Assessment of Heavy Metals and PAHs in Soil from Tyre Pyrolysis Plant located in Egbeda Local Government Area, Oyo State

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Certification

This is to certify that **Christopher OgorchukwuOgbue** with the matriculation number LCU/PG/001962, carried out this research work tittled "Assessment of Heavy Metals and PAHs in Soil from Tyre Pyrolysis Plant located in Egbeda Local Government Area, 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 Degree (M.Sc) 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

This study is aimed to assess heavy metals and PAHs in soil from tyre pyrolysis plant Egbeda, Ibadan Oyo State. Soil samples were collected from seven strategic locations around the plant. Five selected heavy metals name As, Cd, Cr, Pb and Zn were determined using Atomic Absorption Spectrophotometer (AAS). PAHs were extracted from soil samples through an accelerated solvent extraction system (ASE 200, Dionex, Sunny-vale, CA, USA) with a 1:1 (v/v) acetone/dichloromethane solvent mixture. The results of heavy metals showed that the average concentration of the five metals are As-0.2827 mg/kg, Cd-0.2177 mg/kg, Cr-0.1726 mg/kg, Pb-0.6753 mg/kg and Zn-1.0232 mg/kg and in decreasing order of abundance ranked Zn > Pb > As > Cd > Cr. One way ANOVA reveals that all the results were significantly different from one another ($P<0.05$), similarly there was no correlation between all the five metals examined. The degree of contamination and the pollution index of the study site are 13.8 and 2.2 respectively and they implied that the site is moderately contaminated.The PAHs result showed that a total of 18 PAHs were determined with average concentration ranking of Naphthalene -381.25 mg/Kg, 1-Methyl Naphthalene -335.50 mg/Kg, 2-Methyl Naphthalene -236.25 mg/Kg, Anthracene -199.75 mg/Kg, Fluoranthene -173.65 mg/Kg, Phenanthrene -140.00 mg/Kg, Pyrene -78.78 mg/Kg, Chrysene -72.20 mg/Kg, Benzo(a)anthracene -48.78 mg/Kg, Benzo(a)pyrene -45.72 mg/Kg, Acenaphthene -36.68 mg/Kg, Indeno(1,2,3-cd)pyrene -31.26 mg/Kg, Benzo(b)fluoranthene -30.35 mg/Kg, Benzo(k)fluoranthene -27.54 mg/Kg, Fluorene -21.93 mg/Kg, Benzo(g,h,i)perylene -18.51 mg/Kg, Dibenz(a,h)anthracene -15.22 mg/Kg, and Acenaphthylene -12.98 mg/Kg. Seven major carcinogenic and tetratogenic PAHs were detected in slightly elevated levels. One way ANOVA reveals that the concentration of all the PAHs identified were significantly different from one another, although correlation study indicated that there is strong positive correlation between all the PAHs.

Keywords: Pyrolysis, Scrap tyre, PAHs, Heavy metals, Environment, Concentration.

Word Count: 285

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List of Acronyms

Abbreviation	**Meaning**
AAS	Atomic Absorption Spectroscopy
ANOVA	Analysis of Variance
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
ELT	End-of life tyre
ERM	Effects Range Median
FEPA	Federal Environmental Protection Agency
GC	Gas Chromatography
GC-MS	Gas Chromatography Coupled to Mass Spectrometry
HPLC	High Performance Liquid Chromatography
HPLC-FLD	High Performance Liquid Chromatography with Fluorescence Detection
LGA	Local Government Area
NNPC	Nigerian National Petroleum Corporation
PAHs	Polycyclic Aromatic Hydrocarbons
PLE	Pressurized Liquid Extraction
SE	Soxhlet Extraction
SFE	Supercritical Fluid Extraction
SQGs	Sediment Quality Guidelines
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

Chapter One

Introduction

1.1 Background to the Study

The environment as designed by nature takes in all we give in and gives them back to us in another form which could be beneficial or harmful[1]. The reactions that are responsible for these transformations could be physical, chemical, biological or integration of any or all of the aforementioned[2]. Several exchanges or reactions go on all the time from as simple as flow of one river to the other or ponds to lakes to the complex decomposition processes of dead organisms; the environment naturally has a way of cycling substances around it in such a way that every part is affected directly or indirectly by the consequence of the usage of another[3]. If the substance being cycled is a contaminant, other parts of the environment could also be affected; however, the effects could reduce or increase due to the presence of other substances or factors[4].

Heavy metals and Polycyclic Aromatic Hydrocarbons (PAHs) common environmental contaminants of concern because of their toxicity and threat to human life and the environment[5]. Several researches have been conducted on heavy metal and PAHs concentration in soils from various anthropogenic sources such as automobile emissions, industrial waste, agricultural practices, mining activity and petrochemical activity[6]. The presence of PAHs and toxic metals such as lead and cadmium in the environment has been the cause of concern to environmentalist, governmental agencies, and health practitioners[7]. This is mainly due to their health implications since they are carcinogenic and toxic above a certain tolerable level to human, animals and plants[8]. Some heavy metals such as copper and cobalt are essential for enzymatic activities, acting as enzymatic inhibitors at higher concentrations[9].

On the other hand, Road transportation activity, a primal component of economic development and human welfare, is increasing around the world as the economies grow[10]. Road traffic has been highlighted as a major source of heavy metal emissions (such as Copper, Cadmium, Iron, Nickel, Lead and Zinc)[11]. Consequently, the rise of the road transportation activity causes the higher levels of emitted metals, which impact the ecological environment on the roadside and the surrounding areas such as farmlands, pastures, rivers and residences[12]. The heavy metals may enter the food chain as a result of contaminating edible plants or their intake by people. If these levels are excessive, the metals can cause serious health risks[13].

The remarkable worldwide increase in the number of vehicles, and a lack of both technical and economical disposal mechanisms made for waste tyres are being considered as a serious pollution problem[14]. For instance, in Nigeria, over 600 billion naira was spent on the importation of vehicles in the first six months of the year 2021 and the number of tyres which are imported annually for passenger cars, trucks and other vehicles is also rapidly increasing[15]. In order to meet the demand for automobiles, the global market for tyres is predicted to reach 3.5 billion units by 2022[16]. Some of these tyres linger in the transport system as they are used and re-used as fairly-used tyres before they are finally discarded as end of use tyres or scrap tyres[17].

Over 1.5 billion tonnes of tyres per annum are discarded all around the globe weighing 17 million tonnes[18]. This huge quantity of scrap tyres make their way into the environmental cycle each year, so there is an extreme demand to manage and mitigate the environmental impact which occurs from landfilling and burning[19].

Approximately 3.0 billion tyres are generated globally, with a predicted growth rate of at least 1.0 billion tyres each year. Most of which will end up as waste[20]. Also, piles of thousands of tyres at junkyards, landfills and other places are common in many countries and the stockpiles are a burden on the landscape causing environmental and health threats[21].

To solve this problem, a waste-to-fuel approach known as Pyrolysis technology was developed as alternative waste treatment technology in Europe, China and US[22]. Pyrolysis is energy-intensive processes that attempt to reduce the volume of scrap tyres by converting it into synthetic oils (Tyre-Derived Fuel), by combustion in an oxygen-free atmosphere[23].

Tyre-Derived Fuel is the first market for scrap tyres on the global scale and remains the most important end-use even in Nigeria and is mostly used in cement kilns, electric utilities and paper mills as an energy source in the production lines[24].

Many industrial and utility companies have considered waste tyres to be a source of valuable materials and have started to combust scrap tyre as a supplementary fuel due to the higher energy content and lower price of Tyre Derived fuel, relative to other petroleum products[25]. Due to the massive amount of heat generated by the combustion of tyres, pyrolitic reactions take place producing prolytic oil and releasing various chemicals such as, heavy metals volatile organic compounds, polynuclear aromatic hydrocarbon, particulate matter, carbon monoxide, sulphur and many others into the atmosphere[23]. The thick black smoke and toxic residues emitted from the burning tyres may cause environmental harm/ nuisance and pose direct threats to public health and safety[26]. Also, the length and degree of exposure could have direct effects on human health such as Asthma, cancer, nervous depression, high blood pressure and subsequent heart diseases[25].

According to a study conducted to assess the risk from combustion of scrap tyres piles on the US Mexico border, the results reported that air pollution from tyre pile fires poses the greatest threat to the human health and the environment[26].

The heavy metals have non-biodegradable characteristics. They can remain in the roadside environment including the food chain for a very long period of time. It is important to know how the heavy metals are distributed on the roadside. This will suggest us how to protect our health from the heavy metal pollution[27].

Polycyclic Aromatic Hydrocarbons (PAHs) belong to a group of over 100 hazardous substances of organic pollutants consisting of two or more fused-benzene aromatic rings. Formation of PAH is due to incomplete combustion of organic matter through the condensation of ethylenic radicals in the gas phase to form the larger polycyclic compounds[28]. Those containing up to four benzene rings are known as light PAHs (l-PAHs) and those containing more than four benzene rings are known as heavy PAHs (h-PAHs). The h-PAHs are more stable and toxic than the l-PAHs[29]. According to Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) list of hazardous substances, PAHs ranked 7th in 2005 in the biennial ranking of chemicals deemed to pose the greatest possible risk to human health[30]. PAHs have low solubility in water and are highly lipophilic. In water or when adsorbed on particulate matter, PAHs can undergo photodecomposition in the presence of ultraviolet light from solar radiation[31]. In the atmosphere, PAHs can react with ozone, nitrogen oxides and sulphur dioxide, to give diones, nitro- and dinitro-PAHs, and sulphonic acids, respectively. Biologically, PAHs can be degraded by some microorganisms in the soil[32]. Some have been demonstrated to be mutagenic and carcinogenic in humans[33]. Those PAHs that have not been found to be carcinogenic may, however, synergistically increase the carcinogenicity of other PAHs[34].

Therefore, pyrolysis of waste tyres poses a serious public health and an environmental threat[33]. Both heavy metals and PAHs are expected to be released into the environment in large amounts during the tyre combustion[35]. As a result, significant environmental hazard is generated, and pollution of not only the atmosphere but also the surrounding land and the ground water is likely to occur[36].

1.2 Statement of the Problem

Tyre combustions are reported to generate large amounts of hazardous trace elements, toxic, mutagenic and carcinogenic compounds, such as volatile organics, polycyclic aromatic hydrocarbons, heavy metals, particulates and other products of incomplete combustion[37]. Heavy metals are known for their toxicity potential, tendency to bioaccumulation, high mobility and environmental persistence[38].

Similar behaviour has been documented for polycyclic aromatic hydrocarbons. The PAHs were reported to have carcinogenic properties and 16 PAHs have been listed as priority pollutants by the US Environmental Protection Agency[39]. The PAHs are formed during the incomplete burning of coal, oil gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat, coal and gasoline[40]. Once these compounds are released into the air by any process, they are transported to the far areas and may be deposited on soil particles, plants and in water bodies. The PAHs may play a role in the health effects of respirable particulate matter, and are of great concern because they are toxic to aquatic life and because several are suspected human carcinogens, mutagens and some are suspected endocrine disrupters[41].

Soil pollution is rated as one of the worst toxic pollution problems. Pyrolysis of tyres has recently been identified as one of the major sources of pollutants in proximate urban areas[42]. There is therefore a growing concern among developed and developing economies about the need to prevent or reduce harmful environmental effects associated with tyre waste and pyrolysis of waste tyres[43].

1.3 Justification of the Study

There are several studies on water, soil and air quality monitoring due to the transport, industrial and domestic sectors in Ibadan and elsewhere. But very limited study is known regarding then discharge of heavy metals and PAHs due to the combustion of scrap tyres as a potential contributor for environmental degradation.

Hence, this study will reveal the environmental status of soils in and around pyrolysis plant through determination of trace or toxic metals and PAHs content due to the scrap tyre combustion.

All over the world, more yearly deaths are associated to soil pollution and heavy metal poisoning than those related to automobile accidents. According to the study conducted by European Commission in 2005, pollution of reduces the life expectancy of human being by an average of nine months.

Earlier, old tyres were processed and reused. But, with the introduction of radial tyres, the practice had to be discontinued. Now, the option left is to use old tyres as fuel. Nigeria imports waste tyres from other countries but without proper guidelines. Pyrolysis of scrap tyres are now common occurrences in Nigeria. There is need for proper monitoring and enforcement of environmental laws on these plants.

1.4 Aim and Objectives of the Study

Aim

The aim of this study is to determine the level of heavy metals and Polycyclic Aromatic Hydrocarbons (PAHs) in soil around tyre pyrolysis plant at Egbeda Local Government Area Ibadan, Oyo State.

Objectives

The specific objectives of this study are to;

i. determine the concentrations of As, Cd, Cr, Pb and Zn in soil samples around tyre pyrolysis plant Egbeda.

ii. determine and quantify the PAHs in soil samples around tyre pyrolysis plant Egbeda.

1.5 Research Questions

i) What are the levels of heavy metals in tyre pyrolysis plant?

ii) What are the levels of PAHs in soil from the polluted site?

iii) What is the environmental impact of these heavy metals and PAHs?

1.6 Significance of the Study

Heavy metals and Polycyclic Aromatic Hydrocarbons are major pollutants in our environment causing grave and harmful consequences particularly on human health in the past few years. The study area - Ibadan is a populous, commercial and industrial city and it has experienced in the last few years increase in commercial activites one of which is the transport sector and this has consequently lead to the increase in the usage of tyres and consequently increase in end of life tyres otherwise known as scrap tyres which has now create an opportunity for tyre pyrolysis industries to thrive well in the economy of the city. The results of this study will provide a baseline information about the presence of heavy metals and PAHs around the pyrolysis plant in Egbeda and will also indicate the extent of environmental damage caused by these pollutants. Therefore, the study will no doubt increase the plethora of knowledge on heavy metals and PAHs and serve as valuable literature for future research.

1.7 Scope of the Study

There are many heavy metals but this study considered only five metals namely As, Cd, Cr, Pb and Zn, soil samples collected were only top soil at a depth of 0-5cm. The sampling carried out in this study is within the viscinity of the tyre pyrolysis plant in Egbeda Local Government in Ibadan, Southwest Nigeria.

1.8 Limitations of the Study

This study considers the determination of heavy metals and PAHs only in soil samples. The seasonal variation of heavy metals and PAHs could not be determined because the Management of the pyrolysis plant do not permit recurring visit to the premise which would have enabled sample collection in both rainy and dry seasons, so only one series of sampling was carried out.

1.9 Operational Definition of Terms

Environment: The natural world, 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

Pyrolysis: This is the thermal decomposition of materials at very high temperature in an inert environment.

Soil Pollution: The presence of toxic chemicals (pollutants) 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

Tyre: A tyre is a rubber covering, typically inflated and placed round a wheel to provide a flexible cushion and form a soft contact with the road. Used in almost all forms of mechanical vehicles such as passenger cars, bicycles, tricycles, vans, trucks, airplanes, etc.

Endnotes

1. E.C. Ogoko, *Evaluation of Polycyclic Aromatic Hydrocarbons, Total Petroleum Hydrocarbons and Some Heavy Metals in Soils of Nnpc Oil Depot Aba Metropolis, Abia State, Nigeria.* **Journal of Environmental Science, Toxicology and Food Technology**. Volume 8, Issue 5 Ver. III, 2014, 21-27

2. The Global Tyres Market, *Trends drivers and projections, June 2016. Global Industry Analysists Inc.* 2016. Available Online: (http//www.strategyr.com/marketresearch/Tires_Market_Trends.asp)

3. W.C. Wang, C.J. Bai, C.T. Lin & S. Prakash, *Alternative Fuel Produced From Thermal Pyrolysis of Waste Tires and its Use in a Diesel Engine,* **Appl. Therm. Eng.** 93, 2016, 330–338.

4. Y. Su & B. Zhao, *Pyrolysis of Waste Tire Powder and Its Comparison with Shenhua Coal. In Proceedings of the International Conference on Energy and Environment Technology 2019* **ICEET'19**, Guilin, China, 16 (18) 2019; 262–265.

5. P. Parthasarathy, H.S. Choi, H.C. Park, J.G. Hwang, H.S. Yoo, B.K. Lee & M. Upadhyay, *Influence of Process Conditions on Product Yield of Waste Tyre Pyrolysis—A Review.* **Korean J. Chem. Eng.** 33, 2016, 2268–2286.

6. L. Zhang, B. Zhou, P.G. Duan, F. Wang & Y.P. Xu, *Hydrothermal Conversion of Scrap Tire to Liquid Fuel.* **Chem. Eng. J.** 285, 2016, 157–163.

7. R. Eva, S. Rimute, J. Kęstutis, V. Darius, B. Steigvile & Z. Aleksej, *Distribution of Polycyclic Aromatic Hydrocarbons and Heavy Metals in Soil Following a Large Tire Fire Incident: A Case Stud,* **Chemosphere** 286, 2021, 131-556 Available Online: https://doi.org/10.1016/j.chemosphere.2021.131556

8. M. Nadal, J. Rovira, J. Díaz-Ferrero, M. Schuhmacher & J.L. Domingo, *Human Exposure to Environmental Pollutants After a Tire Landfill Fire In Spain: Health Risks,* **Environ. Int.,** 97, 2016, 7–44.

9. Y. Zhu, W. Fan, T. Zhou & X. Li, *Removal of Chelated Heavy Metals from Aqueous Solution: A Review of Current Methods and Mechanisms.* **Sci. Total Environ**. 678, 2019, 253–266.

10. L. Niu, H. Cai, P.H. Van Gelder, P. Luo, F Liu & Q. Yang, *Dynamics Of Polycyclic Aromatic Hydrocarbons (PAHs) in Water Column of Pearl River*

Estuary (China): Seasonal Pattern, Environmental Fate and Source Implication, **Appl. Geochem**. 90, 2018, 39–49.

11. C. Bi, Y. Chen, Z. Zhao, Q. Li, Q. Zhou, Z. Ye & X. Ge, *Characteristics, Sources and Health Risks of Toxic Species (PCDD/Fs, PAHs and Heavy Metals) in PM2.5 During Fall and Winter in an Industrial Area*. **Chemosphere** 12:4, 2020, 6-20.

12. F.O. Ajibade, O.O. Olajire, T.F. Ajibade, N.A. Nwogwu, K.H. Lasisi, A.B. Alo, T.A. Owolabi & J.R. Adewumi, *Combining Multicriteria Decision Analysis with GIS for Suitably Siting Landfills in a Nigerian State*. **Environ. Sustain. Indic**. 3–4, 2019, 100010. https://doi.org/10.1016/j.indic.2019.100010.

13. J.R. Adewumi, O.J. Ejeh, K.H. Lasisi, & F.O. Ajibade, *A GIS-AHP Based Approach in Sitting MSW Landfills in a Nigerian Confluence State*. **SN Appl. Sci**. 1, 2019, 1528. https:// doi.org/10.1007/s42452-019-1500-6.

14. O.O Elemile, M.K.C. Sridhar & O.E. Oluwatuyi, 2019. *Solid Waste Characterization and its Recycling Potential: Akure Municipal Dumpsite, Southwestern, Nigeria*. **J. Mater. Cycles Waste Manag.** 21, 2019, 585–593. https://doi.org/10.1007/s10163-018-00820-2

15. M. Ahmed, M. Matsumoto, & K. Kurosawa, *Heavy Metal Contamination of Irrigation Water, Soil, and Vegetables in a Multi-Industry District of Bangladesh*. **Int. J. Environ. Res.** 12, 2018, 531–542. https://doi.org/10.1007/s41742-018-0113-z.

16. W.H. Gu, J.F. Bai, W.H. Yuan, E. Ma, C.L. Zhang, & J.W. Wang, *Pollution Analysis of Soil Polycyclic Aromatic Hydrocarbons from Informal Electronic Waste Dismantling Areas in Xinqiao, China.* **Waste Manag. Res.** 37, 2019, 394–401.

17. M.J. He, S.Y. Yang, J. Zhao, C. Collins, J.M. Xu, & X.M. Liu, *Reduction in the Exposure Risk of Farmer from E-Waste Recycling Site Following Environmental Policy Adjustment: A Regional Scale View of PAHs in Paddy Fields*. **Environ. Int.** 133, 2019, 105136.

18. H. Huang, C. Cai, S. Yu, X. Li, Y. Liu, S. Tao, & W. Liu, *Emission Behaviours of Nitro- and Oxy-Polycyclic Aromatic Hydrocarbons During Pyrolytic Disposal of Electronic Wastes*, **Chemosphere,** 222, 2019, 267–274.

19. G.A. Ebong, M.M. Akpan, & V.N. Mkpenie, *Heavy Metal Contents of Municipal and Rural Dumpsite Soils and Rate of Accumulation by Carica Papaya and Talinum Triangulare in Uyo, Nigeria.* **E-J. Chem.** 5, 2008, 281–290. https://doi.org/10.1155/2008/ 854103

20. G.A. Ebong, E.U. Dan, E. Inam, & N.O. Offiong, *Total Concentration, Speciation, Source Identification and Associated Health Implications of Trace Metals in Lemna Dumpsite Soil, Calabar, Nigeria.* **J. King Saud Univ. Sci.** 2018, https://doi.org/10.1016/ j.jksus.2018.01.005.

21. M.D. Vaverkova, J. Winkler, D. Adamcova, M. Radziemska, D. Uldrijan, & J. Zloch, *Municipal Solid Waste Landfill – Vegetation Succession in an Area Transformed by Human Impact.* **Ecol. Eng.** 129, 2019, 109–114. https://doi.org/10.1016/ j.ecoleng.2019.01.020.

22. O.O. Ololade, S. Mavimbela, S.A. Oke & R. Makhadi, *Impact of Leachate from Northern Landfill Site in Bloemfontein on Water and Soil Quality: Implications for Water and Food Security*. **Sustainability.** 2019; 11: 4238.

23. N.O. Eddy, S.A. Odoemelem, & A. Mbaba, A. *Elemental Composition of Soil in Some Dumpsites.* **Journal of Environmental Agricultural Food Chemistry,** 5, 2016, 1349-1365

24. M.O. Eze, *Evaluation of Heavy Metal Accumulation in Talinum triangulare Grown Around Municipal Solid Waste Dumpsites in Nigeria*. **Bull. Environ. Pharmacol. Life Sci.,** 4 (1), 2014, 92-100.

25. A. Hammed, L.A. Olayiwola, K. Gbola, M. Adewuyi, & O. Azeez, *Heavy Metal Contents in Soil and Plants at Dumpsites: A Case Study of Awotan and Ajakanga Dumpsite Ibadan, Oyo State, Nigeria.* **J. Environ. Erath Sci.,** 7(4): 2017, 1-14.

26. O.T. Ogunmodede, E. Adewole, & A. Ojo, *Quantitative Changes in Soils Properties and Uptake of Metals on Municipal Solid Waste Dumpsite in Nigeria,* **Int. Lett. Chem., Phys. Astron.,** 52: 2015, 152-162

27. E. Olagunju, O. Badmus, F. Ogunlana, & M. Babalola, *Environmental Impact Assessment of Waste Dumpsite using Integrated Geochemical and Physico-Chemical Approach: A Case Study of Ilokun Waste Dumpsite, Ado Ekiti, Southern Nigeria*, **Civil Eng. Res. J.**, 4(2): 2018, 1-13.

28. S.E. Olatunde & M.O. Onisoya, *Assessment of Heavy Metal Concentrations in Pawpaw (Carica papaya Linn.) around Automobile Workshops in Port Harcourt Metropolis, Rivers State, Nigeria*, **J. Health Pollut**. 14: 2017, 48-61.

29. O.A. Olayiwola, & C.T. Onwordi, *Environmental Fate of Heavy Metals in Soil of Ido-Osun Waste Dump Site, Osogbo, Osun, Nigeria*, **Am. J. Environ. Prot.,** 3(1): 2015, 1-4

30. P.O Oyeleke, O.A. Abiodun, R.S. Salako, O.E. Odeyemi, & T.B. Abejide, *Assessment of some Heavy Metals in the Surrounding Soils of an Automobile Battery Factory in Ibadan, Nigeria,* **Afr. J. Environ. Sci. Technol.,** 10(1): 2016, 1 – 8.

31. M.S. Shokr, A.A. El Baroudy, M.A. Fullen, T.R. El-beshbeshy, A.R. Ramadan, A. Abd El Halim, A.J.T. Guerra, & M.C.O. Jorge, *Spatial Distribution of Heavy Metals in the Middle Nile Delta of Egypt,* **Int. Soil Water Conserv. Res.,** 4: 2016, 293-303

32. R. Twinamatsiko, J. Mbabazi, & H. Twinomuhwezi, *Toxic Metal Levels in Food Crops Grown from Dump-Sites Around Gulu Municipality, Northern Uganda*, **Int. J. Soc. Sci. Technol.,** 1(1): 2016, 22-45.

33. A. Shitandayi, F. Orata & F. Lisouza, *Assessment of Environmental Sources, Levels and Distribution of Polycyclic Aromatic Hydrocarbons Within Nzoia Catchment Area in Kenya*. **Journal of Environmental Protection**, 10(6): 2019, 772-790.

34. N.J. Edokpayi, J.O. Odiyo, O.E. Popoola & T.A.M. Msagati, *Determination and Distribution of Polycyclic Aromatic Hydrocarbons in Rivers, Sediments and Wastewater Effluents in Vhembe District, South Africa*. **Int J Environ Res Public Health,** 13(4): 2016, 387.

35. O.S. Edori, & W.A. Iyama, *Source Identification of Polycyclic Aromatic Hydrocarbons in Water at Point of Effluent Discharge into the New Calabar River, Port Harcourt, Rivers State*, **Nigeria. International Journal of Environment and Climate Change,** 9(6): 2019, 343-349

36. L. Xiaoyan, B. Zhongke, Y. Qinfei, C. Yingui & Z. Wei, *Polycyclic Aromatic Hydrocarbons in the Soil Profiles (0-100cm) from the Industrial District of a Large Open-Pit Coal Mine, China*. **Royal Society of Chemistry Advances** 7(45): 2017, 28029-28037.

37. A.A. Adeyi & P. Oyeleke, *Heavy Metals and Polycyclic Aromatic Hydrocarbons in Soil from E-waste dumpsites in Lagos and Ibadan, Nigeria*. **J Health Pollut** 7(15): 2017, - 84.

38. M.J. He, S.Y. Yang, J. Zhao, C. Collins, J.M. Xu, & X.M. Liu, *Reduction in the Exposure Risk of Farmer from E-Waste Recycling Site Following Environmental Policy Adjustment: A Regional Scale View of PAHs in Paddy Fields,* **Environ. Int**. 133, 2019, 105136bi X. Huang, X. Xu, Y. Dai, Z. Cheng, X. Zheng, & X. Huo, *Association of Prenatal Exposure to PAHs with Anti-Mullerian Hormone (AMH) Levels and Birth Outcomes of Newborns,* **Sci. Total Environ**. 723, 2020, 138009.

39. X. Huo, Y. Wu, L. Xu, X. Zeng, Q. Qin, & X. Xu, *Maternal Urinary Metabolites of PAHs and its Association with Adverse Birth Outcomes in an Intensive E-Waste Recycling Area,* **Environ. Pollut**. 245, 2019, 453–461.

40. L.F. Jiang, Z.N. Cheng, D.Y. Zhang, M.K. Song, Y.J. Wang, C.L. Luo, H. Yin, J. Li, & G. Zhang, *The Influence of E-Waste Recycling on the Molecular Ecological Network of Soil Microbial Communities in Pakistan and China*. **Environ. Pollut.,** 231, 2017, 173–181.

41. R. Jin, G.R. Liu, M.H. Zheng, X.X. Jiang, Y.Y. Zhao, L.L. Yang, X.L. Wu & Y. Xu, *Secondary Copper Smelters as Sources of Chlorinated and Brominated Polycyclic Aromatic Hydrocarbons*, **Environ. Sci. Tech**., 51, 2017, 7945–7953.

42. M. Lin, J. Tang, S. Ma, Y. Yu, G. Li, B. Mai, R. Fan, & T. An, *Simultaneous Determination of Polybrominated Diphenyl Ethers, Polycyclic Aromatic Hydrocarbons and their Hydroxylated Metabolites in Human Hair: A Potential Methodology to Distinguish ExternalfFrom Internal Exposur*e. **Analyst** 144, 2019, 7227–7235.

43. M.O. Onyema, L.C. Osuji & B.O. Isiuku. *Compositional Alteration of Polycyclic Aromatic Hydrocarbons by Burning Oil Spilled Soils,* **Academia Journal of Environmental Science,** vol. 4(11), 2016, 213-219.

Chapter Two

Literature Review

2.1 End of Life Tyres

End of Life Tyre (ELT) or scrap tyre refers to tyre that has ceased to perform its original function having exhausted all its re-use options[1]. It is a non-reusable tyre in its original form. The ELTs are not re-usable as a second hand purchase and are special kind of waste. There are municipal solid wastes rather than hazardous wastes[2]. When it is decided that the used tyre is neither reusable nor re-constructable, it is discarded and the recycling or recovery process begins. The materials of modern pneumatic tyres are synthetic rubber, natural rubber, fabric, wire, carbon black and other chemical compounds. Most times, when tyres have served their original purpose, there are usually discarded in landfills or stockpiled or burned in open field. In many jurisdictions of the world, ELTs are not usually recovered or recycled but stockpiled or burned. ELTs are very problematic because they are non-biodegradable. They do not decay and may take decades to disintegrate naturally. The consequence is resort to green or eco-friendly technologies for sustainable scrap tyre waste disposal and management. The development or adoption of a green tyre waste management and recycling technology depends on the economic and industrial conditions of a country[3].

The increasing pollution caused by the increased use of automobiles and other vehicles has become a cause for alarm around the world. However beneficial tyres may be to mobility, scrap tyres negatively affect the environment when improperly disposed. Landfilling/ Stockpilingare one of the most common methods of scrap tyre waste disposal in the world. Yearly, millions of tons of tyre waste go into already overcrowded landfills. Tyres occupy so much land space in landfills due to their large mass. Tyres are basically non-biodegradable because of their complex chemical and physical composition. Thus, they could take decades to decay and are extremely difficult to compact in landfills because of their buoyancy. When tyre wastes are stockpiled, they tend to collect water and thereby provide suitable breeding ground for malaria causing mosquitoes[1]. The negative environmental impact of landfilling or stockpiling of tyre wastes is huge. Although, landfilling is generally the cheapest and most convenient method of disposing of solid wastes such as ELTs, landfilling of whole or shredded tyres is entirely prohibited in some countries for reasons stated above[4].

2.2 End of Life Tyre Waste Situation in Nigeria

The rapid increase in Nigeria's population growth and income growth has resulted in a corresponding increase in the importation and purchase of all forms of motor vehicles. This change in consumption pattern has caused an increase in the amount of scrap tyres generated periodically. The number of scrap tyres in Nigeria increases monthly thereby amounting to high concentration of this solid waste in environmentally harmful quantity. It is estimated that thousands of tons of scrap tyres are abandoned in various parts of the country[5]. Many ELTs in Nigeria also end up in the waterways and on the streets. Many are also burned during festivities; as roasting material in abattoirs and in extrajudicial killings of suspected criminals[6]. Tyres have been stock piled around the country for years both legally and illegally in landfills and open dumpsites. These open dumpsites, which are usually indiscriminately located near residential settlements, causes leachate to contaminate nearby soil, surface and underground water bodies that are relevant to the residents who completely depend on those resources. This situation is aggravated by the absence of a scrap tyre waste collecting system as well as designated specially constructed landfill sites in the country for tyre wastes[1]. This further highlights the need for a comprehensive national solid waste management policy that would incorporate this present scrap tyre menace[7]. Recycling is still a nascent concept in Nigeria and as such has not received much attention from the government. Material recovery or recycling operations are carried out mostly by the private sector that employ scavengers to sort refuse for a fee and salvage any recyclable waste material prior to the ultimate disposal of the waste. Presently there is no tyre recycling or resource recovery facility in the country. Thus, legislations, policies as well as technologies championing tyre recycling; resource recovery and addressing issues of tyre manufacturing, haulage, disposal, storage, processing, etc. are practically non-existent. Every now and then, the heap is set ablaze in a bid to dispose of them and free up land space. The unregulated landfilling, stockpiling or open burning of tyres in Nigeria for whatever reason negatively affects the Nigerian environment in ways expressed above[4].

2.3 Pyrolysis of Scrap Tyres

Pyrolysis is a thermal decomposition process in which scrap tyre is decomposed at high temperature usually from 450-550 degree Celsius in either an oxygen-free or low-oxygen atmosphere. The purpose of pyrolysis is to break the tyre into its original components of oil, gas, solid residue (char), and low-grade carbon black as shown in Figure 2.1, which cannot be used in tyre manufacture. Pyrolysis of scrap tyres offers an environmentally and economically feasible method for transforming waste tyres into heat and electrical energy[8]. Pyrolysis of scrap is an attractive alternative to disposal in landfills as it saves land space and allows the high energy content of the tyre to be recovered as fuel. Using tyres as fuel produces equal energy as burning oil and 25% more energy than burning coal. Tyre pyrolysis plants are in use in several countries now, including the USA, Japan, India, and France. The carbon black produced by pyrolysis application (CBP) or rubber char is more economical compared to carbon black produced primarily from petroleum and is more price-efficient. It is to be used as a raw material in the following industries such as the electric cable jacketing, the conveyor bands; carrier bands; home and doormats; black nylon bags; hoses, rubber additives; automotive spare parts; heat isolation; plastic pipes; black colourant in industrial rubber products[1] etc.

