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Evaluation of Polycyclic Aromatic Hydrocarbon from Selected Communities in Udu Local Government Area of Delta State

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Abstract

The study presents a design to investigate the concentration profiles and the distribution of polycyclic aromatic hydrocarbons in soil samples within two communities in the Udu local government area of Delta State, Nigeria. Five soil samples suspected to have been contaminated with hydrocarbons were collected from the selected communities and were analyzed for polycyclic aromatic hydrocarbons using gas chromatography equippedwith a mass spectrometry detector (GC-MSD), after extraction and clean-up of the extract with n-hexane/dichloromethane using standard glass column chromatography (190/Piece Ambala, model). The results obtained from the hydrocarbon analysis gave concentration of the ∑17 polycyclic aromatic hydrocarbons (PAHs) in soil samples ranged from 0.11 to 0.83ppm with a mean value of 0.45. The order of the level of PAHs in the soil samples based on their location follows this pattern; mechanic workshop soil > road traffic soil > drainage soil > farm field soil > petrol station soil, while the appearance and profile of PAHs with respect to ring size was in the order of 3-rings > 5-rings >2-rings >4-rings >6-rings. The lower molecular weight (2-3 rings) PAHs and non-carcinogenic PAHs were the main PAHs in these soils. The isometric comparison and principal components analysis used for source apportionment shows that the PAHs in these soil originated from High-temperature combustion of biomass and fossil fuels such as wood as well as emissions from transportation.

Keywords: Hydrocarbon contamination, soil, Udu communities, contamination indices

1. Introduction

Polycyclic aromatic hydrocarbons a prevalent class of contaminants primarily formed during the imperfect or short burning of fossil fuels (petroleum, ecological chat, and coal), the latest environments due to the multiplicity of their sources (Mazeas*et al.*, 2002). These dangerous unsafe pollutants are risky appropriate to their carcinogenic, immunotoxic, mutagenic and teratogenic effects. When they are released into the environment resulting in threat to all forms of life ranging from microorganisms to humans via human activities (Muharram *et al.*, 2019). The aromatic (pungent) hydrocarbons are the complete repeated compounds, the principal repeated formation is the benzene circle, toluene, ethylbenzene and xylene (BTEX) and polycyclic aromatic hydrocarbons (PAHs) (Wang *et al.*, 2006).

As a result of its widespread source and constant nature, PAHs are distributed by atmospheric transport and are found roughly ubiquitously. Humans are exposed to PAHs mixtures in the gas or partial phase- in atmospheric air. Prolonged duration exposure to high PAHs levels is linked with an adverse health challenges. Because some PAHs are considered carcinogenic, inhaling PAHs in particles is a potentially intense health threat associated with an excessive risk of lung cancer (Ibe *et al.*, 2012; Adipah, 2019).

1.1 Study Area

This research work was carried out in Udu local government area of Delta State, Nigeria (Figure 1). Udu is one city located with close propinquityto Warri metropolis, thus, it has become a fast- growing city, urbanizing all the adjoining communities with Warri metropolis. The Udu land is interlocked (mesh) by rivers flowing across; it has weather and rain forest with evergreen vegetation and plantation all year round. Its geographical attribute comprises many streams that interlink into a complex web of rivers, lagoons, swamps and wetlands. Udu has thirty-two Communities, but two of these Communities were chosen for this study amongst these are Egini (5° 27' 44"N and 5° 49' 56"E) and Ubogo (5° 27' 0"N and 5° 49' 60"E).

