Prime Scholars Library

Full Length Research Paper

Available online at https://primescholarslibrary.org/

Journal of Science and Geosciences

Vol. 6 (2), pp. 16 - 26, March, 2018

A similar appraisal of soil contamination by polycyclic aromatic hydrocarbons in Delta communities, Nigeria

Jameson O. E., Ajaino K. L, Ade A. G and Nwonye, S. N

University of Ibadan, Ibadan, Nigeria.

Abstract

This study determined, in comparison with guideline limits, the levels of Polycyclic Aromatic Hydrocarbons (PAH) in the soils at Eleme (highly industrialized) and Ahoada East (less industrialized) communities in the Niger Delta Area. Sixteen grab soil samples with 8 samples each from different locations in each community were collected at depth 0 - 15 cm using an auger. About 500 g of soil from each location were processed and analyzed for pH, moisture content, organic matter, phenol, and PAHs using standard methods. Data were analysed using descriptive statistics viz mean ± standard deviation as well as inferential statistics such as Man Whitney U test and simple regression at 5% level of significance. At Eleme, the highest concentration of phenol (1.04 ± 0.85%) was observed in samples at Ekporo. The highest levels of Benzo(a)pyrene (BaP) (1.54×10^5 ng/kg) were recorded at Onne. Soil samples close to the Petroleum Refinery at Alesa recorded the highest total PAH concentration (2.30×10^6 ng/kg) even though this was slightly lower than the EPA guideline value of 2.5×10^6 ng/kg. At Ahoada East, the highest phenol level (1.48 ± 0.99 mg/kg) was observed at Ula Ehuda. The highest BaP concentrations were observed at Ahoada town (1.57×10^5 ng/kg) . Also the highest total PAH levels (3.67×10^5 ng/kg) were recorded at Odiabidi and this was lower than the levels at Eleme and EPA guideline limits ($P < 0.05$). The mean level of total PAHs at Eleme which recorded the highest number (9) of individual components was 7 fold higher than that recorded at Ahoada East with only 3 components. Also at Eleme four locations compared to none at Ahoada East were classified as high risk sites. The study showed that the communities at Eleme when compared to Ahoada East may be more vulnerable to hazards associated with increased exposure to Soil PAH.

Keywords: Industry, Niger Delta Communities, Nigeria, PAHs, soil pollution.

INTRODUCTION

The main sources of Polycyclic Aromatic Hydrocarbons (PAHs) in soil are atmospheric deposition after local emission, long-range transport, and pollution from combustion gases emitted by industry, power plants, domestic heating and automotive exhausts (Konig et al., 1991). They are also formed during natural combustion like forest fires and volcanic activities (Hites et al., 1980).

The sources of PAH in soil are deposition from sewage (sewage sludge and irrigation water) and particulate waste products (compost); and also from the Carbonization of plant material (Grimmer et al., 1972). PAHs are harmful to environment and health of human being due to their high degree of mutagenicity and carcinogenicity when they enter the human body (Wong et al., 2009). Consequently, PAHs are widely studied with focus on their health- related impacts.

The extent of soil pollution by PAHs depends on factors such as the cultivation and use of the soil, its porosity, its lipophilic surface cover, and its content of humic substances (Windsor and Hites, 1978). In non polluted areas, studies have shown that the PAH concentrations were usually in the range of 5 - 50 ng/kg originating from Industries and other diffuse sources.

The concentration of individual PAH in soil resulting mainly from motor vehicle exhaust usually ranged between 1 and 2000 μg/kg. The PAH content of soil often decreased with increasing depth (Butter et al., 1984). Fritz (1971) reported various levels of PAHs from unspecified diffused sources in soil; Benzo(a)pyrene 800 μg/kg in humus, 100 - 800 μg/kg in garden soil, and 0.8 – 10 μg/kg in sand.

In the Niger Delta Area in Nigeria, studies carried out by Ana and Sridhar (2003) indicated pollution of soils by wastes from a chemical fertilizer industry. Abbas and Brack (2005) studied PAH levels in soils of a Niger Delta community using GC_MS method and found dominant PAHs viz pyrene, naphthalene and Benzo(k)fluoranthene whose concentration ranged between 182 ± 112 to 433 ± 236 ng/kg. In another study Anyakora et al. (2005) determined PAHs in sediment samples in some locations in the Niger Delta using GC-MS method and found concentrations mostly of the 5 - 6 ring PAH compounds ranging from 0 to 28 µg/kg.

In the present study we investigated the extent by which different activities in two communities of the Niger Delta Area affect the physicochemical quality of soils, especially their PAH contents using the HPLC method. The objectives were;

(a) To assess PAH concentration in soils at Eleme (Industrialized area) and Ahoada East (control area).
(b) To compare the values with the guideline limits of environmental agencies.
(c) To develop a risk map for the area.

MATERIALS AND METHODS

Description of the study area

The Niger Delta area located in the Southern part of Nigeria is an intricate, interconnected body of rivers, which drain from central and northern Nigeria through a landmass into the Atlantic Ocean. It consist of a huge deltaic wetland of about 70,000 square kilometers, consisting essentially of Rivers, Bayelsa, Delta, Akwa Ibom, Ondo, Imo, Edo, Cross River and Abia states. It is made up of four distinct ecological zones: coastal ridge barriers, mangroves, freshwater swamp forests, and lowland rain forests each of which offers diversity of settings for ecological resources and human activities. The area, which extends from the coast to about 150 km inland, shares similar climatic characteristics as the Equatorial region. It has two seasons, the wet season March to October, and dry season November to March. Rainfall is between 1500 and 3000 mm per annum with an annual mean of 4000 mm along the coast decreasing to about 2000 mm in the interior. The average temperature range is 17 - 24°C while the relative humidity ranges between 60 - 90%. The people of the area located in different settlements are of multiethnic origin and of diverse culture. The natives are primarily engaged in traditional occupations such as farming and fishing which constitute their dependable source of income and livelihood.

Eleme Local Government Area (LGA) constitutes one of the 24 Local Government Areas in Rivers State. It is located about 20 km away from Port Harcourt city, the Rivers state capital. Eleme as a whole is made up of 10 communities divided into two major tribes viz Nchia and Odido. The choice of Eleme as the main study area from the entire Niger Delta region was justified by the fact that it is the most industrialized semi- urban setting. Apart from oil related facilities such as the Shell Petroleum Development Company (SPDC) oil well at Ebubu, Petrochemical at Akpajo/Agbonjia, Refinery at Alesa/Okirika, it also has additional industries such as the chemical fertilizer plant at Onne and other oil servicing and non oil related companies.

