



## Polycyclic aromatic hydrocarbons in sediments and soils from oil exploration areas of the Niger Delta, Nigeria<sup>☆</sup>

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### ABSTRACT

The distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from rivers and canals adjoining some oil exploration sites in the Niger Delta and surface soils from host communities were examined. The concentrations of 28 target PAHs ranged from 65 to 331 ng/g (average: 168 ng/g) and from 24 to 120 ng/g (average: 80 ng/g) in the sediment and soil samples, respectively. Two-ring PAHs were the dominant components accounting for approximately 45% of the total PAHs detected. Assessment of the PAH compound ratios, phenanthrene/anthracene (Phe/Ant) and fluoranthene/pyrene (Flu/Pyr), suggested that the PAHs in most sediment samples were predominantly of petrogenic origin which may have resulted from incessant oil pipeline leakages in the area. On the other hand, PAHs of pyrogenic sources were present predominantly in surface soils, an indication that gas flaring associated with oil exploration work in the Delta mostly affects the surface soils. An assessment using a set of widely cited sediment quality guidelines indicated that the majority of the sediment samples collected from the rivers of the delta does not pose a serious threat to the ecosystem except for two locations, Imo river and Oginni canal where PAH-contaminated sediments were likely to be acutely toxic to certain sediment dwellers.

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### 1. Introduction

The occurrence of polycyclic aromatic hydrocarbons (PAHs) in surface soil and sediments from the Niger Delta area deserves major attention. Successive oil pollution in the area and natural gas flaring have significantly altered the region's ecology [1,2]. The estuaries located in this area also receive organic pollutants from a number of diverse sources including domestic sewage and wastewater, atmospheric fallouts, and boat engine exhausts [3]. The Niger Delta houses refineries and other petroleum-based industries; therefore, contamination of industrial effluents with oil-related residues is inevitable. At present, protection of streams and rivers from contamination by petroleum and its derivatives in the Niger Delta is one of the greatest ecological challenges in Nigeria.

The Niger Delta is one of the major oil exploring regions in the world, with estimated 36.2 billion barrels of oil and 184 trillion cubic feet of natural gas in reserves [4]. Oil exploration activities started in the region in 1956 when the first oil well was discovered

by Shell-British Petroleum at Oloibiri. These activities have led to the release of various pollutants, including trace elements and PAHs into the soil, air, and water in the region. These pollutants can pose threat to the Nigerian ecosystem and residents. There have been many claims and counter claims by the inhabitants of the Niger Delta on pollution of rivers and streams by oil pipeline spillage, with alleged attendant reduction in the farmland yield which has heated up tension in the area and a great threat to the stability of the Nigeria state. The delta is vibrant with economic activities and accounts for over 30% of Nigeria's gross domestic production, and about 2.5 million barrels of crude oil are drilled daily in the Niger Delta [4]. Numerous studies on the environmental pollution of the Niger Delta have been reported [5–8]. However, most previous studies have been restricted to small areas and usually done on surface water and vegetation.

At present, apparently limited data are available on the occurrence and sources of PAHs in sediments and soils in the region; data available on PAHs in soils in the region covered a small area [9]. Therefore, the present study was conducted to examine the distribution and possible origins of PAHs in surface sediments and soils from some parts of the Niger Delta. It has been known that PAHs in the environment are mainly originated from pyrolytic and petrogenic sources. Pyrolytic PAHs are formed as a consequence of incomplete combustion whereas petrogenic PAHs are mainly

<sup>☆</sup> "Capsule": Occurrence and ecological risk of polycyclic aromatic hydrocarbons in soils and sediments near oil fields of the Niger Delta, Nigeria, are assessed.

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derived from crude oil and its refined products. The Niger Delta stands a great chance of having varying input sources; hence there is an urgent need to decipher the sources of PAHs in the region. Finally, the present study was also intended to assess the ecotoxicological risk stemming from the loadings of PAHs in surface soil/sediments, which is of great significance for protecting human health and eco-environmental system.

## 2. Experimental

### 2.1. Sample collection

The Niger Delta covers an area of approximately 75,000 km<sup>2</sup>, representing 7.5% of Nigeria's total land area. The delta is a vast floodplain built up by the accumulation of sedimentary deposits washed down from the Niger and Benue rivers (Figure S1 in the Supporting Information; "S" designates figures and tables in the Supporting Information hereafter). Sampling was conducted in April and July 2008. Forty-four sediment samples were collected from rivers, streams and canals adjoining the exploration sites in some parts of the Niger Delta at depths ranging from 0 to 20 cm and composited from an average of five sub-samples at each location. The rivers sampled include the Great Kwa River (three tidal episodes—low, medium and high tide), Bakassi River, Calabar River, Imo River and Qua Ibo River, which all flux into the Atlantic Ocean. Twenty surface soil samples were collected from some communities very close to oil installations in the Delta (Figure S1).

Sediment samples were collected in pre-cleaned plastic bags using a hand trowel in shallow water and metallic bucket grab samplers in deep water. Representative samples were prepared by mixing five to eight sub-samples from an area of approximately 4 m<sup>2</sup> and kept in a cooling system prior to analysis. Soils were sampled at 25 m × 25 m sampling plots with five samples from the top 10 cm layer being collected from each location. The samples were transported to the laboratory in pre-cleaned polyethylene bags and stored in a freezer at –20 °C. They were subsequently shipped within 24 h to Guangzhou Institute of Geochemistry, China, in the frozen state and stored in the freezer upon arrival.

### 2.2. Sample preparation and instrumental analysis

Frozen samples were allowed to thaw at room temperature for a few hours upon removal from the freezer and freeze-dried. The freeze-dried samples were further homogenized, lyophilized, ground with a pestle and mortar, and sieved using a 2-mm sieve. Each sample of 20–50 g placed in a pre-extracted thimble was Soxhlet extracted with 200 mL of dichloromethane (DCM) for a minimum of 48 h. Surrogate standards (naphthalene-*d*<sub>8</sub>, acenaphthene-*d*<sub>10</sub>, phenanthrene-*d*<sub>10</sub>, chrysene-*d*<sub>12</sub>, and benzo[*g,h,i*]perylene-*d*<sub>12</sub>) were added prior to extraction. Sulphur was removed by activated copper added to the extract. The extract was concentrated using a rotary evaporator to approximately 1 mL, solvent exchanged to hexane [10], and concentrated again to approximately 1 mL.

