

## Polycyclic aromatic hydrocarbons in Niger Delta soil: contamination sources and profiles

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**ABSTRACT:** The distribution and sources of PAHs in soil as well as PAHs profiles have been investigated in areas with anthropogenic pollution in the Niger Delta (Nigeria) such as Warri and Ughelli. PAHs were identified in 21 soil samples (0- 10cm upper layer) collected in May, 2003. The typical total PAHs level in Niger Delta soil ranged from  $182 \pm 112$  – to  $433 \pm 256$   $\mu\text{g/kg dw}$ . PAH concentrations in soil samples from Warri Refinery, Tanker Loading point and Ugboko via Rapele oil field were quite high ( the mean  $\Sigma$ PAH concentrations were 433, 402 and 384  $\mu\text{g/kg dry weight}$  respectively). The dominant PAHs in soil samples were pyrene, naphthalene and benzo[k]fluoranthene. The soil total PAHs ( $\text{PAH}_{\text{tot.}}$ ) concentration, normalized to organic carbon content (OC), ranged from 11.4 to 47.2  $\text{mg PAH}_{\text{tot.}}/\text{kg OC}$ ; and showed that organic matter of the soil samples from Quality Control Centre, Ughelli West is highly contaminated with PAHs and had a value of  $47.2 \pm 31.2$   $\text{mg PAH}_{\text{tot.}}/\text{kg OC}$ . Two and three ring aromatic hydrocarbons predominated in soil samples from Ughelli West , Tanker Loading point and Delta Steel Company, which is indicative of petrogenic origin.

**Key words:** PAHs, soil, profile, GC/MS, Niger Delta, Nigeria

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### INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) emitted in the environment originate mainly from anthropogenic sources. They are the products of thermal decomposition, formed during incomplete combustion of organic materials and geochemical formation of fossil fuels. The most significant anthropogenic sources of PAH include heat and power generation from coal and other fossil fuels, coal production, petroleum refining, cracking of crude petroleum, incineration of industrial and domestic wastes and chemical manufacturing (Suess, 1976; Neff, 1979). Some PAHs can also be derived from biogenic precursors such as pigments and steroids (Wakeham *et al.*, 1980). PAH in soils can arise from a number of sources, and these include hydrocarbon spillage (Benner Jr. *et al.*, 1990), products of incomplete combustion of fossil fuels, e.g wood burning (Freeman and Catteil, 1990), use of organic waste as compost and fertilizer (Smith *et al.*, 2001) and power plants and blast furnaces (van Brummelen *et al.*, 1996). There are also evidence to indicate that PAH are transported over long distances by atmosphere

movement (Lunde and Bjorseth, 1977; Aamot *et al.*, 1996; Bakker *et al.*, 2001; Halsall *et al.*, 2001). One of the major activities that is known to produce large amounts of PAHs is the cracking and refining of crude oils. In Warri and Ughelli, the major towns in Niger Delta (Nigeria), oil refining, lifting of refined crude oils by tankers and helicopters, petroleum exploration and cracking are among the major activities and therefore, one should expect significant amounts of PAHs in soil of these areas. Limited data are available in the literature on the concentration and distribution pattern of PAHs in soils of the study areas, and it is hoped that this paper will contribute to the database of PAHs contamination impacting the environment of the study area on a global scale. PAH are quite resistant to degradation, and their half-lives as estimated by some researchers vary, dependent on the compound, from 2 months to 2 years (Mackay *et al.*, 1992) and from 8 to 28 years (Wild *et al.*, 1990). Therefore, significant accumulation of PAH is observed in soil, sediments, plants and water bodies when the rate of their emissions

from polluting sources exceeds the degradation capacity. Soil contamination originates mainly from PAH emissions to the atmosphere, which reach the soil via precipitation. Gaseous and particle – bound PAH can be transported over long distances before deposition (Wania and Mackay, 1996). The deposited PAHs are accumulated mainly in the humus layer of soil. The other pathways of PAHs dissipation in contaminated soil may be volatilization, irreversible sorption, leaching, accumulation by plants and biodegradation (Reilley *et al.*, 1996). PAHs with three or more rings tend to be strongly adsorbed to the soil. Therefore strong sorption, low water solubility and low vapor pressures make leaching and volatilization insignificant pathways of PAHs dissipation (Park *et al.*, 1990). The PAHs concentration in soil were found to correlate significantly with the corresponding levels in air (Vogt *et al.*, 1987); house dust (Chuang *et al.* 1995); urban street dust (Takada *et al.* 1990) and plants (Wang and Meresz, 1982), therefore, PAHs determination in soils may provide important information on the state of environmental pollution of an area. Characteristic elemental ratio of PAH and PAH profiles can be used for quantitative and qualitative estimation of the source (Vogt *et al.*, 1987; Yang *et al.*, 1991).

In this study, 16 parent PAHs included in the EPA priority pollutant list were selected for determination because they are considered important in the assessment of the impact of industrialization on public health and/or the environment. No studies have been carried out to assess the accumulation and distribution of PAH in soil of Niger Delta, Nigeria. The objectives of the present study were to assess the level of soil contamination by PAH in the Niger Delta, to relate the PAH compound profiles to different types of anthropogenic input and to examine the relationships between PAH concentrations and soil organic carbon content. The research was conducted in Germany in 2003/2004, the data were interpreted late 2004.

