Assessment of Polycyclic Aromatic Hydrocarbons in Soils from Selected Areas in Agbarho Communities, Delta State, Nigeria.

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Abstract: *Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants of environmental interest due to their established carcinogenic and mutagenic characteristics. In this study, PAHs occurrence in soil within some selected areas in Agbarho community, Delta State, Nigeria was assessed using gas chromatography equipped with a mass spectrometry detector (GC-MSD) after extraction and clean-up of the extracts with n-hexane/dichloromethane. The observed concentrations of $\sum 17$ PAHs in the soils ranged from 16 to 122 $\mu g\,kg^{-1}$, and followed the order: mechanic workshop > barbecue spot > motorway> filling station > traffic point. On the average, the occurrence of the individual PAH compounds followed the order: Naphthalene > Anthracene = Carbazole > Phenanthrene > Fluorene > Benzo(a) pyrene > Acenaphthene = Flouranthene = Pyrene > Benzo(b)fluoranthene = Benzo(k)fluoranthene while the occurrence pattern of the PAHs with respect to ring size increases with increase in the number of aromatic rings (i.e, 2-rings > 3-rings > 5-Rings > 4-rings). The lower molecular weight (2-3 rings) PAHs (and non-carcinogenic PAHs) were the predominant PAHs in the study soils. The isomeric ratios and principal component analysis used for source apportionment indicated that the PAHs in these soils originated from high temperature combustion of biomass and fossil fuels such as wood and coal as well as traffic emissions.*

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1.0   Introduction

Concentrations proportion of specific PAHs pairs is an index for qualitative determination of the PAHs source through the application of PAHs diagnostic ratios, which can be used to evaluate the origin of PAHs in the soil, and other components of the environment (CCME, 2008; Ivwurie *et al*., 2016). The major environmental sources of PAHs in the environment are pyrogenic, petrogenic and biological.sources.

Important routes in which PAHs is introduced to the population are through consumption of meals containing PAHs, inhaling ambient indoor air, cigarettes smoking, or inhaling smoke from open fireplaces, from the fossil fuels that we use to drive cars and cook our food (Zhang *et al*. 2015). Human vulnerability to PAHs can also be attributed to exposure via, automobile exhausts, consumption of barbecued food, industrial emissions, jet fuel, and waste sites hazard. PAHs get to living creatures via water, air and food ingested. PAHs are often atmospherically measured for quality air assessments in biological tissues for health-result monitoring. PAHs are vast environmental pollutants far impossible for

all humans to evade exposure. Non-occupational and occupational dermal contact, inhalation and ingestion settings are all exposure routes (Ravindra *et al.* 2008).

The entrance of PAHs into agricultural soils can constitute severe threats to soil organisms, agricultural food grown in that soil and humans that depend on the primary producers (i.e plants). Consequently, routine examination of PAHs concentrations in the soil is inevitable for the establishment of the safety level of a given soil environment. The present study aims to determine the concentration, distribution, and sources of the 16 EPA priority PAHs in soil from selected areas in Agbarho community of Delta State, Nigeria and to evaluate associated environmental health effects.

1.1   *The study area*

The Studied area is located at Agbarho community within the coordinates of latitude $05^0\ 31^1$N and $05^0\ 37^1$N and longitude $05^0\ 48^1$E and $05^0\ 54^1$E and is about 12 km from Warri city (See Fig. 1). It is situated in the south-south geographical zone of Nigeria with an elevation of about 111 m above the sea. It is made up of several agricultural/rural communities which include Oguname, Ohrerhe, Orhokpokpor, Uwiama, and Orho-Agbarho as the administrative headquarter, with a typical Sombreiro-Warri Deltaic Plain terrain which is lowland, generally flat and slopes gently southward towards the ocean. The coordinates of the sample location are MeWS-Mechanic workshop soil (5°35"N, 5°51"E), MoWs-Motorway soil (5°34"N, 5°52"E), TPS- Traffic Point soil (5°35'N, 5°51"E), BSS- Barbecue Spot soil-(5°34"N, 5°51"E), FSS- Filling Station soil (5°36"N, 5°52"E), FFCS- Farm Field Control soil (5°35"N, 5°50"E) respectively.

Fig. 1: Map showing selected sample sites in Agbarho community.

2.0   Materials and Method

2.1   *Sample collection and preparation*

Five (5) soil samples were collected at 0-10 cm depth from areas suspected to be polluted by hydrocarbons. One (1) control sample was also obtained from farmland with no proximity to hydrocarbon contamination

Samples were kept in aluminum foils and taken to the laboratory, where impurities were removed. Samples were then air-dried at room temperature; ground with mortar and pestle then sieved using a 2 mm mesh.