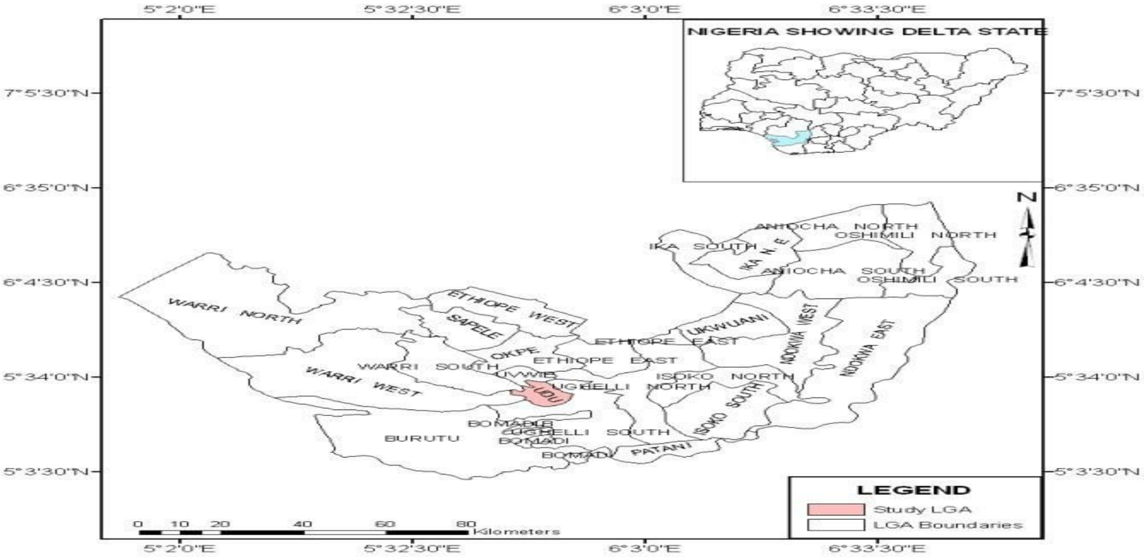

Figure 1 Map of Delta State showing Udu Local Government Area (Ijeomah and Pudie, 2015).

Figure 2 The green dots indicates sampling area and core sites (Google maps 2020).

2. *Materials and Methods*

2.1 Sample collection

Soil samples were collected from the area suspected to have been contaminated with petroleum products in Egini/Ubogo communities in Udu, Delta State as shown in the google map in Figure 2. These areas were investigated to determine the level of aromatic hydrocarbons due to the nature of activities in the locations. The locations include a) Mechanic workshop soil (Egini junction, Udu Road); b) Drainage soil(Close to Egini Secondary School junction); c) Farm field soil (from Egini Community); d) Traffic point soil (Ubogo Market); and e) Petrol station soil (Udu road, close to Ubogo Market).

Similarly, the control sample was collected from virgin land.Topsoil composite samples (including 3 to 4 samples from each site and mixed) from the sites identified above were collected at a depth of 0-10cm using a stainless-steel auger. Samples were transferred to aluminum foil, transported to the laboratory, and stored in a refrigerator with an ice pack. The samples were dried in air and homogenized in the dark at room temperature and foreign matter such as leaves, stems, and stones were removed. The samples were then ground with a mortar and pestle and sieved through a 2mm sieve and stored in clean amber coloured glass bottles that was previously washed before analyses.

2.2 Samples Extraction and Purification

The PAHs extraction was carried out using**ultrasonic extraction** (EPA Method 3550B) (US EPA, 1996). 10gofsoilsamplewasweighedintoa clean 100ml glass beaker and homogenized with 10 grams of anhydrous sodium sulphate until a completely dry homogenate wasobtained. 20 ml of dichloromethane was added to the dry homogenate soil sample inside a 100mlbeaker. This was then shaken for 30 minutes in a mechanical shaker,after which the beaker was removed from the mechanical shaker and then placed in a sonicator and sonicated for 30 minutes at 70°C. After sonication, 5 grams of anhydrous sodium sulphate was added to the samples again to eliminate any leftover water molecules. This was allowed to stand for 15 minutes. The extract was transferred to a rotary evaporator and concentrated to 2ml ready for the clean-up process (US EPA, 1996).

2.3 Preparation of Packed Fractionating Column

Glass columns was packed with chromatograph glass wool and 10g of 60-120 mm mesh silica gel pre-conditioned (baked) at 105°C overnight was dissolved with Dichloromethane to form slurry, and the slurry was added into the column. 5 grams of anhydrous sodium sulphate was added to the fractionating glass column to absorb water and this was conditioned with 10ml of Dichloromethane before extraction (US EPA, 1996).