Ahoada-East Local Government Area which served as the control area is also one of the local government areas in Rivers state. It shares closely similar geographic characteristics as Eleme. These include the rainfall and temperature pattern as well as the vegetation and soil types. The justification for its choice was that it does not have industrial facilities mentioned for Eleme. The LGA is broadly classified into 3 major ethnic settlements namely Upata, Akoh and Ahoada. It is made up of over 20 communities divided into 13 wards.

Soil nature and sampling process

The nature of soils used in this study were of the hydromorphic type comprising formations like the Beach ridge soils, mangrove swamp plain soils, Fresh water swamp soils, Sombrreiro-Warri-deltaic soils and Coastal plain sands (Rivers and Bayelsa States Environmental Action Plan, 1998). A total of 16 grab soil samples were collected purposively from both Eleme and Ahoada East communities as follows: At Eleme and Ahoada East, samples were collected at different locations from 8 communities each.

In each case, 500 g of the top soil (0 - 15 cm) was collected using an auger. Samples were stored in aluminum- foil covered containers and then conveyed to the laboratory for further processing and analysis. The description of sample locations at Eleme and Ahoada East are presented in Tables 1 and 2, respectively.

pH measurement

Fifty ml of distilled water was added to 20 g of soil sample in a glass beaker. The mixture was stirred for 10 min, left to stand for 30 min and stirred again for 2 min. The pH of the supernatant was then determined using an Orion research Digital pH meter model 407 A after prior calibrations (Anderson and Ingram, 1989).

Moisture content

The moisture content of soil is an indication of the amount of water present in the soil. It was determined based on the method described by Anderson and Ingram (1989). 1 g of a representative sample of the moist soil was placed in a clean, dry crucible of known mass with its lid securely in position. The mass of the container and moist soil was determined using a weighing balance model AE 163. Thereafter, the lid was removed and the crucible placed in oven maintained at 110 ± 5°C for 4 h to obtain a constant weight. The measurement was done in duplicate. The moisture content of the soil expressed as follows:

$$\text{Moisture content (\%)} = \frac{Moist\ soil - Dry}{soil} x100^{moist\ soil}$$

Table 1. Description of sample location at Eleme community.

S/NO	Community	Sample code	Location	Coordinates
1	Akpajo	SE 1	2 km away from EPCL	LAT 4803 LON 7.109
2	Agbonjia	SE 2	2 km away from EPCL	LAT 4803 LON 7.109
3	Alesa	SE 3	5 km away from PHRC	LAT4.786 LON7.119
4	Ebubu	SE 4	2 km from an old SPDC contaminated site	LAT 4.780 LON7.152
5	Ogale	SE 5	1 km from SPDC pipeline	LAT 4.788 LON 7.127
6	Eteo	SE 6	1 km away from pedestrian road	LAT 4.751 LON7.184
7	Ekporo	SE 7	location within a farm land	LAT 4.720 LON 7.211
8	Onne	SE 8	500 m away from a solid waste dump site	LAT 4.725 LON 7.153

Table 2. Description of sample location at Ahoada east community.

S/NO	Community	Sample code	Location	Coordinates
1	Igbushi Ahoada	SA1	50 m from the major road within a residential area	LAT 5.094 LON 6.666
2	Ulapata	SA2	50 m away from major road within a church premises	LAT 5.090 LON 6.626
3	Ahoada	SA3	100 m away from a petrol station off the major road	LAT 5.075 LON 6.654
4	Ula Ehuda	SA4	100 m away from the highway	LAT 5.140 LON 6.615
5	Odiabidi	SA5	within the community square	LAT 4.950 LON 6.638
6	Odiemerenyi	SA6	within a residential area	LAT 5.141 LON 6.668
7	Ihuoho	SA7	100 m away from Igboshi stream	LAT 5.159 LON 6.663
8	Edoha	SA8	within a market setting	LAT 5.029 LON 6.632

Organic carbon

The organic carbon content of soils was determined using Wakley-Black acid digestion method as described by Anderson and Ingram (1989). About 1 g of soil sample was placed into a block digester tube (sample weight) and added 5 ml of potassium dichromate solution and 7.5 ml of conc. H_2SO_4 . The tube was placed in a pre-heated block at 145 - 155°C for 30 min then removed and allowed to cool. The digest was quantitatively transferred into a 100 ml conical flask and added 0.3 ml of o-phenanthroline-ferrous complex (Ferroin) indicator solution, then stirred and mixed properly using magnetic stirrer. The digest was then titrated with ferrous ammonium sulphate solution with end point indicating a change from greenish to brown coloration. The organic carbon content expressed in percentage as follows was based on 77% recovery factor:

$$\%\ \text{Organic Carbon} = \frac{N(T - B)}{W} \times 0.390$$

Where N = Normality of $KMnO_4$
T = Volume of $KMnO_4$ used in titration of soil
B = Volume of $KMnO_4$ used in titration of blank
W = Weight of soil in g

Table 3. Physico-Chemical Characteristics of soils at Eleme

Parameter	SE1 Akpajo	SE2 Agbonjia	SE3 Alesa	SE4 Ebubu	SE5 Ogale	SE6 Eteo	SE7 Ekporo	SE8 Onne	Mean ± SD	Critical values
pH value	6.40± 1.16	6.95± 0.89	7.10± 1.04	6.00± 0.98	5.50± 1.67	7.60± 2.03	7.15±1.88	7.55 ± 2..09	6.78 ± 1.47	6-6.5[a]
Moisture Content (%)	7.90± 1.55	7.77± 1.98	12.7± 2.04	19.6± 2.65	14.8± 1.74	14.7± 1.44	15.2± 1.39	9.31± 2.44	12.7 ±1.90	-
Organic matter (%)	7.49± 1.54	67.5± 1.35	24.0± 2.08	56.2± 3.65	29.8± 2.13	4.98± 0.87	44.1± 2.75	10.5± 1.33	30.6 ±1.96	-
C%	4.33± 1.24	39.1± 2.18	13.9± 1.04	32.5± 3.12	13.7± 2.33	2.88± 0.88	25.5± 2.66	6.06± 0.95	17.2 ±1.80	3-5[a]
Phenol (mg/kg)	0.30± 0.12	0.37± 0.09	0.30± 0.05	0.30± 0.12	0.15± 0.19	0.59± 0.23	1.04± 0.85	0.15± 0.09	0.40 ±0.22	-

The different concentrations measured and pH values are expressed as: average ± error, n = 2, [a] Adeoye and Agboola (1985).

