A Survey of Concentrations and Source Characterization of Polycyclic Aromatic Hydrocarbons in Surface Waters of the Imiringi River System

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Author's contribution

The author designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. He also managed the analyses of the study and literature searches. The author read and approved the final manuscript.

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ABSTRACT

Ten water samples were collected along the Imiringi water channel, cutting across several sub-communities of the upstream to downstream sections of the river. All samples were collected in the month of August 2019, reflecting increased tidal movement of water and aggravated pollutants redistribution which is typical of the rainy season. Analysis was carried out using the HP 6890 Plus gas chromatograph – flame ionization detector (GC-FID). The rate of ionization of each PAH component was directly proportional to the obtained concentration. The total concentrations of 14 PAHs ranged from <0.01 to 300.1 µgL^{-1}, with the high molecular mass PAHs (4-6 ring HPAHs) observed as the most important fractions showing 82.4% distribution. Also, the low molecular mass PAHs (2-3 ring LPAHs) were found in trace concentrations, accounting for 17.6% of total PAH mass. The application of PAH source diagnostic ratios revealed vegetation and coal combustion as primary sources, followed by petroleum combustion, and then, petroleum sources. Correlation cluster analysis (CCA) and principal component analysis (PCA) showed discrete localization for

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samples of stations OL1, OB2 and OS4. The pyrogenic inputs are most likely from runoffs of seasonally burnt vegetation at near-coastal farmlands as well as leachates from surrounding waste-dumpsites. Petroleum sources may have resulted from neighbouring oil installations and illegal oil bunkering sites. Overall, the study is aimed at identifying the most important contributing sources of polycyclic aromatic hydrocarbon (PAH) micro-pollutants in the aquatic environment.

1. INTRODUCTION

In Nigeria, coastal communities are mostly engaged in the indiscriminate discharge of municipal wastes along coastlines. Hence, river systems are often prone to contamination, which mostly emanates from anthropogenic activities. Consequently, complex mixtures of persistent organic pollutants (POPs) are released in the form of total petroleum (TPHs), polycyclic aromatic hydrocarbons (PAHs) and volatile aromatic mixtures (VAMs) such as phenol, benzene, toluene, ethylbenzene, xylene [1], inorganic micro-pollutant trace/heavy metals [2–5], as well as proliferating microbial densities [6], amongst others.

Municipal waste dumping, much in the same way as e-waste disposal is known to elevate PAHs in the environment [7–10]. Hence, PAHs have been described as the anthropogenic micro-pollutant with most environmental influence [11]. In the same manner, incineration of waste tends to release semi-volatile hydrocarbon compounds, such as PAHs into the atmosphere [7,12,13], thereby increasing the exposure routes for PAHs in the environment. Overall, the poor waste management practise of dumping un-segregated wastes along river banks tends to release inorganic and organic micro-pollutants directly into the water body, thereby enhancing the movement of such contaminants along coastal waters, before emptying them into the open sea waters.

PAHs are organic compounds with two or more fused aromatic rings that can be found in water [1,14,15], soil and sediment [10,16–19], amongst other environmental matrices. They possess the potential to be suspended in air, depending on prevailing environmental conditions [20–23] and their molecular weights exist as low (petrogenic hydrocarbons) and high fractions (pyrogenic hydrocarbons) [24]. Naturally occurring sources of pyrogenic PAHs release nominal levels in the environment, which emanates mainly from volcanic lava eruptions and incomplete burning of woodland fires, etc [22]. Other sources of PAHs include coal tar and crude oil [21] and electronic wastes [13], amongst others.

The dietary sources of PAHs have been found to include PAH-contaminated soil or water [25], sea foods [24], smoked meat, partially combusted fuels, tobacco smoke, amongst others. Consequently, PAHs depict high carcinogenic and geno-toxic tendencies, which further disrupt the endocrine system in mammals and humans [11,25,26]. Some PAH isomers have also been used to calculate for cancer risk and their hazard indicators [25].

There has been reported increased cancer risk in children, with most hazards emanating from the consumption of contaminated sea food, with variability in exposure, depending on the PAH sources and ingestion pattern, as well as revealing elevated vulnerability amongst the non-Hispanic black population as well as tobacco smokers [25]. Also, increased carcinogenic effects have been revealed from the consumption of shellfish from the Safaga 2 section of the Egyptian Red Sea coast using the benzo(a)pyrene-equivalence (BaPE) [24].

The fingerprinting of crude oil sources and its derivatives has been widely used to decipher potential sources of hydrocarbons in the environment. It has been applied for the identification of pyrogenic and petrogenic sources of pollution. Some of the applicable ratios include Ant/[Ant + Phe], Flr/[Flr + Pyr] and BaA/[BaA + Chr] were applied [7-10,12,18,19, 24].

