Distribution Trends and Source Diagnosis of Polycyclic Aromatic Hydrocarbons (Pahs) In Sediments of Imiringi River

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Abstract

The environmental menace caused by hydrocarbon releasing activities on water bodies have remained a cause for great concern. Such activities are accompanied by the release of highly toxic and carcinogenic polycyclic aromatic hydrocarbons (PAH), which are easily biomagnified across the food chain, ultimately aggravating adverse health conditions in human. This study was aimed at identifying the most important environmental contributors of PAHs in sediments of the Imiringi river. Owing to the activities of oil facilities among other anthropogenic influences, water bodies are inundated with hydrocarbon pollutants which settle within river bed sediments, thereby, playing an important role in the redistribution of contaminants. The applied diagnostic ratios (Phenanthrene/Anthracene, Fluorene/Fluorene + Pyrene, Fluoranthene/Fluoranthene + Pyrene, pyrogenic index and total index) revealed the presence of mixed source of PAHs (pyrogenic and petrogenic). PAH concentrations ranged from <0.01 to 3,965.4 µg/kg with most detected compounds exceeding regulatory limits. The high molecular mass PAHs (4 - 6 ring HPAHs) represents the primary source showing 94.29% distribution, while the low molecular mass PAHs (2 - 3 ring LPAHs) recorded trace concentrations of about 5.71% of total PAHs. Principal component analysis (PCA) revealed Indeno (1,2,3-cd)pyrene and Dibenz (a,h) anthracene as principal PAH components in the environment. In addition, Pearson correlation showed Benzo (k) fluoranthene and Benzo (b) fluoranthene as the most positively correlating PAH species in sediment. Overall, the midstream section of the river was relatively more polluted than the up and down-river locations. Most notably,

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HPAHs recorded higher concentrations than the LPAHs. This may be due to intensive agricultural practices such as bush incineration, while waste dumps along the river bank remain tangible pyrogenic PAH contributors. On the other hand, trace amounts of observed petrogenic PAHs in some locations are possibly spill-over's from oil bunkering activities and infiltrations from nearby oil installations.

Introduction

With around 240,000 barrels of crude oil being spilled across the Niger Delta on annual basis,[1] the water bodies of coastal communities within most of Nigeria's offshore oil and gas installations are often faced with a myriad of environmental and infrastructure-damaging occurrences stemming from associated activities such as crude oil transport and spillage via corroded surface or under-water pipelines, boating emissions, oil bunkering, refuse dumping, industrial effluent discharges, and run-offs from coastal or riverine farmlands, amongst others. These scenarios tend to elevate the levels of micro-pollutants in the aquatic ecosystem, thereby negatively impacting the overall quality of the habitat,[2-8] with the sediment acting as reservoir for organic and inorganic contaminants deposition. The presence of polycyclic aromatic hydrocarbons (PAHs) in aquatic ecosystems often exposes aquatic flora and fauna to the risk of toxicants bioaccumulation. High concentration of PAHs within water bodies mainly exacerbates toxic effects within the environment. Consequently, the overall water quality is adversely affected. Generally, the exploration of crude oil in the region has continued to pose significant socio-economic burden on the wellbeing of local inhabitants of host communities, thereby leading to the degradation of agricultural lands and fishing zones, thus causing food shortage, as well as leading to communal agitations or unrest.[9]

Polycyclic aromatic hydrocarbons (PAHs) belong to a class of ubiquitous organic pollutants that are hydrophobic in nature, posing significant health and ecological risks.[10] PAHs have also been grouped as mutagenic, toxic and carcinogenic compounds.[11-12] They naturally occur from bush burning, volcanic eruptions or during physical and chemical fluxes which accompany sedimentary rock formation.[13] Anthropogenic releases emanate from combustion of liquid petroleum fuels,[14-15] biomass,[16] coal, coal tar and crude oil.[17-19] Also, they are major constituents of crude oil, hence their presence in oil-impacted environments.[2-3] Other natural occurrences like flooding can potentially contribute to the redistribution and spike in concentration of PAHs in the environment.

The prevalence of certain PAH constituents in the environment are determined by their ability to become soluble within a given matrix. Generally, PAHs contain between 2 to 6 fused ring structures, with the 2 to 4-ringed low molecular weight PAHs (LPAHs) assuming increased solubility in water as compared to the high molecular weight PAHs (HPAHs) (4 to 6-ringed types) of poor water-solubility. Again, LPAHs tend to degrade faster in the environment. This is because of its relatively higher rate of evaporation. On the other hand, HPAHs become adsorbed to particles within the environmental matrix due to its increasing lipophilicity.[10, 20] As such, increasing PAH rings reflect reduced solubility and aggravate environmental persistence, while fewer fused-rings are more soluble, thereby portending elevated risk of bioavailabilty. In addition, LPAHs displays synergy in relation to other organic micro-pollutants, while HPAHs are well-known carcinogens,[21-22] hence, depicting toxic tendencies to human health, causing deformities, mutation and interference with hormonal glands.[23-25] Known carcinogens like benzo (a) pyrene are major constituents of spilled crude oil which are easily bio accumulated in food crops, often causing childhood undernourishment, hematoxic and hepatotoxic effects, infertility and cancer in humans and animals.[1]