The concentrated extract was fractionated by a glass column packed with silica–alumina (2:1) into two fractions containing aliphatic hydrocarbons and PAHs/OCPs, respectively, by successive elutions with 20 mL of hexane and 70 mL of hexane/dichloromethane (7/3 in v/v). The PAH/OCP fraction was further concentrated with a rotary evaporator at 30 °C to approximately 1 mL, transferred to a 2-mL vial, and blown down to 0.5 mL under a gentle stream of nitrogen. Internal standards (2-fluoro-1,1-biphenyl, *p*-terphenyl-*d*<sub>14</sub> and dibenzo[*a,h*]anthracene-*d*<sub>14</sub>) were added to the extracts at this point.

GC–MS analyses in the selected ion monitoring mode were performed on a Shimadzu Model 2010 GC–MS (Shimadzu, Japan) with an HP-5MS fused silica column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Ultrapure helium gas was used as the carrier. The mass spectrometer was operated in the electron impact mode at 70 eV. One microliter of sample extract was injected with an autosampler in the splitless/split mode with a split time of 1 min after injection, and the injector temperature was programmed from 100 to 280 °C at the maximum ramping rate (~200 °C/min). The column temperature was initiated at 60 °C, ramped to 200 °C at 5 °C/min, 250 °C at 2 °C/min, and 280 °C at 10 °C/min (held for 20 min), and finally increased to 290 °C at 10 °C/min (held for 5 min). Compound identification was based on comparison of the retention times and fragmented ion profiles of the reference standards with the target analytes, whereas quantification was performed with a conventional internal calibration method [10].

### 2.3. Determination of total organic carbon

Total organic carbon (TOC) contents were determined on freeze-dried, ground sediment and soil samples, following acid treatment with 10% HCl for 24 h to remove carbonate. The carbonate-free samples were rinsed thrice times with distilled water to remove acid residues and dried at 60 °C for 48 h. The measurements were conducted using a combustion method with a PerkinElmer CHN 2400 elemental analyzer [11].

### 2.4. Quality assurance/quality control

Extraction thimbles and silica and alumina used for the cleanup and fractionation were pre-extracted with methanol and DCM before use. All solvents were analytical grade and redistilled. Field blanks, laboratory blanks, spiked blanks, and replicate samples were analyzed along with field samples [10]. Quantification was performed using the internal calibration method based on eight-point calibration curves for individual target compounds. The average recoveries of the surrogate standards ranged from 65 to 99% in all the blanks and from 75 to 98% in the sediment samples with the exception of benzo[*g,h,i*]perylene-*d*<sub>12</sub> which ranged from 90 to 110%. Similarly, the average recoveries of the surrogate standards from the soil samples ranged from 70 to 96%, but for benzo[*g,h,i*]perylene-*d*<sub>12</sub> they ranged from 80 to 105%. All the spiked blanks (standards spiked into solvents) had surrogate standard recoveries in the range of 75–98% and the matrix spiked samples had surrogate standard recoveries in the range of 68–99% excluding perylene-*d*<sub>12</sub> which ranged from 95 to 115% (Table S1). The reporting limits (Table S1) were calculated from the lowest concentrations of the calibration curves divided by the actual sample weights. It should be noted that the measured concentrations were not corrected by the surrogate recovery data.

### 2.5. Data analysis

All the concentrations are presented based on the dry weight equivalent of the samples and the source diagnostic indices are calculated from the interpretative PAH concentration ratios (Table 1). The values of phenanthrene/anthracene (Phe/Ant) and fluoranthene/pyrene (Flu/Pyr) have been used extensively to distinguish between petrogenic and pyrogenic source of PAHs. Values of Phe/Ant and Flu/Pyr greater than 10 and less than 1, respectively, suggest strong petrogenic origin of PAHs [12,13] and vice versa for pyrogenic origin [14]. In addition, Ant/(Ant + Phe) < 0.1 is an indication of petroleum contamination while > 0.1 indicates a dominance of combustion origin [15]. Likewise, a Flu/(Flu + Pyr) value of 0.5 illustrates a petroleum/combustion transitional point [15]. The ratio of Flu/(Flu + Pyr) > 0.5 is ascribed to the combustion of

**Table 1**  
Concentrations of PAHs, total organic carbon (TOC) contents and molecular indices of PAHs in soils and sediments.

