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SOURCE APPORTIONMENT AND DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN IMO RIVER SEDIMENTS NEAR AFAM POWER STATION, S.E. NIGERIA: MOLECULAR INDEX AND MULTI-VARIATE APPROACHES

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ABSTRACT

Surface sediments from Imo River near Afam Power Station were analysed for quantitative determination of polycyclic aromatic hydrocarbons (PAHs) using gas chromatography-mass spectrometry (GC-MS). The total PAH concentrations (excluding perylene) were in the range 1.60 – 67.70 ng/g dry weight (dw).The degree of anthropogenic impacts were considered relatively low when compared to other urban Asian / American coastal sedimentary environments. PAH compositions were dominated by 3 – and 4 – ring types with phenanthrene, anthracene, fluoranthene and pyrene being the dominant species. Relatively high levels of PAHs were found in sediments near the fish settlement while minimum amounts were observed for the remote upstream location. Utilization of five selected PAH molecular ratios such as Fluoranthene/(Fluoranthene + Pyrene) (0.3- 0.5), Anthracene/(Anthracene +Phenanthrene) (0.19 – 1.19), Benzo(a)Anthracene/(Benzo(a)Anthracene+ chrysene) (0.35 – 1.0), Low molecular weight PAHs/High molecular weight PAHs (0.20 – 1.10) and 1,7/(1,7 +2,6 – Dimethylphenanthrene) (0.34 – 0.84) enabled apportionment of sample to source to be made with an observed mixed source dominance scenario. The complication in the molecular ratios may be associated with short/long range transport weathering, and differences in microbial or photo-degradation effects. Cluster analysis employed classified the study area into specific regions and distinguished two main cluster groups with great dissimilarity that are site and source specific. Factor analysis showed that four factors (sources) accounted for 85.1% of total variability.

KEYWORDS: PAHs, source, distribution, molecular ratios and multivariate analysis.

1.0 INTRODUCTION

Contamination of coastal sediments has been identified as a significant health and ecological concern within the past four decades. Prior to the present day, contaminants were routinely discharged into coastal waters. Subsequently, the clean water act placed significant restrictions on the type and amount of waste materials that could be discharged into waste water. However, continuous releases from historically contaminated sites (e.g. Afam power Station), as well as current non-point sources continue to exacerbate the contaminated state of coastal waters (Walker and Dickhut, 2001; Walker *et al*., 2005). Fossil fuel combustion, waste incineration, coal gasification and liquification processes, petroleum cracking and the production of coke, carbon black, coal tar, pitch, and asphalt have been identified as important anthropogenic sources of polycyclic aromatic hydrocarbons (PAHs) in the aquatic environment (McVeety and Hites, 1988) but they can also be released via industrial wastewater, sewage, road runoff and street dust. They are also present in petroleum entering the marine environment through oil spills and ship traffic (McVeety and Hites 1988; Dickhut *et al.,* 2003).

PAHs can be classified into three general categories: petrogenic-derived from slow maturation of organic matter under geothermal gradient conditions; pyrogenic-derived from incomplete combustion of recent (e.g., biomass burning) and fossil (e.g., coal) organic matter; and short term diagenetic products derived from biogenic precursors (Baumard *et al.,* 1998; Soclo *et al*., 2000). However, recent reports by Wilcke *et al*., (2003) and Krauss *et al*., (2005) showed evidence of biological production and/or selective accumulation of PAHs such as naphthalene and perylene in termite nests from different climatic zones.

Techniques used to differentiate pyrogenic and petrogenic sources of PAHs include examining the relative amounts of low molecular weight (LMW) and high molecular weight (HMW) compounds. LMW PAHs compounds predominate in petrogenic sources while HMW compounds predominate in pyrogenic sources (Soclo *et al.,* 2000). Additionally, source discriminant molecular indices have also been developed based on thermodynamic considerations and empirical observations (Baumard et al., 1998; Dickhut *et al*., 2003; Yunker and Mcdonald, 2003; Walker *et al.,* 2005). Generally, two major methods have been used to analyze PAH sources: qualitative and quantitative methods (Rogge *et al*., 1998; Yunker *et al*., 2002). The qualitative method is mostly based on characteristic

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parameter ratio of PAHs. Quantitative method often uses mathematical statistics for source identification e.g, multivariate statistics (Zhihuan et al., 2006). In this present study, multiproxy and multivariate approaches were used for source characterization as well as for the classification of the study area into specific regions with defined characteristics. To the best of our knowledge, this is the first time multivariate statistical tool is used for purposes of source apportionment within the sub-saharan tropical coastal environment. Fluxes of PAHs have been increasing within the past decades with their attendant health risk (Van Metre *et al*., 2000; Schneider *et al.,* 2001; Lima *et al*., 2003; Walker *et al*., 2005; Aichner *et al.,* 2007; Scholz-Bottcher *et al*., 2009), necessitating the identification of the sources of these compounds in the present study. As PAHs released in the study area may be globally distributed, knowledge of PAH sources in this tropical environment is a prerequisite for understanding the global PAH dynamics.

The Imo River has an excellent productive bank rich in fish and other edible organisms. The future of this coastal environment depends on the care and effort spent on its environmental protection. Among the Niger Delta River network, the Imo River was chosen as a model for environmental pollution studies because the river receives organic pollutants from diverse sources. It is hoped that this study will provide baseline data for the preservation of the area under study and will form the basis for future legislation.

1.1 Study Area

Imo River is one of the tributaries of the south Eastern Rivers (Fig. 1). It originates from the hill region of Imo and Anambra States and flows through several towns, villages and farmlands, it empties its water directly into the Bight of Bonny through a bar-built tidal estuary located on the high-energy coast. The study area is located on the South East of Rivers State of Nigeria and lies between latitude 4^{o} 55'N and longitude 7^{o} 1'E. The river has shallow depth ranging from 1.0 to 10.0 m at flood tide and about 8.0 m maximum at ebb tide. The study area belongs to the low-lying coastal deltaic plains of South Eastern Nigeria; the terrain is virtually flat or gently undulating, sloping generally towards the Atlantic (Ezeayim and Okereke, 1996).

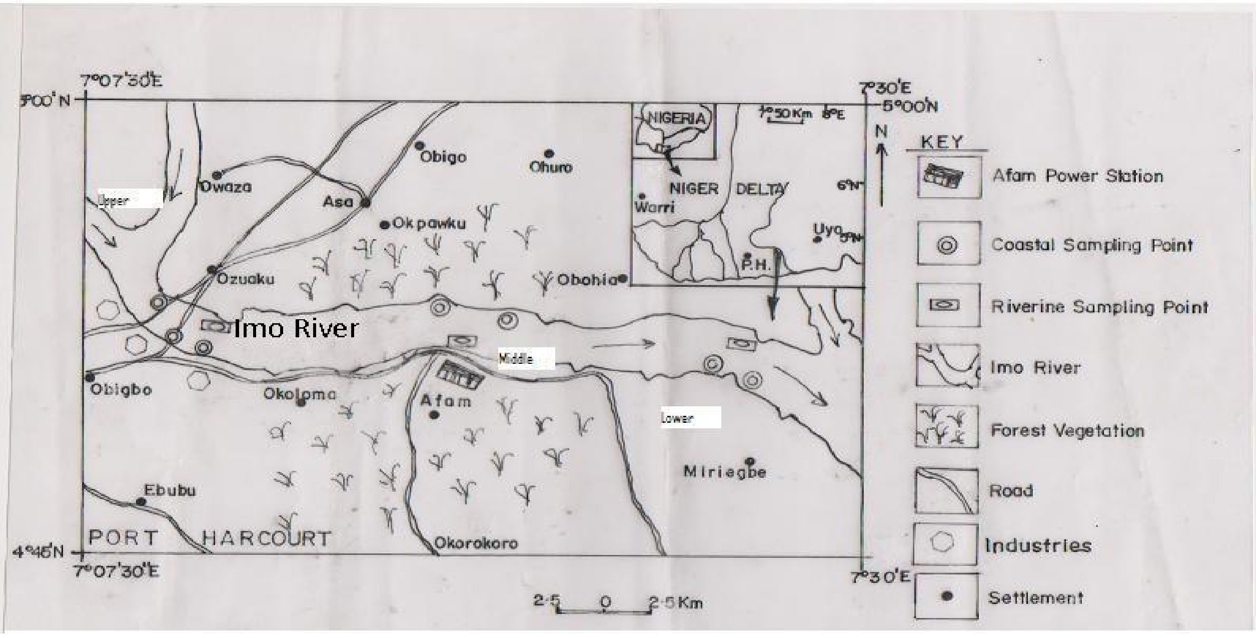
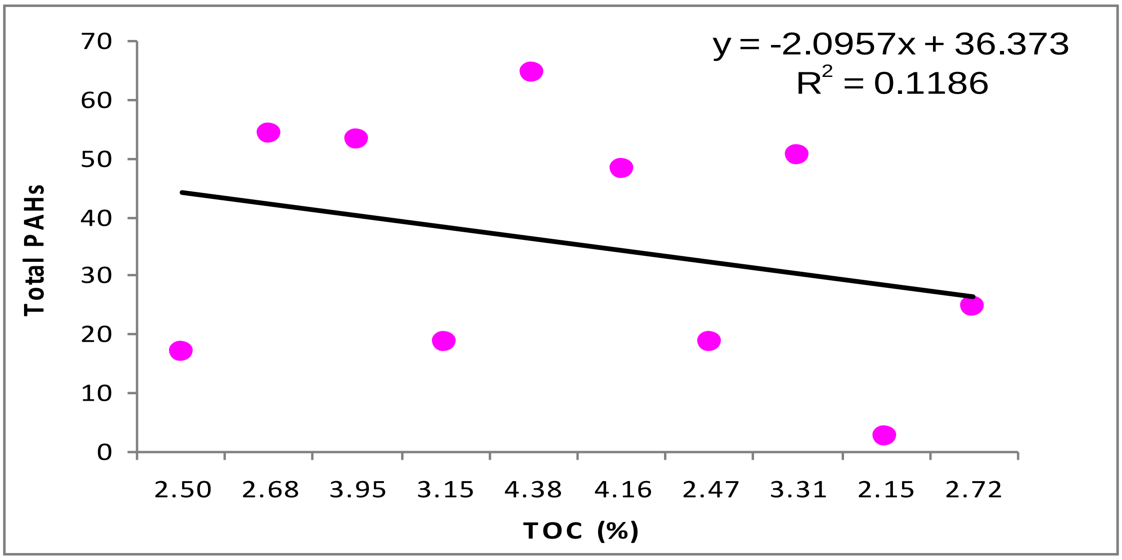


