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Polycyclic Aromatic Hydrocarbons in Asphaltic Coastal Bitumens (Tar Balls) in the Eastern Stretch of the Niger Delta Region of Nigeria

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Abstract:

The concentration, distribution and source of polycyclic aromatic hydrocarbons (PAHs) of nineteen tar ball samples from a part of the eastern coastal line of the Niger Delta were appraised by classical and instrumental methods. The concentration of the PAHs in the tar ball samples ranged from 0.00 – 117.82ng/g. Their concentrations fell into three distinctive classes: >30ng/g; < 30ng/g and no detectable PAHs. Phenanthrene was the most widely distributed PAH among the low molecular weight (LMW) PAHs (di& tricyclic PAHs) while pyrene was the most widely distributed among the high molecular weight (HMW) PAHs (tetra&pentacyclic PAHs). The LMW PAHs were more predominant than the HMW PAHs. The ratio of Phenanthrene and anthracene, a source indicator depicted a high intrusion of combustion products into the tar ball matrix. This is supported by the chromatograms which also reflected different stages of weathering. Crude oil spillage and gas flaring should be curtailed.

Keywords: Tar ball, polycyclic aromatic hydrocarbon, Niger Delta, beach, oil spillage, flaring

1. Introduction

Exploration and production activities of the oil companies operating in the Niger Delta region have severe environmental consequences on the ecosystems. Uncountable number of oil spillage had occurred through the operation of these companies. International vessels that traffic on the Atlantic Ocean also contribute to the pollution through leakage and/ or outright damage of the tanks in which the oils are contained. These spilt/ leaked oils eventually became transformed into petroleum residues which are washed ashore on numerous coastal beaches along the coastline of the Delta (Enyenihi and Antia, 1985). Besides affecting the aesthetics of the coastline, the tar balls are veritable indicators of pollution.

Oil pollution as evidenced by stranded tar balls on beaches has been widely reported, for example, from Canada (Owens, 1977); South Australia and Western Victoria (McKirby et al., 1986) and Nigeria (Enyenihi et al., 1992). Clearly, oil spill-related beach degradation is a problem of global interest and concern. The reports of the various specialized environmental agencies of the United Nations as well as independent studies of some researchers exemplify past efforts aimed at both understanding the impact and predicting the pathways of oil pollution in the marine environment (Antia, 1993).

Tar balls are the final weathering products of crude or refined oils accidentally released into the marine environment through anthropogenic or natural sources (Asuquo and Enyenihi, 1995). The time lag for the weathered products to be stranded on the beach and the quantity depends on a number of environmental and oceanographic factors (Antia, 1993). The processes governing the formation of tar balls in water from the time of accidental release to their final deposition on the beach have been vividly described by several authors (Enyenihi et al., 1992).

Therefore, the evaluation examination of the chemical composition of tar balls especially the sixteen-priority polycyclic aromatic hydrocarbons on some coastal beaches in the Niger Delta will contribute to the understanding of the dynamics of tar ball weathering and transformation processes.

2. Description of the Study Area

The region is densely populated, comprising many ethnic groups spread over closely located communities and settlements covering six states in the south region of Nigeria- Cross River, Akwalbom, River, Bayelsa, Delta and Edo States.

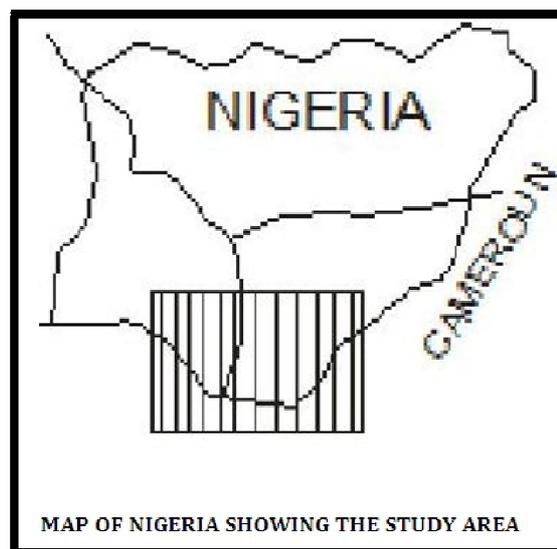


Figure 1: Map of Nigeria Showing The Study Area

3. Materials and Methods

3.1. Sampling

Nineteen tarball samples were collected at selected points along the coastline between the estuaries of Cross River through Qua Iboe River to Imo River. Incidentally, this was the only section within the coastline of the region that had stranded tar balls. The sampling was done in June within the storm season (May – October). According to Antia (1993) larger quantities in stranded beach tar are evident during the storm season due to increased offshore stock. Tucker (1981) indicated that increased sea surface roughness, which is most likely to occur during the storm season, facilitates the emulsification of oil slick and, consequently tar formation.