2.2   *Extraction of sample*

The samples were extracted using the US EPA method 3550B (US EPA, 1996). 10 g of the soil samples and 10.0 g of anhydrous sodium sulphate (Na_2SO_4) were mixed in 100 mL glass beaker until a dry homogenate was obtained. 20 mL of dichloromethane (DCM) was added to the dry homogenate and was shaken in a mechanical shaker (Searchtech instrument, HZ-300 model, USA) for 30 minutes; it was then transferred to a sonicator (Omegasonic quantum series model) and was sonicated for 30 minutes at 70°C. After sonication, 5.0 g of anhydrous Na_2SO_4 was added to the sample to remove any residual water molecule. The extracts were then filtered into 100 ml beaker, and the process was repeated three consecutive times with a fresh mixture of DCM each time with the same sample. A rotary evaporator (Searchtech instrument, RE52-2 model, USA) was then used to concentrate the extracts to 2mL. The resulting extract was fractionated using a glass column packed with glass wool, then silica gel which was preconditioned at 105 °C and mixed with DCM and anhydrous sodium sulphate (Na_2SO_4). The extract was then eluted with 10 mL of DCM for polycyclic aromatic hydrocarbons (PAHs) and concentrated to 1 mL in a rotary evaporator (Searchtech instrument, RE52-2 model, USA). The obtained concentrate was pipetted into a clean 2 mL Teflon screw-cap vial and cap tightly and labeled ready for gas chromatography- mass spectrometry detector (GC-MSD) PAHs analysis.

The extracts were analyzed for 16 priority PAHs using Agilent 6890-5973N GC-MSD. Agilent Technologies Inc MSD chemstation G1701DA D.03.00.611 software was used in quantifying PAHs component results in a suite of 17 priority PAHs recommended by EPA (Accu-standard, 17 PAHs) (Accu-standard) (USEPA, 1996B). The carrier gas was helium, in the split-less mode, the injection volume and injector temperatures were 1.0µl and 250 °C respectively while the oven temperature is set at 300°C and the final temperature is 320 °C.

2.3   *Quality control/assurance*

Quality control and assurance were assessed by sequence analysis for all parameters accompanied by Gas Chromatography measures (such as blanks, duplicates and standards) for validation of analytical procedures used and to ascertain the level of interference.

2.4   *Source identification of PAHs*

Experts have used these ratios for quantitatively interpreting PAH origins and also apportioning contributions of different origins with total PAHs to be examined. A compound is considered to have comparable physicochemical properties when present in the same ratios and has a similar molecular mass. The ratios used for apportioning PAHs source are; Ant/(Ant + Phe) ratio < 0.1 indicates petroleum input, but > 0.1 depicts combustion process; BaA/(BaA+Chry) ratio <0.2 shows petroleum derived source, but 0.2-0.35 reveals petroleum combustion source; BaP/BghiP ratio ranging 0.3-0.4 reveals automobile exhaust source, but 0.9-0.6 indicates coal combustion process; Flt/(Flt + Pyr) ratio < 0.4 shows input from petroleum, but > 0.4 implies petroleum combustion; IndP/(IndP+BghiP) ratio <0.2 shows petroleum input, but 0.2-0.5 shows petroleum combustion; LMW PAH/ HMW PAH ratio < 1 are derived from pyogenic processes such as incomplete combustion, and > 1 shows petrogenic input from refined petroleum products or crude oil; COMB PAHs/TPAHs <1 depicts combustion process, but when >1 petrogenic sources; while total index <4 shows PAHs from low temperature combustion processes, however > 4 shows high temperature combustion processes (Lawal, 2017).

2.5   *Carcinogenicity of PAHs*

The profiling of PAHs rings can be to show its carcinogenicity. The carcinogenicity, mutagenicity and toxicity of PAHs are a function of their molecular structures, where low molecular PAHs (< 3rings) often display acute toxicities and low carcinogenicities; while high molecular PAHs (> 3rings) show low toxicities and very high mutagenicity and carcinogenicities (Ivwurie *et al*., 2016). The

carcinogenic PAHs are BaA, Chry, BbF, BkF, BaP, IndP and DahA.

2.6   Examination of data

The statistical package for social science (SPSS) was used for all statistical data examinations. Descriptive statistics were used to establish the existence of significant variations in the ∑17-PAHs concentrations.

