba-Eku dumpsite. The PAHs are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene. The levels of PAHs in the three vegetable samples varied between 0.95mg/kg and 52.11 mg/kg. Among all the PAHs only Naphthalene was discovered in the three vegetables, acenaphtylene was detected in water leaf and jute mallow alone, acenaphthene and fluorene were detected in water leaf and scent leaf alone, phenanthrene was detected only in jute mallow and anthracene only in scent leaf. Naphthalene highest level (52.11 mg/kg) and lowest (8.15 mg/kg) levels occurred in scent leaf and jute mallow respectively, acenaphthene and acenaphthylene were highest in water leaf sample, fluorene and anthracene were highest in scent leaf while phenanthrene was highest in jute mallow.

Naphthalene recorded the highest concentration of all the PAHs, this is due to the fact that naphthalene has higher solubility in aqueous systems than other PAHs. However, scent leaf contained more naphthalene than other vegetables, this indicate that scent leaf is able to absorb naphthalene through its leaf and root from the atmosphere and the soil. It is noteworthy that all the PAHs recorded higher concentration in the vegetables growing at the dumpsite more than those in the control site. On the overall, Scent leaf accumulated more PAHs than other vegetables. The vegetables ranked in order of total accumulated PAHs is scent leaf > water leaf > jute mallow.

One way analysis of variance indicated that the difference between the concentration of PAHs in the vegetables was significant ($P<0.05$), indicating that the each vegetable possess different affinity to absorb different PAHs from both atmospheric deposition (through their leaves) and the soil (through their roots). The PAHs are less volatile and possess high capacity for sorption (strongly bonded to substrate); this is why they can remain in the soil for a long time[30]. Studies have shown that sediments and soils naturally habour PAHs and around 90% of PAHs with longer half-life are contained in sediments and soil than in the climate or plants[31].

4.2.5 Discussion on PAEs in Soil

The results of determination of PAEs in soil samples is presented in Table 4.20, only two phthalate esters were detected in the soil samples namely dipropyl phthalate and diethyl phthalate. Concentration of phthalate esters in the dumpsite varied between 0.94 mg/kg and 5.75 mg/kg. Generally, the concentration of phthalate esters observed in the soil samples

were scantly and relatively low. Out of the two phthalate esters observed, dipropyl phthalate was more prominent than diethyl phthalate as it was found in all the four locations where soil samples were collected. Dipropyl phthalate recorded the highest and lowest concentration at the 300-meter location and the dumpsite area respectively while diethy phthalate was detected only at the 600-meter location. The overall accumulation at the dumpsite area was 0.94 mg/kg, at the 300-meter location was 5.75 mg/kg, at the 600m location was 6.89 mg/kg and at the river side was 5.34 mg/kg. This observation revealed that the 600-meter location ranked the highest contaminated site followed by the 300-meter location, then the river side location and then the dumpsite area. Also it was only at the 600-meter location that both dipropyl phthalate and diethyl phthalate were detected.

These findings demonstrated that PAE levels in soil samples from the dumpsite may constitute an appreciable threat to human health. The toxic qualities of PAEs may be more harmful in children than in adults, probably due to lower detoxification and metabolic capabilities in children than in adults, as shown by the fact that children showed a greater non-carcinogenic risk and carcinogenic risk than adults[32]. Respiratory illnesses are more common in environments with greater concentrations of phthalate esters than in environments with lower concentrations[33].

4.2.6 Discussion on PAEs in Vegetables

The result of determination of phthalate esters in vegetable samples was presented in Table 4.21. A total of three phthalate esters were determined in edible vegetable samples collected at Aba-Eku dumpsite. The three phthalate esters include dipropyl phthalate, diethyl phthalate

and benzylbutyl phthalate. The concentration of phthalate esters ranged from 0.13 mg/kg to 2.96 mg/kg. The phthalate esters were only present in jute mallow and scent leaf samples as no phthalate ester was detected in water leaf samples. The highest concentration of dipropyl phthalate (2.88 mg/kg) was observed in scent leaf sample. Diethyl phthalate was only detected also in the scent leaf sample while highest concentration of benzylbutyl phthalate (2.96 mg/kg) was observed in the jute mallow sample. Of the two vegetables where phthalate esters were observed, scent leaf had higher overall accumulation of phthalate esters than the jute mallow. In addition, all the three phthalate esters were detected in the scent leaf sample while only two were found in the jute mallow sample.

