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Assessment of Polynuclear Aromatic Hydrocarbon in Marine Sediments Delta State, Southern Nigeria

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Abstract: Sediments from different zones in southern Nigeria were analyzed for the composition of their Polynuclear aromatic hydrocarbon (PAHs). The purpose of this study was to provide information on the presence of PAHs distribution in these sediments for managing waste environment and preserving the health of aquaculture and humans. This was done for 16 PAHS collected from Warri (PC) petrochemicals, Burutu (FS) Finishing, Bomadi (FA) farming and Omasuomar. (CN) – Natural field. A mixture of acetone / dichloromethane / n-hexane was used for the soxhlet extraction of PAH_S from the sediment samples. This was done using gas chromatography –mass spectrometry. The concentrations of E16PAH Varied from 0.00-2. 411, 0.00-0.848, 000-1.695, and 0.00-0.717 µglg for sediments from these zones respectively. The benzo (a) pyrene (BaA) concentration in all samples were below the stated limit of 0.7 µgil for surface and sediment. Since it is an index for the contamination of PAHS. There is need for caution in the discharge of waste, use of pesticides and herbicides since sediment is the final sink before transfer in the food chain. The sources indicated PAHs originated from liquid fossil fuel burning, combustion of wood, biomass and high temperature processes and pyrogenic sources. Therefore, attention should be paid on marine ecosystem by authorities.

Keywords: Assessment, Sources, Polyaromatic Hydrocarbons, Sediments, Southern Nigeria

1. Introduction

Polynuclear aromatic hydrocarbons (PAHs) consist of more than 100 Organic compounds containing two to six fused aromatic rings with various structural arrangements. [1] They comprise the largest class of chemical compounds known to be cancer- causing agents and are included in the priority. Pollutants list due to their mutagenic and carcinogenic properties. [2] PAHs are primarily associated with human activities from industries emissions, vehicular traffic, and combustion of biomass, fossil fuel and oil spillage. Others include national fires, volcanic eruptions, geochemical reactions etc [5]. They can readily be adsorbed onto particulate matter and threat to ecosystem safety and human health [4].

They are classified into compounds that are able to impair endocrine, abnormalities in fetus glands and body metabolism. Aquatic environment especially rivers, oceans, and estuarine system receive significant amount of chemicals through surface run off, waste water discharge and atmospheric precipitation. [8, 10] The slow photolysis and hydrolysis rate of poly aromatic hydrocarbons determines their potentials to bio-accumulate in sediments with regards to ecotoxicity of these compounds to microorganisms, invertebrates, algae, fish, shrimps in saltwater, fresh water or sediments can be a long-term contamination – accumulation sink or through suspension. Human are contacted through diet, bio-accumulation in the fold chain, through industrial processes, storing and transportation [12] PAHs can cause cancer, mutation, abnormalities in fetus, disrupt the endocrine and immune systems [7].

This study evaluates the distribution and accumulation of PAHs in sediments for managing water environments and preserving the health of aquaculture and humans. It evaluated PAHs contaminated sample (sediments) from different locations, since accumulation of pollutants in the marine environment have caused the biodiversity cycle of the region to the constancy under threat.

2. Material and Methods

2.1. The Studied Area

The studied area was within the coastal area at convenient point along southwest delta state Nigerian. Petrochemicals, gas industries, refineries and automobile shops are located along these creeks. In addition we have finishing, municipal services, agricultural activities and wastewater treatment are of environment concern, (Figure 1). It lies in the mangrove belt of Nigerian with thick forest and high humidity. It is 200-500cm above sea level.