2.4 Clean-up Procedure for Aromatic Hydrocarbons and Quantification

The column was eluted with 10ml of Dichloromethane. The eluate was collected in a solvent rinsed 100ml conical flask. The eluate was transferred into a round bottom flask and concentrated to 1ml using a rotary evaporator. The concentrate was pipetted into a clean 2ml Teflon screw-cap vial and cap tightly and labelled ready for GC-MSD PAHs analysis. The sample was then injected into the GC-MSD for PAH analysis using the Agilent 6890-5973N Gas Chromatograph-Mass Selective Detector (GC-MSD) (US EPA 1996).

The separation and detection of compounds in samples were carried out using Agilent 6890- 5973N Gas Chromatograph–Mass Selective Detector (GC-MSD) instrument 1 μl of concentrated sample eluted from column was injected into GC vial. The (Blank) DCM was injected into a micro-syringe of GC to clean the syringe (3 times) before taking the sample for analysis. The micro-syringe was further rinsed with the sample. Then the sample was injected into the column for the separation of compounds (analytes) in the sample. After separation, the compounds were passed through a mass selective detector. MSD detects the compounds (analytes) in the sample. The amount of Aromatics TPH was resolved at a particular chromatogram in ppm (US EPA 1986).

Agilent Technologies Inc MSD Chemstation G1701DA D.03.00.611 software was used in quantifying aromatic component results in ppm (part per million) a suite of 17 priority polycyclic aromatic hydrocarbons recommended by EPA (Accu-standard) was used. Chemstation software was used to quantify normal n-alkanes within C_8-C_{40} and C_{11}-C_{22} including pristine/phytane respectively.

3. *Results and Discussion*

3.1 Mean Concentration of Polycyclic Aromatic Hydrocarbon (PAHs) in Soil

The concentration and distribution of 17-PAHs components in this study are presented in Table 1 (Figure 3). The total concentration ranged from 0.11ppm–0.83ppm, with a mean value of 0.45ppm. The ascending order of PAHs based on their location sites is as follows: Petrol station soil> Farm field soil> Drainage soil> Road traffic soil> Mechanic workshop soil. Analysis of Variance (ANOVA) result is shown in Table 2. There were no significant variations in the PAHs concentrations in the soils (p-value >0.05; Fcal<Fcrit) (Maliszewska-Kordybach 1996; DPR, 2018). A soil has been classified as being non-contaminated when total PAHs concentration is below 0.2ppm, weakly

contaminated when total PAHs concentration falls between 0.6ppm–1.0ppm, and heavily contaminated when total PAHs concentration is greater than 1.0ppm. Based on this classification, Petrol station soil can be regarded as non-contaminated, 0.83ppm at Mechanic workshop soil indicated contamination while all three locations, Drainage soil, Farm field soil and Road traffic soil were all weakly contaminated. Since all PAHs concentrations were lesser than 1.0ppm Benzo(a)pyrene is regarded as the most carcinogenic PAHs congeners, was not detected in any of the sample's locations. This, all the location sites can be regarded as being relatively non-polluted with PAHs compared to previous studies (Onyema *et al.,* 2015)

Table1: Mean concentration and distribution of PAHs in soil.

	MWS Ppm	**FFS Ppm**	**RTS ppm**	**PSS Ppm**	**DS Ppm**	**CS Ppm**
Nap	0.05	0.21	0.07	0.07	0.18	<0.0
Acy	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
Ace	0.03	<0.0	0.03	<0.0	<0.0	<0.0
Flu	0.04	<0.0	0.05	<0.0	<0.0	<0.0
Phen	0.1	<0.0	<0.0	<0.0	<0.0	<0.0
Ant	0.1	<0.0	<0.0	<0.0	<0.0	<0.0
Car	0.07	0.14	<0.0	0.04	0.2	<0.0
Flt	0.06	<0.0	<0.0	<0.0	<0.0	<0.0
Pyr	0.04	<0.0	<0.0	<0.0	<0.0	<0.0
BaA	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
Chry	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
BbF	0.12	<0.0	0.14	<0.0	<0.0	<0.0
BkF	0.12	<0.0	0.14	<0.0	<0.0	<0.0
BaP	0.1	<0.0	0.13	<0.0	<0.0	<0.0
DahA	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
IndP	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
BghiP	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
Total	0.83	0.35	0.56	0.11	0.38	0.0
2-Rings	0.05	0.21	0.07	0.07	0.18	0.0
3-Rings	0.34	0.14	0.08	0.04	0.2	0.0
4-Rings	0.1	0.0	0.0	0.0	0.0	0.0
5-Rings	0.34	0.0	0.4	0.0	0.0	0.0
6-Rings	0.0	0.0	0.0	0.0	0.0	0.0
LMW	0.32	0.21	0.15	0.07	0.18	0.0
HMW	0.44	0.0	0.4	0.0	0.0	0.0
Carcinogenic	0.34	0.0	0.4	0.0	0.0	0.0
Non-carcinogenic	0.49	0.34	0.15	0.11	0.38	0.0

