



DETERMINATION OF HYDROCARBON SOURCES USING N-ALKANE AND PAH DISTRIBUTION INDICES IN SEDIMENTS FROM COASTAL AREAS OF BONNY RIVER IN NIGER DELTA, NIGERIA

Bassey O. Ekpo¹, Ebirien P. Fubara², Okon D. Ekpa¹ and Hab L. Marynowski³

¹Department of Chemistry, Rivers State University of Education, Port Harcourt, Nigeria

²Environmental and Petroleum Geochemistry Research Group, Department of Pure and Applied Chemistry, University of Calabar, C/R State, Nigeria

³Faculty of Earth Science, University of Silesia, Sosnowiec, Poland

E-Mail: baekpo@yahoo.com

ABSTRACT

Surface sediments from coastal areas of Bonny river in the Southeastern Niger Delta region of Nigeria were characterized for n-alkane and polycyclic aromatic hydrocarbon (PAH) compositions using gas chromatography-mass spectrometry (GC-MS) technique. The total n-alkane (TNA) concentrations in the study area ranged from 1.65-12.66 mg/kg dsw. The mean concentrations of n-alkanes C₁₆ - C₂₉ for the sediments ranged from 0.11- 10.31mg/kg dsw, with the highest mean value recorded for n-alkane C₁₇. CPI values ranged from 0.31 - 1.65, and a predominance of odd/even carbon n-alkanes with unimodal distributions were observed for the entire stations. Factor analyses reduced the data set into three principal components (PCs) confirming mixed inputs from biogenic (71.48%), anthropogenic (11.61%) and microbial/bacterial (7.90%) sources of n-alkanes. Twenty four (24) parent and alkylated homologous PAHs of dominant pyrogenic origin were detected in stations from the study area, with total PAH concentrations in the range of 2.13-16.72mg/kg.

Keywords: hydrocarbon sources, n-alkanes, polycyclic aromatic hydrocarbons, PAH distribution indices, factor analysis, Bonny river.

INTRODUCTION

Hydrocarbons are present in worldwide environmental ecosystems, and their potential to cause adverse effects is usually associated with the concentration of polycyclic aromatic hydrocarbons (PAHs). Hydrocarbons found in surface sediments reflect both natural and anthropogenic inputs as well as diagenetic processes taking place within the water column and during transport and sedimentation [1]. Hydrocarbon contaminants have been released, over the years, into the Niger Delta coastal environment from different sources such as untreated effluents, domestic sewages, animal droppings, bush/wood burning, atmospheric fallouts, traffic boat engines and crude oil spills. Understanding contaminant hydrocarbon sources, transport and fate in estuaries is important as these are regions of both high pollution input and resource use. In spite of anthropogenic pressure, estuaries remain dynamic and productive ecosystem of immense ecological, environmental and economic value [2].

Polycyclic aromatic hydrocarbons (PAHs) are one of the major categories of pollutants entering the marine environment and finally accumulating in the sediments. Their occurrence raises major concerns for human health, especially during coastal activities (bathing waters, aquaculture, etc), having combined adverse effects still largely unknown when they are present as mixtures. Moreover, during their remobilization (e.g. dredging activities), their bioavailability can increase resulting in a risk for marine environment [3].

Anthropogenic sources of PAHs are from direct runoff and discharges and indirect atmospheric deposition, i.e., from waste and releases/spills of petroleum and

derivatives such as river runoff, sewage outfalls, maritime transport, pipelines, and combustion or pyrolysis of organic matter such as petroleum, coal, and wood [4-10]. Anthropogenic sources of PAHs can be broadly classified as pyrogenic (combustion origin) and petrogenic (petroleum origin). Whereas pyrogenic sources include combustion processes (e.g., fossil fuel combustion, forest fires, shrub and grass fires), the petrogenic input is closely related to petroleum products (e.g., oil spills, road construction materials). And the pyrogenic inputs (anthropogenic combustions) are largely prevalent in aquatic environments. These compounds tend to interact with different types of environments and are subjected to many processes that lead to geochemical fates such as physico-chemical transformation, biodegradation, and photooxidation. Therefore, PAH characterization and the correlation of PAHs to known or suspected sources become a challenge.

Many PAH molecular ratios have reportedly been used to help to identify the PAH sources, whether petrogenic, biogenic, or pyrogenic in environmental samples [4-8, 11, 12]. The difficulty remains with the complexity of the samples themselves and the weathering effects on the composition of the original source of the compounds. Furthermore, PAHs from pyrogenic and petrogenic sources exhibit different chemical behaviors and distribution in marine sediments. In particular, PAHs from pyrogenic processes are more strongly associated to sediments and much more resistant to microbial degradation than PAHs of petrogenic origin [13]. The presence of high molecular weight (HMW) PAHs indicates likely pyrogenic source, while the presence of low molecular weight (LMW) PAHs implies likely



petrogenic origin of PAHs [14]. However, tracking the sources of PAHs based on the molecular weight of PAHs may not be an accurate procedure [15], since PAHs undergo chemical, physical and biological changes as they are released into the environment [16]. Physical changes, such as evaporation, transport by air or water from one location to another; chemical changes such as photooxidation of PAHs to daughter products; and biological changes such as biotransformation of PAHs, change their profile in the environment. Differentiating the sources of PAHs based on observed PAHs molecular weights may be a useful tool if the samples analyzed for PAHs are assumed not to be affected by any of these changes.

Numerous studies for apportioning sources of hydrocarbons, especially PAHs, in the environment that apply diagnostic indices based on chemical fingerprinting have been made mainly in temperate climate countries [7, 8, 17-21]. In contrast, little is known about the sources and fate of PAHs in tropical environments such as Nigeria [22-24]. Knowledge of PAH sources in the tropics is necessary for understanding the global dynamics of PAHs, because they can be distributed worldwide once released into the tropics [22]. It is against this background that the present study on the sources of PAHs and n-alkanes in surface sediments from coastal areas of Bonny River in Southeastern Niger Delta region of Nigeria was carried out. The objectives of this study are to: (a) quantitatively characterise n-alkanes and polycyclic aromatic hydrocarbons (PAHs) in the solvent extractable lipids of surface sediments from the coastal areas of Bonny river, (b) use PAH source diagnostic indices to distinguish between petrogenic and pyrogenic PAHs, (c) determine the sources of n-alkanes based on some compositional indices. It is our ultimate aim that the results of this study will complement the rather scanty and fragmentary information on the sources and profile of hydrocarbons, especially PAHs, in the Niger Delta coastal environment.

Study area

The fan-shaped Niger Delta, which is the third largest in the world after the Mississippi (USA) and Pantanal (South-West Brazil), lies between latitudes (4 and 6)⁰ north of the equator and longitudes (5 and 9)⁰ east of the Greenwich Meridian. The North-South extension, north of the equator, is expressly defined by the Great Atlantic Ocean in the South to Aboh (Delta State) in the North where River Niger forks in Rivers Nun and Forcados at a village called Obotor [25]. The East-West extension is from the boundary of the Bonny River to River Sapele, Delta State. The Bonny River is one of the major distributaries of the Niger Delta Basin and empties its tidal waters directly into the Atlantic Ocean.

