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Assay of Polycyclic Aromatic Hydrocarbons in Soils from Selected Areas in Ughelli and Its Environs, Delta State, Nigeria

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Abstract

The occurrence of polycyclic aromatic hydrocarbons was investigated in primary sources (pure hydrocarbons) and secondary sources (soils) from selected areas suspected to be contaminated with hydrocarbons in Ughelli and its environs, Delta State, Nigeria. Samples were quantified with gas chromatography equipped with mass spectrometer detector (GC-MSD) after extraction and clean up of the extracts with dichloromethane. The concentrations of ∑17 polycyclic aromatic hydrocarbons ranged from 814 to 103100 µg kg^{-1} in primary sources and 84 to 796 µg kg^{-1} in secondary sources respectively. For the secondary sources, the decreasing order of PAHs based on locations followed the order: Mechanic Workshop Soil > Generator Compound soil > Flow-station Soil > Filling Station Soil > Motor Way Soil. The lower molecular weight (2-3 rings) 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 the secondary sources were from combustion processes of biomass and fossil fuels such as wood and coal.

Keywords: Polycyclic aromatic hydrocarbons, Gas chromatography, Soil, Ughelli,

1. Introduction

Energy consumption pattern of a given environment contributes to the hydrocarbons released in the environment. Hydrocarbons in the environment though originates from different sources but are majorly from fossil fuels such as petroleum, natural gas, and coal released due to incomplete combustion of vehicles and machines, industrial chimney fumes, as well as excessive bush burning, etc. Energy usage in residential buildings and for transportation purpose etc. is known as direct energy consumption (Bin and Dowlatabadi, 2005). However, regardless of the vital contribution of fossil fuel to a nation's development, its societal and environmental cost is significant. Environmental hydrocarbons released either by accident or actions carried out by human are major concerns to soil and water bodies' contamination (Holliger et al., 1997). Hydrocarbon components act as poisonous substance in the environment with adverse effect on both fauna and flora's existence. This poisonous substance gets to human through a given area food chain (Gibson and Parales, 2000). Air, water, and soil are recipient matrices that holds various level of potentially present hydrocarbon.

Polycyclic aromatic hydrocarbons (PAHs) are persistent environmental pollutants with two or more benzenoid rings positioned in different directions. The low molecular weight PAHs (LPAHs) consist of (2-3rings) and high molecular weight (HPAHs) consist of (4-6rings) which gives insight of the source of the PAHs present in the sample and they originate from petrogenic and pyrogenic sources respectively. PAHs present in soil comes from diverse routes, of which human and natural sources have introduced these PAHs contamination into the environment (Emoyan et al; 2008; Iwegbue et al; 2020). Human origin of PAHs includes pyrolytic activity which include; bush burning, organic substance, fumes from industrial processes and non-combustion resultant of petrogenic crude oil. Other sources are vehicular emission, petroleum product spills, solid waste biomass. Its worthy of note that forest fire and volcanic eruption are the main natural origin of PAHs (Keyte et al; 2016; Stapleton et al; 2021).

Much has been documented on PAHs concentrations exposures via inhalation, ingestion, and dermal exposures in environmental matrices as a result of the above listed possible sources of contamination (Ipeaiyeda and Dawodu, 2008). However, there is lack of comprehensive data depicting the occurrence and sources of PAHs found around the study area.

The present study is to investigate the contamination status of soil around mechanic workshop,generator compound, flow-station, filling station, motorway in Ughelli and its environs, Delta State Nigeria in comparison with concentration of pure hydrocarbon compounds which include diesel, fuel, carbon soot and spent engine oil.