Organic matter content

The organic matter content in the soils was determined by multi-ply-ing the organic carbon content from the procedure above by 1.742 (using the assumption that organic matter contains approxi-mately 58% carbon).

Phenol

Phenol in soil was determined using the ASTM method No 1783 (1980) after slight modifications to suit laboratory conditions used in Research and Development (R&D) laboratory at the Nigerian Natio-nal Petroleum Corporation (NNPC). About 10 g of soil was placed in 250 ml conical flask and leached with 100 ml D/W. The mixture was shaken vigorously and allowed to stand for 30 min. Shaking was repeated at intervals. A clear 100 ml of mixture was filtered and used for the phenol test. This method was limited to only soluble phenolic compounds. From 100 ml of the leached sample, 5 ml of NH_4Cl was added and pH adjusted to 9.8 –10.2 using NH_4OH. After this, 2 ml of 4-amino antipyrine and 2 ml of $K_5Fe(CN)_6$ were added and then mixed immediately. After 15 min, reading was taken at an absorbance of 510 nm. This analysis was done in duplicate and the procedure repeated for blank. The concentration of Phenol in soil was expressed in mg/kg

Determination of PAHs

The determination of PAHs was done using HPLC and this entailed several operations including, extraction, purification, concentration and solvent exchange.

Prior to the extraction, soil samples were air- dried openly on the benches in the laboratory for 48 h. The dried soil samples were then sieved using a 0.2 mm sieve and 100 g of sieved sample were introduced into a thimble ready for extraction.

Soil extraction: The extraction of the soil samples was doneaccording to modified standard method described by Blumer and Youngblood (1975). The soil extraction process involved the use of
a soxhlet extractor model-6-4828 manufactured by Supelco and made in Great Britain. About 100 g of the soil samples placed in a thimble were introduced into the soxhlet apparatus with 120 ml of the extracting solvent (Cyclohexane/ Dichloromethane: 3/1); The extraction lasted 2 h at a regulated temperature of 80°C with repea-ted refluxing. Extraction process was made in duplicate.

Concentration, clean up and solvent exchange: The extractsample was concentrated (in a K-D flask concentrator tube with a refluxing column), cleaned up (in a chromatography column) and then concentrated until 5 ml by solvent exchange (acetonitrile) US EPA (1994).

Sample analysis: The analysis of extracts from soil samples wascarried out using an HPLC made up of an auto sampler of model Waters 717, a pump of model Waters 610 for both the fluid unit and valve station and Waters 6.00 E for the pump system controller; a photodiode detector of model Waters IM 996, a fluorescence detec-tor of model Waters 470 all made in Millipore. The software millen-nium 32 was used and the method of operation was of the isocra-tic/gradient type with a combination of acetonitrile and deionised filtered water as the mobile phase and a stationary phase made up of silica gel loaded in 5 µm HPLC column, SUPELCOSIL^{TM} LC-PAH col: 12435-007of dimensions 15 cm x 4.6 mm.

The analysis of unknown samples followed a method set created using a set of standards: 16 WHO prioritized PAH components. The unknown sample was then run against this standard, calibrated, integrated and the concentration of the PAH components based on the size of the peaks quantified. Results were expressed in ng/Kg

Statistical analysis

Data were analysed using descriptive statistics viz range, mean ± standard deviation and subjected to inferential statistics using Man Whitney U test and simple regression at 5% level of significance.

RESULTS

Soil quality at Eleme

The result of the physico-chemical characteristics of the soils at Eleme shows that the highest pH value (7.60 ± 2.03) was recorded in sample SE 6 (Ekporo) while sam-ples SE 2 Agbonjia (67.5 ± 1.35%) and SE 4 Ebubu (56.2 ± 3.65%) recorded the highest organic matter contents, respectively (Table 3). The highest phenol (1.04 ± 0.85 mg/kg) and Pb (0.09 ± 0.13 mg/kg) levels were recorded in samples SE 7 Ekporo and SE 6 Eteo, respectively. The results in Table 4 show that soil samples close to the Refinery at Alesa recorded the highest total PAH concen-tration (2.30 x 10^6 ng/kg). Soils at Ebubu (1.08 x 10^6 ng/kg), Ogale (1.04 x 10^6 ng/kg), Ekporo (1.14 x 10^6 ng/kg) and Onne (7.92 x 10^5 ng/kg) also recorded signifi-

Table 4. Concentration of PAHs in soils at Eleme (Results expressed in ng/kg).

PAH Components	SE1 Akpajo	SE2 Akpanja	SE3 Alesa	SE4 Ebubu	SE5 Ogale	SE6 Eteo	SE7 Ekporo	SE8 Onne	Range
Naphthalene	-	-	3.20×10^{5}	-	-	-	-	-	$0\text{-}3.20\times10^{5}$
Acenaphthene	-	-	-	1.74×10^{5}	-	-	-	1.74×10^{5}	$0\text{-}1.74\times10^{5}$
Acenaphthylene	-	-	-	3.99×10^{-2}	-	-	-	4.45×10^{-3}	$0\text{-}3.99\times10^{-2}$
Fluorene	-	-	3.50×10^{5}	1.61×10^{3}	-	4.37×10^{5}	4.32×10^{5}	4.64×10^{5}	$0\text{-}4.64\times10^{5}$
Anthracene	2.5×10^{-6}	2.5×10^{-6}	7.52×10^{-3}	5.55×10^{-3}	1.59×10^{-2}	-	-	-	$0\text{-}1.59\times10^{-2}$
Phenanthrene	-	-	4.89×10^{5}	-	4.35×10^{5}	-	4.35×10^{5}	-	$0\text{-}4.89\times10^{5}$
Fluoranthene	-	-	1.50×10^{5}	1.73×10^{5}	1.37×10^{5}	-	1.46×10^{5}	-	$0\text{-}1.73\times10^{5}$
Pyrene	-	-	3.81×10^{5}	5.78×10^{5}	4.68×10^{5}	-	-	-	$0\text{-}5.78\times10^{5}$
	-	-	1.36×10^{5}	-	-	-	-	-	$0\text{-}1.36\times10^{5}$
Chrysene	-	-	1.79×10^{5}	-	-	-	-	-	$0\text{-}1.79\times10^{5}$
Benzo(b) fluoranthene	-	2.58×10^{-2}	-	-	-	-	-	-	$0\text{-}2.58\times10^{-2}$
Benzo(k) fluoranthene	9.80×10^{-2}	-		-	-	-	-	-	$0\text{-}9.80\times10^{2}$
Benzo(a) pyrene	-	-	2.73×10^{4}	1.49×10^{5}	-	1.22×10^{5}	1.23×10^{5}	1.54×10^{5}	$0\text{-}1.54\times10^{5}$
Dibenzo(a,h) anthracene	1.96×10^{-3}	-	-	-	-	-	-	-	$0\text{-}1.96\times10^{-3}$
Indeno(1,2,3-cd) pyrene	1.08×10^{-2}	9.07×10^{3}	-	-	-	-	-	-	$0\text{-}1.08\times10^{-2}$
Benzo(g,h,i) perylene	-	-	-	-	-	-	-	-	-