3.0   Results and Discussions

3.1   Concentration of ∑17-PAHs

The concentrations of the ∑17-PAHs in soils suspected to be contaminated are presented in Table 1. The concentrations of the total ∑17 PAHs in the soil presented above (Table 1) range 16 µg kg^{-1} at the mechanic workshop (MoWS) to 122 µg kg^{-1} at the barbecue spot(BSS). No PAHs were detected in the control sample. The total PAHs concentrations obtained in the soils were higher than the total PAHs concentration obtained in the control sample. On the average, the concentrations of the individual ∑17 PAH compounds followed the descending order: Nap > Ant = Car > Phen > Flu > Bap > Ace = Flt = Pyr > BbF = BkF. The descending order of PAHs based on

locations followed the order: mechanic workshop (MeWS) > Barbecue Spot Soil (BSS) > MotorWay Soil (MoWS) > Filling Station Soil (FSS) > Traffic Point Soil (TPS). Concerning soil contamination by PAHs, soils with PAH concentrations < 200 µg kg^{-1} are classified as being uncontaminated; 200-600 µg kg^{-1} are classified as being weakly contaminated; 600-1000 are classified as being contaminated; and > 1,000 µg kg^{-1} is classified as being heavily contaminated (Maliszewska-Kordybach, 1996). Based on this classification, all soil samples from the sites are classified as being uncontaminated; Yet, the PAH concentration in all sites was within the Department of Petroleum Resources- Environmental Guideline for the Petroleum industry in Nigeria DPR-EGASPIN (2002) target value of 1,000 µg kg^{-1}. The concentrations of total PAHs obtained in mechanic workshops and fuel station soils for this study are comparable to those of Nganje et al.,(2007) and Ekanem et al.,(2019) for PAHs in automobile workshop soils from Calabar and Eket metropolis, respectively.

Table 1: Concentrations (µg kg^{-1}) of PAHs in the soils

	MeWS	MoWS	TPS	BSS	FSS	CTR
Nap	22	22	12	36	18	2
Acy	ND	ND	ND	ND	ND	ND
Ace	6	ND	ND	8	2	ND
Flu	8	ND	ND	8	6	ND
Phen	20	ND	ND	4	ND	ND
Ant	20	ND	ND	14	ND	ND
Car	10	4	4	16	ND	ND
Flt	8	ND	ND	8	ND	ND
Pyr	6	ND	ND	10	ND	ND
BaA	ND	ND	ND	ND	ND	ND
Chry	ND	ND	ND	ND	ND	ND
BbF	2	ND	ND	6	ND	ND
BkF	2	ND	ND	6	ND	ND
BaP	2	ND	ND	6	12	ND
DahA	ND	ND	ND	ND	ND	ND
IndP	ND	ND	ND	ND	ND	ND
BghiP	ND	ND	ND	ND	ND	ND
Total	**106**	**26**	**16**	**122**	**38**	**2**
2-Rings	22	22	12	36	18	2
3-Rings	54	ND	ND	34	8	ND
4-Rings	14	ND	ND	18	ND	ND

	5-Rings	6	ND	ND	18	12	ND
	6-Rings	ND	ND	ND	ND	ND	ND
	LMW	76	22	12	70	26	2
ND =	HMW	20	ND	ND	36	12	ND
	Carcinogenic PAHs	6	ND	ND	18	12	ND
	Non-carcinogenic PAHs	100	26	16	104	26	2

not

detected; Naphthalene (NaP), acenaphthalyne (Acy), acenaphthene (Acy), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), CArbazole (Car), fluoranthene (Flt), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IndP), dibenz(a,h)anthracene (DahA) and benzo(g,h,i)pyrene (BghiP), LMW = lower molecular weight; HMW = higher molecular weight

Results obtained from the analysis of variance (ANOVA) indicated that the concentrations of PAHs in these soils varied significantly (p-value < 0.05; Fcal > Fcrit) with sites (Table 2). Variations in the concentrations of PAHs may be related to the length of time for which soil had been contaminated and the volatility of the PAHs.

Edwards (1983) reported that typical endogenous soil PAHs are in the range of 1-10 $\mu g\,kg^{-1}$, and most of them are derived from oil seeps, bitumen, coal, plant debris, forest and prairie fires (Yunker *et al.,* 2002). Concentrations of PAHs in these sites were higher than the background value (Edwards, 1983).