Location	No. <sup>a</sup>	$\Sigma_{28}$ PAH <sup>b</sup>	Min <sup>c1</sup>	Mid <sup>c2</sup>	Max <sup>c3</sup>	TOC (%)	Molecular indices					
							Phe/Ant <sup>d</sup>	Ant/178 <sup>d</sup>	Flu/Pyr <sup>d</sup>	Flu/202 <sup>d</sup>	BaA/228 <sup>d</sup>	Icdp/228 <sup>d</sup>
<b>Sediments</b>												
Uzere	6	97.8	0.100	2.08	26.6	1.26	12.3	0.080	0.800	0.440	0.280	0.230
Calabar	3	180	0.090	0.750	124	2.35	6.87	0.130	1.38	0.580	0.330	0.390
QJRS	3	155	0.180	1.77	36.4	2.40	43.9	0.020	1.36	0.580	0.350	0.140
Bakassi R	3	111	0.070	1.16	20.6	1.29	9.05	0.100	1.34	0.570	0.230	0.450
Imo River	3	286	0.270	1.78	107	3.93	4.85	0.170	1.53	0.600	0.340	0.290
GRT.K.R.L.T	2	67.6	0.670	0.830	17.7	5.09	4.39	0.190	1.44	0.590	0.330	0.400
GRT.K.R.M.T	2	148	0.110	1.40	55.4	6.38	3.57	0.220	1.47	0.590	0.340	0.560
GRT.K.R.H.T	3	65.0	60.11	0.91	17.43	4.65	3.19	0.24	1.69	0.63	0.24	0.53
Great Kwa River (avg.) <sup>e</sup>		93.7	0.110	1.03	21.1	5.37	3.63	0.220	1.20	0.600	0.300	0.500
Oginni	7	331	0.520	6.17	108	1.89	9.85	0.090	0.62	0.380	0.030	0.280
Olomoro	7	306	0.120	4.30	86.4	2.13	12.8	0.070	0.58	0.370	0.070	0.400
Ughelli	5	95.6	0.100	1.81	25.8	1.03	10.1	0.090	0.88	0.470	0.230	0.330
Mean		161				3.15						
<b>Soils</b>												
Oginni	5	112	0.090	1.90	37.10	2.33	7.07	0.120	1.32	0.570	0.180	0.090
Irri	5	23.8	0.040	0.510	7.19	0.330	9.15	0.100	1.19	0.540	0.210	0.260
Olomoro	5	120	0.030	2.23	20.13	1.01	6.02	0.140	1.20	0.540	0.450	0.420
Uzere	5	64.4	0.040	1.36	21.59	1.48	7.38	0.120	1.45	0.590	0.230	0.400
Mean		80.0				1.29						

<sup>a</sup> The number of samples.<sup>b</sup> The total concentration of 28 PAHs in ng/g dry weight to the nearest decimal point.<sup>c1</sup> Indicates the minimum values for individual PAHs.<sup>c2</sup> Indicates the median values for individual PAHs.<sup>c3</sup> Indicates the maximum values for individual PAHs.<sup>d</sup> Phe/Ant is the ratio of phenanthrene/anthracene, Ant/178 is the ratio of anthracene/(phenanthrene + anthracene), Flu/Pyr is the ratio of fluoranthene/pyrene, Flu/202 is the ratio of fluoranthene/(fluoranthene + pyrene), BaA/202 is the ratio of benzo(a)anthracene/(benzo(a)anthracene + chrysene) and Icdp/228 is the ratio of Ideno(123-cd)pyrene (IcdP)/(Ideno(123-cd)pyrene (IcdP) + Benzo(ghi)perylene).<sup>e</sup> The Grt average values were not used in calculating the mean values of  $\Sigma_{28}$ PAH and TOC.

grass, wood, and coal while values between  $0.4 < \text{Flu}/(\text{Flu} + \text{Pyr}) < 0.5$  are attributed mainly to combustion products from petroleum but values less than 0.4 are typical of petroleum contamination [16]. In addition, benzo(a)anthracene/(benzo(a)anthracene + chrysene) (BaA/(BaA + Chr)) of 0.35 and ideno(123-cd)pyrene/ideno(123-cd)pyrene + benzo(ghi)perylene (Icdp/(Icdp + Bghip)) of 0.5 mark the transition point of the petroleum and combustion sources. Specifically,  $\text{BaA}/(\text{BaA} + \text{Chr}) < 0.2$ , between 0.2–0.35 and  $> 0.35$  indicates mainly petroleum input, inputs from both sources and combustion input, respectively. Likewise,  $\text{Icdp}/(\text{Icdp} + \text{Bghip}) < 0.2$ , between 0.2–0.5 and more than 0.5 infers petroleum input, liquid fossil fuel combustion and grass, wood and coal combustion, respectively [17]. Origin 6.1 and SigmaPlot 10.0 were employed in the data analysis.

### 3. Results and discussion

#### 3.1. Occurrence and spatial distribution of polycyclic aromatic hydrocarbons

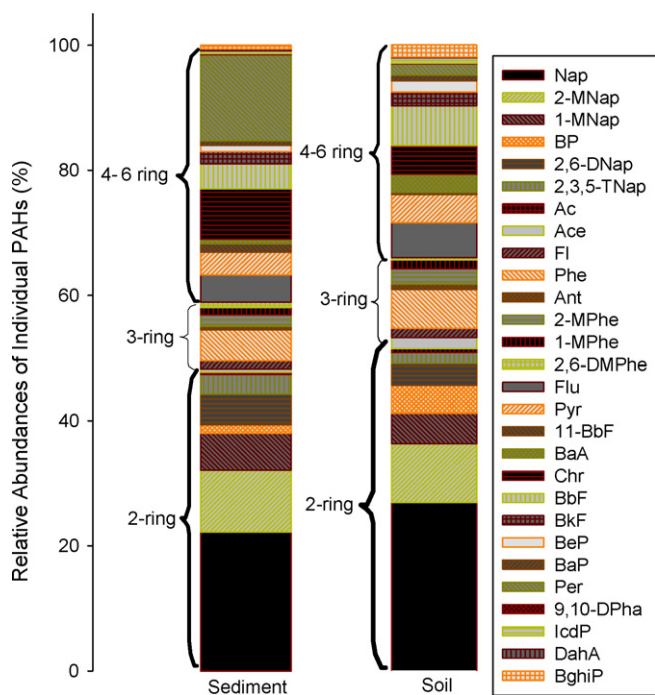
The concentrations of the 28 PAHs, sum of which is defined as  $\Sigma_{28}$ PAH (Table S2), determined in the sediments ranged from 65 to 331 ng/g with a mean value of 168 ng/g (Table 1). The highest concentrations of  $\Sigma_{28}$ PAH were recorded in samples from Oginni (331 ng/g) and Olomoro canals (306 ng/g) (Table 1 and Figure S1) which are located in the hinterland hosting several oil wells and oil installations, and obviously the high concentrations recorded at these locations can be attributed to the intense exploration activities undergoing with occasional oil pipeline leakages in the area. The lowest concentration of 65 ng/g was recorded at Great Kwa River during a high tide (Table 1). In general, sediments from the rivers contained lower PAH concentrations than those from the areas close to oil installations, which can be attributed to the con-

stant flux of the rivers into the Atlantic ocean (Figure S2) resulting in reduced PAH concentrations. This clearly explains the lowest concentration recorded during the high tide in the Great Kwa River.