Figure 2.1: Flow diagram for tyre pyrolysis process

Source: G. Mazloom (2009)

Tyre pyrolysis has been the subject of many studies; a major reason is it is environmentally friendly and its lower emission except for a few equipment leakage and minor fugitive sources[9]. Biomass pyrolysis is a very complex process and performed in two stages. Firstly, the volatile matter or vapour is produced and then secondary cracking starts at higher temperatures. The dominant parameters are temperature, reaction time, gaseous atmosphere type and pressure[10]. Pyrolysis of waste tyres is a favourable way of recycling that converts tyres into bio-oil. The tyre rubber is comprised of the highly complex polymeric structure. When the tyre is heated, the cracking process initially starts at S–S bonds, since S–S bonds need less dissociation energy compared to those of C–C and C–S bonds. The energy required for breaking down the S–S, C–C, and C–S bonds are 429, 607, and 699 kJ/mol, respectively[11].

2.4 Heavy Metals

The term heavy metal refers to metals with a density greater than 5 g/cm3. Heavy metals are generally defined as environmentally stable elements of high specific gravity and atomic weight[12]. They have such characteristics as lustre, ductility, malleability, and high electric and thermal conductivity[13]. Whether based on their physical or chemical properties, the distinction between heavy metals and non-metals is not sharp[14]. Some heavy metals are essential elements for health. Essential elements are chemical nutrients needed by the body in large or tiny amounts and are vital for growth and development, for example Zn, Mn, Cu and Fe[15]. Most of the essential trace elements have unfilled d-orbital and readily form coordination complexes with electron rich elements like nitrogen, oxygen and sulphur thus competing with each other for ligands[16]. The uptake ofheavy metals from the soil is determined by many factors, including their amounts in the soil, genetic makeup of the plant species, physical conditions of the soil and pH of soil[17].

Certain plant species have the ability to accumulate uniquely high concentrations of a particular essential element. Many interactions.

2.4.1 Arsenic (As)

Arsenic is a silver-gray or white metallic solid element found in nature. Arsenic combines with other elements to form organic and inorganic compounds. Inorganic arsenic compounds are thought to be more toxic than organic arsenic compounds. Arsenic exists in oxidation states of −3, 0, 3 and 5. It is widely distributed throughout Earth's crust, most often as arsenic sulfide or as metal arsenates and arsenides. In water, it is most likely to be present as arsenate, with an oxidation state of 5, if the water is oxygenated. However, under reducing conditions (<200 mV), it is more likely to be present as arsenite, with an oxidation state of +3[18].

Arsenic is a naturally occurring element that is found in combination with either inorganic or organic substances to form many different compounds. Inorganic arsenic compounds are found in soils, sediments, and groundwater. These compounds occur either naturally or as a result of mining, ore smelting, and industrial use of arsenic. Organic arsenic compounds are found mainly in fish and shellfish. In the past, inorganic forms of arsenic were used in pesticides and paint pigment. They were also used as wood preservatives and as a treatment for a variety of ailments. Today, usage of arsenic-containing pesticides and wood preservatives is restricted[19]. Arsenicals are used commercially and industrially as alloying agents in the manufacture of transistors, lasers and semiconductors, as well as in the processing of glass, pigments, textiles, paper, metal adhesives, wood preservatives and ammunition. They are also used in the hide tanning process and, to a limited extent, as pesticides, feed additives and pharmaceuticals.

Industry, farming and medicine have all used inorganic arsenic compounds. Arsenic is no longer produced in the United States but it is still imported from other countries. Until the 1940s, inorganic arsenic compounds were often used as agricultural pesticides. Now most uses of arsenic in farming are banned in the United States. The use of chromated copper arsenic to make a wood preservative for pressure-treated wood has been greatly reduced since 2003[19]. Arsenic in soil results from human activities including pesticide use, mining and ore processing operations, operating coal burning power plants, and waste disposal. Sites of former tanneries, which make leather from animal hides, have large amounts of arsenic in the soil. Tanneries once used pits in the ground for preserving the hides or for waste[20].

People who live in an area that was once used for farming, tanning hides or processing oremay have a higher chance of exposure or those who live near a waste site containing arsenic, factories, waste sites or farms where arsenic or pesticides were once used may be exposed. Human beings could also be exposed to arsenic in drinking water if they live in an area where high amounts of arsenic are in soils and mineral deposits.

Human exposure may come through

i. Touching soil that contains arsenic, by digging or playing in the soil.

ii. Eating soil that contains arsenic. Children may eat dirt while playing. Drinking water contaminated from natural sources of arsenic is another possibility.

iii. Breathing dust containing arsenic. Dust can be brought into the home from outside or by breathing air containing sawdust or burning smoke from wood treated with arsenic.

iv. Eye Contact if dust containing arsenic gets into your eyes[21].

High doses of arsenic can be deadly, especially in a short period. While long-term exposure to low levels of arsenic will not cause immediate effects, exposed people can suffer cancer of the skin, bladder, liver, lungs and kidneys[21]. High levels of arsenic in drinking water can cause the skin on the feet, hands and torso to develop sores or turn colour[22]. Children are at more risk of exposure because they put objects in their mouths, eat dirt and spend more time outdoors. Inorganic arsenic is a cancer-causing substance[23].

2.4.2 Cadmium (Cd)

Cadmium is a chemical element with the symbol Cd and atomic number 48[24]. It is soft; bluish-white metal is chemically similar to the two other stable metals in group 12, zinc and mercury[25]. Like zinc, it prefers oxidation state +2 in most of its compounds and like mercury it shows a low melting point compared to transition metals[26]. Cadmium and its congeners are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states[27]. The average concentration of cadmium in the Earth's crust is between 0.1 and 0.5 parts per million (ppm)[28]. There have been a few instances of general population toxicity as the result of long-term exposure to cadmium in contaminated food and water and research is on-going regarding the oestrogen mimicry that may induce breast cancer[29]. Cadmium is very toxic, 50 mg may cause vomiting, diarrhoea, abdominal pains, loss of consciousness. It takes 5–10 years for chronic Cd intoxication[31]. Interest has therefore risen in its bio-hazardous potential[30]. The highest concentration of cadmium has been found to be absorbed in the kidneys of humans, and up to about 30 mg of cadmium is commonly inhaled throughout childhood and adolescence[31]. Kidney damage has long been described to be the main problem for patients chronically exposed to cadmium[32]. Low dosages of cadmium are reported to stimulate ovarian progesterone biosynthesis, while high dosages inhibit it[33].

Maternal exposure to cadmium is associated with low birth weight and an increase of spontaneous abortion[34].

2.4.3 Chromium (Cr)

Chromium is the most abundant mineral in Earth's crust. Cr has an atomic number 24 in periodic table and has a relative atomic mass of 51.996 and it occurs in almost all oxidation states ranging from -2 to +6. But in environment Cr is mostly stable in trivalent and hexavalent form. Cr which is present in 0 oxidation state is biologically inert and is not naturally present in Earth's crust while Cr (III) and Cr (VI) are originated from industries. The available form of chromium is as halides, oxides and sulphides. It is the +2 oxidation state of chromium which is unstable and can be easily be oxidized to +3 forms in the presence of air[35]. Description Chromium is a naturally-occurring element found in rocks, animals, plants, and soil, where it exists in combination with other elements to form various compounds[36].

Chromium (Cr) is a grey, hard metal most commonly found in the trivalent state in nature. Hexavalent (chromium(VI)) compounds are also found in small quantities. Chromite ($FeOCr_2O_3$) is the only ore containing a significant amount of chromium. The ore has not been found in the pure form; its highest grade contains about 55% chromic oxide[37].

Chromium is widely used in manufacturing processes to make various metal alloys such as stainless steel. Chromium can be found in many consumer products such as: wood treated with copper dichromate, leather tanned with chromic sulfate, and stainless steel cookware. Chromium can be found in air, soil, and water after release from industries that use chromium, such as industries involved in electroplating, leather tanning, textile production, and the manufacture of chromium-based products. Chromium can also be released into the environment from the burning of natural gas, oil, or coal. Chromium does not usually remain in the atmosphere, but is deposited into the soil and water. Chromium can change from one form to another in water and soil, depending on the conditions present[35].

Chromium levels in soil vary according to area and the degree of contamination from anthropogenic chromium sources. Tests on soils have shown chromium concentrations ranging from 1 to 1000 mg/kg, with an average concentration ranging from 14 to about 70 mg/kg[36]. Chromium(VI) in soil can be rapidly reduced to chromium(III) by organic matter. As chromium is almost ubiquitous in nature, chromium in the air may originate from wind erosion of shales, clay and many other kinds of soil. In countries where chromite is mined, production processes may constitute a major source of airborne chromium. In Europe, endpoint production of chromium compounds is probably the most important source of chromium in air[38].

2.4.4 Lead (Pb)

Lead is a soft and malleable metal, which is regarded as a heavy metal[37]. Lead is a highly poisonous metal (regardless if inhaled or swallowed), affecting almost every organ and system in the body[38]. The main target for lead toxicity is the nervous system, both in adults and children. Longterm exposure of adults can result in decreased performance in some tests that measure functions of the nervous system[39]. Long-term exposure to lead or its salts (especially soluble salts or the strong oxidant PbO2) can cause nephropathy, and colic-like abdominal pains[40]. In the human body, lead inhibits porphobilinogen synthase and ferro-chelatase, preventing both porphobilinogen formation and the incorporation of iron into proporphrin IX, the final step in heme synthesis[41]. This causes ineffective heme synthesis and subsequent microcytic anaemia[42]. At lower levels, it acts as a calcium analog, interfering with ion channels during nerve conduction. This is one of the mechanisms by which it interferes with cognition[41]. Whenever lead finds its way into the human body, it can cause severe brain damage and malfunctioning of bone marrow which leads to deficiency in the production of blood cells which may cause leukaemia[43]. Of all the lead that enters the human body, a child's body is only able to excrete a third in about two weeks while an adult may excrete up to 99% within the same two weeks[44]. This makes children more susceptible to lead poisoning. When lead in its mobilized form is deposited in the human soft tissues, it may seriously affect the human health[45].

2.4.5 Zinc (Zn)

Zinc is a naturally occurring element found in the earth's surface rocks. Because of its reactivity, zinc metal is not found as the free element in nature. There are approximately 55 mineralized forms of zinc[46]. The most important zinc minerals in the world are sphalerite (ZnS), smithsonite ($ZnCO_3$), and hemimorphite ($Zn_4Si_2O_7(OH_2)H_2O$). Zinc appears in Group IIB of the periodic table and has two common oxidation states, Zn(0) and Zn(+2)[47]. Zinc forms a variety of different compounds, such as zinc chloride, zinc oxide, and zinc sulfate[48]. Zinc is a lustrous, blue-white metal that burns in air with a bluish-green flame. It is stable in dry air, but upon exposure to moist air, it becomes covered with a film of zinc oxide or basic carbonate (e.g., $2ZnCO_3 \cdot 3Zn(OH)_2$) isolating the underlying metal and retarding further corrosion. Bonding in zinc compounds tends to be covalent, as in the sulfide and oxide[49]. In solution, four to six ligands can be coordinated with the zinc ion. Zinc has a strong tendency to react with acidic, alkaline, and inorganic compounds. Since zinc is amphoteric (i.e., capable of reacting chemically either as an acid or a base), it also forms zincates (e.g., $[Zn(OH)_3H_2O]$- and $[Zn(OH)_4]_2$-)[46].

In humans and animals, zinc is an essential nutrient that plays a role in membrane stability, in over 300 enzymes, and in the metabolism of proteins and nucleic acids[48]. Zinc is a trace element found in varying concentrations in all soils, plants and animals and it is essential for the normal healthy growth of higher plants, animals and humans. Zinc is needed in small but critical concentrations and if the amount available is not adequate, plants and/or animals will suffer from physiological stress brought about by the dysfunction of several enzyme systems and other metabolic functions in which zinc plays a part. The total concentration of zinc in soils depends on the composition of the parent material and soil mineralogy, especially the concentration of quartz, which tends to dilute most elements. Only a small fraction of the total zinc is exchangeable or soluble. About one-half of the dissolved zinc exists as the free hydrated cation. The concentration of dissolved complexes of zinc with inorganic ligands can be estimated by computer-implemented models and total concentrations as input. Similar approaches with organic ligands await further research. Most analytical determinations of zinc are made by spectrometric techniques such as atomic absorption spectrophotometry, inductively coupled plasma atomic emission spectroscopy, and inductively coupled plasma mass spectroscopy[50].

2.5 Heavy Metal Pollution

Heavy metal pollution in soils refers to cases where the quantities of the elements in soils are higher than maximum allowable concentrations and this is potentially harmful to biological life at such locations[51]. Heavy metals occur at typical background in all ecosystems, however, anthropogenic releases can result in higher concentrations of these metals relative to their normal background values hence the pollution[51]. Heavy metals released from vehicular emission can accumulate in surface soils and their deposition over time can lead to abnormal enrichment, thus causing metal contamination of the surface soils[52]. High concentrations usually occur in soils below or near landfills and agricultural lands that have been irrigated with contaminated water[53]. Studies have shown that both long term and short term contamination of soils have effects on microbial activity and enzyme activities of the soil [51]. The toxicity and mobility of heavy metals in soils depend not only on the total concentration but also on their specific chemical form, bonding state, metal properties, environmental factors, soil properties and organic matter content[54]. Exposure of children, generally accepted as the highest risk group who have a higher adsorption rate of heavy metals because of their active digestion system and sensitivity of haemoglobin, to heavy metals, can greatly increase ingestion of metal laden soil particles via hand–to-mouth activities. In addition, adults may be exposed to threat since inhalation is easier pathway for toxic metals to enter their body[55].

There are two basic ways through which metals get into the environment: natural and anthropogenic sources. It is difficult to make a quantitative estimate of the anthropogenic input of heavy metals into an environment since no direct evidence exists concerning the heavy metal content of the sediment from the pre-industrial periods[56]. However some groups of workers have been able to make estimate of some metals discharged by human activities[57]. For instance the estimated amount of mercury discharged by human activities equals the amount released by continental weathering[58]. The anthropogenic flux of lead for several inner basins of South California is considerably greater than the natural fluxes by an average factor of four[59]. Also, the anthropogenic input of vanadium into marine and estuarine environments is of the same magnitude as that from natural sources[60]. A large part of the anthropogenic discharged of heavy metals into the environment has been noted to become part of the suspended matter in rivers, which acts as an efficient scavenger for these metals, through which they get into the marine environment[61]. Heavy metals are therefore regarded as one of the most common form of anthropogenic pollution to marine ecosystem[62]. Studies have shown that due to variations in local metal inputs and in the biogeochemical processes operating in different areas, environmental heavy metal concentrations vary both spatially and temporally[63]. Sediments and of course the organisms that dwell and feed on the sediment can then be said to reflect the extent of heavy metal pollution in a given area[64] .

For example in industrialized countries, the trace metal concentrations in fluvial sediments reflect the industrial activity in the drainage areas of the relevant rivers[65]. The origin of the metals found in the marine and estuarine environment has largely been credited to industrial users and storm water runoffs, which thus represent significant sources of this metal[66]. The discharge of municipal wastewater through submarine out-falls is the dominant sources of most toxic trace metals into Southern Californian coastal water[67]. Waste effluents from industries, which include tanning and dyeing, cement, insecticides, fertilizers, petroleum and petrochemicals, plastics, chemicals and various food-processing plants enter the environment through both their main outfall and numerous discharges[68]. Also the contamination and discharge associated with shipping at the ports contribute to the sources of heavy metals in the environment[69]. The discharges from primary and secondary metal sources include smelting activities, ship building and repairs, chemical manufacturing, paper making, municipal effluents from storm drains, combined sewer out-flows and municipal treatment plants have all been shown to contribute to the heavy metal burden of aquatic system[70]. The daily discharges of lead and zinc of about 4.5-6 tons respectively in the Sorfjord in Norway[71]. The use of tetraethyl lead as an anti-knock agent in gasoline and its emission steel plants has greatly increased the flux into the atmosphere by an order of magnitude over the natural flux and has shown that about 831.5 metric tons of lead was used between October and December, 1984 in the forms of tetraethyl lead as anti-knock agent in the three operational refineries in Nigeria[72]. Lead is therefore frequently discharged directly into the atmosphere in the form of smelters and automobile exhaust emission, and the ocean surface receive more lead as a result of precipitation and deposition of air-born aerosols[73]. In local coastal regions, lead pollution has been estimated to originate from sewage contaminated with industrial effluents especially in highly industrialized areas[74]. Another anthropogenic source is untreated industrial and domestic wastewater. For instance, all the 5,500 tons of hazardous waste produced per year in Rivers State are generated mostly by the petroleum industry, including the refinery[75]. Up to 2.1 mg/L of lead concentrations was discovered in storm drain discharges into wastewater ways, high level of copper and zinc observed originated from dry dock activities[75]. In another study, municipal and industrial inputs were noted to contribute 30% of dissolved copper and 37% of dissolved zinc to the main basin in the Puget Sound. These anthropogenic sources were noted to contribute about 23% and 18% of particulate copper and zinc inputs respectively[76]. It was noted these anthropogenic particulate inputs were diluted by inputs from sediments of the lower concentration from erosion sources.

The main natural sources of metal inputs into the environment are through geologic weathering. It is the sources of baseline or background levels. It is to be expected that in areas characterized by metal bearing-formations, these metals will also occur at elevated levels in the water and bottom sediments of the particular areas. Obviously, mineralized zones result in atmospheric pollution[77]. In consequence, the general problem arises of how to distinguish between metal input in an area to be a natural input or an anthropogenic input. Not many examples are known for which the interactions between natural weathering processes and mineralized zones are completely devoid of human contributions. The interactions of natural and anthropogenic metal inputs into an estuary was argued to result from river source (which is assumed to be a natural source) do not presently originate completely from natural weathering processes and that not all atmospheric depositions are man-made, this general classification considered provides an initial insight into man’s impact on an estuary. However they indicated lack of knowledge of the partitioning of metals between dissolved and particulate phase prevent scientists and environmental managers from predicting whether contamination will have greater influence on the water column or on the sediments[78].

The main source for metal input to plants and soils is atmospheric deposition. Volatile metalloids such as As, Hg, Se, and Sb can be transported over long distances in gaseous forms or enriched in particles, while trace metals such as Cu, Pb, and Zn are transported in particulate phases[79]. In terrestrial ecosystems, soils are the major recipient of metal contaminants, while in aquatic systems sediments are the major sink for metals[80]. Freshwater systems are contaminated due to runoff and drainage via sediments or disposal, while groundwater is impacted through leaching or transport via mobile colloids[79]. A number of biogeochemical processes take place at the heterogeneous interface between the rock, soil, water, air and living organisms[80]. These processes or interactions in turn control the solubility, mobility, bioavailability and toxicity of metals[80]. Metal ions may enter the soil solution and be subject to numerous pathways, all of which can potentially overlap. Metals are found in soil solutions as free ions or complexed to inorganic or organic ligands. Both the free ions and the metal-ligand complexes can be taken up by plants, retained on mineral surfaces, natural organic matter and microbes, transported through the soil profile into groundwater via leaching or by colloid-facilitated transport, precipitated as solid phases, and diffused in porous media such as soils. Heavy metal concentration of soils is a far more serious problem than air or water pollution because heavy metals are usually tightly bound by the organic components in the surface layers of the soil. Consequently, the soil is an important geochemical sink, which accumulates heavy metals quickly and usually depletes them very slowly by leaching into groundwater aquifers or bio-accumulating into plants[81].

Heavy metals can also be very quickly trans-located through the environment by erosion of the soil particles to which they are absorbed or bound and re-deposited elsewhere. Their physicochemical forms in water, sediments and soils markedly influence the transport, cycling, fate, bioavailability and toxicity of heavy metals. Whenever a heavy metal or its compound is introduced into an aquatic environment, it is subjected to a wide variety of physical, chemical and biological processes[79]. These include hydrolysis, chelation, complexation, redox, biomethylation, precipitation and adsorption reactions. Often, heavy metals experience a change in the chemical form as a result of these processes and so their distribution, bioavailability and other interactions in the environment are also affected. They can leach into living systems from natural ore deposits and other sources such as waste disposal of heavy metal containing waste[81].

2.6 Health Effects of Heavy Metals

Heavy metals enter the human body mainly through two routes namely: inhalation and ingestion, ingestion being the main route of exposure to these elements in human population[82]. Heavy metals intake by human populations through food chain has been reported in many countries[83]. Soil threshold for heavy metal toxicity is an important factor affecting soil environmental capacity of heavy metal and determines heavy metal cumulative loading limits[84]. For soil-plant system, heavy metal toxicity threshold is the highest permissible content in the soil that does not pose any phytotoxic effects or heavy metals in the edible parts of the crops[85]. Factors affecting the thresholds of dietary toxicity of heavy metal in soil-crop system include: soil type which includes soil pH, organic matter content, clay mineral and other soil chemical and biochemical properties; and crop species or cultivars regulated by genetic basis for heavy metal transport and accumulation in plants[86]. In addition, the interactions of soil-plant root-microbes play important roles in regulating heavy metal movement from soil to the edible parts of crops[87]. Agronomic practices such as fertilizer and water managements as well as crop rotation system can affect bioavailability and crop accumulation of heavy metals. This influences the thresholds for assessing dietary toxicity of heavy metals in the food chain[82]. Heavy metals are not easily biodegradable and it leads to their accumulation in human vital organs causing varying degree of illness on acute and chronic exposure[88].

2.7 Review of Previous Studies on Heavy Metals

In 2014, the range of heavy metal concentrations in soil around oil and service station in Tamale metropolis to be Cr: 2.37-15.00 mg/kg, Hg: 0.01-0.03 mg/kg, Cu: 3.20-22.68 mg/kg, Cd: 0.12-6.63 mg/kg and Pb 4.93-74.20 mg/kg. The enrichment factors for these metals revealed that Cd > Pb > Cr > Cu > Ni >Fe > Zn > As > Hg > Mn, this however is in agreement with degree of contamination, contamination factor and pollution load index. Meanwhile elevated concentration was recorded for some of the metals like Cr, Cu, Pb and Cd. In tamale metropolis, soil contamination by heavy metals observed around oil filling and service stations resulted from anthropogenic sources like corroded vehicles engine materials, oil filling activities, tyre wear, brake wear etc[111].

In a study conducted in 2021 to determine the level of pollution and distribution of pollutants in the surrounding vicinity of a tyre recycling facility in Luthania after a fire incident which happened in October 2019 revealed that the Concentrations of Cr, Zn, Ni, Cu, Pb were in the range of 1.1–93.9; 20.7–227.5; 0.2–35.7; 0.9–21.3; 0.9–102.9 µg/g, respectively. The concentration of Zinc was found to be highest in the fire zone while Zn, Cr, Ni, Pb and Cu also recorded elevated concentration within the area. Principal component analysis (PCA) revealed several locations closest to the fire zone were affected by the fire and were found to be highly contaminated with the heavy metals[112].

A comprehensive analysis of heavy metal was carried out on the soil samples of Industrial creeks located around Surat city, India reveal that cadmium and mercury exceed the limits set for the sediment. Higher values were mainly observed at all sites for Hg. These indicate that heavy metal contamination especially Hg, should be taken into account during development strategies to protect the ecosystem from long term pollution load[113].

In a research to investigate the concentration of some heavy metals in soil sample from Illela garage in Sokoto state using Atomic Absorption Spectroscopy (AAS). The results obtained in dry weight were Fe (1771.00 ±112.73 µg/g), Pb (117.30±7.13 µg/g), Cr (51.75±2.93µg/g), Zn (30.54±0.61 µg/g) and Cd (0.277±0.02 µg/g). The soil pH in waters was 7.12 and in CaCl2 was 6.39 and the moisture content was 5%. The concentration obtained was generally higher than the tolerable limit for safe environment as prescribed by Nigerian Federal Environmental Protection Agency (FEPA) and World Health Organization (WHO). The results of the study revealed that Fe, Pb, and Cr present in the soil sample are in higher concentrations than Zn and Cd, that are in trace amount and were in the following order of abundance Fe > Pb> Cr> Zn> Cd. Fe is present in concentration higher than other metals investigated because of geographicalorigin of the soil. Pb was high due towide use of lead products in storage batteries and its anthropogenic sources being the combustion of leaded gasoline. The higher Fe, Pb and Cr concentrations showed that there is heavy metals pollution at the sampling site where anthropogenic activities such as battery charging, welding are heavier while the lower concentration of Zn and Cd showed that anthropogenic activities are lower and could be as a result of variety of iron salt. In general, the results obtained showed that, the heavy metals concentration in the soil sample can be attributed to leaching of the top soil and unproductive nature of the garage at the time of sampling[114].

In 2013 a study aimed at assessing atmospheric depositions of heavy metals around Nigerian NNPC depots was carried out using the moss (*Barbula lambarenensis*). Concentrations of 7 elements (Cd, Pb, Ni, Cu, Cr, Fe and Zn) were determined in the moss samples by Flame Atomic Absorption Spectrophotometry analysis. Nickel concentrations in the moss samples across the depots, except Mosimi NNPC depot were highest ($p<0.05$). A comparison of the metal depositions among the depots revealed that elemental contents of the mosses were significantly the same ($p<0.01$) in all the depots except for Cd and Cu in Ibadan and Mosimi NNPC depots respectively. This could be attributed to fact that Ibadan depot is situated close to residential areas with major input of Cd from domestic wastes incineration while Mosimi depot serves several other depots around it, so vehicular activities was greater and also the release of Cu. Generally, the pollution level of these depots is high and this calls for their proper monitoring to reduce workers exposure to heavy metal hazards. There is evidence of high pollution of the studied NNPC depots by Ni, Cd, Pb and Cu. The concentrations of these heavy metals could only be attributed to the day-to-day activities around these depots. Monitoring, environmental safety and management of these depots are suggested due to the high concentration of these metal pollutants which could be very hazardous to human health when too much doses are bioaccumulated[115].

In 2015, the level of heavy metals (Pd, Zn, Cr, Cd, Fe and Cu in mg/kg) in the surrounding of automobile battery company in Ibadan was determined. Lead (Pb) concentrations reported decrease of with increase in distance away from the company in all the four different directions (Northwest, Northeast, Southwest and Southeast). The other heavy metals assessed do not show any clear trend with distance away from the factory. The mean concentrations of Pb, Zn, Cr, Cd, Fe and Cu were 59.13±48.9 (range 5.00 - 182.00 mg/kg), 2.68±1.1 (range 0.4 - 5.2 mg/kg), 1.62±2.4 (range ND - 8.7 mg/kg), 0.08±0.09 (range ND - 0.24 mg/kg), 49.44±16.5 (range 12.5 - 70 mg/kg) and 4.94±2.6 mg/kg (range 0.5 - 10.5 mg/kg), respectively. The mean concentration of Pb was far above (four times higher than) the normal crustal average for soils while the other heavy metals were below the normal background level. The concentration of Pb is also the highest at the distance closest to the factory which indicate that Pb is the major heavy metal impacted on soils by the company which elevate the normal background level and thereby contaminate the soils and make it unfit for agricultural purposes as plant take up the leached metals and ultimately find its way into animals and human body through the food chain. Pb concentrations in the soils from the vicinity of the battery factory studied were substantially higher than the normal crustal average (about four times) in soil when compared with Zn, Cd, Cr, Fe and Cu levels. This suggests that activities of the company may have elevated the level of Pb in the soil of the study area due to many years of free discharge of effluents and indiscriminate dumping of wastes containing majorly Pb materials. This finding suggests that the study area is not safe for human to live and for agricultural purposes as these metals accumulate with time and can get into the food chain through plants uptake. They can also contaminate groundwater as a result of leaching. Therefore, the random dumping of wastes and release of effluents on the ground in the study area should be checked by relevant government agencies to reduce the potential threat that may be caused by these heavy metals contaminants. There should also be public awareness on the danger of heavy metals in food chain[116].

In another study to investigate the impact of sawmill activities in the accumulation of heavy metals in soil around some selected sawmill industries in Ekiti State. It was revealed that the concentration of most of the metals at the different sites were almost similar, depicting that these metals are probably of natural origin with mild contribution from anthropogenic source, since the concentration of the metals decreased with distance from the various site. All metals monitored were detected in the soil samples and the values obtained were within the acceptable International Standards for soil/sediment. When compared previous studies of heavy metals in soil with metals (Co, Ni, Cu, Zn, Pb, Mn, Cd, Fe and Cr) from selected sawmill sites in Ekiti State there was arelatively low average content of the metals investigated in sawmill sites in Ekiti state present insignificant exposure risks. This does not ruled out the possibility of increase in concentration of this metals with time, since, the extent of heavy metal pollution varies with age. The concentration of the heavy metal levels in the soil suggests that these metals are of natural origin with contribution from anthropogenic influences. The level of Pb and Cd contents in Fiyinfoluwa Sawmill shows that the soil around this sawmill is moderately polluted. Hence, the cumulative effect through bio-accumulation might be of concern in future, thus calling for urgent attention on regular monitoring of the sawmill activities and its influence on the surrounding environment. Government, both state and local should design emission standards to regulate emission of particulate matters in form of wood dust and volatile organic compounds. This will provide environmental requirements that apply to sawmill industry. Sawmills should be located at least 500 feet from any “sensitive receptors” which include neighbours, place, this include businesses, residences, schools, recreation centres. Environmental protection agencies should help local governments in sharing information; conducting publicity and education on the danger of heavy metal pollution in sawmill industry[117].

Similar study to the one carried out in Ekiti was done to investigate the impacts of automobile workshops on heavy metals concentrations in urban soils of Obio/Akpor Local Government Area (LGA), Rivers State, Nigeria. Thirty three soil samples were collected each at sites close in proximity to selected automobile workshops (experimental sites) and sites that are far from the workshop without the influence of automobile workshop (control sites). The levels of mercury (Hg), lead (Pb) and cadmium (Cd) were determined using atomic absorption spectrophotometer (AAS). Data interpretation involved the use of descriptive statistics and pairwise ttest for test of significance in the levels of heavy metals between the experimental sites and control sites. Findings revealed that heavy metals were generally higher in soils under the influence of automobile workshop than the areas farther but Pb was higher than Hg and Cd. The mean values of Hg, Pb and Cd were 3.07, 91.03 and 5.63 mg/kg respectively in soils under the influence of automobile workshops and 0.03, 60.25 and 1.79 mg/kg, respectively in soils farther from the automobile workshop. There were significant variations in the levels of heavy metals between the experimental sites and the control sites at 0.05 confidence level. It is recommended that mechanic villages should be sited far from residential areas, phyto-remediation of polluted soil using local plants should be encouraged and continuous education and training should be provided for the automobile workers, emphasizing on the environmental implications of their poor occupational waste management. The study concluded that automobile wastes from mechanic workshops accumulated in soils. The study also revealed significant variations in heavy metal levels in soils that were closer to the automobile workshops than the control sites. The usual improper disposal of these wastes now demands attention in order to protect the soil as they render farmlands unfit for agriculture as well as pollute the ground and surface water systems. It is therefore recommended that, mechanic villages should be sited far from residential and farmland areas to avoid the transfer of these metals into the food chain and ground and surface water systems. Bioremediation can be used to clean up the already polluted soil to avoid further transfer of these heavy metals. In addition, the study recommended that the waste effluents from workshops should be recycled and more importantly, environmental education should be encouraged[118].

2.8 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[89]. There are several hundreds of different known PAHs and related compounds and the number of rings could be from two for the lower molecular weight compounds to seven for the higher molecular weight PAHs. For instance, naphthalene has two fused rings and is an example of the lower molecular weight PAHs while pyrene with four rings is an example of high molecular weight PAHs. Some of the known PAHs are: Naphthalene(Naph.), Antracene(Ant.), Chrysene(Chr), Acenaphtylene(Acp), Pyrene(Pyr), Acenaphthene(Acn), Benzo(a)Pyrene(B(a)P, Fluorene(Fluo), Fluoranthene(Fluoran), Benzo(e)Pyrene(B(e)P, Benzo(a)anthracene(B(a)A, Benzo(b)fluoranthene(B(b)F, Phenathrene(Phe), Benzo(a)pyrene(B(a)P, Benzo(k)fluoranthene(B(k)F, Indeno(1,2,3-cd)Pyrene (Ind) and Dibenzo(a,h)Anthracene(Db(ah)A [90]. The structure of the 16 PAHs that are termed as priority pollutants by the World Health Organisation is shown in Figure 2.2:

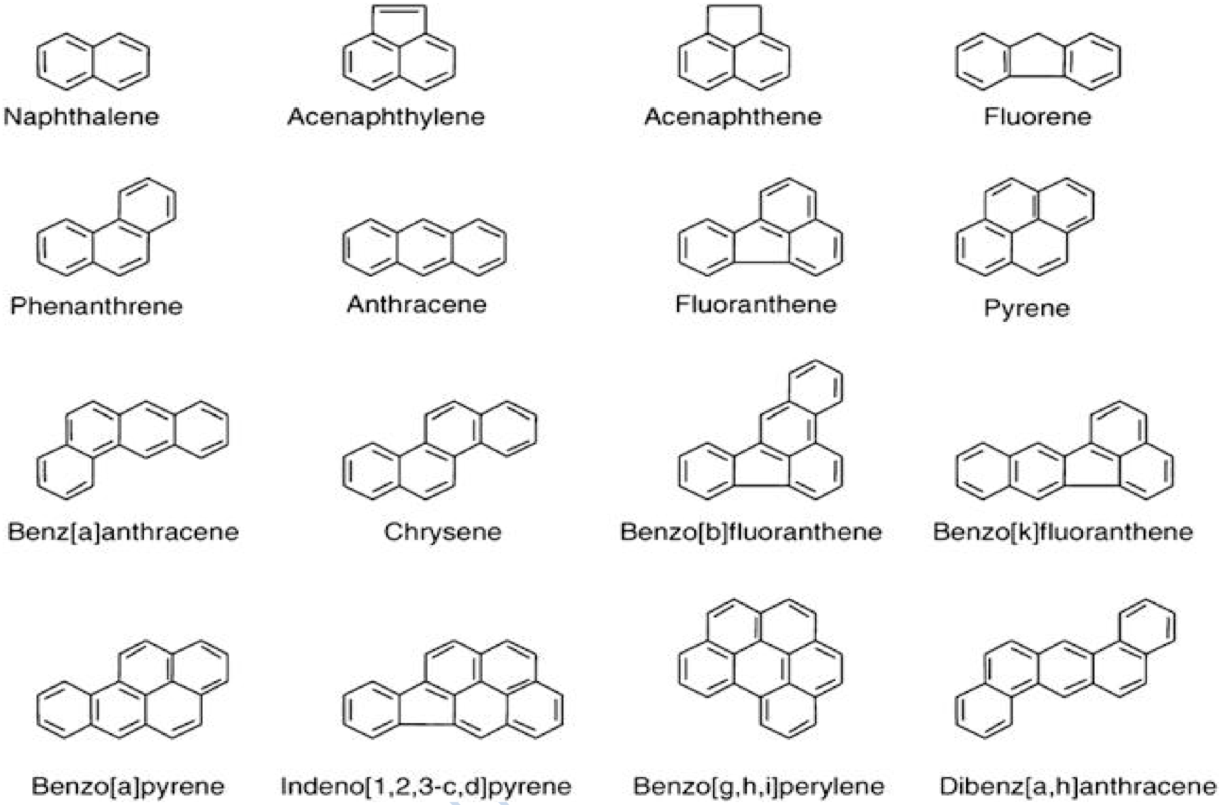

Figure. 2.2: Structure of sixteen PAHs considered by World Health Organisation (WHO) as priority pollutants.