Table 2: ANOVA Result of PAHs concentration in soil

Source of Variation	SS	df	MS	F-cal	P-value	F-crit
Between Groups	560.1882	4	140.0471	3.445441	0.011922	2.485885
Within Groups	3251.765	80	40.64706			
Total	3811.953	84				

3.2 Occurrence and profiles of PAHs in the soil

The occurrence and profiles of the PAHs rings in the soil are displayed in Figure 2. Occurrence and profiles of PAHs in the soils followed the order 2-rings > 3-rings > 5-Rings > 4-rings. 2-ring PAH compound (Nap) was the dominant PAH compound in these soils. Nap was detected in all soil samples at concentrations that ranged from 12 $\mu g\,kg^{-1}$ in Traffic Point Soil (TSS) to 36 $\mu g\,kg^{-1}$ in Barbecue Spot Soil (BSS). Concentration of 3-ring PAHs (Acy + Ace + Flu + Phe + Ant + Car) ranged from 8.0 to 54 $\mu g\,kg^{-1}$ in 60% of the soil samples. Acenaphthalyne (Acy) was not detected in any of the soil samples (<0.01 $\mu g\,kg^{-1}$). The 4-einged PAHs (Flt+Pyr +BaA + Chry)

were detected only in MeWS and BSS at concentrations of 14 $\mu g\,kg^{-1}$ and 18 $\mu g\,kg^{-1}$ respectively. Benzo(a)anthracene (BaA) and chrysene (chry) were not detected in these soils either. Concentration of 5-ring PAHs (BbF + BkF + BaP + DahA) in 60% of the soil samples ranged from 6.0 to 18 $\mu g\,kg^{-1}$. In this study, dibenzo(a,h)anthracene (DahA) was not detected. Also, the 6-ring PAH compounds (IndP and BghiP) were not detected in these soils. Generally, all the soil samples from this location contained higher loads of non-carcinogenic PAHs than carcinogenic PAHs. This observation may be linked to the non-carcinogenic PAHs are majorly the lower molecular weight PAHs (2-3 rings) and are the dominant PAHs in these soils compared to the higher molecular weight PAHs which are majorly the

carcinogenic PAHs. This suggests that humans exposed to these PAHs in all the soils around these locations are not at high risk of cancer.