Values (ng/Kg) are means of two measurements.

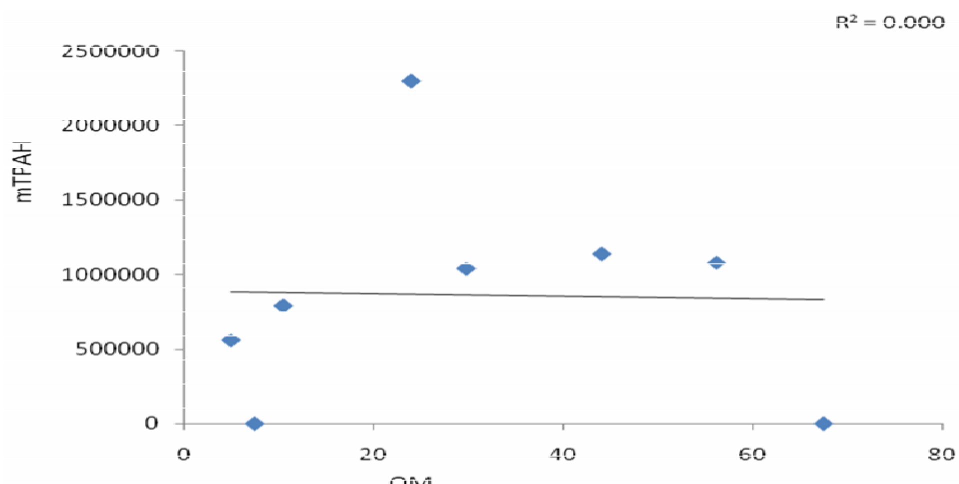

Figure 1. Correlation between OM and PAH at Eleme.

cantly high levels of total PAH. Incidentally, these locations excluding Ogale recorded high levels of Benzo(a)pyrene with the soil at Onne recording the highest concentration (1.54×10^{5} ng/kg). A relationship between the organic matter content of the soil and PAH levels was assessed for the various soil samples. At Eleme there were no correlations between the PAH and the OM levels in the soils ($P > 0.05$) (Figure 1). This probably may be due to some variations soil properties and environmental factors.

Soil quality at Ahoada East

The physico-chemical characteristics of soils at Ahoada

Table 5. Physico-chemical characteristics of soils at Ahoada East.

Parameter	SA1 Igbushi Ahoada	SA2 Ulapata	SA3 Ahoada	SA4 Ula Ehuda	SA5 Odiabidi	SA6 Odiemerenyi	SA7 Ihuoho	SA8 Edoha	Mean ± SD	Critical values
pH value	6.10± 1.97	6.75± 1.56	7.30 ± 2.32	4.40 ±1.96	6.90± 2.33	4.85± 1.96	5.85± 0.87	6.70±1.54	6.11±1.80	6-6.5[a]
Moisture Content (%)	23.2± 2.34	18.1± 2.16	17.9± 3.21	8.03± 1.23	11.9± 2.32	9.17± 2.07	10.3± 2.11	19.4± 1.88	14.8±2.10	-
Organic matter (%)	69.2± 5.74	43.1± 4.32	21.9± 3.28	29.6± 3.26	20.1± 4.34	20.1± 4.34	11.7± 1.96	55.9± 4.56	33.9±3.9	-
C%	40.0± 3.24	24.9± 2.56	12.7± 2.15	17.1± 1.89	11.6± 2.42	11.6± 2.13	6.77± 1.74	32.3± 3.54	19.6±2.30	3-5[a]
Phenol (mg/kg)	0.22± 0.05	0.15± 0.08	0.15± 0.09	1.48± 0.99	0.59± 0.23	4.81± 1.94	0.74± 0.12	0.07± 0.03	1.03±0.44	-

The different concentrations measured and pH values are expressed as: average ± error, n = 2.
[a] Adeoye and Agboola (1985).

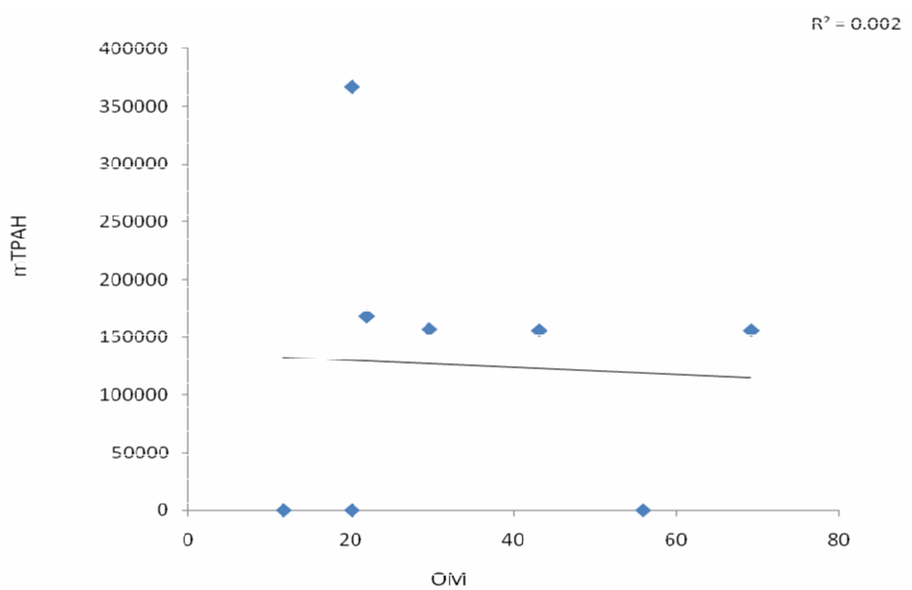

Figure 2. Correlation between OM and PAH at Ahoada East.