ND=Not detected; Nap=Naphthalene, Acy =Acenaphthalyne, Ace=Acenaphthene, Flu=Fluorene, Phen=Phenanthrene, Ant=Anthracene, Car=Carbazole, Flt=Fluoranthene, Pyr=Pyrene, BaA=Benzo(a)anthracene,Chry=Chrysene, BbF=Benzo(b)fluoranthene, BkF=Benzo(k)fluoranthene, BaP=Benzo(a)pyrene, IndP=Indeno(1,2,3-cd)pyrene, DahA=Dibenz(a,h)anthracene and BghiP=Benzo(g,h,i)pyrene, LMW = Lower molecular weight; HMW = higher molecular weigh

Table 2: ANOVA result of PAHs concentrations in soils

Source of Variation	***SS***	***df***	***MS***	***F***	***P-value***	***F crit***
Between Groups	0.016878	4	0.004219	1.642452	0.171732	2.485885
Within Groups	0.205518	80	0.002569			
Total	0.222395	84				

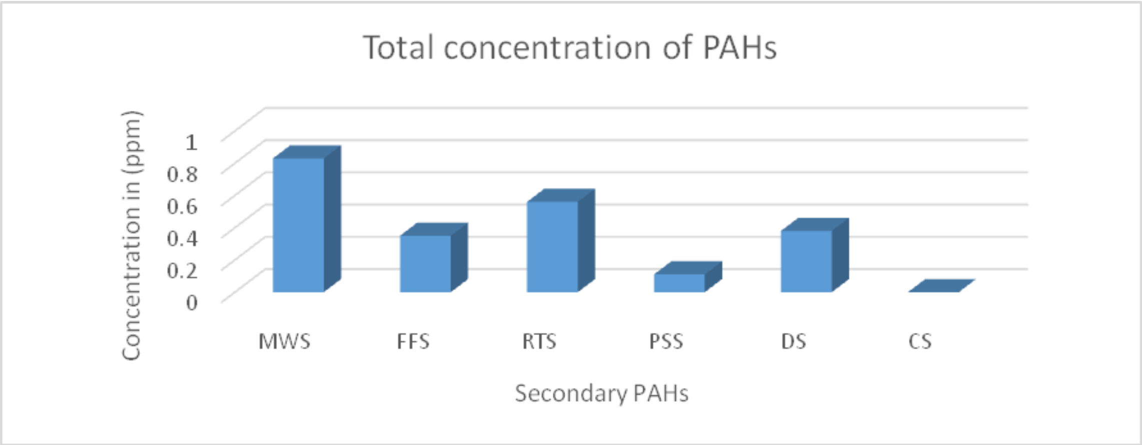

Figure 3 Concentration (ppm) and carbon number distribution of aromatic in all soils

