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Sources and distribution of polycyclic aromatic hydrocarbons in post flooded soil near Afam power station, South East Niger Delta, Nigeria

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Post flooded forest soil profile samples obtained near Afam power station, contiguous to Imo River were analysed for quantitative determination of polycyclic aromatic hydrocarbons (PAHs). Relatively moderate bulk density (1.17 g/cm^3), permeability ($1.79 \text{ cm}^3/\text{s}$) and macro-porosity (60%) values indicate that fluid flow through the soil profile would be unimpeded. PAHs content for the top soil horizon appeared similar to that of one of the point-source samples suggesting possible transport via flooding event on 25th April, 2008. Variation in PAHs content for the lower soil horizons may reflect a record of past PAHs deposition as a consequence of differences in Imo river current trajectory. The decreasing trends in the distribution of Σ thiophenes, Σ alkylPAHs and total PAHs (excluding perylene levels) may be associated with the sorptive character of soil organic matter (SOM) which limits transfer of PAHs deep into the soil. However, the relatively high level of perylene at the bottom soil horizon increases the likelihood of the compound to reach the shallow aquifer and contaminate the ground water. Utilization of six selected molecular ratios such as Fla/(Fla + Pyr) (0.20-0.70), Ant/(Ant + Phe) (0.22-0.41), BaA/(BaA + Chrys) (0.54-0.70), LMW/HMW (0.30-1.47), MPhe/Phe (0.72-1.59) and 1,7/(1,7 + 2,6-DMP) (0.57-0.90) enabled PAH source apportionment to be made. The results indicate a mixed source scenario with predominance of petroleum hydrocarbons input found for the top soil while the lower soil horizons were predominated by PAHs of combustion origin.

Key words: Molecular ratios, natural gas, petroleum condensate, soil, Imo River.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic pollutants because of their chemical stability and the multiplicity of the emission sources (Oros and Simoneit, 2000; Dendooven et al., 2006; Ekpo et al., 2011). The United State Environmental Protection Agency (USEPA, 1994) has listed 16 PAHs as priority pollutants in wastewater and 24 others in soils and sediments (Christensen and Arora, 2006).

Degradation of the soil environment as a result of human activities is the main effect of several pollutions. Unfortunately, the efforts aimed at limiting the harmful effects have not been quite successful. Flooding is a natural process that still occurs, in spite of expensive

protection measures put to minimise its substantial ecological and economic effects (Oleszczuk et al., 2003). Quite often, considerable amounts of PAHs found in ground waters may influence the human food chain or may be taken directly in drinking water (Barbash et al., 1999).

Surface runoff from roads and fields are frequently considered as source of significant amounts of PAHs in soils (Fernandez et al., 2000; Krein and Schorer, 2002; Christensen and Bzdusek, 2005). Flooding is a type of runoff, which causes the transfer of pollutants present in various chemical forms from water to the area covered by the flood. Pollutants remaining in soils after flooding can pollute ground waters as a result of their secondary transfer deep into soil profiles and pose a danger to the human health (Oleszczuk et al., 2003). Thus, it is very important to find out all the consequences of flooding so

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as to be able to minimise them.

In the past two decades, a number of papers shed light on the sources of hazardous PAHs in temperate environments. In contrast, little is known about the sources of PAHs in tropical environments (Wilcke et al., 2003). As persistent organic pollutants released in the tropics may be globally distributed, knowledge of PAH sources in the tropics is a prerequisite for understanding the global dynamics of PAH distribution (Wilcke et al., 2000). Hence, this present investigation from a tropical region should contribute to the knowledge of global PAH distribution.

Although a high level of anthropogenic PAHs to tropical environments is evident, the importance of a biological source input was suggested by Wilcke et al. (2003) on the basis of higher concentrations of certain volatile PAHs (for example, perylene, naphthalene, etc.) in tropics than in temperate environments. Recently, the occurrence of perylene in significant amounts with diagenetically produced PAHs in a tropical environment (Cross River estuary, South East (S.E) Nigeria) bordered by mangrove forest stands was linked to terrestrial organic carbon origin. In contrast to temperate environment, natural PAHs represent the highest percentage (average 76%) of the total PAHs (Ekpo et al., 2011). Finding out the sources of persistent organic pollutants (for example, PAHs) is important in order to legislate the control of influx of these pollutants into the ground water through the soil horizons.

Briefly, the main objectives of this study were to:

- i. Identify and quantify all the PAHs in the soil profile covered by flood.
- ii. Assess the role of geochemistry on the distribution of PAHs in the soil profile.
- iii. Identify the sources of the PAHs using multi-proxy approach.
- iv. Examining the possibility of PAHs transport from potential point-source after the flooding episode on 25th April, 2008.
- v. Establish a chronology of PAHs deposition during the past flooding events.

EXPERIMENTAL METHODS

Materials and quality assurance

The following analytical grade solvents, dichloromethane (DCM), methanol (MeOH), hexane, toluene, as well as molecular sieves, potassium hydroxide (KOH) and bistrimethylsilyltrifluoroacetamide (BSTF) were purchased from Merck (Darmstadt, Germany). Diazald® was provided by Sigma Aldrich (Germany). Perdeuterated polycyclic aromatic hydrocarbons used as internal standards and surrogates: [²H₂]-benzo(a)anthracene, [²H₁₀]-fluoranthene, [²H₁₂]-benzo(ghi)perylene, [²H₁₀]-pyrene and [²H₁₂]-perylene were purchased from Cambridge isotope laboratories (Andover, MA, USA) and [²H₁₀]-anthracene from Dr. Ehrenstofer GmbH (Augsburg, Germany).

The vessels used for analysis were pre-cleaned with ethyl

acetate followed by acetone and heated at 300°C overnight. We ran one analytical blank with every batch of 15 to 20 samples to check background contamination during the extraction and purification steps. To remove background contamination, we corrected PAH concentrations by subtracting the mean of the analytical blanks.

Sample collection and preparation

The study site belongs to the low-lying coastal deltaic plains of South Eastern Nigeria, about 200 m westward from Imo River and is mostly flooded during intense rainfall (Figure 1). The terrain is virtually flat or gently undulating, sloping generally towards the Atlantic (Ezeayim and Okereke, 1996).

Temperature in the area ranges from 25 to 33°C. The coastal rainfall patterns described by Offiong et al. (2008) reveal this region has rainfall throughout the year with the highest rainfall between the months of April and September.