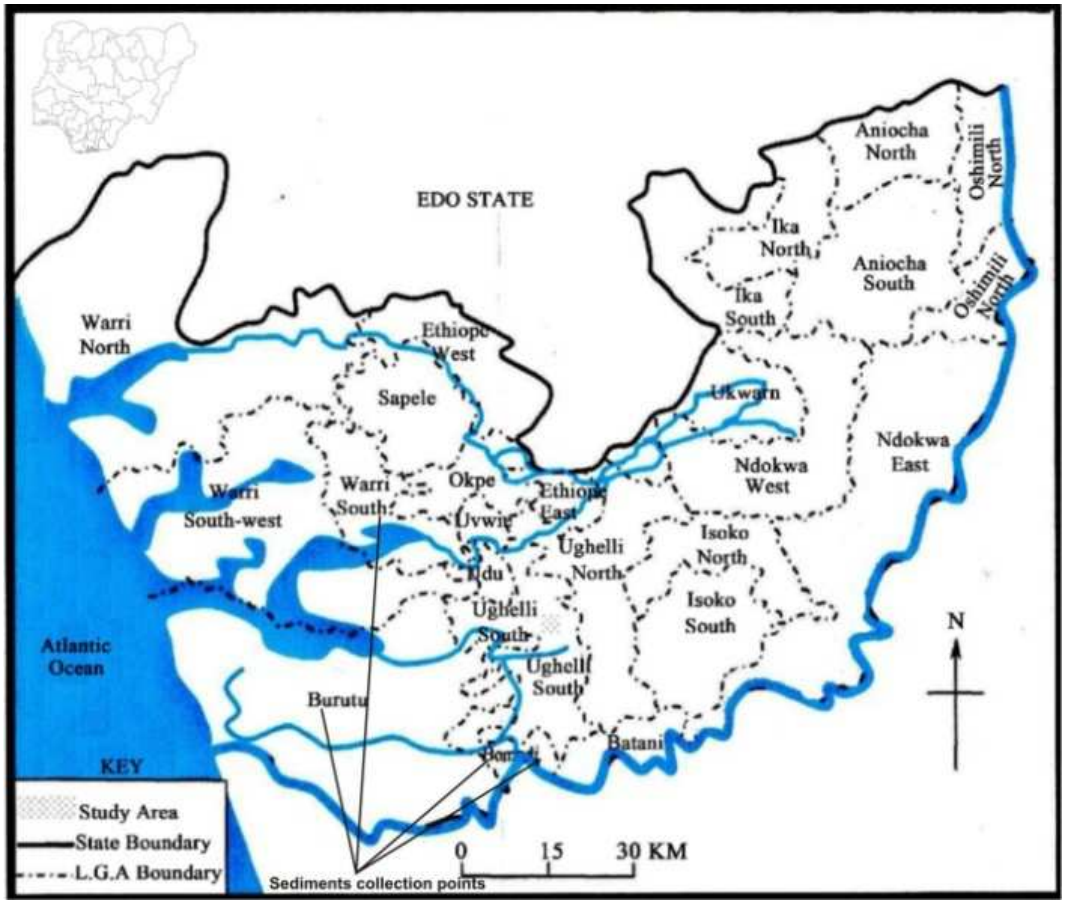

Figure 1. *Map of Delta State showing seawater collection point.*

2.2. Sample Collection

Samples were collected from different sites in the above named regions and were coded Bomadi (FA) Burutu (FS), Omasuomor (CN) and Warri (PC), Steel Grab device was used to collect sediments. They were placed in amber glass containers and transported to the laboratory with dry ice at 4°C and freeze for 72hrs, passed through 0.5mm sieve and kept at 20°C for other analysis.

2.3. Sample Preparation

The PAHs concentration in the sediments was done by soxhet extraction of [16] using 3540c method. 2g of dry and homogenous samples of sediments were taken and poured into clean centrifuges with 4g of anhydrous Na_2SO_4, and spike with 100ng of deuterated PAH standards. Each was soxhlet extracted with 150ml of a 1:1:1 mixture of acetone /DCM/ n-hexane for 16hrs. The extract was reduced to 2ml at 30°C and by rotary evaporation to 250mbar and cleaned on an alumini/silicia gel column. PAHs was eluted from the column with a 30ml mixtureof 1:1 DCM /n-hexane and reduced to 2ml with a mild nitrogen gas flow.

2.4. Physiochemical Properties

Particle size analysis was done using particle size analyzer (Master size 2000, Britain) with a capacity of analyzing sizes between 0.02 – 2000Nm [14]. The percentage of three fractions of clay, silts and sand was determined. The pH of soil was determined using Hach HQ20 pH Britain meter, electrical conductivity (EC) of the samples was measured by HACH DR 4000U, Total organic carbon was done using wet dichromate method of [13].