2. Experimental method

2.1 Description of study area

The studied area was located at Ughelli metropolis, and it lies within latitude 5.500187 and Longitude 5.992834. The city is placed categorically with GPS coordinate 5° 30’ 0.6732” N and 5° 59’ 37.8024” E it is bounded to the North by Ethiope East, Patani to the South, Ughelli South to the west, and Isoko North and South to the east. It houses a population of over 321,028 as published by the National population commission in census conduced in 2006. Ughelli metropolis houses the headquarters of the Ughelli North local government area of Delta state and is one of the fastest growing cities in Delta state as well as an oil producing city with five flow and flare stations which is the highest in the Niger Delta region. The geographical coordinates of each sample sites are FSS- Filling station soil (5°29'45" N,5° 59'40" E), MOWs- Motorway soil (5°28'57" N, 6°1'6" E), FS- Flow station (5°31'33" N, 6°3'4" E), GCS- Generator compound soil (5°28'48" N, 6°1'5" E), MeWS- Mechanic workshop soil (5°29'18" N, 6°1'4" E), CTR- Control (5°36'19"N, 5°52'25"E).

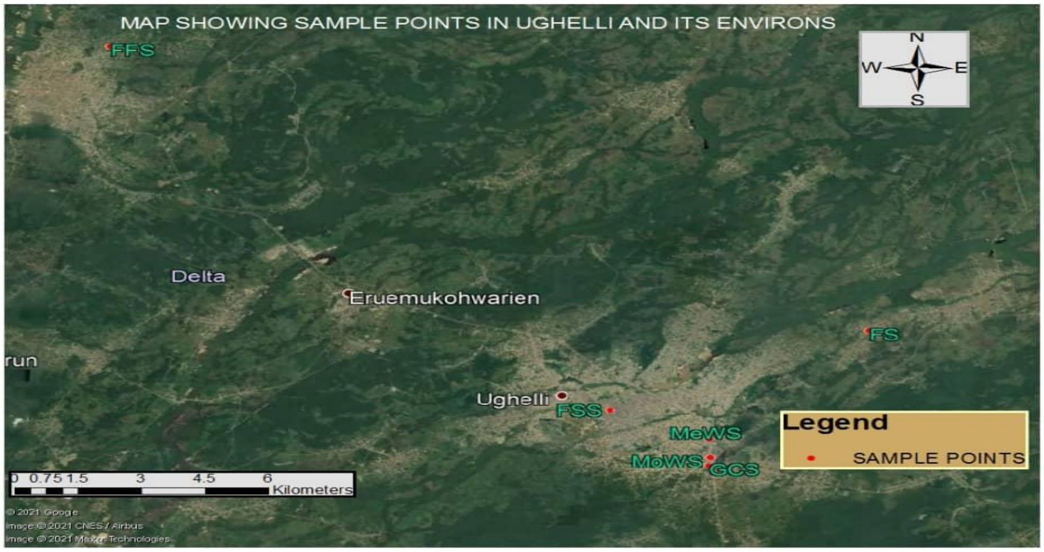

Figure 1:Google Map showing sampling points in Ughelli metropolis and environs.

2.2 Sample collection

Using a clean amber coloured glass bottle a total of eleven (11) samples were collected. With five (5) samples being pure hydrocarbon and six (5) samples being soil collected at the top(0-10cm) depth around areas suspected to be polluted by hydrocarbons. Similarly, one (1) control soil sample was collected from a virgin farmland. Prior to analysis on soil samples, stones and twigs were removed and sample were air-dried at room temperature, ground and sieved using a 2 mm mesh.

2.3 Extraction and analysis

The samples were extracted using the US EPA method 3550B (US EPA, 1996). Thus, 10g of the soil samples and 10grams of anhydrous sodium sulphate(Na_2SO_4)were mixed in an 100mL glass beaker until a dry homogenate was obtained. For Carbon soot, 1.0g was used, while gasoline and diesel required no extraction.

20mL of dichloromethane (DCM)was added to the dry homogenate and was shaken in a mechanical shaker (Searchtech instrument, HZ-300 model, USA)for 30mins, it was then transferred to a sonicator (Omegasonic quantum series model) and was sonicated for 30 minutes at 70°C; after sonication 5g of $Na_2SO_4$was added to the sample again to remove any residual water molecule. The extracts were then filtered into a 100ml beaker, and the process was repeated thrice with fresh mixture of DCMeach time with same sample. A rotary evaporator (Searchtech instrument, RE52-2 model, USA) was then used to concentrate the extracts to 2 mL. The resulting extract was fractionated using a glass column packed with glass wool, then silica gel which was preconditioned at 105°Cand mixed with DCM and Na_2SO_4. The extract was then eluted with 10 mL of DCM for polycyclic aromatic hydrocarbons(PAHs) and concentrated to 1mL in a rotary evaporator (Searchtech instrument, RE52-2 model, USA). The obtained concentrate was pipetted into a clean 2mL teflonscrew-cap vial and cap tightly and labelled ready for gas chromatography- mass spectrometry detector(GC-MSD) PAHs analysis.