PAHs can often become degraded, thereby altering its emission profile or environmental destination. Because of this, the ratio of just two compounds of similar molecular weights and physicochemical attributes is calculated, since the isomeric ratios of both compounds remains unchanged from point of release to sampling.[12, 26] Low temperature processes like wood incineration have been reported to release

LPAHs, while HPAHs are usually formed from the engine-combustion of fuels.[27]

PAH levels were evaluated in surface water, suspended particles and sediments of Upper Iguassu watershed in Parana, Brazil by dos Santos *et al*.[28] The application of diagnostic ratios revealed the predominance of 3 to 4 aromatic ringed compounds in surface waters, but the prevalence of 4 to 6 ringed PAHs were observed in suspended particulate matter and sediment. According to Adeniji *et al*.,[29] PAHs extensively ranged between 0.0003 - 42,350 µg/L and 0 – 1.266 × 10^{9} µg/kg (dry weight) in water and sediments respectively. Results further showed increasing concentrations in regions of enormous crude oil production, boating, commercial and manufacturing ventures. Furthermore, Adeniji *et al*.[30] reported PAH concentrations in surface water,

bottom-profile water and sediment bed samples of Algoa Bay, South Africa, with ranges of <0.01 - 24.66 µg/L, <0.01 – 22.81 µg/L and <0.01 – 5.23 mg/kg respectively. Concentration of PAHs in sediment was significantly greater than the levels found in surface waters of Woji creek in the oil-rich Niger Delta region of Nigeria. In addition, water sample matrices reflected the prevalence of 2 – 3 ringed LPAHs, with sediments showing about 30% and 70% composition for LPAHs and HPAHs respectively. Overall, most of the PAHs revealed petroleum and combustion sources.[31]

The present study is aimed at reporting PAH concentrations and diagnosing its prevalent contributing sources or identifying the various anthropogenic influences that are impacting sediments of the Imiringi River.
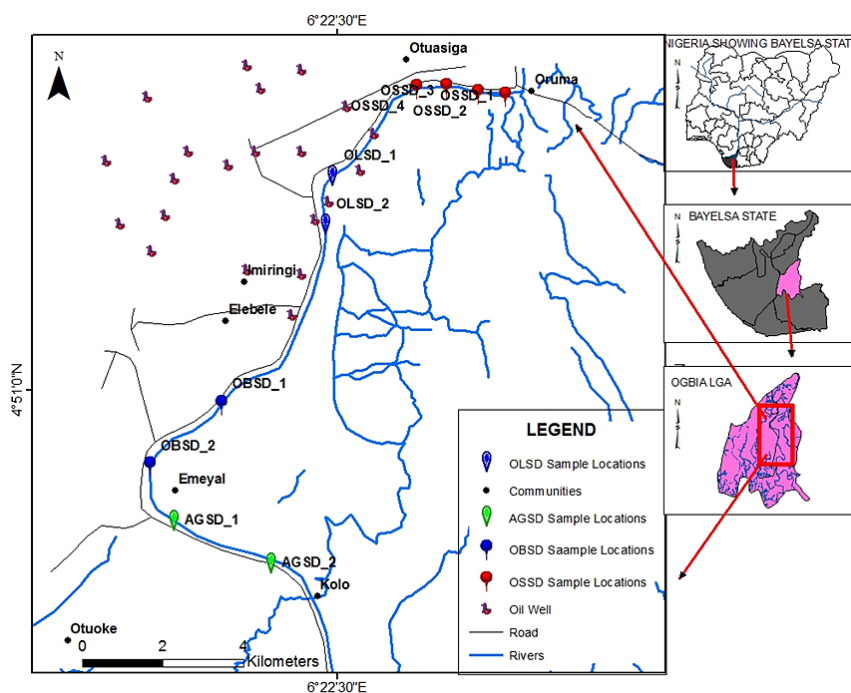

Fig. 1: Geographical map of sampling locations

Materials and Methods
Study Area Description and Sample Collection
The study area cuts across the entire Imiringi community. Mainly, the Imiringi River section of the tributary which traverses across the sub-localities of Oswan (OS), Olem (OL), Obodo (OB) and Agothoman (AG), while the direction of water flow

comes from Otuasega and Oruma colonies, with the water breaking off at the Emeyal 1 and 2 settlements. Each of the sediment sampling points were geo-referenced with a hand-held Garmin Etrex model GPS. The recorded geographical latitudes and longitudes were (OSSD1 – N4.912, E6.412; OSSD2 – N4.917, E6.406; OSSD3 – N4.917, E6.399;

OSSD4 – N4.919, E6.392; OLSD1 – N4.898, E6.374; OLSD2 – N4.887, E6.372; OBSD1 – N4.833, E6.332; OBSD2 – N4.887, E6.372; AGSD1 – N4.822, E6.339; AGSD2 – N4.812, E6.390) (Figure 1). The study area is characterized by two seasons; rainy and dry season. The river is negatively influenced by several anthropogenic inputs such as spilled crude oil from illegal oil bunkering, fuelling of boats and worn-out or failed oil equipment. Also, leachates from farmlands, municipal waste dumps and storm water channels from riverine communities often infiltrate the waterway, thereby contributing to the level of residual contaminants.[32] As a result, field sampling was conducted in the rainy season month of August 2019. This season was chosen in order to capture contaminants deposition on sediments during the most vulnerable period of the year, which is usually characterized by rising water levels and flooding.