2.5. Analysis

The determination of the PAHs concentrations in these samples was with a Finnegan magnum instrument equipped with a CTC A20110 auto sampler a SONm, 0.251DDB5 MS chromatograph with a mass detector fused silica capillary

column (J and W scientific Folson CA) with a mass detector, a capillary column of 30m in high purity degree in agreement with a flow rate of 1.0ml/min 1.0µl was ingested into gas chromatogram, diameter of 0.25 and a film thickness of 0.25Nm. Helium as a carrier gas chromatogram at a temperature of 60°C maintained for 3mins then increased from 180°C at 10°C min^{-1}, from 180°C to 250°C at $5min^{-1}$, finally from 250 – 300°C at $3min^{-1}$. The temperature was programmed at 240°C for ion source that of the injector at 280°C. The retention time of samples were quantified in identification of the PAHs in samples.

2.6. Reagents and Chemicals

A standard solution containing US EPA 16 PAHs and 2-methylnaphthalene (2- MIV ap) New Haven, (USA). A mixture surrogate of four standard solution containing four otopicallylabeled PAHs from (chem service, Westchester, PA) namely acenaphtalene $–d_{10}$, crysene $–d_{12}$, phenanthren $–d_{10}$ and perelened $–d_{12}$ was used as internal standard silica gel and analytical grade anhydrous sodium sulphate, n-hexane (95% purity) all products of sigma- Aldrich (USA), Dichloromethane (DCM) 99.99% purity and alumina of analytical grade were products of Merch (Germany).

2.7. Quality Control / Quality and Statistical Analysis

Blank methods, recoveries of the C-labelled PAHs were used as analytical methods. The PAHs quantification was achieved using an internal calibration. It was based on the ratio of the peak height of the ion to that of internal standard. The analyses of samples were carried out in triplicate and precision measured by the relative standard deviation (RSD) which varies from 0.87 – 16.79. The LODs and LOQs of the PAHs ranged from 0.00 to 1.70 and 0.06 - 5.00µglg respectively. The devices were calibrated on a daily basis. The data obtained are presented in Table 1.

2.8. Statistical Analysis

The results obtained were statistically analyzed using SPSS software version 20.

Table 1. *The mean recovery, LOD and LOQ values for each PAH compound.*

COMPOUND	MEAN RECOVERY (%)	LOD (µglg)	LOQ (µglg)
Nap	71.12	0.06	0.20
2 –Mnap	71.12	0.04	0.10
Acy	71.12	0.02	0.06
Ace	71.12	0.02	0.06
Flu	71.12	0.02	0.06
Phen	91.94	0.03	0.09
Ant	91.94	0.02	0.06
Flt	91.94	0.04	0.12
Pyr	61.92	0.04	0.12
BaA	61.92	0.06	0.20
Cry	64.78	0.06	0.20
Bbf	64.78	0.10	0.30
BKF	64.78	0.15	0.50
BnF	64.78	0.15	0.50
LndP	64.78	1.70	5.00
DahA	64.78	0.00	2.50
BghiP	64.78	0.75	2.70

3. Results and Discussion

3.1. Physiochemical Properties and Land Use Effect

The physiochemical properties of samples of sediments from southern Nigeria in petrochemical, fishing, farming and natural area are as shown below in Table 2; The pH of the sediments lied within the range of 5.01 - 7.10 (± 0.48) for PC, 6.53 – 7.30 (± 0.49) for FS, 6.03 – 7.00 (± 0.17) for FA and 6.23 – 8.63 (± 0.21) for CN. For petrochemical and fishing samples are neutral to acidic level while that of farming and control (natural field) are mild alkaline to neutral level. The low level of pH is traceable to discharges with organic components forming acidic compounds on degradation [17].

Table 2. *Physiochemical parameters of sediments from different land use in Delta state southern Nigeria.*

Parameters	PC		FS		FA		CN	
	Range	Mean + SD	Range	Mean + SD	Range	Mean + SD	Range	Mean + SD
Ph	5.01-7.10	6.32±0.48	6.53-7.30	7.10±0.19	6.02-7.00	7.10±0.17	6.23-8.63	7.40±0.21
TOC	2.20-3.36	2.70± 0.47	1.00-2.93	1.53±0.56	2.12-3.07	3.15±0.46	0.41-1.40	0.60±0.31
Salinity‰	1.21-2.00	1.46±0.03	0.04-1.02	0.00±0.21	1.50-2.10	1.87±0.31	0.06-0.10	0.12±0.02
Total PhosphorusTP µglg	180-300	251.73±45.72	296-720	442±93.10	365-480	402±26.61	8.0-110	91.1±13.32
Clay (%)	15.82-80.53	22.31-60.32	5.80-14.42	10.80±3.02	7.34-40.21	16.12±8.86	7.10-13.30	11.17±2.10
Silt (%)	22.31-60.32	41.70±14.10	26.10-60.10	51.83±13.30	19.21 50.01	33.30±12.60	30-64. 40	41. 62±12.4
Sand (%)	17.00-50.00	37.00±12.31	18.30-52.30	44.51±12.18	13.31-60.14	48.23±18.14	21.16-60.02	43.51±13.1