The prominent facility within this stretch is the oil producing facilities of Exxon Mobil Unlimited. Nineteen tar ball samples were collected within some transects of 1m width set extending between the low tide water line and a backshore reference according to Antia (1993). They were cleaned by scraping all beach tar particulates as outlined in the manual prepared by UNESCO (1977) and contained in ice packs and frozen prior to analysis.

3.2. Separation of the Tar Balls

4.0g of each of the re-frozen tar ball samples was first dissolved in dichloromethane (DCM) to separate the petroleum residue from other impurities like sand, particulates etc. (Huang et al; 2003). The DCM solution was filtered through glass wool to remove the impurities and then concentrated by solvent reduction. The concentrate was deasphalted following the procedure described by Schoell et al. (1983) and Wehner and Teschner (1981) by precipitation in a mixture of dichloromethane- petroleum ether (bp 40 -60°C at 1: 30 ratios in a centrifuge at 3,000rpm for about twenty minutes. The asphaltene was removed by decanting the soluble portion (Maltene). The maltene was desulphurized with a pinch of copper turnings.

The desulphurized extract (maltene) was absorbed in a little silica gel and introduced on the column packed with 6.0g of silica gel slurry over a glass wool and white sand background. The aliphatic fraction was eluted with 50cm³ of n-hexane while the aromatic fraction was eluted with 50cm³ of dichloromethane. To ascertain complete separation of fraction the column was at intervals examined under UV light at 366nm wavelength for the presence of a band using a UV lampe (camag universal – UV lampe 29200).

The solvents were evaporated in a roto- evaporator at 400- 500mbar for hexane and 715- 736 mbar for dichloromethane. The eluents were collected in 10ml vials and the remaining solvents driven off in a stream of nitrogen at a head pressure of 2bars.

3.2.1. Separation of the Polycyclic Aromatic Hydrocarbon

The aromatic hydrocarbon fractions which contain the polycyclic aromatic hydrocarbons were re-dissolved in 50 - 100µl of n-hexane. The separation of individual compounds (16 priority PAHs) was achieved by gas chromatography on a Carlo Erba model chromatograph equipped with a column. The gas chromatograph was programmed at a temperature of 80°C for 30minutes and then a programmed heating rate of 6°C/minute to a temperature of 310°C. The hydrogen gas pressure and the air pressure were set at 0.5kgcm⁻³ and 1.0kgcm⁻³. Thereafter, 1.0µl of the sample was injected into the chromatograph.

Identification of the compounds was achieved by comparison of mass spectra and retention characteristics with literature data and quantification was achieved by adding 5α (H) -cholestane as internal standard of a known concentration (20mg/l) prior to GC analysis.

