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Profiling of Polycyclic Aromatic Hydrocarbons and Diagnostic Ratios of Kpite Oil Spill Impacted Site in Rivers State, Nigeria

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ABSTRACT: Polycyclic Aromatic Hydrocarbon profile of Kpite oil spill impacted site in Rivers state, Nigeria was evaluated to determine the level of contamination of the soil. Four composite oil impacted soil samples were collected at different depths; surface (0-15cm) and subsurface (15-30cm) after a field reconnaissance. Extraction of the oil was carried out on the soil samples and the Polycyclic Aromatic Hydrocarbons were quantified using the Gas Chromatography- flame ionization detector. Results showed that Naphthalene was the most abundant in the range of 0.25 to 1.49 mg kg^{-1}. Fluoranthene followed closely with concentrations in the range of 0.01 to 1.28 mg kg^{-1}. PAHs like Benzo (k) fluoranthene, Benzo (e) pyrene, Dibenzo (a, h)anthracene, Indeno (1, 2, 3-cd) pyrene and Benzo (g, h, i) showed low concentrations of less than 0.01 indicating that strong weathering had occurred. The diagnostic ratios such as Phenanthrene/Anthracene (Phen/Anth), Benzo (a) anthracene Chrysene ((BaA)/Chry) and Fluoranthene/Pyrene (Flth/Py) and sum of chrysene/Phenanthrene ∑Chry/∑Phen were calculated and used to unravel the source of hydrocarbons. Results showed ratios of Flth/Py >1.0 and Phen/Anth ranges from 1.19 to 2.03 (< 10) which denote contamination sources, implying that the hydrocarbon sources are not just petrogenic but rather may due to contamination sources of combustion processes or the area was exposed to bush burning.

Keyword: Hydrocarbons, Pyrogenic, Oil spill, diagnostic ratios, ecosystems.

INTRODUCTION

The hydrocarbons in crude oil are of numerous types, such as polycyclic aromatic hydrocarbons (PAHs), asphaltene, and resin. Oil spills which can emanate from different sources such as ships and oil wells cause severe deleterious effects to both marine and coastal environments. Profiling of PAHs is imperative to comprehend their behavior and effects as a component of crude oil (Hayakawa, 2018). Oil spillage has contaminated the environment with hydrocarbons that are harmful to terrestrial and aquatic ecosystems. Anthropogenic and natural activities which could lead to the release of these hydrocarbons includes accidents during offshore drilling, oil tanker failure, leaking crude oil pipelines to mention but a few (Adelana et al., 2011). When oil spillages occur, a number of toxic

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compounds are released into the environment; many of these constitute negative externalities to the environment and the overall wellbeing of its biodiversity. Some of these persistent compounds find their way into the food chain and some have direct impact on the productivity and quality of the environment (Kadafa, 2012). One of the toxic components of crude oil that possesses the capacity for bioaccumulation in the environment and bio-concentration in the food chain are the Polycyclic Aromatic Hydrocarbons.

Polycyclic aromatic hydrocarbons are organic compounds that have two or more benzene (aromatic) rings fused together. They may be none, singly or multiple alkylated side chains which make it possible for them to take myriads of isomeric forms. This class of natural pollutants has been of interest to several fields of the chemical and environmental sciences and has been studied over a period of time (Yu, 2002). Those that possess high level toxicity and carcinogenicity are considered to be priority pollutants (Lee et al., 2015; Itodo et al., 2019). Polycyclic aromatic hydrocarbons`(PAHs) containing up to four rings are referred to as light PAHs and those that contain more than four rings are heavy PAHs. Heavy PAHs are usually more stable and more toxic than the light PAHs (Lawal, 2017). Polycyclic aromatic hydrocarbons are globally found contaminants and are classified into two main groups' petrogenic and pyrogenic PAHs. Generally, it is a known fact that the main toxic components of crude oils are polycyclic aromatic hydrocarbons (PAHs), which is a set of abundant persistent organic pollutants, composed of two or more fused aromatic rings, arranged in a linear, angular, or cluster form. Environmental pollution due to PAHs has been a topic of interest to scientist because of their mutagenic and carcinogenic effects (Duan, et al., 2018; Gao et al., 2019).