The pH in the neutral area are higher, this could be due to the fact that farming is associated with fertilizers, petrochemical waste and fish farming decrease the pH of this areas [8].

The concentration of organic carbon (TOC) in the sediment samples 2.20 – 3.36 (± 0.47) for PC, 1.00 – 2.93 (± 0.31). The TOC was higher in FA due to farming activities having high organic compounds from pesticides and fertilizers which can alter the carbon cycle [9]. The salinity of the sediments were non-saline materials from the results in Table 2, 1.21 – 2.00 (± 0.03) for PC, 0.40 – 1.02 (±0.21) for FC, 1.50 – 2.10 (±0.31) for FA and 0.06 – 0.10 (±0.02) for CN respectively. The phosphorus levels were with 180-300 (±45.72) for PC, 296 – 720 (±93.10) for FS, 365 – 480 (±36.61) for FA and 80 – 110 (±13.32) µglg for CN.

The concentration of total phosphorus is as FA>FS>PC>CN. The specialization and distribution of phosphorus in sediment is governed by salinity [6]. When salinity increases, phosphorus desorption of the surface of sediments increases and the content of phosphorus desorption

of the surface of sediments increases and the content of phosphorus in sediments decreases. For the clay content lied within the range of 15.82 – 30.53% (±3.78) for PC, 5.80 – 14.42% (±3.02) for FS, 7.34 – 40.21% (±8.86) for FA and 7 - 10 – 13.30% (± 2.10) for CN. The content of silt lied within 22.31 – 60.32% (± 14.10) for PC, 26.10 – 60.10% (±13.30) for FS, 91.21 – 50.51% (±12.60).

For FA and 30 – 64.40% (±12.40) for CN. While the sand content lied within 17.00 – 50.00% (±12.30) for PC, 18.30 – 52.30% (±12.18) for FS and 21.16- 60.02% (±13.10) for CN. The dominant fractionsare sand and silt which could be due to fluctuation of tides which constitute re-suspension in the sediments [15].

3.2. PAHs Concentration Sources and Land Use Effects

The concentration of PAHs in sediments from the four areas are shown in Table 3.

Table 3. *Polynuclear aromatic hydrocarbon concentrations in sediments (mean values).*

COMPONENTS	PC	FS	FA	CN
Nap	0.726	0.610	0.510	0.499
2- MNap	0.911	0.766	0.640	0.627
Acy	0.250	0.210	0.176	0.172
Ace	0.952	0.783	0.655	0.641
Flu	0.852	0.716	0.599	0.586
Phen	1.320	0.110	0.928	0.908
Ant	2.411	0.260	1.695	0.658
Flt	1.009	0.848	0.706	0.694
Pyr	0.348	0.292	0.245	0.239
BaA	0.087	0.730	0.061	0.060
Cry	0.210	0.177	0.148	0.145
Bbf	0.093	0.780	0.065	0.64
BkF	0.052	0.440	0.037	0.36
Bnf	1.042	0.876	0.733	0.717
Indp	0.000	0.000	0.000	0.000
DahA	0.000	0.000	0.000	0.000
BghiP	0.000	0.000	0.000	0.000
Total PAH	10.243	8.609	7.200	6.045
TI	1.681	2.249	1.666	2.756