The Imiringi River is constantly impacted by recreational activities, agricultural run-offs, infiltration of waste dump leachates and crude-oil seepages from nearby oil installations, as well as boating. The need to ascertain the source apportionment and prevailing distribution of carcinogenic PAHs in the surface water channel has made this study one of immense interest. The outcome of this work is aimed at providing vital environmental information, one that will aid the relevant local environmental protection

agencies, waste management authorities, as well as stakeholders in taking proactive steps to forestall future public health emergency.

2. MATERIALS AND METHODS

2.1 Study Area and Sample Collection

The Imiringi River is located in Ogbia local government area of Bayelsa state, which is within the oil hub of the Niger Delta region in Nigeria. It is continuously influenced by activities such as near-shore municipal and domestic waste dumping, infiltration of agricultural runoffs, recreational activities (swimming and bathing), and mixed industrial effluent releases originating from interlinked coastal communities and oil installations, further upstream of the Oswan 1 (OS1) river section. The river lies between latitude 04.8527 and longitude 06.3758, coursing through the Oswan (OS), Olem (OL), Obodo (OB) and Agothoman (AG) neighbouring settlements. Like the rest of the Niger Delta, it is typified by the dry and wet seasons with temperatures reaching about 35°C all through the year [27].

Sampling was done in the rainy season month of August 2019. Water and sediment samples were collected at four different points of the upstream section and labelled (Oswan 1- 4). Two samples were taken at the midstream section and tagged as (Olem 1 and 2). Another four samples were collected from two neighbouring downstream settlements at (Obodo1 and 2) and (Agothoman 1 and 2) respectively. Water samples were collected in clean 250 mL glass bottle containers, fixed with 1 mL sulphuric acid and secured with glass stop corks, before transferring into cooling boxes with ice packs. Sediments from the same water sampling points were collected into 250 mL glass jars, secured with glass lids (all samples being for PAH analysis) before being transferred into ice-coolers. All samples were immediately transported to the laboratory where water samples were kept under cooling conditions, with sediments being air-dried at room temperature.

2.2 PAH Extraction, Cleanup/Separation and Gas Chromatographic Analysis of Water

The liquid-liquid extraction technique was applied to extract PAHs in surface water samples using method [28] with slight modification on the procedure applied by [29]. Firstly, the 250 mL water sample was homogenized before emptying the entire volume into a 500 mL separating funnel. Afterwards, PAHs were extracted by a three-batch extraction process using 20 mL of dichloromethane (DCM)/n-hexane (1:3 v/v) mixed solvents at each time. The sample-solvent mixture in the separating funnel was vigorously agitated with intermittent ejection of built-up pressure from the tap of glass funnel. This was done to eliminate the risk of blowing up the glass material.

Thereafter, the organic extract was dehydrated by filtering through anhydrous sodium sulphate. Organic contaminants in filtered extracts were cleaned by eluting through a 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 1.0 mL, after being concentrated on a temperature regulated water bath at 35 – 40°C. Finally, sample extracts were transferred into glass vials with rubber-crimped caps.

Another 250 mL portion of water sample was transferred into a separating funnel and spiked with pre-deuterated PAHs mixture (naphthalene-d8, phenanthrene-d10, chrysene-d12 and perylene-d12) as internal standards, to establish the efficiency of the extraction protocol. The recovery rates ranged between 92% and 107% (Table 2). Exactly 20 mL of dichloromethane (DCM)/n-hexane (1:3 v/v) mixed solvents were added to the sample mixture, thoroughly mixed and kept standing to allow for adequate phase separation prior to dehydration and filtration, followed by cleanup and elution through a chromatographic column. Afterwards, the eluted extracts were concentrated to 1.0 mL volume and stored in air-tight rubber-crimp cap glass vials.

Exactly 1 µL portion of the reconstituted extract was injected into the gas chromatograph-flame ionization detector (GC-FID) using hypodermic syringe. Nitrogen served as the carrier gas while a combination of hydrogen and air were used to create an ionization environment at the detector head. The various fractions of the aromatic compounds were automatically detected at the FID (whose response is dependent on the composition of the eluted vapour) as they emerged from the column. Results were expressed in µg/L units.

Table 1 shows the pre-set operating conditions of the GC-FID. The instrument conditions above are based on manufacturer recommendations and PAH method suitability for repeatability of

analytical data on the HP 6890 Plus GC-FID, version A.03.08.