East was carried out and involved measurement of pH value, moisture content, organic matter, organic carbon and phenol. Table 5 indicates that sample SA1 (Igbushi Ahoada) recorded the highest levels of moisture content (23.2 ± 2.34%), as well as organic matter (69.2 ± 5.74%) and organic C contents (40.0 ± 3.24%). The highest phenol level was recorded in sample SA4 (Ula Ehuda) 1.48 ± 0.99 mg/kg. At Ahoada-East, the highest total PAH levels were recorded at Odiabidi (3.67×10^5 ng/kg). Benzo-(a)pyrene was found in all the samples at various locations except at Odiemerenyi and Ihuoho. The highest concentrations of Benzo(a)pyrene were found in soils at Ahoada (1.68×10^5 ng/kg) and Ula- Ehuda (1.57×10^5 ng/kg), respectively (Table 6). Similarly at Ahoada East there were no correlations between the PAH and the OM levels ($P > 0.05$) (Figure 2).

Soil PAH burden at Eleme and Ahoada East

From Figure 3, the mean PAH levels at Eleme were 7 folds higher than that recorded at Ahoada East. However, statistically there was no significant differences ($p = 0.208$) between PAH levels recorded at Eleme and Ahoada East. There was also no significant difference ($p > 0.05$) between PAH levels recorded at Eleme and the guideline limits. But there was significant difference ($p>0.05$) between PAH levels observed at Ahoada East and the guideline limits.

Table 6. Concentration of PAHs in soils at Ahoada East (Results expressed in ng/kg).

PAH Components	SA1 Igbushi Ahoada	SA2 Ulapata	SA3 Ahoada	SA4 Ula-Ehuda	SA5 Odiabidi	SA6 Odiemerenyi	SA7 Ihuoho	SA8 Edoha	Range
Naphthalene	-	-	-	-	-	-	-	-	-
Acenaphthylene	-	-	-	-	-	-	-	-	-
Acenaphthene	-	-	-	-	1.59×10^{5}	-	-	-	$0\text{-}1.59 \times 10^{5}$
Fluorene	-	-	-	-	-	-	-	1.16×10^{-3}	$0\text{-}1.16 \times 10^{-3}$
Anthracene	-	-	5.60×10^{3}	-	-	1.69×10^{-2}	-	-	$0\text{-}1.69 \times 10^{-2}$
Phenanthrene	-	-	-	-	-	-	-	-	-
Fluoranthene	-	-	-	-	-	-	-	-	-
Pyrene	-	-	-	-	-	-	-	-	-
Benzo (a) anthracene	-	-	-	-	-	-	-	-	-
Chrysene	-	-	-	-	-	-	-	-	-
Benzo (b) fluoranthene	-	-	1.07×10^{4}	-	-	-	1.33×10^{-2}	2.33×10^{-2}	$0\text{-}1.07 \times 10^{4}$
Benzo (k) fluoranthene	-	-	-	-	5.42×10^{4}	-	-	-	$0\text{-}5.42 \times 10^{4}$
Benzo (a) pyrene	1.56×10^{5}	1.56×10^{5}	1.57×10^{5}	1.57×10^{5}	1.54×10^{5}	-	-	2.78×10^{-3}	$0\text{-}1.57 \times 10^{5}$
Indeno (1, 2, 3, cd) pyrene	-	-	-	-	-	-	7.48×10^{-3}	-	$0\text{-}7.48 \times 10^{-3}$
Dibenzo (a, h) anthracene	-	-	-	-	-	-	-	-	-
Benzo (g, h, i) perylene	-	-	-	-	-	-	-	-	-

Values (ng/Kg) are means of two measurements.

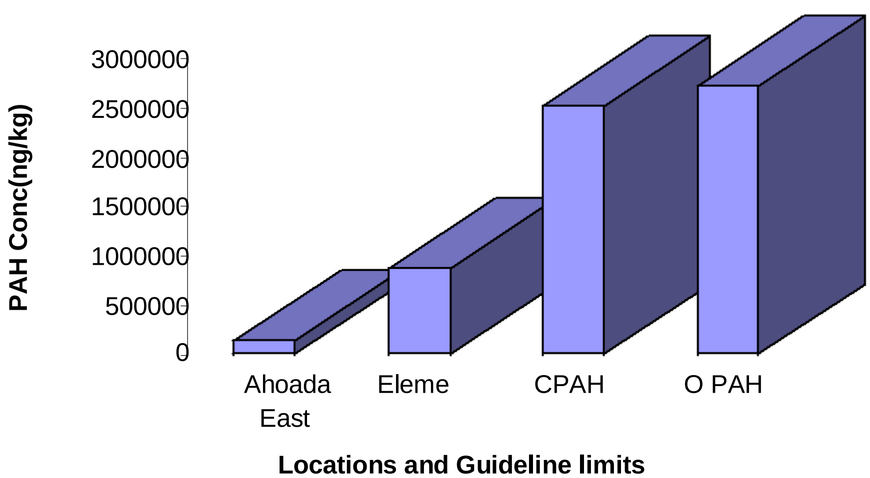

Figure 3. Mean PAH levels at Eleme and Ahoada compared with Swedish EPA limits(Swedish EPA, 2000).
Carcinogenic PAHs (CPAH-Sum of 7): 2.5 x 106 ng/kg
Other PAHs (OPAH-sum of 9):2.7 x 106 ng/kg
From the list of WHO prioritized 16 PAH compounds, 7 are considered carcinogenic