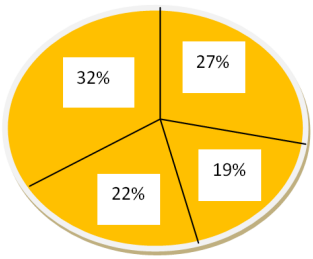

Figure 2. *Distribution of PAHs in Sediments of Delta State Southern Nigeria.*

PAHs compounds found in these sediments did not contained high molecular weights such as benzo (a), perylene, dibenzo (a, h), Anthracene, Indenol (1, 2, 3) perylene and benzo (g, h, i) perylene. High values of PAHs in PC can be attributed to the presence of oil companies/petrochemical followed by fishing (FS) from the total values. Coastal waters in these areas were contaminated by wastewater. This is as a result of transportation, bio-accumulation of PAHs produced by the activities of man, which accumulates in sediments [20]. This is in accordance with contaminants as phthalate acid ester, pesticides. From the four different sites (Ant) occurred highest with mean concentration of 41Nglg for pc, 0.260µglg for Fs, 1695 µglg for and 0.658uglg for CN. The four the different sites and adsorbed by sediments since is not easily degradable. The finally get to the sediment through fine particles, surface runoff effluents and industrial wastes. Ant and Phen had concentrations higher compared with other 3-ring PAHs which is related to thermodynamic stability that is high and high vapor pressure in the gaseous phase [11].

The mean concentration of PAHs of the sequence PC> FS> FA>CN BaA/BaA+Chry) less than 0.2 suggest petroleum source, while ratio values of 0.2__0.35 depictsources associated with liquid fossil fuel burning and values> 0.5 are linked to combustion An Lndp/ (Lndp/Bghip) ratio <0.2 indicate PAH input from petroleum, between 0.2 and 0.5 input from liquid coal / biomass combustion sources, but these were not detected in all the samples in all the studiedareas PC was 0.292 and FA 0.290 suggested PAH input was from burning of liquid fossil fuels while FS and CN>0.5 depict input from coal/ biomass combustion source, but these were not detected in all the sample in all the studied areas PC was 0.292 and FA 0:290 suggested PAH input was from burning of liquid fossil fuels while FS and CN>0.5 depict input from coal / biomass combustion source (wegbue, 2022). Total index (TI) which is the sum total of PHAs isomer ratios of Ant / (Ant +Phen), BaA/(Bah + Chry) Flt (Flt+Pyr) and Indp / (Indp+Bghip). A (TI) value <4 indicates PAH sources are linked to low temperature combustion, while a TI value >4 indicates high temperature combustion processes as source of PAHs in these environments. An Ant/ (Ant+phen) ratio <0.1 represent petrogenic origin. The Ant/ (Ant +phen) ratio were 0.1 which showed that these sediment samples were contaminated by PHAs from pyrogenic sources [3]. If there is continuous discharge into these marine bodies, there could be negative effect on microbial population composition, micro and macro organisms enzymatic activities can be altered [18]. The marine region should be protected.

4. Conclusion

The PAHs concentrations in sediments from these areas followed this order PC>FS>FA>CN i.e. petrochemical, fishing, farming and natural field. The concentration of BaA was present in all the samples were low except FS which exceeded the permissible of 0.7 µglg corresponding to an excess lifetime cancer risk of 10-5 [19]. The concentration of individual PAHs in coastal sediment are in the neighborhood of 0.05NgIl. There was high concentration of PAHs in the sediment. There is need to caution spills (oil), usage of pesticides, herbicides, biomass combustion and gas flaring. Further studies on risk assessment, use of pesticides should be carried out in these areas, in terms of its ecotoxicology, Bait and total PAHs exceeded hazardous level. Wastes containing PAHs should not be discharged into the coastal waters also studies on PAHs in aquatic organisms and plants

are required for principal so that sediments can be protected. This study is an assessment only, the risk assessment and comprehensive bioaccumulation and living organisms will be done for sediment protection.

Abbreviation

PAHs, Polynuclear aromatic hydrocarbons, NAP, Nephalcne, Acy, acenaphthylene, Ace, acenaphthene flu, fluorine, Phen, Phenanthrene, Ant, Anthracene, Flt, Fluoranthene, Pyr, pyrene, BaA, Benzo (a) anthracene, Chry, Chrysene, Bbf, Benzo (b) fluoranthene, Bkf, Benzo (k) fluoranthene, Bap, Benzo (a) pyrene, Bap, Indonal (1,2,3-cd), GcMS, GasChromatograpy with mass dectector; Zones, PC, Petrochemicals, FS, finishing, FA, farming, CN national field; EC, -pelectrical conductivity, TOC, Total organic carbon (TP), Total phosphorus, LOD, Limit of detection, LOQ, limit of quantification TI, Total index ratio, DCM, Dichloromethane.

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