Source: EFCS (2010)

2.8.1 Characteristic of PAHs

Polycyclic Aromatic Hydrocarbons are found in the pure state as white, colourless or pale yellow-green solids at room temperature[91]. They could also have a faint pleasant odour[92]. In the atmosphere, they are usually adsorbed on particles, dust or smoke and are removed from the atmosphere by wet (rainfall or mist) and dry deposition onto soil, water and vegetation[93]. In aqueous environment, PAHs may undergo volatilisation, photodecomposition and biodegradation or bind to suspended particles or sediments or accumulate in aquatic organisms[94]. However, they are generally of low vapour pressure and possess low tendency to vaporise except among the low molecular weight compounds with two to three fused chain (such as naphthalene) which are in the vapour phase, others range from being only semi volatile (four ringed PAHs) and they are mostly non-volatile[95].

Also, PAHs are known to be chemically stable and are poorly degraded by hydrolysis, they are non-polar organic chemicals with low aqueous solubility; this could be attributed to their highly hydrophobic nature and lipophilic characteristics[96]. Studies have shown that the biochemical persistence of PAHs is due to the presence of dense cloud of pi electrons on both sides of the ringed structure making them resistant to nucleophilic attack[97]. Some PAHs such as chrysene, benzo(a)anthracene and benzo(a)fluoranthene have been found to be susceptible to oxidation and photo degradation in light in aqueous environment; this character is however determined by those of the substrates to which they are attached and the medium[97].

Other works conducted on microbial action on PAHs revealed that, microbial biodegradation of PAHs is rapid for the lower molecular weight compounds such as naphthalene and phenanthrene but the higher molecular weight fractions such as chrysene and benzo(a)pyrene strongly oppose biodegradation by microbes in sediments[97]. Further works carried out also showed that volatilisation and adsorption are primary removal processes for medium and high molecular weight PAHs while volatilisation and biodegradation are the major removal processes for low molecular weight fractions in aquatic environment[97]. Also, high molecular weight PAHs (with four rings and above) have been found to be less acutely toxic but more carcinogenic and teratogenic[97].

The characteristics and reactions of PAHs as discussed in this review as well as in several other reviews could be said to explain why they persist and are found in almost every part of the environment (i.e. they are ubiquitous). This is believed to have made them important pollutants that should be investigated just like many other persistent pollutants[98].

2.8.2 Production of PAHs

Polycyclic Aromatic Hydrocarbons PAHs are not usually produced intentionally, but are the products of incomplete organic combustion that arises from sources that spring up from our day to day human activities (such as residential and commercial burning or cooking, industrial or vehicular fumes from diesel and petroleum engines, asphalt production, coking, coal tar production, burning of garbage or incineration) and they are considered to be anthropogenic; they could also be produced naturally from forest fires and volcanoes[89]. Some PAHs such as benzo(a)pyrene had also been found to originate from petroleum hydrocarbons in the environment due to accidental or intentional release of petroleum products or by-products or as a result of activities of refining crude fractions or utilisation of the products[94].

However, certain PAHs such as anthracene, acenaphthene and acenapthylene have been produced commercially in the United States[98]. The process usually involves great heating; for acenaphthene, the process involves heating up ethylene and benzene or naphthalene[98].

$$3C_2H_4 + C_6H_6 + 2O_2 \rightarrow \text{heating} \rightarrow C_{12}H_{10} + 4H_2O$$

(Ethylene) (Benzene) (Oxygen) (Acenaphthene) (Water)

Chemical reactions such as seen above was also described in a report in the document titled – Health Hazards Associated with PAHs, as organic chemical reactions that utilises simple aromatic compounds and occur by a mechanism called HACA- Hydrogen abstraction Acetylene addition[99].

2.9 Sources of PAHs

PAHs have been found to be almost ubiquitous since they are found everywhere even in interstellar medium; their source would therefore be related to almost everything in the environment and its usage or that of it components[100]. Sources of Polycyclic Aromatic Hydrocarbons PAHs in the environment could be grouped into:

i. Natural sources
ii. Anthropogenic sources

2.9.1 Natural Source

The natural sources of PAHs are from thermal geologic reactions that involves rapid chemical and biological transformation of organic precursors from living or recently living plants or animals (biogenic material), such as wood, coal, limestone, pearls or chalk[101]. Natural sources of PAHs also include underground oil seeps, discharge from chlorophylls plants, fungi and bacteria[102]. The natural sources of PAHs are not usually considered as adding to the bulk of the pollutant in the environment[103].

2.9.2 Anthropogenic Source

Anthropogenic has to do with sources that involve human and human interventions in the environment. Such interventions are those that spring up from day to day activities of human that involves utilisation and incomplete combustion of hydrocarbons in oil[104]. Anthropogenic sources of PAHs could be further grouped into two: Petro-genic Sources and Pyrolytic Sources.

2.9.2.1 Petrogenic Sources

Petrogenic sources of PAHs are due to the intentional or accidental release of petroleum or the refined products from workshops and factories that utilise the products, production tank farms, leaking underground storage pipes, pipeline vandals and other oil spillage actions[94].

According to the work done by an author[101], a typical petroleum fraction may contain 0.2 to more than 7% total Polycyclic Aromatic Hydrocarbons. Petrogenic PAHs from unrefined petroleum sources are found to be mostly of the two to three ringed, low molecular weight compounds; the higher molecular weight fractions are usually at low concentration less than 100mg/kg [101]. The refined products contain the same PAHs as in the parent petroleum as well as small amounts produced by catalytic cracking and other refining processes. Also, the PAHs fractions in different refined oils vary depending on the distillation temperature range of the product; consequently, the two ringed PAHs –

naphthalene and alkyl naphthalene are present in gasoline fuels while diesel fuels, home heating oils and engine oils may contain the four ringed PAHs as well as other aromatic hydrocarbons[101]. Most of the PAHs from petrogenic sources contain an alkyl group on one or more of the aromatic carbons and those in the refined products are usually more abundant than those of the parent compounds in petroleum[101]. Benzo(a)pyrene whose origin is from petroleum hydrocarbons is considered to be probably and possibly carcinogenic in human[94].

2.9.2.2 Pyrolytic Sources

This is the major source of PAHs with three or more rings in the environment[101]. Pyrolysis has to do with heating or loosing composition of a substance by heating[102]. PAHs are released into the environment due to incomplete combustion of organic compounds in fossil fuels or hydrocarbon oils[89]. Combustion is said to be complete when the application of heat breaks up molecules with the ultimate production of carbon (iv) oxide and water[103]. When combustion is incomplete, or the combusted fuel products or oil cool quickly, the small organic chemicals may condense to form new chemicals which include PAHs; these are the pyrolytic polycyclic hydrocarbons PAHs[101]. Examples of human activities that generate PAHs from pyrolytic source are: residential or commercial burning or cooking (including frying, broiling, and smoking), asphalt production, coal tar production, industrial or vehicular exhaust from diesel and petroleum engines, vehicular fumes from highway traffic, burning of garbage and incineration[89].

The PAHs from pyrolytic sources are usually complex and are dominated by the four to five and six ringed fractions. The rings usually have their homologous series dominated by the un-alkylated parent compound or they may contain a homologue with only one or two alkyl substituents[101]. This is determined by the temperature of formation in a given pyrolytic PAHs fraction and there exist an inverse relationship between the temperature of formation and the abundance of alkyl carbons. An example is coal tar (which is produced due to high temperature baking of hard coal in a reducing atmosphere to produce coke and manufactured gas); it is a type of high temperature pyrolytic polycyclic aromatic hydrocarbons and will likely contain few alkyl groups and more unalkylated groups[101].

However, further treatment (such as distillation) of the tar could alter the composition and sometimes produce the two and three ringed PAHs fractions (such as creosote)[101]. Pyrolytic-anthropogenic sources of PAHs could also be linked to the natural sources. This is because of the heating or pyrolysis that occurs during diagenesis (conversion of sediments into rocks or reconstitution of crystals to form a new product). This process however happens naturally and is not known to be directly caused by human intervention[103]. Although, diagenesis of biogenic material which is grouped in this report as well as in many other reports as a natural source is sometimes classified as a pyrolytic or pyrogenic PAHs source. The purpose of classification or grouping is for clarity and understanding based on perception of individual and not in any way meant to be contradictory[104].

2.10 Polycyclic Aromatic Hydrocarbons in the Environment

Polycyclic Aromatic Hydrocarbons (PAHs) as mentioned earlier are ubiquitous substances, that is, they are found almost everywhere and can move from one environmental media (air/atmosphere, water and soil) to the other[105]. They can persist in the environment for a long time[89], and have also been found to be toxic with further studies revealing them to be the most toxic pollutants among the hydrocarbon families[91]. The PAHs possess the ability to undergo biotransformation to toxic metabolites thereby resulting in adverse effects on environmental components and make them important environmental pollutants[91]. Figure 2.3 shows the pathway of PAHs in the environment.

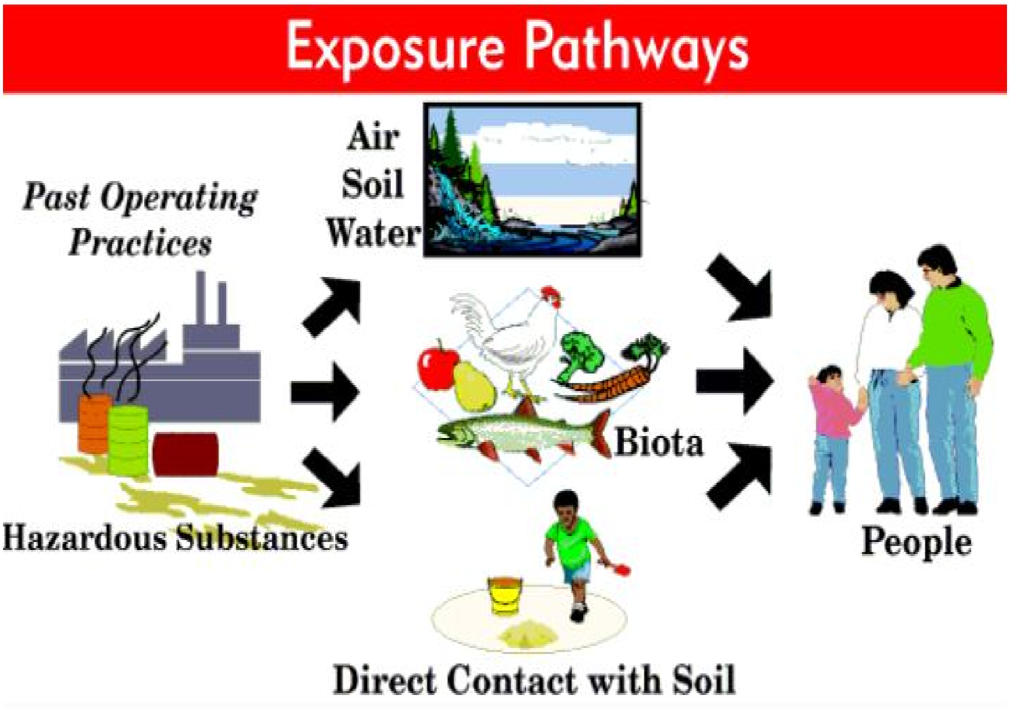

Figure 2.3: PAHs Pathway in the Environment

Source: SRP (2013)

2.10.1 Polycyclic Aromatic Hydrocarbons in Air

Polycyclic Aromatic Hydrocarbons are released into the air from various pyrolytic sources, such as burning of fossil fuels in machines or vehicles and household or commercial burning and incineration, cigarette smoke, or from the natural sources (forest fires and volcanoes); they are usually found attached to dust particles and may be inhaled or due to their heavy molecular weight may be deposited on plants or water surface[106]. PAHs are usually found in ambient air in rural, urban and suburban areas and a wide range can be found in the atmosphere[93]. The air or atmosphere is usually the first point of release of PAHs from several pyrolytic sources and could be inhaled directly by human; this is represented pictorially in Figure 2.4:

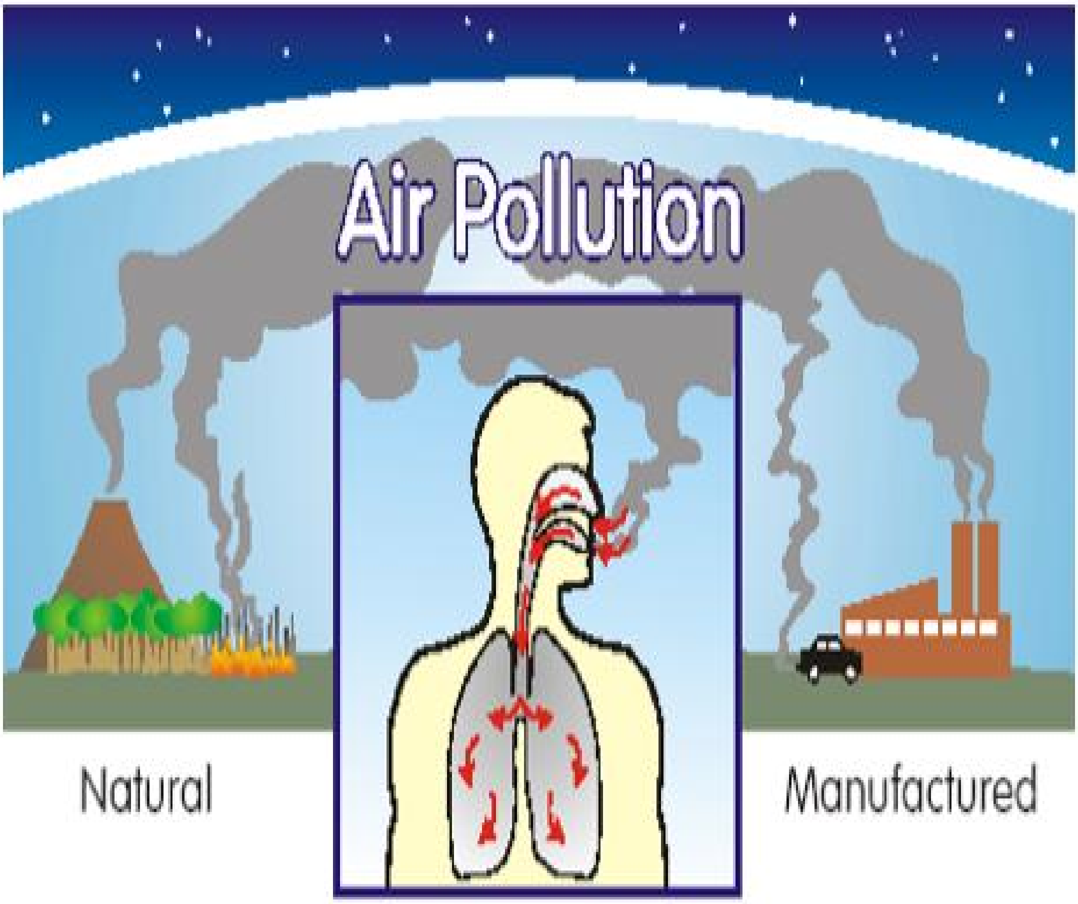

Figure. 2.4: Air Pollution caused by the release of harmful environment Pollutant.

Source: SRP (2013)

In the atmosphere, PAHs could be transformed, degraded or deposited. Deposition could be on vegetation, animals (including birds), humans, aquatic environment and even soil. The processes that transform and degrade PAHs in the atmosphere include photolysis and reaction with NOx, N_2O_5, OH-, ozone, Sulphurdioxide SO_2, and Peroxyacetylnitrate PAN[107]. Possible atmospheric reaction products are oxy-, hydroxy-, nitro- and hydroxynitro-PAH derivatives[107]. Photochemical oxidation of a number of PAHs has also been reported with the formation of nitrated PAHs, quinones, phenols, and dihydrodiols[107]. Reaction with ozone or Peroxyacetylnitrate yields diones; Nitrogen oxide reactions yield nitro and dinitro PAHs[107]. Sulphonic acids have also been formed from reaction with sulphur dioxide. Some of these breakdown products are mutagenic and studies have shown that these products could be more toxic than the parent PAHs compounds[107].

PAHs like many air pollutants reduce air quality. When such air is inhaled, it can produce certain dangerous health defects and this also depends on the length of exposure and the quantity exposed to. Studies have further found that the quantity of PAHs found in the atmosphere in cold season could be more than those found in hot season[93]. This could be related to the absence of sunlight that could act to break down the PAHs (by photodecomposition) and the probable increase in burning to keep warm that could increase heating emissions in the atmosphere. On the contrary however, observation has shown that there is likely to be more fire incidence or outbreak in the dry season than in the wet season which are the two major seasons prevalent in Nigeria (the study area); and could therefore increase the amount of heating emission and probably PAHs in the atmosphere.

2.10.2 Polycyclic Aromatic Hydrocarbons in Soil

The PAHs in soil are usually and mostly from atmospheric deposition due to the pyrolytic sources (such as vehicular exhaust and burning smoke) and the other sources are from the petrogenic sources due to release of petroleum or crude oil from natural oil seeps, spillage and other activities that involve these[107]. In the soil, they are usually found attached to substrates or any oily contaminants present there. They have high sorption capacity (attached strongly to substrate) and are less volatile; as a result, they persist for a long time in the soil[97]. It has been found that the soil as well as sediment are good environmental sink for PAHs and could contain about 90% of these compounds with longer half-life than the atmosphere or in plants[98]. Some PAHs are also sparingly soluble in soil-water and therefore may be found as dissolved there and could enter groundwater and be transported within an aquifer, although this is possible only among the lower molecular weight compounds with two to three rings[108]. PAHs in urban soil may be thought of and have actually been found to be more than that of rural area, due to the increase in vehicular and industrial activities in the urban areas; such PAHs are majorly of the anthropogenic pyrolytic sources[93]. However, most crude oil or petroleum exploits and their related production and activities are usually cited in the rural areas especially in the area under study here (Nigeria); accidental or intentional spillage of oil fractions from various human activities could therefore also increase PAHs in soil from petrogenic sources in addition to those from pyrolytic sources in the rural areas.

2.10.3 Polycyclic Aromatic Hydrocarbons in Aquatic Environment

Polycyclic Aromatic Hydrocarbons from the various sources find their way into aquatic ecosystem by wet and dry atmospheric deposition from incomplete combustion of fossil fuels or hydrocarbons in oil, intake from storm water, drainage water and sewage systems as well as petroleum production, usage and spillage or natural oil seeps[89]. It has also been found that certain plants and animal pigments are able to biosynthesize PAHs in a reducing condition in an aquatic environment (anoxic sediment); this is an indirect biosynthesis of PAHs and it also adds to the bulk of the compound found in such aquatic ecosystem[109]. When PAHs enter aquatic environment, their fate is determined by the type of compound and the characteristics of the substrate to which it is attached; this is because PAHs are complex compounds and they are hardly found as a single substance[109]. Consequently, PAHs in an aquatic environment could evaporate, disperse into the water column, become incorporated into bottom sediments, and concentrate in aquatic biota or experience oxidation and biodegradation[109]. The lower molecular weight polycyclic aromatic hydrocarbons such as naphthalene could easily evaporate and the soluble fractions such as phenanthrene could undergo photo-oxidation and become degraded[109]. Degradation is increased at higher concentration, elevated temperature and oxygen levels and in the presence of much sunlight[109]. The higher molecular weights fractions which are unlikely to dissolve due to their hydrophobic nature are found strongly attached to substrates or particles or adsorb to organic fractions in sediments or absorbed by living organisms in the water; the ultimate fate of such compounds in the sediments is biotransformation and degradation by aquatic organisms[109]. Degradation however occurs very slowly in the absence of oxygen and may persist indefinitely in anaerobic conditions[101].

In addition, studies have shown that all aquatic organisms rapidly bio-concentrate PAHs from low concentration in the ambient water[109]. Other studies conducted also revealed that species lower down on the food chain such as zooplankton, phytoplankton and invertebrates (like mussels and molluscs) can bio-accumulate PAHs. They could still lose much of the accumulated hydrocarbon compounds if clean water is again available. However, if the exposure is chronic, the hydrocarbon may enter more stable tissues (like lipids depot) and as long as the animal is in positive nutritional balance, it will only very slowly release the hydrocarbons[110]. Also, it has been found that colder waters can slow down the metabolism and elimination of hydrocarbons; as a result, animals feeding in arctic waters have a greater chance of bio-accumulating some hydrocarbons[110]. Furthermore, recent studies have shown that biodegradation process which naturally reduces the level of organic pollutant in aquatic environment is mostly effective for the two or three rings PAHs (Naphthalene, Anthracene) while those with more condensed rings are relatively resistant to biodegradation[97].

2.11 Review of Previous Studies on PAHs

In 2015 the total PAHs concentrations at 0-15 cm depth of soil at Igbore, Saje and Alogi dumpsites in Abeokuta metropolis were 29.0 mg/kg, 41.6 mg/kg and 11.9 mg/kg respectively while the corresponding total PAHs concentrations at 15-30 cm depth were 9.3 mg/kg, 28.3 mg/kg and 11.0 mg/kg respectively. These concentrations were slightly lower than the Dutch guideline limits of 40 mg/kg except for that of Saje at 0-15 cm depth. The amounts of fluoranthene at Igbore dumpsite in the two depths were 23.64 mg/kg and 8.02 mg/kg, with a total sum of 10 PAHs compounds of 19.12 mg/kg. The results showed that the highest concentration of a single PAHs compound was at Saje dumpsite with fluoranthene value of 33.75 mg/kg and 22.74 mg/kg at the depths of 0-15 and 15-30 cm respectively. Isomer ratio for fluoranthene/pyrene was 2.69 at Alogi dumpsite, which suggested that the PAHs were from pyrogenic sources. Carcinogenic PAHs constituted about 1.29-15.69% of the total PAHs detected in the dumpsite raising concerns of human exposure through the food chain. The research work showed that there were detectable, variable and non-detectable amounts of the 16 PAHs profile investigated in the soils from three different dumpsites at Saje, Alogi, and Igbore within Abeokuta metropolis. The Saje dumpsite had the highest concentration of PAHs followed by Igbore. The soil samples from Saje and Igbore dumpsites were highly polluted with fluoranthene with an individual mean value (topsoil and subsoil) of 28.25 mg/kg and 15.88 mg/kg respectively and Alogi dumpsite having mean value of 6.28 mg/kg. The total sum for 10 PAHs compounds for Saje dumpsite was 35.49 mg/kg being the highest and only legal dumpsite in Abeokuta metropolis unlike the Alogi and Igbore dumpsites, which are illegal dumpsites. The report also revealed that the dumpsites are principal sources of PAHs in the study area because of the combustion of wastes. Another reason may be due to the increasing vehicular traffic and other human activities around the areas. Uncoordinated and inadequate management of waste material on the dumpsites studied can undoubtedly present a pollution risk and a potential health hazard, therefore improvement in waste management system, restriction on the kind of waste that can be handled, and environmental legislations designed to minimize pollution should all ensure there is no significant risk to the health of the local population. It is recommended that the government should consider a basement treatment for dumpsites before use. This will provide sorption surfaces for pollutant and prevent groundwater contamination. In addition, it is important to ensure longterm safety from hazardous substances generated in the dumpsites[119].

In another study undertaken to determine the influence of compost, bentonite and calcium oxide on the content of polycyclic aromatic hydrocarbons (PAHs) in soils polluted with petrol and diesel oil, using plants as phytoremediators. Contamination of soil with petrol and diesel oil caused an increase in the total PAHs in soil. The effect of diesel oil on the content of PAHs in soil was stronger than that of petrol in the treatments with spring barley and yellow lupine – maize, in reverse to spring rape – oat. Pollution of soil with petroleum substances led to the increased contribution of naphthalene to the total PAHs at the expense of other hydrocarbons. Bentonite and CaO produced an evidently stronger effect on soil properties than compost, in general causing a decline in the content of PAHs in soil. The phytoremediatory effect of plants was the most beneficial in the treatment with spring rape and oat, but the weakest in trials with yellow lupine and maize. Plants were particularly effective in soil polluted with petrol. Plants were particularly effective in soil polluted with petrol. The value of the total PAHs in soil after crop harvest was lower than the permissible values set for soils in Poland. It was only in the treatment with yellow lupine and maize that in some objects polluted with petrol and diesel oil the levels of phenanthrene, fluoranthene and benzo(a)pyrene exceeded the permissible amounts[120].

Soil samples contaminated with spent motor engine oil collected from Abakaliki auto-mechanic site were analysed in 2013 to determine the concentration of polycyclic aromatic hydrocarbon (PAH) components which are often targets in environmental check. Identification and quantification of the PAH components was accomplished using a gas chromatographic system (6890 series and 6890 plus) equipped with a quadrupole Mass Spectrometer (Agilent 5975 MSD) after ultrasonic extraction of the sample and clean up of the extract. The results showed that out of the sixteen USEPA target PAHs (EPA-16) assayed, only six were detected in varying concentrations in mg/kg. These include Phenanthrene with concentration range of 0.0172 ± 0.01 to 0.0193 ± 0.02, fluorene (0.0189 ± 0.01), benzo[a]anthracene (0.0162 ± 0.05), chrysene (0.0209 ± 0.02), benzo[b]fluoranthrene (0.0453 ± 0.02) and benzo[k]fluoranthrene (0.0389 ± 0.1). The concentration of total PAH components detected in the samples ranged from 0.0184 ± 0.02 to 0.1385 ± 0.2 mg/kg. Implications of PAHs on health were discussed. It is evident from the study that the Abakaliki auto-mechanic site is gradually being contaminated with PAHs arising from indiscriminate disposal of spent crankcase engine oils. As the city is expanding with more business outlay emerging, recycling and re-use advocacy is being recommended to track the spread of waste oils in the environment. The risk associated with the PAHs components of the spent engine oils are grave and needed to be tracked and regularly monitored not only in soils but also in water, air, vegetables and other plants in the area[121].

In 2012, the analysis of the 16 polycyclic aromatic hydrocarbons (PAHs) priority pollutant list was carried out in sediment samples of an industrial port in the southern Kaohsiung Harbor of Taiwan which is supposed to be extensively polluted by industrial wastewater discharges. The determination and quantification of PAHs in sediment samples were performed using gas chromatography coupled to mass spectrometry (GC-MS) with the aid of deuterated PAH internal standards and surrogate standards. The total concentrations of the 16 PAHs varied from 4,425 to 51,261 ng/g dw, with a mean concentration of 13,196 ng/g dw. The PAHs concentration is relatively high in the river mouth region, and gradually diminishes toward the harbor region. Diagnostic ratios showed that the possible source of PAHs in the industrial port area could be coal combustion. As compared with the US Sediment Quality Guidelines (SQGs), the various observed levels of PAHs exceeded the Effects Range Median (ERM), and could thus cause acute biological damages. The results can be used for regular monitoring, and future pollution prevention and management should target the various industries in this region for reducing pollution. This indicates that the major sources of sediment PAHs came from the polluted urban rivers. The possible source of PAHs in the industrial port area could be coal combustion. As compared with the US Sediment Quality Guidelines (SQGs), several of the observed PAH levels exceeded the Effects Range Median (ERM), and could thus cause acute biological damage. The results should be useful in designing future strategies for environmental protection of the port, with special focus on the area at industrial zone dock[122].

Recently, the concentration of sixteen polycyclic aromatic hydrocarbons were determined in soil samples at AL-nahrawan bricks factory at Baghdad city, Iraq. The measured period was two seasons' summer and winter. The soil samples collected from surface and depth chosen site and analyzed by GC apparatus. The most abundant compounds in the summer season were naphthalene, acenaphthene, fluorene, pyrene and benzo [a] anthracene, while in the winter were naphthalene, acenaphthene, fluorine, benzo [k] fluoranthene, benzo [a] pyrene. The concentrations of 16 PAH in the summer were higher than in the winter season. The concentration varied in the surface and depth soil as well as in the summer and winter seasons. The most polycyclic aromatic hydrocarbons speared were low molecular weight. The most abundant compound in the summer season was naphthalene[123].

However, in the Marshy soil and sediment within Warri and its environs, Benzo(a)pyrene out of the 16 priority Polycyclic Aromatic Hydrocarbons PAHs had highest total concentration of 3.302mg/kg and mean value of 1.651mg/kg in dry season soil samples. However, sediment samples had highest levels for total concentration of PAHs of 19.362mg/kg and mean of 4.840mg/kg for both dry and rainy seasons within Warri. PAHs concentration was higher in dry than rainy seasons for soil and sediment samples. Source prediction analysis revealed that PAHs in sediments for dry season were pyrolytic while rainy seasons were petrogenic sources. For soils, the dry season was mixed sources while the rainy season was petrogenic[124].

2.12 Atomic Absorption Spectrometry (AAS) Instrumentation

The AAS is a method of elemental analysis that works on the principle of absorption of radiation energy by free atoms. The concentration of an element is measured by the absorption of radiation with a characteristic frequency by free atoms of an element. Light of certain wavelength produced by monochromatic or hollow cathode lamp emits spectral lines corresponding to energy required for excitation of an element of interest[125]. The analytical signal is obtained from the signal between the intensity of the source in the absence of the element of interest and the decreased intensity obtained when the element of interest is present in the optical path. Absorption of light is associated with the transition process from one steady state to another[126]. For instance the case of a steady state O and J, where Eo<Ej, the o-j transition results in the absorption of light with frequency given in Equation 2.1 [13].

$Voj = (Ej-Eo) / h$ ……………………………………………..(2.1)

Where:

h = plank‘s constant

V = frequency

Eo = energy at ground state

Ej = energy at excited state

o-j= transitions stimulated by absorption of external radiation

The number of atoms in the excited state relative to the number in the ground state is given by the Maxwell-Boltzmann law, given in Equation (2.2).

$N_1/N_o = g_1/g_o\exp [E_g-E_1/KT]$………………………………..(2.2)

Where;

N_1 = Number of atoms in excited state

N_o = Number of atoms in ground state

g_1 and g_o = Statistical weight of excited and ground state respectively

K = Boltzman's constant

T= Absolute temperature

E_g = Energy at ground state

E_1 = Energy at excited state

Relative fraction of atoms in excited state is dependent on temperature whereas intensity is independent on temperature. Sample solution is aspirated through nebulizer into the air/acetylene flame or nitrous oxide/acetylene flame[127]. An electrically heated graphite furnace is used when very high sensitivity is required. The sample solution gets dispersed into mist of droplets and then gets evaporated into dry salt. The dry salt goes into vapour then dissociates into atoms that absorb resonance radiation from external source. The unabsorbed radiation is allowed to pass through the monochromator which isolates the existing spectral lines. The isolated analyte line falls on the detector and the output of which is amplified and recorded. The parameter measured is absorbance (A) and related to concentration by Equation (2.3).

$A = \log I_o/I = \varepsilon cl$………………………………………… (2.3)

Where;

A = Absorbance

I_o = Incident radiation

I = Attenuated radiation

ε = molar absorptivity (L mol-1cm -1)

c = Concentration (mol dm-3)

l = Path length (cm)

Since the relationship between absorbance (A) and concentration (C) is linear over a wide range of concentration (Beer‘s law), standards are used to obtain calibration curve from which concentration of analyte is established through interpolation method[128]. The Schematic representation of AAS is shown in Figure 2.5.