Table 2 lists the quality assurance/quality control (QA/AC) parameters applied during GC-FID analysis [30]. The surface water (SW) matrix was used to calculate extraction recovery efficiency for the different PAH compounds: Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flr), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flt), Pyrene (Pyr), Benz (a) anthracene (BaA), Chrysene (Chr), Benzo (b) fluoranthene (BbF), Benzo (k) fluoranthene (BkF), Indeno-1,2,3-cd pyrene (IndP), and Dibenz (a,h) anthracene (DahA). The instrument limit of detection (LOD) and limit of quantification (LOQ) were also calculated using equations 1 to 3. The acceptable recovery range of the equipment was stipulated between 90 and 110%.

$$\% \, recovery \, = \left[concentration \, of \, substance \, obtained \, \left(\tfrac{\mu g}{mL}\right) \div \right.$$
$$\left. spike \, concentration \, \mu g mL x \, 100 \right. \tag{1}$$

$$LOD = \frac{3.3\sigma}{S} \tag{2}$$

$$LOQ = \frac{10\sigma}{S} \tag{3}$$

2.3 Quality Considerations for PAH Analysis

A key quality consideration that was applied for the validation of hydrocarbon extraction method was spike recovery. Trace concentrations of deuterated PAHs were added to measured volumes of test water. Spiked and un-spiked portions of samples were determined for the different aromatic compounds of interest. The ratio of concentrations of determined substance against spike standards was calculated. The percentage recovery of the different PAHs ranged between 92% and 107% with mean recovery of 97.79% ± 3.77%.

2.4 Calculation of PAH Source Identification

In order to characterize the PAHs with respect to their sources, some diagnostic ratios were considered [24,31–33]. To assess the combustion (pyrogenic) and petroleum (petrogenic) contributions, the ratios of some PAHs such as Ant/[Ant + Phe], Flr/[Flr + Pyr] and BaA/[BaA + Chr] were applied by [34-36].

$$\frac{Ant}{[Ant+Phe]} => 0.1 \, (Petrogenic \, PAHs); <$$
$$0.1 \, (pyrogenic \, PAHs) \tag{4}$$

$$\frac{Flr}{[Flr+Pyr]} =< 0.4 \, (petroleum \, source); 0.4 -$$
$$0.5 \, (petroleum \, combustion); >$$
$$0.5 \, (biomass \, and \, coal \, combustion) \tag{5}$$

2.5 Statistical Analysis

In order to identify the sections of the river that were closely associated, the correlation cluster analysis (CCA) was applied with the use of correlation distance which is dependent on average link between groups. Two variables namely: i) sample location and, ii) PAH components were statistically evaluated for the Imiringi river system. PAHs of mutual dependence showed similarities or closeness in features while those of mutual independence reflected diverging characteristics. Similarly, principal component analysis (PCA) was used to identify spatial similarities and dissimilarities, as well as PAH species association and disassociation across the study area.

$$\frac{BaA}{[BaA+Chr]} =< 0.20 \, (petroleum \, source);$$
$$> 0.35 \, (combustion \, of \, coal, grass \, and \, wood); \, 0.2$$
$$- 0.35 \, (petroleum \, combustion, especially \, fossil \, fuel, vehicle \, and \, crude \, oil \, spillage) \tag{6}$$

Table 1. Set-up of the gas chromatograph-flame ionization detector for PAH analysis

GC-FID instrument conditioning for PAH method		
Oven Temperature	Initial (°C)	65
	Final (°C)	320
Injector Temperature (°C)		275
Inlet pressure (psi)		14.8
Detector Temperature (°C)		310
Inlet condition		Splitless
Nitrogen Flow Rate (mL/min)		30
Hydrogen Flow Rate (mL/min)		35
Air Flow Rate (mL/min)		250
Total Run Time (min.)		30.7

Table 2. Spike recovery and measurable detection limits (MDL) for PAHs quantification

GC-FID Quality control checks							
Abbreviations	**Matrix Types**	**Spike concentration, µg/mL**	**Concentration obtained, µg/mL**	**Percentage recovery, %**	**LOD, µg/mL**	**LOQ, µg/mL**	**Acceptable recovery range, %**
Nap	SW	2.0	1.84	92	0.02	0.07	90 – 110
Acy	SW	2.0	1.92	96	0.03	0.10	90 – 110
Ace	SW	2.0	1.93	97	0.02	0.07	90 – 110
Flr	SW	2.0	1.88	94	0.004	0.020	90 – 110
Phe	SW	2.0	2.02	101	0.01	0.04	90 – 110
Ant	SW	2.0	1.94	97	0.01	0.04	90 – 110
Flt	SW	2.0	2.14	107	0.004	0.020	90 – 110
Pyr	SW	2.0	1.98	99	0.005	0.025	90 – 110
BaA	SW	2.0	1.96	98	0.004	0.020	90 – 110
Chr	SW	2.0	1.86	93	0.003	0.015	90 – 110
BbF	SW	2.0	2.02	101	0.005	0.025	90 – 110
BkF	SW	2.0	1.96	98	0.004	0.020	90 – 110
IndP	SW	2.0	1.98	99	0.001	0.004	90 – 110
DahA	SW	2.0	1.94	97	0.008	0.030	90 – 110