## MATERIALS AND METHODS

The study areas, Warri and Ughelli, are the major ports in the Niger Delta (Fig. 1), and they are the largest towns in Urhoboland with population of 218,000 and 54,000 respectively in 1991 (Aweto, 2002). The mineral resources are crude oil and natural gas. There are numerous oil fields in these areas which make a significant contribution to Nigeria's crude oil output. Crude oil exploration has impacted negatively on the

people and economy of the study areas. Periodic spills have resulted in destruction of farmland, rubber plantations and aquatic biota; thereby undermining rural economy and leaving the people unemployed. There are numerous gas flare sites in these areas where natural gas associated with crude oil is burnt off. These sites are chosen in view of various anthropogenic activities in these areas. The major sources of organic contaminants in the selected areas are from petroleum refining and exploration activities, and lifting of petroleum products, including the contributions from heavy and chemical industry, residential and communal heating and transport.

The sampling areas are shown in Fig. 1 and characterized in Table 1. A total of 21 soil samples were collected and analysed. Soil samples (0-10 cm upper layer) were collected in May, 2003. The soil samples were wrapped with aluminium foil to prevent contamination, kept in dry ice and immediately transported to the laboratory and stored at -20°C. Each soil sample was placed in a pre-combusted glass jar, freeze dried, homogenized and sieved through a mesh of 2 mm to remove stones, and stored at -20°C until further analysis.

The dried and sieved samples (50 g) were weighed and spiked with pre-deuterated PAH Cocktail as internal standard (naphthalene-d<sub>8</sub>, acenaphthylene-d<sub>8</sub>, anthracene-d<sub>10</sub>, acenaphthene-d<sub>10</sub>, fluoranthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, fluorine-d<sub>10</sub>, pyrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, benzo[a]pyrene-d<sub>12</sub>, benzo[b] fluoranthene-d<sub>12</sub>, benzo[a]anthracene-d<sub>12</sub>, benzo[ghi]perylene-d<sub>12</sub>, dibenz[a,h] anthracene-d<sub>14</sub> and indenol[1,2,3-cd]pyrene-d<sub>12</sub>) (ES 2528, Promochem, Wesel, Germany), and extracted with dichloromethane ( DCM ) using temperature programmed Soxhlet extractor at 65°C for 24h. The extracts were reduced to dryness and re-dissolved in n-hexane. The extracts were fractionated on a glass column packed with 30 g of alumina deactivated with 4.5% water. Aliphatic and polycyclic aromatic hydrocarbons were eluted with 50 ml of hexane: DCM ( 95/5%, v/v ) and the polar fractions were eluted with DCM. The PAH and the polar fractions were concentrated by rotary evaporation. Before GC/MS analysis, fractions were dried under nitrogen and re-dissolved in DCM.

Polycyclic aromatic hydrocarbons were quantified by gas chromatography (Hewlett-Packard 5890 GC, Waldbronn, Germany) coupled to a mass spectrometer (model 5971, Hewlett-Packard; 70eV, 280°C). A Hewlett-

