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Diagnostic Ratios and Ecological Risk of Non-carcinogenic Polycyclic Aromatic Hydrocarbons (ncPAHs) in Egi Crude Oil Communities, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The loadings of PAHs, its diagnostic ratios and ncPAHs at three cluster communities in Egi sub district of Niger-Delta with geographic coordinates of latitude 15^0 32' 50" N and longitude 6^0 34' 42" E were ascertained using Gas Chromatography (GC-FID, HP 5890 Series). The diagnostic ratios showed that Obagi had an LMW/HMW ratio of 0.2340, Ibewa's was 0.2222, and Obite's was 0.2549. In Obagi, the proportion of Low Molecular Weight (LMW) PAHs compared to High Molecular Weight (HMW) PAHs was 19%, while in Obite it was 18%, and in the Ibewa cluster it was 20%. The sediments of the Obagi, Obite, and Ibewa cluster sites exhibited a significant abundance of PAHs derived from pyrogenic sources, as evidenced by the presence of LMW/HWM ratios below

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1. The identified ncPAHs include: Naphthalene, Acenaphthene, Acenaphthylene, Fluorene, Anthracene, Phenanthrene, Fluoranthene, Pyrene and Benzo(ghi)perylene. According to the results obtained the Obite cluster area exhibited the lowest concentrations (1.503mg/Kg) amongst the ncPAHs, while the Obagi study zone demonstrated the highest concentrations (1.5733mg/Kg). Among the nc(PAHs) examined, benzo (g,h,i) perylene exhibited the highest concentrations (2.086mg/Kg) across all locations, whereas acenaphthylene displayed the lowest concentration (0.123mg/kg) across the three cluster areas. However, none of the three study locations had any ncPAHs that are above the maximum permissible limit. Results from the application of risk quotient models (RQ_{NCs} and RQ_{MPCs}) to assess the ecological risk of ncPAHs as presented indicated that all the sites where these rivers' sediments were tested had RQ_{NCs} values for specific ncPAHs below 1, implying that these ncPAHs pose little or no danger to ecosystems. Also, the RQ_{MPC} score is less than 1, it means that the contamination from individual ncPAHs chemicals do not necessitate immediate remediation. Because the RQ_{NCs} and RQ_{MPCs} for a single PAH molecule are both less than 1, the contamination it generates might be considered low risk. Thus, few measures of control or correction would be required. The ecological risk of non-carcinogenic PAHs using RQ_{MPCs} and RQ_{NCs} indicated a very negligible risk which could be due to factors like heavy flooding that washed away soil surfaces. Application of Detoxification by chemical reaction technology should be used as future remediation method if there is need.

Keywords: Diagnostic ratios; ecology; risk quotient; ncPAHs; RQ_{NCs}; RQ_{MPCs}.

1. INTRODUCTION

The Niger delta region of Nigeria is challenged by enormous ecological risk due to the anthropogenic activities including oil and gas exploration and exploitation [1]. The effect of these activities include air pollution, pollution of marine ecosystem, contamination of surface and ground water and other environmental degradations like introduction of heavy metals, persistent organic pollutants, polycyclic aromatic hydrocarbons (PAHs) and total petroluem hydrocarbons (TPH) have been introduced to sediments, water and air ecosystem in the Niger delta. Altogether, these had giving rise to various public health emergencies overtime [2,3,4,5].

Many researchers have worked extensively on PAHs like [6], they investigated the genotoxicity and carcinogenicity of traditionally roasted meat using indicator PAHs [7,8,9]. Studied the PAHs toxicity profiles and its interaction in animals, while [10] worked on the chemical finger printing, PAHs characterisation and Ecological risks of carcinogenic PAHs in sediments of some oil producing communities of Niger delta, Nigeria. The total potency equivalent concentration of carcinogenic PAHs in soil of Bodo-city was investigated by [11]. The toxicity equivalent (TEQ) concentration of carcinogenic PAHs in soils from Idu Ekpeye playground and some parks in University of PortHarcourt were established by [12,13,14]. The above mentioned researches are mainly directed on the environmental and to an extension the ecological implications of genotoxic and carcinogenic PAHs and their effect were found to be mostly significant and of serious concern.