The predominant coastal vegetation of the Bonny river due to its tidal influence is the mangrove, whose main species are the red and white mangroves which form more than nineteen percent (19%) of the saline swamps [26]. The white mangroves occur scattered among the red mangroves and thrive in less water-logged places. The

Bonny river system is characterized by the interaction of an estuarine and highly saline seawater located seaward of the river mouth (typical of the Niger Delta coastal region), and influenced by tide- and wind-driven surface currents. The coastal areas of Bonny River play host to many fishing settlements while the river itself is a major navigational channel for oil vessels, countless outboard engine boats, maritime and oil-related activities.

MATERIALS AND METHODS

Sampling

Samples of surface sediments were collected at different stations along the coastal areas of Bonny river as depicted in the map of the study area (Figure-1) using a modified grab sampler (0.1m²). Samples were removed from the middle of the grab to avoid contact with the inner metallic surface of the grab sampler, wrapped in aluminium foil and stored frozen at - 4 °C. The sampling was carried out based on the nature of potential anthropogenic inputs (Table-1). Prior to extraction, the samples were freeze-dried, crushed and sieved through a 230 mesh (< 63µm) sieve.

Extraction and fractionation

To minimize contamination, all glassware was cleaned with detergent solution, rinsed with distilled water, heated in an oven at 550°C for eight hours to combust traces of surface organic matter, and finally rinsed with ANALAR grade dichloromethane. The total organic carbon (TOC) contents were determined using a LECO CNS analyzer. Extraction of the crushed and sieved (< 63µm) sediment samples for extractable organic matter (EOM) was carried out using a soxhlet apparatus [27]. The thimbles and glass wool used in the extraction were soxhlet-extracted with dichloromethane for 20 minutes on a water bath. Powdered sediment sample (50g) was then placed in the extracted thimble. The thimble with glass wool was filled with dichloromethane and extracted for 18hrs. Extracts were desulphurized by addition of 30g activated copper (copper immersed in 20ml of 0.1M concentrated hydrochloric acid for ten minutes) into the round-bottom flask during extraction. Extracts obtained were evaporated to near dryness using a vacuum evaporator. The weight of extracts was determined as a measure of the amount of extractable organic matter (EOM), made up of asphaltenes and maltenes. Precipitation of asphaltenes from the extractable organic matter (EOM) was carried out following the procedure described by [28] with a mixture (1:30) of dichloromethane /petroleum ether (b.p. 40-60°C), and centrifuged at 3, 000 rpm for about 20min. The asphaltenes precipitated from EOM were discarded after weighing. The separation of maltenes obtained from the extracts into aliphatic, aromatic and hetero-fractions was carried out by column chromatography (column 30 x1.2cm) using activated silica gel (20g activated by heating in an oven for two hours at 400°C) and alumina (neutral, 10g activated by heating in an oven for two hours



at 500°C) on top of the silica gel. The concentrated extract (2ml) was carefully added to the top of the column already clamped to position. The saturated (aliphatic) fraction was eluted with 50ml hexane, while 200ml of 1:1 dichloromethane/hexane mixture was used for the elution of the aromatic fraction [18]. Finally, a mixture (1: 2, 60ml) of methanol /dichloromethane was used to remove the heterofractions.

Gas chromatography-mass spectrometry (GC-MS) analysis

The gas chromatography-mass spectrometry (GC-MS) analyses of the aliphatic and aromatic fractions from the sediment extracts were performed using an Agilent 6890 Series gas chromatograph (GC) interfaced to an Agilent 5973 Network Mass Selective Detector (MSD) and Agilent 7683 Series Injector. The GC Separation was achieved on a fused silica capillary column coated with DB 35 (60m x 0.25mm i.d., 0.25µm film thickness). The GC oven temperature was programmed from 50°C (isothermal for 1 minute) to 120°C at a rate of 20°C/ min, then to 300°C at a rate of 3°C/ min. The final temperature was held for 45 minutes. Helium was used as the carrier gas. Samples were introduced into the cool on-column injector under electronic pressure control. The GC column outlet was connected directly to the ion source of the mass spectrometer. The GC-MS interface was kept at 280 °C, while the ion source and quadrupole analyzer were at 230 and 150°C, respectively. The mass spectrometer was operated in the electron impact (EI) mode at 70eV ionization energy. Mass spectra were recorded from 45-550 dalton (0 - 40min) and 50 - 700 dalton (above 40 min). Quantification by peak area integration was obtained by acquiring mass chromatograms at the molecular masses for the individual PAHs, and total ion current (TIC) for n-alkanes using the HP-MSD Chemstation Integrator. Individual compounds were identified by comparison of mass spectra with literature and library data.

RESULTS AND DISCUSSIONS

The sampling stations, total organic carbon (TOC) contents, concentrations of different n-alkanes, total n-alkanes (TNAs), total polycyclic aromatic hydrocarbons (TPAHs) as well as some source diagnostic indices derived from n-alkane and PAH compositions are presented in Table-1. The total organic carbon (TOC) contents for the sediments ranged from 0.87 to 1.67%, with a maximum value for station BN05 in the upper zone of the study area. Variations in the total n-alkane (TNA) and mean concentrations of n-alkanes C₁₆ - C₂₉ in sediments from the study area are depicted in Figure-3, while the mean concentrations of individual parent and alkylated homologous PAHs detected in the sediment samples are shown in Figure-4a. Spatial variations in concentrations of TPAHs are given in Figure-4b.

Normal alkane distributions and sources

Normal alkanes in the range C₁₆ - C₂₉ were present in almost all stations from the study area. The total

n-alkane (TNA) concentrations in the entire study area varied between 1.65 - 12.66 mg/kg dsw (Table-1), with an average value of 5.73mg/kg. The maximum TNA value of 12.66 mg/kg dsw was recorded for station BN05 in the upper zone of the study area. The n-alkane envelopes depicted unimodal distribution for sediments from bonny coastal areas with evidence of petroleum contamination (presence of UCM, example Figure-2a). The n-alkanes C₁₆ - C₂₉, maximizing at C₁₇ and C₂₂ (Table-1), detected in virtually all stations along the coastal areas of Bonny river possibly originated from both terrestrial/biogenic and anthropogenic sources, with a stronger biogenic signal. Higher-plant n-alkanes in the range C₂₇ - C₂₉ were barely present in samples from Bonny coastal areas (Figure-3b) giving supportive evidence to other possible biogenic organic matter inputs such as submerged/floating macrophytes as earlier reported by [29].

An odd/even predominance (OEP) in the n-alkanes > C₂₃ has often been used as a marker for a direct input of terrestrial plant waxes into geological and environmental samples [30]. Conversely, an even/odd predominance has been reported to be associated with recent sediments having organic matter input from phytoplanktonic organisms such as diatoms and some bacteria [24, 31]. Our results, however, differ slightly from the even/odd predominance of n-alkanes C₁₄ - C₂₂ reported by [32] for Cretaceous sediments from the upper Benue Trough, Nigeria which was tentatively attributed to hypersalinity. In this study, the odd/even predominances in the C₁₇ - C₂₉ range (Table-1) observed for most stations in the study area was attributed to mixed origin of biogenic, bacterial/microbial and anthropogenic organic source inputs; with stronger biogenic signal based on the results of the factor analysis conducted on the data set.