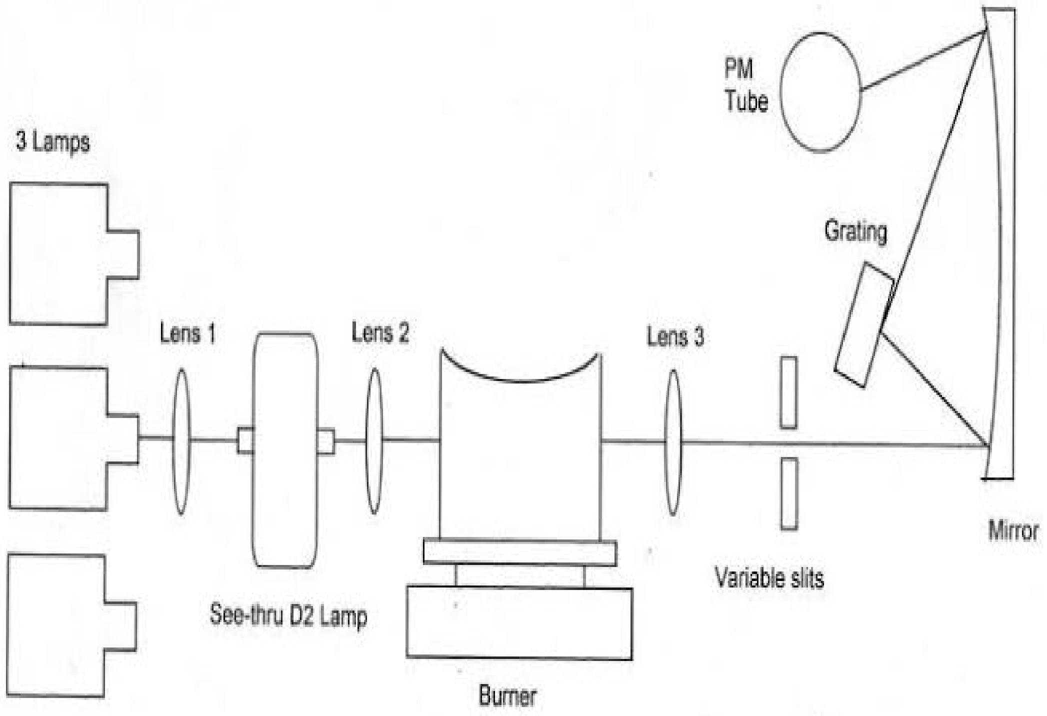

Figure 2.5: Schematic Representation of AAS

Source: S. Taylor (2006)

2.13 Gas Chromatography Analysis of PAHs

Polycyclic Aromatic Hydrocarbons from various samples can be quantified by passing them through chemical analysis in the laboratory. The method applied depends on the sample source; whether it is from food sample or from environmental media. It is also determined by the type of analysis required at a given time. Chemical analysis could be required for legislation, monitoring for detection of frauds or compliance to limits, and monitoring for exposure limits in risk assessment procedure[129]. No matter the sample source of the PAHs, extraction and pre-concentration steps are usually required for sample enrichment especially when the source is from uncontaminated aqueous samples[89]. Several extraction techniques have been used to extract PAHs from various sample sources. For environmental samples, solid-liquid and liquid-liquid extraction have been used for soil, sediment and water samples; some of the methods used are Soxhlet Extraction SE, Supercritical Fluid Extraction SFE and Pressurised Liquid Extraction PLE[129]. Even simpler extraction techniques, such as liquid extraction at room temperature on a shaking device, were shown to be suitable for extracting PAHs from soil. These methods have been proven and approved by US Environmental Protection Agency US EPA has been effective for extracting the 16 PAHs that are considered to be of priority[129].

After extraction, the next stage in the analytical process of PAHs is sample clean-up. This stage is necessary in order to remove any co-extractives (compounds that are extracted together with the PAHs in the extraction process) and produce a pure PAHs sample for chromatographic analysis. Examples of extracts that could be present are: aliphatic hydrocarbons, porphrins, chlorins and carotenoids. Sample clean-up and consequently pre-concentration could take place during adsorption chromatography with silica gel, alumina or florisil[129] and during fractional distillation into aliphatic and aromatic fractions using activated alumina (neutral) column with n-hexane and Dichloromethane. The n-hexane removes the aliphatic hydrocarbons while Dichloromethane separates the aromatic fraction. The clean-up method required depend largely on the selectivity of the applied extraction techniques and on the chromatographic method to be applied later on the pure sample; for instance, SFE extracts of urban air particles in a particular analysis carried out to monitor PAHs contained fewer co-extractives than SE or PLE extracts. And this was attributed to the fact that SE and PLE apply non-polar organic solvents which also dissolves humic acids and aliphatic hydrocarbons; subsequently, silica gel or alumina was used for the clean-up during adsorption chromatography[129]. After the clean-up, a pre-concentrated sample is derived which could still be pass through a further concentration process by placing the extract in a rotary vacuum evaporator or by exposing the extracts to laboratory room temperature for at least 24 hours until a concentrated extract of about 0.5-1.0ml is gotten. The concentration or sample enrichment could also be achieved by means of a suitable enrichment device – under a gentle Nitrogen gas stream[130].

The next stage is the actual analysis of the prepared samples and the method usually employed for PAHs is Chromatography. Gas chromatography with mass spectrometry GC-MS detection operated in selected ion monitoring SIM as well as high performance liquid chromatography with fluorescence detection HPLC-FLD are methods that have been used for analysis of PAHs. The International Standard Organisation ISO standard 13877:1998 describes a method for the determination of PAHs in soil by HPLC, and very recently published standard ISO 18287:2006 for the determination of PAHs in soil by GC-MS[129]. Also, in WHO guidelines report for drinking water quality, gas chromatography with flame ionisation detection GC-FID was used for analysing PAHs in drinking water[89].

2.13.1 Gas Chromatography Instrumentation

Chromatography is a mixture separating technique for compounds containing several solutes. It is suitable for identification of the various compounds present in a mixture of solutes as well as determining the amount present; it is therefore a useful tool for qualitative and quantitative analysis of chemical samples. The method involves the use of a solvent which could be gas, liquid or adsorbent medium (paper or gel) moving over another solvent; they are usually classified as having a stationary and a mobile phase[131]. There are many techniques in Chromatography, and Gas Chromatography GC is one of them; there is also liquid chromatography in which the mobile phase is a suitable solvent and adsorption chromatography in which the mobile phase is a suitable solid. The major difference between them is in the type of mobile phasing used[131]. Gas Chromatography has been extensively utilised in scientific research to analyse and identify substances. It has been estimated that 10-20% of known compounds can be estimated by GC and it is one of the preferred technique for PAHs analysis because of the way it works[132].

Gas chromatography as illustrated in the diagram (Figure. 2.6 and Figure 2.7), works by using a gas called the carrier gas to move the solutes or samples (usually in the liquid state) when they are vaporised in a heating column through a stationary phase such that they are analysed and the result are read through a detector attached to the column.

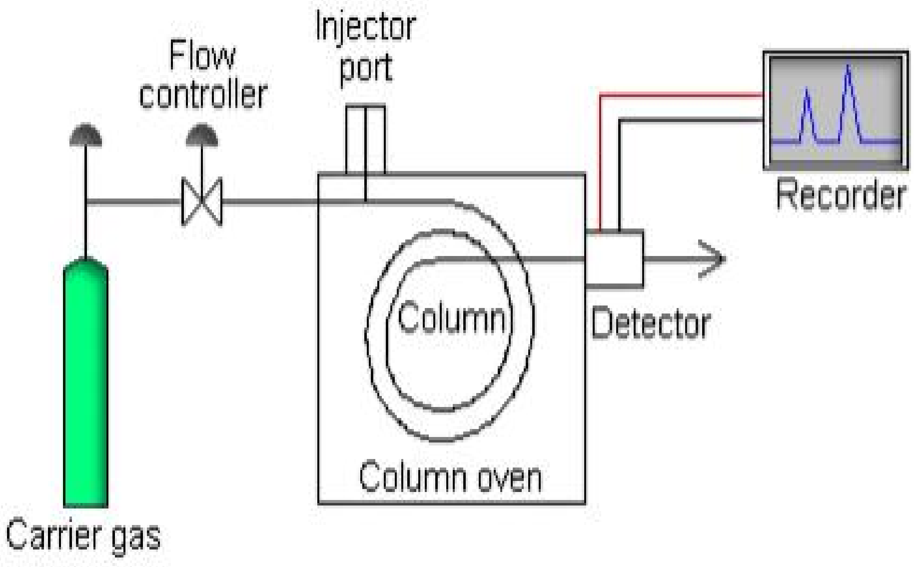

Figure. 2.6: Schematic representation of a Gas Chromatography.

Source: SHU (2013)

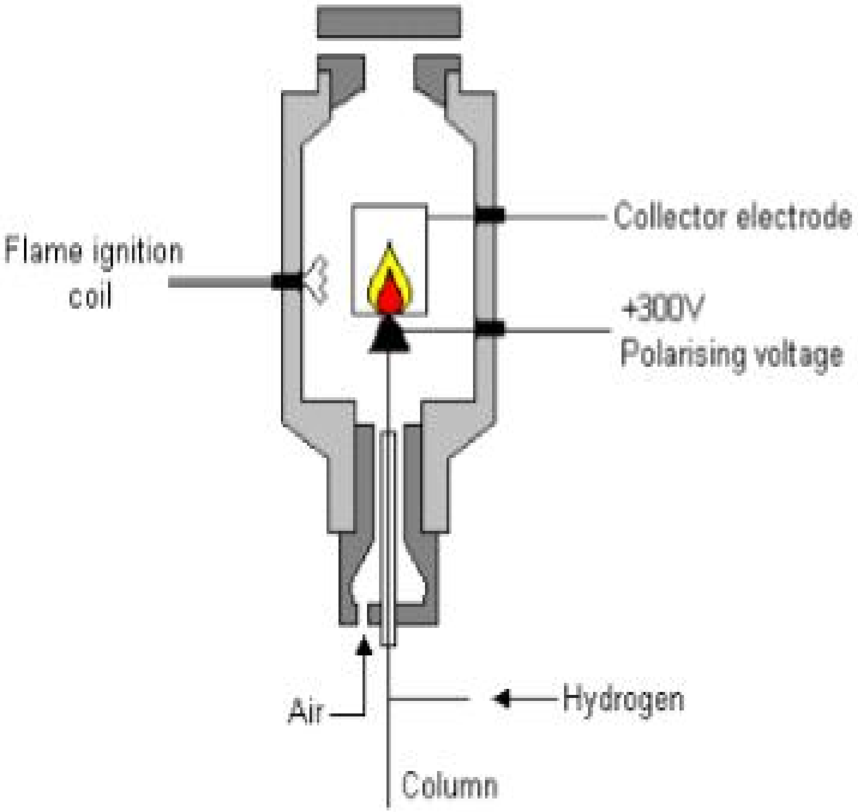

Figure 2.7: Schematic Representation of a Flame Ionisation Detector FID

Source: SHU (2013)

To be suitable for GC, the solutes must be sufficiently volatile and stable to high temperature; if the solutes do not decompose at high temperature when heated, then it is suitable for GC analyses. This is one of the reasons why GC is preferred for analysis of PAHs[132]. The sample to be analysed is introduced into the column through the injector by means of a micro-syringe, it is heated by the oven in the heating column and moved by the carrier gas which is usually an inert gas (such as: nitrogen, argon, helium or carbon (iv) oxide) through the column until they have been analysed and detected by a monitoring device which sends the signal to a recorder. The solute with the lowest temperature emerges first followed by the next until all the compounds present in the sample have been analysed.

The emergence of the samples is determined by their physical properties and temperature and composition of the heating column[133]. As the solutes emerge in the detector, the readings are recorded as electronic signal on the monitor and this is what is read as the chromatogram. The ideal chromatogram is a closely spaced wave signal plotted against the elapse time with different peaks for different solutes. The peak of the chromatogram indicates the quantity of that solute present in the mixture while the retention time which is the time it takes before the sample elapses could be used to determine the type or identify the compound present.

However, using the chromatogram peak and the retention time alone is not enough to know the quantity and type of the solute present. A known standard which is a pure sample containing similar solutes is subjected to similar column condition and the chromatogram peaks and retention times compare with that of the unknown sample and the result is determined. One condition necessary to have good chromatogram peak and hence good result is to ensure that only a small amount of the solutes sample is injected into the column; this will ensure that the emerging chromatograms are not overlapped and therefore measured distinctly.

The detector is also another important part of the GC components as it is the one that determines the type of reading that will be produce by the recorder. It is therefore necessary that the detector be very effective in detecting the result of the analysis and in yielding a good signal for recording. There are a few detectors used with chromatography in PAHs analysis and they include fluorescent detector, flame ionisation detector and mass spectrometry[134].

Endnotes

1. O. Harrison, *Environmental Impact of End of Life Tyre (ELT) or Scrap Tyre Waste Pollution and the Need for Sustainable Waste Tyre Disposal and Transformation Mechanism in Nigeria* **NAUJILJ** 10 (2) 2019.

2. D.R. Chris, *What are the Environmental Impacts of Throwing Away Tires?*' 2018, Available Online: https://homeguides.sfgate.com/environmental-impacts-of-throwing-away-tires-79649.html>

3. A. Merchant & J.M. Torkelson, *Pyrolysis of Scrap Tires,* Chemical Engineering Dept., Northwestern U., Spring, 2020.

4. The Waste & Resources Action Programme, *UK Waste Tyre Management Best Practice: Handling of Post-Consumer Tyres* – **Collection & Storage**: 2016, 1.

5. M.F. Fora, *Scrap Tyre Recycling In Nigeria; The Pre-Feasibility Report'*, 2018, reports/manufacturing-market-research-reports/scrap-tyre-recyclying-in-nigeriathe-pre-feasibility-report-2/>

6. A.C. Friday & J.N. Nwite, *Implications of Roasting Goats with Tyre on Human Health and the Environment in Abakaliki, Ebonyi State Nigeria*, **Journal of Pollution Effects and Control**, 2015, 1-4.

7. M. David, *Tire Pyrolysis is being Rolled Out in the USA', Bridging the Gulf for a Greener Tomorrow*, 2017

8. IPCS, *Arsenic. Geneva, World Health Organization, International Programme on Chemical Safety* (Environmental Health Criteria 18) 2021..

9. S. Kirti, C. Sreemoyee & J. Bhumika, *Chromium Toxicity and its Health Hazards.* **International Journal of Advanced Research,** Volume 3, Issue 7, 2015, 167-172

10. D.H. Klein & E.D. Goldberg, *Mercury in the Marine Environment*. **Environ. Sci. Technol,** 4 2020, 765-768

11. O. Idowu, K.T. Semple, K. Ramadass, W. O'Connor, P. Hansbro & P. Thavamani, *Beyond the obvious: environmental health implications of polar polycyclic aromatic hydrocarbons*, **Environ. Int.,** 123, 2019, 543–557. https://doi.org/10.1016/j.envint.2018.12.0.

12. A. Emmannuel, S.J. Cobbina, D. Adomako, A.B. Dewijuah & W. Asare, *Assessment of Heavy Metals Concentration in Soils Around Oil Filling and Service*

Stations in Tamale Metropolis Ghana. **African Journal of Environmental science and Technology**. Vol 8(4) 2014, pp256-266. Doi:10.6897/AJEST2014.1664

13. R. Eva, S. Rimute, J. Kęstutis, V. Darius, B. Steigvile & Z. Aleksej, *Distribution of Polycyclic Aromatic Hydrocarbons and Heavy Metals in Soil Following A Large Tire Fire Incident: A Case Study*. **Chemosphere** 286, 2021. 131556 Available Online: https://doi.org/10.1016/j.chemosphere.2021.131556

14. V. Alpa & M. Kapila, *Analysis of Heavy Metals in Soil Samples Collected at three Different Industrial Creeks of Surat, India*, **Int.J.Curr.Microbiol.App.Sci.,** 4(6): 2015, 281-286

15. A.J. Yusuf, A. Galadima, Z.N. Garba & I. Nasir, *Determination of some Heavy Metals in Soil Sample from Illela Garage in Sokoto State, Nigeria.* **Research Journal of Chemical Sciences,** Vol. 5(2), 2015, 8-10.

16. P.O. Fatoba, C.O. Ogunkunle, S. Oyedeji & M.B. Salawudeen, *Metal Depositions around some Petroleum Product Depots in Nigeria, using Mosses as Biomonitors*, **The Bioscientist**, Vol. 1(1), 2013, 99-105.

17. P.O. Oyeleke, O.A. Abiodun, R.A. Salako, O.E. Odeyemi & T.B. Abejide, *Assessment of some Heavy Metals in the Surrounding Soils of an Automobile Battery Factory in Ibadan, Nigeri,* **African Journal of Environmental Science and Technology,** Vol. 10(1), 2016, pp. 1-8, DOI: 10.5897/AJEST2015.

18. K.E. Ajibulu, O.S. Adefemi, S.S. Asaolu & G.I. Oyakhilome, *Determination of Heavy Metals in Soil Samples of Selected Sawmills in Ekiti State,* **Nigeria. Journal of Scientific Research & Reports,** 2(2), 2013, 513-521

19. P.B Utang, O.S. Eludoyin & C.L. Ijekeye, *Impacts of Automobile Workshops on Heavy Metals Concentrations of Urban Soils in Obio/Akpor LGA, Rivers State, Nigeria,* **African Journal of Agricultural Research,** Vol. 8(26), 2013, pp. 3476-3482. DOI: 10. 5897/AJAR2013.6753

20. O.O. Olayinka, O.H. Adedeji & R.A. Ipeaiyeda, *Determination of Polycyclic Aromatic Hydrocarbons (PAHs) on Selected Dumpsites in Abeokuta Metropolis, SW, Nigeria***, Applied Environmental Research**, 37 (3), 2015, 33-48

21. M. Wyszkowski & A. Ziółkowska, *Content of Polycyclic Aromatic Hydrocarbons In Soils Polluted With Petrol and Diesel Oil After Remediation With Plants and Various Substances,* **Plant Soil Environ.,** Vol. 59, No. 7, 2013, 287–294

22. U. Obini; C.O. Okafor & J.N. Afiukwa, *Determination of Levels of Polycyclic Aromatic Hydrocarbons in Soil Contaminated with Spent Motor Engine Oil in*

Abakaliki Auto-Mechanic Village. **J. Appl. Sci. Environ. Manage.**, Vol. 17 (2), 2013, 169-175

23. C.D. Dong, C.F. Chen & C.W. Chen, *Determination of Polycyclic Aromatic Hydrocarbons in Industrial Harbor Sediments by GC-MS,* **Int. J. Environ. Res. Public Health,** 9, 2012, 2175-2188; doi:10.3390/ijerph9062175

24. T.K.M. Al-Rudaini & I.M.H. Almousawi, *Determination of Polycyclic Aromatic Hydrocarbons In Soil At Al-Nahrawan Bricks Factory,* **Pak. J. Biotechnol.**, 15 (2) 2018, 445-450

25. A.V. Bayowa, *Levels of Polycyclic Aromatic Hydrocarbons (PAHs) in Marshy Soils and Sediments within Warri and its Environs, Nigeria.* MSc Thesis, University of South Africa 2014.

26. SRP, *Superfund Research Program. OSU Oregon State University, PAH mixtures: New Technologies and Emerging Health Risks,* 2013. Available Online: www.oregonstate.edu/superfund/about-PAHs.

27. SHU, *Sheffield Hallam University SHU, Biosciences homepage, Gas Chromatography,* 2013. Available Online: www.teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm.

28. F.O. Ajibade, O.O. Olajire, T.F. Ajibade, N.A. Nwogwu, K.H. Lasisi, A.B. Alo, T.A. Owolabi & J.R. Adewumi, *Combining Multicriteria Decision Analysis with GIS for Suitably Siting Landfills in a Nigerian State*. **Environ. Sustain. Indic**. 3–4, 2019, 100010. https://doi.org/10.1016/j.indic.2019.100010.

29. J.R. Adewumi, O.J. Ejeh, K.H. Lasisi, & F.O. Ajibade, *A GIS-AHP Based Approach in Sitting MSW Landfills in a Nigerian Confluence State*. **SN Appl. Sci**. 1, 2019, 1528. https:// doi.org/10.1007/s42452-019-1500-6.

30. O.O Elemile, M.K.C. Sridhar & O.E. Oluwatuyi, 2019. *Solid Waste Characterization and its Recycling Potential: Akure Municipal Dumpsite, Southwestern, Nigeria*. **J. Mater. Cycles Waste Manag.** 21, 2019, 585–593. https://doi.org/10.1007/s10163-018-00820-2

31. M. Ahmed, M. Matsumoto, & K. Kurosawa, *Heavy Metal Contamination of Irrigation Water, Soil, and Vegetables in a Multi-Industry District of Bangladesh.* **Int. J. Environ. Res.** 12, 2018, 531–542. https://doi.org/10.1007/s41742-018-0113-z.

32. W.H. Gu, J.F. Bai, W.H. Yuan, E. Ma, C.L. Zhang, & J.W. Wang, *Pollution Analysis of Soil Polycyclic Aromatic Hydrocarbons from Informal Electronic Waste Dismantling Areas in Xinqiao, China.* **Waste Manag. Res.** 37, 2019, 394–401.

33. M.J. He, S.Y. Yang, J. Zhao, C. Collins, J.M. Xu, & X.M. Liu, *Reduction in the Exposure Risk of Farmer from E-Waste Recycling Site Following Environmental Policy Adjustment: A Regional Scale View of PAHs in Paddy Fields*. **Environ. Int.** 133, 2019, 105136.

34. H. Huang, C. Cai, S. Yu, X. Li, Y. Liu, S. Tao, & W. Liu, *Emission Behaviours of Nitro- and Oxy-Polycyclic Aromatic Hydrocarbons During Pyrolytic Disposal of Electronic Wastes*, **Chemosphere,** 222, 2019, 267–274.

35. G.A. Ebong, M.M. Akpan, & V.N. Mkpenie, *Heavy Metal Contents of Municipal and Rural Dumpsite Soils and Rate of Accumulation by Carica Papaya and Talinum Triangulare in Uyo, Nigeria.* **E-J. Chem.** 5, 2008, 281–290. https://doi.org/10.1155/2008/ 854103

36. G.A. Ebong, E.U. Dan, E. Inam, & N.O. Offiong, *Total Concentration, Speciation, Source Identification and Associated Health Implications of Trace Metals in Lemna Dumpsite Soil, Calabar, Nigeria.* **J. King Saud Univ. Sci.** 2018, https://doi.org/10.1016/ j.jksus.2018.01.005.

37. M.D. Vaverkova, J. Winkler, D. Adamcova, M. Radziemska, D. Uldrijan, & J. Zloch, *Municipal Solid Waste Landfill – Vegetation Succession in an Area Transformed by Human Impact.* **Ecol. Eng.** 129, 2019, 109–114. https://doi.org/10.1016/ j.ecoleng.2019.01.020.

38. O.O. Ololade, S. Mavimbela, S.A. Oke & R. Makhadi, *Impact of Leachate from Northern Landfill Site in Bloemfontein on Water and Soil Quality: Implications for Water and Food Security*. **Sustainability.** 2019; 11: 4238.

39. N.O. Eddy, S.A. Odoemelem, & A. Mbaba, A. *Elemental Composition of Soil in Some Dumpsites.* **Journal of Environmental Agricultural Food Chemistry,** 5, 2016, 1349-1365

40. M.O. Eze, *Evaluation of Heavy Metal Accumulation in Talinum triangulare Grown Around Municipal Solid Waste Dumpsites in Nigeria*. **Bull. Environ. Pharmacol. Life Sci.,** 4 (1), 2014, 92-100.

41. A. Hammed, L.A. Olayiwola, K. Gbola, M. Adewuyi, & O. Azeez, *Heavy Metal Contents in Soil and Plants at Dumpsites: A Case Study of Awotan and Ajakanga Dumpsite Ibadan, Oyo State, Nigeria.* **J. Environ. Erath Sci.,** 7(4): 2017, 1-14.

42. O.T. Ogunmodede, E. Adewole, & A. Ojo, *Quantitative Changes in Soils Properties and Uptake of Metals on Municipal Solid Waste Dumpsite in Nigeria,* **Int. Lett. Chem., Phys. Astron.,** 52: 2015, 152-162

43. E. Olagunju, O. Badmus, F. Ogunlana, & M. Babalola, *Environmental Impact Assessment of Waste Dumpsite using Integrated Geochemical and Physico-Chemical Approach: A Case Study of Ilokun Waste Dumpsite, Ado Ekiti, Southern Nigeria*, **Civil Eng. Res. J.**, 4(2): 2018, 1-13.

44. S.E. Olatunde & M.O. Onisoya, *Assessment of Heavy Metal Concentrations in Pawpaw (Carica papaya Linn.) around Automobile Workshops in Port Harcourt Metropolis, Rivers State, Nigeria*, **J. Health Pollut**. 14: 2017, 48-61.

45. O.A. Olayiwola, & C.T. Onwordi, *Environmental Fate of Heavy Metals in Soil of Ido-Osun Waste Dump Site, Osogbo, Osun, Nigeria*, **Am. J. Environ. Prot.,** 3(1): 2015, 1-4

46. P.O Oyeleke, O.A. Abiodun, R.S. Salako, O.E. Odeyemi, & T.B. Abejide, *Assessment of some Heavy Metals in the Surrounding Soils of an Automobile Battery Factory in Ibadan, Nigeria,* **Afr. J. Environ. Sci. Technol.,** 10(1): 2016, 1 – 8.

47. M.S. Shokr, A.A. El Baroudy, M.A. Fullen, T.R. El-beshbeshy, A.R. Ramadan, A. Abd El Halim, A.J.T. Guerra, & M.C.O. Jorge, *Spatial Distribution of Heavy Metals in the Middle Nile Delta of Egypt,* **Int. Soil Water Conserv. Res.,** 4: 2016, 293-303

48. R. Twinamatsiko, J. Mbabazi, & H. Twinomuhwezi, *Toxic Metal Levels in Food Crops Grown from Dump-Sites Around Gulu Municipality, Northern Uganda*, **Int. J. Soc. Sci. Technol.,** 1(1): 2016, 22-45.

49. A. Shitandayi, F. Orata & F. Lisouza, *Assessment of Environmental Sources, Levels and Distribution of Polycyclic Aromatic Hydrocarbons Within Nzoia Catchment Area in Kenya*. **Journal of Environmental Protection**, 10(6): 2019, 772-790.

50. N.J. Edokpayi, J.O. Odiyo, O.E. Popoola & T.A.M. Msagati, *Determination and Distribution of Polycyclic Aromatic Hydrocarbons in Rivers, Sediments and Wastewater Effluents in Vhembe District, South Africa*. **Int J Environ Res Public Health,** 13(4): 2016, 387.

51. O.S. Edori, & W.A. Iyama, *Source Identification of Polycyclic Aromatic Hydrocarbons in Water at Point of Effluent Discharge into the New Calabar River, Port Harcourt, Rivers State*, **Nigeria. International Journal of Environment and Climate Change,** 9(6): 2019, 343-349

52. L. Xiaoyan, B. Zhongke, Y. Qinfei, C. Yingui & Z. Wei, *Polycyclic Aromatic Hydrocarbons in the Soil Profiles (0-100cm) from the Industrial District of a Large Open-Pit Coal Mine, China*. **Royal Society of Chemistry Advances** 7(45): 2017, 28029-28037.

53. A.A. Adeyi & P. Oyeleke, *Heavy Metals and Polycyclic Aromatic Hydrocarbons in Soil from E-waste dumpsites in Lagos and Ibadan, Nigeria*. **J Health Pollut** 7(15): 2017, - 84.

54. M.J. He, S.Y. Yang, J. Zhao, C. Collins, J.M. Xu, & X.M. Liu, *Reduction in the Exposure Risk of Farmer from E-Waste Recycling Site Following Environmental Policy Adjustment: A Regional Scale View of PAHs in Paddy Fields,* **Environ. Int**. 133, 2019, 105136bi X. Huang, X. Xu, Y. Dai, Z. Cheng, X. Zheng, & X. Huo, *Association of Prenatal Exposure to PAHs with Anti-Mullerian Hormone (AMH) Levels and Birth Outcomes of Newborns,* **Sci. Total Environ**. 723, 2020, 138009.

55. X. Huo, Y. Wu, L. Xu, X. Zeng, Q. Qin, & X. Xu, *Maternal Urinary Metabolites of PAHs and its Association with Adverse Birth Outcomes in an Intensive E-Waste Recycling Area,* **Environ. Pollut**. 245, 2019, 453–461.

56. L.F. Jiang, Z.N. Cheng, D.Y. Zhang, M.K. Song, Y.J. Wang, C.L. Luo, H. Yin, J. Li, & G. Zhang, *The Influence of E-Waste Recycling on the Molecular Ecological Network of Soil Microbial Communities in Pakistan and China*. **Environ. Pollut.,** 231, 2017, 173–181.

57. R. Jin, G.R. Liu, M.H. Zheng, X.X. Jiang, Y.Y. Zhao, L.L. Yang, X.L. Wu & Y. Xu, *Secondary Copper Smelters as Sources of Chlorinated and Brominated Polycyclic Aromatic Hydrocarbons*, **Environ. Sci. Tech**., 51, 2017, 7945–7953.

58. M. Lin, J. Tang, S. Ma, Y. Yu, G. Li, B. Mai, R. Fan, & T. An, *Simultaneous Determination of Polybrominated Diphenyl Ethers, Polycyclic Aromatic Hydrocarbons and their Hydroxylated Metabolites in Human Hair: A Potential Methodology to Distinguish ExternalfFrom Internal Exposur*e. **Analyst** 144, 2019, 7227–7235.

59. M.O. Onyema, L.C. Osuji & B.O. Isiuku. *Compositional Alteration of Polycyclic Aromatic Hydrocarbons by Burning Oil Spilled Soils,* **Academia Journal of Environmental Science,** vol. 4(11), 2016, pp. 213-219.
60. O.S. Edori, O.A. Ekpete, & W.A. Iyama, *Concentrations of Polycyclic Aromatic Hydrocarbons from Selected Dumpsites Within Port Harcourt Metropolis, Rivers State, Niger Delta, Nigeria.* **International Journal of Environmental Science & Natural Resources**. 2 (4) 2019, 556066. DOI: 10.19080/IJESNR.2019.21.556066.

61. C. Peng, M. Wang, Y. Zhao, & W. Chen, *Distribution and Risks of Polycyclic Aromatic Hydrocarbons in Suburban and Rural Soils of Beijing with Various Land Uses,* **Environmental Monitoring and Assessment**, 188: 2016, 162.

62. D.B. Bahiru, E. Teju, T. Kebede & N. Demissie, *Levels of Some Toxic Heavy Metals (Cr, Cd and Pb) in Selected Vegetables and Soil Around Eastern Industry Zone, Central Ethiopia,* **African Journal of Agricultural Research,** 14(2), 2019, pp. 92-101.

63. O.B. Akintan, J.A. Olusola, & A.M. Azeez, *Heavy Metals Loads in Soil, Farmlands and Plant Crop at Open Dumpsite*. **Global J. Environ. Sci. Manage.,** 5(4): 2019, 449-460.

64. G.A. Ebong, M.M. Akpan & V.N. Mkpenie, *Heavy Metals Contents of Municipal and Rural Dumpsite Soils and Rate of Accumulation By Carica papaya and Talinun triangulare in Uyo, Nigeria*, **E-J. Chem**., 5(2): 2018, 281 – 290.

65. S.S. Olubunmi, J.A. Olufemi, Augustus O. A. I., Abidemi O. F. and Adetola, T. A. *Heavy Metal Contamination of a Dumpsite Environment as Assessed with Pollution Indices*. **International Journal of Agricultural and Biosystems Engineering**.12(1): 2018, 1-7

66. F.O. Ajibade., B. Adelodun, T.F. Ajibade, K.H. Lasisi, C. Abiola, J.R. Adewumi, & C.O. Akinbile, *The Threatening Effects of Open Dumping on Soil at Waste Disposal Sites of Akure City, Nigeria*. **Int. J. Environ. Waste Manag**. 2019b (Manuscript accepted) https://www.inderscience.com/info/ingeneral/forthcoming.php?jcode¼ijewm

67. A. Cesaro, V. Belgiorno, G. Gorrasi, G. Viscusi, M. Vaccari, G. Vinti, G., Jandric, A., Dias, M.I., Hursthouse, A., & Salhofer, S., *A Relative Risk Assessment of the Open Burning of WEEE*. **Environ. Sci. Pollut. Res**. 26, 2019, 11042–11052. https://doi.org/ 10.1007/s11356-019-04282-3.

68. Republic of Lebanon – Ministry of Environment, *Brief on the Proposed Policy for Integrated Solid Waste Management. Unofficial Translation by Human Rights Watch*, 2018. https://www.hrw.org/sites/default/files/supporting_resources/brief_proposed_policy_isw_managementenglish.pdf.

69. The Daily Star, *NGOs to Get Say in Environment Body*, 2018. https://www.dailystar.com.lb/News/Lebanon-News/2018/Jan-16/433899-ngos-to-get-say-in-environment-body.ashx.

70. C.E. Dirisu, E. Biose, & I.T. Aighewi, *Heavy Metal Contamination of Ewhare Dumpsite Environment in Nigeria's Niger Delta*. **SCIREA Journal of Environment**, Volume 3, Issue 2, 2019, 44-46.

71. J.R. Adewumi, & F.O. Ajibade, *Periodic Determination of Physicochemical and Bacteriological Characteristics of Wastewater Effluents for Possible Reuse as*

Irrigation Water. **Int. J. Energy Water Resour**. 3 (4), 2019, 269–276. https://doi.org/10.1007/s42108- 019-00036-6.

72. J.R. Adewumi, O.J. Ejeh, K.H. Lasisi, & F.O. Ajibade, *A GIS-AHP Based Approach in Sitting MSW Landfills in a Nigerian Confluence State.* **SN Appl. Sci**. 1, 2019, 1528. https:// doi.org/10.1007/s42452-019-1500-6.

73. O.O. Elemile, M.K.C. Sridhar, & O.E. Oluwatuyi, *Solid Waste Characterization and its Recycling Potential: Akure Municipal Dumpsite, Southwestern, Nigeria.* **J. Mater. Cycles Waste Manag**. 21, 2019, 585–593. https://doi.org/10.1007/s10163-018-00820-2

74. M. Ahmed, M. Matsumoto, & K. Kurosawa, *Heavy Metal Contamination of Irrigation Water, Soil, And Vegetables in a Multi-Industry District of Bangladesh.* **Int. J. Environ**. Res. 12, 2018, 531–542. https://doi.org/10.1007/s41742-018-0113-z.