4. Results

S.No	Nap	Any	Ace	Flu	Phe	Ant	Fth	Py	B(a)A	Chr	B(b)F B(k)F	B(a)P	Indeno	B(ah) A	B(ghi) P	ΣPAH
1	ND	ND	ND	ND	9.0	3.0	5.21	3.53	ND	ND	ND	ND	ND	ND	ND	20.74
2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00
3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00
4	ND	ND	ND	ND	ND	ND	ND	14.21	ND	ND	ND	ND	ND	ND	ND	14.21
5	ND	ND	ND	ND	67.23	8.52	ND	ND	ND	9.12	ND	ND	ND	ND	ND	84.87
6	4.68	6.21	8.53	10.14	35.26	3.51	18.11	29.65	ND	25.41	ND	7.81	ND	28.51	ND	177.82
7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00
8	ND	ND	ND	5.13	10.12	18.32	ND	ND	ND	ND	ND	ND	ND	ND	ND	33.57
9	ND	2.15	ND	ND	70.38	38.17	ND	10.27	ND	ND	ND	ND	ND	ND	ND	120.97
10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00
11	ND	ND	2.51	ND	5.27	6.11	ND	9.23	ND	ND	ND	ND	ND	ND	ND	23.11
12	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00
13	ND	ND	3.51	ND	28.34	8.33	ND	ND	ND	13.10	ND	ND	ND	ND	ND	53.28
14	ND	ND	ND	ND	76.35	34.81	ND	ND	ND	3.23	ND	ND	ND	ND	ND	114.39
15	ND	5.28	7.53	ND	5.82	8.36	ND	10.21	ND	ND	ND	ND	ND	ND	ND	37.20
16	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00
17	ND	ND	ND	ND	33.73	15.27	ND	ND	ND	ND	ND	ND	ND	ND	ND	49.00
18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00
19	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00
Mean	0.28	0.80	1.30	0.90	20.09	8.32	1.37	4.54	0.00	2.99	0.00	0.46	0.00	1.68	0.00	
Std	2.75	1.88	2.65	2.61	26.43	11.59	4.36	7.82	0.00	9.95	0.00	1.84	0.00	7.06	0.00	

Table 1: Concentrations of Polycyclic Aromatic Hydrocarbons in Tarballs (Ng/G)

4.1. Legend

Nap – Naphthalene, Any – Acenaphthylene, Ace – Acenaphthene, Flu – Fluorene
 Phe – Phenanthrene, Ant – Anthracene, Fth – Fluoranthene, Py – Pyrene
 B(a)A – Benz(a)anthracene, Chr – Chrysene, B(b)F – Benzo (b) fluoranthene
 B(k)F – Benzo (k) fluoranthene, B(a)P – Benzo (a) pyrene, Ind – Indeno (1, 2, 3 - c-d) pyrene
 B(ah)A – Benzo (ah) anthracene, B(ghi)P – Benzo (ghi) perylene, ND – Not detected

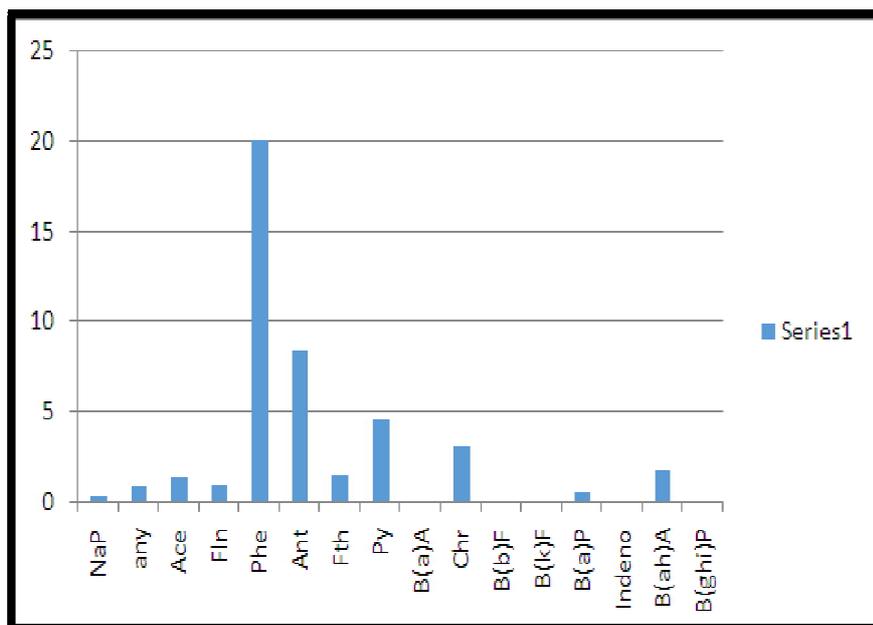


Figure 2: Mean Distribution of PAHs in Tar Balls

Station	Phe / Ant
1	3.00
2	0.00
3	0.00
4	0.00
5	7.89
6	10.04
7	0.00
8	0.55
9	1.84
10	0.00
11	0.86
12	0.00
13	3.40
14	2.19
16	0.70
17	2.21
18	0.00
19	0.00
20	0.00