The identification of the homologous n-alkanes in the hydrocarbon fractions allowed the determination of the carbon preference index (CPI) and Carbon maximum (C_{max}) for each sample set, which give supportive evidence for the relative incorporation of the different n-alkane sources. The CPI, a measure of biologically synthesized n-alkanes [33, 34], indicates the relative contributions of n-alkanes from natural (biogenic/terrestrial; CPI > 1) compared to anthropogenic (CPI < 1) sources. The carbon preference index (CPI) was calculated according to [35] using the same odd-carbon and even-carbon number n-alkane concentrations in the respective samples as follows:

$$CPI = (C_{23} + C_{25} + C_{27} + C_{29} + C_{31}) / (C_{24} + C_{26} + C_{28} + C_{30})$$

Values of CPI ranged from 0.31-1.65 for the entire stations, with maximum value (1.65) for station BN15 in the lower zone (Table-1), suggesting terrigenous/biogenic sedimentary sources of n-alkanes. Conversely, the calculated CPI values for stations BN02, BN08 and BN15 were less than one, indicating a relatively higher proportion of n-alkanes from anthropogenic (mostly petroleum) sources. These results corroborate earlier reports by [35, 36].



In order to evaluate the origin of long-chain n-alkanes (i.e., whether the long-chain n-alkanes are derived from either higher plant waxes or macrophytes) in coastal sediments from the study area, the parameter, Alkane Proxy (P_{aq}) was calculated according to [29] as follows:

$$P_{aq} = (C_{23} + C_{25}) / (C_{23} + C_{25} + C_{29} + C_{31})$$

Values of P_{aq} (Table-1) ranged from 0.7-1.60 for the entire stations. According to [29], values of P_{aq} ranging from 0.01 to 0.23 are linked to terrestrial plant waxes whereas those in the range of 0.48 to 0.94 are associated with submerged/floating species of macrophytes. Results of this study showed the contributions of submerged/floating species of macrophytes to the long-chain sedimentary n-alkanes in our study area.

Factor analysis

For a better understanding of the principal sources and biogeochemical processes responsible for the sedimentary n-alkanes in coastal sediments from Bonny river, South eastern Niger Delta of Nigeria, varimax rotated factor analysis using Statistica version 7.0 was carried out for the data suites. The varimax rotated factor analysis was calculated using eigen values greater than 1.0 and sorted by results having values greater than 0.6 being considered significant influences towards the principal sources. Three factors or principal components (PCs) explained 90.99% for the n-alkanes in stations from bonny coastal areas, with different percentages of total variance for the entire data structure. Factor 1, which was positively loaded with CPI, accounted for 71.48% of the total variance for n-alkanes in stations from coastal areas of Bonny River. This factor was attributed to biogenic/terrestrial sources. The second factor obtained using n-alkanes and compositional indices explained 11.61% of the total variance for n-alkanes in stations from coastal areas of Bonny River; and were found to be negatively associated with compositional indices (CPI, OEP, Paq) in the entire data structure. This factor was attributed to petrochemical sources. The third factor contributed 7.90% of the total variance for n-alkanes in stations from coastal areas of Bonny River. This factor, which was negatively loaded with CPI, OEP and P_{aq} , was attributed to microbial/bacterial source inputs to sedimentary n-alkanes.

PAH distributions and sources

Twenty four (24) parent and alkylated homologous PAHs were detected and quantified in aromatic fractions of sediments from coastal areas of the study area. The range of 2.13 - 16.72mg/kg recorded as total PAH concentrations in this study are comparable to some values reported in literature (Table-2). Highest mean concentration of methylfluorene (C1F) was recorded while naphthalene (N) and its C1- and C2-alkylated homologues (C1N and C2N) were not detected in coastal sediments from the study area (Figure-4a). Spatial variations in the concentrations of total PAHs were equally observed in the

entire sample stations, with station BN05 at the lower zone of the study area recording a maximum value of 16.72mg/kg (Table-1). The high total PAH concentration observed at the lower course of Bonny river (station BN05) could be attributed to the mixing of sea and river water (which causes particles in the river water to rapidly flocculate, leading to elevated accumulation of sedimentary PAHs), sediment resuspension and tidal changes. Highest levels of total PAHs in outer shelf and coastal areas of East China Sea due to sediment resuspension, tidal changes and lateral transport have been reported [20]. Our results corroborate earlier report by [37] on high total anthropogenic PAHs at the mouth of lower Cross River estuary. On global comparison (Table-2), total PAH concentrations recorded for stations from coastal areas of Bonny river are categorized as low to moderate with pyrogenic sources most probably derived from wood burning and emissions from outboard engine boats due to intense maritime transport. Characteristic isomeric series of four- or five-ring PAHs are considered to be produced by microbial and oxidative degradation or transformation of pentacyclic triterpenoids present in vascular plant waxes or woody tissues [38]. Four-ring PAHs, for example parent and alkylated homologous fluoranthene and pyrene, were barely present in stations from our study area (Figure-4a). Thus, the likelihood of contributions from microbial and oxidative degradation or transformation of pentacyclic triterpenoids present in vascular plant waxes or woody tissues to sedimentary PAHs detected in this study is rather tenuous. The significant differences ($p < 0.05$) recorded in the mean concentrations of individual PAHs with respect to compound types and stations further underscore the effects of fluvial geochemistry (tidal changes and lateral transport) on PAH distributions [20, 39] at the different stations along the coastal areas of Bonny river.

Generally, the proportions of parent and alkyl PAHs depend on the combustion temperature [40]. Petrochemicals or vehicular emissions usually exhibit a pattern of low amounts of phenanthrene and maximum at C1-homologues, and a direct input from crude oil spill is characterized by a distribution increasing uniformly from less to more alkylated homologues up to C5 [40]. Our results showed relatively high amounts of phenanthrene and an erratic distribution pattern for the alkylated homologues up to C4, which unarguably reduces the possibility of petrochemicals or vehicular emissions as major source input to the PAH profile in the sediments from the study area. Typical examples of the mass spectra of anthracene and phenanthrene detected in our samples are shown in Figure-2. The absence of dibenzothiophene (Figure-4a), a constituent of coal, crude oil and coal products [6, 41] in stations from the study area also suggests that they did not contribute to the total PAH profile. The coastal vegetation of Bonny River is dominated by swamp with thick mangrove forest (the inhabitants utilize wood obtained from this forest for cooking and agricultural purposes). When grass is burned, it produces a higher proportion of high molecular weight



PAHs than wood [42]. The PAHs detected in coastal areas of Bonny river are low molecular weight (LMW), reducing the likelihood of a significant contribution from grass burns. The presence of C2-phenanthrene (C2-Phe) is particularly useful for identifying wood combustion-derived PAHs as reported by [37]. Several scholars have reported a strong effect of TOC contents on distribution of PAHs [19, 20, 37]. Results from this study clearly showed a strong and positive relationship ($r = 0.88$) between TOC contents and total PAH concentrations (Figure-4d), which is supportive of earlier reports.

In order to distinguish between pyrogenic and petrogenic sources of PAHs in marine sediments, several scholars [6, 7, 8, 10, 18, 19, 43] have relied on the use of PAH diagnostic indices.