75. E.I. Michaela, A.O. Odohb , E.I. Chukwura, & M.G. Bend, *Heavy Metal and Microbial Load Properties of Dumpsite Leachate: Case Study of Onitsha Dumpsite, South-East, Nigeria.* **Journal of Toxicology Annual**. 1: 2018, 1- 6.

76. B.T. Olowookere, O. Oyibo, & G.T. Oyerinde. *Heavy Metals Concentration in Dumpsites at Gwagwalada, Abuja: Implications on Sustainable Environmental Management.* **Greener Journal of Soil Science and Plant Nutrition**. 1(5): 2018, 001-004.

77. J.P,E. Tsuma, S.O. Wandiga, & D.A. Abong'o , *Methane and Heavy Metals Levels From Leachates at Dandora Dumpsite, Nairobi County, Kenya*. **IOSR Journal of Applied Chemistry,** Volume 9, Issue 9 Ver. II, 2016, PP 39-46 DOI: 10.9790/5736-0909023946

78. A. N. Daniel, I. K. Ekeleme, C. M. Onuigbo, V. O. Ikpeazu, & S. O. Obiekezie, *Review on Effect of Dumpsite Leachate to the Environmental and Public Health Implication*. **GSC Advanced Research and Reviews**, 07(02), 2021, 051–060

79. A. R. Ishak, S. Mohamad, T.K. Soo, & F.S. Hamid, *Leachate and Surface Water Characterization and Heavy Metal Health Risk on Cockles in Kuala Selangor.* **Procedia - Social and Behavioral Sciences** 222, 2016, 263 – 271

80. J.A. Ojodomo, I.O. Ocholi, A.O. Ahmadu, & P.N. Uzoma . *Assessment of Heavy Metals Levels and Leaching Potentials in Dumpsites Soils in Wukari, North-Eastern Nigeria.* **International Journal of Modern Analytical and Separation Sciences**, 5(1): 2016, 20-31

81. J. Borjac, M. El Joumaa, R. Kawach, L. Youssef, & D. A. Blake, *Heavy Metals and Organic Compounds Contamination in Leachates Collected from Deir Kanoun Ras El Ain Dump and its Adjacent Canal in South Lebanon.* **Heliyon** 5, 2019 e02212

82. A. Godwin, & E. Oghenekohwiroro, *Leachate Characterization and Leachate Pollution Index from Landfill Dump Sitesin Warri Metropolis, Nigeria.* **International Letters of Natural Sciences** Vol. 57, 2016, pp 41-48

83. K. Wieczorek, A, Turek, J. Kubicki, & W.M. Wolf, *The Long-Term Effect of Industrial Waste Landfill on Surface Water: An Example from Central Poland*. **Minerals,** 11, 2021, 861. https:// doi.org/10.3390/min11080861

84. Geoflint, *Environmental and Social Impact Assessment.* Plot Number/765/ Ain Baal, Tyre South Lebanon, 2017. www.cdr.gov.lb/stuy/EISAAinbaalFina.pdf.

85. K. Rehman, F. Fatima, I. Waheed, & M.S.H. Akash, *Prevalence of Exposure of Heavy Metals and their Impact on Health Consequences,* **J. Cell. Biochem**. 119 (1), 2018, 157–184.

86. S. Sobhanardakani, *Potential Health Risk Assessment of Heavy Metals via Consumption of Caviar of Persian Sturgeon*. **Marine Pollution Bulletin** 123(1-2), 2017a, 34–38.

87. S. Sobhanardakani, L. Tayebi, & S.V. Hosseini, *Health Risk Assessment of Arsenic and Heavy Metals (Cd, Cu, Co, Pb, And Sn) through Consumption of Caviar of Acipenser Persicus from Southern Caspian Sea.* **Environmental Science and Pollution Research** 25(3), 2018, 2664–2671.

88. O. E. Oluwatuyi F.O. Ajibade, T.F. Ajibade, B. Adelodun, A.S. Olowoselu, J.R. Adewumi, & C.O. Akinbile, *Total Concentration, Contamination Status and Distribution of Elements in a Nigerian State Dumpsites Soil*. **Environmental and Sustainability Indicators** 5, 2020, 100021 https://doi.org/10.1016/j.indic.2020.100021

89. J.N. Ihedioha, P.O. Ukoha, & N.R. Ekere, *Ecological and Human Health Risk Assessment of Heavy Metal Contamination in Soil of a Municipal Solid Waste Dump in Uyo, Nigeria*. **Environ. Geochem. Health**, 39, 2017, 497–515. https://doi.org/10.1007/ s10653-016-9830-4.

90. O.O. Ojuri, F.O. Ayodele, & O.E. Oluwatuyi, *Risk Assessment and Rehabilitation Potential of a Millennium City Dumpsite in Sub-Saharan Africa.* **Waste Manag**. 76, 2018, 621–628. https://doi.org/10.1016/j.wasman.2018.03.002.

91. A.M. Odukoya, & T. Laniyan, *Health Risk Assessment of Heavy Metals in Soils and Vegetables Grown Around a Dumpsite in Lagos, Southwest, Nigeria*. **J. Appl. Geochem.** 18, 2016, 258–270.

92. L.M. Yanez, J.A. Alfaro, N.A. Carreras, & G.B. Mitre, *Arsenic Accumulation in ~ Lettuce (Lactuca Sativa L.) and Broad Bean (Vicia Faba L.) Crops and its Potential Risk for Human Consumption*. **Heliyon** 5, 2019, e01152. https://doi.org/10.1016/ j.heliyon.2019.e01152.

93. S.S. Mahipal, K. Mayuri, N. Manisha, M. Shriyash, P.S. Gaurav, C. Bhaskar, & R. Kumar, *Effect of Electronic Waste on Environmental and Human Health- A Review.*

Journal of Environmental Science, Toxicology and Food Technology. 10: 2016, 98-104.

94. P.O. Njoku, J.N. Edokpayi, & J.O. Odiyo, *Health and Environmental Risks of Residents Living Close to a Landfill: A Case Study of Thohoyandou Landfill, Limpopo Province, South Africa*. **International Journal of Environmental Research and Public Health.** (16): 2019, 21-25

95. O.B. Akintan, J.A. Olusola, & A.M. Azeez, *Heavy Metals Loads in Soil, Farmlands and Plant Crop at Open Dumpsite*. **Global J. Environ. Sci. Manage**. 5(4): 2019, 449-460

96. A.O. Afolayan, *Accumulation of Heavy Metals from Battery Waste Topsoil Surface Water, and Garden Grown Maize at Omilende Area, Olodo, Nigeria,* **Global Challenges**, 2: 2018, 1-12.

97. O. Akintan, S. Jewitt, & M. Clifford, *Culture, Tradition, and Taboo: Understanding the Social Shaping of Fuel Choices and Cooking Practices in Nigeria*, **Energy Res. Social Sci**., 40(C): 2018, 14 – 22.

98. S. Prakash & A.K. Verma, *Arsenic: It's Toxicity and Impact on Human Health* . **IJBI** 3 (1): 2021, 38-47

99. S. Prakash & A.K. Verma *Acute toxicity and Behavioural responses in Arsenic Exposed Mystus vitatus (Bloch).* **International Journal on Agricultural Sciences**. 10(1): 2019, 1-3.

100. S. Dwivedi . *Evaluation of Drinking Water Quality Status by Water Quality Index: A Case Study of Shikhar Water Fall, Dehradun (UK), India*. **International Journal of Biological Innovations.** 2 (2): 2020, 214-219. https://doi.org/10.46505/IJBI.2020.2218

101. G. Genchi, M. S. Sinicropi, G. Lauria, A. Carocci, & A. Catalano, *The Effects of Cadmium Toxicity*. **Int. J. Environ. Res. Public Health,** 17, 2020, , 3782; doi:10.3390/ijerph17113782

102. M.R. Rahimzadeh, M.R. Rahimzadeh, S. Kazemi, & A.A. Moghadamnia, *Cadmium Toxicity and Treatment: an Update*. **Caspian J. Intern. Med.** 8, 2017, 135–145

103. A.A. Tinkov, V.A. Gritsenko, M.G. Skalnaya, S.V. Cherkasov, J. Aaseth, & A.V. Skalny, *Gut as a Target for Cadmium Toxicity*. **Environ. Pollut**. 235, 2018, 429–434.

104. Z. Liu, L. Cai, Y. Liu, W. Chen, & Q. Wan, *Association Between Prenatal Cadmium Exposure and Cognitive Development of Offspring: A Systematic Review.* **Environ. Pollut.**, 254, 2019, 113081.

105. K. Shekhawat, S. Chatterjee, & B. Joshi, *Chromium Toxicity and its Health Hazards*. **International Journal of Advanced Research**, Volume 3, Issue 7, 2015, 167-172

106. H.J. Lunk, *Discovery, Properties and Applications of Chromium and its Compounds.* **ChemTexts** 1:6, 2015. DOI 10.1007/s40828-015-0007-z

107. J.J. Beaumont, R.M. Sedman, S.D. Reynolds, C.D. Sherman, L.H. Li, R.A. Howd, M.S. Sandy, L. Zeise, & G.V. Alexeeff, *Cancer Mortality in a Chinese Population Exposed to Hexavalent Chromium in Drinking Water*. **Epidem.**, 19(1): 2018, 12- 23.

108. M. Kosiorek, & M. Wyszkowski: *Effect of Cobalt on Environment and Living Organisms - A Review* - 11420 - **Applied Ecology and Environmental Research** 17(5): 2019, 11419-11449.

109. B.H. Chaudhari, J.K. Parmar, R.H. Mali, & N.H. Bumbadiya, *Effect of Co Level and FYM on Growth and Yield of Fodder Maize.* – **International Journal of Chemical Studies** 5(1): 2017, 327-329.

110. N. Defarge, J. S. de Vendômois, & G.E. Séralinia, *Toxicity of Formulants and Heavy Metals in Glyphosate-Based Herbicides and other Pesticides*. – **Toxicology Reports** 5: 2018, 156-163. https://doi.org/10.1016/j.toxrep.2017.12.025.

111. S. Jadoon, & A. Malik, *A Review of Formation, Toxicity of Reactive Oxygen Species by Heavy Metals and Tolerance in Plants.* – **International Journal of Biochemistry Research & Review** 21(2): 2018, 1-12. https://doi.org/10.9734/IJBCRR/2018/38670.

112. S. Cheng, H. Mao, Y. Ruan, C. Wu, Z. Xu, G. Hu, X. Guo, C. Zhang, H. Cao, & P. Liu, *Copper Changes Intestinal Microbiota of the Cecum and Rectum in Female Mice by 16S Rrna Gene Sequencing*. **Biol Trace Elem Res** 193(2) 2020, :445-455. 10.1007/s12011-019-01718-2

113. E. Cholewinska, K. Ognik, B. Fotschki, Z. Zdunczyk, & J. Juskiewicz, *Comparison of the Effect of Dietary Copper Nanoparticles and One Copper (II) Salt on the Copper Biodistribution and Gastrointestinal and Hepatic Morphology and Function in a Rat Model.* **PLoS One** 13(5): 2018, e0197083. 10.1371/journal.pone.0197083.

114. L. Ciacci, T. Fishman, A. Elshkaki, T.E. Graedel,I. Vassura, & F. Passarini, *Exploring Future Copper Demand, Recycling and Associated Greenhouse Gas Emissions in the EU-28*. **Global Environ Change** 63: 2020, 102002093

115. ATSDR. *Copper. Full SPL Data. Substance Priority List (SPL) Resource Page.* **Agency for Toxic Substances and Disease Registry, Centers for Disease Control and Prevention**. 2019 https://www.atsdr.cdc.gov/SPL/resources/index.html. February 20, 2020.

116. V. Sharma, & P Singh., *Heavy Metals Pollution and its Effect on Environment and Human Health*. **International Journal of Recent Scientific Research** Vol. 6, Issue, 12, 2015, pp. 7752-7755

117. B. Ravindhran, K. Karthikeyan, V. Jayakumar, N. Mitta, & S. Subramanyam *Early Intestinal Obstruction in Iron Toxicity – An Unheard of Occurrence*. **JCDR**. 12(1): 2018. http://jcdr.net/article_fulltext.asp?issn=0973-709x&year=2018&volume=12&issue=1&page=PD01&issn=0973-709x&id=11094

118. R.A. Ávila, M.A.S.C. Silva, J.V. Peixoto, I. Kassouf-Silva, R.T.H. Fogaça, & L. dos Santos, *Mechanisms Involved in the In Vitro Contractile Dysfunction Induced by Different Concentrations of Ferrous Iron in the Rat Myocardium.* **Toxicology in Vitro**. 2016 Oct;36:38–45.

119. D.N. Bateman, V. Eagling, E.A. Sandilands, G. Jackson, C. Crawford, L. Hawkins, T. Cheung, G. Cooper, S.M. Bradberry, J.P. Thompson, S.H.L. Thomas, & M. Eddleston, *Iron Overdose Epidemiology, Clinical Features and Iron Concentration-Effect Relationships: The UK Experience 2008–2017*. **Clinical Toxicology**. 2 (11): 2018, 1098–106.

120. ATSDR. *Lead Toxicity: Case Studies in Environmental Medicine (CSEM).* **Environmental Health and Medicine Education**. 2017. Available online: https://www.atsdr.cdc.gov/csem/lead/docs/CSEM-Lead_toxicity_508.pdf

121. A,L, Wani, A. Ara, & J.A. Usmani, *Lead Toxicity: A Review.* **Int. Toxicol**. 8, 2015, 55–64.

122. H.F. Gomez, D,A, Borgialli, M. Sharman, K.K. Shah, A.J. Scolpino, J.M. Oleske, & J.D. Bogden, *Blood Lead Levels of Children in Flint, Michigan: 2006-2016*. **J Pediatr** 197: 2018, 158-164. http://doi.org/10.1016/j.jpeds.2017.12.063.

123. G.H. Kang, J.Y. Uhm, Y.G. Choi, E.K. Kang, S.Y. Kim, W.O. Choo, & S.S. Chang, *Environmental Exposure of Heavy Metal (Lead and Cadmium) and Hearing Loss: Data from the Korea National Health and Nutrition Examination Survey (KNHANES 2010-2013).* **Ann Occup Environ Med** 30: 2018, 22. http://doi.org/10.1186/s40557-018- 0237-9.

124. J.W. Lee, H. Choi, U.K. Hwank, J.C. Kang, Y.J. Kang, K.I. Kim, & J.H. Kim, *Toxic Effects of Lead Exposure on Bioaccumulation, Oxidative Stress, Neurotoxicity, and Immune Responses In Fish: A Review*. **Environ. Toxicol. Pharmacol.** 68, 2019, 101–108.

125. M. Hussain, S. Haider, Y. Abbas, Q. Khan, B. Hussain, S.W. Hussain, & A. Ali, *A Study of Source Specific Quantification, Composition and Disposal Methods of Municipal Solid Waste at Konodas Gilgit City, Pakistan.* **J. Biodivers. Environ. Sci.**, 8(5), 2016, 20162222- 20166663.

126. A. Zul, O.A. La, & N. Muhammad, *Heavy Metal Content of Cocoa Plantation Soil in East Kolaka, Indonesia*. **Oriental Journal of Chemistry,** 33(3), 2017, 1164-1170.

127. S. Srigirisetty, T. Jayasri, & C. Netaji, *Open Dumping of Municipal Solid Waste-Impact on Groundwater and Soil*. **Tech. Res. Organ. India,** 4(6), 2017, 26-33.

128. H.K. Ozcan, S.Y. Guvenc, L. Guvenc, & G. Demir, *Municipal Solid Waste Characterization According to Different Income Levels: A Case Study.* **Sustainability,** 8(10), 2016, 1044.

129. A. Phothisansakul, & T. Runguphan, *Remediation of Domestic Wastewater Runoff using Vermi-Biofiltration*. **Int. J. Environ. Bioremediation Biodegrad,** 5(2), 2017, 60-64.

130. H. Yasin, & M. Usman, *Site Investigation of Open Dumping Site of Municipal Solid Waste in Faisalabad*. **Earth Sciences Pakistan** 1(1), 2017, 23-25.

131. V.F. Nascimento, A.C. Sobral, P.R. Andrade, N. Yesiller, & J.P. Ometto, *Natural Disaster Risk in Municipal Solid Waste Disposal Sites using GIS: A Case Study in São Paulo State, Brazil*. **Journal of Water Resource and Protection,** 9(11), 2017, 1213.

132. O.A. Agbede, & S.A. Ojelabi, *Heavy Metal Contamination Assessment of Selected Water Sources in Ibadan Metropolis,* .**MAYFEB Journal of Civil Engineering**, volume 1, 2017, 1-14

133. Y.F.M. Benedicta, A. Emmanuel, Y.T. Dzidzo, & N. Frank, *Heavy Metals Concentration and Distribution in Soils and Vegetation at Korle Lagoon Area in Accra, Ghana* . **Cogent Environmental Science**, 3(1): 2017, 1405887

134. J.B. Kowalska, R. Mazurek, & M. Gasiorek, *Pollution Indices as Useful Tools for the Comprehensive Evaluation of the Degree of Soil Contamination*. **A review Environ Geochem Health** 40 (6) 2018, 2395-2420.

Chapter Three

Methodology

3.1 Research Design

This research involved the determination of two environmental pollutants namely heavy metals and Polycyclic Aromatic Hydrocarbons (PAHs) and was carried out in two phases. The first phase was the site inspection to seek concent, determine location profile and sample collection while the second phase was the analytical stage which involves sample preparation, laboratory bench work and instrumental analysis.

3.2 Study Site

Shri Balaji Industries Limited, a small scale industry founded in 2009, designed to extract Low Pour Fuel Oil, carbon and steel wires from used tyres located at Olopomeji Village, Egbeda Local Government Area of Oyo State.

The facility is spatially located at North N070 21.761, Easting E0040 06.620 and Elevation 605 m as shown in Figure 3.1. The facility has stockpile of old/used tyres as shown in Figure 3.2 and it is surrounded by farms settlement and close to Asejire dam.

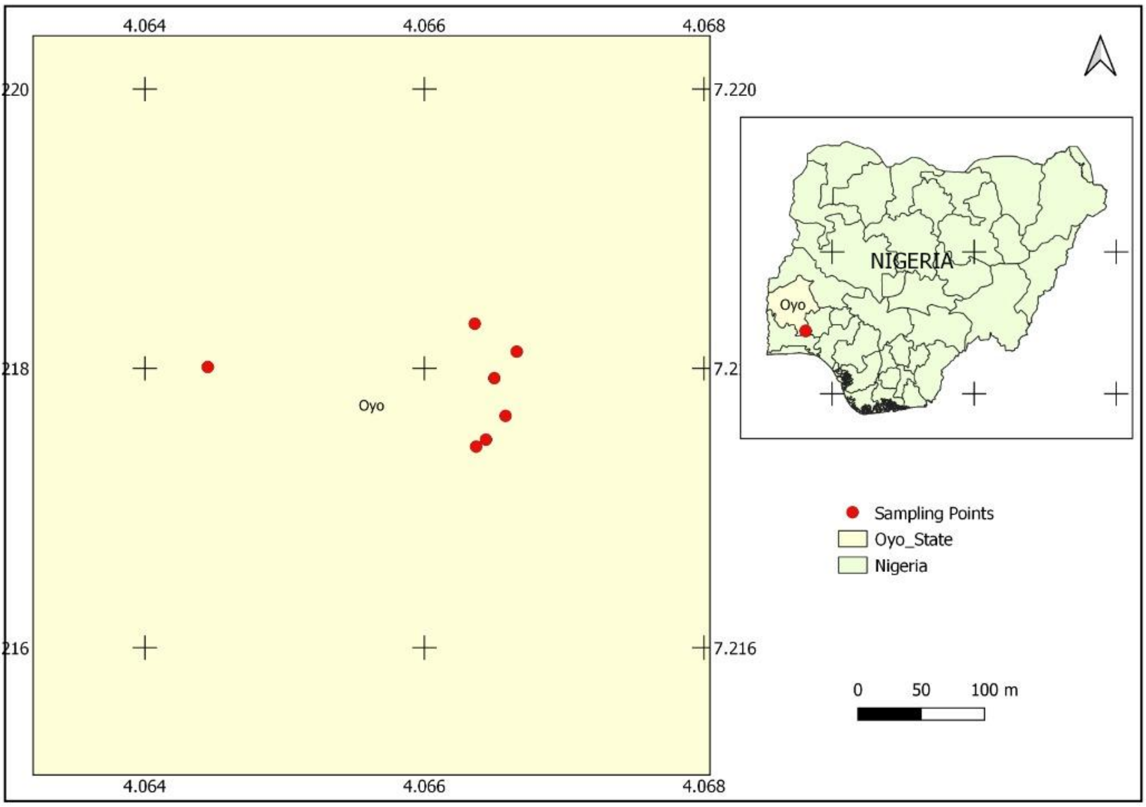

Figure 3.1: Map of the Study Site

Source: Author's Field Work, 2022

Figure 3.2: Stock pile of waste tyres at the pyrolysis plant

Source: Author's Field Work, 2022

3.3 Sample Collection

Soil samples were collected very early in the morning by 6:30 am. A total of 22 soil samples were collected from seven different locations strategically mapped out in and around the factory namely; Burning Spot (BS), Iron Removing spot (IR), Tyre Point (TP), Middle Point (MP), Dark Spot (DS), Non-Dark Spot (NDS) and nearby Farm Settlement (FS). Control soil samples were also collected at the Botanical Garden, University of Ibadan, Ibadan. At each sampling spot, top soil samples were collected at a depth of 0-5 cm using a hand trowel into a properly labelled aluminium foil and were transferred into the laboratory. After being brought to the laboratory, the soil samples were air-dried in a clean laboratory room. Subsequently, they were homogenized and sieved through a 2 mm stainless steel sieve prior to analysis.

3.4 Chemicals and Reagent Used

All chemicals used were of Analar grade and of highest purity. Reagents used include;

n-Hexane, dichloromethane, alumina (GC grade) as desiccant, concentrated nitric acid (HNO_3),perchloric acid ($HClO_4$) and sulphuric acid (H_2SO_4), anhydrous sodium sulphate, activated copper powder, 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 18 PAHsdetermined in the study.

3.5 Heavy Metals Analysis

3.5.1 Digestion of Samples

Soil samples from the various sites were air dried, sieved through a 2-mm mesh and digested according to United States Environmental Protection Agency (USEPA) method 3050b[1]. Two grams of air dried soil samples were weighed using electronic Sartorius

Analytical balance Model 2842. The weighed soil samples were placed in 50 ml volumetric flask and to each was added 3 ml of concentrated nitric acid (HNO_3), 1 ml perchloric acid ($HClO_4$) and 1 ml sulphuric acid (H_2SO_4) in the ratio of 3:1:1 and heated on a hot plate to near dryness. The content of each flask was diluted with 10ml of distilled water up to the mark and then filtered with Whatman No 1 filter paper. The filtrates were then preserved in sample bottles for few days before being analysed for the heavy metals using Atomic Absorption Spectrophotometer.

3.5.2 Heavy Metal Determination

The filtrates obtained from digestion were being analysed for the heavy metals, Lead, Zinc, Chromium, Cadmium and Arsenic using Atomic Absorption Spectrophotometer. The digested sample was fed into the AAS. The reading of the metal concentration for each sample was obtained and recorded.

3.5.3 AAS Condition

The model of the Atomic Absorption Spectrophotometer (AAS) employed in the analysis of heavy metals is: Buck 211VGP, made by Buck Scientific.

The analytical condition of the AAS is summarized in Table 3.1 below

Table 3.1: AAS Buck 211VGP working conditions

Element	Wavelength (nm)	Slit Width (nm)	Working Range (µg/mL)	Sensitivity (µg/mL)	Lamp Current	Flame Type
As	193.7	0.7	1-100	45	300	MHS
Cd	228.8	0.5	0.5-5	0.03	15	Air-C_2H_2
Cr	357.9	0.2	2.0-20	0.2	25	Air-C_2H_2
Pb	283.3	0.5	4.0-40	0.2	440	Air-C_2H_2
Zn	213.9	0.5	0.5-5	0.03	15	Air-C_2H_2

Source: Author's Field Work, 2022

3.6 Extraction and clean up of Polycyclic Aromatic Hydrocarbons

Sixteen target PAHs were analysed using Gas Chromatography-Mass Spectrometry (GS/MS) following modified USEPA methods (method 8270 C)[2].

3.6.1 Solvent Extraction

Approximately 5 g of each soil 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 twice with another 25 mL dichloromethane. The three 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 determined by calculating the amount of analyte[8].

2 g of the soil samples were spiked with deuterate surrogate standards (1-methylnaphthalene-d8, fluorine-d10, anthracene-d10, pyrene-d10, p-terphenyl-d14, benzo[a]pyrene-d12, and benzo(g.h.i)pyrene-d12), and then mixed with anhydrous magnesium sulphate for extraction. An appropriate amount of activated copper powder was also added to each extraction cell in order to remove sulphur during extraction. The PAHs were extracted from soil samples through an accelerated solvent extraction system (ASE 200, Dionex, Sunny-vale, CA, USA) with a 1:1 (v/v) acetone/dichloromethane solvent mixture[8]. Samples were extracted three times under the following conditions: Oven temperature 100°C, Pressure-1700 psi, Heat time- 5min, Static time- 10min and a 60 % flash.The three extracts were pooled, concentrated with a rotatory evaporator and solvent exchange with 5ml of n-hexane.

3.6.2 Sample Clean-up Procedure

Sample clean-up was done on a silica gel-aluminium oxide glass column (10 cm x 6 mm ID), and elution was conducted by successively loading 5 ml n-hexane and 20 ml n-haxane-dichloromethane (3:7, v/v) and the elution was collected for PAH dtermination. 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 andkept at -4°C until further analysis.

3.6.3 Polycyclic Aromatic Hydrocarbons Quantification

Polycyclic Aromatic Hydrocarbons quantification was conducted using an Agilent 7890-5975c gas chromatography-mass spectrometer (GC-MS). A DB-5 column (30 m x 0.25 mm x 0.10 um) was used. The injection volume was 1 µL. Helium was used as the carrier gas at a flow rate of 1 mL/min. The column temperature was set to 50 ^{o}C for the first 1 min, increased 20 ^{o}C /min to a temperature of 120 ^{o}C, then increased 4 ^{o}C /min – 130 ^{o}C, and maintained at 310 ^{o}C for 30 min. The mass spectrometer conditions were: electron impact, electron energy 70 eV; filament current 100 µA; multiplier voltage of 1200 v and in full scan mode.

Quantification of individual PAHs was performed in MS/MS scan mode at normal speed, based both on retention time and characteristic ions. Concentration of each PAH was finally calculated and calibrated using the standard calibration curve. 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.

3.7 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 .

3.8 Data Analysis

3.8.1 Statistical Tools for 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 toolsused to test significant difference in mean levels of pollutants/variables.

3.8.2 Degree of Soil Contamination

The degree of contamination of the sampling-sites' soils and the control-site soils was evaluated using two indices, Contamination Factor and Pollution Load Index.

3.8.2.1 Contamination Factor

The Contamination Factor (C_f^i) was used by Hakanson to assess soil contamination by comparing the contaminant concentration in the surface layer to a background value[4]. We used a modified C_f^i formula, using metals concentrations in the control samples instead of background values, which are currently lacking for Nigeria[5]. It is expressed using Equation 1.

Contamination factor, $\mathbf{C_f^i = C^i_{0\text{-}1} / C_n^i}$..........................Equation 1

where,

$\mathbf{C_f^i}$ = contamination factor;

$\mathbf{C^i_{0\text{-}1}}$ = mean concentration of each metal in the soil;

$\mathbf{C_n^i}$ = baseline or background value (concentration of each metal in the control sample was used);

n = number of analysed elements;

i = ith element (or pollutants).

We then classified the $\mathbf{C_f^i}$ using descriptive categories:

$\mathbf{C_f^i} < 1$, low contamination;

$1 \leq \mathbf{C_f^i} < 3$, moderate contamination;

$3 \leq \mathbf{C_f^i} < 6$, considerable contamination; and

$6 \leq \mathbf{C_f^i}$, very high contamination.

3.8.2.2 Pollution Load Index (PLI)

Pollution Load Index (PLI) was also used to assess the metal accumulation and multi-element contamination resulting in increased overall metal toxicity[6]. Heavy metal contamination is associated with a mixture of contaminants rather than one metal contaminant[7]. The higher the PLI, 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 2 as shown below.

$$\mathbf{PLI} = (\mathbf{C_f^i}\,\mathrm{Zn} \times \mathbf{C_f^i}\,\mathrm{Cd} \times \mathbf{C_f^i}\,\mathrm{Pb} \times \mathbf{C_f^i}\mathrm{As} \times \mathbf{C_f^i}\,\mathrm{Cr})^{1/5} \text{..............................Equation 2}$$

Endnotes

1. Method 3050B, *Acid Digestion of Sediments, Sludges, and Soils, Revision 2*. Washington, DC. **United States Environmental Protection Agency**, 1996. Available from: https://www.epa.gov/sites/ production/files/2021-12/documents/epa-3050b.pdf

2. Method 8270C, *Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/ MS).* Washington, DC**. United States Environmental Protection Agency,** 1996. Available from: https://www.epa.gov/sites/production/files/2015-07/documents/epa-8270d.pdf.

3. L. Hakanson, *An Ecological Risk Index for Aquatic Pollution Control. A Sedimentological Approach*. **Water Res.** 14(8): 1980, 975-1001. Available from: http://www.sciencedirect.com/ science/article/pii/0043135480901438.

4. W.H. Liu, J.Z. Zhao, Z.Y. Ouyang, L. Söderlund & G.H. Liu, *Impacts of Sewage Irrigation on Heavy Metal Distribution and Contamination in Beijing, China.* **Environ Int.** 31(6): 2005, 805-12. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0160-4120(05)00113-3.

5. A.A. Adeyi & N. Torto, *Profiling Heavy Metal Distribution and Contamination in Soil of Old Power Generation Station in Lagos, Nigeria.* **Am J Sci Technol.** ;1(1): 2014, 1-10. Available from: http://www.fulviofrisone.com/attachments/ article/532/9020729.pdf

6. A.H. Al Obaidy & A.A. Al Mashhadi, *Heavy Metal Contaminations in Urban Soil within Baghdad City*, **Iraq. J Environ Prot**. 4(1): 2013, 72-82. Available from: https://file.scirp.org/ Html/8-6701677_27185.htm 51.

7. M.C. Jung, *Heavy Metal Contamination of Soils and Waters in and Around the Imcheon Au–Ag Mine*, **Korea. Appl Geochem** 2021, 1369-75. Available from: http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.553.6821&rep=rep1&type=pdf

8. P. Peter, K. Petra, M. Monika, P. Albrecht, T. Uwe, *Application of Accelerated Solvent Extraction Followed by Gas Chromatography, High-Performance Liquid Chromatography and Gas Chromatography–Mass Spectrometry for the Determination of Polycyclic Aromatic Hydrocarbons, Chlorinated Pesticides and Polychlorinated Dibenzo-P-Dioxins and Dibenzofurans in Solid Wastes*. **Journal of Chromatography A**, 774, 1997, 203–211

Chapter Four

Results and Discussion of Findings

4.1 Results of Heavy Metal Analysis

The mean concentration of As, Cd, Cr, Pb and Zn analysed in the soil samples are presented in Table 4.1. Metals concentrations across the sampling location varied slightly from one another. Metals concentrations in the control sample were generally lower than what was detected in waste tyre burning site, which might have resulted from the burning/pyrolysis of tyre activity at the sampling site.

Table 4.1: Mean Concentration of As, Cd, Cr, Pb and Zn in the Soil sample

Soil Sample	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)
BS1	0.683	0.340	0.097	0.350	0.640
BS2	0.100	0.430	0.020	0.727	1.623
BS3	0.597	0.180	0.107	0.247	0.503
BS4	0.113	0.773	0.220	0.633	0.430
IR5	0.270	0.107	0.170	0.300	2.220
IR6	0.340	0.170	0.037	0.463	1.250
IR7	0.250	0.490	0.203	0.677	0.930
IR8	0.127	0.310	0.120	0.397	0.247
TP9	0.680	0.080	0.083	0.127	1.050
TP10	0.207	0.153	0.130	0.670	1.420
TP11	0.250	0.117	0.203	0.147	1.993
TP12	0.227	0.067	0.220	0.800	2.010
MP13	0.280	0.083	0.310	1.620	2.233
MP14	0.350	0.133	0.030	1.573	0.907
MP15	0.100	0.143	0.420	0.983	0.477
MP16	0.480	0.293	0.180	1.637	1.403
DS17	0.383	0.127	0.147	1.020	1.017
DS18	0.100	0.040	0.610	0.633	0.480
ND19	0.117	0.020	0.040	0.950	0.340
ND20	0.217	0.187	0.200	0.523	0.680
FR21	0.147	0.300	0.100	0.150	0.207
FR22	0.203	0.247	0.150	0.230	0.450
Mean	**0.283**	**0.218**	**0.173**	**0.675**	**1.023**
S.D	**0.182**	**0.176**	**0.136**	**0.466**	**0.658**
Sum	**6.220**	**4.790**	**3.797**	**14.857**	**22.510**
Min	**0.100**	**0.020**	**0.020**	**0.127**	**0.207**
Max	**0.683**	**0.773**	**0.610**	**1.637**	**2.233**
CSS	**0.090**	**N.D**	**0.010**	**0.098**	**0.102**

S.D = Standard deviation; CSS = Control site sample; ND= Not detected

Source: Author's Field Work, 2022

4.2 Result of PAHs Analysis

The result for determination and quantification of PAHs is presented in Table 4.2. A total of 18 PAHs were determined and quantified.