Petrogenic PAHs are introduced naturally into the environment by oil seeps, or anthropogenically by spills of crude or refined petroleum product. They usually have 2-3 member rings. Pyrogenic PAHs are formed from the incomplete combustion of fossil fuel or biomass and are commonly distributed by atmospheric deposition and urban runoff. They usually have 4-6 member rings. The persistence and toxicity of PAHs make them a target for remedial investigations (Bobak, 2010; Itodo et al., 2019). Many Marine organisms with the inclusion of vertebrates and invertebrates have been shown to be affected by PAHs from their larvae and embryo stages up to the stage of reproduction and maturity.

Generally, PAHs tend to resist biological breakdown in the environment, in comparison to their hydrocarbons (n-alkanes and isoprenoids) and volatile alkyl benzene counterpart compounds. This makes them very useful in the identification of oil spills (fingerprinting). The more stable high molecular weight PAHs containing 4 to 6 benzene find importance in diagnosing the components of petroleum (Onojake et al., 2016). The 2 or 4- ringed PAHs exhibit higher solubility in water with respect to the higher molecular weight PAHs (containing more than 4 rings) and at such are more readily distributed in soil and groundwater. High molecular weight PAHs, exhibit lower levels of solubility and mainly adsorb to particles in the environmental compartments (Itodo et al., 2019). Petrogenic and pyrogenic PAHs can be differentiated using the calculation of different ratios. Some of the ratios used for this include phenanthrene/anthracene (Phen/Anth), fluoranthene/pyrene (Flth/Py) and benzo (a) anthracene/chrysene (BaA/Chrys). The objective of this article is to profile the level of polycyclic aromatic hydrocarbons (PAHs) and determine their impact on arable soil within the study vicinity.