A marked distribution pattern of the PAH concentrations in sediments was apparent (Table S2 and Fig. 1) with predominance of 2-, 4-, and 5-ring PAHs. The 2-ring PAHs accounted for approximately 45% of  $\Sigma_{28}$ PAH with naphthalene dominating with about 22% of the total, whereas the 3- and 4–6-ring PAHs contributed approximately 10 and 42%, respectively (Fig. 1). Perylene, likewise, was the dominant constituent in the 4–6-ring PAHs, which may be hypothesized that perylene has biogenic origin and could be generated in situ through biotransformation of some precursors most likely diatoms [18]. No correlation ( $r^2 = -0.18$  and  $p = 0.58$  with a two-tailed test) was found between the concentrations of perylene and the 5–6-ring parent PAHs compounds supposed to originate from anthropogenic combustion/pyrolysis processes, which implies that perylene in these sediment samples are of biotic and natural origins. A similar trend was observed in the soils, with the exception of perylene that had lower relative abundances in the 4–6-ring PAHs compared to those in the sediments (Table S2 and Fig. 1). Suffice to say that all 28 target compounds were detected in virtually all the samples analyzed. The concentrations of total PAHs and individual PAHs in the soil samples are presented in Table 1 and Table S2, respectively. The total concentration of  $\Sigma_{28}$ PAH in the soil samples ranged from 24 to 120 ng/g with a mean value of 80 ng/g.

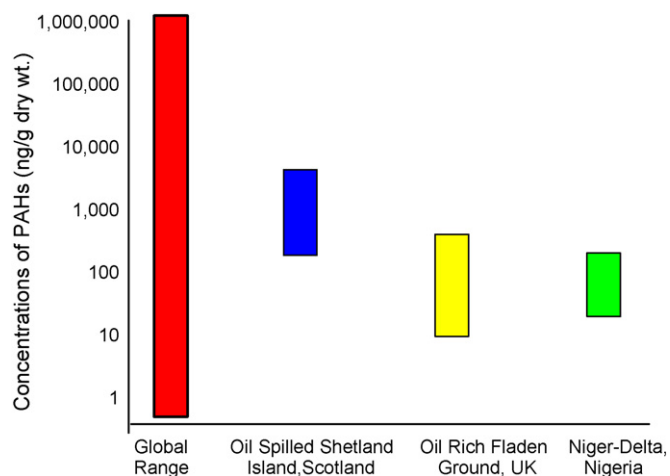
#### 3.2. Comparison with PAH levels from other parts of the globe

Though data on PAHs in oil fields around the world are scanty, the sediments investigated in the present study can be considered to be moderately polluted with PAHs as compared to those reported for similar samples from other parts of the world (Table 2 and Fig. 2) [19–21]. In comparison with estuarine sediments in the



**Fig. 1.** Relative distribution pattern and percent compositions of individual PAHs in sediment and soil of the Niger Delta, Nigeria.

U.K. (Table 2) [22], the PAH concentrations in the present study were relatively low. In the rivers Blythe, Tyne, Wear and Tees, the total concentrations of 15 parent PAHs (Supporting Information) in sediments were in excess of 10,000 ng/g dry wt. [23]. Total PAH (2- to 6-ring parent and branched components) concentrations found in the Firth of Clyde, UK, ranged from 3900 to 27,000 ng/g dry wt. [24]. High PAH concentrations (>2000 ng/g dry wt.) are often found in sediments in estuarine and harbor sites and areas close to industrial or urban activities [23–25]. Total concentrations of PAHs (2- to 6-ring parent and branched) at ~10,000 ng/g dry wt. were reported in estuarine sediments from the Pearl River Delta of South China [25] though lower values of 31–133 ng/g were obtained in sediment samples from Yellow River, China (Table 2). However, Notar et al. [26] reported lower total PAH (2- to 6-ring parent and branched)



**Fig. 2.** PAH concentrations in Nigeria (the present study), oil rich/spilled Shetland Island, Scotland, and oil rich Fladen Ground, UK sediments in comparison to those reported for rivers, lakes, and coastal zones around the world. Data for Shetland Island, Fladen Ground and global sediments are adopted from [19,21] and [20], respectively.

concentrations of between 30 and 600 ng/g dry wt. in sediments from the Gulf of Trieste, an area heavily utilized for tourism and industrial and agricultural activities, and classified samples with total PAH concentrations >500 ng/g dry wt. as being relatively contaminated.

Likewise, the levels of  $\Sigma_{28}$ PAH in the soil samples were lower than those reported for soils from some parts of the world. The total concentrations of  $\Sigma_{13}$ PAH (Supporting Information) in soils from two industrial zones in Korean Peninsula, South Korea, ranged from 109 to 178 ng/g [27]. Surface soils from the outskirts of Beijing, China, contained total concentrations of 16 PAHs (16 priority pollutants proposed by the United States Environmental Protection Agency; Table S2) ranging from 16 to 3884 ng/g with a mean value of 1347 ng/g [28]. In addition, Wild and Jones [22] reported a mean concentration of 187 ng/g for the 16 PAHs in rural soils of the U.K. Table 2 further compares the global PAH concentrations in soil and sediments.