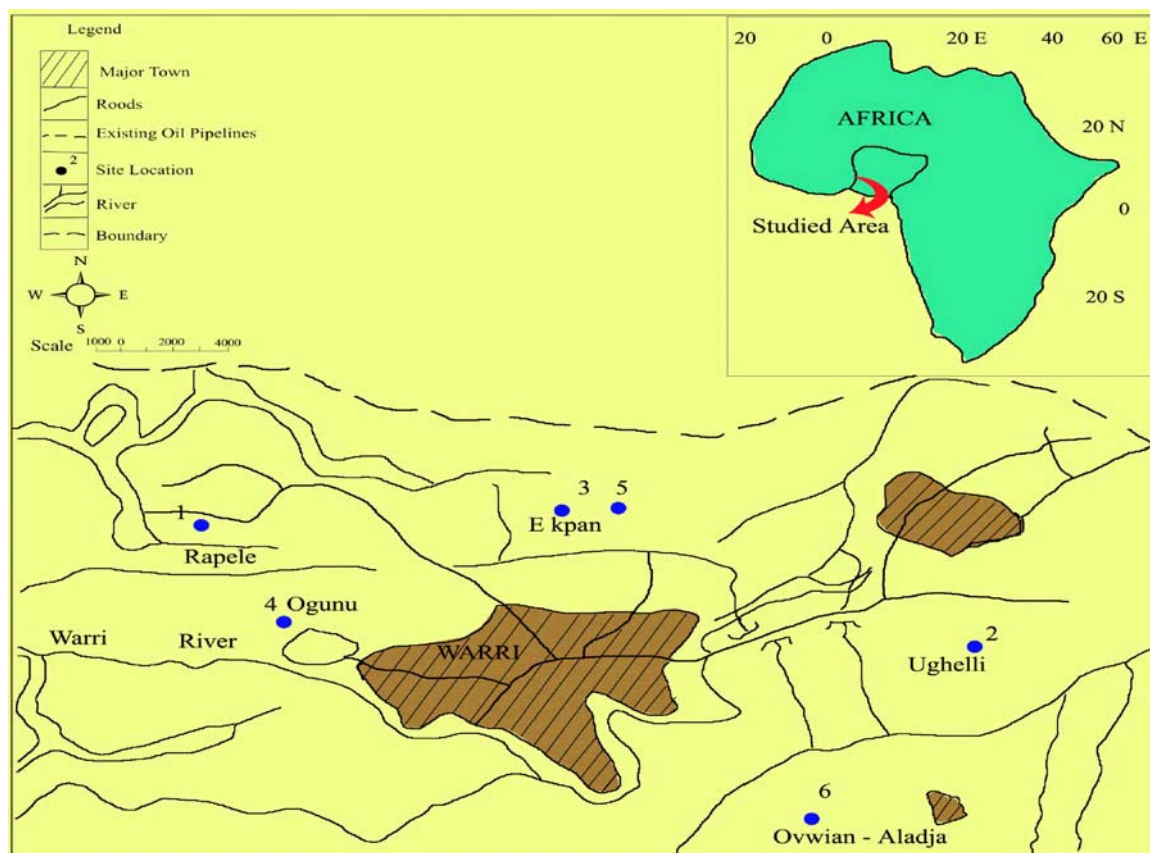


Fig. 1: The location of studied area

Packard-MS 5 column (length, 30 m; inner diameter, 0.25mm; film thickness, 0.25 $\mu$ m) was used for compound separation. The injector temperature was 280°C. The column temperature was held at 70°C for 4 min. and then increased with a rate of 7° / min. to 280°C and held for 20 min. The PAH were determined in selective ion-monitoring mode with an ionization energy of 70eV. The m/z peaks corresponding to the molecular weights of the individual PAH were used for identification and quantification. Concentrations of PAH were calculated relative to the pre-deuterated internal standard.

Total carbon of the soil samples was determined by combustion oxidation method with RC-412 Multiphase analyzer. Soil sample (5.00 mg) were combusted in a high temperature furnace, using the following temperature programme: initial temperature, 580°C for 200 s; heating: 200°C/min to 1000°C, and was maintained at this temperature for 30 s. The results were expressed as percent total organic and inorganic carbons (TOC and TIC), per gram of dried soil.

Table 1: The Sampling sites and their descriptions

| Site No. | Acronym of the samples | Description of the site                                |
|----------|------------------------|--|
| 1        | SSUGBO                 | Ugboko via Rapele oil field                            |
| 2        | SSUGH                  | Quality Control Centre, Ughelli West                   |
| 3        | SSTLP                  | Tanker Loading point, Ekpan Ogunu Shell main area      |
| 4        | SSOGN                  | office, Warri  |
| 5        | SSWRR                  | Warri Refinery area, Ekpan                             |
| 6        | SSALD                  | Delta Steel Company, Ovwian-Aladja, Outskirt of Warri. |

## RESULTS

The means and standard deviations of PAHs concentrations in soil from different sampling locations are given in Table 2. The total PAH values of all the soil samples ranged from 15.4 to 750  $\mu$ g/kg dw.

Table 2: The mean concentrations ( $\mu\text{g/kg dw}$ ) of PAH and total organic carbon (%) in soils of the Niger Delta, Nigeria