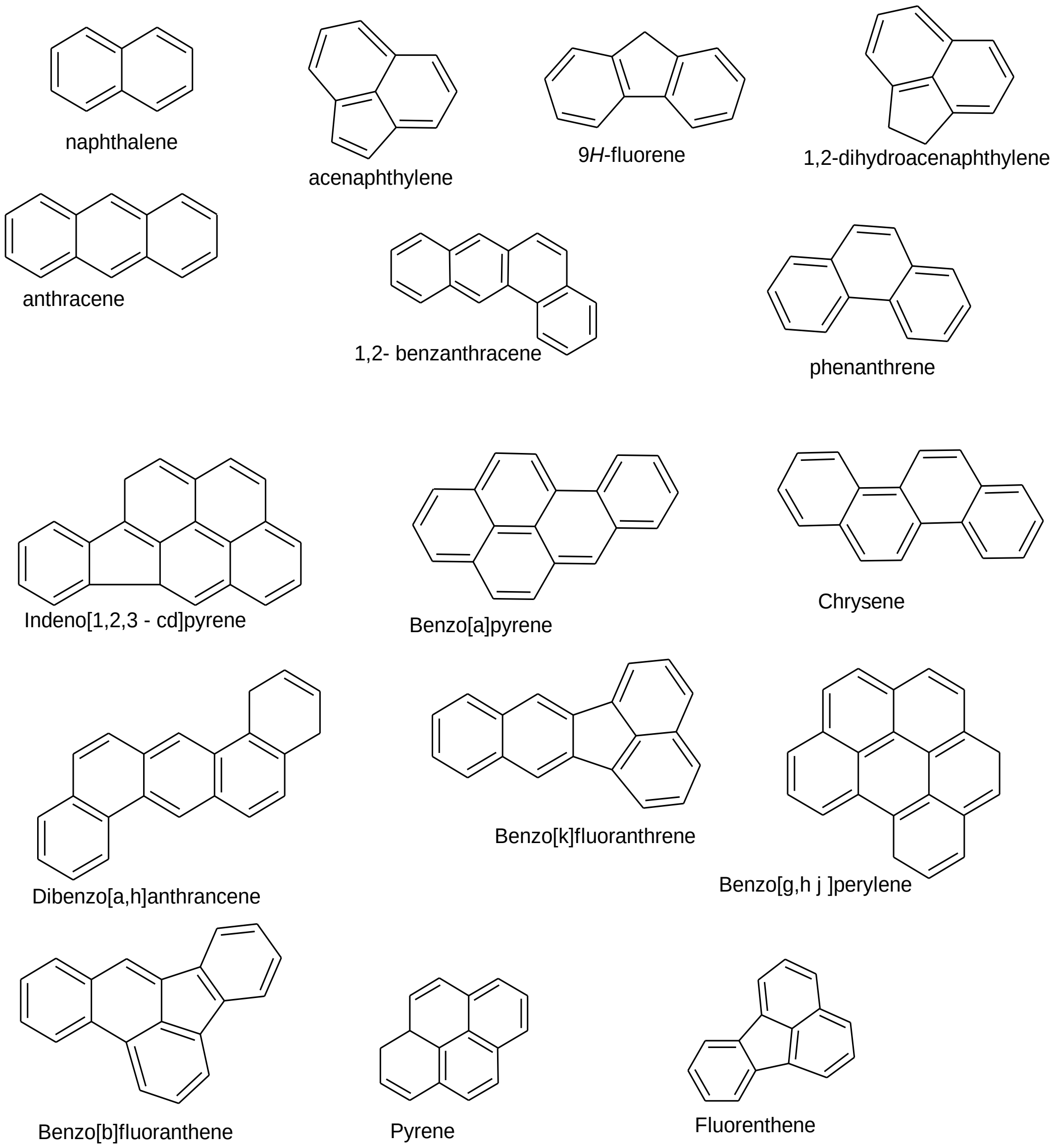

Fig. 1. Structures of sixteen (16) USEPA priority PAHs

MATERIALS AND METHODS

Four composite quadrants of surface and sub-surface soil were collected from an oil spill impacted site in Kpite community, Tai Local Government of Rivers State, at two depths surface (0-15 cm) and sub-surface (15-30 cm) using a soil auger. The sampling was done randomly from a sampling plot of 200 m × 200 m. The sampling area of 200 m × 200 m was divided into 100 grid plots. Surface and subsurface soils were randomly selected from each plot and homogenized to four (4) representative composite samples and taken to the laboratory for analysis. The soil samples were subjected to analysis using USEPA 8015C. 30 g of wet soil samples were homogenized using a spatula. The homogenized soil samples were dried using Na_2SO_4 and 30 ml of dichloromethane was then added to the dry sample as extraction solvent. The samples were agitated for 30 minutes, filtered and concentrated to 1ml, the filtrate from the samples was then analyzed using Gas Chromatography- flame ionization detector (Tongo et al., 2017). Figure 2 is the map of the study area.