The ecological risk posed by non-carcinogenic PAHs in the sediments of Egi crude oil producing communities of Niger Delta have not been extensively researched despite the fact that the sediments provides benthic organisms home, it also acts as repository of both cPAHs and Non-cPAHs, both which are by products of lithogenic and anthropogenic activities [15].

This long-term study established the loading of non cPAHs in the sediments of Obagi, Obite and Ibewa communities in Egi area of Rivers state and ecological risk posed by Non-cPAHs in the sediments using risk quotient models. The diagnostic ratios as well as the relationship between the carcinogenic and non carcinogenic PAHs were also highlighted. Our findings helped us know the overall ecological risk posed by the presence of Non-cPAHs in the study area and make appropriate recommendations.

2. MATERIALS AND METHODS

2.1 Study Area

Description of the study area: The study area covers streams around Obagi flow station, Obite gas plant, Ibewa cluster and contaminated freshwaters around oil wells in the study area (Egi communities). Egi community is located in Ogba/Egbema/Ndoni Local Government Area, Rivers State. The area is located in the northern part of the state and shares boundary with Imo

and Delta State respectively. It is a growing city with an estimated population of about 400,000. The economy of the area relies mainly on agriculture and oil and gas, being one of the highest oil and gas producing communities in Rivers State. The climate is typically tropical with dry (November – March) and wet (June – October) seasons. Average temperature of the area ranges between 27^{O}C – 32^{O}C, while average humidity is between 69% and 96%, EPNL (ELF Petroleum Nigeria Ltd).

Obagi flow station is an onshore oil field located on OML 58, 85 km north-west of Port-Harcourt, Nigeria. It is composed of 26 stacked reservoir levels with an estimated total OOIP(original oil in place) of 1.2 Gbbls. It was discovered in 1964 and has been producing since 1966 through 123 wells and 257 completions. 21 layers have been developed. The Obite Gas Plant processes Non-Associated Gas (from HP-high pressure Gas wells) and Associated Gas (from Obagi Gas Compression) which it exports on an extended capacity of 10.65 Million Standard Metric Cubes of Gas to the Nigeria LNG Plant in Bonny.

2.2 Soil Sample Collection

Sediment samples were collected from freshwater around Obagi flow station, Obite gas plant, Ibewa cluster and contaminated sediments around oil wells between July and December 2022, to reflect the dominant seasons in the study area – wet and dry seasons.

Twenty-seven (27) grab sediment samples (about 1kg each) were collected at different depth from the various sampling stations. The sediments were collected in an aluminium foil using soil auger. Each sampling was carried out in triplicate. With the exception of suspected source point, the sampling points were evenly spread in order to give a true representative sample of the study area. The samples were kept in a cooler containing dry ice (≤4^{o}C) to initiate cooling process and sample preservation prior to transportation to the laboratory for preparation and analysis. Control samples were taken 100 meters away from each sample site.

2.3 Sample Preparation

The sediment samples were air-dried for more than 48 hours until there was no visible moisture remaining. Each of the air-dried samples were thoroughly homogenized in a mortar and then sieved with a 2mm metal sieve. Sonication extraction technique was used to extract the PAHs in the sediment. 1:1 solvent mixture of acetone and dichloromethane was prepared. About 10 g aliquot of the well homogenized sediment sample was measured into a solvent rinsed beaker. 50 ml of the solvent mix was added to the sample. The sample was then place in a Sonicator and sonicated for about 10-15 minutes at 70^{o}C. About 10 g of anhydrous sodium sulphate was added to the sample until a clear extract developed. The extracted solvent was poured into a round bottom flask and concentrated to about 2ml using vacuum rotary evaporator. Clean up of PAHs extracts from the sediment was achieved through solid phase extraction with alumina/silica gel. The 2 ml concentrated solvent was transferred into the packed column and fractionated with 10 ml dichloromethane. Saturated aliphatic hydrocarbons were eluted with 20 ml of n-hexane and the aromatic hydrocarbons eluted with 30 ml of a mixture of hexane and dichloromethane (90:10) (v/v). The eluted solvent (aromatic hydrocarbon) was re-concentrated and then transferred to the vial bottle. The elute (aromatic fraction) was analyzed using an “HP5890 Series ii’’ Gas chromatography equipped with a flame ionization detector (GC/FID).