Fig. 1: Location of the sampling points on map of the study area.



The coastal rainfall patterns described by Adefolalu (1981) reveal this region as having rainfall throughout the year with the highest rainfall between the months of April and September. A combination of heavy rains and good sunshine coupled with adequate soil nutrients have generated thick vegetation cover in the study area. The vegetation is made up of mangrove swamp forest, tall evergreen trees including pines with prolific undergrowth of entangled shrubs. The main occupations of the native inhabitants of the area are farming (wood burning for agricultural and domestic purposes is the common practice) and fishing. However, there are few industries aligned near the Imo River bank of which the Afam Power generating station is one. Geologically, the study area belongs to the south east part of the Tertiary sedimentary basin of southern Niger Delta (Ezeayim, and Okereke, 1996).

2.0 Experimental Methods

2.1 Materials

The following analytical grade solvents, dichloromethane (DCM), methanol (MeOH), hexane (C_6H_{14}), toluene (C_7H_8), as well as molecular sieves, potassium hydroxide (KOH), bistrimethylsilyltrifloroacetamide (BSTF) were purchased from Merck, Darmstad, Germany. Diazald® was provided by Sigma Aldrich Germany. Perdeuterated Polycyclic aromatic hydrocarbons (PAHs) used as internal standards and surrogates: [$^2H_2$]-benzo(a)anthracene, [$^2H_{10}$]-fluoranthene, [$^2H_{12}$]-benzo(ghi)perylene, [$^2H_{10}$]-pyrene and [$^2H_{12}$]-perylene were purchased from Cambridge Isotope Laboratories Andoyer, MA, USA and [$^2H_{10}$]-anthracene supplied by Dr. Ehrenstofer GmbH(Augsburg, Germany).

2.2 Samples Collection and Organic Carbon analysis

Prior to sediment sample collection, two potential point-source soil samples (PS1 and PS2) were obtained near natural gas combustion turbine and petroleum condensate spills respectively within the Afam power station premises. A total of eight other sediment samples were collected from the Imo River using a Van-Veen grab sampler. In order to ensure homogeneity in grain size of samples collected, each sediment sample was a composite of three samples from different assessment points.

The sampling stations were divided into three zones (I, II and III). Sediment samples from zone I (IR1 and IR2) were collected near Afam Power Station; zone II sediment samples were collected at the other bank of the river near the fish settlement (IR3 and IR4); while sediment samples from zone III were obtained downstream about 3.5Km from Afam Power Station near the residential area (IR5, IR6 and IR7). One remote upstream sediment sample (IR8) was also collected about 5Km northward from Afam Power Station in order to have insight into the background contamination levels. Organic carbon was determined by the dichromate wet oxidation method (Nelson and Sommers, 1996).

2.3 PAHs Analysis

Extraction of 1g of sample in a test tube was performed sequentially by sonication with DCM/MeOH (2:1) and DCM in triplicate. The extracts were hydrolysed overnight at room temperature in a 10% w/v solution of KOH in MeOH. Extraction with hexane yielded a fraction enriched in neutral compounds. After lowering the pH to 2, the acid fraction was extracted with acetone. Hydroxy containing neutral compounds were converted to trimethylsilyl ethers with N,O-Bis(trimethylsilyl)Trifluoroacetamide (BSTFA) and the fatty acid fraction treated with diazomethane distilled from diazald according to standard procedure (Albaiges *et al,* 2006).

2.4 GC-MS Analysis

Identification and quantification of lipids was done by GC-MS on a Trace GC-MS (THERMO instruments, Manchester, UK). A 60m capillary column coated with 5% phenyl-95% methyl-polysiloxane (0.25mm internal diameter (id) and 0.25μm film thickness; HP-5, Hewlett-Packard, CA, USA) was used. The carrier gas was helium at a flow of 2.1ml/ min. Injection port and transfer line temperatures were 300°C. Samples in toluene were injected in splitless mode. The oven temperature programs used, started at 90°C/min., raised to 150°C/min. and then at 4°C/min. to 320°C and a final holding time of 30min. The quadrupole mass spectrometer was operated in EI mode (70eV), with an ion source temperature of 200°C and scanning from 50 to 700 m/z in one second. For polycyclic aromatic compounds (PAHs), selected ion monitoring (SIM) of the molecular ions of each analyte and the deuterated internal standards were recorded using retention time windows.

Calibration curve (detector response versus amounts injected) were performed for each compound to be quantified. The range of linearity of the detector was evaluated from the curve generated by plotting detector signal/amounts injected versus amount injected. All measurements were performed in the ranges of linearity found for each compound. In a few cases the samples were re-diluted and re-injected to fit within the linear range of the instrument. The quantitative data were corrected for surrogate recovery; recoveries ranged from 70% to 110 %(average 85%). Procedural blanks were lower than 5ng/g, the limit of detection (LOD) in the full scan mode ranged from 0.004 to 0.013 ng/g dw. The analytical procedure was validated with the IAEA-417 reference material obtaining accuracy from 75% to 107% compared with the certified value.

3.0 RESULT AND DISCUSSION

3.1 Relationship between total PAH levels, organic carbon contents and sediment grain size distribution

Bulk properties such as sediment grain size distribution, soluble organic matter (SOM), and total organic carbon (TOC) are presented in Table 1. The surface sediments covering the study area are mostly composed of terrigenic materials which consist of admixture of sand, silt and clay, probably due to its sheltered basin morphology and apparent high energy current conditions. The Imo River stretch covered in this study is characterised by a high percentage of sand fraction (Table 1). Average percentage sand in the sediments was rather high at stations near the residential area and remote upstream location where they were 89.3% and 90.2%, respectively. Potential point source and those sediment samples collected near Afam Power Station had mean percentage sand of 63.9% and 57.8%, respectively.

Table 1: Sediment sample locations, particle size distribution, geochemical properties and characteristic features of the environment.