A combination of heavy rains and good sunshine along with adequate soil nutrients has 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 are farming (wood burning for agricultural and domestic purposes is the common practice) and fishing. However, there are some industries aligned near the Imo river bank including the Afam power generating station. Geologically, the study site belongs to the south east part of the cretaceous and tertiary sedimentary basin in southern Niger Delta (Ezeayim and Okereke, 1996).

Hydrogeology of the area aforementioned is directly related to the structural setting of the Benin Formation which constitutes part of the water-producing layer for ground water supplies. The layer consists of sands and gravels that are enhanced by high hydraulic conductivity and transmissivity of the water-producing layer (aquifer) such that the water table is invariably at shallow depth level.

To get a deep insight into the sources, transport of PAHs and to assess its impact on ground water through the soil column as well as establish a chronology of PAHs deposition via flooding episodes, two potential point-source top soil samples and one forest soil profile sample were obtained. The potential point-source samples, PS₁ and PS₂ were collected near natural gas combustion turbine and petroleum condensate spill respectively within the Afam power station premises while the soil profile sample was obtained about 1 km southward from Afam power station. Both samples were collected within 24 h after the intense rainfall event on 25th April, 2008 (wet season) as this site keeps being inundated by outflow from the Imo river water through its low-lying bank, especially during wet season. For purposes of comparison as well as examining if diagenetic formation of perylene occurs, another one top soil sample (FS) was taken (about 1.5 km northward from Afam power Station, near the fish settlement) from a non-flooded area.

A 100 cm depth soil profile was dug using an auger (post-hole) sampler after clearing the sampling site of surface debris and removing the first 3 to 6 inches surface soil. Periodically, the accumulated soil of described horizons (5 sections) were removed from the withdrawn auger and thoroughly mixed to obtain homogenized sample representative after discarding about 1 inch of the top soil sample. Samples were placed in pre-cleaned screw-capped bottles and kept in refrigerator at -4°C until laboratory time. Bulk soil sample was collected using a trowel for particle size analysis, determination of hydraulic conductivity, bulk density and micro-porosity. The bulk soil samples were sieved to pass through a 2 µm mesh. Infiltration rate was measured using double-ring infiltrometer method and transmissivity were computed according to Ogban and Ekerette (2001). A total of 8 soil samples were used for the study, 5 of which were sections from the core while the remaining 3 were surface soil samples.

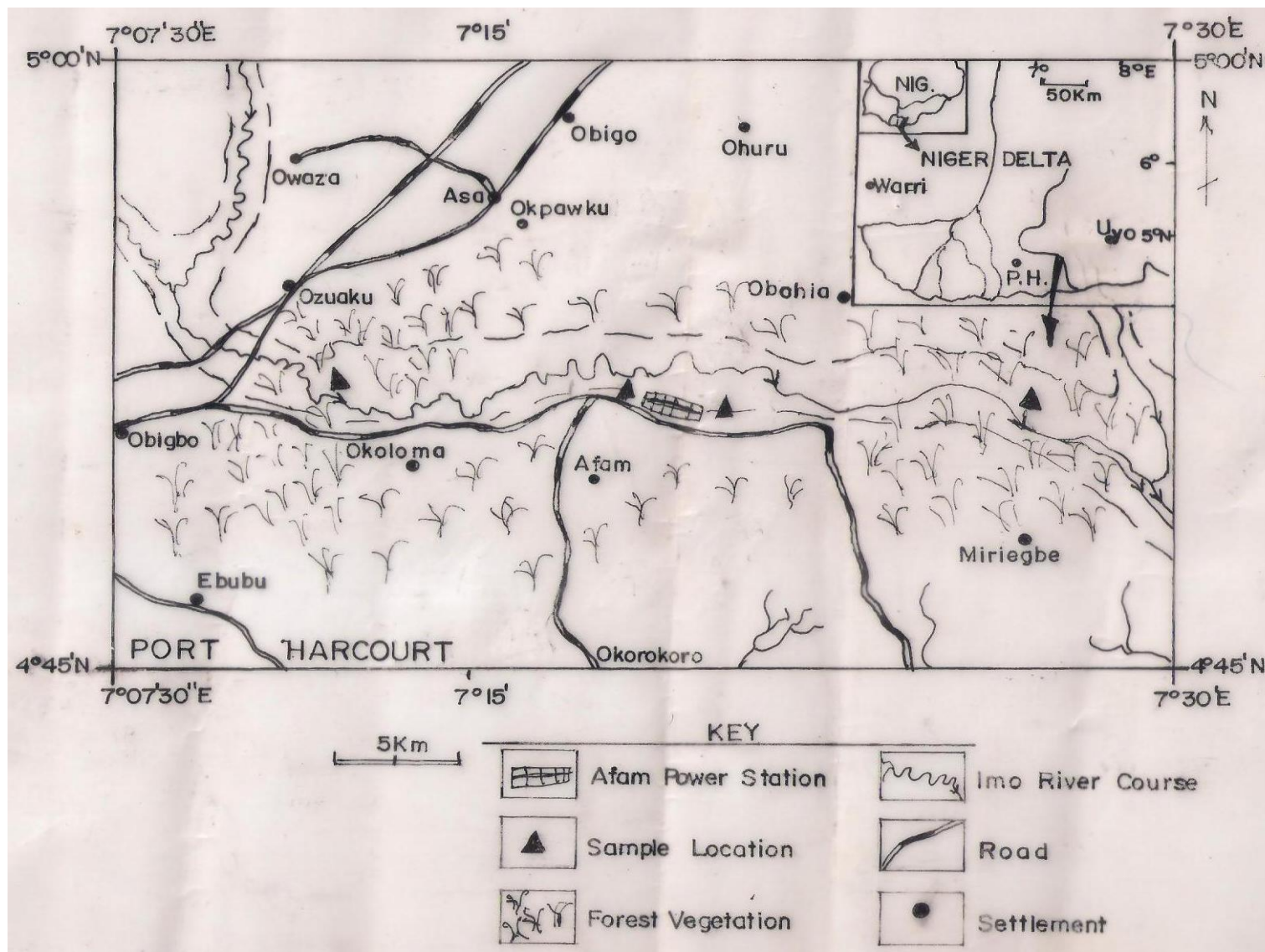


Figure 1. Map of the study area showing sampling locations.