2.4 Risk Quotient Models and Diagnostic Ratios

The risk posed to the ecosystem by the concentrations of ncPAHs found in sediments from the study areas was evaluated by making use of the risk quotient (RQ) approach with the modifications introduced by [16,17]. The risk assessment was based on a set of negligible concentrations (NCs) and a set of maximum permissible concentrations (MPCs) for PAHs in sediment which were developed by [17]. The RQs for PAHs in these river sediments were determined by using Equations below

$$RQ_{NCs} = \frac{C_{PAHs}}{C_{QV(NCs)}} \quad (1)$$

and

$$RQ_{MPCs} = \frac{C_{PAHs}}{C_{QV(MPCs)}} \quad (2)$$

Where:

RQ_{MPCs} is the Risk quotient for maximum permissible concentration
RQ_{NCs} is the Risk quotient for negligible concentration
C_{PAHs} is the concentrations of PAHs in the sediments

C_{QV} is the corresponding sediment quality value concentration for these PAHs.

The maximum permissible concentration (MPCs) is the concentration above which the risk of adverse effects is considered to be unacceptable. The negligible concentration (NCs) is defined as the MPC/100. Important details regarding the RQ values are as follows: A low RQ_{NCs} value suggests that the individual PAH chemicals are probably not a major concern. But, if RQ_{MPCs} is equal to or greater than 1, it indicates that the contamination produced by the specific PAH compound is significant, and prompt action is required to regulate and remediate the problem so that the threat can be reduced. Contamination caused by a single PAH molecule can be classified as a moderate concern when RQ_{NCs} are greater than or equal to 1.0 and RQ_{MPCs} are less than 1, which means that control and remediation measures will be needed.

The ratios of sediment PAHs are used for diagnoses called Diagnostic rations. In order to distinguish between polycyclic aromatic hydrocarbons (PAHs) associated with petrogenic origins and those that are pyrogenic, the LMW/HMW ratio might be employed. A LMW/HMW ratio below 1 is indicative of sources associated with pyrogenic origins, while a ratio above 1 indicates sources associated with petrogenic origins.