Table 2: Ratios of Phenanthrene and Anthracene (Phe/Ant) in Tar Balls

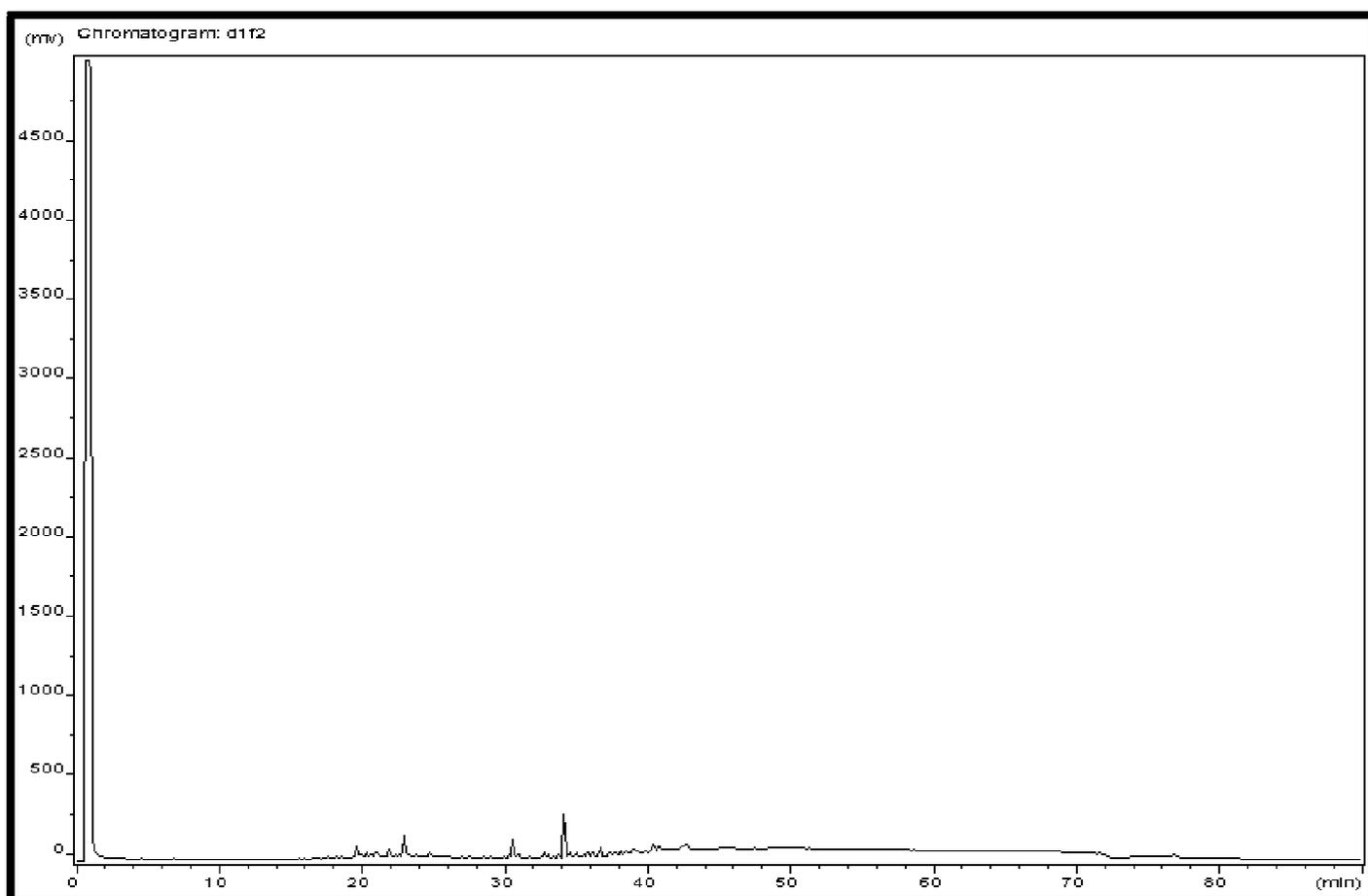


Figure 3: Representative Chromatograms of Tar Ball Samples

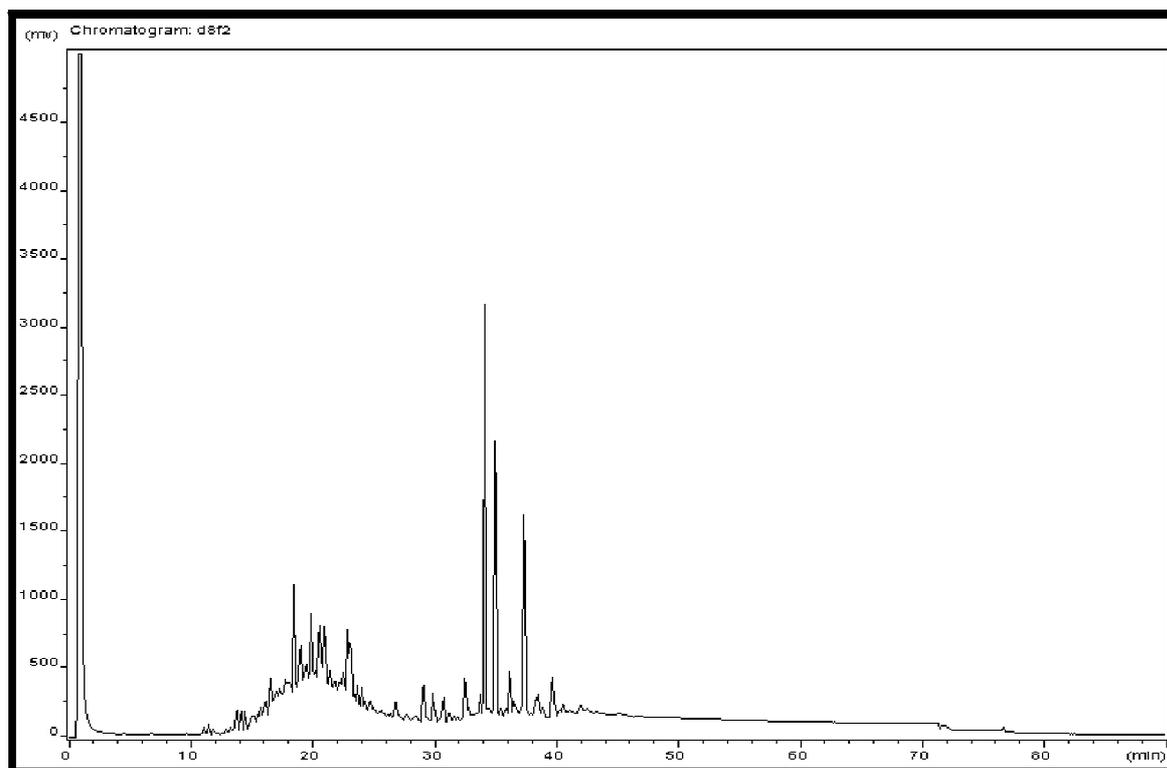


Figure 4: Representative Chromatograms of Tar Ball Samples

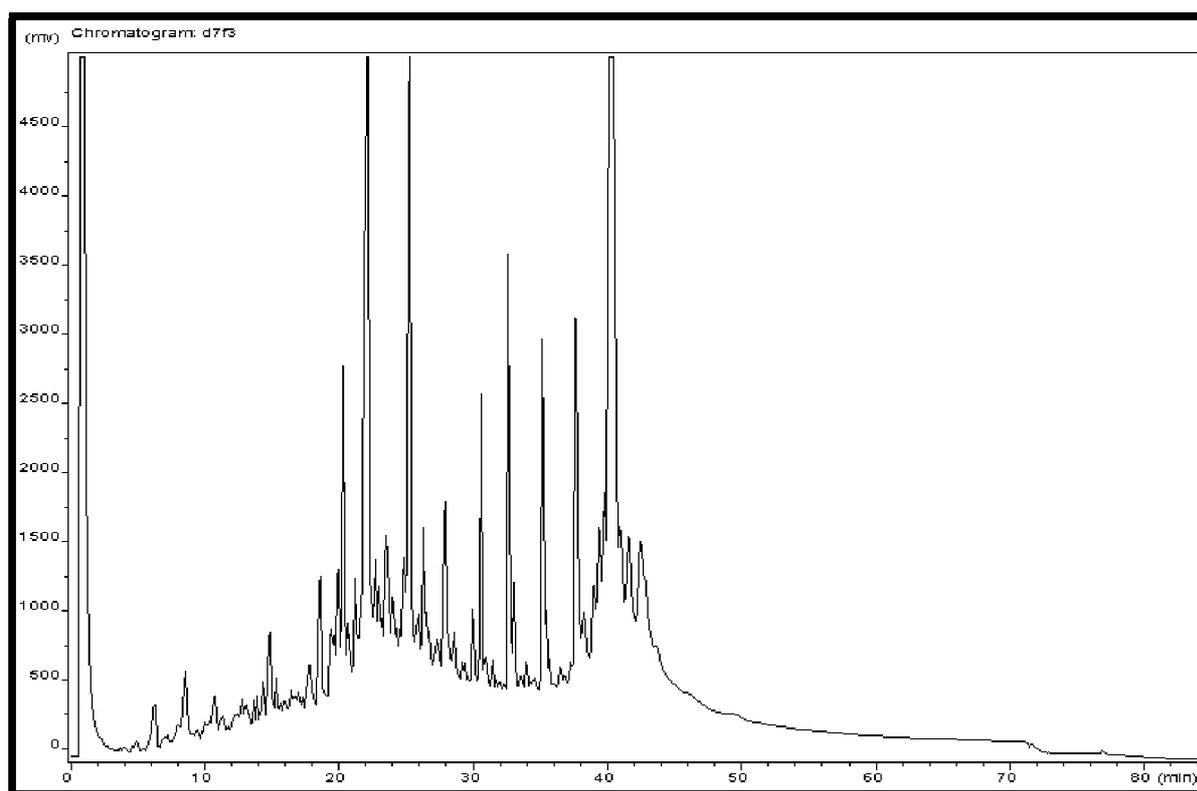


Figure 5: Representative Chromatograms of Tar Ball Samples

5. Discussion

5.1. Distribution of PAHs

The sum of the sixteen-priority polycyclic aromatic hydrocarbons studied ranged from 0.00 – 117.82ng/g. According to the empirically determined response concentration estimates, 0.03 – 15.8 μ g/g (concentration at or above which significant biological effects were always found) developed by Anderson et al. (1989) the concentration ranges in some of the sediment and soil samples could be toxic to the benthic macro fauna.

As shown on table 1 and figure 2, tar balls 1, 4 and 11 have PAH concentrations <30ng/g. Tar balls 5, 6, 8, 9, 13, 14, 15, and 17 have PAH concentrations > 30ng/g while tar balls 2, 3, 7, 10, 12, 16, 18, 19 did not contain detectable level of PAH.