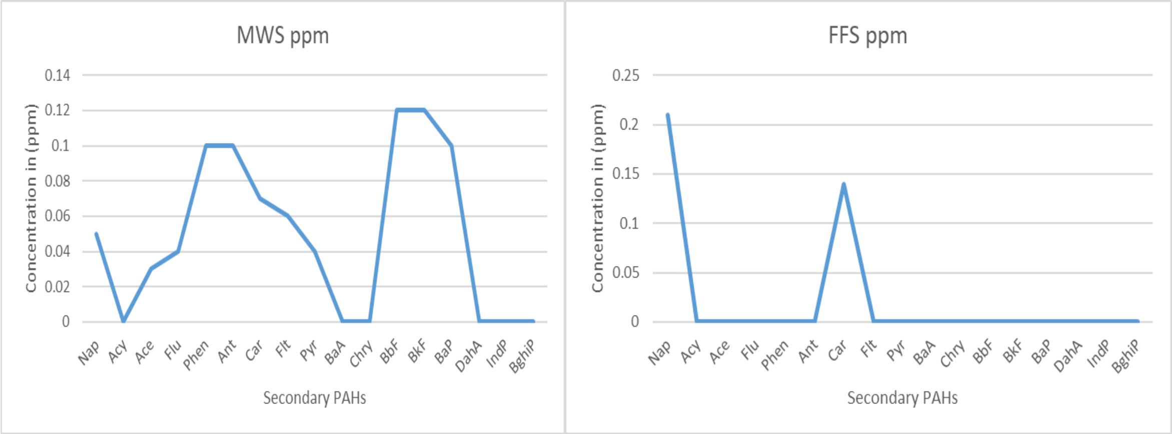

Figure 4Concentration (ppm) and distribution of PAHs in MWS and FFS in soil

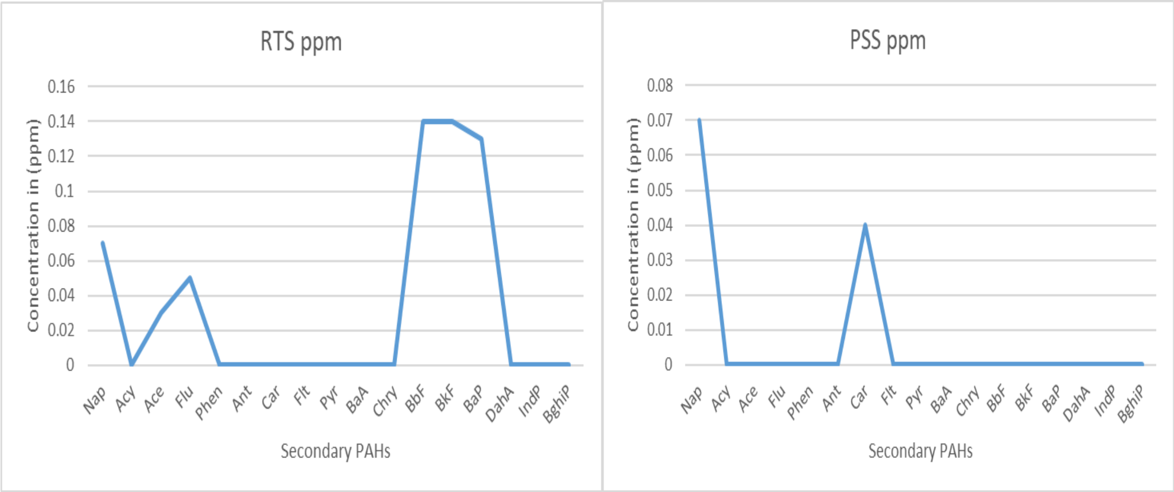

Figure 5Concentration (ppm) and distribution of PAHs in RTS and PSS in soil

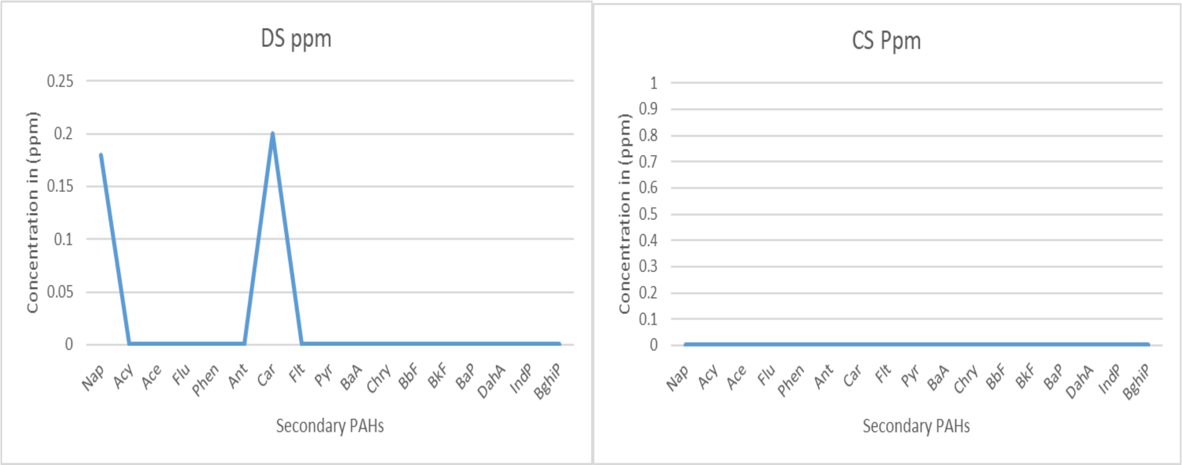

Figure 6Concentration (ppm) and distribution of PAHs in DS and CS in soil

3.2 Source identification of PAHs

The isometric ratio of PAHs has been used to distinguish between pyrogenic and petrogenic sources by several researchers (Tesi *et al*., 2016; Iwegbue*et al*., 2020). For instance, Flt/(Flt+Pyr) ratio <0.4 indicates petroleum origin, but >0.4 implies petroleum combustion; LMWPAH/HMWPAH ratio <1 are derived from pyrogenic processes such as incomplete combustion, and >1 shows petrogenic origin from crude oil or refined petroleum products. COMB PAHs/TPAHs < 1 = combustion of fossil fuels or wood and > 1 = petroleum origin. Total index is the summation of the indices standardized by their individual limits between low and high temperature processes (Iwegbue*et al*., 2016). The total index = (BaA/(BaA+ Chry))/0.2 + (IndP/(IndP + BghiP))/0.5 + (Ant/(Ant

+Phen))/0.1 + (Flt/(Flt + Pyr))/0.4. Total index value < 4 = low temperature combustion processes and > 4 = high temperature combustion processes. In this study, the different computed isometric ratio is shown in Table 3

The Ant/(Ant+Phen) ratio ranged from 0.0–0.5. This ratio was > 0.1 in Mechanic workshop soil. Combustion processes are common in this environment, and the results show that combustion processes a major source of PAHs. The ratio of Flt/(Flt+Pyr ranged from 0.0–0.6. only one location (Mechanic workshop soil) had a value that was not 0.0. The value obtained (0.6) indicated that the source of PAHs in this environment was coal and biomass/diesel, which are commonly found in Mechanic workshop soil (MWS).