Ten (10) sediments were collected with the use of an Eckmann grab. Samples were transferred into 250 mL glass vials before been transferred into a cooling box packed with ice chips (4 ± 2°C). At the laboratory, sediment samples were immediately air-dried at room temperature (28 ± 2°C) to eliminate moisture. Afterwards, samples were pulverized (crushed and sieved through a 2 mm mesh sieve) before sub-sampling for PAH extraction.

Sample Preparation and Analysis
The extraction method previously applied by Zhao *et al*.[33] was adopted for this study. Sediments were air-dried at room temperature, crushed and sieved through a 2 mm mesh sieve. 5 grams of adequately homogenized sample was weighed and transferred into 50 mL glass vials with Teflon crimp caps, mixed with 2 grams of anhydrous sodium sulphate and vigorously agitated with 15 mL n-hexane/acetone (2:1 v/v) for 10 minutes, before leaving it further submersed in the mixed solvent for an hour. The supernatant was transferred into glass vials; then the residue (sediment) was re-extracted with 15 mL n-hexane/DCM (3:1 v/v). The recovered supernatants were combined into another 50 mL glass vial. Thereafter, the organic partition was rid of moisture by straining through anhydrous sodium sulphate. The organic phase of filtered extract was rinsed by eluting viz; 10 mm I.D (internal diameter) x 250 mm long chromatographic column packed with glass wool, slurry of silica gel and anhydrous sodium

sulphate. The cleaned up extract was reconstituted to about 10 mL before being concentrated to about 1.0 mL using a thermally regulated water bath at temperatures between 35°C and 40°C. Results were expressed in concentration units of µg/kg.

Another 5 grams portion of sediment was ceded into a 50 mL glass vial with Teflon crimp caps. The sediment was spiked with pre-deuterated PAH internal standards mix (naphthalene-d8, phenanthrene-d10, chrysene-d12 and perylene-d12). Thereafter, sample mixture was extracted[33] and analyzed. The recovery percentage of the internal standard mix was used to as certain the extraction efficiency (88.0% - 103.0%) (Table 2).

With the use of hypodermic syringe, exactly 1 µL portion of the reconstituted extract was introduced into the injection port of the gas chromatograph - flame ionization detector (GC-FID). PAH components were eluted through the capillary column based on their individual boiling points (BP) and molecular weights (MW). Hence, PAH species of lower BP and MW are known to elute faster. Results were recorded in µg/kg units. The pre-set instrument conditions of the HP 6890 Plus GC-FID are: initial oven temperature (65°C), final oven temperature (320°C), injector temperature (275°C), inlet pressure (14.8 psi), detector temperature (310°C), inlet condition (split-less), nitrogen flow amount (30 mL/min), hydrogen flow amount (35 mL/min), and air flow rate (250 mL/min). The total analysis run time lasted 30.7 minutes.

Statistical Analysis
Statistical Package for Social Science (SPSS) was used for the descriptive and inferential statistics. By applying hierarchical cluster analysis (HCA), the different PAH compounds were grouped in such manner as to reflect those in the same group, showing similarities to each other (cluster). In addition, the Pearson correlation coefficient matrix (PCCM) and principal component analysis (PCA) were used to perform statistical validation.

Results
PAH Source Identification Ratios
Ratios that were applied for the delineation of PAH sources in the environment included Phe/Ant, Flu/Pyr, Fla/Pyr and LPAH/HPAH (PI) (Table 1).

Table 1: Source diagnostic ratios of PAHs in Imiringi sediment

PAH diagnostic ratios	PAH source delineation		
	Pyrogenic	**Petrogenic**	**Combustion**
Phe/Ant	<5	>5	-
Flu/Pyr	+1	<1	-
Fla/Pyr	<1	>1	-
LPAH/HPAH (PI)	-	-	<1
TI	-	<4	>4

Source: Neff *et al.*[34]; Motelay-Massei *et al.*[35]; Zhang *et al.*[36]; Magi *et al.*[37]

Measurement of Equipment Response/quality Condition

Standard solutions of the different PAH species tested were introduced into samples as spikes, and the recovery rate was determined as a means of ensuring optimum performance of the gas chromatograph – flame ionization detector (GC-FID) instrument. Table 2 depicts the percentage recovery values, as well as the limits of detection and quantification.