For example, ratios of phenanthrene/anthracene, fluoranthene/pyrene, anthracene/(anthracene + phenanthrene), and fluoranthene/(pyrene + fluoranthene) have been reportedly used in source determination of sedimentary PAHs globally. To determine the principal sources of sedimentary PAHs detected in this study, two PAH diagnostic indices, pyrogenic index (PI) and An/(An + Phe), were calculated and used. The PI was calculated according to [18] as follows:

$PI = \Sigma(3-6 \text{ ring PAHs}) / \Sigma(4 \text{ alkylated PAH series})$, where (4 alkylated PAH series = Alkylated naphthalenes, fluorenes, dibenzothiophenes, phenanthrenes).

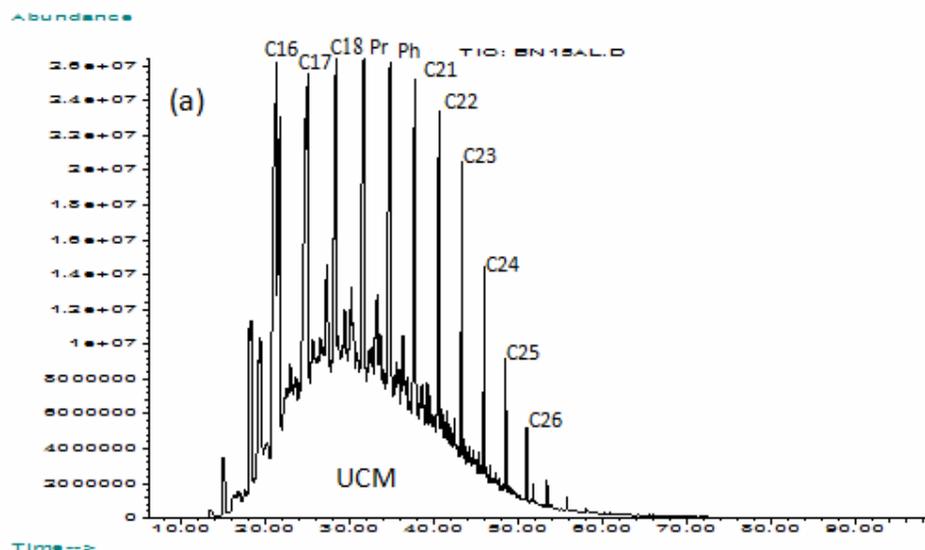
These indices were used because they are very effective in discriminating pyrogenic from petrogenic PAHs [18, 44]. According to these scholars, PI values greater than 0.5 suggests petrogenic; while values less than 0.5 indicate pyrogenic sources of PAHs. All the stations in the study area recorded PI values less than 0.5 suggesting pyrogenic sources. Another reliable and effective diagnostic ratio, An/(An + Phe), was also used in source

determination of PAHs in the study area. Values of An/(An + Phe) greater than 0.1 indicate pyrogenic, and less than 0.1 petrogenic [45]. Again, all the stations recorded An/(An + Phe) values greater than 0.1 (Table-1), pointing to pyrogenic sources of sedimentary PAHs.

The double-ratio plot of phenanthrene/anthracene (Phe/An) versus fluoranthene/pyrene (Fl/Py) has been frequently used to distinguish a mixture of petrogenic and pyrogenic input for sediments [10, 46] despite the low discrimination capacity of Phe/An. A similar parental double ratio plot of anthracene/(anthracene + phenanthrene) versus fluoranthene/(fluoranthene + pyrene) was proposed and used by [7, 44]. In this study, the double-ratio plot of PI and An/(An + Phe) clearly shown in Figure-4c was proposed and used to distinguish between pyrogenic and petrogenic sources of sedimentary PAHs in sediments from coastal areas of Bonny river. A strong correlation ($r = 0.72$) between PI and An/(An + Phe), and the fact that PAHs from pyrogenic processes are more strongly associated to sediments thereby resisting microbial degradation than PAHs of petrogenic origin [13], provide additional support to the pyrogenic source input of PAHs in sediments from coastal areas of Bonny river.

CONCLUSIONS

Hydrocarbons from different sources are prevalent in coastal areas of the Bonny River, Southeastern Niger Delta. The present study showed that sedimentary n-alkanes $C_{16} - C_{29}$ in stations from the study area were of mixed biogenic, anthropogenic and microbial/bacterial sources. Anthropogenic PAHs detected in sediments from the study area were predominantly pyrogenic in origin; with the highest total PAH concentration recorded for station close to the mouth (lower zone) of the Bonny River.



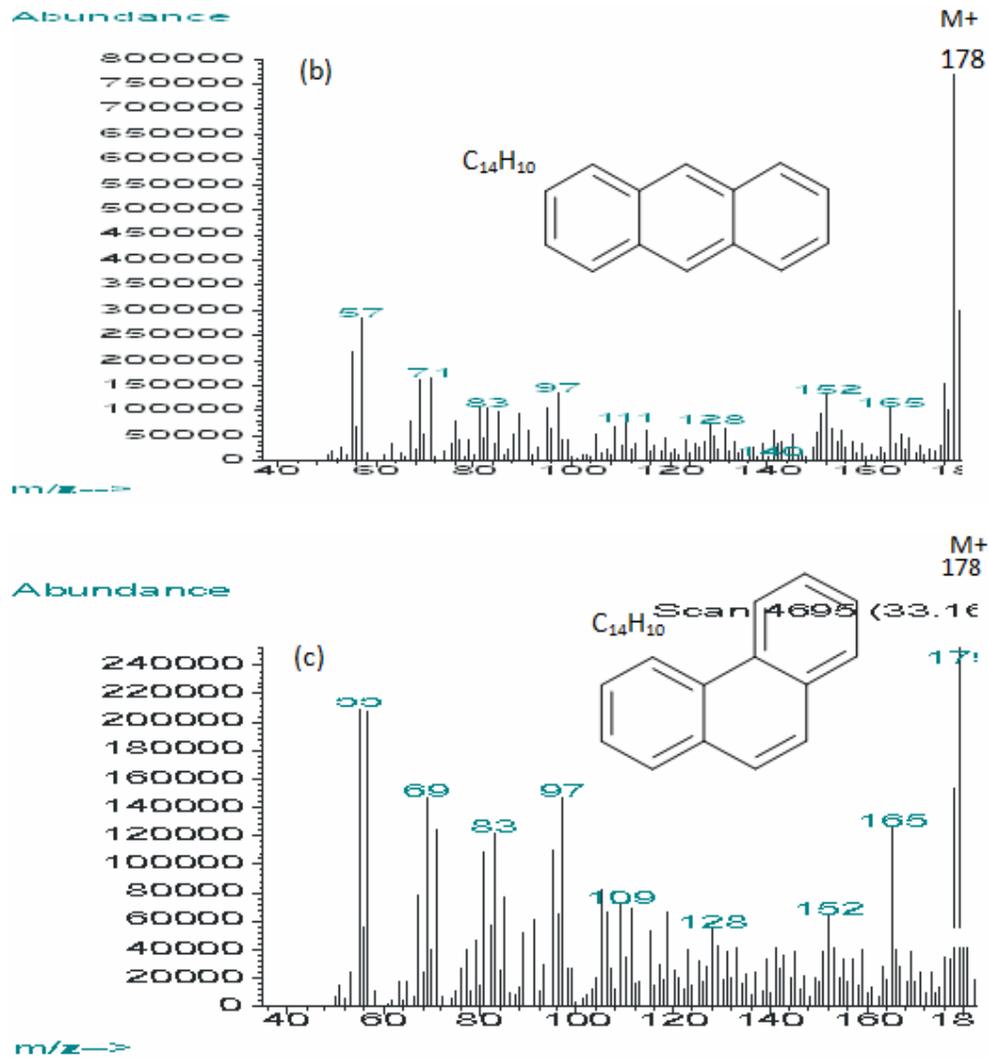
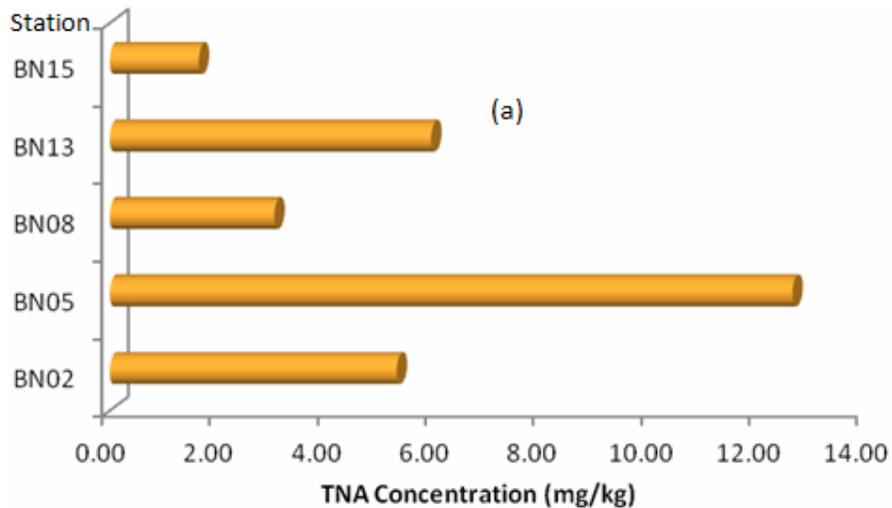