3.3   Correlation analysis of PAHs

Pearson correlation analysis was performed to evaluate the relationship among individual PAH compounds. This is to evaluate possible sources on the assumption that two or more components may correlate either due to atmospheric behavior or common origin. The Pearson correlation coefficients of the individual PAHs are shown in Table 4. As shown in Table 4, a substantial positive correlation ($r^2 > 0.5$) between individual PAHs at either 0.01 or 0.05 level of significance suggests similar behavior or a common source.
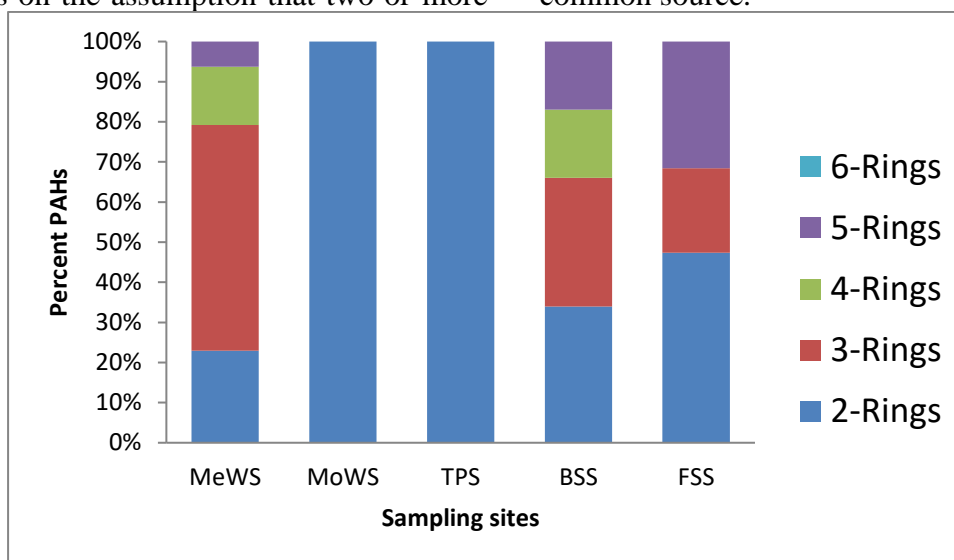
Fig. 2: Occurrence and profiles ring compositional percentage pattern of PAHs in all soils
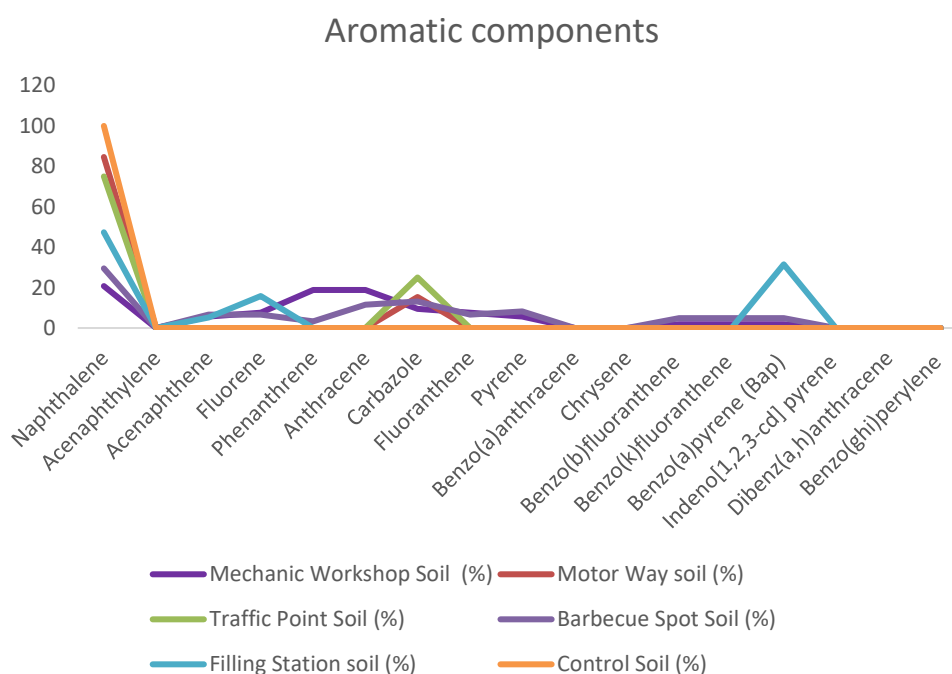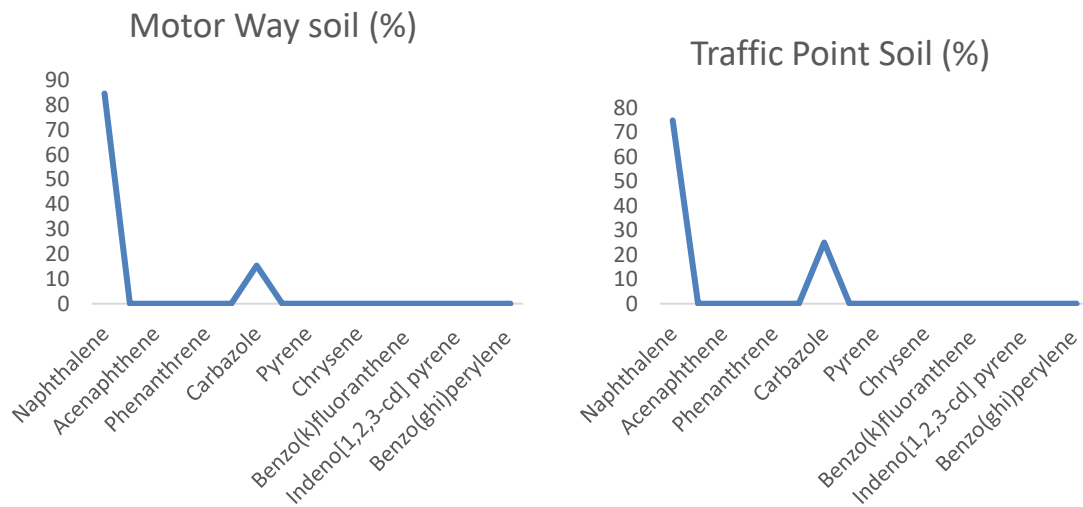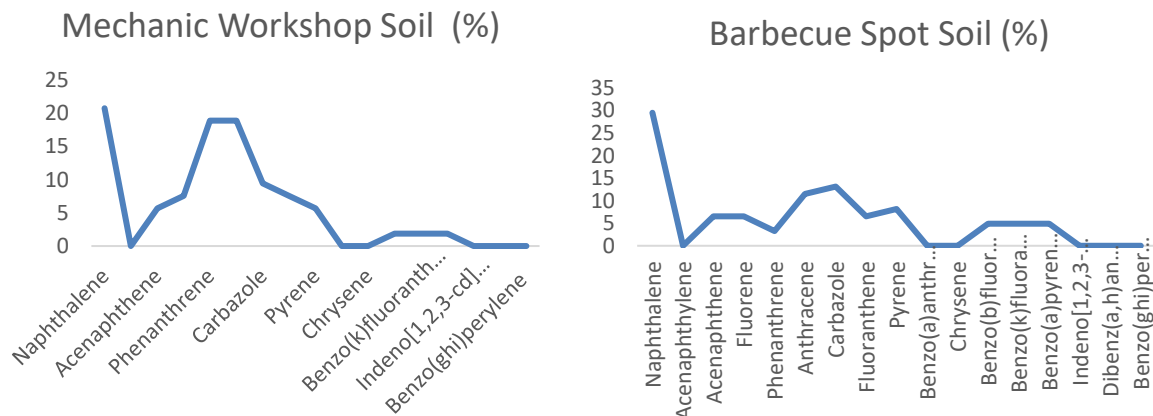