Table 2: Quality assurance and control considerations for PAH analysis

PAH compounds	Concentration of spike, µg/mL	Detected concentration, µg/mL	Percentage recovered, %	LOD, µg/mL	LOQ, µg/mL
Nap	2	1.76	88.0	0.020	0.070
Acy	2	1.80	90.0	0.030	0.100
Ace	2	1.83	91.5	0.020	0.070
Flu	2	1.79	89.5	0.004	0.020
Phe	2	1.99	99.5	0.010	0.040
Ant	2	1.82	91.0	0.010	0.040
Fla	2	2.06	103.0	0.004	0.020
Pyr	2	1.90	95.0	0.005	0.025
BaA	2	1.86	93.0	0.004	0.020
Chr	2	1.78	89.0	0.003	0.015
BbF	2	1.98	99.0	0.005	0.025
BkF	2	1.85	92.5	0.004	0.020
InP	2	1.88	94.0	0.001	0.004
DaA	2	1.81	90.5	0.008	0.030

Nap = Naphthalene, Acy = Acenaphthylene, Flu = Fluorene, Phe = Phenanthrene, Ant = Anthracene, Fla = Fluoranthene, Pyr = Pyrene, BaA = Benzo (a) anthracene, Chr = Chrysene, BbF = Benzo (b) fluoranthene, BkF = Benzo (k) fluoranthene, InP = Indeno (1,2,3-cd) pyrene, DaA = Dibenz (a,h) anthracene.

Trends in PAH Species Distribution

Sediment PAHs ranged between <0.01 and 3,965.4 µg.kg^{-1} across the selected sediment sampling locations of the Imiringi river. The low molecular weight PAHs (LPAHs) consisting of Nap, Acy, Ace, Flu, Phe and Ant, showed a 5.72% distribution, while the high molecular weight PAHs (HPAHs) comprising Fla, Pyr, BaA, Chr, BbF, BkF, InP and DaA accounted for 94.28% of the total PAH mass concentration. Concentrations obtained from this study were lower

than the levels of 489 to 5,616 µg.kg^{-1} recorded by Parra *et al.*[38] for soils and sediments in Southwest Nigeria. Similarly, the range of 44 to 39,000 ng/g reported by Nieuwoudt *et al.*[39] for soils and sediments of Central South Africa mostly exceeded concentrations reported for this study. Contrary to the reported prevalence of 2-, 3- and 4-ring PAHs in the riverine wetland sediments of Chaohu, China, by Wu *et al.*,[40] PAHs in the current study environment were dominated by the 5-6 ring PAHs (74.06%), followed by the 4-ring PAHs (20.23%). The least important fractions were the 2-3 ring PAHs (5.71%)

(Figure 2). Also, Wu *et al.*[40] reported the uniform distribution of 2-, 3- and 4-ring PAHs in sediments, whilst revealing the predominant concentration of 5 and 6-ring PAHs in surface soil, while Iwegbue *et al.*[41] had reported the PAH-rings distribution order (4 > 6 > 5 > 3 > 2) for household dusts around urban zones in the Niger Delta province, Nigeria. Results of this study compared with Yang *et al.*[42] The author's had reported the total concentration of 16 PAHs within the range of 3.55 to 3,200 µg.kg^{-1} with the 4-6 ring HPAHs dominating the PAH profiles at about 83.3% of the total PAH mass.
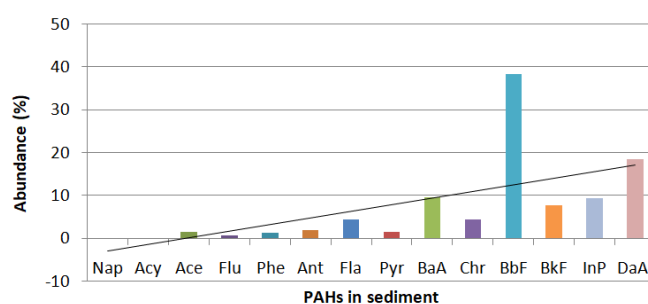

Fig. 2: Percentage abundance of different PAH species in sediment

Trends In Spatial Composition of Pah Compounds
The highest spatial distribution of PAH was observed at the midstream and downstream locations of OLSD1 (45.95%) and OBSD2 (25.56%) respectively (Figure 3). The high tidal movement of water and increased dumping of municipal wastes (trash or garbage) by the riverine communities located towards the mid and downstream sections of the river may have contributed to the increased redistribution of organic pollutants and relative spike in residual PAHs.
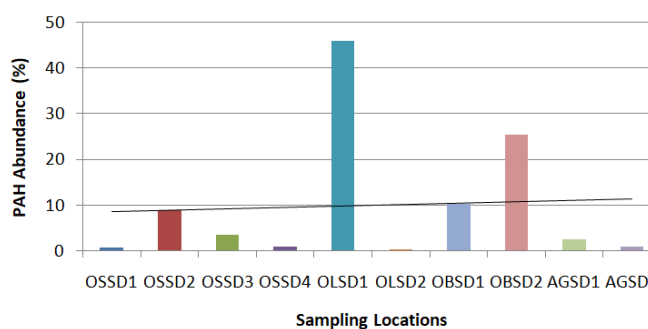

Fig. 3: Percentage spatial delineation of PAHs in sediment

Apart from Nap and Acy which showed PAH concentrations below stipulated environmental regulations, the other LPAHs revealed levels exceeding the interim standard quality guidelines (ISQG) and probable effect levels (PEL) of the Canadian Council of Ministers of the Environment (CCME) (Table 3). Furthermore, the total cumulative PAHs mostly exceeded sediment target values (STV), but remained within sediment intervention values (SIV) recommended by the department of petroleum resources (DPR) in Nigeria.