The extracts were analyzed for 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)using Agilent 6890-5973N gas chromatography- mass selective detector (GC-MSD). Agilent technologies Inc MSDchemstation 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 temperature were 1.0µl and 250°C respectively. While the oven temperature is set at 300°C and the final temperature (i.e outlet) is 320°C.

2.4 Quality control/assurance

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

2.5 Source identification of PAHs

Experts have used these ratios for quantitatively elucidating PAH origins and also apportioning contributions of different origins with total PAHs be examined. A compound is considered having comparable physico chemical properties when present in the same ratios and has 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).

2.5.1 Carcinogenicity of PAHs

The profiling of PAHs rings can be to show its carcinogenicity. The carcinogenicity, mutagenicity and toxicity of PAHs is a function of their molecular structures, wherein 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 Data Examination

The statistical package for the social science (SPSS) was used for all statistical data examination. Descriptive statistics was 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 concentration of the ∑17-PAHs in the pure hydrocarbons and sites suspected to be contaminated are presented in table 1.

Table 1: PAHs concentration and distribution in pure hydrocarbons and soil samples.

	Pure hydrocarbon samples					**Soil Samples**					
	Diesel exhaust (µg kg^{-1})	Diesel (mg/L)	Motor exhaust (µg kg^{-1})	Spent oil (mg/L)	Petrol (mg/L)	FSS (µgkg^{-1})	MoWS (µgkg^{-1})	GCS (µgkg^{-1})	MeWS (µgkg^{-1})	FS(µg kg^{-1})	CTR (µg kg^{-1})
Nap	72	3976	ND	9038	16339	106	80	76	42	52	ND
Acy	742	362	ND	256	9	ND	ND	298	ND	ND	ND
Ace	1676	591	ND	196	ND	ND	ND	ND	72	8	ND
Flu	2784	903	ND	1560	57	88	ND	94	174	82	ND
Phen	7198	1881	ND	2958	15	6	ND	ND	40	ND	ND
Ant	3320	479	ND	2266	55	6	ND	ND	38	ND	ND
Car	2940	64	112	2668	ND	ND	4	8	16	178	ND
Flt	8352	83	56	538	ND	ND	ND	ND	ND	10	ND
Pyr	8674	87	134	866	ND	ND	ND	ND	ND	12	ND
BaA	6468	14	32	192	ND	ND	ND	ND	ND	ND	ND
Chry	9362	16	ND	14	ND	ND	ND	ND	ND	ND	ND
BbF	11596	28	246	126	ND	ND	ND	ND	188	ND	ND
BkF	13500	26	2	192	ND	ND	ND	ND	226	ND	ND
BaP	6350	40	144	ND	ND	ND	ND	212	ND	266	ND
DahA	4320	ND	64	ND	ND	ND	ND	ND	ND	ND	ND
IndP	6848	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BghiP	8898	ND	24	ND	ND	ND	ND	ND	ND	ND	ND
Total	**103100**	**8550**	**814**	**20870**	**16475**	**206**	**84**	**688**	**796**	**608**	**ND**
2-Rings	72	3976	ND	9038	16339	106	80	76	42	52	ND
3-Rings	18660	4280	112	9904	136	100	4	400	340	268	ND
4-Rings	32856	200	222	1610	ND	ND	ND	ND	ND	22	ND
5-Rings	35766	94	456	318	ND	ND	ND	212	414	266	ND
6-Rings	15746	ND	24	ND	ND	ND	ND	ND	ND	ND	ND
LMW	18732	8256	112	18942	16475	206	84	476	382	320	ND
HMW	84368	294	702	1928	ND	ND	ND	212	414	288	ND
Carcinogenic	58444	124	488	524	ND	ND	ND	212	414	266	ND
Non-carcinogenic	18732	8256	112	18942	16474	206	84	476	382	320	ND