Soil physicochemical properties

Particle size analysis was performed using Bouyoucos hydrometer. Hydraulics conductivity, bulk density and micro-porosity were determined according to the conventional method. Permeability was computed using the equation:

$$K_p = \frac{K_h \Pi}{g \ell g}$$

Where K_p = permeability (cm^3/s); K_h = hydraulic conductivity, (cmh^{-1}); Π = fluid viscosity, ($\text{gcm}^{-1} \text{s}^{-1}$); ℓ = fluid density, (gcm^{-3}); g = acceleration due to gravity, (cms^{-2}).

The permeability classes were determined according to Ogban and Ekerette (2001). Soil pH was measured following equilibration of the glass electrode meter in a 1: 2 soil (20 g) to water (40 g) suspension after calibration with buffer solutions of pH 7.0 and 10. Organic carbon was determined by the dichromate wet oxidation method (Nelson and Sommers, 1996).

Extraction and PAHs analysis

Extraction of 1 g sample in a test tube was performed sequentially by sonification with DCM/MeOH (2:1) and DCM in triplicate (Grimalt et al., 2004). 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 derivatized to trimethylsilyl ethers with BSTFA and the fatty acids with diazomethane distilled from diazald according to standard procedure (Albaiges et al., 2006).

GC-MS analysis

Identification and quantification of PAHs were carried out by GC-MS (Trace GC-MS, THERMO instruments, Manchester, UK). A 60 m capillary column coated with 5% phenyl-95% methyl-polysiloxane (0.25 mm id and 0.25 μm film thickness; HP-5, Hewlett-Packard, CA, USA) was used. The carrier gas was helium at a flow of 2.1 ml/min. Injection port and transfer line temperatures were 300°C. Samples in toluene were injected in splitless mode. The following oven temperature program was used: the program started at 90°C and held for a minute, raised to 150°C and held for another 1 min, then at incremental rates of 4°C held for 1 min to 320°C and a final holding time of 30 min. 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. Selected ion monitoring (SIM) of the PAH and the deuterated internal standards molecular ions were carried out using retention time windows.

A calibration curve (detector response versus amounts injected) were performed for each compound to be quantified. The lineal range of the detector was estimated from the curve generated by plotting detector signal versus amount injected. All measurements were performed in the lineal ranges for each target analyte. In few cases, the samples were re-diluted and re-injected for fitting within the lineal 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 5 ng/g, the limit of detection (LOD) in the full scan mode ranged from 0.004 to 0.013 ng/g dw. The lower limit of determination of PAHs was estimated from the smallest peak (signal-to-noise ratio > 3:1 in the

chromatograms) that could be integrated. We validated the accuracy of PAHs quantification by analysing with the certified reference materials "CRM-104" (Resource Technology Corporation, USA), obtaining accuracy from 75 to 107% compared with the certified value (Grimalt et al., 2004).

RESULTS AND DISCUSSION

Bulk properties

The soils bulk properties including particle size, bulk density, micro-porosity, permeability and pH as well as extractable organic matter (EOM) and total organic carbon (TOC) contents are given in Table 1. Bulk density, micro-porosity and permeability did not vary with soil profile depth and reflected the predominance of the sand fraction particle in the size distribution. The observed relatively moderate bulk density and micro-porosity values when compared with soil profile study reported by Oleszczuk et al. (2003) in Poland are attributed to the fact that sand particles were not completely in close contact because of minor bridging organic material (TOC ~ 1.38 to 2.35%; Table 1).

Morphologically, the soils were loose when moist indicating that root penetration would not be hindered. As a consequence, PAHs in flooding rain water could easily leach deep into the soil horizons. Generally, permeability was moderately rapid in the soil horizon studied which indicates that fluid flow would be un-hindered (Table 1).

PAHs content and distribution in flooded and non-flooded forest soils

Concentrations expressed in ng/g dry weight (dw) in the study are representative as they were estimated from homogenized soil samples at each interval of soil profile. Among the 16 USEPA priority listed PAHs, 10 were found in the entire forest soil profile inundated by flood (Figure 2a to e) and the concentrations estimated (2.01 to 5.20 ng/g dw) were in sum lower than those found for the potential point-source samples PS₁ (11.33 ng/g dw) and PS₂ (47.07 ng/g dw) (Figure 3a, b) and higher than those for the non-flooded forest soil (4.43 ng/g dw). The parent PAH sum determined for the top forest soil was low (5.20 ng/g dw) and was about 40 order of magnitude higher than those for the forest top soil horizon in Poland and other European areas with limited anthropopressure. These PAHs include acenaphthylene (Acy), fluorene (F), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chrys), indene(1,2,3-cd)pyrene (IcdP) and dibenzo(a,h)anthracene (DBA). Other non-priority listed PAHs identified were perylene (Pery), retene (Ret), benzo(e)pyrene (BaP), dibenzothiophene (DBT), and isomeric naphto(1,2-b) thiophenes.

Other various alkyl PAHs also identified at low

Table 1. Soil horizons, geochemical characteristics and bulk properties.

Sample code	Horizon (cm)	Coordinate	pH	Micro porosity (%)	Permeability (cm ³ /s)	Particles density (g/cm ³)	Bulk density (g/cm ³)	Colour	Particle size distribution (%)			TOC (%)	EOM (mg/kg)
									Sand	Silt	Clay		
AS1	A _p (0-15)	04°51'N 07°16'E	5.52	60.10	1.79	2.55	1.17	Dark grey	33.80	46.00	30.20	2.35	1020.00
AS2	A ₂ (15-45)	04°51'N 07°16'E	5.54	60.10	1.79	2.55	1.17	Dark grey	33.80	46.00	30.20	2.08	700.00
AS3	BA ₁ (45-55)	04°51'N 07°16'E	5.60	60.10	1.79	2.55	1.17	Brownish grey	33.80	46.00	30.20	1.87	450.00
AS4	BA ₂ (55-80)	04°51'N 07°16'E	5.62	60.10	1.79	2.55	1.17	Brownish grey	33.80	46.00	30.20	1.40	100.00
AS5	BA ₃ (80-100)	04°51'N 07°16'E	5.71	60.10	1.71	2.65	1.19	Brown	33.80	46.00	30.20	1.38	290.00
FS	A _p (0-15)	04°59'N 07°15'E	6.20	-	-	-	-	Dark grey	43.50	40.00	16.50	2.65	1860.00
PS ₁	A _p (0-15)	04°51'N 07°18'E	5.10	-	-	-	-	Dark grey	68.90	6.000	15.10	2.50	2150.00
PS ₂	A _p (0-15)	04°50'N 07°18'E	5.10	-	-	-	-	Dark grey	58.90	22.00	19.20	2.68	1150.00
Standard deviation			0.35	31.10	0.92	1.33	0.61		13.86	15.12	6.96	0.52	735.02
Standard error (+/-)			0.12	11.00	0.32	0.47	0.21		4.90	5.34	2.46	0.19	259.87