The concentrations of benzo(a)pyrene (BaP), the most carcinogenic PAH in the present study, ranged from 0.17 to 10.21 ng/g with

**Table 2**  
Global distribution of polycyclic aromatic hydrocarbons in soils and sediments.

Location	No. of PAHs	$\Sigma$ PAHs (ng/g)	Source type	Reference
<b>Soils</b>				
Beijing, China	16 EPA	467–5,470	Urban soils	[44]
Canada	17	1,400	Highway	[45]
United Kingdom	7	20,000	Motorway	[46]
United States	14	3,000	Highway	[47]
Australia	18	300–79,000	Chemical plant	[48]
Japan	8	1,300 <sup>a</sup>	Urban soils	[49]
United Kingdom	16	2,700 <sup>a</sup>	Urban soils	[50]
New Orleans (United States)	16	3,730	Urban soils	[51]
West Macedonia (Greece)	16	55.2–495	Lignite fire power plant	[52]
Linz (Austria)	18	1450 <sup>a</sup>	Industrial area	[48]
Zelzate (Belgium)	7	3,000–14,000	1.3–4.2 km from an oil refinery	[53]
Five cities (Tallinn, Helsinki, Vilnius, Chicago and London)	16	1,090 <sup>a</sup>	Urban soils	[54]
Novi Sad (Serbia and Montenegro)	16	47,900 <sup>a</sup>	Oil refinery	[55]
Tokushima (Japan)	13	611 <sup>a</sup>	Urban soils	[56]
Niger Delta, Nigeria	28	23.8–120	Close to oil installations	This study
<b>Sediments</b>				
England and Wales	16 EPA	nd–102,000	Surface	[23]
Thailand	14	6–8,400	Surface	[57]
Yellow River, China	13	31–133	Surface	[16]
Niger Delta, Nigeria	28	65–331	Close to oil installations	This study

<sup>a</sup> Mean values.

a mean value of 1.25 ng/g in sediments and from 0.09 to 2.05 ng/g with a mean value of 0.75 ng/g in soils (Table S1). Again, these values were lower than those reported for the industrial zones in Korean Peninsula with values between 5 and 270 ng/g with a mean concentration of 55 ng/g [27]. Varying values of BaP were reported in commercial areas (90–4190 ng/g) and industrial areas (170–6030 ng/g) in Tokyo [29] and in the city of Chiang-Mai of Thailand (22 ng/g) [30]. The soils studied in this work can be regarded as being moderately polluted with PAHs compared to similar samples from other parts of the world.

### 3.3. Correlation between polycyclic aromatic hydrocarbons and total organic carbon

The wide disparity in the total PAH concentrations among the sediment samples was also reflected in the TOC contents which ranged from 1.03 to 6.38% with a mean value of 2.95%; TOC contents in the soil samples ranged from 0.33 to 2.33% with a mean value of 1.29% (Table 1). It is apparent from Figure S3 that no significant correlation exists between the total PAH concentrations and TOC contents ( $r^2 = 0.082$  and  $p = 0.60$  based on a two-tailed test) in the sediment samples. On the other hand, a significant correlation exists between the total PAH concentrations and TOC in soil samples ( $r^2 = 0.64$  and  $p = 0.0022$  with a two-tailed test). Several researchers have reported a linear relationship between the abundances of PAHs and TOC in sediments [31,32]. However, several factors such as organic matter composition and temperature have been suggested to affect yields and distribution of PAHs formed during incomplete combustion of organic matter or during its thermal maturation [33]. The nonlinear relationship between the TOC and PAH concentrations in the sediments indicates that the PAHs were recently generated and therefore were yet to fully partition into organic matter in the sediments. On the other hand, PAHs in the soils may have fully integrated into the soil matrix; therefore, a good correlation between the concentrations of PAHs and TOC can be expected.

### 3.4. Source diagnostics

Generally, the prevalence of alkylated PAHs (e.g. 2-MNap and 1-MNap approximately 15%; in sediments and approximately 14% in the soils; Fig. 1) indicates contamination from petrogenic inputs [34]. However, several molecular indices such as Flu/Pyr and Phe/Ant have also been used to ascertain emission sources [17,35]. The Phe/Ant and Flu/Pyr values in the sediments under investigation ranged from 3.2 to 44 and from 0.58 to 1.7, respectively (Table 1). The Phe/Ant and Flu/Pyr values in sediments from Uzere stream, Olomoro, and Ughelli canals ranged from 10 to 13 and 0.58 to 0.88 (Table 1), respectively, suggesting a predominant petrogenic origin for PAHs in these sediments. However, sediments from Calabar River, Imo River, Great Kwa River, and Bakassi River had Phe/Ant and Flu/Pyr ratios ranging from 3.65 to 9.05 and from 1.2 to 1.53, respectively. These values suggest a mixed petrogenic and pyrolytic origin for PAHs in the sediments. Based on the Ant/(Ant + Phe) values (Table 1), the input sources of PAHs in sediments of Uzere Stream, Qua Ibo River, Bakassi River, Oginni, Olomoro, and Ughelli canals were mainly petrogenic while those from Calabar River, Imo River, and Great Kwa River were considerably pyrogenic. This observation is consistent with the conclusion drawn from the assessment of Phe/Ant and Flu/Pyr given above. The BaA/(BaA + Chr) values ranged from 0.03 to 0.35 in sediment and 0.18 to 0.45 in soil samples (Table 1), indicating that sediment samples from Oginni, Olomoro and Ughelli are predominantly contaminated with PAHs of petrogenic origin while those from other locations contain PAHs from both petroleum and combustion sources. The PAHs are likewise of petrogenic origin in the soil

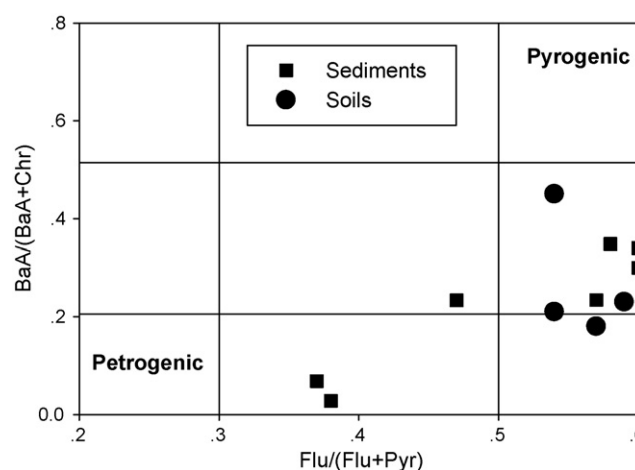


Fig. 3. Plot of anthracene/(anthracene + phenanthrene) (Ant/(Ant + Phe)) versus fluoranthene/(fluoranthene + pyrene) (Flu/(Flu + Pyr)) in sediments of the Niger Delta, Nigeria.

samples from Oginni, of mixed sources in Irri and Uzere soils and of combustion source in soils from Olomoro. The Icdp/(Icdp + Bghip) values ranged from 0.14 to 0.56 and 0.09 to 0.42 in the sediments and soils, respectively (Table 1), implying that PAHs in sediments from Qua Iboe River (QIRS) are largely petrogenically derived while those in sediments from other locations could be contributed from fossil fuel combustion.