FSS = Filling Station Soil, MoWS = Motor Way Soil, GCS = Generator Compound Soil, MeWS = Mechanic Workshop Soil, FS = Flowstation Soil, ND = 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

The concentration of 17 PAHs detected had a minimum of 72 and maximum of 13,500 µg kg^{-1} for diesel exhaust; <0.01 to 3,976 mg/L diesel; <0.01 to 246 µg kg^{-1} for motor exhaust; < 0.01 to 9,038 mg/L for spent oil and <0.01 to 16,339 mg/L for petrol. Naphthalene was the dominant PAH congener in diesel, spent oil and petrol, and this was in unity with the findings of Marr et al. (1999), Lim et al. (2005). Benzo[a]pyrene (BaP) was not detected in petrol and spent oil. Diesel fuel however contained 2-5 ringed PAHs, with benzo(a)anthracene being the least dominant PAHs (Viera de Souza and Correa, 2016), but no 6-ringed PAH was detected. The PAHs in spent engine oil was similar to that of diesel. Diesel exhaust contained 2-6 ringed PAHs unlike motor exhaust that contained 3-6 ringed PAHs. The PAHs concentrations in soils presented above has concentrations of the ∑17 PAHs ranging from 84 µg kg^{-1} at motorway soil (MoWS) to 796µg

kg^{-1} at mechanic workshop (MeWS). No PAHs were detected in the control sample. The decreasing order of PAHs based on locations followed the order: mechanic workshop (MeWS) > generator compound soil (GCS) > flow station (FS) > Filling station soil (FSS) > Motorway soil (MoWS). With respect to 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, soils from generator compound, flow-station, and mechanic workshop are contaminated, filling station soil is weakly contaminated; while only motorway soil is relatively uncontaminated; However, the PAH concentration in all sites were 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 is comparable to Akporhonor et al. (2021) with range of 140 to 1372 µg kg-1 and 115 to 981µg kg-1 respectively, but much lower than those of Nganjeet al.(2007) and Ekanem et al.(2019) for PAHs in automobile workshop soils from Calabar and Eket metropolis, respectively.

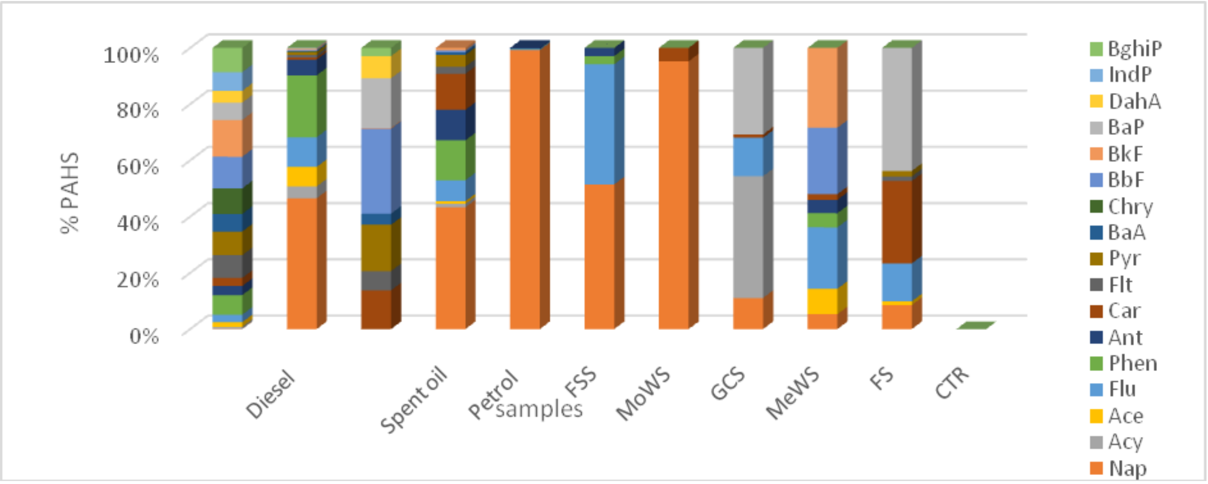

Figure 2: Individual PAHs compositional (%) pattern in hydrocarbons sources.