Table 4.2: Result of PAHs analysis in (mg/Kg)

Individual PAHs (mg/Kg)	**Iron removing point**	**Tyre point+ mid point**	**Burningspot + Dark spot**	**Non dark spot +Farm**	**Average PAH**	**Control site**
Naphthalene	315	333	556	321	381.25	10.7
1-Methyl Naphthalene	237	340	485	280	335.5	16.1
2-Methyl Naphthalene	144	383	263	155	236.25	9.79
Acenaphthylene	7.75	16.7	17.8	9.66	12.98	1.58
Acenaphthene	26.7	50.2	42	27.8	36.68	1.26
Fluorene	20.7	17.4	24.2	25.4	21.93	2.21
Phenanthrene	140	195	84	141	140	5.68
Anthracene	191	80	336	192	199.75	1.9
Pyrene	62.8	102	102	48.3	78.78	2.52
Fluoranthene	68.8	392	165	68.8	173.65	2.84
Benzo(a)anthracene	16.4	65.7	88.9	24.1	48.78	2.52
Chrysene	25	117	113	33.8	72.2	2.21
Benzo(k)fluoranthene	9.47	32.9	53.3	14.5	27.54	2.52
Benzo(b)fluoranthene	10.3	36	58.2	16.9	30.35	2.84
Benzo(a)pyrene	9.47	60.8	96.9	15.7	45.72	2.52
Benzo(g,h,i)perylene	6.02	16.7	40.4	10.9	18.51	2.21
Dibenz(a,h)anthracene	6.88	12.4	30.7	10.9	15.22	2.21
Indeno(1,2,3-cd)pyrene	7.75	28.5	74.3	14.5	31.26	2.21
Minimum	**6.02**	**12.4**	**17.8**	**9.66**	**12.98**	**1.26**
Maximum	**315**	**392**	**556**	**321**	**381.25**	**16.1**
Mean Per Site	**72.5**	**126.63**	**146.15**	**78.35**	**105.91**	**4.1**
∑ Total PAH	**1305.04**	**2279.3**	**2630.7**	**1410.26**	**1906.33**	**73.82**

Source: Author's Field Work, 2022

4.3 Discussion of Findings

4.3.1 Discussion on Heavy Metals

The mean concentration of metals at each of the sampling spots (shown in Table 4.3 to Table 4.9) revealed that the average concentration of arsenic in the tyre pyrolysis plant ranged between 0.1000 and 0.6833 mg/Kg. However, higher concentration of arsenic was observed in samples collected from middle spot and tyre point. This could be attributed to deposition of metal that might occur during the storage stage of the pyrolysis and accumulated stockpile of tyres. The non-spot and non-dark spot sampling spot recorded the lowest concentration of Arsenic which ranges between 0.1000 - 0.2167 mg/kg. The overall mean Arsenic concentration observed in the tyre pyrolysis plant was 0.2827 mg/kg. The distribution of arsenic in soil is widely associated to geological inputs, although many other locations do experience anthropogenic inputs. Some of these anthropogenic inputs include usage of pesticides made with arsenic and the combustion of fossil fuels. The latter is an extremely important additional input as we have it the tyre pyrolysis plant. Arsenic is highly carcinogenic and the health effects mainly include kidney, lung, skin and bladder disorders[2]. Arsenic contamination in soil is of public concern owing to its carcinogenic and toxic nature, it can accumulate in plants which will be transferred to human body system via the food chain[1].

Cadmium concentration observed in the pyrolysis plant ranged from 0.0200 - 0.7700 mg/kg, with an average of 0.2177 mg/kg. High level of cadmium were observed in samples collected from the middle spot and iron removing point while the lowest concentration of cadmium was observed at the non-dark spot. However, few samples from the burning point and tyre point also showed relatively low level of cadmium. Cadmium had a high mobility and widespread which make it a potential contaminant in soil and other natural environment. Sources of cadmium pollution may be from iron smelters, industrial usage of cadmium in the production of pigments, alloys, plastics and in batteries. Cadmium exposure is a threat to environment and human safety as it is obvious that the operations of tyre pyrolysis plant is contributing to the concentration of cadmium in soils. Other anthropogenic sources that might also contribute to rise in cadmium concentration include oil leaking from underground storage tanks, sewage sludge, machinery and baking enamels, waste batteries and paints metal plating and coating operations. Accumulation of cadmium in the body also have negative effects on kidney, liver, lungs, placenta, bones and brain[2].

Chromium concentration observed ranged from 0.0200 to 0.6100 mg/kg. Lower concentrations were observed at the middle spot and the iron removing spot while high levels of Chromium were observed at the dark spot and the burning point. The mean concentration of chromium in the study area was 0.1726 mg/kg. The combustion activities undertaken in the pyrolysis plant and other varieties of industrial activities are reported to contribute to chromium levels[3].

Very high levels of Lead were observed in the middle point and the dark spot. However, the concentration of Lead in the plant varied from 0.1267-1.6367 mg/kg , this is the second highest range observed in all the heavy metal analysed. Meanwhile, Lead levels were observed in lower concentration at the tyre point. Indiscriminate disposal of waste tyres, waste tyre incineration, used oil, scrap and junk auto part are various sources of Lead in soil[5]. Leachate stockpile and dumpsites are also source of lead input into the soil. Lead is in no way beneficial biologically to the human system but can affect body system in various ways causing failure in nervous and reproductive systems, kidney failure, anaemia and high blood pressure[4].

Zinc concentration observed was lowest at the non-spot site while elevated levels were recorded at burning point, tyre point, iron removing point and the middle spot. Zinc concentration varied from 0.2067 to 2.2333 mg/kg. Mean level of Zinc recorded in the plant was 1.0232 mg/kg. Zinc contamination in soil is majorly by anthropogenic causes many of which are related to combustion of tyre waste, composted wastes, industrial waste, use of liquid manures, pesticides and agrochemicals like fertilizers[5].

Table 4.3: Mean concentrations of As, Cd, Cr, Pb and Zn at the burning spot

Soil Sample	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)
BS1	0.683	0.340	0.097	0.350	0.640
BS2	0.100	0.430	0.020	0.727	1.623
BS3	0.597	0.180	0.107	0.247	0.503
BS4	0.113	0.773	0.220	0.633	0.430
MEAN	0.373	0.431	0.111	0.489	0.799
SD	0.310	0.250	0.082	0.227	0.556

Source: Author’s Field Work, 2022

Table 4.4: Mean concentrations of As, Cd, Cr, Pb and Zn at the iron removing point

Soil Sample	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)
IR5	0.270	0.107	0.170	0.300	2.220
IR6	0.340	0.170	0.037	0.463	1.250
IR7	0.250	0.490	0.203	0.677	0.930
IR8	0.127	0.310	0.120	0.397	0.247
MEAN	0.247	0.269	0.133	0.459	1.162
SD	0.089	0.170	0.072	0.160	0.820

Source: Author's Field Work, 2022

Table 4.5: Mean concentrations of As, Cd, Cr, Pb and Zn at the tyre point.

Soil Sample	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)
TP9	0.680	0.080	0.083	0.127	1.050
TP10	0.207	0.153	0.130	0.670	1.420
TP11	0.250	0.117	0.203	0.147	1.993
TP12	0.227	0.067	0.220	0.800	2.010
MEAN	0.341	0.104	0.159	0.436	1.618
SD	0.227	0.039	0.064	0.349	0.468

Source: Author's Field Work, 2022

Table 4.6: Mean concentrations of As, Cd, Cr, Pb and Zn at the middle point

Soil Sample	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)
MP13	0.280	0.083	0.310	1.620	2.233
MP14	0.350	0.133	0.030	1.573	0.907
MP15	0.100	0.143	0.420	0.983	0.477
MP16	0.480	0.293	0.180	1.637	1.403
MEAN	0.303	0.163	0.235	1.453	1.255
SD	0.158	0.091	0.168	0.315	0.754

Source: Author's Field Work, 2022

Table 4.7: Mean concentrations of As, Cd, Cr, Pb and Zn at the dark spot

Soil Sample	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)
DS17	0.383	0.127	0.147	1.020	1.017
DS18	0.100	0.040	0.610	0.633	0.480
MEAN	0.242	0.084	0.379	0.827	0.749
SD	0.200	0.062	0.327	0.274	0.380

Source: Author's Field Work, 2022

Table 4.8: Mean concentrations of As, Cd, Cr, Pb and Zn at the non-dark spot

Soil Sample	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)
ND19	0.117	0.020	0.040	0.950	0.340
ND20	0.217	0.187	0.200	0.523	0.680
MEAN	0.167	0.104	0.120	0.737	0.510
SD	0.071	0.118	0.113	0.302	0.240

Source: Author’s Field Work, 2022

Table 4.9: Mean concentrations of As, Cd, Cr, Pb and Zn at the farm spot

Soil Sample	**Arsenic (mg/kg)**	**Cadmium (mg/kg)**	**Chromium (mg/kg)**	**Lead (mg/kg)**	**Zinc (mg/kg)**
FR21	0.147	0.300	0.100	0.150	0.207
FR22	0.203	0.247	0.150	0.230	0.450
MEAN	0.175	0.274	0.125	0.190	0.329
SD	0.040	0.037	0.035	0.057	0.172

Source: Author's Field Work, 2022

Table 4.10: Correlation matrix of heavy metals

	Arsenic	*Cadmium*	*Chromium*	*Lead*	*Zinc*
Arsenic	1				
Cadmium	-0.1350	1			
Chromium	-0.3330	-0.1090	1		
Lead	-0.0750	-0.1057	-0.0053	1	
Zinc	0.0973	-0.2765	-0.1269	0.2360	1

Source: Author's Field Work, 2022

Table 4.11: Metal Contamination Factors, Pollution Load Index and Degree of Contamination in the pyrolysis plant

Metals	**C^f_i**
Arsenic	1.9
Cadmium	0.7
Chromium	1.7
Lead	4.5
Zinc	5.0
Degree of Contamination($\sum C^f_i$)	13.8
PLI	**2.2**

C^f_i= Contamination Factor; PLI= Pollution Load Index

Source: Author's Field Work, 2022

Table 4.12: Comparison of Heavy Metal Concentrations with literatures

Study Site	Arsenic	Cadmium	Chromium	Lead	Zinc	Reference
	(mg/Kg)					
Tyre pyrolysis plant	0.283	0.218	0.173	0.675	1.023	This study
Oil filling station	0.33	2.29	7.35	19.51	5.57	2014
Motor garage	NA	NA	51.75	117.30	30.54	2015
Saw mills	NA	0.21	0.96	1.21	4.50	2013
Battery company	NA	0.08	1.62	9.13	2.68	2016
WHO	0.5	0.02	1.3	2.0	50.0	2022

NA= Not Analysed

Source: Author’s Field Work, 2022

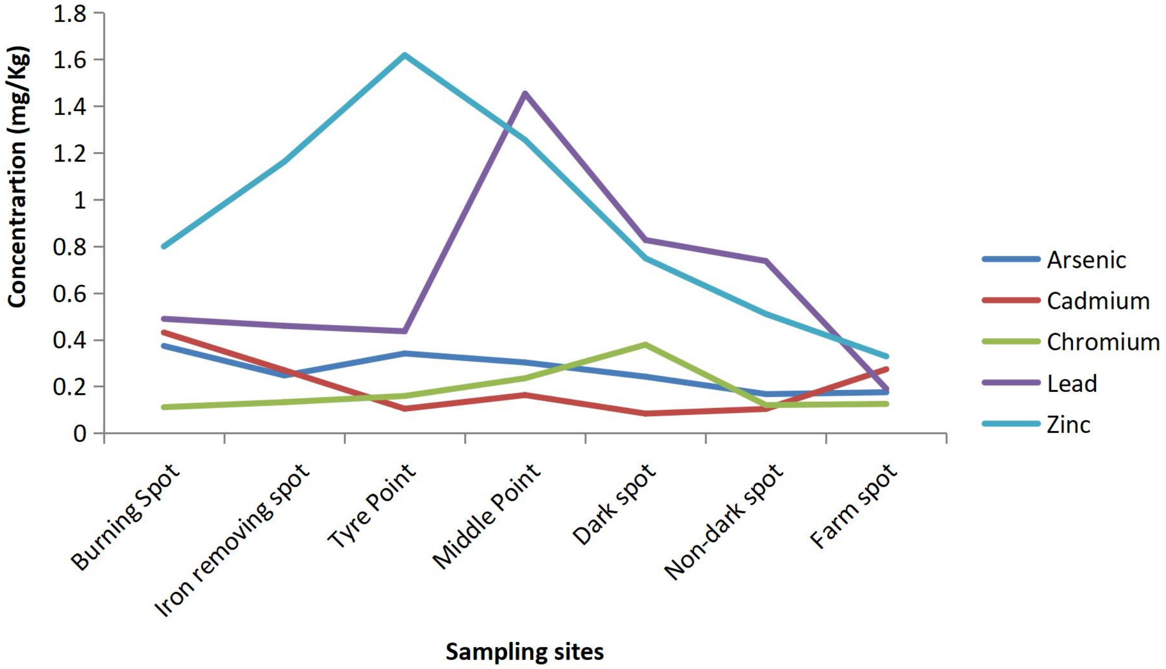

Figure 4.1: Distribution of metals across the tyre pyrolysis plant

Source: Author's Field Work, 2022

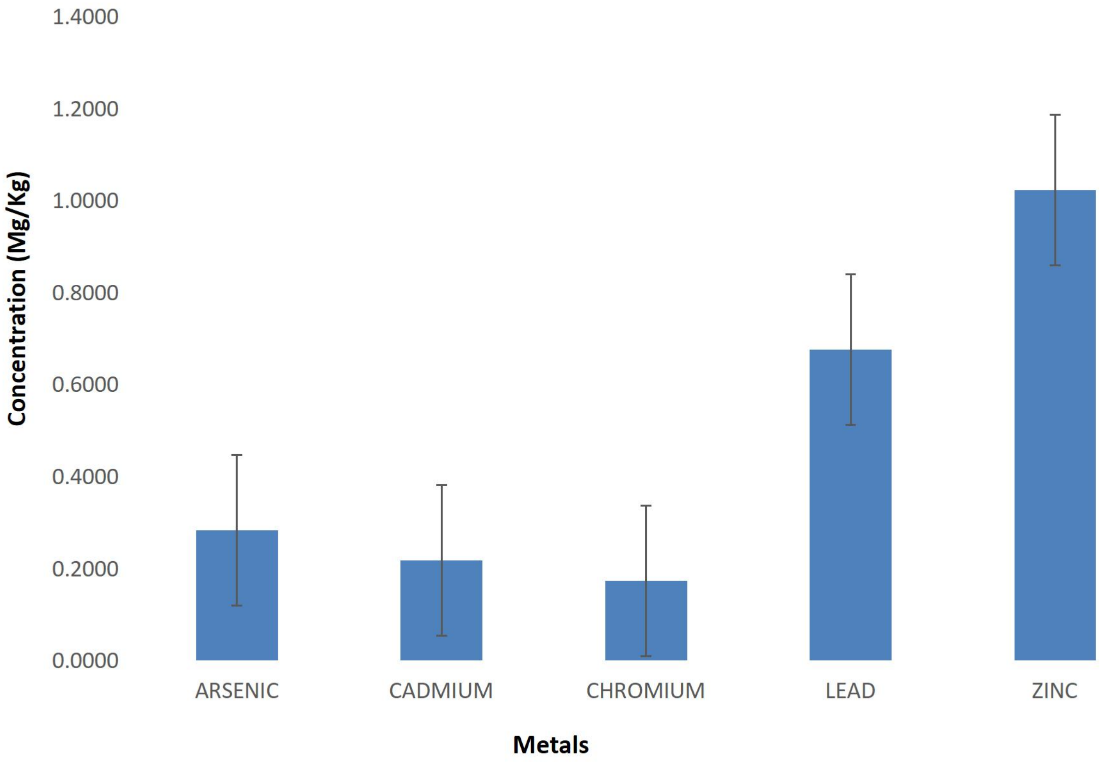

Figure 4.2: Mean concentrations of heavy metals in the study area

Source: Author’s Field Work, 2022

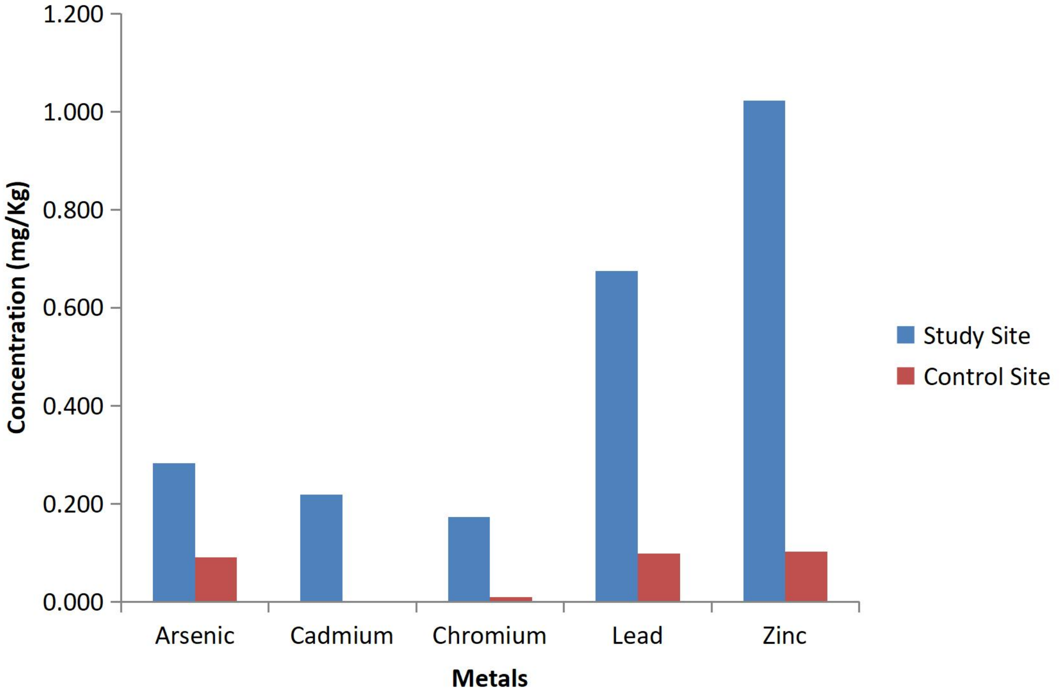

Figure 4.3: Comparison of heavy metals in study site with control site

Source: Author's Field Work, 2022

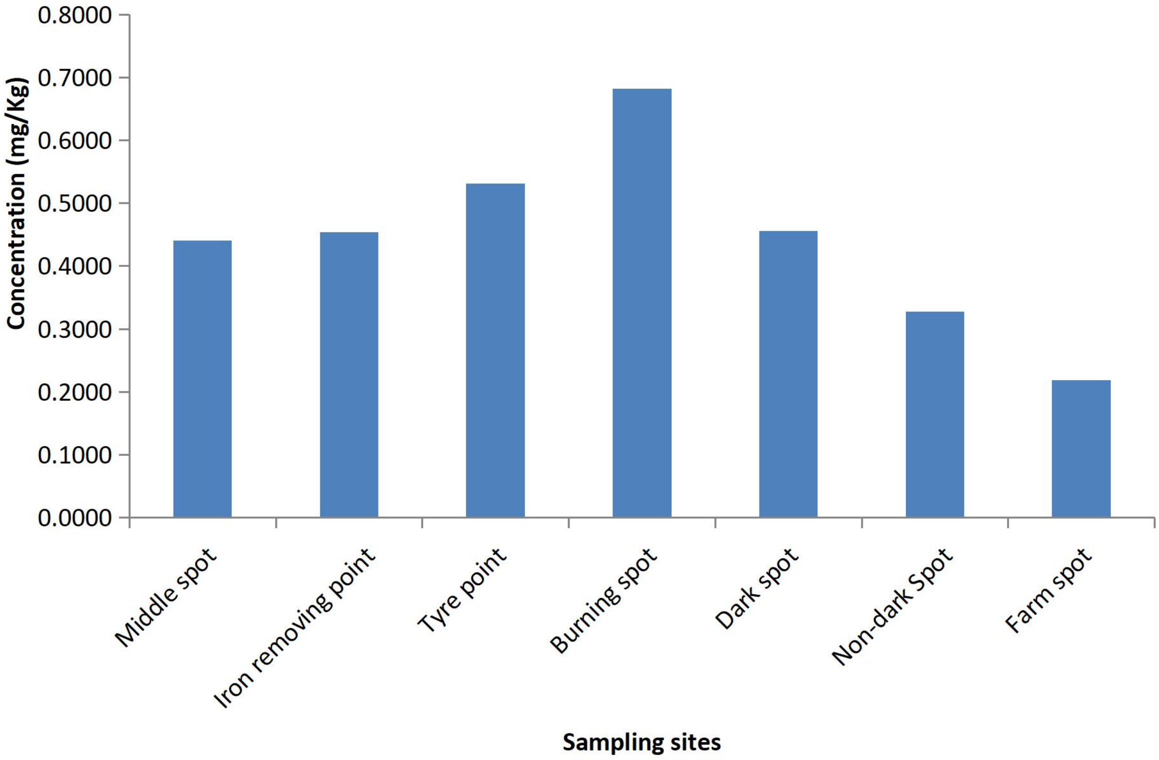

Figure 4.4: Cummulative of heavy metals concentration at each sampling site of the pyrolysis plant

Source: Author's Field Work, 2022

From Figure 4.1 and 4.4, the heavy metals of study were found to be present in the soil from all the sites. In general, the results obtained showed that, the heavy metals concentration in the soil samples can be attributed to combustions of scrap tyres and are reported to generate large amounts of hazardous trace elements, toxic, mutagenic and carcinogenic compounds, such as volatile organics, polycyclic aromatic hydrocarbons, heavy metals, particulates and other products of incomplete combustion[6]. Heavy metals are known for their toxicity potential, tendency to bioaccumulation, high mobility and environmental persistence[7].

The results of the study revealed that Zn and Pb present in the soil sample were in higher concentrations than Cr and Cd, that were in trace amount as shown in Figure 4.2. When compared to what was reported in automobile battery companies in Ibadan, the value of Zn, Pb and Cr observed in this study were lower.

The Zn was present in concentration higher than other metals investigated because of anthropogenic sources origin of the soil[8]. The Pb was high due to wide use of lead products in scrap tyres, storage batteries. The higher Zn and Pb concentrations showed that the pollution at the sampling sites were due to high anthropogenic activities such as battery charging, welding while the lower concentration of Cr and Cd showed that activities resulting in their contamination are lower.

However, the concentration of heavy metals ranged from 0.1000 to 0.6833 mg/kg for As, 0.0200 to 0.7700 mg/kg for Cd, 0.0200 to 0.6200 mg/kg for Cr, 0.1267 to 1.6367 mg/kg for Pb and 0.2067 to 2.2333 mg/kg for Zn. The mean concentration (mg/kg) for each of the metal ranked As-0.2827 Cd-0.2177, Cr-0.1726, Pb-0.6753 and Zn-1.0232. In this study, the availability of heavy metals was in the following order of abundance Zn > Pb> As> Cd> Cr. This distribution pattern is similar to what was reported in some previous studies except that the concentrations were not in the same range[9]. The level of heavy metals recorded in this study were lower compared to what was observed by various authors which was reported in oil filling stations, motor garage, saw mills and automobile battery company (Table 4.12). Also, the concentration of heavy metals observed in this study were within WHO limits (Table 4.12) for the concentration of Cadmium which exceeded the WHO limit.

One way analysis of variance of mean of all the metals showed that there was a significant difference between the metal concentration ($P<0.05$). The concentration of Zn and Pb were significantly higher than the other metals (As, Cd and Cr). This indicates that anthropogenic sources have great impact on their concentration. However, there was no significant difference between the mean values of As, Cd and Cr ($P>0.05$); suggesting minimal effect from anthropogenic sources. From Table 4.10, the result of the Pearson correlation analysis carried out indicated that there was no correlation either positive or negative between all the five metals (As, Cd, Cr, Pb and Zn) that are being studied. It can then be implied that the concentration of each metal (As, Cd, Cr, Pb and Zn) is independent of one another. This result is similar to what was reported by some authors except that the latter established a negative and positive correlation between Pb and Cd and then Pb and As respectively[10].

From Figure 4.4, the burning point is the most polluted site in the pyrolysis plant followed by the tyre point. The concentration heavy metals in these two sits were higher compared to other sites.

From Table 4.11, Zinc has the highest contamination factor followed by Lead. Both metals have considerately contaminated the study site, Arsenic and Chromium have moderate contamination while cadmium has low contamination. The degree of contamination and the pollution load index of the study site were 13.8 and 2.2 respectively and they implied that the site was moderately contaminated.

In general, when the mean concentration of heavy metal was compared with that of the control site, there was a clear indication that the heavy metal concentration observed in the pyrolysis plant was greater than that of the control site (Figure 4.3). It can however be explained that the effect of operational activities and combustion of scrap tyres in the pyrolysis plant is largely responsible for the elevated levels observed for each of the metals.

4.3.2 Discussion on PAHs

The results for the determination and quantification of PAHs in the pyrolysis plant as well as the control site is presented in Table 4.6. A total of eighteen (18) PAHs were determined and quantified across four identified locations in the pyrolysis plant and the control site including all the sixteen (16) PAHs that are considered by the World Health Organization as priority pollutants. The eighteen (18) PAHs are Naphthalene, 1-Methyl Naphthalene,2-Methyl Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Pyrene, Fluoranthene, Benzo(a)anthracene, Chrysene, Benzo(k)fluoranthene, Benzo(b)fluoranthene, Benzo(a)pyrene, Benzo(g,h,i)perylene, Dibenz(a,h)anthracene and Indeno(1,2,3-cd)pyrene.

At the Iron Removing Point, Naphthalene had the highest concentration of 315.00 mg/kg while benzo(g,h,i)perylene had the lowest concentration 6.02 mg/kg. The total concentration of PAHs detected at the iron removing point was 1305.04 mg/kg. Similarly, in the burning point and non-dark spot, Naphthalene ranked highest with 556.00 and 321.00 mg/kg respectively. Acenaphthene ranked the lowest at these two points with

17.80 and 9.66 mg/kg respectively. At the tyre point, Fluoranthene had the highest concentration (392.00 mg/kg) and Dibenz(a,h)anthracene with the lowest concentration (12.40 mg/kg). Out of all the sampling sites, the Burning Point recoreded the highest concentration of PAHs (Figure 4.6).

The mean concentration of all the PAHs in the pyrolysis plant ranged from 12.98 to 381.25 mg/kg. It was observed that in the whole pyrolysis plant Naphthalene had the highest mean concentration, this agrees with the findings of researchers while Acenaphthylene had the minimum concentration[11].

It was observed that PAHs with two-rings exhibits higher concentration compared to PAHs of higher rings. This indicates that the pyrolysis activities in the plant contaminate the environment with more two-rings PAHs. This observation was also due to the fact that Naphthalene is very soluble and easily disintegrates in aqueous solution; it can therefore be transformed to the N-Methylated derivatives like 1-Methylnaphthalene and 2-methylnaphthalene[12]. These methylated derivatives have been found to be highly harmful compared to the parent compound but they are susceptible to microbial degredation[13]. The order of concentration among the two-rings PAHs wass Naphthalene > 1-Methyl naphthalene > 2-Methylnaphthalene.

Among the three-rings PAHs, the mean concentration of Anthracene observed was the highest in the series. Although Anthracene was the most persistent among the three-rings PAHs in the study area, Phenanthrene was found predominantly in the tyre point. The order of concentration among the three-rings PAHs was Anthracene > Phenathrene > Acenaphthene > Fluorene > Acenaphthylene.

Similarly, Fluoranthene had the highest concentration among the four-rings PAHs. The order of concentration among the four-rings PAHs was Fluoranthene > Pyrene >

Chrysene > Benzo(a)anthracene. These four-rings PAHs have been reported to be liable to photo degredation and oxidation in mild aqueous environment, however this majorly influenced the medium and substrate they are attached to. But they strongly oppose microbial biodegradation. The four rings PAHs are less toxic but carcinogenic[11].

Benzo(a)pyrene had the highest concentration among the five rings PAHs, while their order of concentration was Benzo(a)pyrene > Benzo(b)fluoranthene > Benzo(k)fluoranthene > Dibenz(a,h)anthracene. Indeno(1,2,3-cd)pyrene had the highest among the six rings PAHs followed by Benzo(g,h,i)perylene.

In this study (Figure 4.5), the concentrations of all the identified PAHs were in the order Naphthalene > 1-Methyl Naphthalene > 2-Methyl Naphthalene > Anthracene > Fluoranthene > Phenanthrene > Pyrene > Chrysene > Benzo(a)anthracene > Benzo(a)pyrene > Acenaphthene > Indeno(1,2,3-cd)pyrene > Benzo(b)fluoranthene > Benzo(k)fluoranthene > Fluorene > Benzo(g,h,i)perylene > Dibenz(a,h)anthracene > Acenaphthylene.

Across this trend, many of the higher rings PAHs had lower concentration, this also agrees with some literatures who reported that the more rings the less soluble PAHs are; which indicates that the fewer rings PAHs were more soluble[14].