Figure-2. Examples of (a) Gas chromatogram (TIC) showing distributions of n-alkanes and UCM in aliphatic fraction of station BN15, (b) Mass spectrum of anthracene, and (c) Mass spectrum of phenanthrene in aromatic fraction of sediments from coastal areas of Bonny River.





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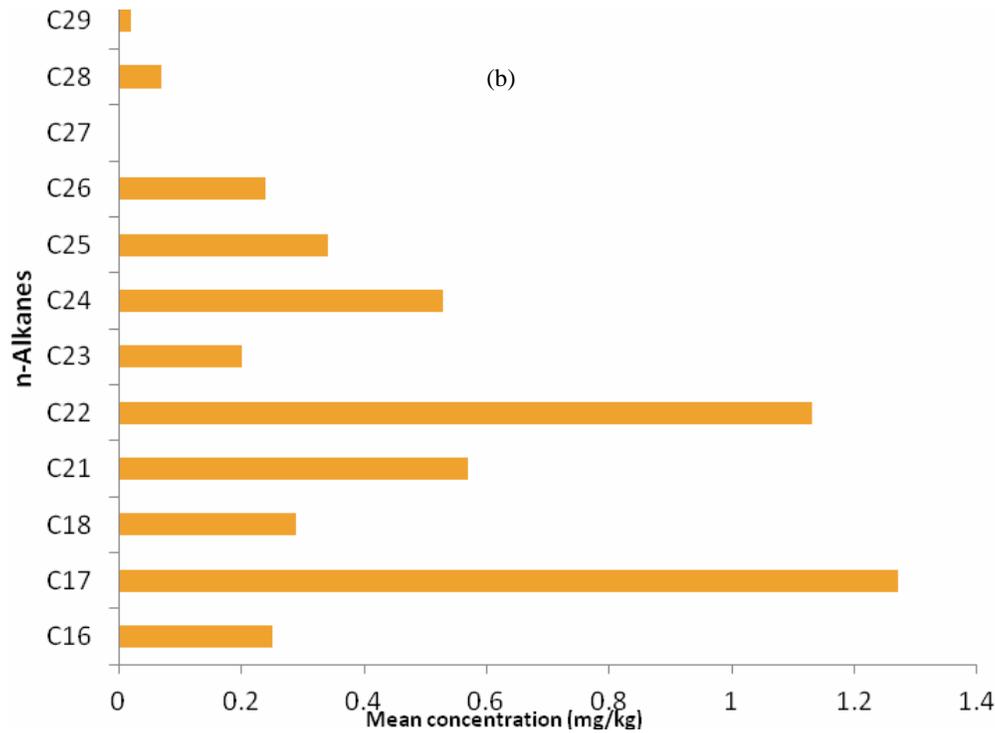
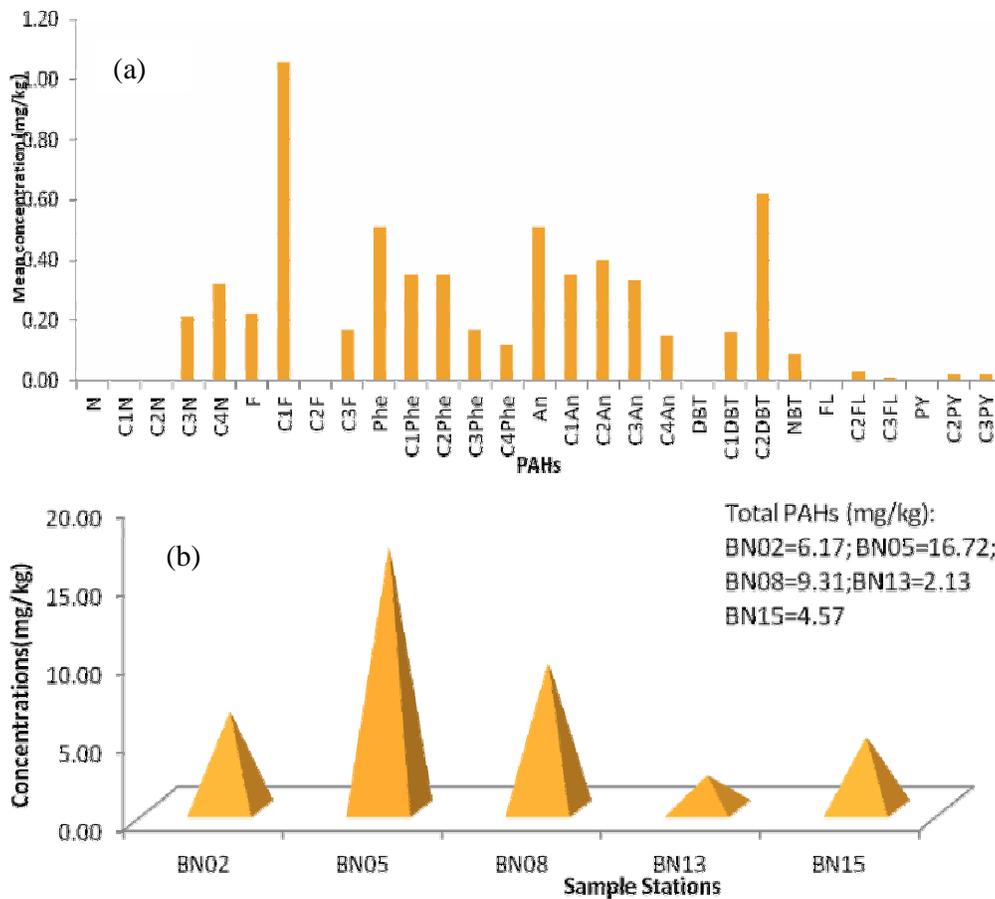