Fig. 3: Concentration percentage and carbon number distribution of aromatics in all soils.
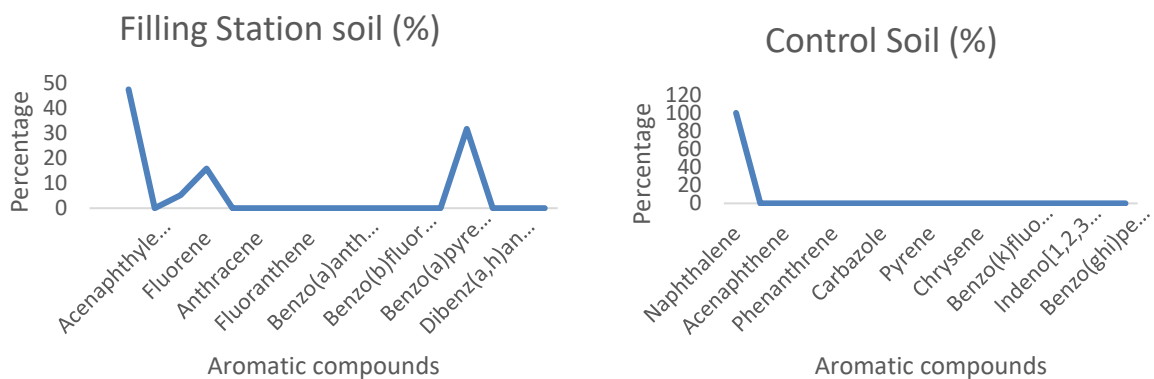
Fig. 4: Concentration percentage and aromatic distribution in Motor Way Soil and Traffic Point Soil.

Fig. 5: Concentration percentage and aromatic distribution in Mechanic Workshop Soil and Barbecue Spot Soil.

Fig. 6: Concentration percentage and aromatic distribution in Filling Station Soil and Control Soil.

Table 3: Pearson correlation of PAHs in soils

	Nap	Ace	Flu	Phen	Ant	Car	Flt	Pyr	BbF	BkF	BaP
Nap	1.00										
Ace	0.81**	1.00									
Flu	0.61*	0.90**	1.00								
Phen	0.18	0.60*	0.61*	1.00							
Ant	0.58*	0.89**	0.78**	0.88**	1.00						
Car	0.83**	0.87**	0.57*	0.46*	0.81**	1.00					
Flt	0.72**	0.95**	0.80**	0.76**	0.98**	0.90**	1.00				
Pyr	0.86**	0.97**	0.76**	0.52*	0.86**	0.96**	0.95**	1.00			
BbF	0.91**	0.91**	0.67*	0.28	0.70**	0.94**	0.84**	0.97**	1.00		
BkF	0.91**	0.91**	0.67*	0.28	0.70**	0.94**	0.84**	0.97**	1.00**	1.00	
BaP	0.20	0.27	0.57*	-0.18	-0.06	-0.16	0.00	0.09	0.15	0.15	1.00

**Pearson's correlation significant at 0.01 level of significance
*Pearson's correlation significant at 0.05 level of significance

3.4 Source apportionment of PAHs using isomeric ratio

The isomeric ratios of PAHs in hydrocarbon sources of this study are shown in Table 4. The Ant/(Ant + Phen) ratio in mechanic workshop soil and Barbecue Spot soil were above 0.1 indicating that the PAHs sources are combustion processes. The Flt/(Flt + Pyr) ratio in mechanic workshop soil was > 0.5 suggesting petroleum combustion while the Flt/(Flt + Pyr) ratio for barbecue spot was between 0.4 and 0.5 suggesting coal and biomass combustion. LMW/HMW ratios were greater than 1.0 suggesting that the source of PAHs in these soils is petroleum origin. However, the ratios of COMB PAHs/TPAHs were < 1.0 indicating the combustion of fossil fuels as the source of PAHs. The total index values for the mechanic workshop and barbecue Spot soils were > 4.0. This indicates that the sources of PAHs were high temperature combustion processes.