Since air deposition is a well-known source of soil PAEs, it is possible that this was one of the origins of the PAEs in the vegetable samples[34]. However, organic chemicals with higher vapour pressure, such as diethyl phthalate and dipropyl phthalate, are more likely to exchange at the leaf-soil interface, causing greater absorption and volatilization of these pollutants throughout the vegetable[35].

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Chapter Five

Conclusion

5.1 Summary of Findings

Considerate levels of heavy metals were observed in soil samples. This could be due to the presence of waste products like batteries, electronics, or industrial waste that contain these metals. Among all the four locations where samples were collected, the dumpsite area sampling location had the highest degree of contamination and highest accumulation of heavy metals and thus the most polluted out of all the sampling locations, the reason is obvious because the dumpsite area constituted where majority of refuse and waste items were being discharged or dumped. The average concentration of heavy metals observed in Aba-Eku MSW dumpsite were Copper: 1.01 mg/kg, Cadmium: 0.03 mg/kg, Lead: 0.12 mg/kg, Manganese: 0.48 mg/kg and Iron: 4.31mg/kg. The contribution of each individual metal to the pollution at the Aba-Eku MSW dumpsite was rated by their contamination factor in decreasing order as follow Iron (4.49) > Copper (3.73) > Manganese (3.45) > Cadmium (2.50) > Lead (1.50). Iron had the highest concentration and contamination factor among all the metals considered in this study making iron the biggest metal pollutant in Aba-Eku MSW dumpsite. These high levels of heavy metals in soil can have a number of negative impacts, including reducing soil fertility, harming plant growth, and potentially leaching into groundwater.

Considerate levels of Heavy metal were also observed in plant samples. Among all the three edible vegetables investigated in this study, Iron concentration was the highest while water

leaf had highest accumulation of heavy metals. In decreasing order of their heavy metal content the vegetables ranked as follow; Water leaf > Jute mallow > Scent leaf.

This is an indication that plants growing at the dumpsite are taking up these heavy metals from the soil. If so, this could imply that these plants could pose a risk to animals or humans that consume them, as heavy metals can be toxic in high doses. Additionally, the presence of heavy metals in plants can also indicate that the metals are being transported through the food chain, potentially impacting other organisms in the ecosystem.

The PAHs observed in soil samples were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene. The average concentration of PAHs in the soil samples were naphthalene- 36.15 mg/kg, acenaphthylene- 33.18 mg/kg, acenaphthene- 8.02 mg/kg, fluorene- 3.48mg/kg, phenanthrene- 3.94 mg/kg and anthracene- 1.14 mg/kg. Majority of the PAHs had strong positive correlation and are significantly different from one another ($P<0.05$). The study area is characterized by dominance of 2-rings and 3-rings PAHs, this suggest that the dumpsites may contain waste products that have been burned or contain materials like tar, or petroleum derivatives like plastics, polyvinyl chloride and polyethylene goods, motor oil, etc. or chemicals that are formed when organic matter is burned or otherwise heated at high temperatures which can contribute to high levels of PAHs in the soil.

It was also observed that three edible vegetables investigated at the dumpsite have different levels of PAH uptake. Some plants may be more tolerant of PAHs, while others may avoid taking them up altogether. The three vegetables contain more naphthalene than any other PAH. In this research, Scent leaf accumulated more PAHs than other vegetables. The vegetables ranked in order of total accumulated PAHs is scent leaf > water leaf > jute mallow.

Dipropyl phthalate and diethyl phthalate were the phthalate esters observed in the soil samples around Aba-Eku MSW dumpsite. the concentration of phthalate esters observed in the soil samples were scantly and relatively low. Out of the two phthalate esters observed, dipropyl phthalate was more prominent than diethyl phthalate as it was found in all the four locations where soil samples were collected.

5.2 Conclusion

This study identified the levels of some heavy metals, PAHs and PAEs in the soil and plants around Aba-Eku Municipal Dumpsite, Ibadan. In view of the findings there is potential risks of exposure to heavy metal, PAHs and PAEs in the environment to the waste pickers, dumpsite workers, residents in the neighborhood and animals by direct contact or indirect exposure through the food chain. Municipal Solid Waste (MSW), however, constitutes a serious environmental problem with varying degrees of direct as well as indirect negative effects on the environment and its ecosystems. Its handling across the different functional elements requires greater attention as it raises concerns not only about cost but also about environmental health and pollution.