Zone	Sample code	Coordinate	SOM (mg/kg)	TOC (%)	TPAH (ng/g)	Nature of environment	Particle size (%)		
							Clay	Silt	Sand
Point-source	PS1	04°58’N 07°13’E	2150	2.50	11.54	Power station	15.1	6.0	68.9
	PS2	04°59’N 07°14’E	1150	2.68	46.93		19.2	22.0	58.9
I	IR1	04°59’N 07°15’E	2850	3.95	36.16	Near power station	20.2	28.0	51.8
I	IR2	04°59’N 07°15’E	3000	3.15	13.85		21.2	26.0	63.8
II	IR3	04°59’N 07°19’E	2950	4.38	60.10	Near fish settlement	23.6	28.4	48.0
II	IR4	04°59’N 07°18’E	1700	4.16	42.70		22.8	30.0	47.2
III	IR5	04°50’N 07°14’E	2250	2.47	10.10	Near residential area	3.1	6.8	90.0
III	IR6	04°51’N 07°13’E	406	3.31	13.82		4.6	9.0	86.8
III	IR7	04°51’N 07°14’E	556	2.27	18.47		4.0	4.8	91.2
Upstream	IR8	05°11’N 07°20’E	200	2.16	1.53	Remote	5.4	4.4	90.2

PAH levels may be influenced by physical sediment factors as well as proximity to source. The organic carbon content of 2.15% - 4.38% observed for the sediments are typical of coastal environments (Unlu and Alpa, 2006; Albaiges et al., 2006). No significant correlation ($r^2 = 0.12$; $p<0.01$) was found between total PAH concentrations and organic carbon contents beyond a slight positive relationship that confirms the presence of elevated total PAH levels in sediments with high levels of TOC (eg. stations IR8 and IR3 with low and high TOC contents exhibited low and high total PAH concentrations, respectively; Table 1). Probably the production of varied benthic microfauna in the lower River (not the upper River) contributed high amounts to the organic carbon level in the coastal sediment samples, masking any relationship which may exist between total PAH and organic carbon contents (Ghosh *et al.,* 2000; Unlu and Alpa, 2006). In support of this assertion, Dublin-Green (1990) showed that A*renaceous foraminiferal fauna* strongly dominated the total living fauna assemblages of the Bonny estuary which is the southern/lower extension of the Imo River. In general, sediments with more clay percentage and higher TOC content have higher total PAH contents than sandy sediments with low TOC.

3.2 PAH contents

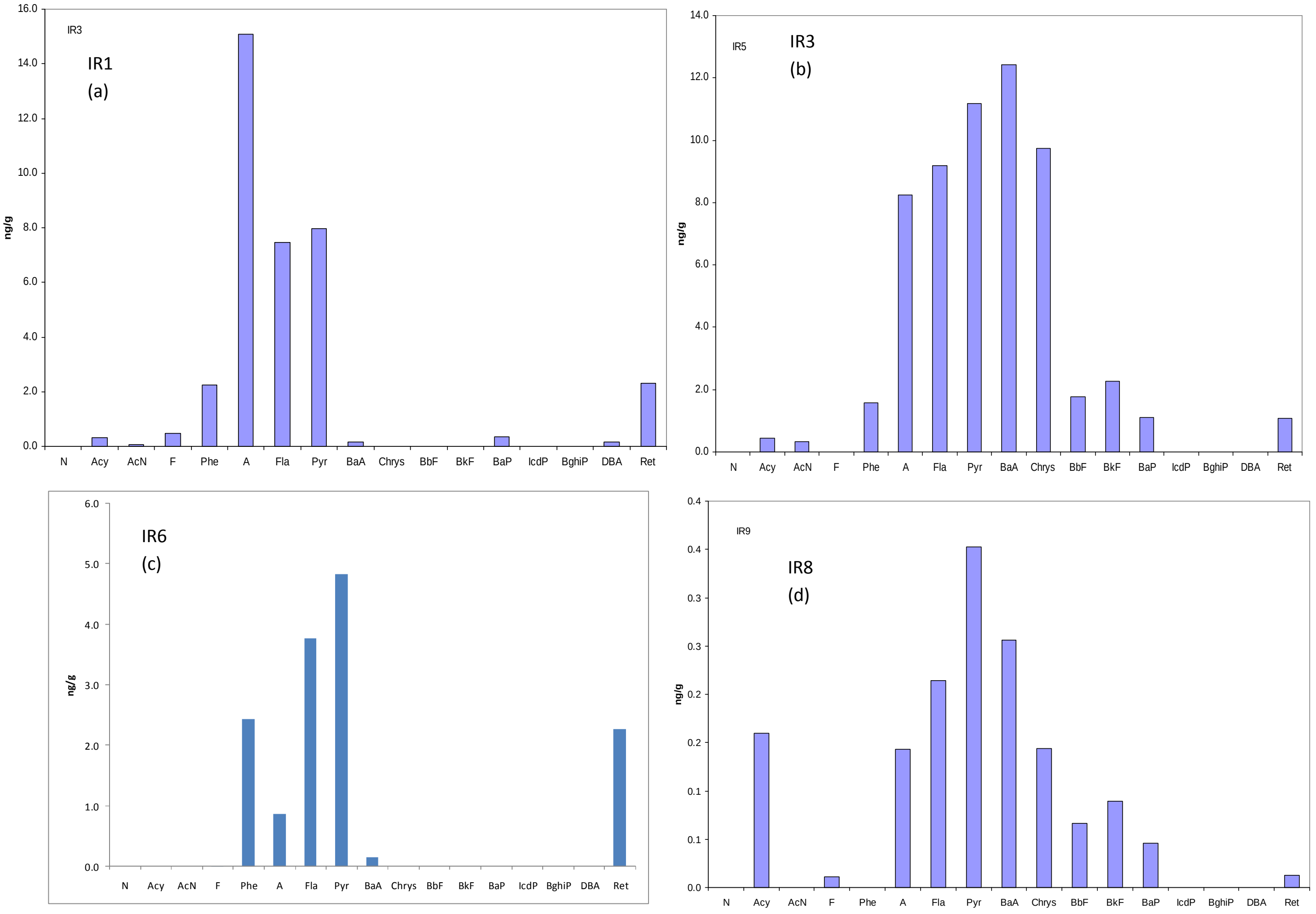
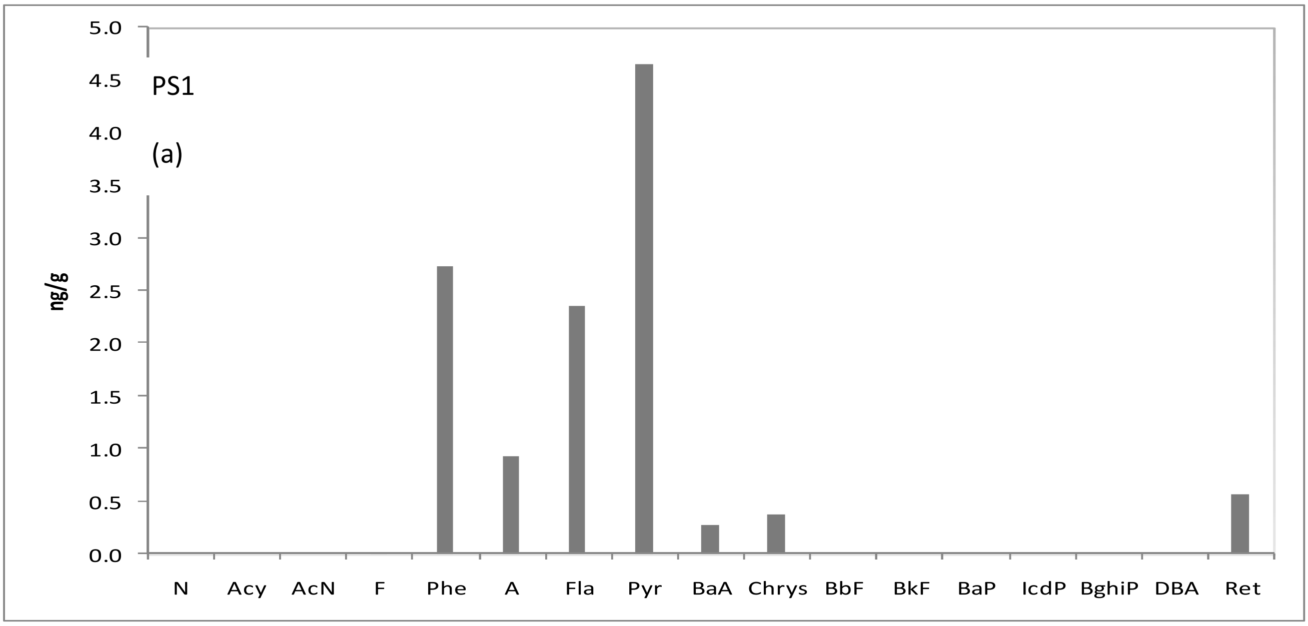


Fig. 2a, b, c and d: PAH contents in sediment samples collected near (a) Afam power station, (b) fish settlement (c) residential area and (d) remote upstream location.