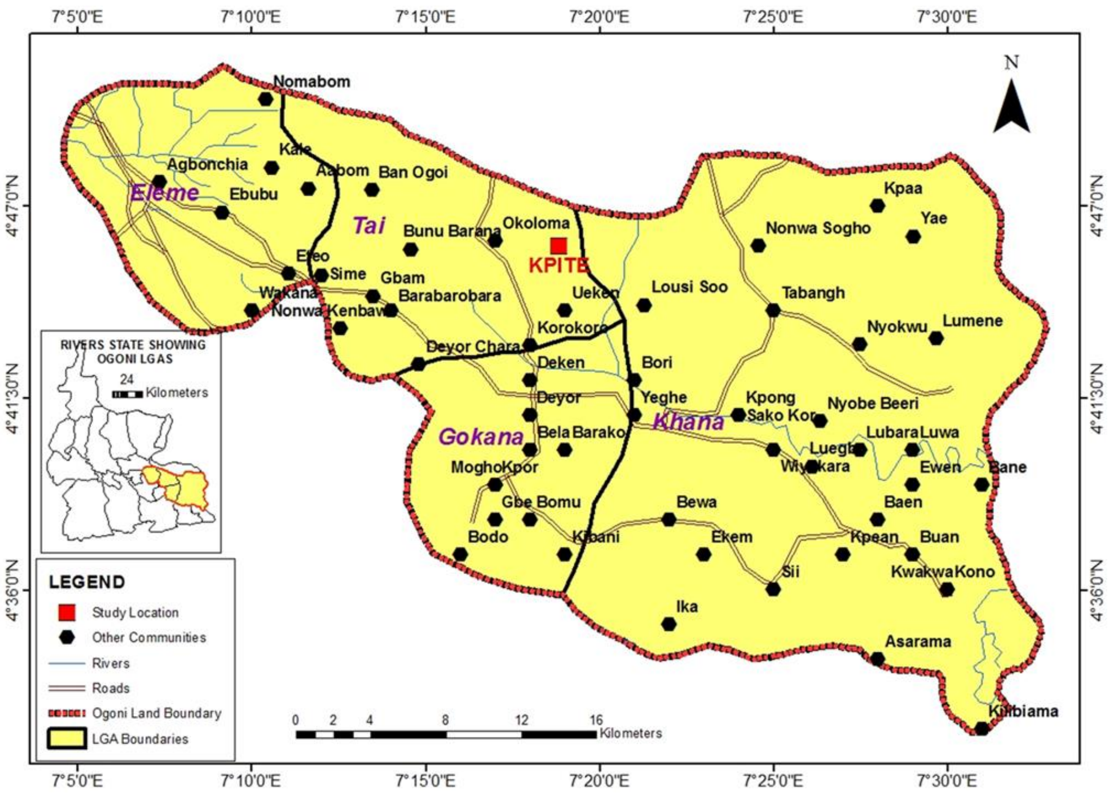

Fig. 2. Map of the study area showing Kpite community

The polycyclic aromatic hydrocarbons were determined using a Gas Chromatograph (Agilent 6890 N) with HP-5 fused silica column of dimensions 30 m × 250 µm × 250 µm film thickness and 5% phenyl methyl siloxane capillary column. The oven temperature program was maintained at 400 ^{o}C for 2 min and then increased at a rate of 100 ^{o}C/min until a temperature of 3200 ^{o}C was reached. The final temperature was held for 2 min with Nitrogen carrier gas maintained a flow rate of 2.6 ml/min and pressure of 10.4 psi which was ma. PAH analysis of the aromatic hydrocarbon fraction of the samples extract was performed with Agilent 7820 GC with FID to identify Polycyclic Aromatic Hydrocarbons (PAHS). Hydrogen was used as the carrier gas (Onojake et al., 2013).

Quality control/assurance measures were ensured by rinsing the separating apparatus used with a mixture of acetone and dichloromethane. All solvents used (dichloromethane, acetone, etc.) were of analytical grade. After the concentration of samples, the round bottom flask was always rinsed with acetone before concentration of the next sample. Upon spiking (addition of known concentration to the sample) the helium gas (carrier gas) was released and allowed to sweep out impurities that could cause an error before the chemical analysis of the sample. The blank and spiked matrix samples alongside with samples were analyzed while PAHs extraction was evaluated by spiked recovery method, in which selected and already analyzed samples were spiked with individual polycyclic aromatic hydrocarbons whose concentrations are determined. The recoveries for the PAHs compounds ranged from 89.5% to 99.7%.