Table 3: PAH (µg.kg⁻1 DW) (levels from current study versus regulatory guidelines)

PAHs	OS SD1	OS SD2	OS SD3	OS SD4	OL SD1	OL SD2	OB SD1	OB SD2	AG SD1	AG SD2	CCME[43] ISQG	CCME[43] PEL	DPR[44] STV	DPR[44] SIV	Carcinogenic Potential USEPA[45]
Nap	0.02	0.9	0	0	0	0	0	0	0	0	34.6	391	-	-	0
Acy	0.7	0	0.9	0	0	0	0	0	0	0	5.87	128	-	-	0
Ace	1.2	14.2	0.5	0	0	0	0	169.4	6.3	0	6.71	88.9	-	-	0
Flu	4	10.7	0.6	10.9	0	0	0	43.6	6.4	0	21.2	144	-	-	0
Phe	2.3	14.5	1.3	28.2	1.5	3.6	107.1	0	1.5	10.3	41.9	515	-	-	0
Ant	4.8	45.7	7.6	2.9	12.6	11	62.3	78.7	8.8	2	46.9	245	-	-	0
Fla	7	46	7.5	3.1	33.6	8.9	50.5	350	7.2	17.7	111	2355	-	-	0
Pyr	2.8	16.9	29.5	17.7	68.6	6.3	13.5	17	7	8.3	53	875	-	-	0
BaA	9	33.5	27.4	15.2	320.2	7.9	241.4	485.8	7.3	1.5	31.7	385	-	-	++
Chr	14	28.8	47.9	1.5	246.6	1.6	8.4	179.8	2.3	0.6	57.1	862	-	-	++
BbF	13.1	109.2	29.7	7	3,965.40	0.8	208	167.7	17.2	4.2	-	-	-	-	++
BkF	1.5	52.9	16.3	3	636.2	3	98.3	93.4	20.1	4.7	-	-	-	-	++
InP	6.4	373.8	172.1	12.7	32.8	2.3	121	198.3	176.8	11.2	-	-	-	-	+ + +
DaA	18.1	306.8	76.9	19.9	117.3	3.4	317.6	1,240.30	44.2	48.6	6.22	135	-	-	+++
Total PAHs	84.9	1,053.90	418.2	122.1	5,434.80	48.8	1,228.10	3,024.00	305.1	109.1	-	-	1,000	40,000	NA

CCME (Canadian Council of Ministers of the Environment); ISQG (Interim Standard Quality Guidelines); PEL (Probable Effect Levels); USEPA (United States Environmental Protection Agency); DPR (Department of Petroleum Resources); STV (Sediment Target Value); SIV (Sediment Intervention Values); NA (Not Applicable); 0 (Not carcinogenic); ++, +++ (Strongly carcinogenic)

Discussion
Correlating Relationships among PAH Species in Sediment

Figure 3 reveals the spatial distribution of PAHs in sediment. The most contaminated sections of the river were OLSD1 midstream (45.95%), OBSD2 downstream (25.56%), OBSD1 downstream (10.38%) and OSSD2 upstream (8.91%). The reasonable level of HPAHs in the midstream section can be attributed to the high tidal movement of organic pollutants from the oil installations located upstream, coupled with the effect of bush burning from nearby farmlands, as well as leachates from waste dumps along river banks. In addition, the influx of storm water draining via community flood channels may have elevated the pyrogenic inputs of the river. Pearson's correlation coefficient results mostly indicated weak and strong negative correlations among the LPAHs. Some of the identified positive LPAH inter-correlations included Nap/Flu ($r = 0.079$, $p < 0.05$), Nap/Ant ($r = 0.273$, $p < 0.05$), Ace/Flu ($r = 0.960$, $p < 0.01$), Ace/Ant ($r = 0.714$, $p < 0.05$), Flu/Ant ($r = 0.663$, $p < 0.05$) and Phe/Ant ($r = 0.424$, $p < 0.05$). Amongst the LPAHs being studied, Acy and Phe were the most negatively correlating. Overall, HPAHs showed comparatively higher positive inter-correlations with LPAHs. The most significant positive LPAH-to-HPAH inter-correlations are Nap/InP ($r = 0.754$, $p < 0.05$), Fla/Ace ($r = 0.982$, $p < 0.01$), BaA/Ace ($r = 0.740$, $p < 0.05$), DaA/Ace ($r = 0.910$, $p < 0.01$), BaA/Ant ($r = 0.742$, $p < 0.05$) and DaA/Ant ($r = 0.869$, $p < 0.01$). The strongest positive correlation between Fla and Ace is evidence of the similarity of sources (petrogenic), probably due to their closely similar molecular masses (LPAHs). The HPAHs were apparently more positively correlating. Strong positive HPAH inter-correlations were exhibited by BaA/Fla ($r = 0.829$, $p < 0.01$), Chr/Fla ($r = 0.552$, $p < 0.05$), DaA/Fla ($r = 0.966$, $p < 0.01$), Chr/Pyr ($r = 0.808$, $p < 0.01$), BbF/Pyr ($r = 0.920$, $p < 0.01$), BkF/Pyr ($r = 0.919$, $p < 0.01$), BbF/Chr ($r = 0.799$, $p < 0.01$), BkF/Chr ($r = 0.836$, $p < 0.01$), DaA/Chr ($r = 0.511$, $p < 0.05$) and BkF/BbF ($r = 0.991$, $p < 0.01$) (Table 4). The strongest HPAH-to-HPAH correlation was between the two isomeric PAH compounds (BkF and BbF). As such, both pyrogenic species are likely being released from a similar source.