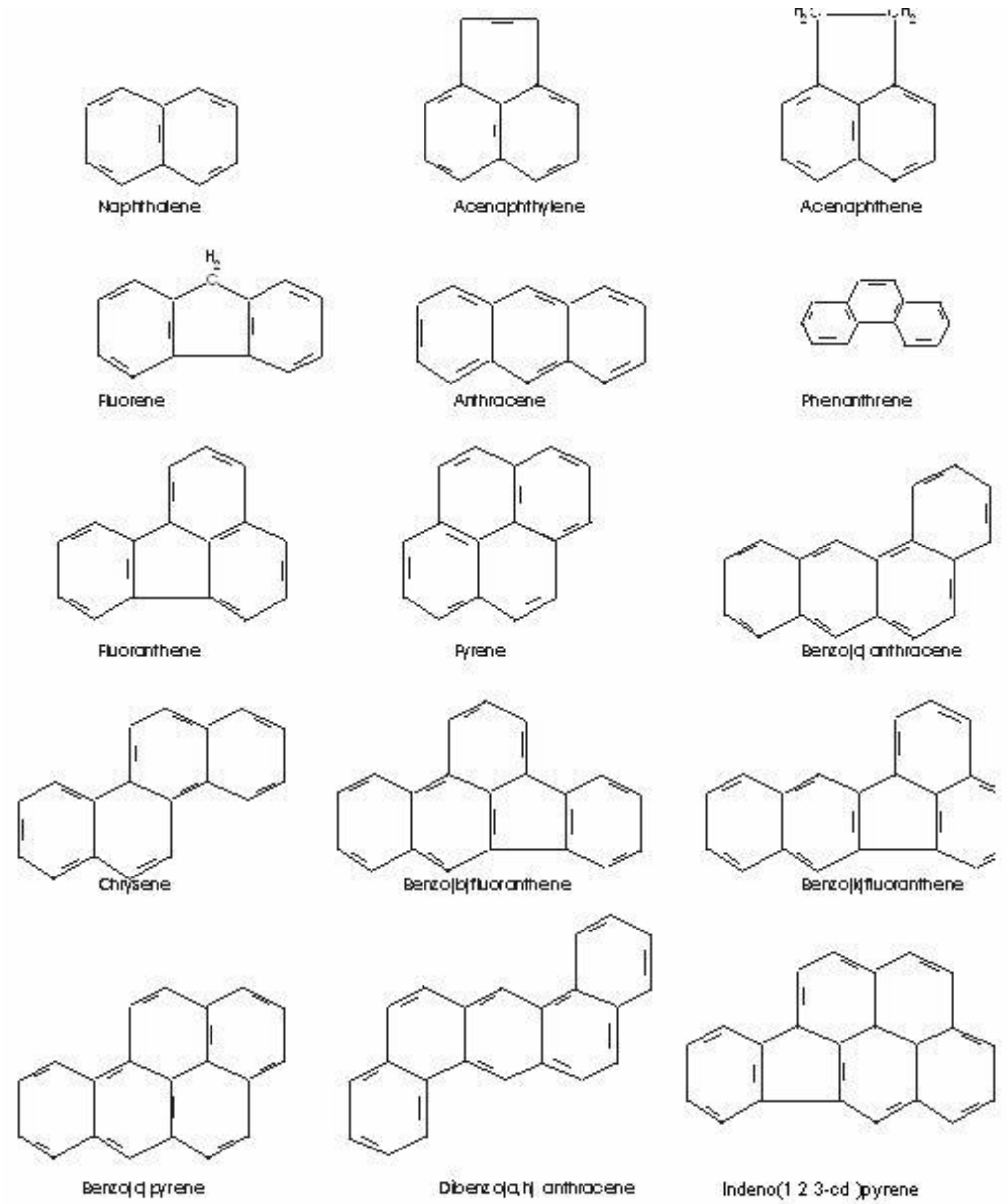

Figure 4. Structures of 15 identified PAHs in soil samples.

The PAH analysis shows that with the exception of benzo(ghi)perylene 15 out of the 16 PAHs prioritized by EPA/WHO were present in soils at Eleme while at Ahoada East only 7 of the PAHs namely acenaphthene, fluorene, anthracene, benzo(b)fluoranthene, benzo(k) fluoranthene, benzo(a)pyrene and indeno(I 2 3-cd)pyrene were present. The structures of the identified PAHs are shown in Figure 4.

Soil PAH risk map

The risk map (Figure 5) was developed based on a classification of the soil PAH concentrations into the following >1.0 x 10^6 ng/kg, 1.0 - 1.0 x 10^6 ng/kg and < 1.0 ng/kg for High Risk (HR), Medium Risk (MR) and Low Risk (LR) respectively. Communities with red codes have high PAH concentrations and belong to high risk group, those with purple code have moderate PAH concentrations and belong to the medium risk group while communities with the blue code have low PAH concentrations and belong to the low risk group.

By implication 4 locations namely Alesa, Ogale, Ebubu and Eteo at Eleme and non at Ahoada East recorded soil PAH levels classified as high risk with pockets of both medium and low risk soil PAH levels also recorded in the two study communities.