| Analyte                               | Sampling area (site No.) |                 |                 |                 |                 |                 |
|---------------------------------------|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                       | UGBO No.1                | UGH No.2        | TLP No.3        | OGN No.4        | WRR No.5        | ALD No.6        |
| 2- 3ring PAHs                         | Naphthalene              | 32.8 $\pm$ 27.3 | 40.3 $\pm$ 33.3 | 17.5 $\pm$ 10.3 | 23.3 $\pm$ 15.3 | 72.8 $\pm$ 57.9 |
|                                       | Acenaphthalene           | 5.1 $\pm$ 3.7   | 7.8 $\pm$ 5.3   | 16.4 $\pm$ 11.5 | 14.1 $\pm$ 7.2  | 8.4 $\pm$ 5.1   |
|                                       | Acenaphthene             | 13.9 $\pm$ 13.6 | 45.1 $\pm$ 36.2 | 28.6 $\pm$ 20.6 | 6.3 $\pm$ 3.2   | 28.4 $\pm$ 25.3 |
|                                       | Fluorene                 | 7.3 $\pm$ 5.7   | 7.5 $\pm$ 5.9   | 11.8 $\pm$ 9.6  | 3.7 $\pm$ 2.8   | 2.0 $\pm$ 1.7   |
|                                       | Phenanthrene             | 8.4 $\pm$ 4.3   | 22.4 $\pm$ 13.6 | 41.9 $\pm$ 28.7 | 10.1 $\pm$ 6.7  | 25.3 $\pm$ 15.2 |
|                                       | Anthracene               | 23.4 $\pm$ 4.3  | 16.9 $\pm$ 13.7 | 95.4 $\pm$ 48.0 | 69.0 $\pm$ 48.4 | 13.9 $\pm$ 9.8  |
| 4- ring PAHs                          | Fluoranthene             | 11.0 $\pm$ 9.0  | 9.4 $\pm$ 5.0   | 61.4 $\pm$ 49.4 | 78.4 $\pm$ 45.2 | 44.7 $\pm$ 40.6 |
|                                       | Pyrene                   | 45.9 $\pm$ 37.4 | 9.2 $\pm$ 2.9   | 61.6 $\pm$ 45.1 | 41.5 $\pm$ 34.5 | 25.3 $\pm$ 17.4 |
|                                       | Benzo[a]anthracene       | 10.0 $\pm$ 5.5  | 3.8 $\pm$ 1.9   | 10.3 $\pm$ 6.9  | 12.4 $\pm$ 7.5  | 22.8 $\pm$ 20.9 |
|                                       | Chrysene                 | 53.9 $\pm$ 21.6 | 11.6 $\pm$ 5.3  | 8.1 $\pm$ 2.3   | 13.6 $\pm$ 10.7 | 11.8 $\pm$ 7.3  |
| 5- ring PAHs                          | Benzo[b]fluoranthene     | 0.72 $\pm$ 0.15 | 7.4 $\pm$ 3.4   | 8.8 $\pm$ 6.5   | 20.1 $\pm$ 18.0 | 27.7 $\pm$ 23.5 |
|                                       | Benzo[k]fluoranthene     | 70.5 $\pm$ 68.2 | 28.9 $\pm$ 10.4 | 13.5 $\pm$ 10.2 | 26.1 $\pm$ 17.3 | 38.2 $\pm$ 28.9 |
|                                       | Benzo[a]pyrene           | 41.2 $\pm$ 34.8 | 4.1 $\pm$ 1.4   | 3.2 $\pm$ 2.1   | 9.4 $\pm$ 8.0   | 29.5 $\pm$ 22.7 |
|                                       | Dibenzo[a,h]anthracene   | 55.8 $\pm$ 39.4 | 1.9 $\pm$ 0.7   | 9.0 $\pm$ 6.8   | 2.3 $\pm$ 0.3   | 8.0 $\pm$ 6.7   |
|                                       | Benzo[g,h,i]perylene     | 2.6 $\pm$ 1.4   | 4.3 $\pm$ 2.6   | 9.3 $\pm$ 6.3   | 12.5 $\pm$ 10.7 | 60.8 $\pm$ 45.2 |
| 6-ring PAH                            | Indeno[1,2,3-cd]pyrene   | 2.0 $\pm$ 1.2   | 3.6 $\pm$ 1.6   | 5.1 $\pm$ 3.7   | 4.9 $\pm$ 2.9   | 12.9 $\pm$ 10.3 |
| $\Sigma$ PAHs (2-3 ring)              |                          | 90.9 $\pm$ 31.2 | 140 $\pm$ 97.6  | 212 $\pm$ 179   | 127 $\pm$ 65.7  | 151 $\pm$ 119   |
| $\Sigma$ PAHs (4-6 ring)              |                          | 294 $\pm$ 120   | 84.2 $\pm$ 32.8 | 191 $\pm$ 158   | 221 $\pm$ 131   | 282 $\pm$ 160   |
| $\Sigma$ PAHs                         |                          | 385 $\pm$ 146   | 224 $\pm$ 122   | 403 $\pm$ 209   | 348 $\pm$ 229   | 433 $\pm$ 256   |
| $\Sigma$ CPAHs <sup>a</sup>           |                          | 180 $\pm$ 137   | 57.5 $\pm$ 39.6 | 75.2 $\pm$ 8.6  | 38.5 $\pm$ 12.8 | 139 $\pm$ 83.1  |
| % Organic carbon                      |                          | 2.3 $\pm$ 0.1   | 0.9 $\pm$ 0.6   | 1.4 $\pm$ 0.4   | 1.1 $\pm$ 0.7   | 1.5 $\pm$ 0.5   |
| $\Sigma$ PAHs/OC (mg/kg) <sup>b</sup> |                          | 16.7 $\pm$ 6.4  | 47.2 $\pm$ 31.2 | 28.7 $\pm$ 15.8 | 31.6 $\pm$ 21.7 | 28.9 $\pm$ 21.6 |
| Number of samples                     |                          | 3               | 3               | 3               | 4               | 4               |

Table 3: Some diagnostic elemental ratios of PAHs in soil samples of the Niger Delta, Nigeria

| Stations | N/A  | P/A  | FLT/<br>PYR | BaA/<br>CHR | BaA/<br>BaP | PYR/<br>BaP | BaP/<br>BPE | INP/<br>BPE |
|----------|------|------|-------------|-------------|-------------|-------------|-------------|-------------|
| UGBO 1   | 1.2  | 0.4  | 2.5         | 5.9         | 0.4         | <0.1        | 87.0        | 0.8         |
| UGBO 2   | 0.3  | 0.2  | 0.4         | 0.1         | 7.3         | 7.3         | 0.9         | 4.3         |
| UGBO 3   | 2.3  | 0.4  | 0.2         | <0.1        | <0.1        | 2.0         | 10.7        | <0.1        |
| UGH 1    | 1.9  | 2.1  | 1.5         | 0.1         | 0.7         | 2.4         | 0.3         | 1.1         |
| UGH 2    | 2.7  | 0.4  | 0.5         | 1.2         | 1.0         | 1.9         | 1.9         | 0.2         |
| UGH 3    | 4.0  | 5.2  | 1.2         | 0.8         | 1.0         | 2.5         | 1.5         | 0.8         |
| OGN 1    | 1.7  | 0.2  | 0.1         | 1.3         | 0.5         | 0.6         | 64.1        | 3.5         |
| OGN 2    | 0.2  | <0.1 | 2.4         | 1.1         | 12.1        | 71.2        | 0.1         | <0.1        |
| OGN 3    | 1.7  | 6.3  | 1.3         | 0.8         | 1.1         | 2.5         | 1.0         | 0.8         |
| ALD 1    | 36.0 | 3.8  | 1.1         | 0.9         | 1.1         | 2.9         | 1.6         | 0.8         |
| ALD 2    | 3.4  | 0.8  | 2.6         | 0.4         | <0.1        | 0.1         | 19.8        | 0.1         |
| ALD 3    | 5.5  | 7.0  | 1.5         | 0.7         | 1.4         | 6.4         | 0.7         | 0.5         |
| ALD 4    | 22.1 | 14.0 | 1.1         | 0.6         | 1.2         | 2.3         | 0.6         | 0.7         |
| WRR 1    | 4.3  | 0.2  | 0.9         | 1.7         | 4.3         | 2.2         | 0.1         | 0.4         |
| WRR 2    | 0.7  | 13.7 | 4.0         | 4.0         | 0.5         | 0.2         | 0.6         | 0.1         |
| WRR 3    | 0.7  | 4.6  | 1.3         | 0.8         | 1.1         | 4.7         | 1.1         | 0.8         |
| WRR 4    | 27.2 | 2.6  | 1.6         | 0.8         | 1.2         | 4.4         | 1.0         | 0.4         |
| TLP 1    | 0.1  | 0.4  | 0.3         | 2.0         | 16.2        | 51.5        | 1.9         | 0.4         |
| TLP 2    | 1.8  | 8.5  | 0.4         | 0.3         | 1.5         | 21.9        | 0.5         | 2.3         |
| TLP 3    | 2.3  | 4.7  | 1.3         | 0.8         | 1.1         | 3.1         | 1.4         | 0.8         |
| TLP 4    | 0.6  | <0.1 | 1.4         | 2.1         | 4.8         | 55.4        | 0.1         | 0.3         |