Figure-3. Variations in (a) concentrations of total n-alkanes (TNA), and (b) mean concentrations of n-alkanes in sediments from coastal areas of Bonny river





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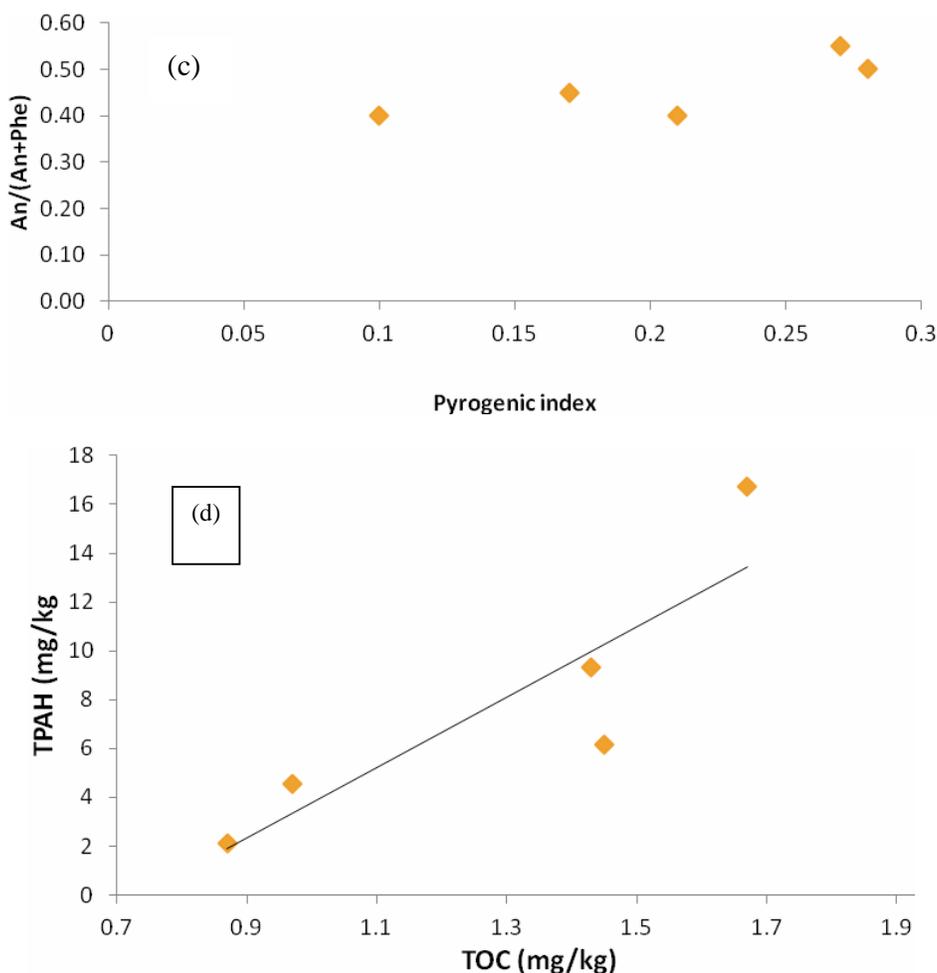


Figure-4. (a) Mean concentrations of PAHs, (b) spatial variations in concentrations of total PAHs, and (c) Double ratio plot of PI versus An/(An + Phe) in sediments from coastal areas of Bonny river (d) Effects of TOC on TPAHs.

REFERENCES

- [1] Wakeham S.G. and Farrington J.W. 1980. Hydrocarbons in contemporary aquatic sediments. In: Baker, R.A. (ed.) Contaminants and Sediments 1. Ann Arbor Science Publishers, Ann Arbor, Michigan. pp. 3-32.
- [2] Dickhut R.M., Canuel E.A. and Countway R.E. 2003. PAHs distributions and associations with organic matter in surface waters of the York River, VA Estuary. *Journal of Organic Geochemistry*. 34, 209-224.
- [3] Nikalaou A., Kostopoulou M., Lofrano G. and Meric S. 2009. Determination of PAHs in marine sediments: Analytical methods and environmental concerns. *Global NEST Journal*. 11(4): 391-405.
- [4] Lipatou E. and Albaiges J. 1994. Atmospheric deposition of hydrophobic organic chemicals in the north western Mediterranean Sea: Comparison with the Rhone River input. *Marine Chemistry*. 46, 153-164.
- [5] Budzinski H., Jones I., Bellocq J., Pierard C. and Garrigues P. 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde Estuary. *Marine Chemistry*. 48, 85-97.
- [6] Wang Z.D., Fingas M. and Page D.S. 1999. Oil spill identification. *Journal of Chromatography*. A. 843, 369-411.
- [7] Yunker M. B., Macdonald R. W., Brewer R. Sylvestre S., Tuominen T., Sekela M., Mitchell R.H., Paton D.W., Fowler B.R., Gray C., Goyette D. and Sullivan D. 2000. Assessment of natural and anthropogenic inputs using PAHs as tracers. The Fraser River Basin and Strait of Georgia 1987-1997. Report DOE FRAP, Vancouver, BC: Environment Canada, Fisheries and Oceans, Canada. 128.