Table 4: Pearson correlation coefficients for residual PAH fractions in sediments of Imiringi river

	Nap	Acy	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	InP	DaA
Nap	1													
Acy	-0.153	1												
Ace	-0.036	-0.181	1											
Flu	0.079	-0.216	0.960**	1										
Phe	-0.031	-0.243	-0.194	-0.206	1									
Ant	0.273	-0.323	0.714*	0.663*	0.424	1								
Fla	-0.149	-0.204	0.982**	0.908**	-0.079	0.746*	1							
Pyr	-0.041	-0.026	-0.045	-0.105	-0.131	-0.038	0.020	1						
BaA	-0.171	-0.290	0.740*	0.629	-0.153	0.742*	0.829**	0.462	1					
Chr	-0.102	-0.120	0.499	0.402	-0.280	0.320	0.552	0.808**	0.812**	1				
BbF	-0.100	-0.181	-0.096	-0.173	-0.128	-0.081	-0.015	0.920**	0.462	0.799**	1			
BkF	-0.076	-0.223	-0.012	-0.097	-0.059	0.047	0.076	0.919**	0.559	0.836**	0.991**	1		
InP	0.754*	-0.048	0.325	0.382	0.015	0.570	0.230	-0.026	0.146	0.057	-0.194	-0.119	1	
DaA	0.078	-0.233	0.962**	0.910**	0.023	0.869**	0.966**	0.013	0.819**	0.511	-0.051	0.055	0.441	1

*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

Application of Pah Isomeric Ratios and Observed Trends

Figure 3 reveals the spatial distribution of PAHs in sediment. The most contaminated sections of the river were OLSD1 midstream (45.95%), OBSD2 downstream (25.56%), OBSD1 downstream (10.38%) and OSSD2 upstream (8.91%). The reasonable level of HPAHs in the midstream section

can be attributed to the high tidal movement of organic pollutants from the upstream oil installations, coupled with the effect of bush burning from nearby farmlands and leachates from waste dumps along river banks. In addition, the influx of storm water from communities, draining via flood channels may have elevated the pyrogenic inputs of the river.

Apart from the upstream (OSSD4) and downstream (AGSD2) locations which revealed petrogenic inputs, the Phe/Ant ratios were mostly less than 5

(< 5), an indication that PAHs are mainly derived from pyrogenic sources (Figure 4). Similarly, the author's of Gereslassie *et al.*[25] indicated that 14 of the 18 soil sampling stations from Wuhan, Central China had Phe/Ant values less than 5 (< 5), hence PAH sources were sparsely petrogenic. This trend portends that the Imiringi river system is mostly impacted by pyrogenic PAHs emanating from bush burning activities, as well as waste dump leachates, and agricultural run-offs.
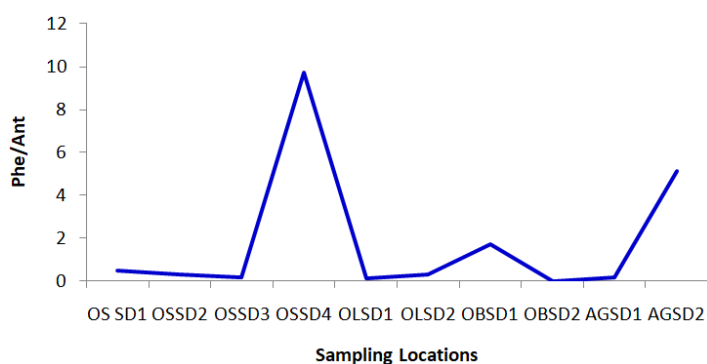

Fig. 4: Phe/Ant ratio in sediments of Imiringi River

Figure 5 shows the distribution trend for Flu/Pyr ratio across the different sampling locations. This ratio was not applicable across all ten sampling stations due to the absence or non-detection of Flu in sediments of OLSD1, OLSD2, OBSD1 and AGSD2 (Table 4). This may be due to evaporation effect.[10] However, two stations (OSSD1 and OBSD2) and 4 stations (OSSD2, OSSD3, OSSD4 and AGSD1) reflected pyrogenic and petrogenic PAH sources respectively. As a result, PAH in the environment can be predominantly attributed to petrogenic inputs. Applying the same ratio, Gereslassie *et al.*[25] reported

the predominance of petrogenic PAHs in soils from Wuhan, China. Similarly, sediments of the Adriatic Sea were sampled by Magi *et al.*[37] The Chioggia section of the coastal environment depicted Flu/Pyr ratios ranging between 0 and 0.12, thereby signifying petrogenic inputs, while the Ancona section depicted a range between 0 and 1.27. Only one sampling point showed a value greater than 1 (> 1), hence, increasing the suspicion that most of the LPAHs may have emanated from either the nearby oil installations or makeshift/artisanal refineries.
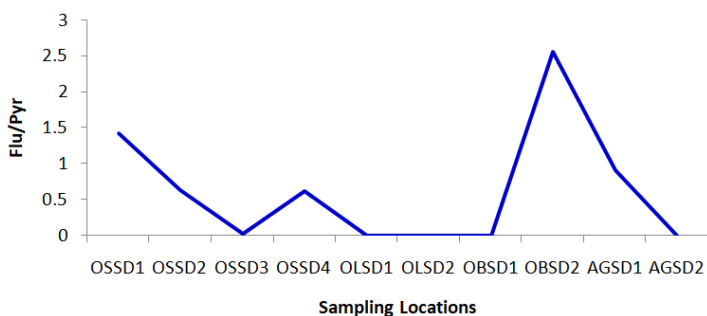