Phenanthrene is the most widely distributed PAH even among the low molecular weight PAHs (Di α tricyclic PAH). Among the high molecular weight PAHs (tetra α pentacyclic) pyrene is the most widely distributed (Fig.2). The lower molecular weight PAHs were more predominant in the tar balls than the high molecular weight PAHs. The hydrodynamics of the adjoining Atlantic Ocean seems complex and may to a large extent influence the retention of the polycyclic aromatic hydrocarbon content of tar balls both from oil slick and other sources. Processes of solubilisation, evaporation, dispersion etc. are common physical processes that may affect the content of oil slick after release in the marine environment.

Although there is no standard, established for the toxicity of PAHs in tar balls unlike sediments, soils and water, eight of the studied tar ball samples had PAH concentration above 30ng/g, empirically determined response concentration estimate established by Anderson et al. (1989), the concentration range above which the PAH in sediment and soil could be toxic to macro fauna. The potential human health impact of PAHs established by Canadian Ministers of the Environment (CCME) in 2008, usually predicted with benzo(a) pyrene potency equivalent could not be calculated here because of the paucity of benzo(a) pyrene (BaP) in most of the samples.

It is the opinion of the authors that toxicity of PAHs in tar balls should be considered like that of soils since most tar balls are sometimes found buried in beach sand irrespective of whether the beach is dissipative or reflective.

5.2. Origin Of PAH in Tar Balls

Studies on source identification employed ratios of some PAH to distinguish PAHs from various sources (Budzinski et al., 1997) except biological source. These criteria are based on peculiarities in PAH composition and distribution pattern as a function of emission source. Phenanthrene is a thermodynamically more stable tricyclic aromatic isomer than anthracene. Hence, petroleum contains more phenanthrene than anthracene. Therefore, the PAHs of petrogenic input are generally characterised by high Phe / Ant ratio (>15) (Benner et al., 1990). In the tar ball samples where phenanthrene and anthracene were detected, the Phe / Ant ratios were all less than 15 (Table 2). Thus, suggesting an intrusion of other PAH sources into the tar ball matrix. Since the sampled area is a major navigational channel to ships and boats and there is also a huge gas flaring at the Mobil Qua Iboe Terminal base within the study area, flaring may have been the major source of PAH intrusion into the tar balls.