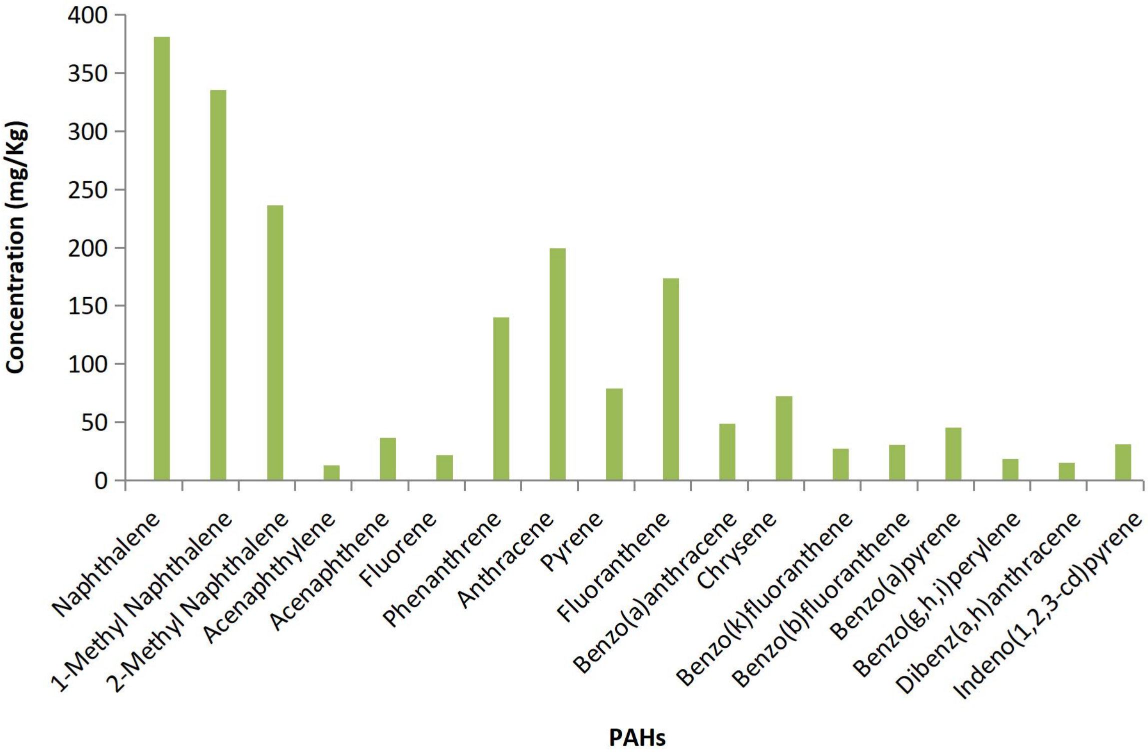

Figure 4.5: PAHs Concentration in the soil sample from the study site

Source: Author's Field Work, 2022

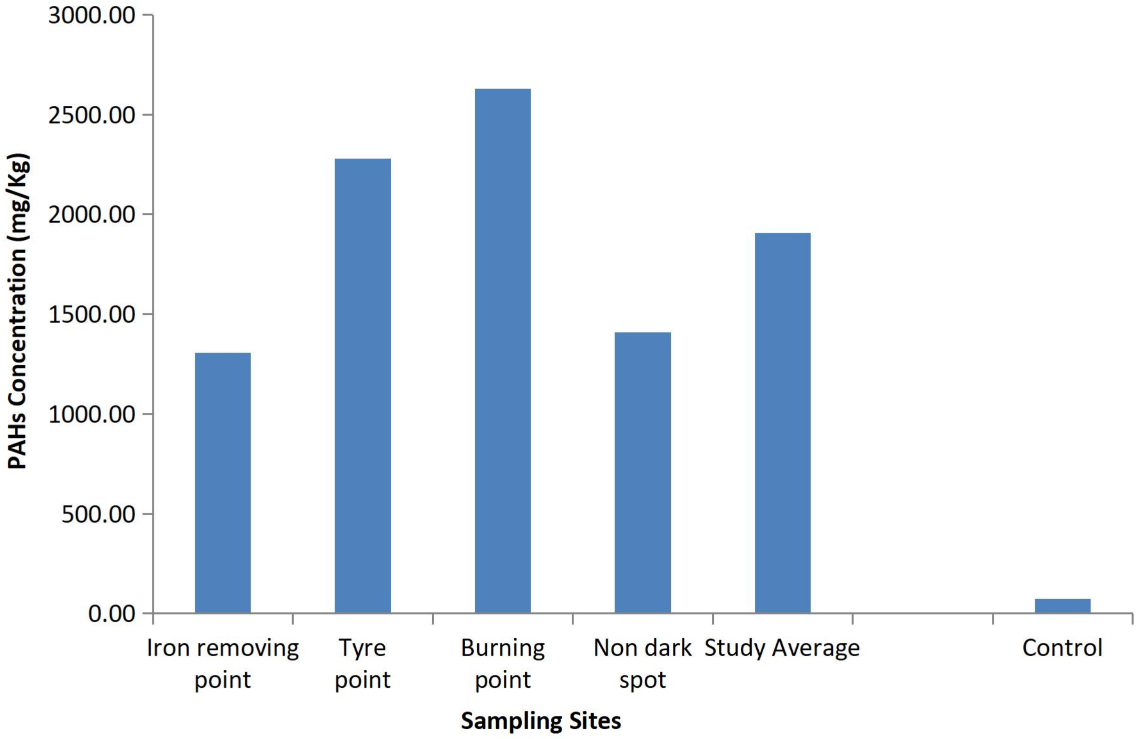

Figure 4.6: Cummulative PAH concentration at each sampling site

Source: Author’s Field Work, 2022

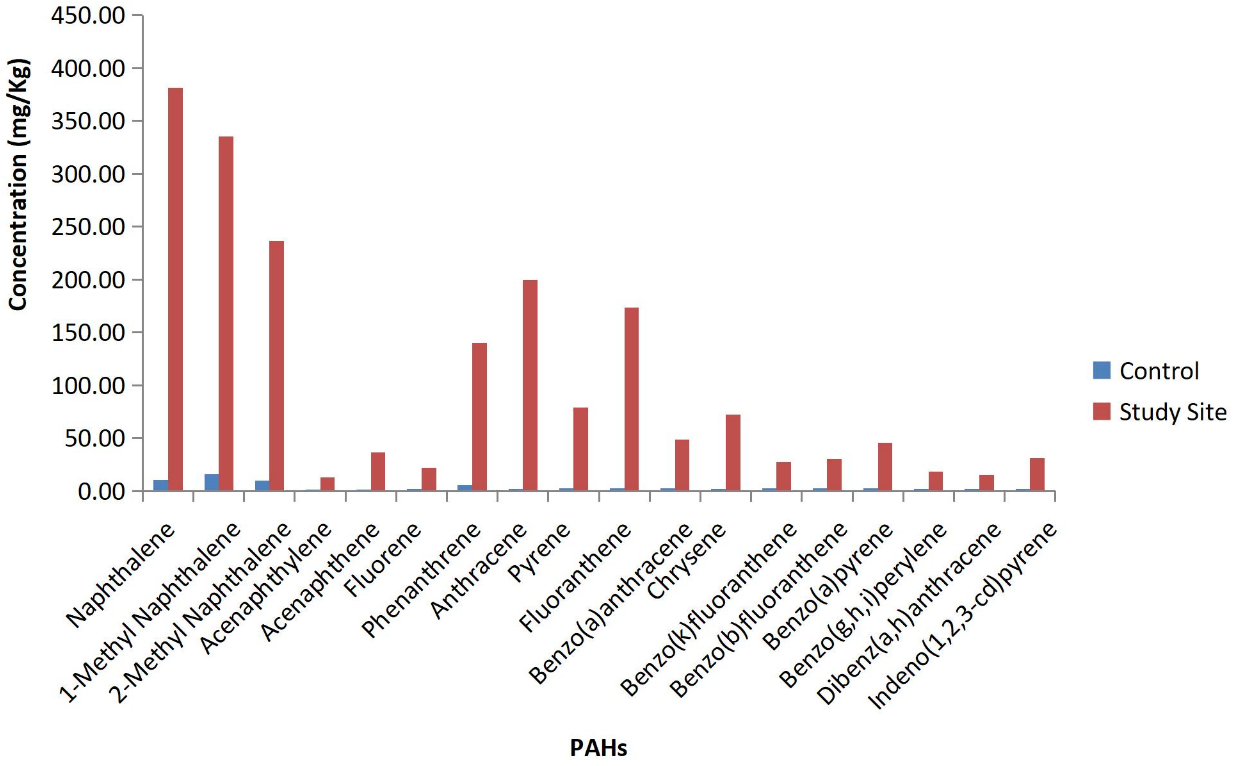

Figure 4.7: Comparison of concentration of each PAH at study site with control site

Source: Author's Field Work, 2022

Table 4.13: Correlation matrix of PAHs

	Naphthalene	*1-Methyl Naphthalene*	*2-Methyl Naphthalene*	*Acenaphthylene*	*Acenaphthene*	*Fluorene*	*Phenanthrene*	*Anthracene*	*Pyrene*	*Fluoranthene*	*Benzo(a)anthracene*	*Chrysene*	*Benzo(k)fluoranthene*	*Benzo(b)fluoranthene*	*Benzo(a)pyrene*	*Benzo(g,h,i)perylene*	*Dibenz(a,h)anthracene*	*Indeno(1,2,3-cd)pyrene*
Naphthalene	1																	
1-Methyl Naphthalene	0.98	1																
2-Methyl Naphthalene	0.70	0.80	1															
Acenaphthylene	0.88	0.95	0.93	1														
Acenaphthene	0.83	0.89	0.97	0.96	1													
Fluorene	0.87	0.83	0.53	0.67	0.70	1												
Phenanthrene	0.49	0.53	0.77	0.60	0.79	0.65	1											
Anthracene	0.91	0.83	0.33	0.61	0.51	0.83	0.19	1										
Pyrene	0.88	0.93	0.94	0.97	0.98	0.68	0.68	0.61	1									
Fluoranthene	0.44	0.57	0.95	0.79	0.85	0.25	0.70	0.02	0.79	1								
Benzo(a)anthracene	0.84	0.91	0.83	0.96	0.85	0.51	0.35	0.61	0.90	0.71	1							
Chrysene	0.76	0.85	0.94	0.97	0.91	0.46	0.50	0.44	0.93	0.86	0.97	1						
Benzo(k)fluoranthene	0.85	0.91	0.76	0.93	0.79	0.53	0.26	0.68	0.86	0.61	0.99	0.93	1					
Benzo(b)fluoranthene	0.86	0.91	0.76	0.93	0.79	0.54	0.26	0.68	0.86	0.61	0.99	0.93	1.00	1				
Benzo(a)pyrene	0.80	0.87	0.76	0.91	0.77	0.44	0.22	0.61	0.84	0.64	0.99	0.94	0.99	0.99	1			
Benzo(g,h,i)perylene	0.86	0.88	0.60	0.84	0.66	0.54	0.10	0.78	0.75	0.41	0.93	0.81	0.97	0.97	0.96	1		
Dibenz(a,h)anthracene	0.89	0.90	0.57	0.83	0.66	0.61	0.12	0.84	0.75	0.36	0.91	0.78	0.95	0.96	0.93	0.99	1	
Indeno(1,2,3-cd)pyrene	0.84	0.86	0.59	0.82	0.65	0.50	0.07	0.76	0.74	0.41	0.93	0.81	0.97	0.97	0.96	1.00	0.99	1

Source: Author's Field Work, 2022

One way analysis of variance carried out on all the PAHs indicated that all the PAHs were significantly different from one another ($P<0.05$). This implies that each PAH concentration was influenced by anthropology sources which is as a result of the tyre pyrolysis plant operation.

Correlation analysis (Table 4.13) also revealed that majority of the PAHs had strong positive correction with one another. Comparing the concentration of PAHs in the study site and that of the control site (Figure 4.7), the concentration of all the PAHs were higher in the pyrolysis plant than the control site, this further buttress the fact that the pyrolysis plant is a major source of PAH contamination. Similar to what was observed in the study site, the concentration of two rings PAHs in the control site were higher than the PAHs of higher rings. The source of PAHs in the control site would be largely attributed to natural sources which are not usually regarded as adding to bulk of the pollutants in the environment[15]. Some of these sources arise from thermal geologic reactions which may entails chemical or biological trans formation of organic materials from living or recently died plants and animals[16].

The PAHs with higher molecular weight especially the four rings and above are less acutely toxic but are highly teratogenic and carcinogenic[17]. These carcinogenic PAHs namely; Benzo(a)anthracene, Chrysene, Benzo(k)fluoranthene, Benzo(b)fluoranthene, Benzo(a)pyrene, Dibenz(a,h)anthracene and Indeno(1,2,3-cd)pyrene were all present in the study site at varying concentration[17]. These PAHs are in elevated levels and therefore have harmful effects on the health of human being and the environment because of their high degree of carcinogenicity and mutagenicity[18]. The three or more rings PAHs are majorly released into the environment via pyrolytic sources due to incomplete combustion or burning of either hydrocarbon oils or fossil fuel[19].

Endnotes

1. O.S. Edori, & W.A. Iyama, *Source Identification of Polycyclic Aromatic Hydrocarbons in Water at Point of Effluent Discharge into the New Calabar River, Port Harcourt, Rivers State*, **Nigeria. International Journal of Environment and Climate Change,** 9(6): 2019, 343-349

2. L. Xiaoyan, B. Zhongke, Y. Qinfei, C. Yingui & Z. Wei, *Polycyclic Aromatic Hydrocarbons in the Soil Profiles (0-100cm) from the Industrial District of a Large Open-Pit Coal Mine, China*. **Royal Society of Chemistry Advances** 7(45): 2017, 28029-28037.

3. A.A. Adeyi & P. Oyeleke, *Heavy Metals and Polycyclic Aromatic Hydrocarbons in Soil from E-waste dumpsites in Lagos and Ibadan, Nigeria*. **J Health Pollut** 7(15): 2017, - 84.

4. M.J. He, S.Y. Yang, J. Zhao, C. Collins, J.M. Xu, & X.M. Liu, *Reduction in the Exposure Risk of Farmer from E-Waste Recycling Site Following Environmental Policy Adjustment: A Regional Scale View of PAHs in Paddy Fields,* **Environ. Int**. 133, 2019, 105136bi X. Huang, X. Xu, Y. Dai, Z. Cheng, X. Zheng, & X. Huo, *Association of Prenatal Exposure to PAHs with Anti-Mullerian Hormone (AMH) Levels and Birth Outcomes of Newborns,* **Sci. Total Environ**. 723, 2020, 138009.

5. X. Huo, Y. Wu, L. Xu, X. Zeng, Q. Qin, & X. Xu, *Maternal Urinary Metabolites of PAHs and its Association with Adverse Birth Outcomes in an Intensive E-Waste Recycling Area,* **Environ. Pollut**. 245, 2019, 453–461.

6. L.F. Jiang, Z.N. Cheng, D.Y. Zhang, M.K. Song, Y.J. Wang, C.L. Luo, H. Yin, J. Li, & G. Zhang, *The Influence of E-Waste Recycling on the Molecular Ecological Network of Soil Microbial Communities in Pakistan and China*. **Environ. Pollut.,** 231, 2017, 173–181.

7. R. Jin, G.R. Liu, M.H. Zheng, X.X. Jiang, Y.Y. Zhao, L.L. Yang, X.L. Wu & Y. Xu, *Secondary Copper Smelters as Sources of Chlorinated and Brominated Polycyclic Aromatic Hydrocarbons*, **Environ. Sci. Tech**., 51, 2017, 7945–7953.

8. M. Lin, J. Tang, S. Ma, Y. Yu, G. Li, B. Mai, R. Fan, & T. An, *Simultaneous Determination of Polybrominated Diphenyl Ethers, Polycyclic Aromatic Hydrocarbons and their Hydroxylated Metabolites in Human Hair: A Potential Methodology to Distinguish ExternalfFrom Internal Exposur*e. **Analyst** 144, 2019, 7227–7235.

9. M.O. Onyema, L.C. Osuji & B.O. Isiuku. *Compositional Alteration of Polycyclic Aromatic Hydrocarbons by Burning Oil Spilled Soils,* **Academia Journal of Environmental Science,** vol. 4(11), 2016, pp. 213-219.

10. O.S. Edori, O.A. Ekpete, & W.A. Iyama, *Concentrations of Polycyclic Aromatic Hydrocarbons from Selected Dumpsites Within Port Harcourt Metropolis, Rivers State, Niger Delta, Nigeria.* **International Journal of Environmental Science & Natural Resources**. 2 (4) 2019, 556066. DOI: 10.19080/IJESNR.2019.21.556066.

11. C. Peng, M. Wang, Y. Zhao, & W. Chen, *Distribution and Risks of Polycyclic Aromatic Hydrocarbons in Suburban and Rural Soils of Beijing with Various Land Uses,* **Environmental Monitoring and Assessment**, 188: 2016, 162.

12. D.B. Bahiru, E. Teju, T. Kebede & N. Demissie, *Levels of Some Toxic Heavy Metals (Cr, Cd and Pb) in Selected Vegetables and Soil Around Eastern Industry Zone, Central Ethiopia,* **African Journal of Agricultural Research,** 14(2), 2019, pp. 92-101.

13. O.B. Akintan, J.A. Olusola, & A.M. Azeez, *Heavy Metals Loads in Soil, Farmlands and Plant Crop at Open Dumpsite.* **Global J. Environ. Sci. Manage.,** 5(4): 2019, 449-460.

14. G.A. Ebong, M.M. Akpan & V.N. Mkpenie, *Heavy Metals Contents of Municipal and Rural Dumpsite Soils and Rate of Accumulation By Carica papaya and Talinun triangulare in Uyo, Nigeria*, **E-J. Chem**., 5(2): 2018, 281 – 290.

15. S.S. Olubunmi, J.A. Olufemi, Augustus O. A. I., Abidemi O. F. and Adetola, T. A. *Heavy Metal Contamination of a Dumpsite Environment as Assessed with Pollution Indices.* **International Journal of Agricultural and Biosystems Engineering**.12(1): 2018, 1-7

16. P.O. Fatoba, C.O. Ogunkunle, S. Oyedeji & M.B. Salawudeen, *Metal Depositions Around some Petroleum Product Depots in Nigeria, using Mosses as Biomonitors.* **The Bioscientist**: Vol. 1(1): 2013, 99-105.

17. A. Emmannuel, S.J. Cobbina, D. Adomako, A.B. Dewijuah & W. Asare, *Assessment of Heavy Metals Concentration In Soils Around Oil Filling and Service Stations in Tamale Metropolis Ghana.* **African Journal of Environmental science and Technology.** Vol 8(4), 2014, pp256-266. Doi:10.6897/AJEST2014.1664.

18. K.M.A. Thamera & H.M.A. Israa, *Determination of Polycyclic Aromatic Hydrocarbons in Soil at Al-Nahrawan Bricks Factory.* **Pak. J. Biotechnol.** VOL. 15 (2) 2018, 445-450.

19. V. Popovici, L. Bucur, S.I. Calcan, E.I. Cucolea, T. Costache, D. Rambu, V. Schröder, C.E. Gîrd, D. Gherghel, G. Vochita, A. Caraiana & V. Badea, *Elemental Analysis and In Vitro Evaluation of Antibacterial and Antifungal Activities of Usnea barbata (L.) Weber ex F.H.* Wigg from Călimani Mountains, Romania. **Plants**, 11, 2022, 32. https://doi.org/ 10.3390/plants11010032

20. A. Emmannuel, S.J. Cobbina, D. Adomako, A.B. Dewijuah & W. Asare, *Assessment of Heavy Metals Concentration in Soils Around Oil Filling and Service Stations In Tamale Metropolis Ghana*. **African Journal of Environmental science and Technology.** Vol 8(4) 2014, pp256-266. Doi:10.6897/AJEST2014.1664

21. A.J. Yusuf, A. Galadima, Z.N. Garba & I. Nasir, *Determination of some Heavy Metals in Soil Sample from Illela Garage in Sokoto State, Nigeria*. **Research Journal of Chemical Sciences** Vol. 5(2), 2015, 8-10.

22. K.E. Ajibulu, O.S. Adefemi, S.S. Asaolu & G.I. Oyakhilome, *Determination of Heavy Metals in Soil Samples of Selected Sawmills in Ekiti State,* **Nigeria. Journal of Scientific Research & Reports,** 2(2): 2013, 513-521

23. P.O. Oyeleke, O.A. Abiodun, R.A. Salako, O.E. Odeyemi & T.B. Abejide, *Assessment of Some Heavy Metals in the Surrounding Soils of an Automobile Battery Factory in Ibadan, Nigeria,* **African Journal of Environmental Science and Technology,** 10(1), 2016, pp. 1-8. DOI: 10.5897/AJEST2015

Chapter Five

Conclusion

5.1 Summary of Findings

From this study, it was observed that the mean concentration of the five metals were As-0.2827, Cd-0.2177, Cr-0.1726, Pb-0.6753 and Zn-1.0232 mg/kg. The tyre pyrolysis plant was highly concentrated with Zinc followed by Lead while the availability of the heavy metals in decreasing order were Zn > Pb> As> Cd> Cr. In the tyre pyrolysis plant, out of all the sites examined, the burning point harbours the highest concentrations of heavy metals and the next to it was the tyre point. One way ANOVA reveals that all the results of heavy metals were significantly different from one another ($P<0.05$), similarly there was no correlation between all the five metals examined, although the concentration of all the metals were higher in the pyrolysis plant site than the control site. Zinc had the highest Contamination Factor followed by Lead. Both metals had considerately contaminated the pyrolysis site, Arsenic and Chromium had moderate contamination while cadmium has low contamination. The Degree of Contamination of the study site was 13.8 which reveal that the site was moderately contaminated. This was further established by the Pollution Load Index of 2.2 attesting that the pyrolysis site had suffered deterioration.

The findings of this study also revealed that the soil around the pyrolysis plant contained PAHs in decreasing order of abundance: Naphthalene -381.25, 1-Methyl Naphthalene -335.50, 2-Methyl Naphthalene -236.25, Anthracene -199.75, Fluoranthene -173.65, Phenanthrene -140.00, Pyrene -78.78, Chrysene -72.20, Benzo(a)anthracene -48.78, Benzo(a)pyrene -45.72, Acenaphthene -36.68, Indeno(1,2,3-cd)pyrene -31.26, Benzo(b)fluoranthene -30.35, Benzo(k)fluoranthene -27.54, Fluorene -21.93, Benzo(g,h,i)perylene -18.51, Dibenz(a,h)anthracene -15.22 and Acenaphthylene -12.98

mg/Kg. The concentrations of PAHs in the pyrolysis site were observed to be higher than the control site. Naphthalene had the highest concentration and similarly the concentration of the two rings PAHs were higher than three rings and above. Seven carcinogenic PAHs namely Benzo(a)anthracene, Chrysene, Benzo(k)fluoranthene, Benzo(b)fluoranthene, Benzo(a)pyrene, Dibenz(a,h)anthracene and Indeno(1,2,3-cd)pyrene were also identified among the PAHs that were determined.

5.2 Conclusion

The soil in and around the pyrolysis plant were observed to be moderately contaminated by both the heavy metals and PAHs. Among all the sampling points in the pyrolysis plant site considered in this study, the burning point and the tyre point had the highest concentrations of heavy metals. Similar trend was also observed for the PAHs indicating that operational activites carried out in both section of the pyrolysis plant constitute the highest contamination. However, the concentrations of the heavy metals were significantly different. In the same vain, concentrations all the PAHs identified were also significantly different from one another, although correlation study indicated that there was strong positive correlation between all the PAHs. This suggests that the observed concentrations were as a result of anthropogenic activies (cutting of tyres, removing of iron, burning of tyres etc) in and around the pyrolysis plant.

5.3 Recommendations

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

1. The general public needs to be well sensitized and enlightened on heavy metals and PAHs, their source, health effects and how to check their discharge into the environment.

2. Remediation should be carried out on areas that are highly polluted with heavy metals and PAHs.
3. Factories, plants and companies should be made to realise that environmental management is far above paying dues to regulatory bodies but needs to put in place a robust Environmental Management System and conduct regular Environmental Audit.
4. Factories, Plants and companies should also be encouraged to adopt the use of environment friendly technologies that reduce the release of contaminants into the environment.

5.4 Contribution to Knowledge

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

1. Pyrolysis plant constitutes heavy metal and PAHs contamination to the environment.
2. The level of Zinc and Lead constitute the highest heavy metal contamination in and around the pyrolysis plant
3. The two rings PAHs concentration is higher than the concentrations of higher rings PAHs.
4. The results of this study have generated baseline information about the presence of heavy metals and PAHs around pyrolysis plants/factories in Ibadan and Nigeria at large for both policy formulation and other literary studies.

5.5 Suggested Areas for Further Research

1. Further research needs to be carried out on the water and vegetable samples around the pyrolysis plant for holistic environmental review of heavy metals and PAHs.
2. Research needs to be carried out to determine possible remediation techniques most suitable for the areas that are highly polluted with heavy metals and PAHs.

Bibliography

Journals

Adewumi J.R., & Ajibade F.O., *Periodic Determination of Physicochemical and Bacteriological Characteristics of Wastewater Effluents for Possible Reuse as Irrigation Water.* **Int. J. Energy Water Resour**. 3 (4), 2019, 269–276. https://doi.org/10.1007/s42108- 019-00036-6.

Adewumi J.R., Ejeh O.J., Lasisi K.H., & Ajibade F.O., *A GIS-AHP Based Approach in Sitting MSW Landfills in a Nigerian Confluence State*. **SN Appl. Sci**. 1, 2019, 1528. https:// doi.org/10.1007/s42452-019-1500-6.

Adeyi A.A. & Oyeleke P., *Heavy Metals and Polycyclic Aromatic Hydrocarbons in Soil from E-waste dumpsites in Lagos and Ibadan, Nigeria*. **J Health Pollut** 7(15): 2017, - 84.

Afolayan A.O., *Accumulation of Heavy Metals from Battery Waste Topsoil Surface Water, and Garden Grown Maize at Omilende Area, Olodo, Nigeria,* **Global Challenges**, 2: 2018, 1-12.

Agbede O.A., & Ojelabi S.A., *Heavy Metal Contamination Assessment of Selected Water Sources in Ibadan Metropolis,* .**MAYFEB Journal of Civil Engineering**, volume 1, 2017, 1-14

Ahmed M., Matsumoto M., & Kurosawa K., *Heavy Metal Contamination of Irrigation Water, Soil, And Vegetables in a Multi-Industry District of Bangladesh*. **Int. J. Environ**. Res. 12, 2018, 531–542. https://doi.org/10.1007/s41742-018-0113-z.

Ajibade F.O., Olajire O.O., Ajibade T.F., Nwogwu N.A., Lasisi K.H., Alo A.B., Owolabi T.A. & Adewumi J.R., *Combining Multicriteria Decision Analysis with GIS for Suitably Siting Landfills in a Nigerian State*. **Environ. Sustain. Indic**. 3–4, 2019, 100010. https://doi.org/10.1016/j.indic.2019.100010.

Ajibade. F.O., Adelodun B., Ajibade T.F., Lasisi K.H., Abiola C., Adewumi J.R., & Akinbile C.O., *The Threatening Effects of Open Dumping on Soil at Waste Disposal Sites of Akure City, Nigeria*. **Int. J. Environ. Waste Manag**. 2019b (Manuscript accepted) https://www.inderscience.com/info/ingeneral/forthcoming.php?jc ode¼ijewm

Ajibulu K.E., Adefemi O.S., Asaolu S.S. & Oyakhilome G.I., *Determination of Heavy Metals in Soil Samples of Selected Sawmills in Ekiti State,* **Nigeria. Journal of Scientific Research & Reports,** 2(2), 2013, 513-521

Akintan O., Jewitt, S., & Clifford M., *Culture, Tradition, and Taboo: Understanding the Social Shaping of Fuel Choices and Cooking Practices in Nigeria*, **Energy Res. Social Sci**., 40(C): 2018, 14 – 22.

Akintan O.B. Olusola. J.A., & Azeez A.M., *Heavy Metals Loads in Soil, Farmlands and Plant Crop at Open Dumpsite*. **Global J. Environ. Sci. Manage**. 5(4): 2019, 449-460

Al Obaidy A.H. & Al Mashhadi A.A., *Heavy Metal Contaminations in Urban Soil within Baghdad City*, **Iraq. J Environ Prot**. 4(1): 2013, 72-82. Available from: https://file.scirp.org/ Html/8-6701677_27185.htm 51.

Alpa V. & Kapila M., *Analysis of Heavy Metals in Soil Samples Collected at three Different Industrial Creeks of Surat, India*, **Int.J.Curr.Microbiol.App.Sci.,** 4(6): 2015, 281-286

Al-Rudaini T.K.M. & Almousawi I.M.H., *Determination of Polycyclic Aromatic Hydrocarbons In Soil At Al-Nahrawan Bricks Factory,* **Pak. J. Biotechnol**., 15 (2) 2018, 445-450

ATSDR. *Copper. Full SPL Data. Substance Priority List (SPL) Resource Page.* **Agency for Toxic Substances and Disease Registry, Centers for Disease Control and Prevention**. 2019 https://www.atsdr.cdc.gov/SPL/resources/index.html.

ATSDR. *Lead Toxicity: Case Studies in Environmental Medicine (CSEM).* **Environmental Health and Medicine Education**. 2017. Available online: https://www.atsdr.cdc.gov/csem/lead/docs/CSEM-Lead_toxicity_508.pdf

Ávila R.A., Silva M.A.S.C., Peixoto J.V., Kassouf-Silva I., Fogaça R.T.H., dos Santos& L., *Mechanisms Involved in the In Vitro Contractile Dysfunction Induced by Different Concentrations of Ferrous Iron in the Rat Myocardium.* **Toxicology in Vitro**. 2016 Oct;36:38–45.

Bahiru D.B., Teju E., Kebede T. & Demissie N., *Levels of Some Toxic Heavy Metals (Cr, Cd and Pb) in Selected Vegetables and Soil Around Eastern Industry Zone, Central Ethiopia,* **African Journal of Agricultural Research,** 14(2), 2019, pp. 92-101.

Bateman D.N., Eagling V., Sandilands E.A., Jackson G., Crawford C., Hawkins L. C., Cheung T., Cooper G., Bradberry S.M., Thompson J.P., Thomas S.H.L., & Eddleston M., *Iron Overdose Epidemiology, Clinical Features and Iron Concentration-Effect Relationships: The UK Experience 2008–2017*. **Clinical Toxicology**. 2 (11): 2018, 1098–106.

Beaumont J.J., Sedman R.M., Reynolds S.D. , Sherman C.D., Li L.H., Howd R.A., Sandy M.S., Zeise L., & Alexeeff G.V., *Cancer Mortality in a Chinese Population Exposed to Hexavalent Chromium in Drinking Water*. **Epidem.**, 19(1): 2018, 12- 23.

Benedicta Y.F.M., Emmanuel A., Dzidzo Y.T., & Frank N., *Heavy Metals Concentration and Distribution in Soils and Vegetation at Korle Lagoon Area in Accra, Ghana* . **Cogent Environmental Science**, 3(1): 2017, 1405887

Bi C., Chen Y., Zhao Z., Li Q., Zhou Q., Ye Z. & Ge X., *Characteristics, Sources and Health Risks of Toxic Species (PCDD/Fs, PAHs and Heavy Metals) in PM2.5 During Fall and Winter in an Industrial Area*. **Chemosphere** 12:4, 2020, 6-20.

Borjac J., El Joumaa M., Kawach R., Youssef L. & Blake D. A., *Heavy Metals and Organic Compounds Contamination in Leachates Collected from Deir Kanoun*

Ras El Ain Dump and its Adjacent Canal in South Lebanon. **Heliyon** 5, 2019 e02212

Cesaro A., Belgiorno V., Gorrasi G., Viscusi G., Vaccari M., Vinti G., Jandric G.,, Dias A., Hursthouse M.I., A., & Salhofer, S., *A Relative Risk Assessment of the Open Burning of WEEE.* **Environ. Sci. Pollut. Res**. 26, 2019, 11042–11052. https://doi.org/ 10.1007/s11356-019-04282-3.

Chaudhari B.H., Parmar J.K., Mali R.H., & Bumbadiya N.H., *Effect of Co Level and FYM on Growth and Yield of Fodder Maize.* – **International Journal of Chemical Studies** 5(1): 2017, 327-329.

Cheng S., Mao H., Ruan Y., Wu C., Xu Z., Hu G., Guo X., Zhang C., Cao H., & Liu P., *Copper Changes Intestinal Microbiota of the Cecum and Rectum in Female Mice by 16S Rrna Gene Sequencing*. **Biol Trace Elem Res** 193(2) 2020, :445-455. 10.1007/s12011-019-01718-2

Cholewinska E., Ognik K., Fotschki B., Zdunczyk Z., & Juskiewicz J., *Comparison of the Effect of Dietary Copper Nanoparticles and One Copper (II) Salt on the Copper Biodistribution and Gastrointestinal and Hepatic Morphology and Function in a Rat Model.* **PLoS One** 13(5): 2018, e0197083. 10.1371/journal.pone.0197083.

Ciacci L., Fishman T., Elshkaki A., Graedel, T.E. Vassura I., & Passarini F., *Exploring Future Copper Demand, Recycling and Associated Greenhouse Gas Emissions in the EU-28*. **Global Environ Change** 63: 2020, 102002093

Daniel A. N., Ekeleme I. K., Onuigbo C. M., Ikpeazu V. O., & Obiekezie S. O., *Review on Effect of Dumpsite Leachate to the Environmental and Public Health Implication*. **GSC Advanced Research and Reviews**, 07(02), 2021, 051–060

David M., *Tire Pyrolysis is being Rolled Out in the USA', Bridging the Gulf for a Greener Tomorrow*, 2017, accessed 14 July 2018

Defarge, N. de Vendômois J. S., & Séralinia G.E., *Toxicity of Formulants and Heavy Metals in Glyphosate-Based Herbicides and other Pesticides*. – **Toxicology Reports** 5: 2018, 156-163. https://doi.org/10.1016/j.toxrep.2017.12.025.

Dirisu C.E., Biose E., & Aighewi I.T., *Heavy Metal Contamination of Ewhare Dumpsite Environment in Nigeria's Niger Delta*. **SCIREA Journal of Environment**, Volume 3, Issue 2, 2019, 44-46.

Dwivedi S. . *Evaluation of Drinking Water Quality Status by Water Quality Index: A Case Study of Shikhar Water Fall, Dehradun (UK), India*. **International Journal of Biological Innovations.** 2 (2): 2020, 214-219. https://doi.org/10.46505/IJBI.2020.2218

Ebong G.A., Akpan M.M. & Mkpenie V.N., *Heavy Metals Contents of Municipal and Rural Dumpsite Soils and Rate of Accumulation By Carica papaya and Talinun triangulare in Uyo, Nigeria*, **E-J. Chem**., 5(2): 2018, 281 – 290.

Ebong G.A., Dan E.U., Inam E., & Offiong N.O., *Total Concentration, Speciation, Source Identification and Associated Health Implications of Trace Metals in Lemna Dumpsite Soil, Calabar, Nigeria.* **J. King Saud Univ. Sci.** 2018, https://doi.org/10.1016/ j.jksus.2018.01.005.

Eddy N.O., Odoemelem S.A., & Mbaba A., A. *Elemental Composition of Soil in Some Dumpsites.* **Journal of Environmental Agricultural Food Chemistry,** 5, 2016, 1349-1365

Edokpayi N.J., Odiyo J.O., Popoola O.E. & Msagati T.A.M., *Determination and Distribution of Polycyclic Aromatic Hydrocarbons in Rivers, Sediments and Wastewater Effluents in Vhembe District, South Africa.* **Int J Environ Res Public Health,** 13(4): 2016, 387.

Edori O.S., & Iyama W.A., *Source Identification of Polycyclic Aromatic Hydrocarbons in Water at Point of Effluent Discharge into the New Calabar River, Port Harcourt, Rivers State*, **Nigeria. International Journal of Environment and Climate Change,** 9(6): 2019, 343-349

Elemile O.O, Sridhar M.K.C. & Oluwatuyi O.E., *Solid Waste Characterization and its Recycling Potential: Akure Municipal Dumpsite, Southwestern, Nigeria.* **J. Mater. Cycles Waste Manag.** 21, 2019, 585–593. https://doi.org/10.1007/s10163-018-00820-2

Eva R., Rimute S., Kęstutis J., Darius V., Steigvile B. & Aleksej Z., *Distribution of Polycyclic Aromatic Hydrocarbons and Heavy Metals in Soil Following a Large Tire Fire Incident: A Case Stud,* **Chemosphere** 286, 2021, 131-556 Available Online: https://doi.org/10.1016/j.chemosphere.2021.131556

Eze M.O., *Evaluation of Heavy Metal Accumulation in Talinum triangulare Grown Around Municipal Solid Waste Dumpsites in Nigeria***. Bull. Environ. Pharmacol. Life Sci.,** 4 (1), 2014, 92-100.

Friday A.C. & Nwite J.N., *Implications of Roasting Goats with Tyre on Human Health and the Environment in Abakaliki, Ebonyi State Nigeria*, **Journal of Pollution Effects and Control**, 2015, 1-4.

Genchi G., Sinicropi M. S., Lauria G., Carocci G., & Catalano A., *The Effects of Cadmium Toxicity.* **Int. J. Environ. Res. Public Health,** 17, 2020, , 3782; doi:10.3390/ijerph17113782

Godwin A., & Oghenekohwiroro E., *Leachate Characterization and Leachate Pollution Index from Landfill Dump Sitesin Warri Metropolis, Nigeria.* **International Letters of Natural Sciences** Vol. 57, 2016, pp 41-48

Gomez H.F., Borgialli D,A,, Sharman M., Shah K.K., Scolpino A.J., Oleske J.M., & Bogden J.D., *Blood Lead Levels of Children in Flint, Michigan: 2006-2016.* **J Pediatr** 197: 2018, 158-164. http://doi.org/10.1016/j.jpeds.2017.12.063.

Gu W.H., Bai J.F., Yuan W.H., Ma E., Zhang C.L., & Wang J.W., *Pollution Analysis of Soil Polycyclic Aromatic Hydrocarbons from Informal Electronic Waste Dismantling Areas in Xinqiao, China.* **Waste Manag. Res.** 37, 2019, 394–401.