Of the 16 USEPA listed priority PAHs, fourteen were detected in sediment samples from Imo River (Fig. 2a-d) and eight were found to be present in the potential point-source samples (PS$_1$ and PS$_2$)(Fig.3a and b). These PAHs include acenapthylene (Acy), acenapthene (AcN), fluorene (F), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chrys), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene, indene(1,2,3-cd)pyrene (IcdP) and dibenzo(a,h)anthracene (DBA). Other identified non-priority listed PAHs were perylene (Pery), retene (Ret), benzo(e)pyrene (BeP), dibenzothiophene (DBT), and isomeric naphto(1,2-b)thiophenes. Also identified in appreciable concentrations were various alkyl PAHs (isomeric alkylphenanthrenes) including 3-methylphenanthrene (3-MP), 2-methylphenanthrene (2-MP), 9/4-methylphenanthrene (9/4-MP), 1-methylphenanthrene (1-MP), 1-ethylphenanthrene (1-EP), 3,5-dimethylphenanthrene (3,5-DMP), 2,6-dimethylphenanthrene (2,6-DMP), 2,7-dimethylphenanthrene (2,7-DMP), 1,3-dimethylphenanthrene (1,3-DMP), 1,6-dimethylphenanthrene (1,6-DMP), 1,7-dimethylphenanthrene (1,7-DMP), 2,3-dimethylphenanthrene (2,3-DMP), 4,9-dimethylphenanthrene (4,9-DMP), 1,8-dimethylphenanthrene (1,8-DMP) and 9,10-dimethylphenanthrene (9,10-DMP).

In the entire samples under study naphthalene and its alkylated analogs were not detected. As a low molecular weight PAH, this compound is more volatile and remains in the atmosphere for a longer time, and is thus more susceptible to long distance transport compared to higher molecular weight PAHs. This phenomenon especially in a typical tropical environment as ours may be responsible for the non detection of naphthalene and its alkylated analogs as well as the low levels of acenapthylene and acenapthene (Baran and Oleszczuk, 2002). For the 3-ring PAHs, the concentrations ranged between 0.01 and 32.61ng/g dry weight (dw) (average 2.29 ± 6.17ng/g) maximizing in phenanthrene in the potential point source sample PS2 (Fig. 3b) while 4-ring PAHs had concentrations that ranged between 0.14 and 17.18ng/g dw (average 3.84 ± 4.0ng/g) maximizing in benzo(a)anthracene at station IR3(Fig. 2b) with a minimum value for chrysene at station IR8 (Fig.2d). Concentrations range of 0.05-9.73ng/g dw (average 1.50 ± 3.17ng/g) were detected for the 5-ring PAHs (excluding perylene) maximizing in benzo(k)fluoranthene at station IR3 (Fig. 2b) and minimizing in benzo(a)pyrene at station IR8 (Fig. 2d). PAHs with 6-ring nucleus was absent in all samples studied. Benzo(a)pyrene, the most carcinogenic PAH was detected only at stations IR3, IR4, IR7 and IR8.



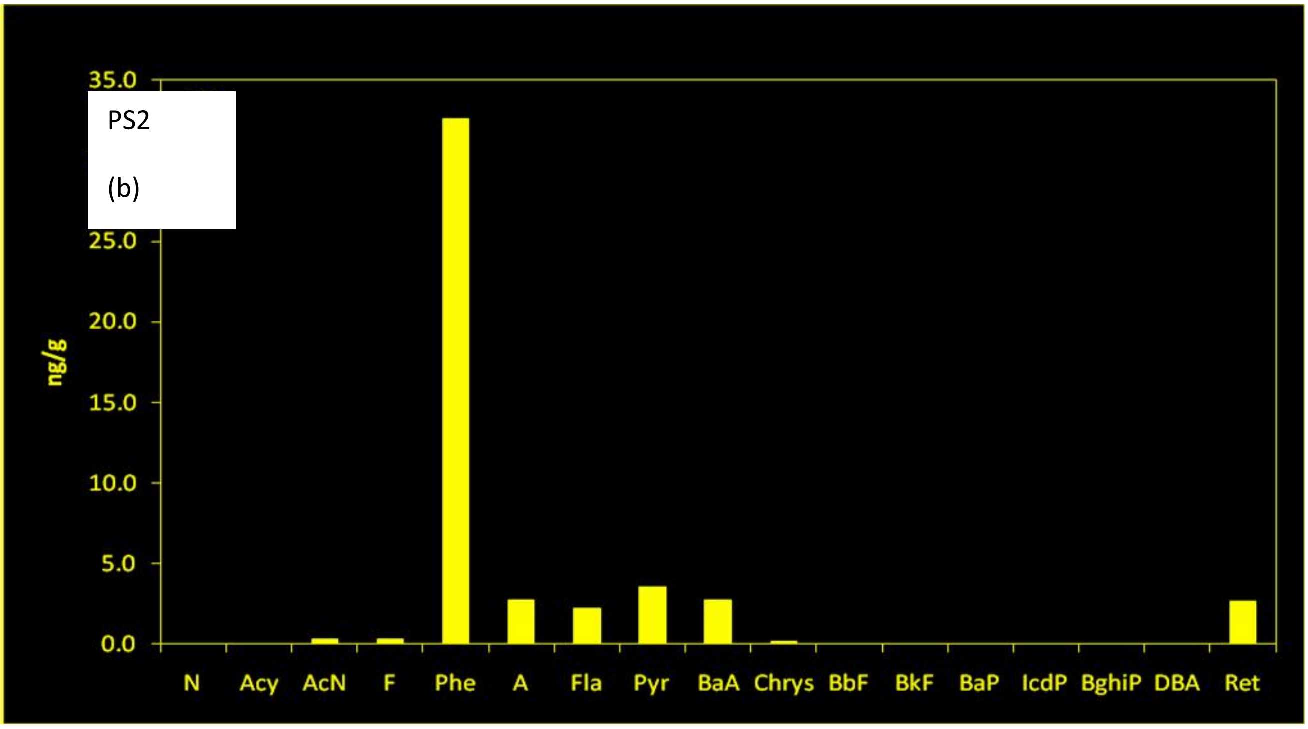


Fig. 3a, b: PAH contents for (a) potential point source near gas turbine and (b) potential point source near petroleum condensate spill.

Amongst the non-priority USEPA listed parent PAHs, perylene was found to have the highest concentration for both the potential point-source and sediment samples (1,601.72 and 391.3ng/g dw), respectively with lowest and highest values observed for potential point-source samples.

3.3 PAH source identification

A large number of parent and alkyl PAH have been used in interpreting PAH distribution and assessing their sources in sediments (Yunker *et al*., 2002; Yunker and McDonald, 2003; Wilcke *et al.,* 2003; Aichner *et al.,* 2007; Bechtel *et al.,* 2007). Based on our study, limited set of five PAH ratios were selected using parent, alkyl and PAH molecular masses that exhibited the best potential for interpreting PAHs' geochemistry.

3.3.1 Fla/Fla+Pyr

To assess combustion versus petroleum inputs, proportions of fluoranthene (Fla) to fluoranthene (Fla) plus pyrene (Pyr) ratio was used. Ratios of these PAHs have been proved to be more diagnostic of different PAHs formation processes than ratios of other commonly quantified parent PAHs (Yunker *et al*., 2002). Fla/(Fla + Pyr) ratios less than 0.40 usually indicate petroleum input such as crude oil, diesel, between 0.40 and 0.50 indicate liquid fossil fuel combustion such as vehicular exhaust emission. Ratios over 0.50 are attributed to grass, wood or coal combustion. In our case, Fla/Fla + Pyr ratios were in the range 0.30 – 0.50, clearly indicating a dominance of petroleum fuel influence at stations near the residential area (e.g. IR6 and IR7) as well as the upstream location (IR8) while other stations were mainly affected by pyrogenic influence (Table 2).

3.3.2 Ant/Ant + Phe and BaA/BaA + Chrys

Fla/Fla + Pyr ratio is supplemented by Ant/Ant + Phe and BaA/BaA + Chrys ratios (Yunker et. al. 2001). Ant/Ant + Phe ratio was developed on the basis that though phenanthrene and anthracene are structural isomers, phenanthrene is more thermodynamically stable compared to anthracene (Doong and Lin, 2004). Thus Ant/Ant + Phe ratios <0.10 are usually taken as indicative of petroleum input while ratios>0.10 indicate combustion source input, although ratios >0.10 have been reported for shale oil and coal (Radke *et al.,* 1991). In our case, besides the potential point source sample PS2 with Ant/Ant + Phe value of 0.07 (supporting petroleum condensate component of the sample), the entire sediment sample had Ant/Ant + Phe values range of 0.19 – 1.19 with minimum values determined for stations near the residential area (suggesting dominant petroleum pollution) and higher values recorded for other stations (indicating mainly pyrogenic source input). A boundary plot of Ant/Ant + Phe versus Fla/Fla + Pyr used in this study supports the observed source apportionment (Fig 4a).