Table 4: Isomeric ratio of PAHs in the soils

	MeWS	MoWS	TPS	BSS	FSS
BaA/(BaA+Chry)	0.00	0.00	0.00	0.00	0.00
IndP/(IndP+BghiP)	0.00	0.00	0.00	0.00	0.00
Ant/(Ant+Phen)	0.50	0.00	0.00	0.78	0.00
Flt/(Flt+Pyr)	0.57	0.00	0.00	0.44	0.00
LMW/HMW	3.80	0.00	0.00	1.94	2.17
COMB PAHs/TPAHs	0.19	0.00	0.00	0.30	0.32
BaP/BghiP	0.00	0.00	0.00	0.00	0.00
Total Index	6.43	0.00	0.00	8.89	0.00

MeWS = Mechanic Workshop Soil, MoWS = Motor Way Soil, TPS = Traffic Point Soil, BSS = Barbecue Spot Soil, FSS = Filling Station Soil

3.5 Principal component analysis (PCA) of PAHs in the soil

The principal component analysis (PCA) result of the PAHs in the soils is shown in Table 5 and Figure 3. Three components were identified and accounted for 98.849 % of the variability in the data set. Component 1 explained 53.737% of the total variance and was characterized by high loading of Nap, Ace, Car, Flt, Pyr, BbF and BkF. Nap, Ace, and BbF were associated with wood combustion (Khalili *et al*. 1995; Kavouras *et al*. 2001); Flt and Pyr are indicators for coal combustion (Larsen and Baker, 2003; Dong and Lee 2009), while BkF is a marker for traffic emissions (Simcik *et al*. 1999; Yang *et al*. 2012). Thus Component 1 indicated that PAHs were from pyrogenic processes such as wood, coal and traffic emissions. Component 2 explained 30.842 % of the total variance

and has high loading of Phen, Ant and Flt with moderate loading of Ace and Flu. Phen, Ant, Ace and Flu are tracers for wood combustion (Khalili *et al*. 1995; Kavouras *et al*. 2001) while Flt is an indicator of coal combustion (Larsen and Baker, 2003; Dong and Lee 2009). Thus Component 2 indicated that PAHs were from wood and coal combustion. Component 3 explained 14.270 % of the total variance and has high loading

of Bap and moderate loading of Flu. BaP and Flu are indicators for coal and wood combustions respectively (Kavouras *et al*. 2001; Larsen and Baker, 2003; Dong and Lee, 2009). Thus Component 3 also indicated that PAHs were from wood and coal combustion. The PCA result was in agreement with Pearson's correlation coefficient (Table 3).

Table 5: Principal Component Analysis (PCA) result of PAHs in these soils

	Components		
	1	**2**	**3**
Nap	.928	.097	.178
Ace	.770	.55	.295
Flu	.471	.626	.621
Phen	0.84	.990	.0.83
Ant	.532	.847	.002
Car	.908	.383	.159
Flt	.702	.711	.042
Pyt	.879	.463	.094
BbF	.963	.221	.131
BkF	.093	.221	.131
BaP	.042	.101	.994
Variance %	53.737	30.843	14.270
Cumm %	53.737	84.579	98.849
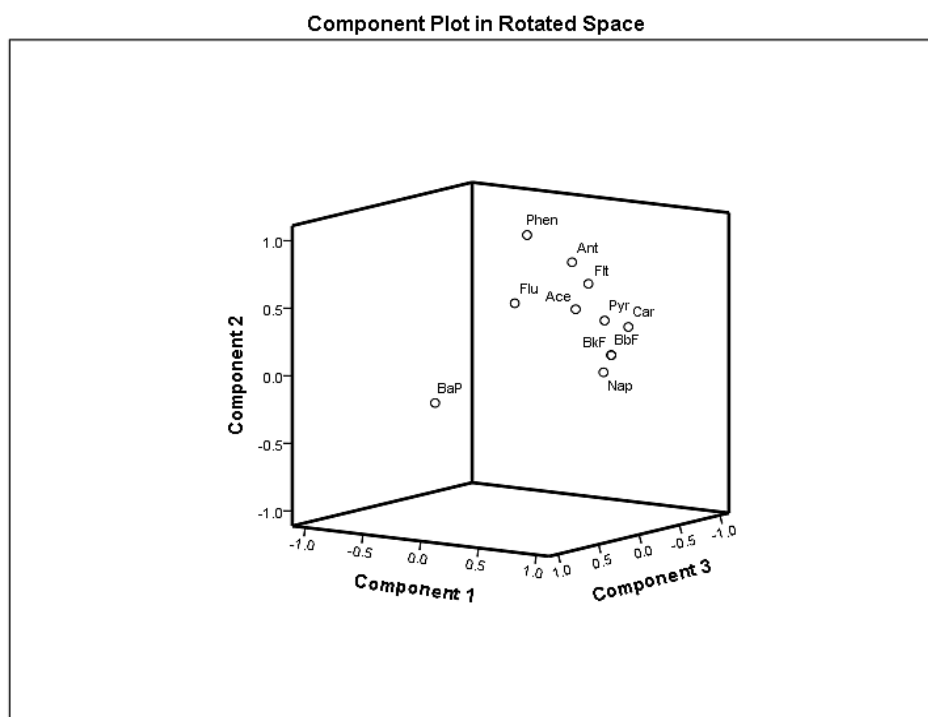
Fig. 3: Principal Component Analysis (PCA) plot of PAHs in the soils