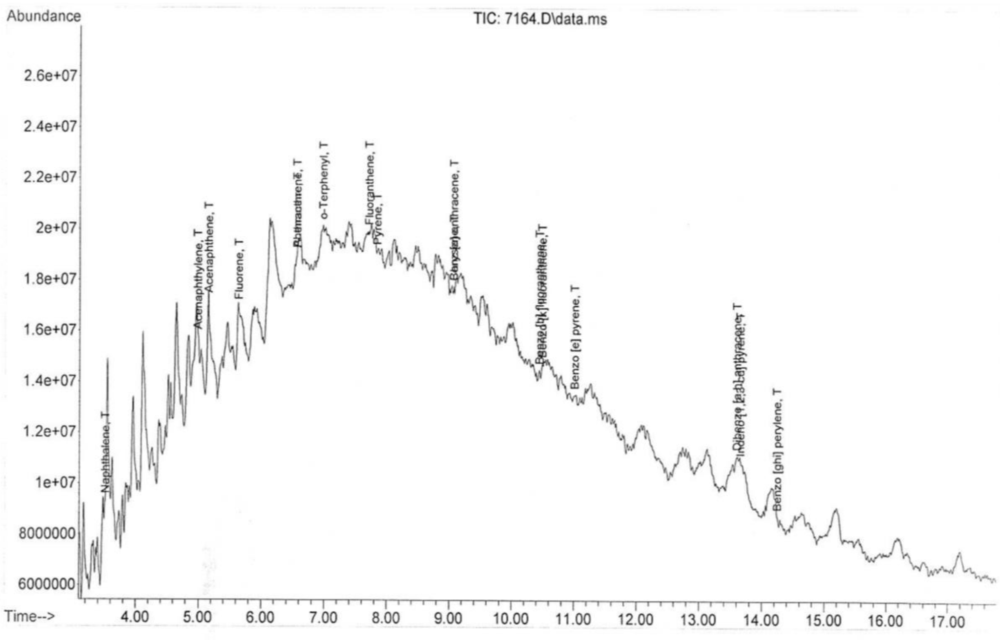

Fig. 3. Representative chromatogram of oil spill soil samples

RESULTS AND DISCUSSION

The distribution of polycyclic aromatic hydrocarbons (PAHs) is the utmost technique for distinguishing pyrogenic hydrocarbons from petrogenic hydrocarbons. This study applied diagnostic ratios in ascertaining the specific source information of polycyclic aromatic hydrocarbons (PAHs) in Kpite oil spill impacted site, in the Niger Delta. The sixteen (16) USEPA priority PAHs (Figure 1) were the main focus in computing the diagnostic ratios. Diagnostic ratios were computed for Phenanthrene and Anthracene (Phen/Anth), fluoranthene and Pyrene (Flth/Py) and Benzo (a) Anthracene, Chrysene (BaA/Chry) and the sum of chrysene and the sum of phenanthrene (∑Chry/∑Phen), (Table 2).

Table 1. Result of Polycyclic Aromatic Hydrocarbons (PAHs) in oil spill impacted soils

PAHs	A (mg/kg)	B (mg/kg)	C (mg/kg)	D (mg/kg)
Naphthalene	0.25	1.49	0.81	0.34
Acenaphthylene	0.35	0.05	0.25	0.12
Acenaphthene	0.01	0.09	0.01	0.01
Fluorene	0.01	0.17	0.01	0.01
Anthracene	0.04	0.37	0.01	0.38
Phenanthrene	0.06	0.44	0.01	0.77
Fluoranthene	0.89	1.28	0.79	0.01
Pyrene	0.18	0.34	0.01	0.06
Benzo(A)Anthracene	0.01	0.03	0.01	0.07
Chrysene	0.05	0.07	0.01	0.06
Benzo(B) fluoranthene	0.03	0.06	0.01	0.01
benzo (k) fluoranthene	0.01	0.01	0.01	0.01
Benzo (e) pyrene	0.23	0.13	0.05	0.01
Dibenzo (A, H)Anthracene	0.01	0.01	0.01	0.01
Indeno (1, 2, 3-cd) Pyrene	0.01	0.01	0.01	0.01
Benzo (g, h, i) Perylene	0.07	0.01	0.01	0.01

Table 2. Diagnostic ratios of Polycyclic Aromatic Hydrocarbon compound

PAH	Sample A	Sample B	Sample C	Sample D
Phen/Anth	1.50	1.19	1.00	2.03
BaA/Chry	0.02	0.43	1.00	1.17
Flth/Py	4.94	3.28	1.00	0.17
∑Chry/∑Phen	0.83	0.16	1.00	0.08

The PAHs diagnostic ratios were used to distinguish pyrogenic and petrogenic source of hydrocarbons. When the calculated ratio of phenanthrene/anthracene has a value less than 10, then hydrocarbon source is pyrogenic. Conversely, values above 10 are said to be from petrogenic sources (Boehm and Saba, 2008).