concentrations in the soil profile were isomeric alkylphenanthrenes [including 3-methylphenanthrene (3-MPbe), 2-methylphenanthrene (2-MPhe), 9/4-methylphenanthrene (9/4-MPhe), 1-methylphenanthrene (1-MPhe), 1-ethylphenanthrene (1-EPhe), 3,5-dimethylphenanthrene (3,5-DMPhe), 2,6-dimethylphenanthrene (2,6-DMPhe), 2,7-dimethylphenanthrene (2,7-DMPhe), 1,3-dimethylphenanthrene (1,3-DMP), 1,6-dimethylphenanthrene (1,6-DMPhe), 1,7-dimethylphenanthrene (1,7-DMPhe), 2,3-dimethylphenanthrene (2,3-DMPhe), 4,9-dimethylphenanthrene (4,9-DMPhe), 1,8-dimethylphenanthrene (1,8-DMPhe) and 9,10-dimethylphenanthrene (9,10-DMPhe)]. Low molecular weights PAHs were predominant, for instance, the percentage content of phenanthrene was 20% with respect to the total parent priority listed PAHs determined. A clear differentiation in PAH content was observed. Unlike the top horizons, higher content levels of high molecular weight PAHs were found in the bottom horizon. The concentrations of 3-ring priority listed PAHs

varied between 0.01 and 1.30 ng/g dw, with their maximum value recorded for phenanthrene at the top soil horizon [A_p – (0 to 15 cm)]. For the 4-ring PAHs, concentrations were in the range 0.14 to 0.95 ng/g dw, maximizing in flouranthene at the A₂ horizon (15 to 45 cm) while 0.01 to 0.17 ng/g dw were recorded for the 5-ring PAHs, maximizing in dibenzo(a,h)anthracene (DBA) at the bottom horizon [BA₃ – (80 to 100 cm)](Figure 2a to e). The higher contribution of PAHs with high molecular weight (for example, DBA and IcdP) at the bottom horizon can be explained by the limitation of biodegradation processes towards heavy PAHs compared to the light counterparts and the higher leaching tendency of light PAHs (for example, flourene, acenaphthylene and acenaphthene) through the soil profile to much deeper depth than their heavy counterparts (Oleszcuk et al., 2003).

To establish a chronology of PAHs deposition during past flooding events, we examine the distribution of individual PAH compositions down the soil horizons. The top soil horizon (A_p ~ 0 to 15 cm) had PAH composition similar to that found for one of the potential point-source top soil samples (PS₂) (except the detection of low level of

acenaphthylene and high level of retene), indicating that the top soil horizon was mostly influenced by petroleum related PAHs transported in flooded water through the potential point source sites following the intense rainfall event on 25th April, 2008. Despite the low solubility of PAHs in water, high molecular weight PAHs such as benzo(a)anthracene are transferred in the form adsorbed on particles, carried away by water (in general, only very fine grained particles < 63 μm are transported by river current) (Dorzd et al., 2002; Oleszcuk et al., 2003; Zhihuan et al., 2006). The detection of retene at high levels in the top soil horizon may be indicative of pine wood combustion source to the soil profile study site (Zhihuan et al., 2006). Retene concentration profiles reveal a decreasing trend down core except at BA₂ horizon (55 to 80 cm) (Figure 4a). The retene level at this horizon may reflect higher retene production, a consequence of past increased utilization/burning of pine wood for agricultural and domestic purposes.

Similar PAH composition and distribution were observed for the lower soil horizons (A₂ - BA₃ ~ 15 to 100 cm) except in the case of