3. RESULTS AND DISCUSSION

3.1 PAHs Distribution and Source Identification in Surface Waters of Imiringi River

PAHs ranged between <0.01 and 300.1 µgL^{-1} across the selected surface water sampling locations of the river. The organic micro-pollutants were delineated according to their molecular masses, the 2-3 ring species being the LPAHs (Nap, Acy, Ace, Flr, Phe and Ant) showed a 17.6% distribution in the water body, while the HPAHs (Flt, Pyr, BaA, Chr, BbF, BkF, IndP and DahA) which were the most important PAH fractions accounted for 82.4% of the total PAH mass concentration. Concentrations obtained from this study were lower than levels recorded for Atlas cove in Lagos Nigeria. It was also inconsistent with the accounted fractions of 63.64% (2-3 ring PAHs), 27.27% (4-ring PAHs) and 9.09% (5-6 ring PAHs) [37]. Also, the current work showed lower concentrations than those obtained from hand-dug wells at Ile-Oluji, Nigeria, where concentrations ranged from <0.01 to 11.3 ng/µL. Furthermore, LPAHs (2-3 aromatic rings) consisted of about 95% of the total PAH mass, with the remaining 5% being associated with the 4-6-membered aromatic rings [38].

The Flt/(Flt+Pyr) ratios were only applicable for Agothoman SW1 (AG1), which is located at the downstream zone of river. Value of the ratio (0.83) showed pyrolytic input of PAHs. Also, the Ant/(Ant+Phe) ratios were greater than 0.1 with values ranging from 0.14 to 0.96 across all the sampling points, hence, reflecting the derivation of PAHs from combustion sources. In addition, BaA/(BaA+Chr) exceeded 0.35 in all stations apart from AG1 where the value of 0.32 was recorded. Consequently, station AG1 is most likely receiving PAH inputs from nearby petroleum sources. Finally, Phe/Ant ratios varied between 0.05 and 6.19, thereby signifying the impact of combustion residues (Figs. 1 to 3). El Nemr et al. [24] had reported Phe/Ant ratios <10 for shell fishes from the Egyptian Red Sea coast, being an indication of pyrolytic contributions. Generally, the application of different PAH diagnostic ratios revealed pyrolytic/combustion activities as the most important source of PAHs in the Imiringi river, while the overall PAH concentrations for all sampling locations exceeded comparable regulatory limits, including USEPA's maximum contamination level (MCL) for drinking water (Table 3). The findings from this study corroborated the report of pyrogenic and petrogenic PAHs at levels exceeding maximum tolerable standards outlined by different regulatory bodies [9]. Contrary to this study, the increased level of LPAHs found in waters of the Atlas cove in Lagos State in Nigeria was an indication of increased petrogenic inputs [37], and the predominance of petrogenic LPAHs in hand-dug wells of South-Western Nigeria [38].

3.1.1 PAH ratios across locations of Imiringi surface water

Fig. 1 shows the PAHs diagnostic ratios in water samples collected across different sampling sections of the Imiringi River. Ant/(Ant+Phe) ratios in all the studied locations were greater than 0.1 with a mean ratio of 0.27 ± 0.32, except for stations OS4, OL1, OL2, OB1 and AG1 where the values were 0. The ratio's information suggests that PAHs might be derived from pyrogenic sources. The Flt/(Flt+Pyr) ratios were mostly greater than 0.5 with a mean value of 0.47 ± 0.37, except for 0 values observed at locations OS4, OL1 and OB4, thereby revealing the vegetation and coal combustion processes as the most important sources of PAHs in the Imiringi river, this is closely followed by the petroleum source. The observed prevalence of pyrogenic PAH sources in the various sampling station is an indication of vegetation and coal combustion flares and runoffs from seasonal bush burning activities along the river shoreline. Also, petroleum sources may have emanated from the redistribution of spilled crude from oil installations that are located further upstream of the river.

Similarly, BaA/(BaA+Chr) ratios revealed the prevalence of coal, grass and wood combustion sources, followed by petroleum combustion, most likely resulting from gas flare particulates released from starks of neighbouring oil fields or nearby oil bunkering sites. On the other hand, Flt/(Flt+Pyr) ratios in all the studied locations showed the prevalence of biomass and coal combustion, after which petroleum source and petroleum combustion inputs subsequently occurred (Fig. 2). In addition, the Flr/(Flr+Pyr) ratio was only recorded for station AG1, reflecting petroleum combustion inputs as the most important source of PAHs (Fig. 3). Surrounding waste dumpsites of an effluent receiving river in South Lebanon were reportedly responsible for the presence of petrogenic and pyrogenic PAHs [9]. The authors had deemed the water unsafe for irrigation and public consumption. Furthermore, observations from this study are partially consistent with petroleum