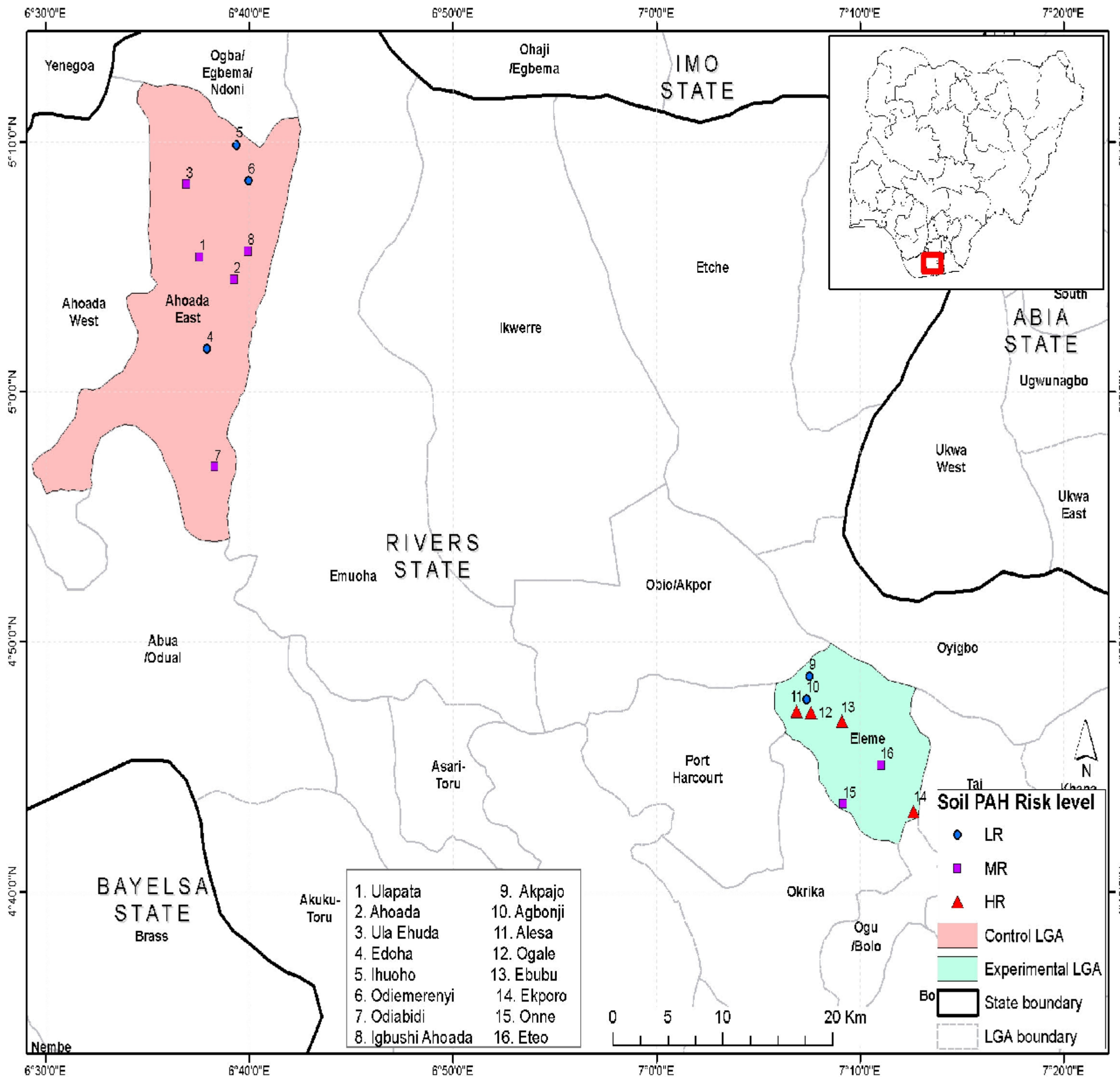

Figure 5. Risk Map for Soil PAHs at Eleme and Ahoada East.

DISCUSSION

The physicochemical characteristics of the soils at Eleme indicated that most of the parameters such as pH value and percentage organic carbon were within the critical levels. At Ahoada East, soils at Ula Ehuda and Odiemerenyi recorded low pH values, which were below critical levels while other parameters were within critical levels. Soils at Ahoada East were also richer in organic matter content than those at Eleme.

For PAH levels, all the 16 PAH components except Benzo(ghi)perylene were found in soils obtained from selected locations at Eleme. Altogether 9 components were recorded in soils near the Port Harcourt Refinery at Alesa with anthracene and Benzo(a)pyrene being the most dominant in soils found in that locality. This location also recorded the highest total PAH level (2.30 x 10^6 ng/kg) which was found to be within the guideline limits (2.5 x 10^6 ng/kg) given by Swedish EPA (2000). The source of these PAHs may have been from pollution arising from the petroleum tanker deposits close to the vicinity or from combustion by-products emitted by industry or nearby power plants as reported by Hembrock-Heger and Konig (1990) and Konig et al. (1991).

However, one of the highest total PAH levels (1.08 x 10^6 ng/kg) was recorded in soil samples close to an old SPDC oil field at Ebubu. This location recorded 7 components and was the next highest number. The increased pollution load of PAH in Ebubu soils may have been associated with the rich organic soil: its lipophilic surface nature and high content of humic substances according to Windsor and Hites (1978). The highest levels of Benzo(a)pyrene, a PAH toxicity indicator were found at Alesa, Ebubu and Onne which collectively harbour the highest number of industries in the whole area. The range of values of the PAH components recorded in majority of the soil samples were comparable to values reported by Thomas (1986) and Jones et al. (1989a, b).

Soils from Ahoada East particularly at Ahoada, Odiabidi and Edoha communities were found to contain the highest number (3) of individual PAH components with Benzo(a)pyrene [B(a)P] being the most dominant in soils found in that locality. B(a)P occurred in 6 out of the 8 soil samples and the highest concentration was recorded in soils close to the village square at Odiabidi. Also the highest concentration of total PAH was recorded in soils close to the village square at Odiabidi.

The soils at Ahoada main town close to the motorway and a petrol station recorded the next highest concentration for Benzo(a)pyrene. This may have originated from the petrol station spills. Even though the soils in this area were not exposed to the high levels of pollution as observed at Eleme, it is believed that the sources of PAH may have been from deposition from sewage, irrigation water, particulate waste products from compost (Konig et al., 1991), carbonization of plant material (Grimmer et al., 1972) or unspecified diffused sources in soil (Fritz, 1971).

Although the Mann-whitney test did not indicate any significant differences in the PAH levels between Eleme (experimental area) and Ahoada East (control area), the range of values succinctly showed that Ahoada East recorded lower values as depicted by the risk map. Nevertheless, these values were also higher than those reported in America and parts of Europe for Benzo(a) pyrene (2 μg/kg) by Van et al. (1998).

Conclusion

The present research assessed the levels of PAHs in a highly industrialized community, Eleme, and compared the outcome with observations at Ahoada East, a less industrialized community still found within Nigeria's Niger Delta Area.

The study revealed that most of the physico-chemical parameters were within guideline limits and that most levels at Eleme were expectedly higher than values obtained for Ahoada East. The most contaminated soils at Eleme was at Alesa community where the petroleum refinery is located . This location recorded the highest number of individual PAH components (9) with the highest total PAH level (2.30 x 10^6 ng/kg). This value though slightly lower than the EPA guideline limits could portend serious health hazard to the community.

Statistically there were no significant differences between the total PAH levels recorded at Eleme and Ahoada East, even though in real values the levels recorded for the former were 7 folds higher than that recorded in the later. The heavily industrialized communities of Alesa, Ebubu and Onne at Eleme area recorded the highest levels of Benzo(a)pyrene (the main PAH toxic indicator). This suggests that populations at Eleme may be at higher level of health risk compared to those at Ahoada East.