It is also known that the fluoranthene/pyrene (Flth/Py) less than one (<1.0) indicates contamination source of hydrocarbons (Anyakora et al., 2011). Results in Table 2 shows that the ratio of Flth/Py of PAHs for the four oil spill impacted soil samples were greater than unity (>1.0). Sample D was the only sample with a concentration less than one (< 1.0). In other separate research, Onojake et al. (2016) postulated also Flth/Py ratio less than unity (<1.0) to be an indication of the petrogenic source of PAHs, while a Flth/Py ratio greater than one (>1.0) is an indication of pyrogenic or pyrolytic PAHs. The results in Table 2 therefore suggest that the PAHs are majorly of pyrogenic source which may be due to combustion, with the exception of sample D, which may have a petrogenic hydrocarbon input from oil spill activities in the study area. Furthermore, the research of Benlahcen et al. 1997 reported the use of Phen/Anth < 10 and Flth/Py >1.0 to denote contamination sources of combustion of processes. The results in Table 2 shows that all oil spill samples have Flth/Py >1.0 excerpt sample D. The implication is that the hydrocarbon sources are not just petrogenic but rather may have combustion (pyrogenic sources) or other contamination sources. Result of the BaA/Chy ratios ranged from 0.02 to 1.17. High ratios of BaA/Chy are attributed to more pyrogenic sources, while lower ratios of BaA/Chy are attributed to more petrogenic sources (Nwaichi and Ntorgbo, 2015). The Phen/Anth ratios of the crude oil samples range from 1.00 to 2.03 (< 10). This implies the source of the PAHs in the oil spill site have other sources such as combustion processes within the area under study. The diagnostic ratios of PAHs shows that though there was incidence of oil spill, leading to a petrogenic source of PAHs, the area under study would have been exposed to bush burning just before the occurrence of oil spillage.

Weathering is a major process that can lead to significant alteration in the chemical and physical characteristics of spilled oils. The calculated sum of the ratio of ∑Chry/∑Phens, which is a weathering indicator, is 0.16 (Table 2). Main chemical compositional alterations caused by weathering are significant loss in the low-molecular-weight n-alkanes ethylbenzene and xylenes. Weathering can lead to partial or complete loss of the aromatic compound including the benzene, toluene. In many cases, it is pronounced decrease in the concentration of the naphthalenes relative to other alkylated PAH series or increase the amount of chrysenes relative to other PAH series and substantial reduction in the relative ratios of the sum of naphthalenes, phenanthrenes, dibenzothiophenes, and fluorenes to chrysenes (Wang et al., 1999). A visual observation of the representative chromatograms (Figure 3) for oil spill sample indicates that substantial amount of weathering had occurred in the area. Some of the weathering processes includes evaporation, dissolution, spreading, photochemical oxidation, water-oil emulsification, microbial degradation, adsorption onto suspended particulate materials, oil-mineral aggregation, sinking, and sedimentation. These processes can alter the chemical composition of the spilled oil and impact negatively on environment.

CONCLUSION

Profiling PAHs distribution has made it possible to identify the probable sources of these hydrocarbons in Kpite oil spill impacted site. The PAHs diagnostic ratios were used to distinguish between pyrolytic, pyrogenic and petrogenic sources. In heavily impacted by oil spill, these ratios are expected to be higher suggesting the dominant presence of petrogenic PAHs, But in this case there were diverse sources of PAHs which contributed their quota to the total of hydrocarbons in the study area. The hydrocarbon sources from Kpite oil spillage were more of pyrogenic source with substantial contributions from petrogenic sources. It was also established that the study area was exposed to combustion or bush burning before the oil. It was also inferred that multiple source contamination might have occurred at the site.

The diagnostic ratio of the weathering index also depicted that considerable amount of weathering had occurred in the area. All these may affect arable Agricultural land leading to low crop yield in the area. Proper depollution measures must be instituted to mitigate the environmental impact of the hydrocarbons if the loss of agricultural viability in the area is to avoided.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest concerning the publication of this manuscript. We declare that all ethical issues such as plagiarism, false information, misconduct, data fabrication or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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