The LMWPAH/HMWPAH ratio ranged from 0.4–0.7. The values obtained were 0.4 for Road traffic soil and 0.7 for Mechanic workshop soil. Base on this classification for this isometric ratio, the source of PAHs from both Road traffic soil and Mechanic workshop soil are the combustion of fossil fuels or wood (Lawal, 2017). The ratio of CombPAHs/TPAHs was 0.5 at Mechanic workshop soil and 0.7 at Road traffic soil, these values were <1 indicating that the source of PAHs was from combustion processes while the total index value for Mechanic workshop soil was 6.5 >4.0 indicating that the PAHs in this location was from high- temperature combustion processes

Table 3:Isometric ratios of PAHs in the soil and primary sample

	MWS ppm	**FFS ppm**	**RTS ppm**	**PSS ppm**	**DS ppm**
BaA/(BaA+Chry)	0.0	0.0	0.0	0.0	0.0
IndP/(IndP+BghiP)	0.0	0.0	0.0	0.0	0.0
Ant/(Ant+Phen)	0.5	0.0	0.0	0.0	0.0
Flt/(Flt+Pyr)	0.6	0.0	0.0	0.0	0.0
LMW/HMW	0.7	0.0	0.4	0.0	0.0
Phen/Ant	1.0	0.0	0.0	0.0	0.0
Flt/Pyr	1.5	0.0	0.0	0.0	0.0
BaP/BghiP	0.0	0.0	0.0	0.0	0.0
CombPAHs/TPAHs	0.5	0.0	0.7	0.0	0.0
Total index	6.5	0.0	0.0	0.0	0.0

ND =Not detected; Nap=Naphthalene, Acy =Acenaphthalyne, Ace=Acenaphthene, Flu=Fluorene, Phen=Phenanthrene, Ant=Anthracene, Car=Carbazole, Flt=Fluoranthene, Pyr=Pyrene, BaA=Benzo(a) anthracene,Chry=Chrysene,BbF=Benzo(b)fluoranthene,BkF=Benzo(k)fluoranthene, BaP=Benzo(a)pyrene, IndP=Indeno(1,2,3-cd)pyrene, DahA=Dibenz(a,h)anthracene and BghiP=Benzo(g,h,i)pyrene, LMW = Lower molecular weight; HMW = higher molecular weight