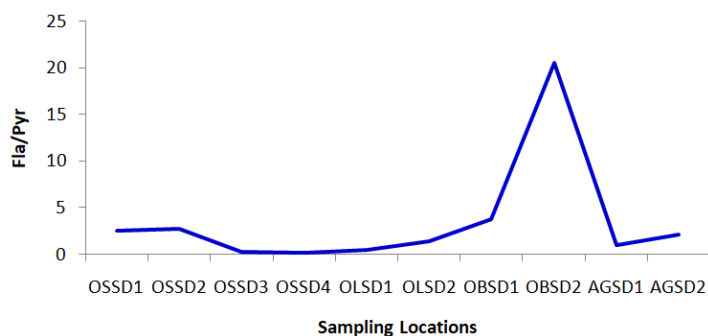**Fig. 5: Flu/Pyr ratio in sediments of Imiringi River**

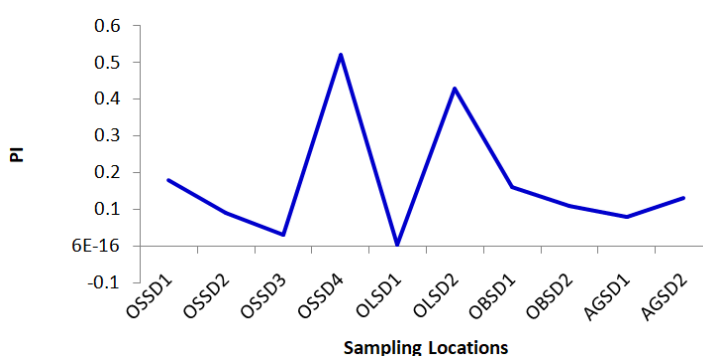**Fig. 6: Fla/Pyr ratio in sediments of Imiringi River**

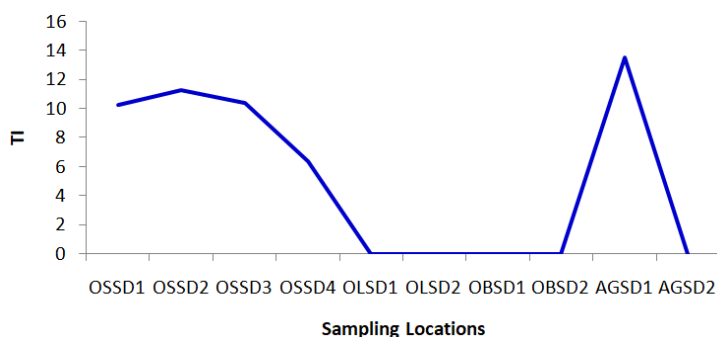**Fig. 7: PI ratio in sediments of Imiringi River**

Fig. 8: TI ratio in sediments of Imiringi River

The Fla/Pyr ratio reflected superseding pyrogenic influences in the sediment (Figure 6). The sampling stations were dominated by pyrogenic PAHs with values mostly greater than 1 (> 1). Most notably, the downstream location at OBSD2 recorded a ratio of 20.59, showing a considerable spike in pyrogenic inputs in that section of the river. The spike in pyrogenic inputs at the downstream area of the river may have resulted from increased water movement and contaminant deposition, which is typical of the rainy season. Magi *et al*.[37] had reported values

ranging from 1.03 and 2.00 for Chioggia and 1.07 to 2.17 for the Ancona section of the Adriatic Sea. The author's had attributed the presence of PAHs to pyrolytic sources.

Figure 7 shows the pyrogenic index (PI) or LPAH/HPAH ratio. PI values for all sampling locations are less than 1 (< 1), thereby depicting combustion sources. Result of this study was concurrent with those reported in other works.[5, 37] Similarly, values of total index (TI) ratio were greater than 4

(Figure 8), hence, depicting combustion sources as well. A similar report was published by Gereslassie *et al.*[25] The author's had observed the primary source of residual PAHs in soils form Wuhan, China, to be of combustion origin. Also, Han *et al.*[46] had reported open biomass combustion emissions to be mostly responsible for the prevailing distribution of pyrogenic HPAHs found in air ccaround urban areas of China.
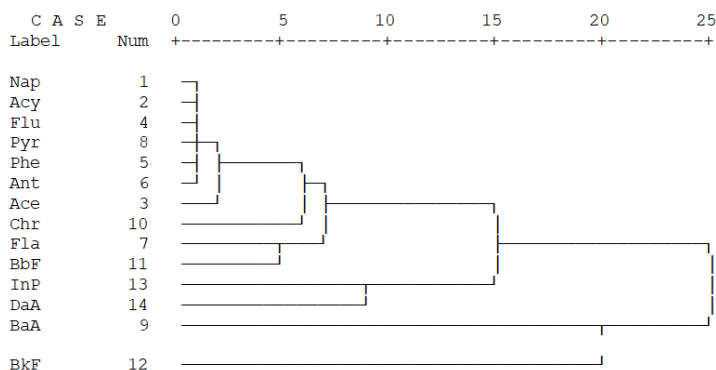