The Phe/Ant and Flu/Pyr ratios in the soils from all the locations ranged from 6.0 to 9.2 and from 1.2 to 1.5, respectively (Table 1). These values strongly affirmed a predominant pyrogenic origin, with minor petrogenic contributions, of PAHs in the soil samples. However, the plot of BaA/(BaA + Chr) versus Flu/(Flu + Pyr) (Fig. 3) suggest that some sediment samples contain PAHs of mixed sources while others have PAHs of pyrogenic origin. On the other hand, PAHs in the soil samples are mainly of pyrogenic origin, consistent with the conclusions drawn based on other diagnostic indices. Our results show that PAHs in sediments of the Niger Delta are predominantly derived from petrogenic sources with some level of pyrogenic inputs in some areas which is evident in Great Kwa River, Imo River and Calabar River and surface soils (Fig. 4). Sediments from the hinterland hosting the majority of oil installations are mainly contaminated by PAHs of petrogenic origin which obviously has resulted from incessant oil pipeline leakages. About 1.5 million tons of crude oil were estimated to have spilled in different parts of the Niger Delta since the inception of oil exploration in 1958 [36]. Gas flaring – where an obsolete “open pipe flare” method

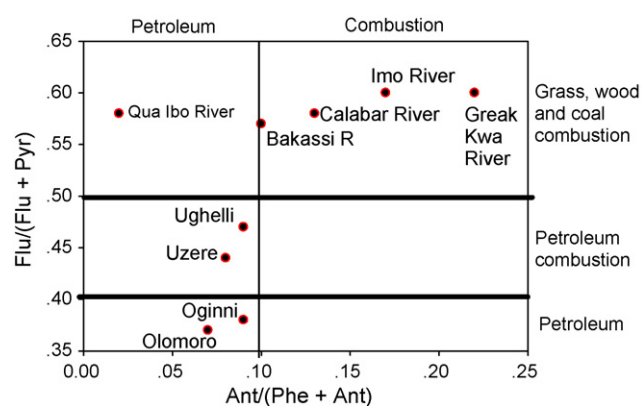


Fig. 4. Plot of benzo(a)anthracene/(benzo(a)anthracene + chrysene) (BaA/(BaA + Chr)) versus fluoranthene/(fluoranthene + pyrene) (Flu/(Flu + Pyr)) in the sediments and soils of the Niger Delta, Nigeria.

is being used by oil companies – is also believed to be responsible for the occurrence of PAHs of pyrogenic origin in some of the samples.

### 3.5. Assessment of potential ecological risk

The main concern about the occurrence of PAHs in the environment stems from the fact that they are mostly carcinogenic, both in humans and other mammals, whereas some PAHs have also been classified as mutagenic, e.g. dibenz[a,h]anthracene, benzo[a]pyrene and benzo[g,h,i]perylene [37,38]. There has been strong concern about the impact of crude oil exploration on the pollutant loads in the Niger Delta, which has caused and is still causing unrest among the citizenry and various interest groups in the area [36]. The dominant view blames oil production and its attendant consequences for the declining productivity of local economies that are mainly based on fisheries and agriculture [39,40], while some others say otherwise [8]. On the other hand, the World Bank in 1997 [41] disagreed with the popular view noted above, but attributed the productivity declines to the consequences of population increase and construction of upstream dams, among others [41]. With these conflicting claims, it should be beneficial to assess the possible impact of the PAH loads in sediments/soils on the ecosystem in the study area.

Based on the sediment quality guidelines (Table S3) which have been extensively tested and validated in several previous studies, such as that of Woodhead et al. [23], the majority of the sediments under investigation did not seem to pose adverse ecotoxicological effects, because the concentrations of all individual PAHs but naphthalene and chrysene were below the effect range low (ERL) and threshold effect level (TEL) (Tables S2 and S3). Conversely, the concentrations of naphthalene and chrysene were high enough to pose potential biological impairments in two main locations, Imo River and Oginni canal (Tables S2 and S3). The concentrations of both compounds were above the TEL values in the respective locations [42,43]. With the daily oil production output of 2.5 million barrels per day compared with the highest recorded value of 331 ng/g for total PAHs in the present study, it appears that crude oil exploration in the Niger Delta has a minimal impact on the PAH load in the area. This, however, does not undermine the need to ascertain other environmental pollution indices in the region.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.09.099.