REFERENCES

Adeoye GO, Agboola AA (1985). Critical levels for soil pH, available P, K, Zn and Mn and Maize ear leaf content of P, Cu, and Mn in Sedimentary soils of South western Nigeria, Agronomy Experimental Manual, University of Ibadan, Ibadan, Nigeria.

ASTM American Society for Testing and Materials (1982). Annual book of ASTM standards part 31, water: Philadelphia, ASTM. p. 789.

AmericanAcademy of Pediatrics, AAP (1987). (Committee on Environmental Hazards and Committee on Accident and Poison Prevention of the American Academy of Pediatrics). Statement on childhood lead poisoning. Pediatrics. 79: 457-65.

Ana OE (2003). Polycyclic Aromatic Hydrocarbons and the Risk of Human Exposure in Selected Communities of the Niger Delta Area, Nigeria. Unpublished Ph.D Thesis. University of Ibadan, Ibadan, Nigeria

Ana GREE, Sridhar MKC (2004). Soil quality near a chemical fertilizer Industry at Port Harcourt, Nigeria. African Journal of Environmental Assessment and Management (AJEAM) 8: 19-26.

Anderson JM, Ingram JSI (1989). Tropical Soil Biology and Fertility: A Handbook of Methods. CAB International, UK. 1-100.

Anyakora C, Ogbeche A, Palmer P, Coker H, Ukpo G, Ogah C (2005). GC-MS Analysis of Polynuclear Aromatic Hydrocarbons in Sediment samples from the Niger Delta Region. Chemosphere. 60(7): 990-997.

BlummerM, Youngblood WW (1975). Polycyclic Aromatic Hydrocarbons in Soils and Recent Sediments. Sci. 188: 53-55.

Bowen JM (1979). Environmental Chemistry and Elements. Academic Press, London, UK, 220-237.

ButlerJD, Butler WV, Kellow SC, Robinson HG (1984). Some observations on the polycyclic aromatic hydrocarbons (PAH) content of surface soils in urban areas. Sci. Total Environ. 33: 75-85.

Dorn CR, PiierceJO, Chase GR, Philips PE (1975). Environmental Contamination by lead, cadmium, zinc and copper in a New LEAD-Producing Area. Environmental Res. 9: 159-172.

Fritz W (1971). The extent sources of contamination of our food with carcinogenic hydrocarbons] *Ernahrungs for schung*, 16: 547-557 [in German].

Grimmer G, Jacob J, Hildebrandt A (1972). [Hydrocarbons in the human enviroment. 9. Content of polycyclic hydrocarbons in Icelandic soil.*] Zkrebsforsch*. 78: 65-72 (in German).

Grova N, Feidt C, Crepineau C, Laurent C, Lafargue PE, Hachimi A Rychen G (2002). Detection of polycyclic aromatic hydrocarbon level in milk collected near potential contamination sources, J. Agricult. Food Chem. 50 (1): 4640–4642.

Hembrock-Heger A, Konig W (1990). Vorkommen und Transfer von polycycclischen aromatischen kohlenwasserstoffen in Boden und pflanzen.VDI Berichte 837: 815-830.

HitesRA, Lafamme RE, Windsor JG (Jr)(1980). Polycyclic aromatic hydrocarbons in marine/aquatic sediments: Their Ubiliquity. In: petakisl and Weiss FTed. Petroleum in the Marine enviroment (Advances in Chemistry Series No. 185). Washington DC, American Chemical Society, pp. 283 – 311.

Howari FM, Au-Rukah Y, Goodell PC (2004). Heavy metal pollution of soils along North Shuna-Aqaba Highway, Jordan. Int J. Environ Pollu. 22(5): 597-607.

Jones KC, Grimmer G, Jacob J, Johnson AE (1989b). Changes in the polynuclear aromatic hydrocarbon content of wheat grain and pasture grassland over the last century from site in the UK Sci. Tech. Environ. 8: 117-130.

Jones KC, Statford JA, Waterhouse KS, Vogts NB (1989a). Organic contaminants in Welsh soils: Polynuclear Aromatic hydrocarbons. Env Sci. Technol. 23: 540-550.

Konig W, Hembrock -Heger A, Wilkens M (1991). (Persistent organic chemicals in soil – routes of entry and occurrence]. Umweltwissensch schadstoff – Forsch, 3: 33-36 (in German).

Lardon JR (1991). Booker tropical soil Mannual. A handbook for soil survey and Agricultural land Evaluation in the Tropics and sob-tropics. Longman Scientific and technical Harlow.

Monicke R (1982). Multi-layer study of heavy metal transfer soil/plant and consequences for agricultural use. R. Saclisische Lan dessanstalt for land wirtschaft, 04159 Leipzig, Germany, VDL-UFA-Verlag.

Mottier P, Parisod RJ, Turesky J (2000). Quantitative determination of polycyclic aromatic hydrocarbons in barbecued meat sausages by gas chromatography coupled to mass spectrometry, J. Agric. Food Chem. 48(1): 1160–1166.

Olajire A, Brack W (2005). Polycyclic Aromatic Hydrocarbons in Niger Delta Soil: Contamination Source and Profiles. Int Journal of Environ Sci Technol. 2(4): 343-352.

Rivers and Bayelsa States Env Action plan (1998). (Description of soil types in the State Environmental Action plan report for Rivers and Bayelsa states in the Niger Delta Area, Nigeria.

Thomas W (1986). Principal component analysis of trace substance concentration in rain-water samples. Atmos Environ. 20: 995-1000.

US EPA (1994). Soxhlet Extraction—Method 3541.Methods in Soil Extraction for PAHs and Purification.

Van BTC, StwijfzSC (1993). Effects of benzo (a) pyrene on survival, growth and energy reserves in terrestrial isopods omiscus asellus and porcellio scaber. Sci Total Environ. Suppl (Part II): 921-930.

Wang Y, Liu CS, Li FB, Liu CP, Liang JB (2009). Photodegradation of polycyclic aromatic hydrocarbon pyrene by iron oxide in solid phase. J. Hazardous Mater. 162: 716–723.

Windsor JG (Jr), Hites RA (1978). Polycyclic aromatic hydrocarbons in Gulf of marine sediments and Nova Scotial Soils. Gochini, Cosmochim Acta. 41: 27-33.