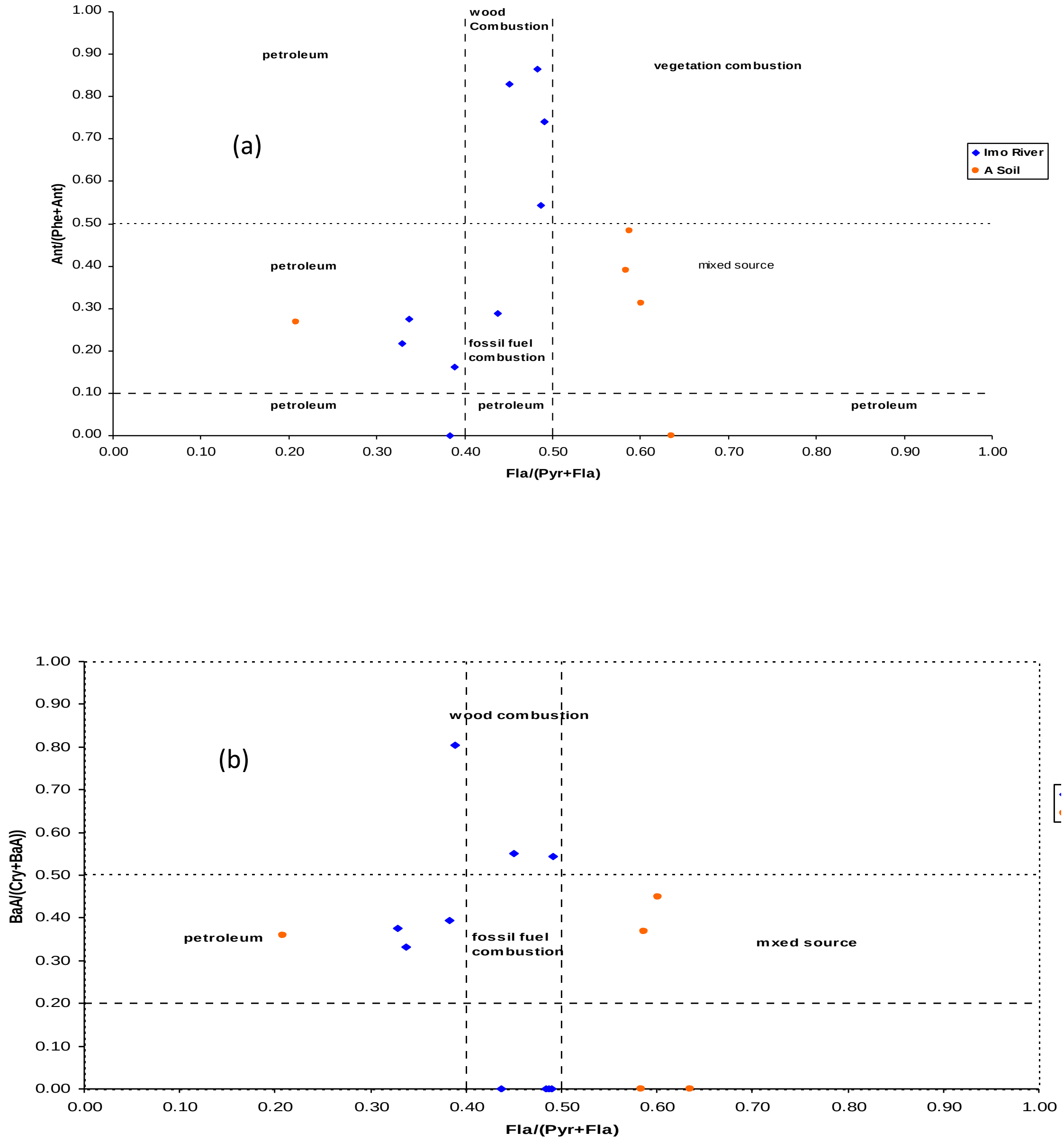


Fig. 4a & b: Boundary plots of (a) Ant/(Ant + Phe) versus Fla/(Fla + Pyr) and (b) BaA/(BaA + Chrys) versus Fla/(Fla + Pyr) ratios showing apportionments of PAH source to samples.

Similarly, according to Yunker *et al*., (2002), BaA/BaA + Chrys ratios < 0.20 imply petroleum source input; between 0.20 and 0.35 indicate either petroleum or fossil fuel combustion while ratios > 0.35 imply combustion (coal or biomass). In this study, sediment samples from all stations exhibited BaA/BaA + Chrys ratios>0.35 (Table 2) indicating that hydrocarbon derived from pyrolytic or combustion processes contributed dominantly to the PAH sources in the portion of the Imo river under study. A boundary plots of BaA/BaA + Chrys versus Fla/Fla + Pyr supporting apportionment of sediment samples to source is shown in Fig 4b.The complication observed for these molecular ratios suggests consequences of (i) a mixed source scenario of greater petrogenic and minor pyrogenic source input for stations near the residential area while stations near the fish settlement and Afam Power Stations were dominated by pyrogenic derived hydrocarbons with a minor petrogenic source input, (ii) short and/or long range transport weathering and (iii) differences in microbial/photo degradation effects (Doong and Lin, 2004; Walker *et al*, 2005).

3.3.3 LMW/HMW and 1,7/1,7 + 2,6 DMP

Ratio calculations are traditionally restricted to PAHs within a given molecular mass to minimise differences arising from volatility, water solubility, adsorption, etc. (McVeety and Hites, 1988). Despite variations in solubility in water among PAH isomers in most cases, mass ratios appear to reflect faithfully the source characteristic of PAHs, likely because only strongly bound refractory phase compounds, protected from dissolution or degradation remain after transport (McVeety and Hites, 1988).

Since an abundance of high molecular weight PAH (e.g 4-, 5- and 6-ring) species is typically a characteristic of pyrogenic origin while low molecular weight PAHs (e.g. 2- and 3-ring species) are more abundant in petroleum source, ratios of low molecular weight (LMW)/high molecular weight (HMW) were calculated to further distinguish petroleum from combustion source inputs. LMW/HMW ratios>1 indicate petroleum source while values<1 imply combustion source(Walker *et al*., 2005). Sediment samples in the present study show this ratio to range from 0.20 – 1.10 (Table 2). The LMW/HMW ratios for the potential point-source samples (PS1 and PS2) were 0.48 and 4.12, respectively. These support the inference that one of the point-source samples (PS1) contains PAHs mainly as a result of the combustion of natural gas, while the other (PS2) showed evidence of PAHs derived mainly from petroleum condensates. Among the sediment samples studied, sample IR1 (collected near Afam Power Station) exhibited characteristic LMW/HMW ratio of 1.10 somewhat similar to that of petroleum condensates. This probably is as a result of runoff and its proximity to the point-source. Others showed characteristics attributable to combustion sources with greater impact at stations IR3 and IR4 (near the fish settlement), probably due to additional input from wood/grass or coal combustion (Table 2).

Table 2: PAH source indices from Imo River Sediments and from potential point-source samples.

Parameter	PS1	PS2	IR1	IR2	IR3	IR4	IR5	IR6	IR7	IR8
Fla/Fla + Pyr	0.30	0.40	0.50	0.50	0.50	0.50	0.50	0.40	0.30	0.40
BaA/BaA + Chrys	0.42	0.93	1.0	1.0	0.56	0.35	1.0	1.0	0.46	0.64
Ant/Ant + Phe	0.25	0.70	0.87	0.54	0.83	0.74	0.75	0.26	0.19	1.19
LMW/HMW	0.48	4.12	1.10	0.52	0.20	0.32	0.98	0.80	0.33	0.26
1,7/(1,7+2,6)DMP	0.61	0.65	0.60	0.67	0.76	0.84	0.53	0.34	0.68	0.57

The molecular ratio 1,7/1,7 + 2, 6- DMP has been specifically used to characterise input from wood burning (Yunker and Mcdonald, 2003). 1,7/1,7 + 2,6-DMP > 0.70 indicates wood combustion, those less than 0.45 indicates vehicle exhaust emission while ratios between 0.45 and 0.7 may imply other combustion sources or the presence of shale oil or coal. In the samples studied, 1,7/1,7 + 2,6 – DMP ratio ranged between 0.34 – 0.84 with greater influence of wood burning emission input at the stations near fish settlement (>0.70) where the inhabitants of the settlement utilize pine wood for domestic cooking and agricultural purposes via tree logging (Table 2). Other stations exhibited 1,7/1,7 + 2,6-DMP ratios between 0.53 -0.68 typical of other combustion processes except IR6 (near the residential area) with a value 0.34 characteristic of vehicle exhaust emission, most likely as a result of runoff from street dust.