### References

- [1] C.N. Ifeadi, J.N. Nwankwo, Oil spill in Nigerian petroleum industry—a critical analysis, *Napector* (1989) 11–45.
- [2] C.O. Dublin-Green, Benthic foraminifera as pollution indicators in Bonny estuary, Niger Delta. <http://hdl.handle.net/1834/2430> (accessed September 2009).
- [3] B.O. Ekpo, O.E. Oyo-Ita, H. Wehner, Even-n-alkane/alkene predominances in surface sediments from the Calabar River, SE Niger Delta, Nigeria, *Naturwissenschaften* 92 (2005) 341–346.
- [4] Energy Information Administration, Country analysis brief: Nigeria, <http://www.eia.doe.gov/emeu/cabs/Nigeria/Oil.html> (accessed April 2009).
- [5] S.E. Kakulu, O. Osibanjo, Pollution studies of Nigerian rivers: trace metal levels of surface waters in the Niger delta area, *Int. J. Environ. Stud.* 41 (1992) 287–292.
- [6] K. Howard, M. Horsfall, I.A. Spiff, S.C. Tene, Heavy metal levels in surface waters and sediments in an oilfield in the Niger delta, *Global J. Pure Appl. Sci.* 12 (2006) 79–83.
- [7] C.M.A. Iwegbue, F.E. Egbueze, K. Opuene, Preliminary assessment of heavy metals levels of soil of an oil field in the Niger delta, Nigeria, *Int. J. Environ. Sci. Technol.* 3 (2006) 167–172.
- [8] L.A. Daniel, S.A. Braide, The impact of accidental oil spill on cultivated and natural vegetation in a wetland area of Niger delta, Nigeria, *J. Hum. Environ.* 31 (2002) 441–442.
- [9] A.O. Abbas, W. Brack, Polycyclic aromatic hydrocarbons in Niger Delta soil: contamination sources and profiles, *Int. J. Environ. Sci. Technol.* 2 (2005) 343–352.
- [10] J.-Z. Wang, Y.-F. Guan, H.-G. Ni, X.-L. Luo, E.Y. Zeng, Polycyclic aromatic hydrocarbons in riverine runoff of the Pearl River Delta (China): concentrations, fluxes and fate, *Environ. Sci. Technol.* 41 (2007) 5614–5619.
- [11] H.G. Ni, F.H. Lu, X.L. Luo, H.Y. Tian, E.Y. Zeng, Riverine inputs of total organic carbon from the Pearl River Delta to the South China Sea, *Mar. Pollut. Bull.* 56 (2008) 1150–1157.
- [12] P.M. Gschwend, R.A. Hites, Fluxes of the polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States, *Geochim. Cosmochim. Acta* 45 (1981) 2359–2367.
- [13] J.C. Colombo, E. Pelletier, C. Brochu, M. Khalil, J.A. Catoggio, Determination of hydrocarbon sources using n-alkanes and polycyclic aromatic hydrocarbon indexes, *Environ. Sci. Technol.* 23 (1989) 888–894.
- [14] M.A. Sicre, J.C. Marty, A. Saliot, X. Aparicio, J. Grimalt, J. Albaiges, Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: occurrence and origin, *Atmos. Environ.* 21 (1987) 2247–2259.
- [15] H. Budzinski, I. Jones, J. Bellocq, C. Piérard, P. Garrigues, Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary, *Mar. Chem.* 58 (1997) 85–97.
- [16] G.C. Li, X.H. Xia, Z.F. Yang, R. Wang, N. Voulvoulis, Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River, China, *Environ. Pollut.* 144 (2006) 985–993.
- [17] M.B. Yunker, R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette, S. Sylvestre, PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition, *Org. Geochem.* 33 (489) (2002) 515.
- [18] G.-P. Yang, Polycyclic aromatic hydrocarbons in the sediments of the South China Sea, *Environ. Pollut.* 108 (2000) 163–171.
- [19] L. Webster, A.D. McIntosh, C.F. Moffat, E.J. Dalgarno, N.A. Brown, R.J. Fryer, Analysis of sediments from Shetland Island voes for polycyclic aromatic hydrocarbons, steranes and triterpanes, *J. Environ. Monit.* 2 (2000) 29–38.
- [20] National Oceanic Atmospheric Administration, Summary of Chemical Contaminant Levels at Benthic Surveillance Project Sites (1984–1992), US Department of Commerce, Maryland, 1998.
- [21] M. Russell, L. Webster, P. Walsham, G. Packer, E.J. Dalgarno, A.D. McIntosh, C.F. Moffat, The effects of oil exploration and production in the Fladen Ground: Composition and concentration of hydrocarbons in sediment samples collected during 2001 and their comparison with sediment samples collected in 1989, *Mar. Pollut. Bull.* 50 (2005) 638–651.
- [22] S.R. Wild, K.C. Jones, Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget, *Environ. Pollut.* 88 (1995) 91–108.
- [23] R.J. Woodhead, R.J. Law, P. Matthiessen, Polycyclic aromatic hydrocarbons in surface sediments around England and Wales, and their possible biological significance, *Mar. Pollut. Bull.* 38 (1999) 773–790.
- [24] P. Hess, The determination and environmental significance of planar aromatic compounds in the marine environment, Ph.D. Thesis, Robert Gordons University, 1998.
- [25] B.-X. Mai, J.-M. Fu, G.-Y. Sheng, Y.-H. Kang, Z. Lin, G. Zhang, Y.-S. Min, E.Y. Zeng, Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China, *Environ. Pollut.* 117 (2002) 457–474.
- [26] M. Notar, H. Leskovsek, J. Faganeli, Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the gulf of Trieste, northern Adriatic sea, *Mar. Pollut. Bull.* 42 (2001) 36–44.
- [27] I. Hashmi, G.K. Jong, S.K. Kyoung, P. Ji-Soo, Polycyclic aromatic hydrocarbons (PAHs) levels from two industrial zones (Sihwa and Banwal) located in An-san city of the Korean peninsula and their influence on lake, *J. Appl. Sci. Environ. Manage.* 9 (2005) 63–69.
- [28] L.L. Ma, S.G. Chu, X.T. Wang, H.X. Cheng, X.F. Liu, X.B. Xu, Polycyclic aromatic hydrocarbons in the surface soils from outskirts of Beijing, China, *Chemosphere* 58 (2005) 1355–1363.
- [29] Y.K. Matsushita, Y. Hisamatsu, Distribution of benzo[a] pyrene content in soil in urban area, *Jpn. Soc. Air Pollut.* 15 (1980) 348–352.
- [30] T. Amagai, Y. Takahashi, H. Matsushita, D. Morknoy, P. Sukasem, M. Tabucanon, A survey on polycyclic aromatic hydrocarbon concentrations in soil in Chiang-Mai Thailand, *Environ. Int.* 25 (1999) 563–572.
- [31] J.M. Neff, Polycyclic aromatic hydrocarbons in the aquatic environment sources, fates and biological effects in Applied Science, London, 1979, pp. 262.
- [32] J.P. Knezovich, F.L. Harrison, R.G. Wilhelm, The bioavailability of sediment-sorbed organic chemicals, *Water Air Soil Pollut.* 32 (1987) 233–245.
- [33] P. Baumard, H. Budzinski, P. Garrigues, H. Dizer, P.D. Hansen, Polycyclic aromatic hydrocarbons in recent sediments and mussels (*Mytilus edulis*) from the western Baltic sea: occurrence, bioavailability and seasonal variations, *Mar. Environ. Res.* 47 (1999) 17–47.
- [34] E.Y. Zeng, C. Vista, Organic pollutants in the coastal environment off San Diego, California. 1. Source identification and assessment by compositional indices of polycyclic aromatic hydrocarbons, *Environ. Toxicol. Chem.* 16 (1997) 179–188.
- [35] M.B. Yunker, L.R. Snowdon, R.W. Macdonald, J.N. Smith, M.G. Fowler, D.N. Skibo, F.A. Mclaughlin, A.I. Danyushevskaya, V.I. Petrova, G.I. Ivano, Polycyclic aro-