A comparison of the chromatograms (Fig.3, 4, 5,) shows that the tar balls might have originated from different source inputs and underwent different weathering and transformational processes prior to stranding.

6. Conclusion

The concentration of the polycyclic aromatic hydrocarbons (PAHs) in the tar balls fell into three categories: > 30ng/g; <30ng/g and 0.00ng/g. This suggests that the PAHs came from different petroleum sources. The chromatograms support this preliminary conclusion as well as divergent transformation processes prior to stranding. However, PAH pollution or contamination may be deduced.

7. Acknowledgement

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8. References

- i. Anderson, J. W., Bay, S. M. and Thompson, B. E. (1989) Characteristics and effects of contaminated sediments from Southern California. In: An International Conference addressing methods for understanding the global oceans 1989, Seattle, Washington, 18 – 21, September, 1989, 2, Ocean Pollution 448 - 451.
- ii. Antia, E.E. (1993). A morphodynamic model of sandy beach susceptibility to tar pollution and self – cleansing on the Nigerian Coast. *Journal of Coastal Research*, 9(4), 1065- 1074.
- iii. Asuquo, F.E. and Enyenihi, U.K. (1995). Tar balls monitoring- A unique tool for the assessment and evaluation of marine pollution by petroleum. *Journal of Applied Science and Education*, 2(1): 20-26.
- iv. Benner, B. A., Bryner, N. P., Wise, S. A., Mulholland, G. H., Lao, R. C. and Fingas, M. F. (1990). Polycyclic aromatic hydrocarbon emissions from combustion of crude oil on water. *Environmental Science and Technology*, 24, 1418 – 1427.
- v. 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*, 58, 85 – 97.
- vi. CCME (2008). Canadian soil quality guidelines for the protection of the environment and human health: carcinogenic and other PAHs. In: Canadian Environmental Quality Guidelines, 1- 11
- vii. Enyenihi, U.K. and Antia, E.E. (1985). Tar balls as indicator of crude petroleum pollution of the beaches of Cross River State, Nigeria. *IOC(UNESCO) Workshop Report 41, annex 9, 1-8.*
- viii. Enyenihi, U.K; Asuquo, F.E. and Antia, E.E. (1992). The levels of stranded pelagic tar residues on Ibeno Beach, Nigeria. *Tropical Journal of Applied Sciences*, 2, 52-55.

- ix. Huang, H., Larter, S. R. and Love, G. D. (2003). Analysis of wax hydrocarbon in petroleum source rocks from Damitumdepression, Eastern China using high temperature Gas Chromatography. *Organic Geochemistry*, 34,1073-1687.
- x. McKirdy, D.M., Cox, R.E., Volkman, J.K. and Howell, V. J. (1986).Botryococcane in a new class of Australian non marine crude oils. *Nature*, 320, 57-59.
- xi. Owens, E.H.(1977). Coastal environments of Canada: The impact and cleanup of oil spills, Ottawa, Canada: Department of Fish and Environment, 413p.
- xii. Schoell, M., Teschner, M., Wechner, H., Durand, B., and Oudin, J. L. (1983). Maturity related biomarker and stable isotope variations and their application to oil / source rock correlation in the Mahakam Delta, Kalimantan. In: *Advances in organic geochemistry 1981* (M. BjorØy et al. eds.). Wiley and Sons, New York, 156 – 163pp.
- xiii. Tucker, M.J.(1981). The importance of oceanography to the oil industry. *Proceedings of Petromar'80 London: Graham and Trotman Ltd.*, 497- 512pp.
- xiv. UNESCO (1997). IOC/WMO/UNEP Manuals and Guides No.7 (supplement), *Manuals for Monitoring of oil and Petroleum Hydrocarbons in Marine Waters and on Beaches*. New York: UNESCO, 50 -60pp
- xv. Wehner H. and Teschner, M. (1981).Correlation of crude oils and source rocks in the German Molasse Basin. *Journal Chromatography*, 204, 481- 490.