3.4 PAH distribution

Distribution of total PAHs (sum of parent and alkyl) among sampled stations is presented in Fig. 5a. PAH levels were higher in those samples collected near the fish settlement (IR3 and IR4) than those from the residential area (IR5, IR6, IR7) and are comparable to that of potential point-source sample, PS2. The highest concentration of total PAHs in sediments was found at station IR3 (67.70ng/g dw). This value was more than 50 order of magnitude higher than that measured at the remote upstream station (IR8). The high total PAH concentration detected at this station may be a result of additional input of atmospheric deposits arising from engine boat exhaust emission and wood/grass or coal burning processes. The measured TOC content at this station was 4.38% (Table 1) and is about twice higher than the TOC content measured at the relatively pristine upstream location (IR8). This shows that station IR3 is seriously polluted with micropollutants in relation to other stations.

According to Baumard *et al.* (1998), PAH levels can be classified as low, moderate, high and very high when ΣPAH (parent) levels are 0-100, 100-1000, 1000-5000 and >5000ng/g dw, respectively. According to these authors, PAH levels >1000ng/g dw correspond to chronically polluted industrialised areas and harbours. However, this parameter is questionable in areas where significant inputs from petroleum occurs since it does not take account of all alkylated homologue compounds derived from fossil sources (Unlu and Alpa, 2006). In our study, total PAHs (sum of parent and alkyl PAHs) were preferred due to the appreciable proportion of fossil PAHs detected. Perylene levels were not considered because it is generally believed that perylene is naturally produced biologically via a diagenetic process in sediments and its concentrations in the present study were considered outliers. On the basis of classification adopted by Baumard *et al*. (1998) and modified in our study, the levels of PAH pollution in the sediments from Imo River can be considered low especially in relation to other urban and industrialised Asian and American countries. For instance, levels exceeding 1000 ng/g dw have been reported in sediments from Elizabeth River (Walker and Dickhut 2001) and Prince Williams Sound, Alaska USA (Page *et al*., 1996). Although the levels of anthropogenic impact on sediment samples obtained for this study are not representative of the entire river, they could at least represent a major portion of the river as most of the upstream portion is remote except the lower portion where anthropogenic activities are expected to be high.

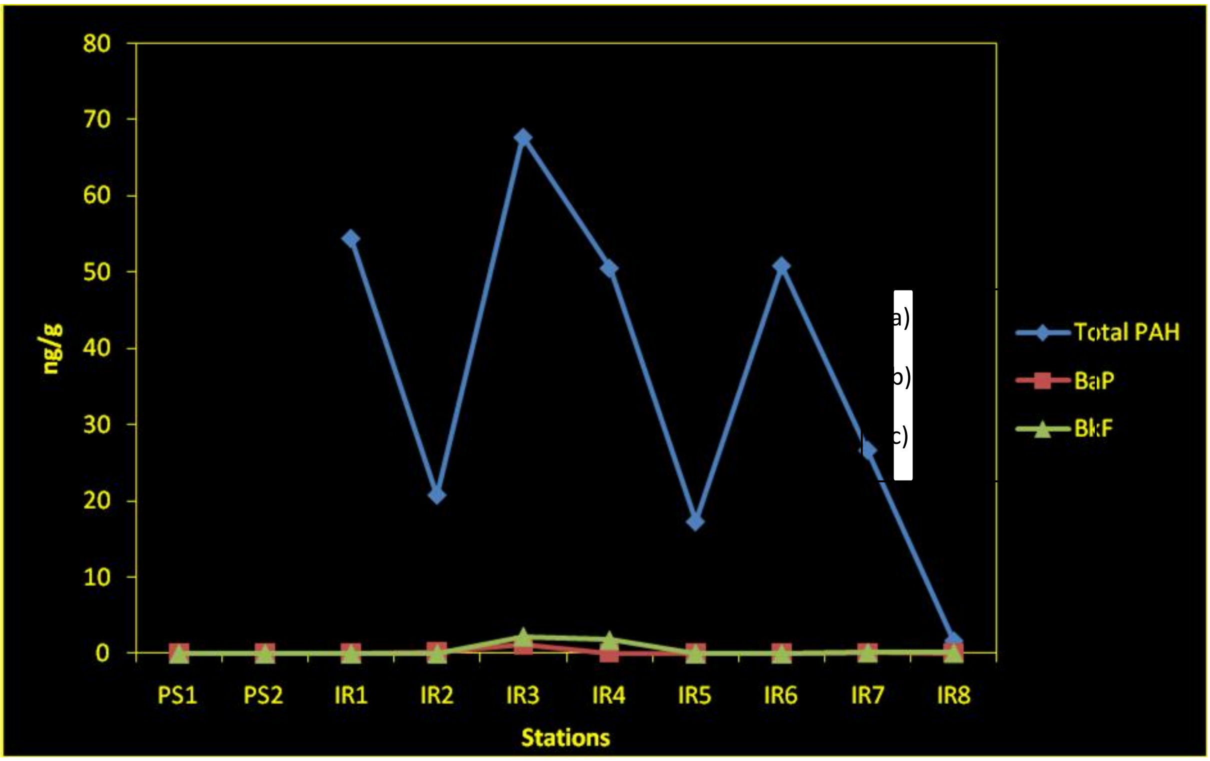


Fig.5a, b & c: Distribution of (a) Total PAHs, (b) Benzo(a)pyrene, and (c) Benzo(k)fluoranthene amongst sampling stations.

For the individual PAH concentrations in relation to those of potential point-source samples, evidence that natural gas combustion processes and petroleum condensates from Afam Power Station were not the only sources of PAHs to the area under study are observable in the distribution patterns shown in Figs. 5b and c. For instance, the absence of benzo(a)pyrene and benzo(b)fluoranthene in potential point-source samples including sediment samples collected near the Afam Power Station and their detection in other sediment samples support contribution from other sources. In addition to this source, retene is observed to be present in appreciable levels in all samples obtained for this study (e.g. Figs. 1a,b c and d). Retene has not been previously reported to be present either as a component of natural gas combustion or petroleum condensate. It is a typical compound emitted from brushwood and vegetable cover (Zhihuan *et al*., 2006). Pine trees are ubiquitous in the vicinity of the study area and burning of pinewood by the inhabitants of the fish settlement provides an effective and veritable source of fuel for domestic cooking. Major PAHs in pinewood smoke are retene, acenaphthene and benzo(a)anthracene (Rogge *et al*., 1998). Thus, burning of pinewood may be responsible for the prevalence of retene in all samples studied.

In order to assess the extent of petroleum pollution among the sampling stations, the distribution of the sum of methylphenanthrenes, and dibenzothiophene was evaluated. These PAHs were chosen on the premise that they are present in high levels in petroleum compared to combustion products.

Dibenzothiophenes are present in crude oil, coal and its products and coal combustion emissions (Oros and Simoneit, 2000) but are absent in wood and kerosene/fuel oil combustion products (Lee *et al*., 1997). Comparing Fig.6a and b, it can be seen that station IR6 was mostly influenced by petroleum residues as this station had the highest ∑methylphenanthrene and dibenzothiophene concentrations. Beyond this, the dissimilarity in the distribution patterns of Σmethylphenanthrenes and dibenzothiophene (Fig. 6a, b) among the stations suggests that petroleum might not have been the only source of these PAHs and that other source(s) such as coal combustion and coal products utilisation may be involved. In support of this deduction is a weak relationship observed between ∑methylphenanthrenes and dibenzothiophenes (r^2 =

0.54; p< 0.01) indicating that these paired variables might not have originated from a common source.

Perylene was detected in high levels in sediment samples and in much a higher level in the potential point-source sample (PS1) (Fig.6c). Besides the natural biogenic production, perylene could also be produced by fossil fuel combustion (Wang *et al*., 1999). High levels of perylene in temperate soils have been linked with frequent water logging arising from frequent flooding (Wilcke *et al*., 2000). No evidence of natural biogenic perylene production was apparent even though the site where potential point source soil samples were obtained is frequently flooded especially during intense rain fall (wet season) arising from out flow of the Imo river water through its low-lying bank (Oyo-Ita et al., 2011). Therefore, due to the extremely high level of perylene in the potential point source soil sample obtained near natural gas combustion turbine, the perylene levels in the sediments most likely have a fossil fuel (natural gas) combustion origin. Therefore, perylene could be utilised as marker for natural gas production in the region. Fig. 6c shows the distribution of perylene in sediments of Imo River. The minimum amounts found in sediments near Afam Power Station (IR1) and the maximum at IR6 may be attributed to variations in the dominant north-easterly wind trajectory as sediment sample (IR6) was obtained at downstream location about 3.5km Southward from the gas turbine.