An average of  $\Sigma$  PAHs concentration in soil samples from Warri Refinery (site no.5; 433 $\pm$ 256  $\mu\text{g/kg dw}$ ) was higher than the corresponding data from other sampling sites. The average PAH concentrations in soils from Tanker Loading point, Ekpan (site no.3; 402 $\pm$ 209  $\mu\text{g/kg dw}$ ); Ugboko via Rapele oil field (site no.1; 385 $\pm$ 146  $\mu\text{g/kg dw}$ ) and Ogunu Shell main area office (site no.4; 348 $\pm$ 229  $\mu\text{g/kg dw}$ ) were higher than those from Ughelli West (site no.2; 224 $\pm$ 112  $\mu\text{g/kg dw}$ ) and Delta Steel Company (site no.6; 182 $\pm$ 112  $\mu\text{g/kg dw}$ ). The lowest concentrations of PAH was found in soil samples from Delta Steel Company (182 $\pm$ 112  $\mu\text{g/kg dw}$ ). PAH profiles are shown in Figure 2 as bar diagrams of PAH as normalized average concentrations in soil for six sampling sites of the Niger Delta, Nigeria. The bar diagrams indicate that samples from different sampling sites have different pattern. The dominant PAH found in soil are pyrene, naphthalene and benzo[k]fluoranthene in all the sites under study. They formed 4-12, 4-42 and 1-18% of the  $\Sigma$ PAH, respectively. 2-3 ring PAH (defined as 128<m/z <192) dominate in samples UGH