3.3 Profile and Distribution of PAHs in theSoil Samples

The cumulative results of the secondary sources were further characterized according to the distribution of the ring structures, and they are presented in Figure 7. It could be observed that Mechanic workshop soil (0.39ppm) occupied the highest concentration in 2 and 3 membered ring PAHs and the least concentration in Petrol station soil (0.11ppm). The 4-membered ring PAHs (Flt &Pyr), were detected only in Mechanic workshop soil with a concentration of 0.1ppm but absent in the other 4-sites. Similarly, the concentration of 5-membered ring PAHs (BbF, BkF, and BaP) was highest in Road traffic soil (0.41ppm), followed by Mechanic workshop soil (0.34ppm) and 6-membered ring were not detected in any of the location including the control sample. The carcinogenicity, mutagenicity and toxicity of PAHs is a function of their molecular structures, wherein low molecular weight PAHs (<3 rings) often display acute toxicities and low carcinogenicities; while, high molecular weight PAHs (>3 rings) show low toxicities and very high carcinogenicities and mutagenicity (Ivwurie*et al.*, 2016). All secondary sources except those from Mechanic workshop soil and Road traffic soil were typically non-carcinogenic, since the carcinogenic congeners were not detected in any of those other 3-sites.

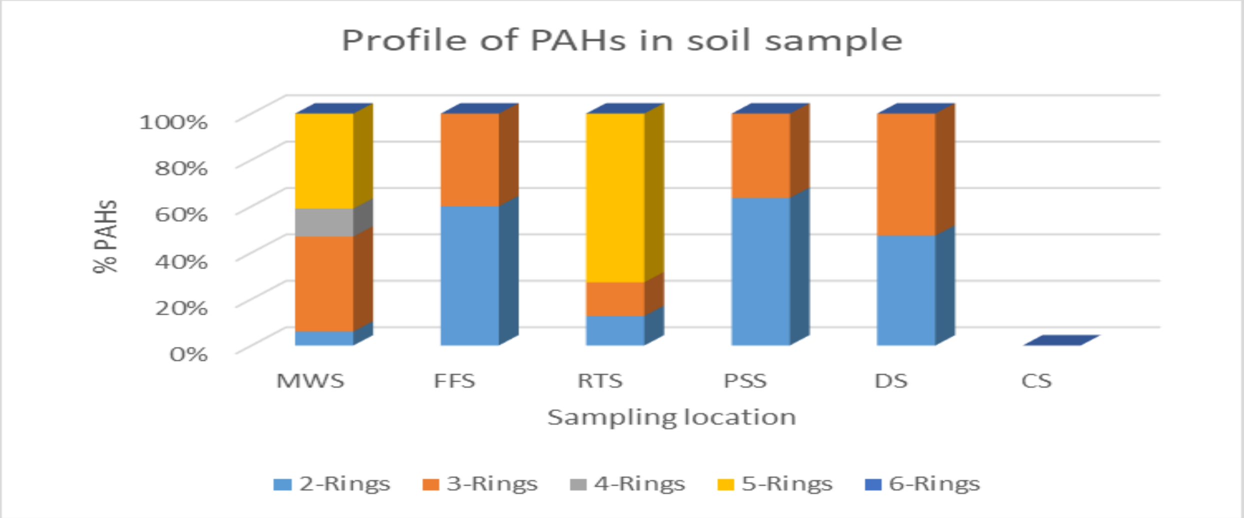

Figure 7 Profile of PAHs in the soil samples

Conclusion

The results of this study provide firsthand information about the presence and sources of hydrocarbons in the soil of the study area. The total PAH concentration in this soil ranged from 0.11ppm–0.83ppm, and is included in the uncontaminated category. There was the predominance of low molecular weight and non-carcinogenic PAHs. The Isometric ratios used for source apportionment suggest that the PAHs in these soils originates from biomass/diesel, combustion of fossil fuels or wood, coal and high- temperature combustion processes. The soils of the Udu metropolis, had Benzo(a)pyrene total potency equivalent below the Canadian council of ministers of environment (CCME) threshold value, suggesting negative human health impact.