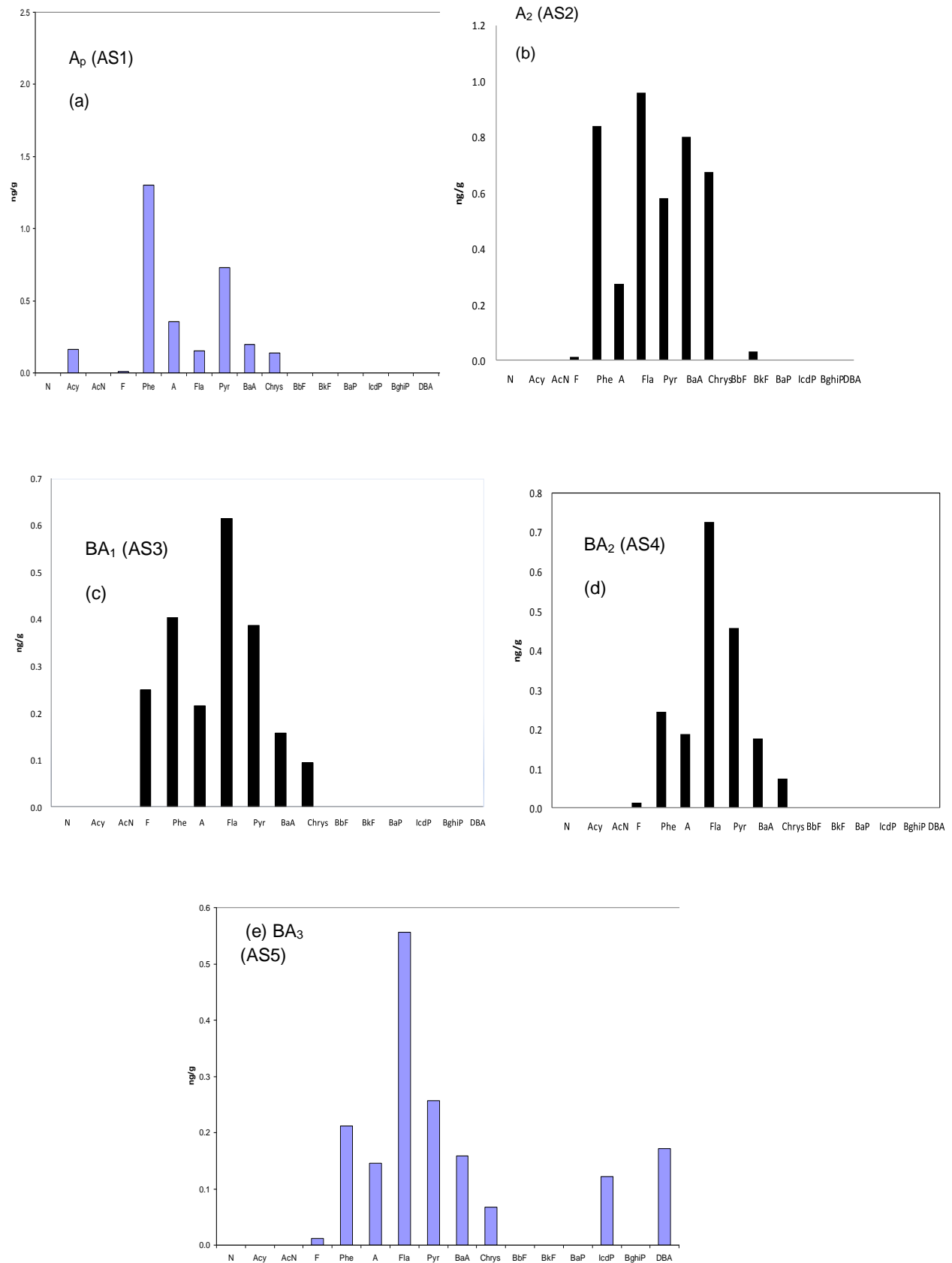


Figure 2. Distribution of individual PAH compositions down the forest soil profile; a) A_p (AS1); b) A_2 (AS2); c) BA_1 (AS3); d) BA_2 (AS4); e) BA_3 (AS5).

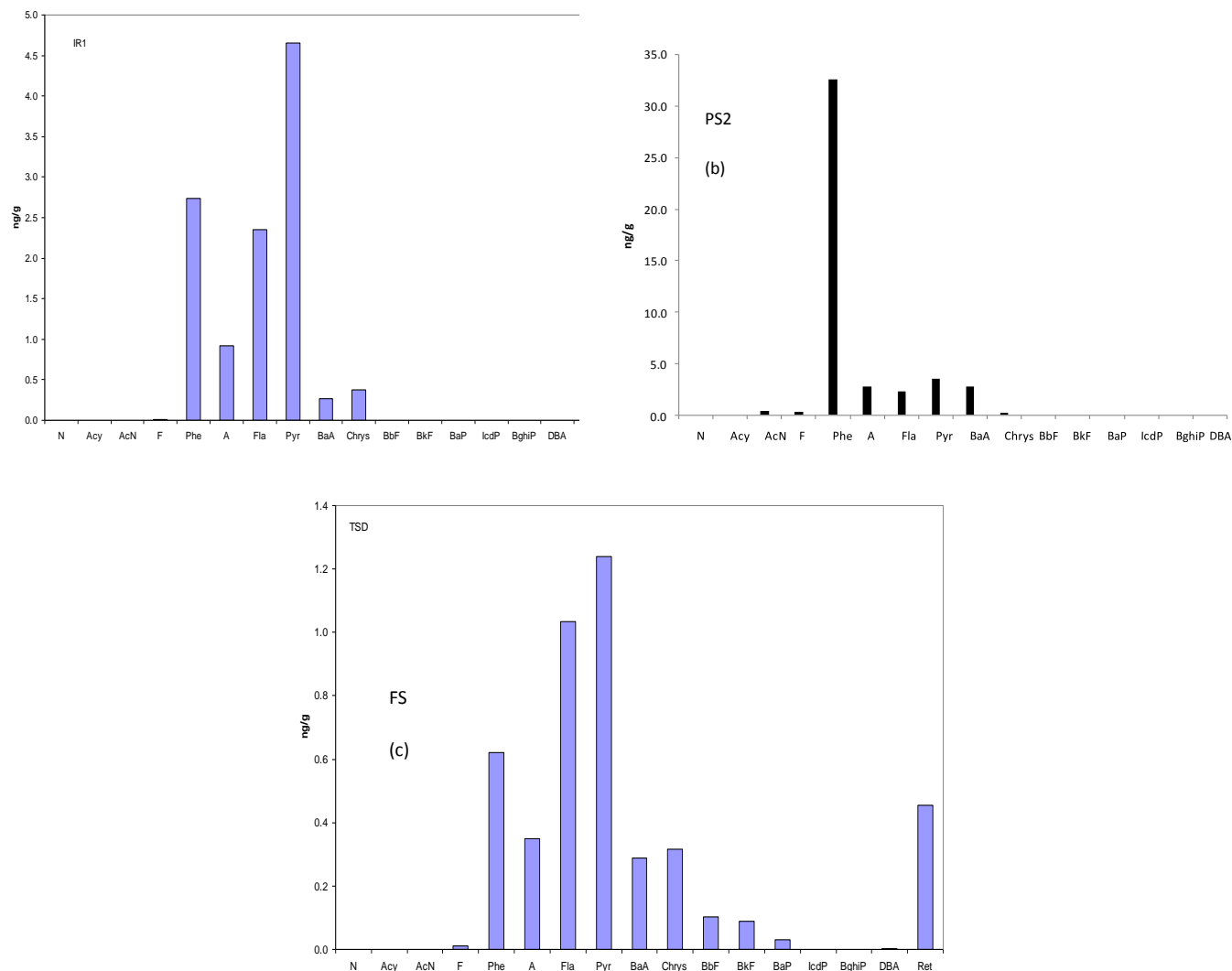


Figure 3. PAH contents for (a) potential point-source sample collected near gas turbine, (b) potential point-source sample collected near petroleum condensate spill and (c) non-flooded top soil sample collected near fish settlement.

benzo(k)fluoranthene at A_2 horizon as well as indeno(123-cd)pyrene and dibenzo(a,h)anthracene at the bottom horizon (BA_3). These mixed source scenario at A_2 soil horizon may be associated with additional input of vehicular exhaust emission linked to boat traffic, carried away by the Imo River current during past flooding events (Harrison et al., 1996; Simcik et al., 1999; Yunker et al., 2002; Zhang et al., 2004). The detection of dibenzo(a,h)anthracene and indeno(123-cd)pyrene at the bottom horizon (BA_3) also suggests additional input from gasoline exhaust emission and diesel spill besides natural gas combustion /petroleum condensate spill inputs (Rogge et al., 1998; Zhihuan et al., 2006). Variation in PAHs content for the lower soil horizons may reflect a record of past PAHs deposition via flooding caused by differences in Imo river current trajectory.