3.2 Statistical Analysis

3.2.1 Analysis of variance for PAHs concentration in Soil

Analysis of Variance (ANOVA) result showed that the concentrations of PAHs in these soils varied significantly (p-value < 0.05; Fcal>Fcrit) with respect to sites (Table 2). The significant variation observed might be due to nature, proximity, and strength of input sources; traffic volume and vehicular speeds; direction of wind and prevailing weather conditions; and degradation and transformation during transportation (Xu *et al*; 2018; Baalbaki *et al*; 2018).

Table 2: ANOVA result of PAHs concentrations in soils

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	23019.48	4	5754.871	1.424295	0.233521	2.485885
Within Groups	323240.5	80	4040.506			
Total	346260	84				

3.2.2 Pearson Correlation coefficient of PAHs in pure hydrocarbons and soil

Pearson correlation analysis was performed to assess 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 result of the inter-relationship between PAHs in both primary and secondary samples are shown in Tables 3 and 4 below, respectively.

Table 4,shows significant positive correlation(r^2> 0.5) between individual PAHs at either 0.01 or 0.05 level of significance suggesting similar behavior or a common source.

TABLE 3: Pearson correlation coefficient of PAHs in pure hydrocarbons.

	Nap	**Acy**	**Ace**	**Flu**	**Phen**	**Ant**	**Car**	**Flt**	**Pyr**	**BaA**	**Chry**	**BbF**	**BkF**	**BaP**	**DahA**	**IndP**	**BghiP**
Nap	1.00																
Acy	-0.49	1.00															
Ace	-0.53	0.97*	1.00														
Flu	-0.39	0.95*	0.89*	1.00													
Phen	-0.44	0.96*	0.94*	0.99*	1.00												
Ant	-0.30	0.85*	0.78*	0.97*	0.95*	1.00											
Car	-0.23	0.71*	0.62*	0.90*	0.85*	0.97*	1.00										
Flt	-0.47	0.87*	0.94*	0.86*	0.92*	0.82*	0.70*	1.00									
Pyr	-0.47	0.87*	0.94*	0.87*	0.93*	0.84*	0.73*	1.00*	1.00								
BaA	-0.47	0.86*	0.94*	0.84*	0.91*	0.80*	0.68**	1.00*	1.00*	1.00							
Chry	-0.47	0.86*	0.94*	0.83*	0.90*	0.79*	0.66**	1.00*	1.00*	1.00*	1.00						
BbF	-0.48	0.85*	0.94*	0.83*	0.90*	0.79*	0.66**	1.00*	1.00*	1.00*	1.00*	1.00					
BkF	-0.47	0.86*	0.94*	0.84*	0.91*	0.79*	0.67**	1.00*	1.00*	1.00*	1.00*	1.00*	1.00				
BaP	-0.49	0.85*	0.94*	0.82*	0.90*	0.78*	0.65**	1.00*	0.99*	1.00*	1.00*	1.00*	1.00*	1.00			
DahA	-0.48	0.85*	0.94*	0.83*	0.90*	0.78*	0.66**	1.00*	1.00*	1.00*	1.00*	1.00*	1.00*	1.00*	1.00		
IndP	-0.47	0.86*	0.94*	0.83*	0.90*	0.79*	0.66**	1.00*	1.00*	1.00*	1.00*	1.00*	1.00*	1.00*	1.00*	1.00	
BghiP	-0.47	0.86*	0.94*	0.83*	0.90*	0.78*	0.66**	1.00*	1.00*	1.00*	1.00*	1.00*	1.00*	1.00*	1.00*	1.00*	1.00