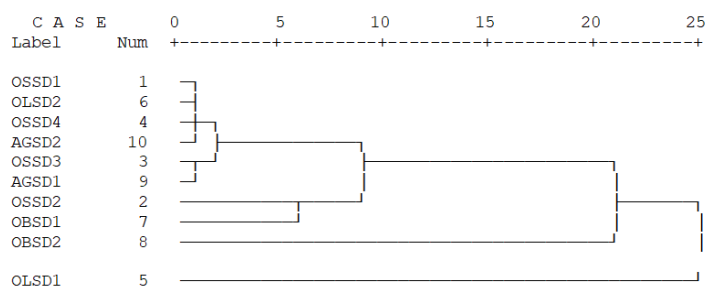**Fig. 9: Hierarchical cluster analysis of PAHs in sediment**

Fig. 10: Hierarchical cluster analysis of sediment sampling locations

The dendogram of hierarchical cluster analysis (HCA) of PAH distribution (Figure 9) showed the relationship existing among the different PAH compounds in Imiringi sediment. Results showed strong similarities among the LPAH compounds (2 – 3 membered rings). BkF and BaA revealed strongest dissimilarity with Nap. This may have been due to the undetected levels of Nap in the environment, owing probably to its comparatively higher evaporation or degradation rate.[10,20] Correlation statistics of different spatial locations of the river (Figure 10) showed strong dissimilarities between the upstream location (OSSD1) and midstream location (OLSD1). This may have resulted from the prevalence of pyrogenic HPAHs in the midstream location. Also, the slight differences observed among other sampling locations can be attributed to variations in petrogenic and pyrogenic inputs. Ilechukwu *et al.*[22] had shown distinct spatial dissimilarities for soils containing reasonable HPAHs within asphalt production plants in Port Harcourt, Nigeria.

Identification of Principal Pah Species In Sediments of Imiringi River
PCA revealed twelve (12) of all fourteen (14) PAH fractional species examined to be discretely distributed within the cluster: (Nap, Acy, Ace, Flu, Phe, Ant, Fla, Pyr BaA, Chr, BbF, and BkF). On the other hand, two (2) PAH species (InP and DaA) showed the strongest dissimilarity across the field locations (Figure 11). This difference can be attributed to the relatively higher concentrations of "InP" and "DaA", the principal PAH components found in the sediments. Also, the outlier concentrations of InP and DaA are responsible for the spatial delineation in the PCA plot. Evidently, both PAHs are high molecular weight pyrogenic species. The PCA result compares with the PAH source identification ratios

which revealed the predominance of pyrogenic PAHs within the sediment environment (Table 1, Figures 4 - 8). Similarly, hierarchical cluster analysis showed close association between InP and DaA (Figure 9). In addition, InP and DaA showed positive correlation (r = 0.441, p < 0.05) (Table 4).
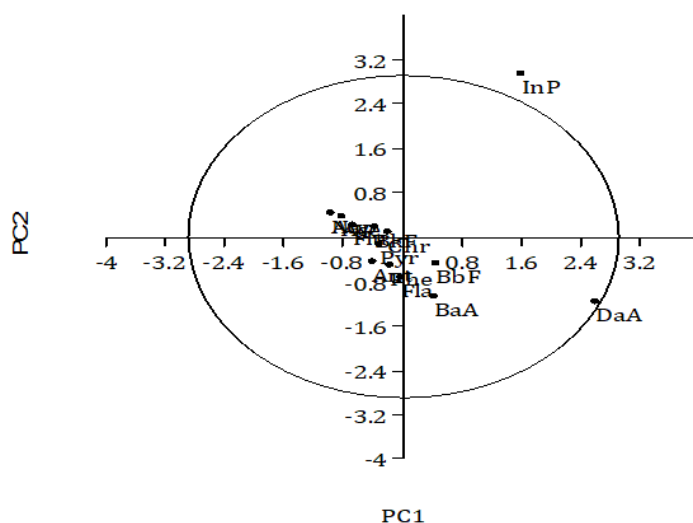

Fig. 11: Principal component analysis of PAH fractions/species

Conclusion

Whilst the results of this study shows petrogenic PAHs to have emanated from spilled crude oil from illegal make-shift refineries and neighbouring oil production facilities, and pyrogenic PAHs to have resulted from agricultural run-offs, deposition of fly-ash from seasonal bush incineration and the leaching of municipal waste or garbage along creek and coast lines. The most significant source of PAHs was biomass and bush incineration. Based on the foregoing, anthropogenic activities within the study area appear to be impacting negatively on the overall quality of the aquatic environment. In order to mitigate the rising PAH levels in the environment, it is pertinent to ensure improved sanitary conditions, as well as discourage bush and biomass combustion within proximity of the Imiringi River.

Conflict of interest

The authors do not have any conflict of interest.

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