sourced PAHs that are dispersed from oil spills during ship refuelling [37]. However, the petroleum source and petroleum combustion inputs from this study though present, depicted comparatively lesser spread when compared to the PAHs from pyrogenic sources.
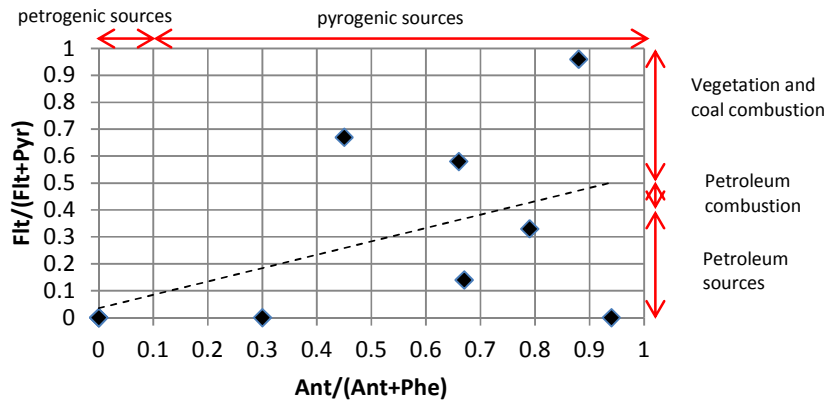

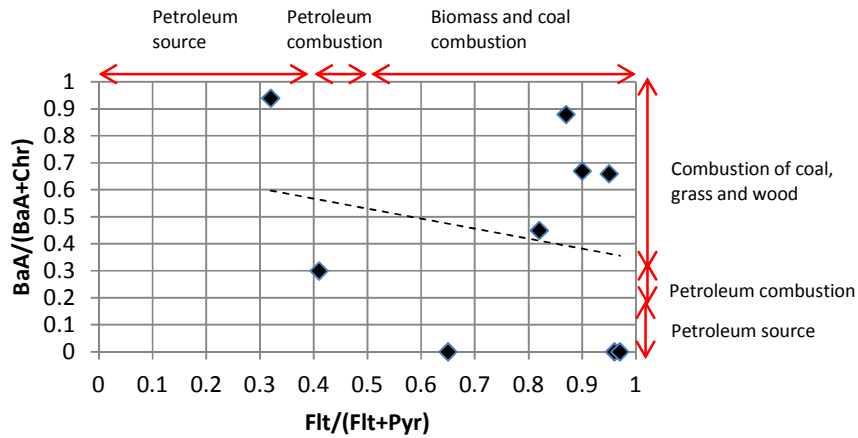**Fig. 1. Scatterplot of Flt/(Flt+Pyr) versus Ant/(Ant+Phe)**

Fig. 2. Scatterplot of BaA/(BaA+Chr) versus Flt/(Flt+Pyr) in Imiringi water
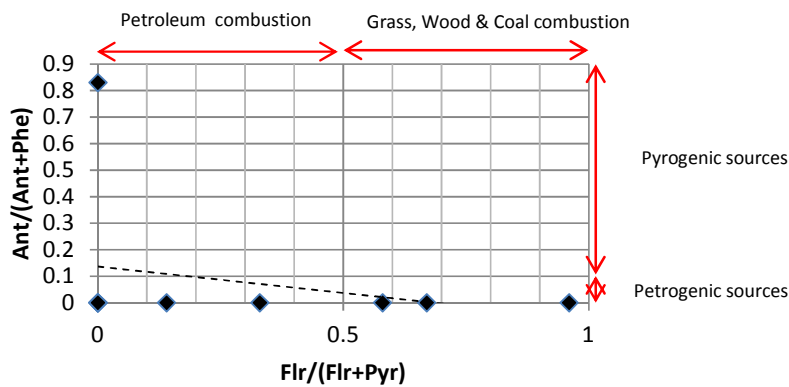