*Pearson correlation significant at 0.01 level of significance

**Pearson correlation significant at 0.01 level of significance

Table 4: Pearson correlation of PAHs in secondary sources of hydrocarbons

	Nap	Acy	Ace	Flu	Phen	Ant	Car	Flt	Pyr	BbF	BkF	BaP
Nap	1.00											
Acy	0.11	1.00										
Ace	-0.71	-0.28	1.00									
Flu	-0.51	0.06	0.79**	1.00								
Phen	-0.55	-0.30	0.98**	0.81**	1.00							
Ant	-0.54	-0.30	0.98**	0.81**	1.00**	1.00						
Car	-0.49	-0.24	-0.07	0.00	-0.23	-0.24	1.00					
Flt	-0.43	-0.25	-0.14	-0.05	-0.30	-0.30	1.00**	1.00				
Pyr	-0.43	-0.25	-0.14	-0.05	-0.30	-0.30	1.00**	1.00**	1.00			
BbF	-0.65	-0.25	0.99**	0.78**	0.99**	0.99**	-0.18	-0.25	-0.25	1.00		
BkF	-0.65	-0.25	0.99**	0.78**	0.99**	0.99**	-0.18	-0.25	-0.25	1.00**	1.00	
BaP	-0.31	0.49*	-0.33	0.00	-0.48	-0.48	0.72**	0.72**	0.72**	-0.40	-0.40	1.00

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

*Pearson's correlation significant at 0.05 level of significance

3.3 Profiling of rings to depict toxicity and carcinogenicity

The occurrence and profiles of the PAHs rings are displayed in Figure 3.The 2-ring PAHs (i.e. Nap) was detected in all locations, with a maximum concentration at filling station soil (106 ug/kg) and least in mechanic workshop soil (42 ug/kg).The concentration of 3-ring PAHs (Acy + Ace + Flu + Phe + Ant + Car) ranged from 4 to 400 µg kg^{-1}.The 4-ringed PAHs (Flt + Pyr+ BaA + Chry) were detected only in flow-station soil with a concentration of 22 µg kg^{-1} The concentration of 5-ring PAHs (BbF + BkF + BaP + DahA) ranged from 212 to 414µg kg^{-1}. 6-ring PAHs were not detected in any of the locations.

The concentrations of the carcinogenic PAHs (Sum of BaA, Chry, BbF, BkF, BaP, IndP and DahA) ranged from not detected to 414 µg kg-1 while the non-carcinogenic PAHs ranged from 84 to 476 µg kg^{-1}. Generally, the soils of filling station, motor way and generator compound contained higher loads of non-carcinogenic PAHs than carcinogenic PAHs while the soil of mechanic workshop and flow station contained higher loads of carcinogenic PAHs than non-carcinogenic PAHs. This observation is because the non-carcinogenic PAHs are majorly the lower molecular weight PAHs while the higher molecular weights PAHs are majorly the carcinogenic PAHs. This suggests that humans exposed to these PAHs in soils of filling station and motor way are not at high risk of cancer whereas those exposed to soils of generator compound, mechanic workshop and flow station are at risk of cancer.