3.6   Implications of PAHs in the soil on environmental and human health

The ∑17-PAHs concentration and occurrence studied show that they were all below the DPR-EGASPIN target value of 1000 µg kg^{-1} and are classified as the not contaminated category (DPR-EGASPIN, 2002). Though the continuous deposition of combustion fuels on soils along motorways, mechanic workshop, traffic points, barbecue spot and filling station have its potential risk for non-cancer and cancer risk when people are wide-open to them. Though, these are reliant on the path of exposure, concentration rates and exposure length. These routes range from ingestion, inhalation and dermal exposures to the soil in the soil sites.

4.0   Conclusion

The ∑17-PAHs concentration rates determined from these soils based on the location of land use in decreasing order are Mechanic Workshop Soil > Barbecue spot soil > Motorway soil > Filling Station Soil > Traffic point soil. The lower molecular weight (2-3rings PAHs) and non-carcinogenic PAHs were the predominant PAHs in these soils. The isomeric ratios and principal component analysis used for source apportionment indicate that the PAHs in these soils originated from high temperature combustion of biomass and fossil fuels such as wood and coal as well as traffic emissions. The study has shown that the occurrence of the ∑17-PAHs falls within the DPR-EGASPIN not contaminated category. This study has contributed to knowledge by showing the source and distribution of aromatic hydrocarbons as well as concentration rates in the land-use sites of hydrocarbons in Agbarho communities of Delta State, Nigeria.

5.0   Acknowledgements

6.0   References

CCME (2008). *Canada soil quality guidelines for the protection of the environment and human health: Carcinogenic and other PAHs in Canadian* Environmental Quality Guidelines. PP 1-11.

Dong T. T. T. & Lee, B.K. (2009). *Characteristics, toxicity and source apportionment of polycyclic PAHs (PAHs) in road dust of Ulsan, Korea. Chemosphere 74, pp. 1245-1253.*

DPR-EGASPIN. (2002*). Environmental guidelines and standards for the petroleum industry in Nigeria (revised edition. Department of Petroleum Resources, Ministry of Petroleum and Mineral Resources, Abuja Nigeria 320.* https://ngfcp.dpr.gov.ng/media/1066/dprs-egaspin-2002

Edwards, N. T. J. (1983). *Polycyclic PAHs (PAHs) in the terrestrial environment: A review. Journal Environmental Quality,12, pp. 427-441.*

Ekanem, A.,Ikpe, E. & Ekwere, I. (2019). *Assessment of polycyclic aromatic hydrocarbons level in soils around automobile repair workshops within Eket metropolis, Akwa-Ibom State, Nigeria. International Journal of Research and Scientific Innovation 6, 1, pp. 102-107*

Ivwurie, W., Emelife, S. C. & Snape, C. (2016*). Polycyclic PAHs in soils within selected communities In Delta State. Journal of sciences and Multidisciplinary Research, 8, 1, pp. 13-18.*

Kavouras, I. G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E. G. , Von Baer, D. & Oyola P. (2001). *Source apportionment of urban particulate aliphatic and polynuclear PAHs (PAHs) using multivariate methods. Environmental Science and Technology 35, pp. 2288-2294.*

Khalili N.R, Scheff P.A, and Holsen T.M. (1995). *PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. Atmospheric Environment 9(4): 533-542.*

Larsen, R. K., & Baker, J. E. (2003*). Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environmental Science and Technology 37: 1873-1881.*

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.*

Nganje, T. N., Edet, A, & Ekwere, S.J. (2007). *Distribution of PAHs in surface soils from petroleum handling facilities in Calabar. Environmental Monitoring and Assessment, 130: 27-34*

Ravindra, K., Sokhi, R., & Van Grieken, R. (2008). *Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmospheric Environment, 42, 2895–921.*

Simcik, M. F, Eisenreich, S. J&, Lioy, P. J. (1999). *Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. Atmos Environ 33: 5071–5079.*

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

United States Environmental Protection Agency (US EPA) (1996). *Method 8015B. Nonhalogenated organics using GC/FID. Washington: US EPA.*

Yang, B., Xue, N., Zhou, L., Li, F., Cong, X., Han, B., Li, H., Yan, Y., & Liu, B. (2012). *Risk assessment and sources of polycyclic aromatic hydrocarbons in agricultural soils of Huanghuai plain, China. Ecotoxicity and Environmental Safety,* 84*, pp.* 304-310.

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