The levels and types of PAHs in flooded top soil (A_p) and non-flooded top soils (FS) varied and depended

upon the nature of anthropogenic activities in these areas (Figures 2a and 3c). First, there were clear differences in the PAH compositions for these two sites with higher levels recorded for the flooded top soil. Comparing data in Figures 2a and 3c, it can be seen that 5-ring PAHs (for example, benzo(b)fluoranthene and benzo(a)pyrene) were detected in appreciable levels for the non-flooded soil only. Furthermore, there were clear differences in the framework of Σ thiophenes, Σ alkylphenanthrenes and total PAHs (sum of parents and alkyl PAHs) contents for the flooded soil profile down core (Figure 4b, c and d). The decreasing trends down core observed are a natural phenomenon reported by many researchers (Olesczuk et al., 2003) arising mainly from sorptive character of soil organic matter in relation to organic pollutants. Organic matter is a strong sorbent which limits transfer of PAHs deep into the soil. This influence had already been observed in soils with organic carbon contents above

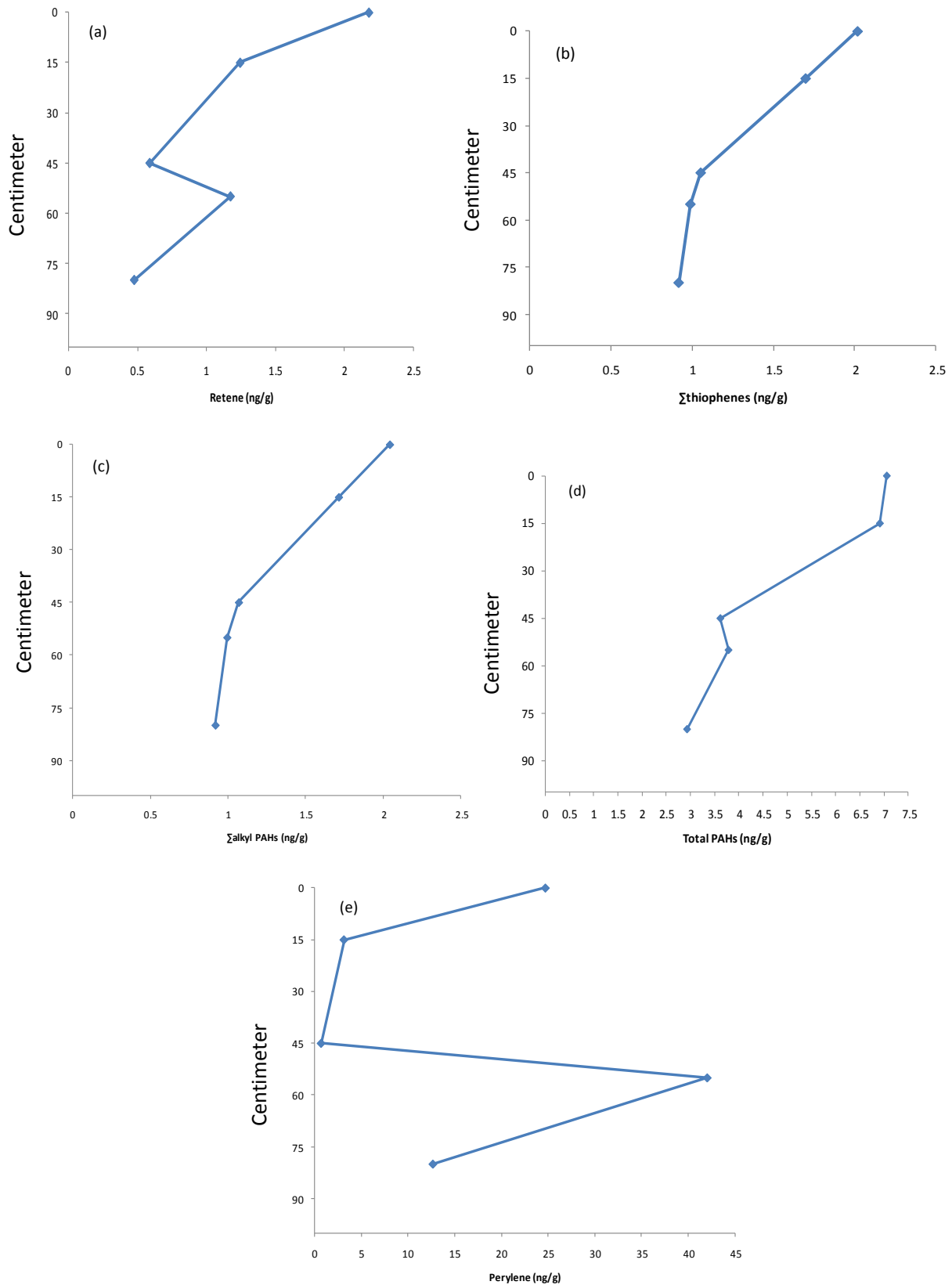


Figure 4. Distribution of (a) retene, (b) Σ thiophenes, (c) Σ alkylphenanthrenes, (d) total PAHs and (e) perylene in flooded soil profile.

0.1% as in our case study (Table 1). These result profiles indicate that the levels of PAHs leaching through the soil profiles would be insignificant at a depth close to the shallow aquifer if extrapolated and their possible health effect would be negligible.

Generally, naphthalene and its alkylated analogues were not detected in the entire soil profile. As low molecular weight PAH, these compounds are more volatile and remain in the atmosphere for a longer time, and are thus more susceptible to long distance transport compared to high molecular weights PAHs. In North America, climatic condition was shown to modify the PAH pattern in topsoil (Wilcke et al., 2003). The contribution of naphthalene according to these authors to the sum of the PAH concentrations in a climatically different zone (tropical) decreased in increasing mean annual temperature because of enhanced volatilisation and degradation with increasing temperature. This phenomenon may partly be responsible for the non-detection of naphthalene and its alkylated analogues as well as the low levels of acenaphylene besides leaching as previously mentioned above in the entire soil profile studied (Baran and Oleszczuk, 2002).