The study also showed that, in conjunction with the burning of waste materials on the dumpsite, the trash disposed of at the dumpsite served as the primary source of heavy metals, PAHs, and PAEs in the study region. Uncoordinated and insufficient waste management at the dumpsite obviously poses a pollution risk as well as a potential health hazard. As a result, environmental laws aimed at reducing pollution should be enforced, waste management systems should be improved, and there should be no significant risk to the local population's health.

5.3 Recommendations

Based on the findings of this study, the followings are therefore recommended.

i. Promote public awareness and education on potential risks of exposure to toxic chemicals and the importance of proper waste disposal.

ii. Educate proximate residents, waste pickers and dumpsite workers on the potential hazards and best practices for waste disposal can help minimize the risk of toxic chemical exposure.

iii. Prior to waste depositing, it should be encouraged to separate waste into biodegradable and non-biodegradable categories.

iv. In order to prevent heavy metal poisoning due to biomagnification, proper remediation work should be done on any site proven to have high levels of heavy metals before it can be used for the production of edible food crops.

v. In order to prevent waste-related problems in the food chain, adequate education and laws on waste treatment in society should also be strengthened.

vi. In order to prevent further sources of pollution issues, education and laws regarding the management of dumpsites should be strengthened.

5.4 Contributions to Knowledge

From this study, there are appreciable findings which are key contribution to knowledge as follows;

i. Fe and Cu respectively ranks the highest heavy metal pollutant in the soil samples in and around Aba-Eku MSW dumpsite, in decreasing order the heavy metals ranked Fe>Cu>Mg>Pb>Cd

ii. Heavy metal accumulation was highest in water leaf, followed by scent leaf and then jute mallow, which suggest that water leaf has more capacity to absorb heavy metals from soil

iii. Fe concentration was highest in all the vegetable samples

iv. The dumpsite is characterized by two rings and three rings PAHs

v. The concentration of Naphthalene was higher than other PAHs in the dumpsite

vi. Scent leaf contains the highest accumulation of PAHs and the vegetables ranks Scent leaf>water leaf>jute mallow

vii. Dipropyl Phthalate is the most prominent phthalate ester in the Aba-Eku Dumpsite

viii. Water leaf and scent leaf demonstrated high capacity and are capable of accumulating heavy metals, PAHs and PAEs and can be used for phytoremediation.

ix. The information obtained can be used by policy makers to develop effective strategies for mitigating the risk and protecting public health.

x. Additionally, the study can provide insights into the effectiveness of different remediation techniques.

5.5 Suggested Areas for Further Research

i. Additional research is needed to better understand the impact of heavy metals, PAHs and PAEs on human health particularly the dumpsite workers and the immediate environment.

ii. Further studies can be conducted to explore the behavior of pollutants in different environments and to develop effective strategies for remediation.

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Appendix I

Result of Triplicate Analysis of Heavy Metals in Soil Samples at the Dumpsite Location

Metals	AAS 1	AAS 2	AAS 3	Mean	SD
Cu (mg/Kg)	0.09	0.08	0.08	0.08	0.01
Cr (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Cd (mg/Kg)	0.08	0.07	0.06	0.07	0.01
Pb (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Mn (mg/Kg)	0.92	0.95	0.92	0.93	0.02
Fe (mg/Kg)	7.62	7.64	7.62	7.63	0.01

Source: Author's Field Work, 2023

Appendix II

Result of Triplicate Analysis of Heavy Metals in Soil Samples at 300m Location

Metals	AAS 1	AAS2	AAS3	Mean	SD
Cu (mg/Kg)	2.21	2.20	2.21	2.21	0.01
Cr (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Cd (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Pb (mg/Kg)	0.38	0.35	0.39	0.37	0.02
Mn (mg/Kg)	0.04	0.04	0.06	0.05	0.01
Fe (mg/Kg)	1.33	1.35	1.32	1.33	0.02