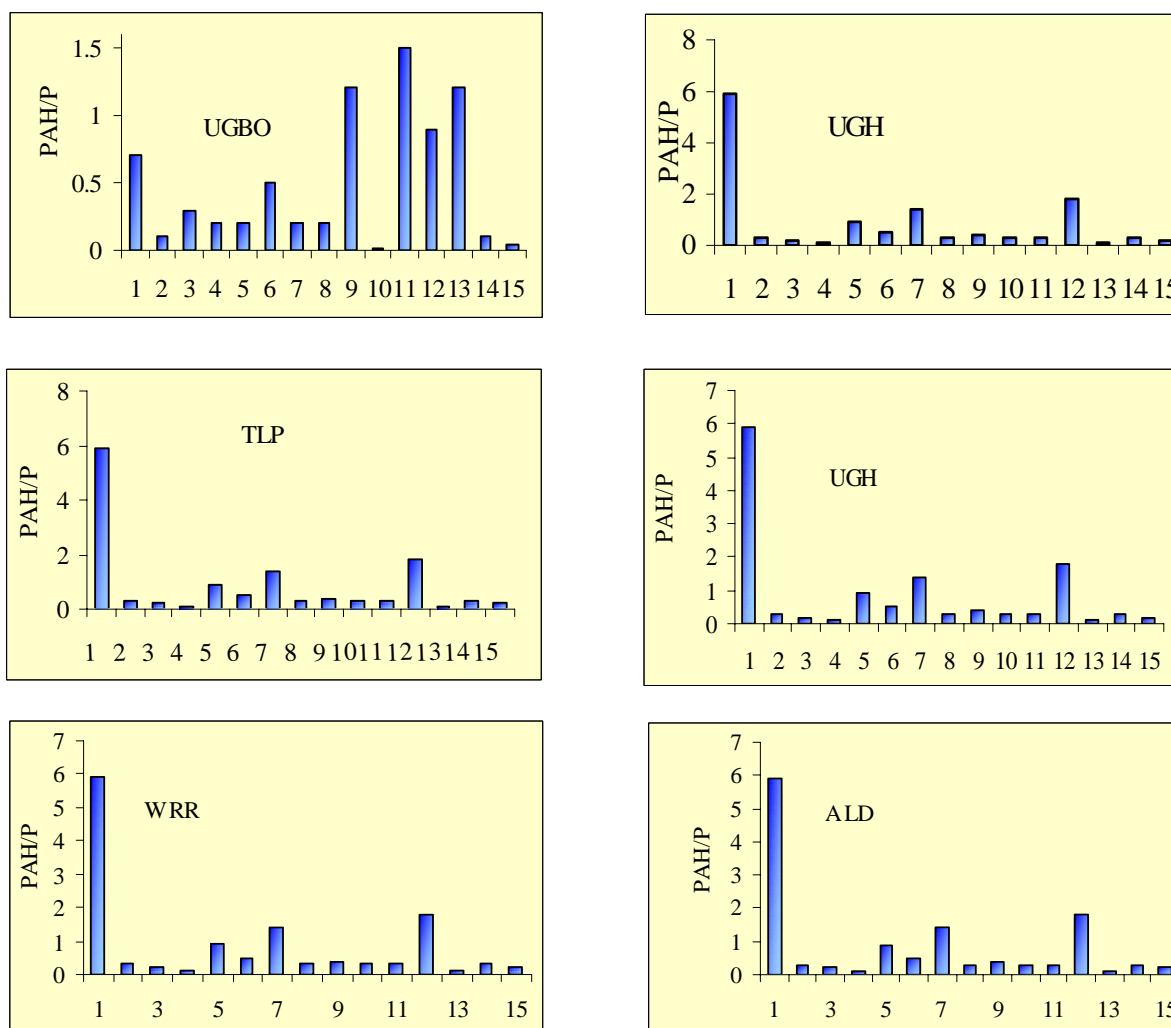


Fig. 2: Bar diagram of normalized average polycyclic aromatic hydrocarbons (PAHs) concentrations in soil from different sampling sites. Normalization has been done by dividing the average concentration for each PAH by the concentration of pyrene (P) in each separate sampling site. PAH: 1, naphthalene; 2, acenaphthalene; 3, acenaphthene; 4, fluorene; 5, phenanthrene; 6, anthracene; 7, fluoranthene; 8, pyrene; 9, benzo[a]anthracene; 10, chrysene; 11, benzo[b]fluoranthene; 12, benzo[k]fluoranthene; 13, benzo[a]pyrene; 14, dibenzo[a,h]anthracene; 15, benzo[g,h,i]perylene; 16, indeno[1,2,3-cd]pyrene.

( $140 \pm 97.6 \mu\text{g/kg dw}$ ); TLP ( $212 \pm 179 \mu\text{g/kg dw}$ ) and ALD ( $103 \pm 75.3 \mu\text{g/kg dw}$ ) while 4-6 ring (defined as  $202 < m/z < 292$ ) PAH dominate in other samples. The ratio of the 2-3 ring PAH to that of 4-6 ring PAH ranged from 0.3:1 (in UGBO, site no.1) to 1.7:1 (in UGH, site no.2). Benzo[g,h,i]perylene forms 0.9-26.5% of  $\Sigma\text{PAH}$  in soil samples from Warri Refinery whilst at other sites, it varied from 0.1 to 6.6% of the total PAH content. Total concentrations of potentially carcinogenic PAHs ( $\Sigma\text{CPAH}$ ), which include benzo[a]anthracene,

benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and dibenzo[a,h]anthracene [IARC,1987] varied from  $38.5 \pm 12.8$  to  $180 \pm 137 \mu\text{g/kg dw}$  (Table 2).

The organic carbon-normalized  $\text{PAH}_{\text{tot}}$  concentration ranged from  $11.4 \pm 8.7$  to  $47.2 \pm 31.2 \text{ mg PAH}_{\text{tot.}}/\text{kg OC}$ . The soil samples collected from UGH had the highest value, amounted to  $47.2 \pm 31.2 \text{ mg PAH}_{\text{tot.}}/\text{kg OC}$ , while soil samples from ALD had the least value of  $11.4 \pm 8.7 \text{ mg PAH}_{\text{tot.}}/\text{kg OC}$ .

## DISCUSSION AND CONCLUSION

The study of soil pollution in Warri Refinery indicated very high soil PAH pollution level. The average  $\Sigma$ PAH concentration in soil samples from Warri Refinery (site No. 5;  $433 \pm 256 \mu\text{g/kg dw}$ ) was higher than the corresponding data from other sampling sites. The influence of refinery operations amongst other anthropogenic sources on the soil PAHs pollution was quite clear. The average PAH concentrations in soils from Tanker Loading Point, Ekpan (site No. 3); Ugboko via Rapele oil field (site No. 1) and Ogunu Shell main area office (site No. 4) were higher than those from Ughelli West (site No. 2) and Delta Steel Company (site No. 6). These results are quite reasonable and expected. It is most likely that soil samples collected from these areas were contaminated in varying degrees by spillage of fuels or oils from heavy trucks and vehicles containing PAH of interest. Other activities that may produce PAHs in these areas include electrical generation from diesel-fueled generators, emissions from petrochemical and heavy chemical industries, light and heavy vehicles burning gasoline and diesel. The soil samples from Delta Steel Company (ite No. 6) had the least concentration of PAH. This concentration is typical in area with little anthropogenic pollution sources, and emissions from Steel Processing plants may be an important source of soil PAH in this area. Based only on the predominant parent PAH compounds, similarities are observed between the soil samples studied. The 2-3 ring PAH dominate in samples UGH (site no. 2), TLP (site No. 3) and ALD (site No. 6) while 4-6 ring dominate in other samples (site Nos. 1, 4 and 5). The samples from UGBO contain relatively high concentrations of heavy PAH- dibenzo[a,h]anthracene, benzo[k]fluoranthene and benzo[a]pyrene. The highest concentrations of  $\Sigma$ CPAH were found in UGBO, the site with the highest 4-6 ring PAHs and the least occurred in samples collected from OGN (site No.4). The soil samples collected from UGH (site No. 2) had the highest value of organic carbon-normalized  $\text{PAH}_{\text{total}}$  concentration of  $47.2 \pm 31.2 \text{ mg PAH}_{\text{total}}/\text{kg OC}$  while soil samples from ALD 9site no. 6) had the least value of  $11.4 \pm 8.7 \text{ mgPAH}_{\text{total}}/\text{kg OC}$ . Our results showed clearly that the organic matter of the soil samples from UGH is highly contaminated with PAHs.