Hammed A., Olayiwola L.A., Gbola K., Adewuyi M., & Azeez O., *Heavy Metal Contents in Soil and Plants at Dumpsites: A Case Study of Awotan and Ajakanga Dumpsite Ibadan, Oyo State, Nigeria.* **J. Environ. Erath Sci.,** 7(4): 2017, 1-14.

Harrison O., *Environmental Impact of End of Life Tyre (ELT) or Scrap Tyre Waste Pollution and the Need for Sustainable Waste Tyre Disposal and Transformation Mechanism in Nigeria* **NAUJILJ** 10 (2) 2019.

He M.J., Yang S.Y., Zhao J., Collins C., Xu J.M., & Liu X.M., *Reduction in the Exposure Risk of Farmer from E-Waste Recycling Site Following Environmental Policy Adjustment: A Regional Scale View of PAHs in Paddy Fields,* **Environ. Int**. 133, 2019, 105136bi

Huang H., Cai C., Yu S., Li X., Liu Y., Tao S., & Liu W., *Emission Behaviours of Nitro- and Oxy-Polycyclic Aromatic Hydrocarbons During Pyrolytic Disposal of Electronic Wastes*, **Chemosphere,** 222, 2019, 267–274.

Huang X., Xu X., Dai Y., Cheng Z., Zheng X., & Huo X., *Association of Prenatal Exposure to PAHs with Anti-Mullerian Hormone (AMH) Levels and Birth Outcomes of Newborns,* **Sci. Total Environ**. 723, 2020, 138009.

Huo X., Wu Y., Xu L., Zeng X., Qin Q., & Xu X., *Maternal Urinary Metabolites of PAHs and its Association with Adverse Birth Outcomes in an Intensive E-Waste Recycling Area,* **Environ. Pollut**. 245, 2019, 453–461.

Hussain M., Haider S., Abbas Y., Khan Q., Hussain B., Hussai S.W. n, & Ali A., *A Study of Source Specific Quantification, Composition and Disposal Methods of Municipal Solid Waste at Konodas Gilgit City, Pakistan.* **J. Biodivers. Environ. Sci**., 8(5), 2016, 20162222- 20166663.

Idowu O., Semple K.T., Ramadass K., O'Connor W., Hansbro P. & Thavamani, *Beyond the obvious: environmental health implications of polar polycyclic aromatic hydrocarbons*, **Environ. Int.,** 123, 2019, 543–557. https://doi.org/10.1016/j.envint.2018.12.0.

Ihedioha J.N., Ukoha P.O., & Ekere N.R., *Ecological and Human Health Risk Assessment of Heavy Metal Contamination in Soil of a Municipal Solid Waste Dump in Uyo, Nigeria.* **Environ. Geochem. Health**, 39, 2017, 497–515. https://doi.org/10.1007/ s10653-016-9830-4.

Ishak A. R., Mohamad S., Soo T.K., & Hamid F.S., *Leachate and Surface Water Characterization and Heavy Metal Health Risk on Cockles in Kuala Selangor.* **Procedia - Social and Behavioral Sciences** 222, 2016, 263 – 271

Jadoon S., & Malik A., *A Review of Formation, Toxicity of Reactive Oxygen Species by Heavy Metals and Tolerance in Plants.* – **International Journal of Biochemistry Research & Review** 21(2): 2018, 1-12. https://doi.org/10.9734/IJBCRR/2018/38670.

Jiang L.F., Cheng Z.N., Zhang D.Y., Song M.K., Wang Y.J., Luo C.L., Yin H., Li J., & Zhang G., *The Influence of E-Waste Recycling on the Molecular Ecological Network of Soil Microbial Communities in Pakistan and China.* **Environ. Pollut.,** 231, 2017, 173–181.

Jin R., Liu G.R., Zheng M.H., Jiang X.X., Zhao Y.Y., Yang L.L., Wu X.L. & Xu Y., *Secondary Copper Smelters as Sources of Chlorinated and Brominated Polycyclic Aromatic Hydrocarbons*, **Environ. Sci. Tech**., 51, 2017, 7945–7953.

Jung M.C., *Heavy Metal Contamination of Soils and Waters in and Around the Imcheon Au–Ag Mine*, **Korea. Appl Geochem** 2021, 1369-75. Available from: http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.553.6821&rep=rep1&type=pdf

Kang G.H., Uhm J.Y., Choi Y.G., Kang E.K., Kim S.Y., Choo W.O., & Chang S.S., *Environmental Exposure of Heavy Metal (Lead and Cadmium) and Hearing Loss: Data from the Korea National Health and Nutrition Examination Survey (KNHANES 2010-2013).* **Ann Occup Environ Med** 30: 2018, 22. http://doi.org/10.1186/s40557-018- 0237-9.

Kirti S., Sreemoyee C. & Bhumika J., *Chromium Toxicity and its Health Hazards.* **International Journal of Advanced Research,** Volume 3, Issue 7, 2015, 167-172

Klein D.H. & Goldberg E.D., *Mercury in the Marine Environment*. **Environ. Sci. Technol,** 4 2020, 765-768

Kosiorek, M. & Wyszkowski M.: *Effect of Cobalt on Environment and Living Organisms - A Review* - 11420 - **Applied Ecology and Environmental Research** 17(5): 2019, 11419-11449.

Kowalska J.B., Mazurek R., & Gasiorek M., *Pollution Indices as Useful Tools for the Comprehensive Evaluation of the Degree of Soil Contamination.* **A review Environ Geochem Health** 40 (6) 2018, 2395-2420.

Lee J.W., Choi H., Hwank U.K., Kang J.C., Kang Y.J., Kim K.I., & Kim J.H., *Toxic Effects of Lead Exposure on Bioaccumulation, Oxidative Stress, Neurotoxicity, and Immune Responses In Fish: A Review*. **Environ. Toxicol. Pharmacol.** 68, 2019, 101–108.

Lin M., Tang J., Ma S., Yu Y., Li G., Mai B., Fan R., & An T., *Simultaneous Determination of Polybrominated Diphenyl Ethers, Polycyclic Aromatic Hydrocarbons and their Hydroxylated Metabolites in Human Hair: A Potential Methodology to Distinguish ExternalfFrom Internal Exposur*e. **Analyst** 144, 2019, 7227–7235.

Liu Z., Cai L., Liu Y., Chen W., & Wan Q., *Association Between Prenatal Cadmium Exposure and Cognitive Development of Offspring: A Systematic Review.* **Environ. Pollut.**, 254, 2019, 113081.

Lunk H.J., *Discovery, Properties and Applications of Chromium and its Compounds.* **ChemTexts** 1:6, 2015. DOI 10.1007/s40828-015-0007-z

Mahipal S.S., Mayuri K., Manisha N., Shriyash M., Gaurav P.S., Bhaskar C., & Kumar R., *Effect of Electronic Waste on Environmental and Human Health- A Review.* **Journal of Environmental Science, Toxicology and Food Technology**. 10: 2016, 98-104.

Merchant A. & Torkelson J.M., *Pyrolysis of Scrap Tires,* **Chemical Engineering Dept**., Northwestern U., Spring, 2020.

Michaela E.I., Odohb A.O., Chukwura, E.I., & Bend M.G., *Heavy Metal and Microbial Load Properties of Dumpsite Leachate: Case Study of Onitsha Dumpsite, South-East, Nigeria.* **Journal of Toxicology Annual**. 1: 2018, 1- 6.

Nada M. l, Rovira J., Díaz-Ferrero J., Schuhmacher M. & Domingo J.L., *Human Exposure to Environmental Pollutants After a Tire Landfill Fire In Spain: Health Risks,* **Environ. Int.,** 97, 2016, 7–44.

Nascimento V.F., Sobral A.C., Andrade P.R., Yesiller N., & Ometto J.P., *Natural Disaster Risk in Municipal Solid Waste Disposal Sites using GIS: A Case Study in São Paulo State, Brazil.* **Journal of Water Resource and Protection,** 9(11), 2017, 1213.

Nishimura C., Horii Y., Tanaka S., Asante K.A., Ballesteros F.Jr, Pham Hung V., Itai T., Takigami H., Tanabe S. & Fujimori S., *Occurrence, Profiles, and Toxic Equivalents of Chlorinated and Brominated Polycyclic Aromatic Hydrocarbons in e-waste Open Burning Soils,* **Environ. Pollut.**, 225, 2017, 252–260.

Niu L., Cai H., Van Gelder P.H., Luo P., Liu F & Yang Q., *Dynamics Of Polycyclic Aromatic Hydrocarbons (PAHs) in Water Column of Pearl River Estuary (China): Seasonal Pattern, Environmental Fate and Source Implication*, **Appl. Geochem**. 90, 2018, 39–49.

Njoku P.O., Edokpayi J.N., & Odiyo J.O., *Health and Environmental Risks of Residents Living Close to a Landfill: A Case Study of Thohoyandou Landfill, Limpopo Province, South Africa.* **International Journal of Environmental Research and Public Health.** (16): 2019, 21-25

Odukoya A.M., & Laniyan T., *Health Risk Assessment of Heavy Metals in Soils and Vegetables Grown Around a Dumpsite in Lagos, Southwest, Nigeria.* **J. Appl. Geochem.** 18, 2016, 258–270.

Ogoko E.C., *Evaluation of Polycyclic Aromatic Hydrocarbons, Total Petroleum Hydrocarbons and Some Heavy Metals in Soils of Nnpc Oil Depot Aba Metropolis, Abia State, Nigeria.* **Journal of Environmental Science, Toxicology and Food Technology**. Volume 8, Issue 5 Ver. III, 2014, PP 21-27

Ogunmodede O.T., Adewole E., & Ojo A., *Quantitative Changes in Soils Properties and Uptake of Metals on Municipal Solid Waste Dumpsite in Nigeria,* **Int. Lett. Chem., Phys. Astron.,** 52: 2015, 152-162

Ojodomo J.A., Ocholi I.O., Ahmadu A.O., & Uzoma P.N., *Assessment of Heavy Metals Levels and Leaching Potentials in Dumpsites Soils in Wukari, North- Eastern Nigeria*. **International Journal of Modern Analytical and Separation Sciences**, 5(1): 2016, 20-31

Ojuri O.O., Ayodele F.O., & Oluwatuy O.E. i, *Risk Assessment and Rehabilitation Potential of a Millennium City Dumpsite in Sub-Saharan Africa.* **Waste Manag**. 76, 2018, 621–628. https://doi.org/10.1016/j.wasman.2018.03.002.

Olagunju E., Badmus O., Ogunlana F., & Babalola M., *Environmental Impact Assessment of Waste Dumpsite using Integrated Geochemical and Physico-Chemical Approach: A Case Study of Ilokun Waste Dumpsite, Ado Ekiti, Southern Nigeria*, **Civil Eng. Res. J.**, 4(2): 2018, 1-13.

Olatunde S.E. & Onisoya M.O., *Assessment of Heavy Metal Concentrations in Pawpaw (Carica papaya Linn.) around Automobile Workshops in Port Harcourt Metropolis, Rivers State, Nigeria*, **J. Health Pollut**. 14: 2017, 48-61.

Olayinka O.O., Adedej O.H. i & Ipeaiyeda R.A., *Determination of Polycyclic Aromatic Hydrocarbons (PAHs) on Selected Dumpsites in Abeokuta Metropolis, SW, Nigeria*, **Applied Environmental Research**, 37 (3), 2015, 33-48

Olayiwola O.A., & Onwordi C.T., *Environmental Fate of Heavy Metals in Soil of Ido-Osun Waste Dump Site, Osogbo, Osun, Nigeria*, **Am. J. Environ. Prot.,** 3(1): 2015, 1-4

Ololade O.O., Mavimbela S., Oke S.A. & Makhadi R., *Impact of Leachate from Northern Landfill Site in Bloemfontein on Water and Soil Quality: Implications for Water and Food Security*. **Sustainability.** 2019; 11: 4238.

Olowookere B.T., Oyibo O., & Oyerinde G.T.. *Heavy Metals Concentration in Dumpsites at Gwagwalada, Abuja: Implications on Sustainable Environmental Management.* **Greener Journal of Soil Science and Plant Nutrition**. 1(5): 2018, 001-004.

Olubunmi S.S., Olufemi J.A., Augustus O. A. I., Abidemi O. F. and Adetola, T. A. *Heavy Metal Contamination of a Dumpsite Environment as Assessed with Pollution Indices*. **International Journal of Agricultural and Biosystems Engineering**.12(1): 2018, 1-7

Oluwatuyi O. E. Ajibade F.O., Ajibade T.F., Adelodun B., Olowoselu A.S., Adewumi J.R., & Akinbile C.O., *Total Concentration, Contamination Status and Distribution of Elements in a Nigerian State Dumpsites Soil*. **Environmental and Sustainability Indicators** 5, 2020, 100021 https://doi.org/10.1016/j.indic.2020.100021

Onyema M.O., OsujI L.C. & Isiuku B.O.. *Compositional Alteration of Polycyclic Aromatic Hydrocarbons by Burning Oil Spilled Soils,* **Academia Journal of Environmental Science,** vol. 4(11), 2016, pp. 213-219.

Oyeleke P.O, Abiodun O.A., Salako R.S., Odeyemi O.E., & Abejide T.B., *Assessment of some Heavy Metals in the Surrounding Soils of an Automobile Battery Factory in Ibadan, Nigeria,* **Afr. J. Environ. Sci. Technol.,** 10(1): 2016, 1 – 8.

Oyeleke P.O., Abiodun O.A., Salako R.A., Odeyemi O.E. & Abejide T.B., *Assessment of some Heavy Metals in the Surrounding Soils of an Automobile Battery Factory in Ibadan, Nigeri,* **African Journal of Environmental Science and Technology,** Vol. 10(1), 2016, pp. 1-8, DOI: 10.5897/AJEST2015.

Ozcan H.K., Guvenc S.Y., Guvenc L., & Demir G., *Municipal Solid Waste Characterization According to Different Income Levels: A Case Study.* **Sustainability,** 8(10), 2016, 1044.

Parthasarathy P., Choi H.S., Park H.C., Hwang J.G, Yoo H.S., Lee B.K. & Upadhyay M., *Influence of Process Conditions on Product Yield of Waste Tyre Pyrolysis—A Review.* **Korean J. Chem. Eng.** 33, 2016, 2268–2286.

Peng C., Wang M., Zhao Y., & Chen W., *Distribution and Risks of Polycyclic Aromatic Hydrocarbons in Suburban and Rural Soils of Beijing with Various Land Uses,* **Environmental Monitoring and Assessment**, 188: 2016, 162.

Phothisansakul A., & Runguphan T., *Remediation of Domestic Wastewater Runoff using Vermi-Biofiltration.* **Int. J. Environ. Bioremediation Biodegrad,** 5(2), 2017, 60-64.

Popovici V., Bucur L., Calcan S.I., Cucolea E.I., Costache T., Rambu D., Schröder V., Gîrd C.E., Gherghel D., Vochita G., Caraiana A. & Badea V., *Elemental Analysis and In Vitro Evaluation of Antibacterial and Antifungal Activities of Usnea barbata (L.) Weber ex F.H.* Wigg from Călimani Mountains, Romania. **Plants**, 11, 2022, 32. https://doi.org/ 10.3390/plants11010032

Prakash S. & Verma A.K. *Acute toxicity and Behavioural responses in Arsenic Exposed Mystus vitatus (Bloch).* **International Journal on Agricultural Sciences**. 10(1): 2019, 1-3.

Prakash S. & Verma A.K., *Arsenic: It's Toxicity and Impact on Human Health* . **IJBI** 3 (1): 2021, 38-47

Rahimzadeh M.R., Rahimzadeh G., Kazemi S., & Moghadamnia, A.A. *Cadmium Toxicity and Treatment: an Update*. **Caspian J. Intern. Med.** 8, 2017, 135–145

Ravindhran B., Karthikeyan K., Jayakumar V., Mitta N., & Subramanyam S. *Early Intestinal Obstruction in Iron Toxicity – An Unheard of Occurrence*. **JCDR**. 12(1): 2018. http://jcdr.net/article_fulltext.asp?issn=0973-709x&year=2018&volume=12&issue=1&page=PD01&issn=0973-709x&id=11094

Rehman K., Fatima F., Waheed I., & Akash M.S.H., *Prevalence of Exposure of Heavy Metals and their Impact on Health Consequences,* **J. Cell. Biochem**. 119 (1), 2018, 157–184.

Sharma F., & Singh P., *Heavy Metals Pollution and its Effect on Environment and Human Health*. **International Journal of Recent Scientific Research** Vol. 6, Issue, 12, 2015, pp. 7752-7755

Shekhawat K., Chatterjee S., & Joshi B., *Chromium Toxicity and its Health Hazards*. **International Journal of Advanced Research**, Volume 3, Issue 7, 2015, 167-172

Shitandayi A., Orata F. & Lisouza F., *Assessment of Environmental Sources, Levels and Distribution of Polycyclic Aromatic Hydrocarbons Within Nzoia Catchment Area in Kenya*. **Journal of Environmental Protection**, 10(6): 2019, 772-790.

Shokr M.S., El Baroudy A.A., Fullen M.A., El-beshbeshy T.R., Ramadan A.R., Abd El Halim A., Guerra A.J.T., & Jorge M.C.O., *Spatial Distribution of Heavy Metals in the Middle Nile Delta of Egypt,* **Int. Soil Water Conserv. Res.,** 4: 2016, 293-303

Sobhanardakani S., *Potential Health Risk Assessment of Heavy Metals via Consumption of Caviar of Persian Sturgeon*. **Marine Pollution Bulletin** 123(1-2), 2017a, 34–38.

Sobhanardakani S., Tayebi L., & Hosseini S.V., *Health Risk Assessment of Arsenic and Heavy Metals (Cd, Cu, Co, Pb, And Sn) through Consumption of Caviar of Acipenser Persicus from Southern Caspian Sea.* **Environmental Science and Pollution Research** 25(3), 2018, 2664–2671.

Srigirisetty S., Jayasri T., & Netaji C., *Open Dumping of Municipal Solid Waste-Impact on Groundwater and Soil*. **Tech. Res. Organ. India,** 4(6), 2017, 26-33.

Su Y. & Zhao B., *Pyrolysis of Waste Tire Powder and Its Comparison with Shenhua Coal. In Proceedings of the International Conference on Energy and Environment Technology 2019* **ICEET'19**, Guilin, China, 16 (18) 2019; pp. 262–265.

Thamera K.M.A. & Israa H.M.A., *Determination of Polycyclic Aromatic Hydrocarbons in Soil at Al-Nahrawan Bricks Factory.* **Pak. J. Biotechnol.** VOL. 15 (2) 2018, 445-450.

Tinkov A.A., Gritsenko V.A., Skalnaya M.G., Cherkasov S.V., Aaseth J., & Skalny A.V., *Gut as a Target for Cadmium Toxicity*. **Environ. Pollut**. 235, 2018, 429–434.

Tsuma J.P,E., Wandiga S.O., & Abong'o D.A., *Methane and Heavy Metals Levels From Leachates at Dandora Dumpsite, Nairobi County, Kenya*. **IOSR Journal of Applied Chemistry,** Volume 9, Issue 9 Ver. II, 2016, PP 39-46 DOI: 10.9790/5736-0909023946

Twinamatsiko R., Mbabazi J., & Twinomuhwezi H., *Toxic Metal Levels in Food Crops Grown from Dump-Sites Around Gulu Municipality, Northern Uganda*, **Int. J. Soc. Sci. Technol.,** 1(1): 2016, 22-45.

Vaverkova M.D., Winkler J., Adamcova D., Radziemska M., Uldrijan D., & Zloch J., *Municipal Solid Waste Landfill – Vegetation Succession in an Area Transformed by Human Impact.* **Ecol. Eng.** 129, 2019, 109–114. https://doi.org/10.1016/ j.ecoleng.2019.01.020.

Wang W.C., Bai C.J., Lin C.T. & Prakash S., *Alternative Fuel Produced From Thermal Pyrolysis of Waste Tires and its Use in a Diesel Engine,* **Appl. Therm. Eng.** 93, 2016, 330–338.

Wani A,L,, Ara A., & Usmani J.A., *Lead Toxicity: A Review.* **Int. Toxicol**. 8, 2015, 55–64.

Wieczorek K., Turek A,, Kubicki J., & Wolf W.M., *The Long-Term Effect of Industrial Waste Landfill on Surface Water: An Example from Central Poland*. **Minerals,** 11, 2021, 861. https:// doi.org/10.3390/min11080861

Xiaoyan L., Zhongke B., Qinfei Y., Yingui C. & Wei Z., *Polycyclic Aromatic Hydrocarbons in the Soil Profiles (0-100cm) from the Industrial District of a Large Open-Pit Coal Mine, China*. **Royal Society of Chemistry Advances** 7(45): 2017, 28029-28037.

Yanez L.M., Alfaro J.A., Carreras N.A., & Mitre G.B., *Arsenic Accumulation in ~ Lettuce (Lactuca Sativa L.) and Broad Bean (Vicia Faba L.) Crops and its Potential Risk for Human Consumption.* **Heliyon** 5, 2019, e01152. https://doi.org/10.1016/ j.heliyon.2019.e01152.

Yasin H., & Usman M., *Site Investigation of Open Dumping Site of Municipal Solid Waste in Faisalabad*. **Earth Sciences Pakistan** 1(1), 2017, 23-25.

Yusuf A.J., Galadima A., Garba Z.N. & Nasir I., *Determination of some Heavy Metals in Soil Sample from Illela Garage in Sokoto State, Nigeria.* **Research Journal of Chemical Sciences,** Vol. 5(2), 2015, 8-10.

Zhang L., Zhou B., Duan P.G., Wang F. & Xu Y.P., *Hydrothermal Conversion of Scrap Tire to Liquid Fuel*. **Chem. Eng. J.** 285, 2016, 157–163.

Zhu Y., Fan W., Zhou T. & Li X., *Removal of Chelated Heavy Metals from Aqueous Solution: A Review of Current Methods and Mechanisms.* **Sci. Total Environ**. 678, 2019, 253–266.

Zul A., La O.A., & Muhammad N., *Heavy Metal Content of Cocoa Plantation Soil in East Kolaka, Indonesia*. **Oriental Journal of Chemistry,** 33(3), 2017, 1164-1170.

Periodical Articles

The Waste & Resources Action Programme, *UK Waste Tyre Management Best Practice: Handling of Post-Consumer Tyres* – **Collection & Storage**: 2016, p 1

UNEP, *United Nations Environment Program, Marine Pollution UNEP Regional Seas Report and Studies* No .4 2013.

USEPA, *Health Assessment Document for Chromium. Research Triangle Park,* NC, (Final report No. EPA600/8-83-014F), 2014.

WHO, *Water, Sanitation and Health.* **World Health Organization, Geneva**, 2012.

Textbooks

Cheremisinoff N.P., *Handbook of Air Pollution Prevention and Control*. Butterworth-Heinemann, 2011.

Theses/Dissertations (Unpublished)

Bayowa A.V., *Levels of Polycyclic Aromatic Hydrocarbons (PAHs) in Marshy Soils and Sediments within Warri and its Environs, Nigeria.* MSc Thesis, University of South Africa 2014.

Skudi J.B., *Effect of Alum Treatment and pH Adjustment on Turbidity and of Selected Ions In Grey Water From Githurai, Kenya.* MSc. Thesis. 2011, pp 20-38.

Websites

AGILENT, *What is Gas Chromatography,* 2021. Available Online: https://www.chem.agilent.com/cag/cabu/whatisgc.htm. What is Gas Chromatography?

Chris D.R., *What are the Environmental Impacts of Throwing Away Tires?'* 2018, Available Online: https://homeguides.sfgate.com/environmental-impacts-of-throwing-away-tires-79649.html>

Fora M.F., *Scrap Tyre Recycling In Nigeria; The Pre-Feasibility Report'*, 2018, reports/manufacturing-market-research-reports/scrap-tyre-recyclying-in-nigeriathe-pre-feasibility-report-2/>

Geoflint, *Environmental and Social Impact Assessment.* Plot Number/765/ Ain Baal, Tyre South Lebanon, 2017. www.cdr.gov.lb/stuy/EISAAinbaalFina.pdf.

Method 3050B, *Acid Digestion of Sediments, Sludges, and Soils, Revision 2*. Washington, DC. **United States Environmental Protection Agency**, 1996. Available from: https://www.epa.gov/sites/ production/files/2021-12/documents/epa-3050b.pdf

Method 8270C, *Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/ MS).* Washington, DC. **United States Environmental Protection Agency,** 1996. Available from: https://www.epa.gov/sites/production/ files/2015-07/documents/epa-8270d.pdf.

Republic of Lebanon – Ministry of Environment, *Brief on the Proposed Policy for Integrated Solid Waste Management. Unofficial Translation by Human Rights Watch*, 2018. https://www.hrw.org/sites/default/files/supporting_resources/brief _proposed_policy_isw_managementenglish.pdf.

SHU, *Sheffield Hallam University SHU, Biosciences homepage, Gas Chromatography,* 2013. Available Online: www.teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm.

SRP, *Superfund Research Program. OSU Oregon State University, PAH mixtures: New Technologies and Emerging Health Risks,* 2013. Available Online: www.oregonstate.edu/superfund/about-PAHs

The Global Tyres Market, *Trends drivers and projections, June 2016. Global Industry Analysists Inc.* 2016. Available Online: (http//www.strategyr.com/marketresearch/Tires_Market_Trends.asp)

The Daily Star, *NGOs to Get Say in Environment Body*, 2018. https://www.dailystar.com.lb/News/Lebanon-News/2018/Jan-16/433899-ngos-to-get-say-in-environment-body.ashx.

Appendix I

Result of triplicate analysis of arsenic in soil samples

Samples	AAS1 (mg/Kg)	AAS2 (mg/Kg)	AAS3 (mg/Kg)	MEAN (mg/Kg)	SD
1	0.680	0.680	0.690	0.683	0.006
2	0.090	0.100	0.110	0.100	0.010
3	0.580	0.600	0.610	0.597	0.015
4	0.100	0.120	0.120	0.113	0.012
5	0.260	0.270	0.280	0.270	0.010
6	0.330	0.340	0.350	0.340	0.010
7	0.240	0.250	0.260	0.250	0.010
8	0.110	0.140	0.130	0.127	0.015
9	0.670	0.680	0.690	0.680	0.010
10	0.190	0.210	0.220	0.207	0.015
11	0.240	0.250	0.260	0.250	0.010
12	0.210	0.240	0.230	0.227	0.015
13	0.270	0.280	0.290	0.280	0.010
14	0.340	0.350	0.360	0.350	0.010
15	0.090	0.100	0.110	0.100	0.010
16	0.470	0.480	0.490	0.480	0.010
17	0.390	0.370	0.390	0.383	0.012
18	0.090	0.100	0.110	0.100	0.010
19	0.100	0.130	0.120	0.117	0.015
20	0.200	0.220	0.230	0.217	0.015
21	0.150	0.140	0.150	0.147	0.006
22	0.180	0.230	0.200	0.203	0.025
Mean	**0.272**	**0.286**	**0.291**		

Source: Author's Field Work, 2022

Appendix II

Result of triplicate analysis of cadmium in soil samples

Samples	AAS1 (mg/Kg)	AAS2 (mg/Kg)	AAS3 (mg/Kg)	MEAN (mg/Kg)	SD
1	0.330	0.340	0.350	0.340	0.010
2	0.420	0.430	0.440	0.430	0.010
3	0.170	0.180	0.190	0.180	0.010
4	0.770	0.770	0.780	0.773	0.006
5	0.100	0.100	0.120	0.107	0.012
6	0.100	0.200	0.210	0.170	0.061
7	0.180	0.640	0.650	0.490	0.269
8	0.620	0.160	0.150	0.310	0.269
9	0.130	0.050	0.060	0.080	0.044
10	0.040	0.300	0.120	0.153	0.133
11	0.080	0.140	0.130	0.117	0.032
12	0.110	0.040	0.050	0.067	0.038
13	0.020	0.110	0.120	0.083	0.055
14	0.090	0.150	0.160	0.133	0.038
15	0.140	0.140	0.150	0.143	0.006
16	0.280	0.290	0.310	0.293	0.015
17	0.110	0.130	0.140	0.127	0.015
18	0.030	0.040	0.050	0.040	0.010
19	0.010	0.030	0.020	0.020	0.010
20	0.120	0.300	0.140	0.187	0.099
21	0.310	0.290	0.300	0.300	0.010
22	0.230	0.260	0.250	0.247	0.015

Source: Author's Field Work, 2022

Appendix III

Result of triplicate analysis of chromium in soil samples

Samples	AAS1 (mg/Kg)	AAS2 (mg/Kg)	AAS3 (mg/Kg)	MEAN (mg/Kg)	SD
1	0.080	0.100	0.110	0.097	0.015
2	0.010	0.020	0.030	0.020	0.010
3	0.090	0.110	0.120	0.107	0.015
4	0.210	0.220	0.230	0.220	0.010
5	0.160	0.170	0.180	0.170	0.010
6	0.030	0.030	0.050	0.037	0.012
7	0.180	0.210	0.220	0.203	0.021
8	0.110	0.120	0.130	0.120	0.010
9	0.080	0.080	0.090	0.083	0.006
10	0.120	0.130	0.140	0.130	0.010
11	0.190	0.200	0.220	0.203	0.015
12	0.210	0.220	0.230	0.220	0.010
13	0.300	0.310	0.320	0.310	0.010
14	0.020	0.030	0.040	0.030	0.010
15	0.410	0.420	0.430	0.420	0.010
16	0.170	0.180	0.190	0.180	0.010
17	0.130	0.160	0.150	0.147	0.015
18	0.610	0.600	0.620	0.610	0.010
19	0.030	0.040	0.050	0.040	0.010
20	0.190	0.200	0.210	0.200	0.010
21	0.090	0.110	0.100	0.100	0.010
22	0.140	0.160	0.150	0.150	0.780

Source: Author’s Field Work, 2022

Appendix IV

Result of triplicate analysis of Lead in soil samples

Samples	AAS1 (mg/Kg)	AAS2 (mg/Kg)	AAS3 (mg/Kg)	MEAN (mg/Kg)	SD
1	0.340	0.350	0.360	0.350	0.010
2	0.710	0.730	0.740	0.727	0.015
3	0.230	0.250	0.260	0.247	0.015
4	0.620	0.630	0.650	0.633	0.015
5	0.290	0.300	0.310	0.300	0.010
6	0.470	0.450	0.470	0.463	0.012
7	0.670	0.670	0.690	0.677	0.012
8	0.380	0.400	0.410	0.397	0.015
9	0.120	0.120	0.140	0.127	0.012
10	0.670	0.660	0.680	0.670	0.010
11	0.130	0.150	0.160	0.147	0.015
12	0.800	0.790	0.810	0.800	0.010
13	1.610	1.620	1.630	1.620	0.010
14	1.560	1.570	1.590	1.573	0.015
15	0.980	0.980	0.990	0.983	0.006
16	1.630	1.630	1.650	1.637	0.012
17	1.010	1.020	1.030	1.020	0.010
18	0.630	0.630	0.640	0.633	0.006
19	0.940	0.950	0.960	0.950	0.010
20	0.510	0.520	0.540	0.523	0.015
21	0.140	0.160	0.150	0.150	0.010
22	0.220	0.240	0.230	0.230	0.010

Source: Author's Field Work, 2022

Appendix V

Result of triplicate analysis of Zinc in soil samples

Samples	AAS1 (mg/Kg)	AAS2 (mg/Kg)	AAS3 (mg/Kg)	MEAN (mg/Kg)	SD
1	0.630	0.640	0.650	0.640	0.010
2	1.610	1.620	1.640	1.623	0.015
3	0.490	0.500	0.520	0.503	0.015
4	0.420	0.430	0.440	0.430	0.010
5	2.210	2.220	2.230	2.220	0.010
6	1.240	1.250	1.260	1.250	0.010
7	0.930	0.920	0.940	0.930	0.010
8	0.240	0.240	0.260	0.247	0.012
9	1.040	1.050	1.060	1.050	0.010
10	1.410	1.420	1.430	1.420	0.010
11	1.990	1.990	2.000	1.993	0.006
12	2.000	2.010	2.020	2.010	0.010
13	2.400	2.140	2.160	2.233	0.145
14	0.900	0.900	0.920	0.907	0.012
15	0.470	0.470	0.490	0.477	0.012
16	1.390	1.400	1.420	1.403	0.015
17	1.000	1.020	1.030	1.017	0.015
18	0.470	0.480	0.490	0.480	0.010
19	0.340	0.330	0.350	0.340	0.010
20	0.680	0.670	0.690	0.680	0.010
21	0.190	0.220	0.210	0.207	0.015
22	0.450	0.460	0.440	0.450	0.010

Source: Author's Field Work, 2022

Appendix VI

Tyre grading point at the pyrolysis plant

Source: Author's Field Work, 2022

Appendix VII

Tyre loading point at the pyrolysis plant

Source: Author's Field Work, 2022

Appendix VIII

Iron removing point at the pyrolysis plant

Source: Author's Field Work, 2022

Appendix IX

Tyre cutting point at the pyrolysis plant

Source: Author's Field Work, 2022

Appendix X

Carbon dust by-product at the pyrolysis plant being stored in sacks

Source: Author’s Field Work, 2022

Appendix X

Water recycling point at the pyrolysis plant

Source: Author's Field Work, 2022

Bio-data

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❖ Personal Business	2016 till date

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- Sindiku O. and Ogbue C.O., *Assessment of Heavy Metals and PAHs in Soil from Tyre Pyrolysis Plant located in Egbeda Local Government Area, Ibadan, Oyo State,* **FASCON International Conference**, 2022.

E. Date and Signature

University Compliance Certification

This is to certify that, this Thesis written by **Christopher Ogorchukwu, OGBUE with Matric No. LCU/PG/001962** 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.

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