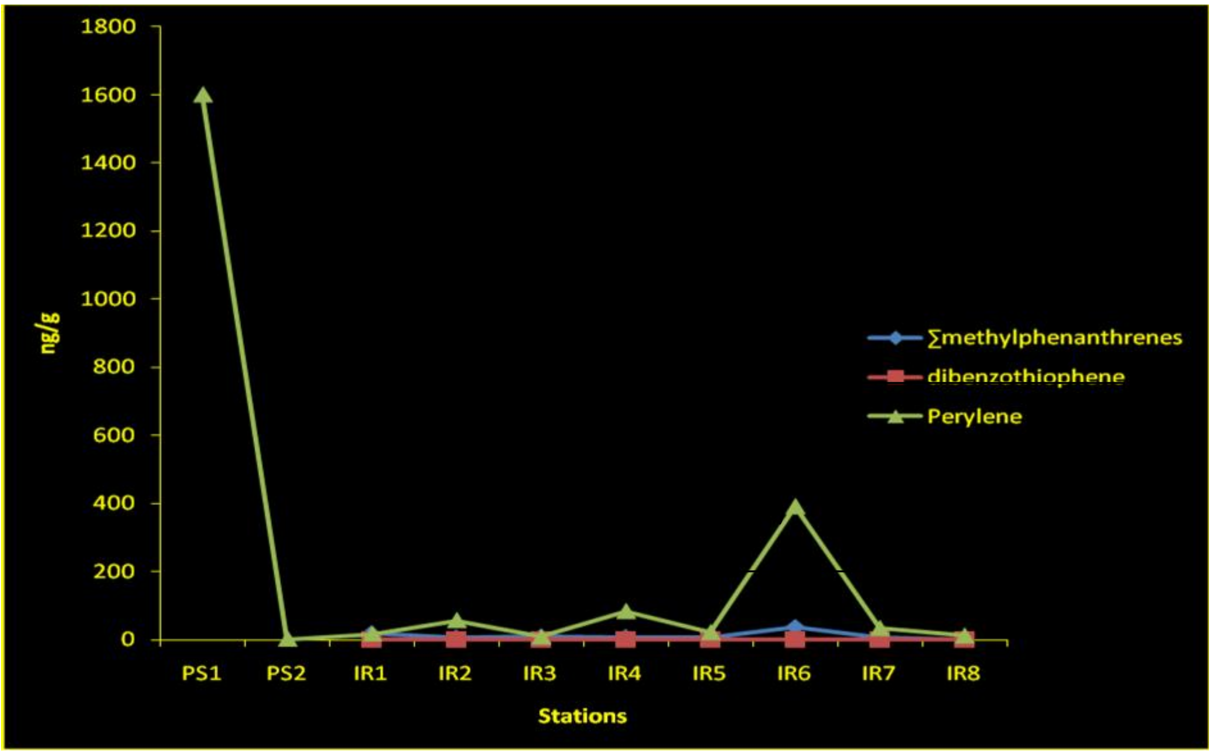
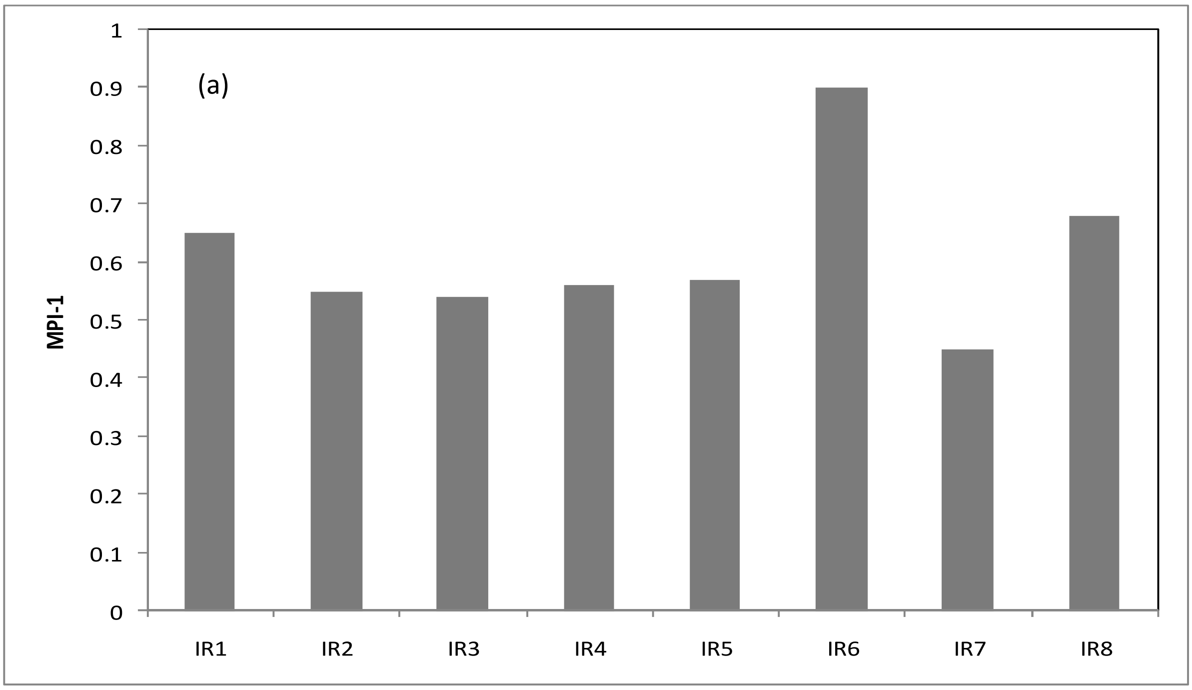


Fig.6a, b & c: Distribution of (a) ∑methylphenanthrenes, (b) dibenzothiophene and (c) perylene amongst sampling stations.

An assessment of petroleum maturity in environmental samples using methylphenanthrene indices provides insight into ascertaining if the environment under study is contaminated by petroleum from different origins (reservoirs). This can be achieved by evaluating the proportion of 2-, and 3-methylphenanthrenes to the methylphenanthrene total (2-, 3-, 1-, 9-and 4-methylphenanthrenes) (Yawanarajah and Krudge, 1994). The 1- and 9-methylphenathrenes are less thermodynamically stable than their 2- and 3-methyl isomers and with increasing temperature, 1-, 9- and 4-methylphenanthrenes are gradually converted into the more stable 2- and 3-methylephenanthrenes. The uniformity in the distribution of MPI-1 and MPI-2 among the sampling stations (Figs. 7a and b) suggests that the sediments from Imo River near Afam Power Station were polluted by petroleum residues of similar thermal maturity history.



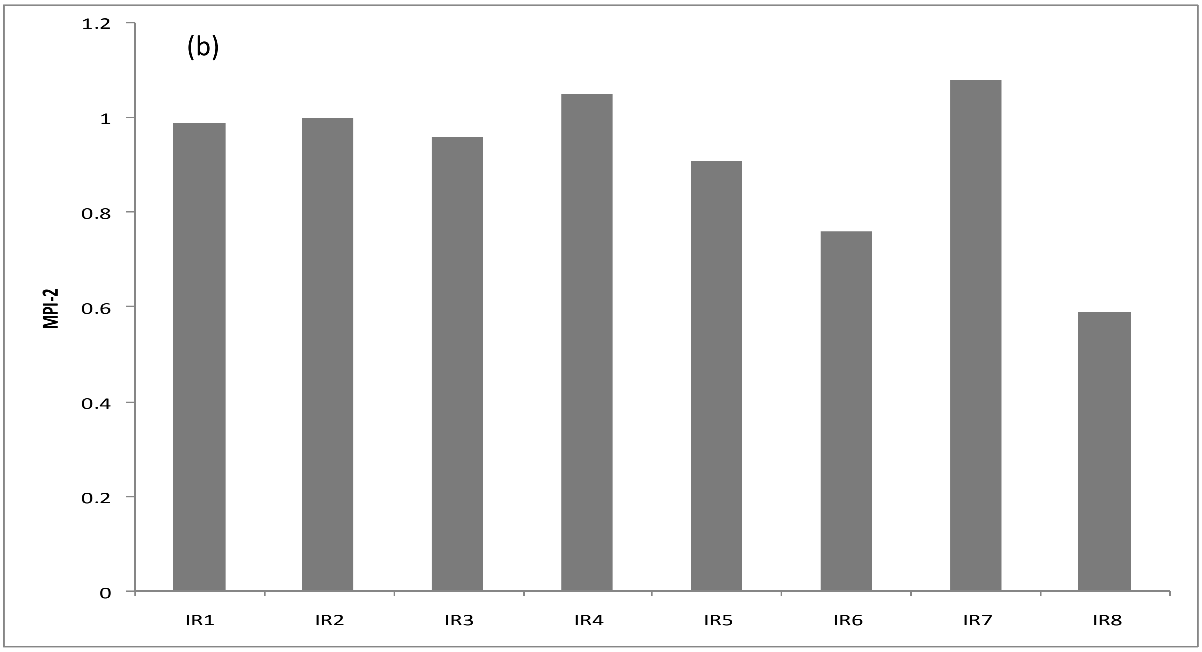


Fig.7a & b: Distribution of methyl phenanthrene indices: (a) MPI1 and (b) MPI2 from Imo River sediments and potential point source samples.