The partitioning concept of soil sorption implies that the sorption of hydrophobic organic molecules is determined by the content of the organic carbon of the substrate (Karickhoff and Brown, 1979; Means *et al.*,

1980). The relationship between the mean 2-3 ring, 4-6 ring, total PAHs and naphthalene with soil organic carbon content (%C) was investigated by linear regression analysis. Plots of  $\Sigma$  2-3 ring PAH, 4-6 ring PAH,  $\Sigma$ PAH and naphthalene (Figs. 3-6) showed no significant correlation ( $r^2 = 0.0055, 0.0432, 0.0078$  and  $0.2593$  respectively) with soil organic carbon content. This actually suggests different and site-specific levels of contamination of the organic matter rather than simple dilution with inorganic soil components. The non-correlativity of PAHs and soil organic carbon could also be attributed to weather condition, soil properties or easy degradation of PAHs in soil. Exact identification of PAH sources to the Niger Delta soils is not feasible due to the variety of processes contributing to the formation and preservation of PAHs in soils of this area. However, the general distributions of the PAH group profile (Table 2) are assumed to represent both anthropogenic combustion (pyrolytic) and the production, transport and use of oil and its refined products (petrogenic). Ratios between pairs of individual PAHs have often been employed as a method of determining the most significant sources of PAHs detected in environmental samples. In order to characterize PAHs with respect to specific source, we have considered some diagnostic elemental ratios conventionally reported in the literature to this objective (Soclo *et al.*, 1986; Budzinski *et al.*, 1997; Baumard *et al.*, 1998). Yang *et al.*, (1991) reported a ratio of about 3 for PHEN/ANT was indicative of PAH arising from motor vehicle exhaust whereas a ratio of over 50 implied that the major source was mineral oil. Similarly, a ratio of 1 for FLT/PYR indicated the PAH origin was likely to be from combustion processes and ratio of more than 1 suggested the origin to be petroleum derived. Also, BaA/BaP of 1 and BaP/BPE of 0.2-0.5 were indicative of vehicle exhaust while BaP/BPE of greater than 1 was indicative of coal combustion. The INP/BPE of 0.37 was suggestive of traffic exhaust and PYR/BaP of less than 1 to 50 implied that the major source was diesel fuel-powered truck exhaust. On the basis of these observations and the data presented in Table 3, it would appear that both the pyrogenic origin such as motor vehicle exhaust and heavy industry emissions and petrogenic inputs are the dominant sources of PAH in Niger Delta soils.

Finally, it was considered the ratio NAPH/PHEN, that was used to assume the presence of fresh and unweathered petroleum if it is greater than 1 (Dahle *et*

*al*, 2003]. In this study, NAPH/PHEN ratios ranged from greater than 1 to 36.0 for most of the soil samples analyzed, further evidence in support of petrogenic inputs for soil PAHs from these sites.

As previously suggested [Edward, 1983] that typical endogenous  $\Sigma$ PAH in soil, resulting from plant synthesis and natural fires, is in the range 1-10  $\mu\text{g}/\text{kg}$ . It can be concluded from this study that typical Niger Delta soils are contaminated with PAH above the natural level. This may be attributed to long-range atmospheric transport of PAH from the hotspot to these sites. Also, the PAHs in soils of the Niger Delta can be characterized by both petrogenic and pyrolytic sources. The PAH group profile shows the predominance of 2-3 ring PAHs

in soils of UGH, TLP and ALD while 4-6 ring PAHs predominated in other soil samples.

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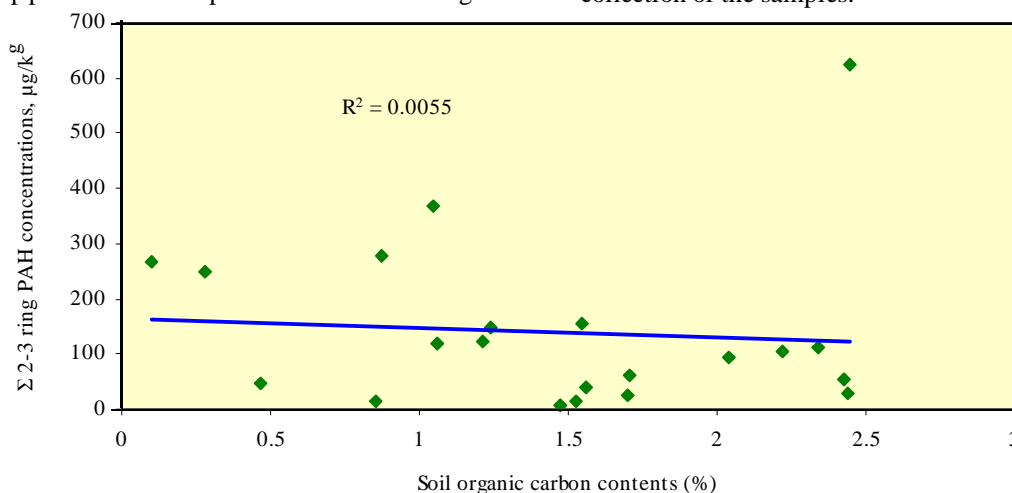