References

Adipah, S. (2019). Introduction of Petroleum Hydrocarbons Contaminants and its Human Effects. Journal of Environmental Science and Public Health 3, pp. 001-009.

Department of Petroleum Resources (DPR). (2018). *Environmental guidelines and standard for the petroleum industry in Nigeria (Revised Edition).* Department of Petroleum Resources, Ministry of Petroleum and Mineral Resources, Abuja Nigeria.

Ibe, K.A., Nganje, T.N., Edet, A.E., Ibok, U.J., Ukpabio, E.J., Neji, P. (2012). Polycyclic aromatic hydrocarbons in surface water and soil in the vicinity fuel-oil spillage from a tank farm distribution facility. EsukUtan, Calabar Municipality, Nigeria. Environ Earth Sci. 67:81-90.

Ijeomah, H.M. and Pudie, A. (2015). Ultilization of tortoise chelonoidesngra, quo and gaimard 1824 in five selected communities in Udu Local Government Area of Delta State, Nigeria. 2141-1778

Ivwurie, W., Emelife, S.C. and Snape, C. (2016). Polycyclic aromatic hydrocarbons in soil within selected communities in Delta State. Journal of Science and Multidisciplinary Research, 8(1):13–8.

Iwegbue CMA., Ehigbor MJ, Tesi GO, Eguavoen OI, Martincigh BS. (2020). Occurrence, sources and exposure risk of polycyclic aromatic hydrocarbons (PAHs) in street dusts from the Nigerian megacity, Lagos. Polycyclic Aromatic Compounds http:///doi.org/10.1080/10406638.2020.1716027

Iwegbue, C.M.A., Arimoro, F.O., Nwajei, G.E. and Eguavoen, O.I. (2016). Concentration and distribution of trace metals in water and stream bed sediments of Orogodo River, Southern Nigeria. Soil Sediment contamination, 21(3):382–406.

Lawal, A.T. (2017). Polycyclic aromatic hydrocarbons. A review, Cogent Environmental Science, 3: 1339841.

Maliszewska-Kordybach, B. (1996). Polycyclic aromatic hydrocarbons in agricultural soils in Poland: preliminary proposals for criteria to evaluate the level of soil contamination. *Applied Geochemistry*, 11 (1–2): 121–127.

Mazeas, L., Budzinski, H. and Raymond, N. (2002). Absence of stable carbon isotope fractionation of saturated and polycyclic aromatic hydrocarbons during aerobic bacterial biodegradation. Organic Geochemistry. 33, 1259-1272.

Muharrem, I. & Olcay Kaplan, I. (2019). Introductory chapter: sources, health impact, and environment effect of hydrocarbons, Hydrocarbon Pollution and its Nelson Effect on the Environment, DOI: 10.5772/intechopen.89039., P.F. (1989). Combustion generated polycyclic aromatic hydrocarbons in diesel exhaust emissions. Fuel. 68:283-286.

Onyema, M.O., Ofodili, S.O. and Osigi, I.C. (2015). Characterization of petroleum hydrocarbons in post-born crude oil-spilled soils, Gokana, Rivers State, Nigeria. Journal of Applied Science and Environmental Management, 19(4):719–724.

Tesi, G.O.,Iwegbue, C.M.A., Emuh, F.N. and Nwajei, G.E. (2016).Ladgo Dam floods disaster of 2012: An assessment of the concentrations, sources and risks of polycyclic aromatic hydrocarbons in floodplain soils of the lower reaches of River Niger, Nigeria. *Journal of Environmental Quality* 45: 305-314.

United States Environmental Protection Agency (US EPA 1996). Method 3550B. Ultrasonic extraction.Washington: US EPA.

United States Environmental Protection Agency (US EPA 1986). Method 8100. Polynuclear Aromatic Hydrocarbons using GCMS. Washington:

Wang, G., Huang, L.., Zhao, X., Niu, H., & Dai, Z. (2006). Aliphatic and polycyclic aromatic hydrocarbons of atmospheric aerosols in five locations of Nanjing urban area, China. Atmospheric Research 81, 4583-4591.