- [8] Yunker M. B., Macdonald R. W., Brewer R., Vingarzan R., Mitchell R.H., Goyette D. and Sylvestre S. 2002. PAHs in the Fraser Basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*. 33, 489-515.
- [9] Stout S.A., Uhler A.D. and McCarthy K.J. 2001. A Strategy and methodology for defensibly correlating spilled oil to source candidates. *Environmental Forensics*. 2, 87-98.
- [10] Readman J.W., Fillman G., Tolosa I., Bartocci J., Villeneuve J.P., Catinni C. and Mee L.D. 2002. Petroleum and PAH contamination of the Black Sea. *Marine Pollution Bulletin*. 44, 48-62.
- [11] Baumard P., Budzinski H., Mchin Q., Garrigues P., Burgeot T. and Bellocq J. 1998. Origin and bioavailability of PAHs in Mediterranean Sea from mussel and sediment records. *Estuarine, Coastal and Shelf Science*. 47, 77-90.
- [12] Sicre M.A., Marty J.C., Saliot A., Aparico X., Grimalt J. and Albaiges J. 1987. Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: Occurrence and origin. *Atmospheric Environment*. 21, 2247-2259.
- [13] Perra G., Renzi M., Guerranti C. and Focardi S.E. 2009. Polycyclic aromatic hydrocarbons pollution in sediments: distribution and sources in a lagoon system (Orbetello, Central Italy). *Transitional Waters Bulletin*. 3(1): 45-58.
- [14] Boehm P.D. and Farrington J.W. 1984. Aspects of the polycyclic aromatic hydrocarbon geochemistry of the recent sediments in the Georges Bank region. *Environmental Science and Technology*. 18, 840-845.
- [15] Pitt R.E., Field R., Lalor M. and Brown M. 1995. Urban Stormwater Toxic Pollutants: Assessment, Sources, and Treatability. *Water Environment Research*. 67(3): 260-275.
- [16] Countway R.E., Dickhut R.M., Canuel E.A. 2003. Polycyclic aromatic hydrocarbon (PAH) distributions and associations with organic matter in surface waters of the York River, VA Estuary. *Organic Geochemistry*. 34, 209-224.
- [17] Yim U.H., Hong S.H., Shim W.J., Oh J.R. and Chang M. 2005. Spatio-temporal distribution and characteristics of PAHs in sediments from Masan Bay, Korea. *Marine Pollution Bulletin*. 50, 319-326.
- [18] Meniconi M.G. and Barbanti S.M. 2007. Evaluation of hydrocarbon sources in Guanabara Bay, Brazil. In: Wang, Z. and Stout, S.A. (eds.). *Oil spill environmental forensics: Fingerprinting and source identification*, Elsevier, USA. pp. 505-536.
- [19] Liu Y., Chen L., Jianfu Z., Qinghui H., Zhiliang Z. and Hongwen G. 2008. Distribution and sources of polycyclic hydrocarbons in surface sediments of rivers and an estuary in Shanghai, China. *Environmental Pollution*. 154, 298-305.
- [20] Hung C.C., Gong G.C., Ko F.C., Lee H.J., Chen H.Y., Wu J.M., Hsu M.L., Peng S.C., Nan F.H. and Santschi P.H. 2011. Polycyclic aromatic hydrocarbons in surface sediments of the East China Sea and their relationship with carbonaceous material. *Marine Pollution Bulletin* (Website: [http:// www.ncbi.nlm.nih.gov/pubmed](http://www.ncbi.nlm.nih.gov/pubmed)).
- [21] Alebic-Juretic A. 2011. Polycyclic aromatic hydrocarbons in marine sediments from the Rijeka Bay area, Northern Adriatic, Croatia, 1998-2006. *Marine Pollution Bulletin*. 62(4): 863-869.
- [22] Wilcke W., Amelung W., Krauss M. and Martins C. 2003. PAH patterns in climatically different ecological zones of Brazil. *Journal of Organic Geochemistry*. 3, 1450-1477.
- [23] Anyakora C., Ogbeche A., Palmer P., Coker H., Ukpo G. and Ogah C. 2005. GC/MS analysis of polynuclear aromatic hydrocarbons in sediment samples from the Niger Delta region. *Chemosphere*. 60, 990-997.
- [24] Ekpo B.O., Oyo-Ita O.E. and Wehner H. 2005. Even n-alkane/alkene predominances in surface sediments from the Calabar River, S.E. Niger Delta, Nigeria. *Naturwissenschaften*. 92(7): 341-346.
- [25] Tamuno T.T. 2008. The Geographical Niger Delta. *Proceedings of the International Conference on the Nigerian state, Oil Industry and the Niger Delta*. pp. 916-930.
- [26] Nwilo P.C. and Badejo O.T. 2008. Impacts and management of oil spill in Nigerian coastal environment. *Proceedings of the International Conference on the Nigerian State, Oil Industry and the Niger Delta*. pp. 1217-1232.
- [27] 1986. EPA-540, Soxhlet extraction. In: *Test Method Evaluation Solid Waste, Physical/Chemical Methods, Laboratory Manual*, Washington DC, Environmental Protection Agency, v. 1-B.
- [28] Schoell M., Teschner M., Wehner H, Durand B. and Oudin J.L. 1983. Maturity related biomarkers and stable isotope variation and their application to oil/source rock correlation in the Mahakam Delta, Kalimantan. In: Bjoroy, M. (ed.), *Advances in Organic Geochemistry 1981*, Chichester, Wiley. pp. 156-163.



- [29] Ficken K.J., Li B., Swain D.E. and Eglinton G. 2000. An n-alkane proxy for sedimentary input of submerged/floating fresh water aquatic macrophytes. *Organic Geochemistry*. 31, 745-759.
- [30] Simoneit B.R.T., Grimalt J.O., Hayes J.M. and Hartman H. 1987. Low temperature hydrothermal maturation of organic matter in sediments from the Atlantis II Deep Red Sea. *Geochimica et Cosmochimica Acta*. 51, 879-894.
- [31] Elias V.O., Simoneit B.R.T. and Cardoso J.N. 1997. Even n-alkane predominances on the Amazon Shelf and a Northeast Pacific Hydrothermal System. *Naturwissenschaften*. 84, 415-420.
- [32] Pearson M.J. and Obaje N.G. 1999. Onocerane and other triterpenoids in Late Cretaceous sediments from the Upper Benue Trough, Nigeria: Tectonic and palaeoenvironmental implications. *Organic Geochemistry*. 30, 583-592.
- [33] Simoneit B.R.T. 1978. The organic chemistry of marine sediments. In: Riley, J.P. and Chester, R. (eds), *Chemical oceanography*, Vol. 7, 2nd edition, Academic Press, New York. pp. 233-311.
- [34] Simoneit B.R.T., Sheng G., Chen X., Fu J., Zhang H. and Xu Y. 1991. Molecular marker study of extractable organic matter in aerosols from the urban areas of China. *Atmospheric Environment*, 25A, 2111-2129.
- [35] Zhu Y., Liu H., Cheng H., Xi Z., Liu X. and Xu X. 2005. The distribution and source apportionment of aliphatic hydrocarbons in soils from the outskirts of Beijing. *Organic Geochemistry*. 36, 475-483.
- [36] Oyo-Ita O.E., Ekpo B.O., Oros D. R. and Simoneit B.R.T. 2010. Distribution and sources of aliphatic hydrocarbons and ketones in surface sediments from the Cross River estuary, S.E. Niger Delta, Nigeria. *Journal of Applied Sciences in Environmental Sanitation*. 5(1): 13-24.
- [37] Ekpo B.O., Oyo-Ita O.E., Oros D.R. and Simoneit B.R.T. 2011. Distributions and sources of polycyclic aromatic hydrocarbons in surface sediments from the Cross River estuary, S.E. Niger Delta, Nigeria. *Environmental Monitoring and Assessment*. DOI 10.1007/s 10661-011-2019-5.
- [38] Jaffe R., Rushdi A.I., Medeiros P.M. and Simoneit B.R.T. 2006. Natural product biomarkers as indicators of sources and transport of sedimentary lipids in a subtropical river. *Chemosphere*. 64, 1870-1884.
- [39] Short J.W., Kolak J.J., Payne J.R. and van Kooten G.K. 2007. An evaluation of petrogenic hydrocarbons in Northern Gulf of Alaska continental shelf sediments-The role of coastal oil seep inputs. *Organic Geochemistry*. 38, 643-670.
- [40] Aboul-Kassim T.A.T. and Simoneit B.R.T. 1995. Aliphatic and aromatic hydrocarbons in particulate fallout of Alexandria, Egypt. Sources and implications. *Environmental Science and Technology*. 29, 2473-2482.
- [41] Oros D.R. and Simoneit B.R.T. 2000. Identification and emission rates of molecular tracer's coal smoke particulate matter. *Fuel*. 79, 515-536.
- [42] Jenkins B.M., Turn S.Q. and Williams R.B. 1996. Emission factors for polycyclic aromatic hydrocarbons from biomass burning. *Environmental Science and Technology*. 30, 2462-2469.
- [43] Gui-peng Y. 2000. Polycyclic aromatic hydrocarbons in the sediments of the South China Sea. *Environmental Pollution*. 108, 63-71.
- [44] Yunker M. B. and Macdonald R. W. 2003. Petroleum biomarker sources in suspended particulate matter and sediments from the Fraser River Basin, Canada. *Journal of Organic Geochemistry*. 34(11): 1525-1542.
- [45] Li G., Xia X., Yang Z., Wang R., Voulvoulis N. 2006. Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River, China. *Environmental Pollution*. 144, 985-993.
- [46] Ke L., Wong T.W.Y., Wong Y.S. and Tam N.F.Y. 2002. Fate of polycyclic aromatic hydrocarbon (PAH) contamination in a mangrove swamp in Hong Kong following an oil spill. *Marine Pollution Bulletin*. 45, 339-347.
- [47] Pereira W.E., Hostettler F.D. and Rapp J.B. 1996. Distributions and fate of chlorinated pesticides, biomarkers and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco Bay, California. *Marine Environmental Research*. 41, 299-314.
- [48] Kayal S.I. and Connel D.W. 1989. Occurrence and distribution of polycyclic aromatic hydrocarbons in surface sediments and water from the Brisbane River Estuary, Australia. *Estuarine Coastal and Shelf Science*. 29, 473-487.
- [49] El Nemr A., Said T.O., Khaled A., El-Sikaily A. and Abd-Allah A.M. 2007. The distribution and sources of polycyclic aromatic hydrocarbons in surface sediments along the Egyptian Mediterranean coast. *Environmental Monitoring Assessment*. 124(1-30): 343-3.