Fig. 3 :  $\Sigma$  2-3 ring PAH concentrations versus soil organic carbon-Niger Delta, Nigeria (all soil data)

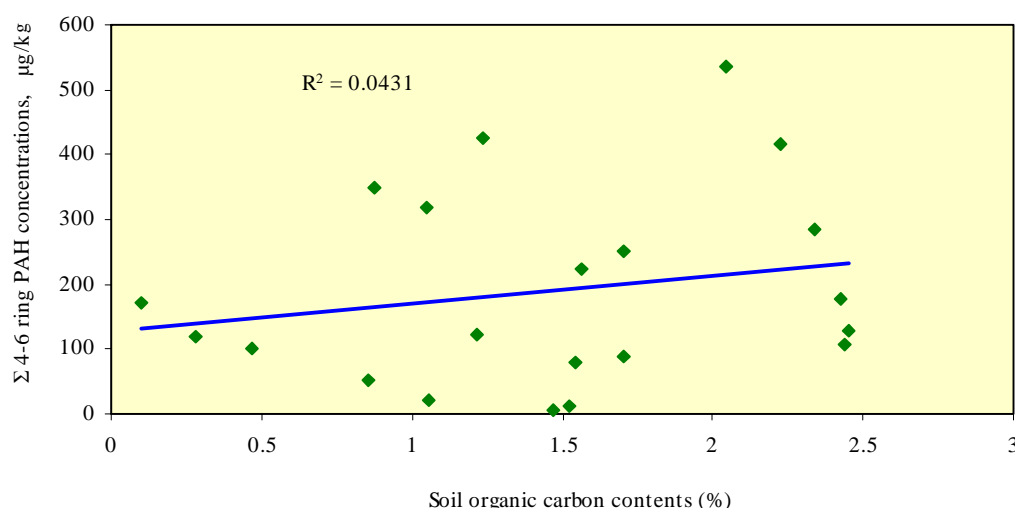


Fig. 4:  $\Sigma$  4-6 ring PAH concentrations versus soil organic carbon- Niger Delta, Nigeria (all soil data)

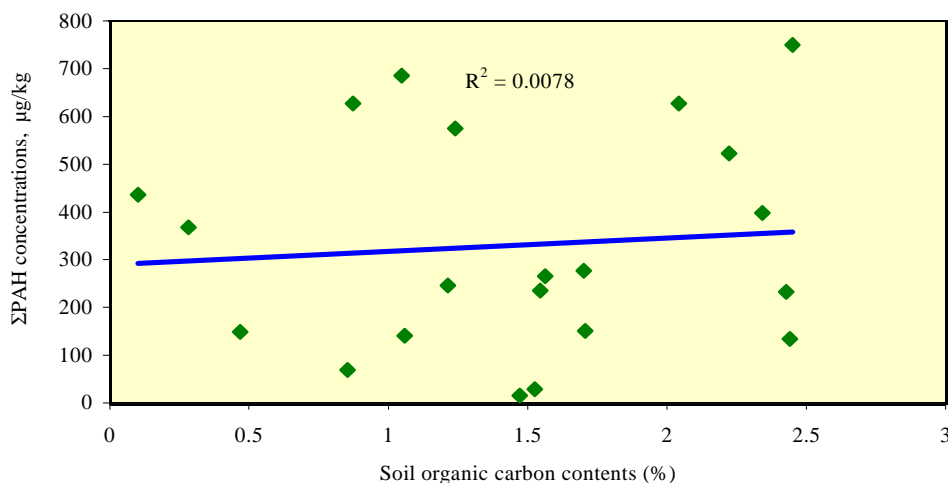


Fig. 5:  $\Sigma$  PAH concentrations versus soil organic carbon- Niger Delta, Nigeria (all soil data)

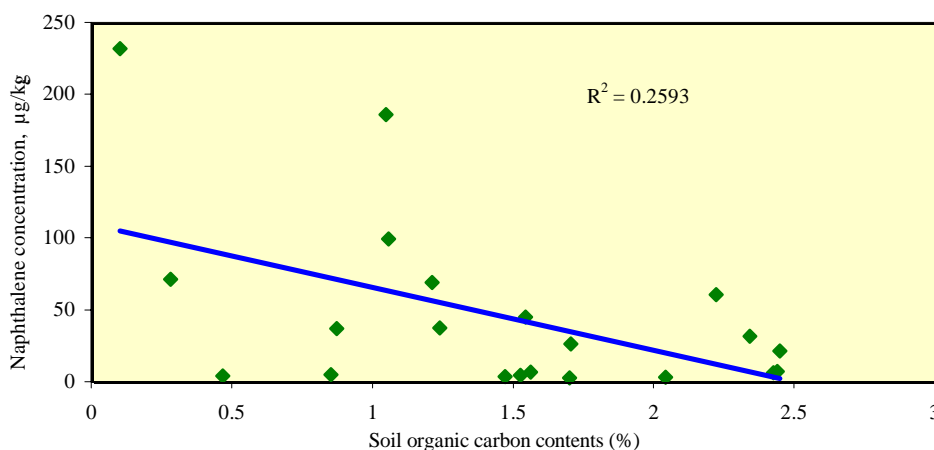


Fig. 6: Naphthalene concentration versus soil organic carbon- Niger Delta, Nigeria (all soil data)

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