Among the non-priority listed PAHs identified, perylene showed the highest concentrations (0.73 to 41.99 ng/g dw) for the soil profile under study. Perylene concentrations were not included in the calculations of the total PAHs down core because perylene is reported in many environments to have biological/diagenetic origin (Wilcke et al., 2003) and its concentrations were considered outliers especially for the point-source sample PS₁ (1601.72 ng/g dw). In a near shore area of Prince Williams sound, Alaska, for example, perylene levels exceeding several hundred ppm were attributed to abundant supply of terrigenous organic debris in combination with a restricted circulation regime (Page et al., 1996). Besides this natural biogenic production, perylene could also be produced by fossil fuel (for example, natural gas) combustion (Wang et al., 1999). According to these authors and others (Wilcke et al., 2000), high level of perylene in temperate soils have been consistently linked with frequent water logging arising from frequent flooding. However, in the present study, perylene concentrations for the flooded top soil profile and well aerated non-flooded top soil (near fish settlement) were not consistent with this hypothesis as the flooded top soil horizon had lower perylene concentration (24.69 ng/g dw) than the well aerated non-flooded forest top soil (64.65 ng/g dw). These results indicate that perylene concentrations in the soil profile were not of biogenic origin but rather exclusively derived from fossil fuel (for example, natural gas) combustion origin. This is supported by the extremely high perylene concentrations detected in one of the potential point-source samples (PS₁) obtained near natural gas combustion turbine. The distribution of perylene down core reveals an irregular pattern. This irregularity may reflect a record of PAHs production pattern from

natural gas combustion process taking place within Afam power station occasioned by past flooding events. Therefore, perylene could be utilized as marker for natural gas combustion pollution for the region. It appears there is an extent to which soil organic matter could limit sipping of organic pollutants down the soil profile. At high concentrations, the sorptive capacity of soil organic matter (SOM) dwindles, thus increasing the likelihood of perylene to reach the shallow aquifer.

PAH source identification in soils

A large number of parent and alkyl PAH has been used for interpreting PAH distribution and assessing their sources in soils and sediments (Yunker et al., 2002; Wilcke et al., 2003; Yunker and McDonald, 2003; Aichner et al., 2007; Bechtel et al., 2007; Ekpo et al., 2011). Based on our study, limited set of six PAH ratios were selected using parent, alkyl and PAH molecular masses that exhibited the best potential for interpreting PAHs' geochemistry in soils near Afam power station.

To assess combustion versus petroleum inputs, the ratio of Fla to Fla +Pyr was used. This ratio has demonstrated to provide a better diagnostic index of PAHs formation processes than ratios of other commonly quantified parent PAHs (Yunker et al., 2002). Fla/(Fla + Pyr) ratios smaller than 0.40 usually indicate petroleum input such as crude oil, diesel, etc., 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 (Yunker and McDonald, 2003). As the soil profile sample including the point-source samples were collected within 24 h after flooding episode accompanying the intense rainfall event that occurred on 25th April, 2008, only the top soil horizon (A_p) was observed to exhibit a Fla/(Fla + Pyr) ratio < 0.40 similar to that of one of the point-source samples (PS₂). This similar characteristic petroleum source input suggests transport of PAHs via flood water (Table 2). Other lower horizons (A₂-BA₃) had Fla/(Fla + Pyr) ratios > 0.50 characteristic of combustion source input. The non-flooded forest soil sample had Fla/(Fla + Pyr) ratio of 0.5, typical of liquid fossil fuel combustion input associated with utilization of gasoline engine boat for commercial fishery activities by the inhabitants of the fish settlement (Table 2).

Methylphenanthrene to phenanthrene (MPhe/Phe) ratio has been widely used by many researchers as a diagnostic index for petroleum hydrocarbons contamination in different compartments of the environment (Zakaria et al., 2002; Walker et al., 2005). This ratio is defined as a sum of 3-methylphenanthrene(3-MP) + 2-methylphenanthrene (2-MP) + 9/4-methylphenanthrene (9/4-MP) + 1-methylphenanthrene (1-MP) relative to phenanthrene concentrations. The basis for this index is on the observation that alkylated homologues are typically present

Table 2. PAH source indices in forest soil profile near Afam power station.

Parameter	AS1 (A _p)	AS2 (A ₂)	AS3 (BA ₁)	AS4 (BA ₂)	AS5 (BA ₃)	FS (A _p)	PS ₁ (A _p)	PS ₂ (A _p)
Fla/(Fla + Pyr)	0.20	0.60	0.60	0.60	0.70	0.50	0.30	0.40
BaA/(BaA + Chrys)	0.58	0.54	0.62	0.70	0.69	0.47	0.42	0.93
Ant/(Ant + Phe)	0.22	0.25	0.31	0.41	0.40	0.36	0.25	0.07
1,7/(1,7+2,6DMP)	0.80	0.60	0.57	0.90	0.88	0.95	0.61	0.60
LPAH/HPAH	1.47	0.30	0.73	0.30	0.31	0.31	0.48	4.12
MPhe/Phe	1.59	1.57	0.96	0.86	0.93	0.72	0.35	2.24

in higher proportions relative to their parent PAHs (for example, methylphenanthrene > phenanthrene) in petrogenic source. In contrast, higher temperature combustion processes form PAHs through condensation reactions and/or ring fusion limiting the presence of alkyl groups (Walker et al., 2005). Consequently, MPhe/Phe ratios of > 1 is indicative of petrogenic source input while ratios < 1 implies input from pyrogenic origin. In our study, the MPhe/Phe ratios for the soil profile were in the range 0.72 to 1.59 with the lowest value found for the bottom soil horizon whereas the top soil sample exhibited the highest MPhe/Phe value. The results show a decreasing trend of petroleum hydrocarbon input down core with a corresponding gradual increase in pyrogenic source input.

Fla/(Fla+Pyr) ratio is supplemented by Ant/(Ant+Phe) and BaA/(BaA+Chrys) ratios. 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 the soil profile under study, the Ant/(Ant+Phe) ratio for the top soil horizon (A_p) had the least value (0.22) compared to those for the lower horizons (A₂-BA₃) (> 0.22), supporting predominant petroleum source input to the top soil while the lower horizons were predominated by PAHs of combustion origin (Table 2).

However, a boundary plot of Ant/(Ant+Phe) versus Fla/(Fla+Pyr) indicating apportionment of soil profile samples to source shows that top soil sample was mainly influenced by petroleum while the lower horizons had a mixed source origin dominated by combustion source (Figure 5a). These results are consistent with the distribution pattern down the soil profile.