**Table-1.** Concentrations of n-alkanes and hydrocarbon source diagnostic indices for sediments from coastal areas of Bonny River.

Zone ^a	Station	TOC (%)	n-alkane concentrations (mg/kg)													Source diagnostic indices						
			C ₁₆	C ₁₇	C ₁₈	C ₂₁	C ₂₂	C ₂₃	C ₂₄	C ₂₅	C ₂₆	C ₂₇	C ₂₈	C ₂₉	TNA	*TPAH	C _{max}	CPI	OEP	P _{aq}	PI	An/An +Phe
Upper	BN15	0.97	-	0.16	-	0.26	0.26	0.21	0.21	0.08	0.04	-	0.01	-	1.65	4.57	C ₂₂	0.31	0.78	1.00	0.17	0.45
Middle	BN02	1.45	0.20	1.32	0.08	0.37	0.83	0.96	0.29	0.37	0.45	-	0.12	-	5.32	6.17	C ₁₇	0.90	1.18	1.00	0.28	0.50
	BN08	1.43	0.08	0.82	0.76	1.24	0.17	0.47	0.15	0.08	0.01	-	0.05	-	3.05	9.31	C ₁₇	0.50	3.16	1.00	0.27	0.55
Lower	BN13	0.87	0.32	1.27	0.59	0.42	1.13	1.00	0.53	0.34	0.24	-	0.07	0.05	5.96	2.13	C ₁₇	1.65	1.06	1.60	0.10	0.40
	BN05	1.67	0.67	2.76	-	0.75	3.25	2.34	1.45	0.83	0.46	-	0.10	0.05	12.66	16.72	C ₁₇	1.60	0.83	0.70	0.21	0.40

^a Based on possible anthropogenic inputs: Upper zone = Domestic sewage as a result of fishing settlements, Middle zone = Engine boat pollution and fishing activities, Lower zone = Oil spills, pollution from maritime transport, oil vessels and untreated sewage.

*Sum of PAHs detected in each station, CPI = Carbon Preference Index, OEP = Odd/even predominance (C₂₁ - C₂₅),

PI = Pyrogenic Index, An/An +Phe = Anthracene/ (Anthracene + Phenanthrene)

P_{aq} = n-Alkane Proxy, C_{max} = Carbon maximum

Table-2. Literature data on total PAH concentrations (mg/kg dsw) of sediments from some coastal sites in the world.

Location	No. of PAHs analysed	Concentration range (mg/kg)	References
May Bay, Korea	24	0.21 - 2.67	[17]
San Francisco Bay, USA	17	2.65 - 27.68	[47]
Brisbane River Estuary, Australia	17	2.84 - 13.47	[48]
Guanabara Bay, Brazil	38	0.56 - 58.44	[18]
Egyptian Mediterranean coast	16	0.09 - 6.34	[49]
Rivers and Estuaries in Shanghai, China	17	0.11 - 1.71	[19]
Rijeka Bay Area, Northern Adriatic, Croatia	16	3.01 - 6.31	[21]
Bonny Coastal Area, Niger Delta, Nigeria	24	2.13 - 16.72	Present study

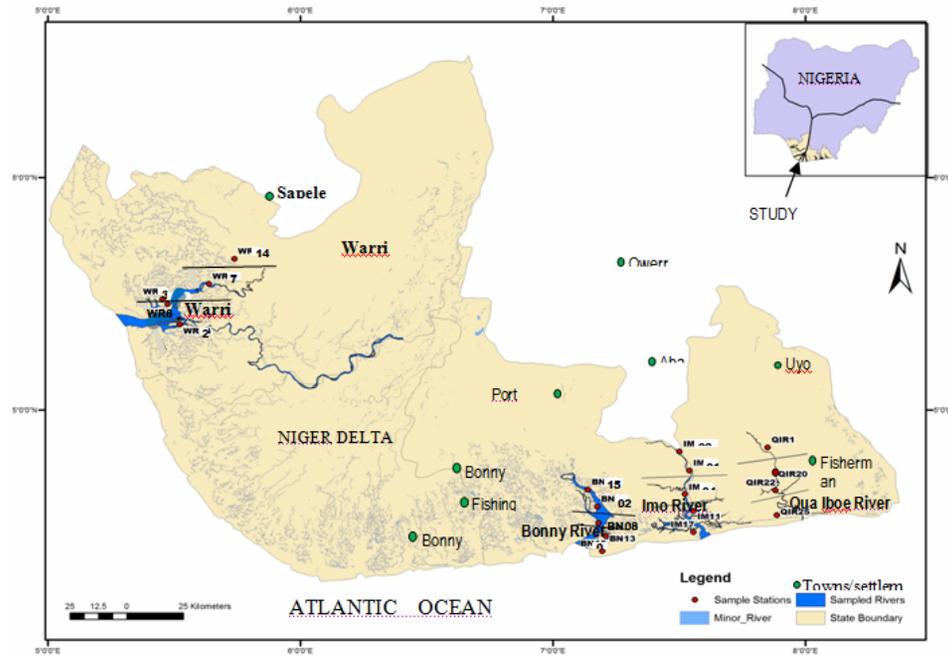


Figure-1. Map of study area showing sample stations.