Fig. 3. Scatterplot of Ant/(Ant+Phe) versus Flr/(Flr+Pyr) in Imiringi water

Table 3. Characteristics and distribution of PAHs in Imiringi surface water

PAH components	Unit	No. of rings	Carcinogenicity (USEPA, 2011)	OS1	OS2	OS3	OS4	OL1	OL2	OB1	OB2	AG1	AG2	USEPA (USEPA, 2002)	EC (EC, 1998)	WHO (WHO, 2003)	DPR (DPR, 2018)
Nap	µg/L	2	0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	0.02
Acy	µg/L	3	0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	-
Ace	µg/L	3	0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	-
Flr	µg/L	3	0	ND	ND	ND	ND	ND	ND	ND	ND	18.5	ND	0.2 (MCL)	-	-	-
Phe	µg/L	3	0	0.7	2.2	9.9	ND	ND	ND	ND	2.0	ND	5.9	0.2 (MCL)	-	-	0.005
Ant	µg/L	3	0	1.4	3.1	1.6	300.1	ND	ND	ND	44.4	2.2	2.9	0.2 (MCL)	-	-	0.02
Flt	µg/L	4	0	0.5	10.5	12.4	ND	ND	7.0	ND	34.3	55.7	10.9	-	0.03	-	0.005
Pyr	µg/L	4	0	0.6	5.5	6.0	1.6	12.3	16.0	5.3	4.9	3.7	2.9	0.2 (MCL)	-	-	-
BaA	µg/L	4	++	4.2	10.9	6.3	10.9	109.0	4.5	9.4	27.7	1.6	9.9	0.2 (MCL)	-	-	-
Chr	µg/L	4	++	0.9	0.6	0.7	0.4	3.3	6.5	5.0	4.3	3.4	1.7	0.2 (MCL)	-	-	-
BbF	µg/L	5	++	50.1	8.9	92.7	13.3	3.8	17.0	7.3	16.2	19.6	8.5	0.2 (MCL)	0.03	-	-
BkF	µg/L	5	++	0.8	2.5	13.2	1.5	2.4	11.0	0.7	6.3	4.7	5.0	0.2 (MCL)	0.03	-	-
IndP	µg/L	6	+++	4.2	5.7	15.9	2.7	4.1	13.5	16.8	29.7	9.9	16.1	0.2 (MCL)	0.03	-	-
DahA	µg/L	5	+++	20.7	55.6	42.1	89.4	286.3	169.5	78.3	114.7	135.7	45.2	0.2 (MCL)	-	-	-
Total PAHs	µg/L	NA	NA	84.1	105.5	200.8	122.1	421.2	245.0	122.8	284.5	255.0	109.0	2.0 (MCL)	0.12	0.05	0.1

MCL = Maximum Contaminant Level; USEPA = United States Environmental Protection Agency; EC = European Communities; WHO = World Health Organization; DPR = Department of Petroleum Resources; ND = Not Detected; NA = Not Applicable; 0 = Not carcinogenic; ++, +++ = strongly carcinogenic

3.1.2 Mutual dependence and independence among locations and distribution of PAH species in surface water

Correlation cluster analysis was applied in the identification of variables (sample location and PAH species distribution) of close affinities within the study location. PAH species of common relationship depicted homogeneity in species prevalence while those of independent relationship reflected diverging distribution in the water system. Test PAH components showed strong similarities between the following groups of PAH compounds: (Pyr and Chr), (BaA and DahA), (Ant, Ace, Acy and Nap), (Phe and BbF), (Flr and Flt) and (BkF and IndP). The strongest dissimilarity existed between (Pyr and Flt) (Fig. 4). Similarities can be attributed to homogeneity in sources releasing these PAHs. On the other hand, the distinction between Pyr and Flt is indication that activities releasing these compounds are heterogenous in nature. In addition, strongest spatial similarities were observed for (OL2 and OB1) and (OS1 and

OS3), with OL1 showing the strongest disassociation with OS4 (Fig. 5). The observed spatial distinction of the upstream stations may have resulted from the reasonable levels of low molecular weight PAHs (LPAHs) such as "Phe" and "Ant" (Table 3). Overall, the midstream section of the river at OL1 appears to be most contaminated with a cumulative PAH concentration of 421.2 µg/L (Table 3). Observation from this study is partially consistent with the findings of Borja et al. [9]. In their work, PAH sources were reported to emanate from a combination of petrogenic and pyrogenic wastes. Furthermore, Ant, Ace and Acy showed strong similarities as they were below detection limit during the dry season.

3.1.3 Identification of principal PAH components in Imiringi surface water

PCA revealed all ten locations examined were discretely located with closest similarity between two clusters: (OS1 – OS3, OL2, OB1) and (AG1 and AG2), while the most dissimilarity was
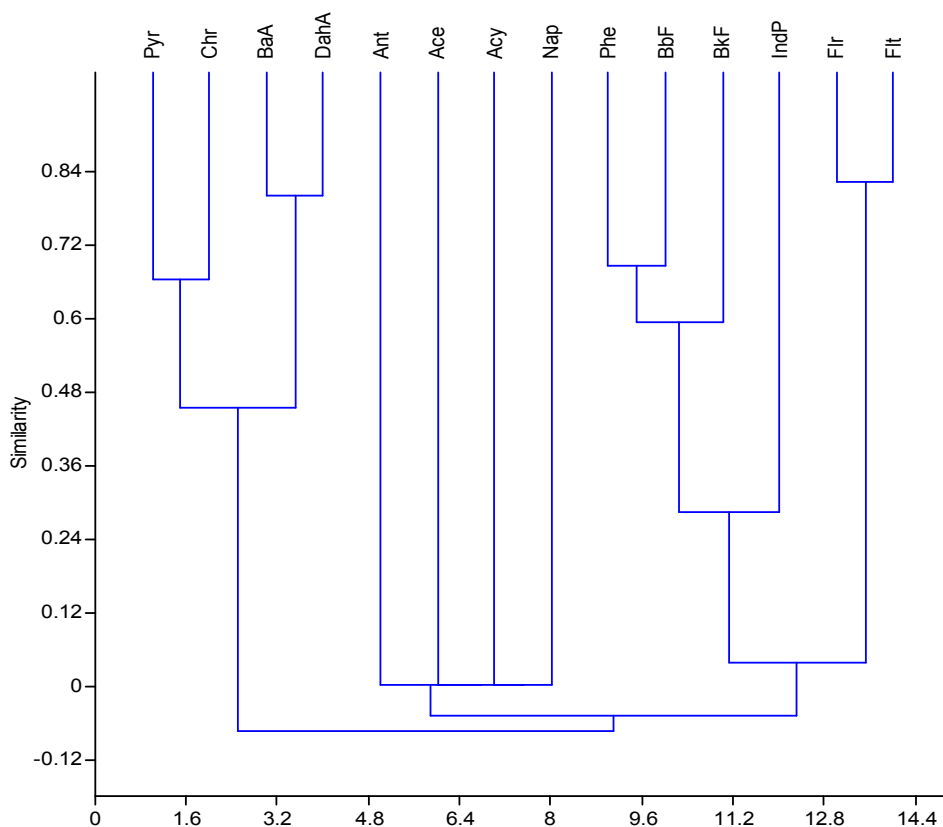