Similarly, according to Yunker et al. (2002), values of BaA/(BaA+Chrys) ratio < 0.20 imply petroleum source input, between 0.20 and 0.35 indicate either petroleum or combustion input whereas ratios > 0.35 imply combustion. In the present study, the lower horizons had BaA/(BaA+Chrys) values that are consistent with above mentioned indices for combustion input except for the top soil horizon. As many possible contamination sources co-exist in the soil profile, the observed complication in molecular ratios may be linked to weathering processes associated with microbial or photo-degradation effect (Doong and Lin, 2004) as well as leaching through the soil profile.

A boundary plot of BaA/(BaA+Chrys) versus Fla/(Fla+Pyr) shows apportionment of soil profile samples to source (Figure 5b) where the top soil horizon sample was mainly influenced by petroleum and the lower horizons by a mixed source, dominated by combustion source input. Fla/(Fla+Pyr), Ant/(Ant+Phe) and BaA/(BaA+Chrys) ratios for the non-flooded forest top soil sample (obtained near fish settlement) show values (0.50, 0.36 and 0.47 respectively) that are typical of liquid fossil fuel combustion source, a consequence of utilization of gasoline engine boat for commercial fishery activity.

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 water solubility among PAH isomers in most cases, mass ratios seem to reflect faithfully the characteristic source of PAHs, likely because only strongly bound refractory phase compounds, protected from dissolution or degradation, remain after transport (McVeety and Hites, 1988).

As an abundance of high molecular weight PAH (for example, 4-, 5- and 6- ring) is typically characteristic of pyrogenic origin whereas low molecular weight PAHs (for example, 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 whereas values < 1 imply combustion (Walker et al., 2005). For the soil profile under study, only the forest top soil horizon exhibited LMW/HMW ratio > 1 supporting the dominant petroleum source input. Other lower horizons including the non-flooded forest top soil had LMW/HMW ratios < 1, supporting major combustion source input (Table 2).

Although several studies have shown that some low molecular weight PAHs are biosusceptible and could be degraded more rapidly than their high molecular weight counterparts, this ratio has been proven useful for source discrimination. 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 indicate wood combustion, those less than 0.45 indicate vehicle exhaust emission while ratios in between may imply other combustion sources or the

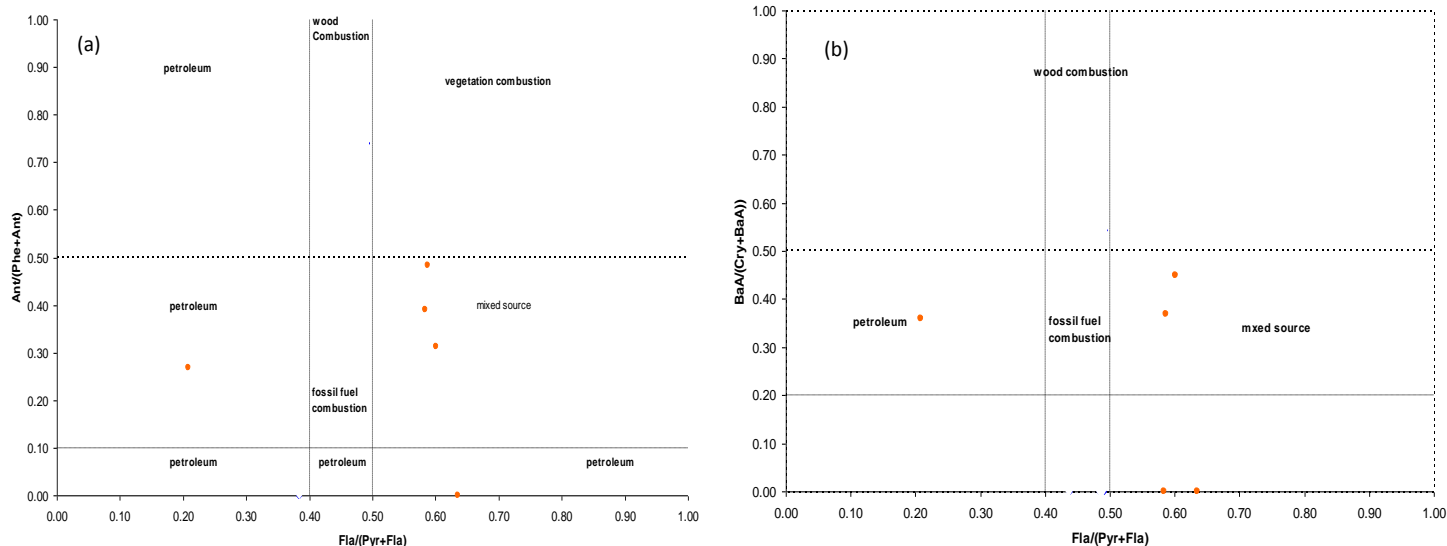


Figure 5. Boundary plots between (a) Ant/(Ant + Phe) and Fla/(Fla + Pyr) and (b) BaA/(BaA + Chrys) and Fla/(Fla + Pyr) for the forest soil profile showing apportionments of samples to source.

presence of shale oil or coal. In the soil profile under study, the top soil horizons (A_p and BA_2) exhibited 1,7/(1,7 + 2,6-DMP) ratios typical of input from wood burning while the lower soil horizons were predominated with PAHs of combustion origin.

Conclusion

Flooding had a slight impact on the total PAH concentrations of the forest soil profile sample obtained near Afam power station contiguous to Imo River. The flooded forest top soil horizon was characterised by a higher contribution of PAHs of 3- and 4-ring types compared to content of the non-flooded forest top soil with additional 5- and 6-ring species, indicating differences in the nature of anthropogenic activity in these two sites. The similarity in PAHs content in flooded top soil with that of one of the potential point-source samples suggest transport of PAHs via flood water following the intense rainfall event on 25th April, 2008.

Due to the observed decreasing trends in the concentrations of Σ thiophenes, Σ alkylphenanthrene and total PAHs (excluding perylene concentrations), no excessive levels which could reach the shallow water table and threaten human health was observed. However, the relatively high perylene concentration at the bottom horizon increases the likelihood of the compound to reach the shallow aquifer.

Variation in PAH contents observed for the lower soil horizons may reflect a record of past PAHs deposition via flooding, a consequence of differences in Imo river current trajectory. Utilization of six selected PAHs molecular ratios enabled source apportionment to be made. The

results indicate a mixed source scenario with predominance of petroleum source input for the top soil horizon while the lower soil horizons were predominated with PAHs of combustion origin.

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