- matic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents seas, *Environ. Sci. Technol.* 30 (1996) 1310–1320.
- [36] J. Brown, Niger Delta bears brunt after 50 years of oil spills. <http://www.corpwatch.org/article.php?id=14202> (accessed September 2009).
- [37] M. Hall, P.L. Glower, in: C.S. Cooper, P.L. Glower (Eds.), *Chemical Carcinogenesis and Mutagenesis*, Springer, Berlin, 1990, p. 327.
- [38] J.C. Colombo, C. Barreda, N.C. Bilos, M.C. Migoya, C. Skorupka, Oil spill in the Rio de la Plata estuary, Argentina: hydrocarbon disappearance rates in sediments and soils, *Environ. Pollut.* 134 (2005) 267–276.
- [39] K.K. Aaron, Human rights violation and environmental degradation in the Niger Delta, in: E. Porter, B. Offord (Eds.), *Activating Human Rights*, Oxford, Barne, New York, 2006, pp. 193–215.
- [40] O. Ibeanu, Democracy, environment and security in Nigeria: reflections on environment and governance in the post-military era, in: *Annuals of the Social Science Academy of Nigeria*, 2002.
- [41] The World Bank, *Defining an Environmental Development Strategy for the Niger Delta*, Washington, DC, World Bank, 1997, p. 150.
- [42] E.R. Long, D.D. Macdonald, S.L. Smith, F.D. Calder, Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments, *Environ. Manage.* 19 (1995) 81–97.
- [43] A. Liu, Y. Lang, L. Xue, J. Liu, Ecological risk analysis of polycyclic aromatic hydrocarbons (PAHs) in surface sediments from Laizhou Bay, *Environ. Monitor. Assess.* (2009), doi:10.1007/s10661-008-0640-8.
- [44] X. Li, L. Ma, X. Liu, S. Fu, H. Cheng, X. Xu, Polycyclic aromatic hydrocarbon in urban soil from Beijing, China, *J. Environ. Sci.* 18 (2006) 944–950.
- [45] D.T. Wang, O. Meresz (Eds.), *Occurrence and Potential Uptake of Polynuclear Aromatic Hydrocarbons of Highway Traffic Origin by Proximally Grown Food Crops*, Springer Verlag, New York, 1982.
- [46] J.D. Butler, V. Butterworth, S.C. Kellow, H.G. Robinson, Some observations on the polycyclic aromatic hydrocarbon (PAH) content of surface soils in urban areas, *Sci. Total Environ.* 33 (1984) 75–85.
- [47] S.Y.N. Yang, D.W. Connell, D.W. Hawker, S.I. Kayal, Polycyclic aromatic hydrocarbons in air, soil and vegetation in the vicinity of an urban roadway, *Sci. Total Environ.* 102 (1991).
- [48] P. Weiss, A. Riss, E. Gschmeidler, H. Schentz, Investigation of heavy metal, PAH, PCB pattern and PCDDrF profiles of soil samples from an industrialized urban area (Linz, upper Austria) with multivariate statistical methods, *Chemosphere* 29 (1994) 2223–2236.
- [49] T. Spitzer, S. Kuwatsuka, Residue levels of polynuclear aromatic compounds in urban surface soil from Japan, *J. Chromatogr.* (1993) 305–643.
- [50] A.A. Meharg, J. Wright, H. Dyke, D. Osborn, Polycyclic aromatic hydrocarbon (PAH) dispersion and deposition to vegetation and soil following a large scale chemical fire, *Environ. Pollut.* 99 (1998) 29–36.
- [51] H.W. Mielke, G. Wang, C.R. Gonzales, B. Le, V.N. Quach, P.W. Mielke, PAH and metal mixtures in New Orleans soils and sediments, *Sci. Total Environ.* 281 (2001) 217–227.
- [52] C.D. Stalikas, C.I. Chaidou, G.A. Pilidis, Enrichment of PAHs and heavy metals in soils in the vicinity of the lignite-fired power plants of West Macedonia, *Sci. Total Environ.* 204 (1997) 135–146.
- [53] M.I. Bakker, B. Casado, J.W. Koerselman, J. Tolls, C. Koloffel, Polycyclic aromatic hydrocarbons in soil and plant samples from the vicinity of an oil refinery, *Sci. Total Environ.* 263 (2000) 91–100.
- [54] Z. Saltiene, D. Brukstiene, A. Ruzgyte, Contamination of soil by polycyclic aromatic hydrocarbons (PAH) in some urban areas, *Polycycl. Aromat. Compd.* 22 (2002) 23–35.
- [55] B. Skrbic, N. Miljevic, An evaluation of residues at an oil refinery site following fires, *J. Environ. Sci. Health A* 37 (2002) 1029–1039.
- [56] Y. Yang, X.X. Zhang, T. Korenaga, Distribution of polynuclear aromatic hydrocarbons (PAHs) in the soil of Tokushima, Japan, *Water Air Soil Pollut.* 138 (2002) 51–60.
- [57] B. Ruchaya, W. Gullaya, T. Ayako, H. Takada, Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand, *Mar. Pollut. Bull.* 52 (2006) 942–956.