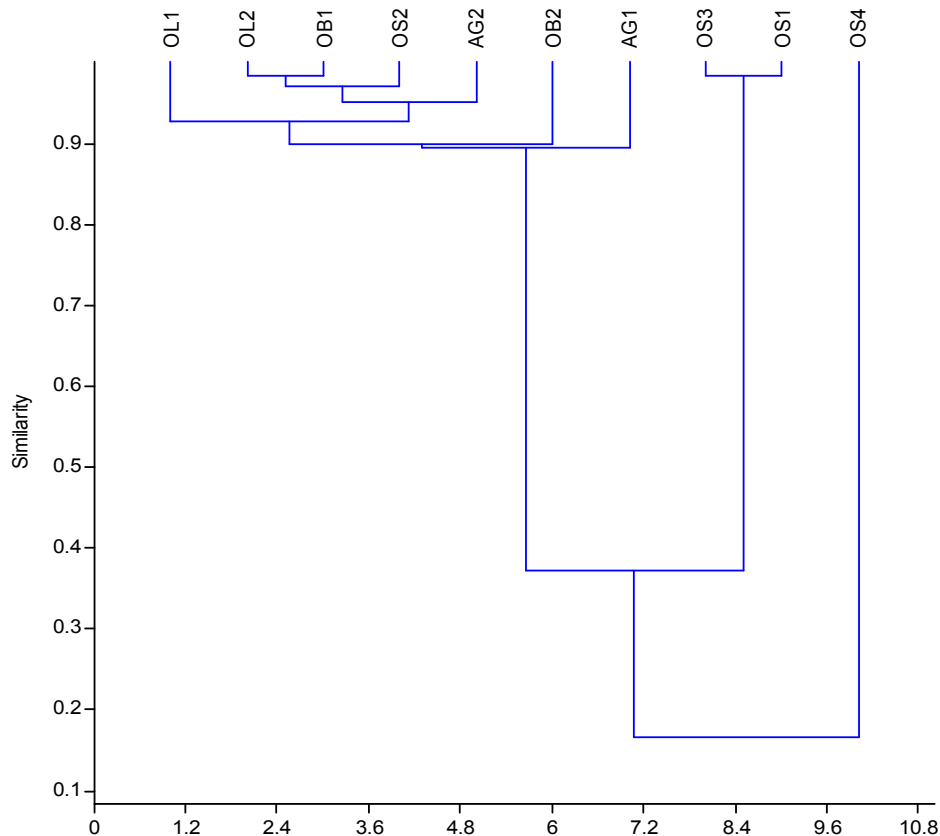**Fig. 4. Correlation cluster analysis of PAH components in water**

Fig. 5. Correlation cluster analysis of water sampling locations

observed for stations OL1, OB2 and OS4. The relatively higher concentrations of Anthracene (Ant) in OS4, Indeno(1,2,3-cd)pyrene (IndP) in OB2 and Dibenz(a,h)anthracene (DahA) in OL1 were responsible for the spatial delineation in the PCA result. The elevated level of LPAH (Ant) at upstream station OS4 can be attributed to the activities of illegal oil bunkers, and oil installations located further upstream of OS community, while the spike in HPAHs (IndP and DahA) at OB2 (downstream) and OL1 (midstream) may have stemmed from the open incineration of biomass from waste dumpsites and vegetation from farmlands located in fragments along this section of the river. On the other hand, "Ant" and "DahA" were distinguished from the 14 PAHs studied because of the spike in their cumulative concentration. However, the comparatively greater concentration of DahA accounted for its isolation from Ant (Fig. 6).