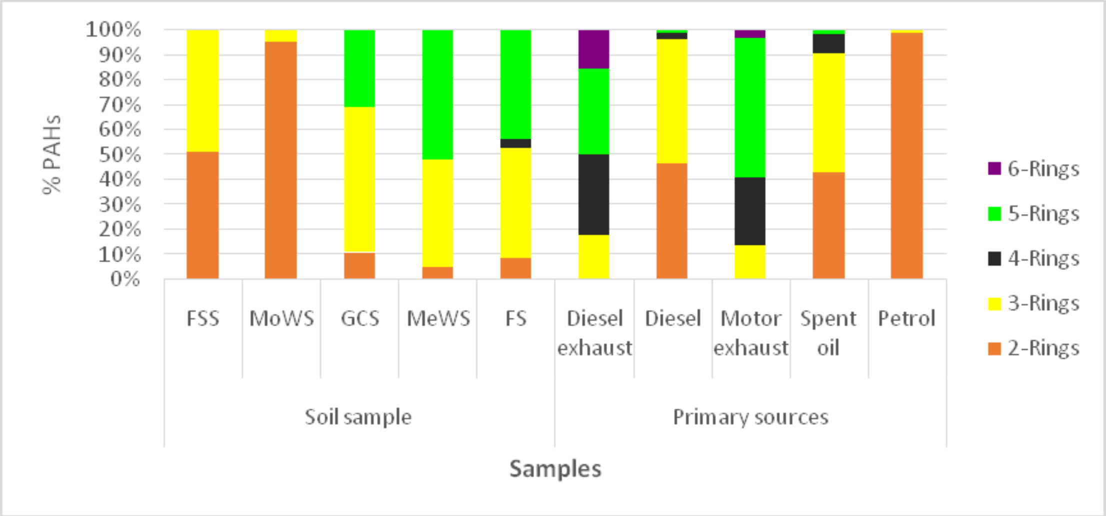

Figure 3: Ring based compositional (%) pattern of PAHs in hydrocarbon sources.

3.4 Source identification of PAHs

The isomeric ratios of PAHs in hydrocarbon sources of this study are shown in Table 6. The Ant/(Ant + Phen) ratio was above 0.1 in soils from filling station and mechanic workshop, indicating that the PAHs sources are combustion processes, which are associated with these environments. The Flt/(Flt + Pyr) ratio was 0.45 in flow-station suggesting petroleum combustion while the ratio was 0.0 in the other locations. The ratio of LMW/HMW > 1 in soils from generator compound and flow-station only, suggesting that the source of PAHs in these soils is petrogenic. The ratio of COMB PAHs/TPAHs in soils of generator compound, mechanic workshop, and flow-station were < 1 suggesting that the source of PAHs was combustion of fossil fuels or wood. The total index value for filling station and mechanic workshop soils were above 4 indicating that the PAHs in these two sites are from high temperature combustion processes. However, the total index value for flow-station was < 4 indicating that the PAHs are from low temperature combustion processes.

Table 5: Isomeric ratios of PAHs in primary and secondary sources of HCs

	Primary sources					**Secondary sources**				
	Diesel exhaust	**Diesel**	**Motor exhaust**	**Spent oil**	**Petrol**	**FSS**	**MoWS**	**GCS**	**MeWS**	**FS**
BaA/(BaA+Chry)	0.4	0.5	1.0	0.9	0.0	0.00	0.00	0.00	0.00	0.00
IndP/(IndP+BghiP)	0.4	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.00	0.00
Ant/(Ant+Phen)	0.3	0.2	0.0	0.4	0.8	0.50	0.00	0.00	0.49	0.00
Flt/(Flt+Pyr)	0.5	0.5	0.3	0.4	0.0	0.00	0.00	0.00	0.00	0.45
LMW/HMW	0.2	27.9	0.2	9.8	0.0	0.00	0.00	2.25	0.92	1.11
COMB PAHs/TPAHs	0.8	0.0	0.8	0.1	0.0	0.00	0.00	0.31	0.52	0.47
BaP/BghiP	0.7	0.0	6.0	0.0	0.0	0.00	0.00	0.00	0.00	0.00
Total Index	7.3	0.0	0.0	0.0	0.0	5.00	0.00	0.00	4.9	1.13

3.5 Principal Component Analysis (PCA) of PAHs in Secondary Sources of Hydrocarbons.

Principal component analysis (PCA) result of the PAHs in the soils is shown in Table 5 and Figure 3. Three components were detected and accounted for, 96.845 % of the variability in the data set. Component 1 explained 53.679 % of the total variance and was characterized by high loading of Ace, Flu, Phen, Ant, BbF and BkF and negative loading with Nap. Ace, Flu, Phen, Ant, and BbF are PAHs associated with low temperature burning processes including burning of grass, wood and other biomass (Dong and Lee, 2009) while BkF is a marker for traffic emissions (Yang et al; 2012). Thus component 1 suggests that the PAHs were from burning of grass, wood and other biomass and traffic emissions. Component 2 explained 31.497% of the total variance and has high loading of Car, Flt, Pyr and BaP. These are indicators for coal combustion (Larsen and Baker, 2003; Dong and Lee 2009). Component 3 explained 11.669% of the total variance and has high loading of Acy which is a tracer for wood combustion. Thus, component 3 suggests that the PAHs are from wood combustion.