Source: Author's Field Work, 2023

Appendix III

Result of Triplicate Analysis of Heavy Metals in Soil Samples at 600m Location

Metals	AAS 1	AAS2	AAS3	Mean	SD
Cu (mg/Kg)	1.62	1.60	1.65	1.62	0.03
Cr (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Cd (mg/Kg)	0.01	0.01	0.02	0.01	0.01
Pb (mg/Kg)	0.10	0.11	0.13	0.11	0.02
Mn (mg/Kg)	0.33	0.35	0.31	0.33	0.02
Fe (mg/Kg)	2.80	2.84	2.80	2.81	0.02

Source: Author's Field Work, 2023

Appendix IV

Result of Triplicate Analysis of Heavy Metals in Soil Samples at the River Area Location

Metals	AAS 1	AAS2	AAS3	Mean	SD
Cu (mg/Kg)	0.11	0.14	0.12	0.12	0.02
Cr (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Cd (mg/Kg)	0.01	0.05	0.01	0.02	0.02
Pb (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Mn (mg/Kg)	0.61	0.63	0.61	0.62	0.01
Fe (mg/Kg)	5.47	5.48	5.50	5.48	0.02

Source: Author's Field Work, 2023

Appendix V

One-way Analysis of Variance of Heavy Metals in Soil Samples

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Cu (mg/kg)	4	4.03	1.0075	1.156358
Cd (mg/kg)	4	0.1	0.025	0.000967
Pb (mg/kg)	4	0.48	0.12	0.030467
Mn (mg/kg)	4	1.93	0.4825	0.143158
Fe (mg/kg)	4	17.25	4.3125	7.840558

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	51.14397	4	12.78599	6.970496	0.002227	3.055568
Within Groups	27.51453	15	1.834302			

Total	78.6585	19

Source: Author's Field Work, 2023

Appendix VI

Analysis of Variance of Heavy Metals across Sampling Locations

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Dumpsite	5	8.71	1.742	10.98007
300 meters	5	3.96	0.792	0.91402
600 meters	5	4.88	0.976	1.46968
river soil	5	6.24	1.248	5.66052

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2.561335	3	0.853778	0.179513	0.908728	3.23887
Within Groups	76.09716	16	4.756073			

Total	78.6585	19

Source: Author's Field Work, 2023

Appendix VII

One-way Analysis of Variance of PAHs in Soil Samples

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Naphthalene (mg/kg)	4	144.6	36.15	328.1475
Acenaphthylene (mg/kg)	2	66.36	33.18	312.0002
Acenaphthene (mg/kg)	4	32.08	8.02	5.979133
Fluorene (mg/kg)	1	3.48	3.48	#DIV/0!
Phenanthrene (mg/kg)	3	11.83	3.9433	1.796933
Anthracene (mg/kg)	3	3.41	1.1366	0.195733

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3718.544	5	743.7089	6.205258	0.00569	3.203874
Within Groups	1318.365	11	119.8514			
Total	5036.91	16				

Source: Author's Field Work, 2023

Appendix VIII

One-way Analysis of Variance of PAHs across Sampling Locations

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Dumpsite	5	120.52	24.104	767.7819
300m	4	64.48	16.12	191.6281
600m	4	45.17	11.2925	176.3175
River side	4	31.59	7.8975	62.81249

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	673.5078	3	224.5026	0.668767	0.586064	3.410534
Within Groups	4363.402	13	335.6463			
Total	5036.91	16				

Source: Author's Field Work, 2023

Appendix IX

Result of Triplicate Analysis of Heavy Metals in Water Leaf Samples

Metals	AAS 1	AAS2	AAS3	Mean	SD
Cu (mg/Kg)	0.99	1.00	0.98	0.99	0.01
Cr (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Cd (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Pb (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Mn (mg/Kg)	12.87	12.85	12.84	12.85	0.02
Fe (mg/Kg)	15.73	15.70	15.69	15.71	0.02

Source: Author's Field Work, 2023

Appendix X

Result of Triplicate Analysis of Heavy Metals in Jute Mallow Samples

Metals	AAS 1	AAS2	AAS3	Mean	SD
Cu (mg/Kg)	1.21	1.19	1.25	1.22	0.03
Cr (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Cd (mg/Kg)	0.01	0.01	0.02	0.01	0.01
Pb (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Mn (mg/Kg)	4.32	4.29	4.33	4.31	0.02
Fe (mg/Kg)	11.10	10.80	11.10	11.00	0.17