3.5 Statistical data interpretation

Cluster analysis was employed in this study to classify the study area into specific regions with defined characteristics. The whole of USEPA priority listed parent PAH data set and retene was subjected to this analysis. The complete linkage method (Fig. 8) indicated that stations such as IR7 as well as one of the potential point-source samples (PS1) were combined first with the smallest distance (or greatest similarity) between them. The combining distances then increase to station IR6, IR2 and finally to station IR8. These later stations show the greatest dissimilarity to the former stations (PS1 and IR7). For the sediment, two main groups were distinguished based on the type and quantity of PAHs, and the distance between them proves their great dissimilarity. The first cluster group (IRA) comprised of samples collected from zones I and III (near Afam Power Station and residential area respectively) as well as samples collected near the gas turbine (PS1). This suggests significant contribution of natural gas combustion PAHs to these zones. The second cluster group (IRB) consists of sediment samples located in zone II (near the fish settlement), this has significant contribution of PAHs derived from wood burning and engine boat exhaust emission (diesel combustion). All samples within the two main cluster groups (IRA and IRB) were combined at short distances because of the great similarity between these samples having a common PAH source input.

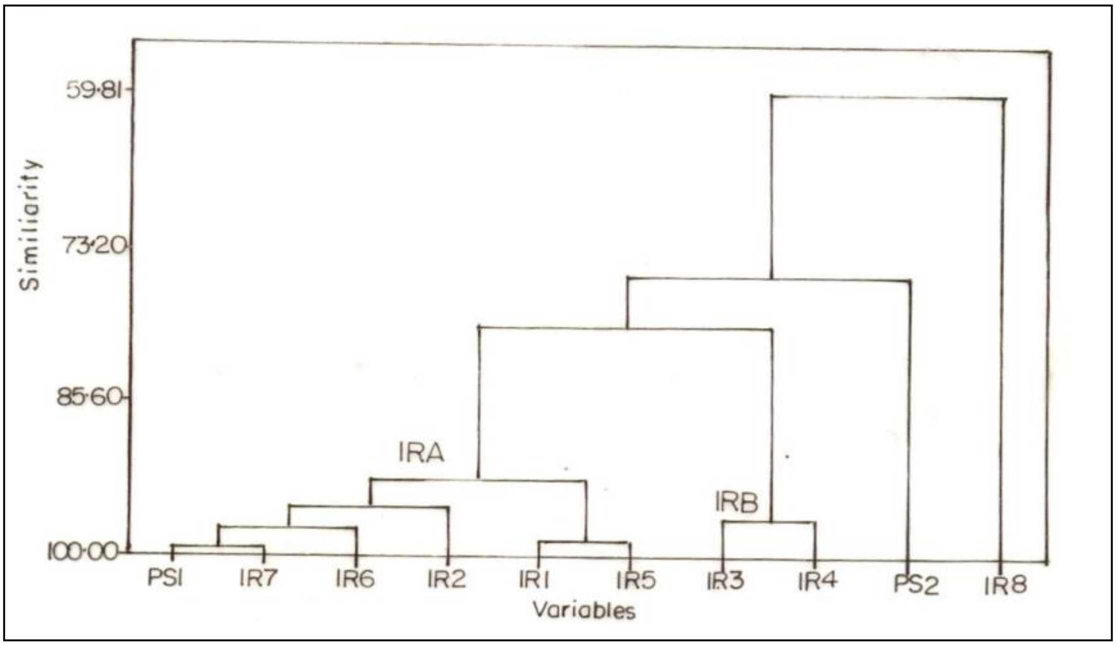


Fig. 8: Cluster dendogram showing relationship among sampling stations

Sample IR8 taken from the remote upstream site exhibited the greatest dissimilarity in relation to other sediment samples and indicates quite different PAH source input at this site. The other point-source sample (IR2) taken within Afam Power Station near the petroleum condensate spill also exhibited significant variation in relation to other sediment samples and indicates a minor PAHs contribution from petroleum condensates.

In general, the IRA (larger group) corresponds to samples characterised by relatively high levels of low molecular weight PAHs (3-ring). These features define samples affected mainly by high levels of petroleum residues and natural gas combustion pollution (zones I and II). The IRB are characterised by high concentrations of high molecular weight PAHs (4 – 5 ring) derived mainly from wood burning process and engine boat exhaust (diesel combustion) emission.

In order to investigate variances in the distribution of PAHs and subsequently characterise further the different PAH sources in the Imo River, levels of USEPA priority listed parent PAHs and retene were used. Common principal component analysis with varimax rotation was performed on these PAH levels. A factor was ignored if its variance was less than 6%. Loading of 0.70 was selected as a standard for prominent loading. Numbers of factors for the surface sediments from Imo river were four (Table 3). In order words, the pollutant causes for the sediments may be explained by four main factors.

Table 3: Factor analysis of surface sediment from Imo River indicating factor loading scores (varimax rotated, significant loadings are >0.700000).

	Factor 1	**Factor 2**	**Factor 3**	**Factor 4**
Acenapthylene	0.713864	0.069123	-0.628916	0.121513
Acenapthene	0.560997	0724206	-0.088216	0.176956
Flourene	0.072455	0.902962	-0.032380	0.173655
Phenanthrene	-0.152600	0.465274	0.382794	0.752950
Anthracene	0.696860	0.495965	-0.097075	-0.202513
Fluoranthene	0.856239	0.290301	-0.129751	-0.205079
Pyrene	0.744759	0.266058	-0.101401	-0.217331
Benzo(a)anthracene	0.848562	-0.302821	0.327310	0.201423
Chrysene	0.855459	-0.376267	0.283047	0.066139
Benzo(b)fluoranthene	0.847183	-0.401146	0.266776	0.054306
Benzo(k)fluoranthene	0.860449	-0.389792	0.232665	0.080797
Benzo(a)pyrene	0.862984	-0.012586	-0.369698	0.109769
Indene(1,2,3-cd)pyrene	-0.398842	0.183069	-0.772039	0.179865
Benzo(ghi)perylene	-0.501607	0.363832	0.451337	-0.254625
Dibenzo(a,h)anthracene	0.307150	0.698120	0.255433	-0.283498
Retene	0.046457	0.769119	0.349436	-0.035327
Variance (%)	42.58	23.45	12.64	6.36
Pollution source	Mixed source	Wood burning	Diesel engine exhaust emission	Petroleum condensate

The four factors accounted for 85.14% of the total variability in the data set and separated the PAHs into these identifiable source categories. Factor 1, which accounted for 42.58% of the total variance was highly loaded on acenaphthylene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene. Since it was highly loaded with both low molecular weight and high molecular weight PAHs, factor 1 was considered to represent a typical mixed source that was mainly caused by dominant amount of fossil fuel (natural gas) combustion and minor petroleum residues.

Factor 2 could be used to explain 23.45% of the total variance and was characterised by loading of retene, acenaphthene, fluorene and dibenzo(a,h)anthracene. The major PAHs in pinewood combustion (prevalent in the study area) are retene and acenaphthene (Rogge *et al.,* 1998). Therefore, factor 2 represents contributions from wood burning process.

Factor 3, accounted for 12.64% of the total variance and had no significant loading except that this factor explained the moderate level of indene (1,2,3-cd)pyrene, a high molecular weight PAH usually detected as a main product of incomplete combustion of liquid fossil fuel and in diesel engine exhaust. Thus this factor was taken to represent diesel engine exhaust emission.

Factor 4 contributed 6.36% of the total variance and was dominated by phenanthrene. This factor was selected to represent slight surface runoff of petroleum condensate into sediments of the Imo River.

CONCLUSION

Total and individual PAH contents for sediments from the Imo River near Afam Power Station varied significantly and depended on the nature of the anthropogenic activity around the sampling stations. Napthalene and its alkylated analogues were absent whereas 3- and 4- ring PAHs were the major species. On the other hand, 5- ring PAHs occurred in low abundance.

The distributions of PAHs were site-specific and proximity to source was the most important determining factor for the distribution of these contaminants. PAH levels were highest at those stations wheree samples were obtained near the fish settlement compared to those collected near the residential area and Afam Power Station. Calculation of five selected PAH molecular ratios showed evidence of a mixed source scenario dominated by pyrogenic and a minor petrogenic source inputs.

Cluster analysis employed distinguished the study area into two main cluster groups with great dissimilarity that is site and source-specific. Factor analysis explained four different PAH sources consisting of mixed, wood burning, diesel exhaust emissions and petroleum condensate spill inputs.

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