Table 6: PCA results of PAHs in soils

	Component		
	1	**2**	**3**
Nap	**-.729**	-.553	-.080
Acy	-.148	-.187	**.969**
Ace	**.986**	-.034	-.153
Flu	**.871**	.041	.232
Phen	**.958**	-.204	-.194
Ant	**.956**	-.207	-.196
Car	-.048	**.996**	-.061
Flt	-.118	**.987**	-.080
Pyr	-.118	**.987**	-.080
BbF	**.977**	-.143	-.141
BkF	**.977**	-.143	-.141
BaP	-.213	**.753**	.622
Variance %	**53.679**	**31.497**	**11.669**
Cumm Var. %	**53.679**	**85.176**	**96.845**

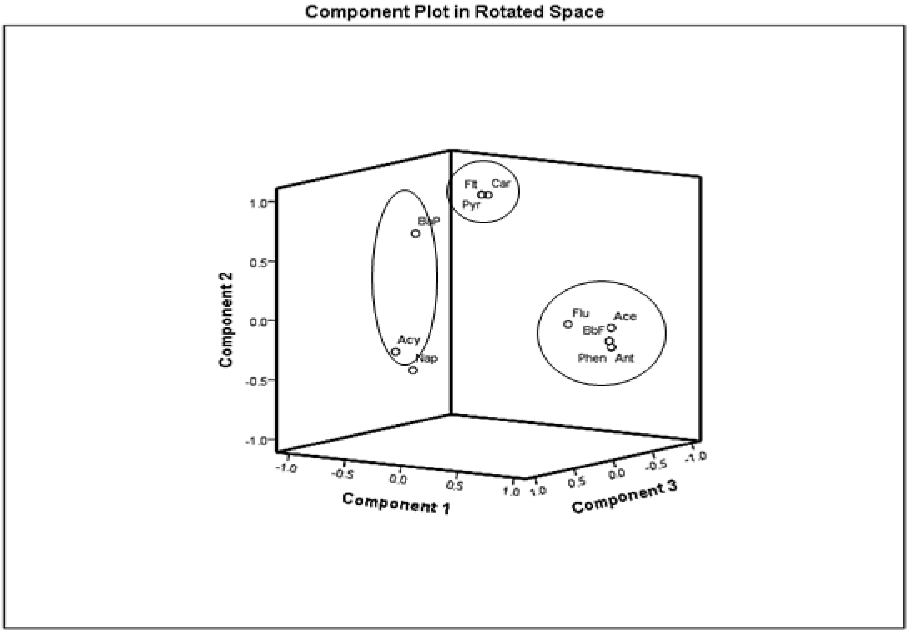

Figure 4: PCA plot of PAHs in soils

3.6 Implications for environmental and human health

The ∑17-PAHs concentration and occurrence studied shows that they were all below the DPR-EGASPIN target value of 1000 µg kg^{-1} and falls into the not contaminated category (DPR-EGASPIN, 2002). Though the continual usage of land-use for combustion fuels like in filling station, generator compound and flow station have its potential risk for cancer and non-cancer-risk when inhabitants are exposed to them. However, these are dependent on route of exposure, concentration loads andexposure duration. These routes range from ingestion, inhalation and dermal exposures to soil in these land-use sites.

Conclusion

The ∑17-PAHs concentration loads determined from these soils based on location of land use in decreasing order is mechanicworkshop soil >generator compound soil >flow-station soil >filling station soil >motor-way 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 occurrence of the ∑17-PAHs falls within the DPR-EGASPIN not contaminated category. This study has contributed to knowledge by showing the distribution and source of aromatic hydrocarbons concentration load in the land-use sites of hydrocarbons in Ughelli and its environs area of Delta state Nigeria.

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