Source: Author's Field Work, 2023

Appendix XI

Result of Triplicate Analysis of Heavy Metals in Scent Leaf Samples

Metals	AAS 1	AAS2	AAS3	Mean	SD
Cu (mg/Kg)	0.86	0.86	0.87	0.86	0.01
Cr (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Cd (mg/Kg)	0.00	0.00	0.00	0.00	0.00
Pb (mg/Kg)	0.01	0.0.4	0.02	0.02	0.01
Mn (mg/Kg)	1.45	1.40	1.46	1.44	0.03
Fe (mg/Kg)	8.07	8.00	8.11	8.06	0.06

Source: Author's Field Work, 2023

Appendix XII

One-way Analysis of Variance of Heavy Metals in Vegetable Samples

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Cu (mg/kg)	3	3.07	1.023333	0.033233
Cd (mg/kg)	3	0.01	0.003333	3.33E-05
Pb (mg/kg)	3	0.02	0.006667	0.000133
Mn (mg/kg)	3	18.6	6.2	35.2261
Fe (mg/kg)	3	34.77	11.59	14.8917

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	308.8554	4	77.21384	7.698105	0.004227	3.478005
Within Groups	100.3024	10	10.03024			
Total	409.1578	14				

Source: Author's Field Work, 2023

Appendix XIII

One-way Analysis of Variance of Heavy Metal Load between the Vegetable Groups

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
		29.5		59.566
Watre leaf	5	5	5.91	55
		16.5		21.587
Jute mallow	5	4	3.308	57
		10.3		11.557
Scent leaf	5	8	2.076	08

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	38.312 97	2	19.156 49	0.6198 76	0.5543 81	3.8852 94
Within Groups	370.84 48	12	30.903 73			
Total	409.15 78	14				

Source: Author's Field Work, 2023

Appendix XIV

One-way Analysis of Variance of PAHs in the Vegetable Samples

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Naphthalene (mg/kg)	3	84.71	28.23667	493.8745
Acenaphthylene (mg/kg)	3	10.61	3.536667	20.57003
Acenaphthene (mg/kg)	3	13.34	4.446667	27.71773
Fluorene (mg/kg)	3	2.34	0.78	0.4627
Phenanthrene (mg/kg)	3	0.87	0.29	0.2523
Anthracene (mg/kg)	3	0.95	0.316667	0.300833

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1784.018	5	356.8036	3.941289	0.023973	3.105875
Within Groups	1086.356	12	90.52969			
Total	2870.375	17				

Source: Author's Field Work, 2023

Appendix XV

A Cross Section of Aba-Eku Municipal Dumpsite

Source: Author's Field Work, 2023

Appendix XVI

Researcher at Aba-Eku Municipal Dumpsite

Source: Author's Field Work, 2023

Appendix XVI

Researcher at Aba-Eku Municipal Dumpsite

Source: Author's Field Work, 2023

Appendix XVII

Collection of Soil Samples at Aba-Eku Municipal Dumpsite

Source: Author's Field Work, 2023

Bio-data

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4. State of Origin Oyo State

5. Name and Address of Next of Kin: Makinde Ademola Samuel
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B. Educational Background:

Educational Institution Attended with Dates and Qualification:

School Attended	Dates	Qualifications
❖ Greater Heights School	2000-2002	Pre School
❖ Sure Foundation Model High School.	2002-2008	First Leaving Sch. Cert.
❖ Providence High School, Ibadan.	2008-2014	West African Exam. Cert.
❖ Olabisi Onabanjo University Ago-Iwoye	2014-2018	B.Sc. Pharmacology
❖ Lead City University, Ibadan	2021-2023	MSc in View

C. Working Experiences with Dates:

❖ Teacher, Luminous Star Academy	2019 - 2022
❖ Project Officer, National Sugar Development Council	Feb 2023 till Date

D. Awards and Fellowship: Nil

E. Membership of Professional Bodies:

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- Sindiku O.& Makind I.M, *Assessment of Toxic Chemicals/Pollutants in Undergound Water from Aba-Eku Mucipal Soil Waste Dumpsite*, FASCON International Conference 2022.
-

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The University Compliance Certification

This is to certify that, this Thesis written by **Ifeoluwa Mayowa Makinde** with Matric No**. LCU/PG/002352,** in the Department of Biological Science, Faculty of Natural and Applied Sciences, Lead City University, Ibadan is in full compliance with the approved University format and style.

_____ _____

Signature **Date**