The box plot was used to show trends in the mean concentrations of test PAH compounds across different locations. The observations revealed "Nap", "Acy" and "Ace" at concentrations below detection limit, while "Flr" showed an outlier concentration (<40 µg/L). Even though "Ant" showed the highest outlier concentration between 280 and 320 µg/L, majority of its concentration were within the same range as compounds such as "Flr", "Phe", "Flt", "Pyr", "Chr", "BkF" and "IndP" (<80 µg/L). "BaA" and "BbF" showed outlier concentrations ranging between 40 and 80 µg/L, but with more consistency at the upper concentrations. Even though "DahA" showed the least consistency and most variability in distribution within the different locations of the Imiringi water body, it still represented the component with the highest 25% distribution than nearly all other PAHs in the river, thereby showing the greatest consistency at its upper concentration levels. Similar upper level concentrations reflected consistency for "Flt", "BaA", "BbF" and "DahA" (Fig. 7).
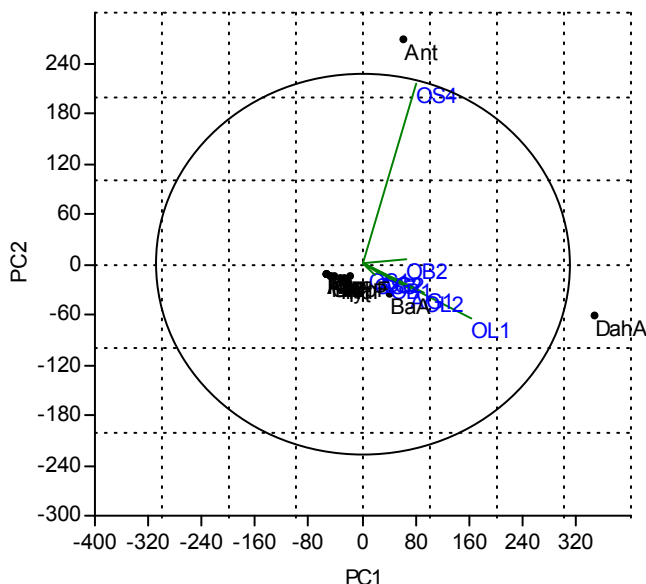
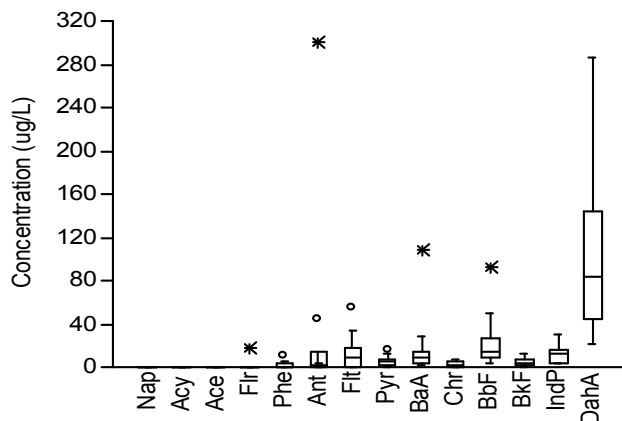**Fig. 6. Principal component analysis (PCA) of PAHs and locations in Imiringi water**

Fig. 7. Box plot of PAH components in water

4. CONCLUSION

PAHs in the Imiringi water environment revealed a combination of petrogenic and pyrogenic sources, with pyrogenic (combustion sources) being the most impacting activity. The loss of reasonable LPAHs may have been due to the effect of photolysis and increased tidal movement of water during the rainy sampling period, hence, the occasional presence of some petrogenic LPAHs at midstream and downstream stations may have resulted from increased water-mixing and redistribution from areas of active petroleum mining. On the other hand, the predominance of carcinogenic and environmentally persistent HPAH fractions in the environment is a source of concern because of its associated public health risks. Generally, the cumulative PAH concentration in all sampling stations exceeded the USEPA, EC, WHO and USEPA regulatory limits of 2.0 µg/L, 0.12 µg/L, 0.05 µg/L, and 0.1 µg/L for drinking water respectively, thereby, potentially exposing recreational users to dermal ingestion, especially the locals who bath and swim in it. Overall, owing to the increasing vulnerability of coastlines to organic micro-pollutants from waste dumps, a waste collection system should be reconstituted by the relevant waste management authorities, while legislation and infringement fines must be

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considered as a deterrent measure for defaulters. Similarly, improved coastal surveillance by the government and stakeholders will limit the incidence of accidental oil spill from faulty underwater pipelines, as well as dissuade illegal oil bunkers. Additional caution should be exercised while consuming seafood from the river in order to avoid the effect of bio-magnification of persistent organic pollutants across the food chain.

DISCLAIMER

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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