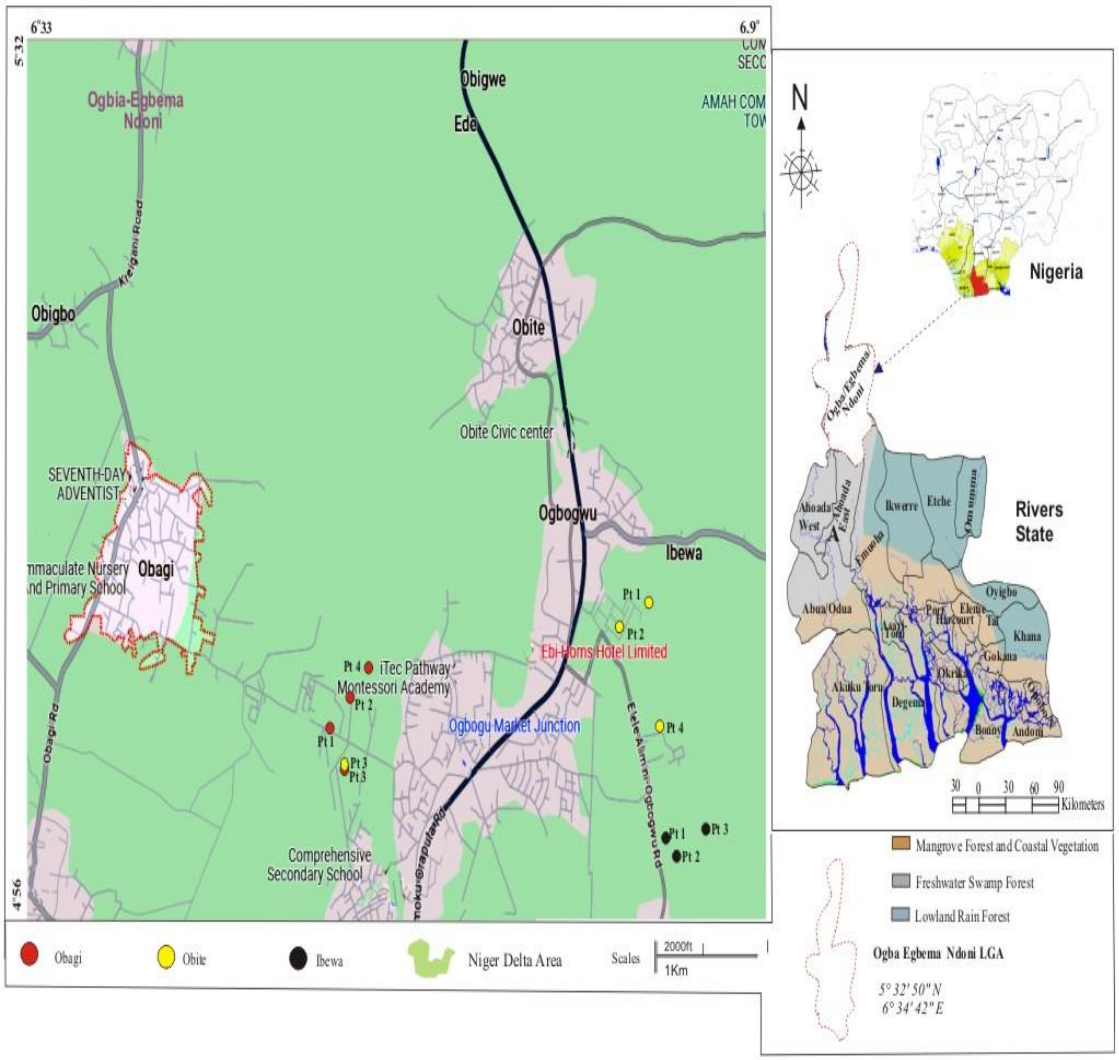

Fig. 1. Map of Rivers state, Nigeria showing study area

3. RESULTS AND DISCUSSION

The ncPAHs detected as shown in Table 1 are: Naphthalene, Acenaphthene, Acenaphthylene, Fluorene, Anthracene, Phenanthrene, Fluoranthene, Pyrene and Benzo(ghi)perylene.. The mean concentrations of PAHs that were determined to be non-carcinogenic (ncPAHs) in the research regions of Obagi, Obite, and Ibewa Cluster are displayed in Table 1. The ncPAHs levels at the Obagi, Obite and Ibewa Cluster research sites were 1.5733, 1.5030, and 1.5723 mg/kg, respectively. The concentration of benzo (g,h,I)perylene was 0.783 mg/kg, the highest of all ncPAHs, in the Obagi study region. Benzo (g,h,I)perylene was the most abundant ncPAH in the Obite Cluster at 0.7100 mg/kg and in the Ibewa Cluster at 0.5930 mg/kg. Obagi recorded almost same ncPAHs concentration of (0.0530 mg/kg) for naphthalene, acenaphthylene, and pyrene. Obite area had the lowest ever ncPAHs content of at 0.0200 mg/kg (acenaphthylene), whereas the Ibewa cluster had the lowest concentration of pyrene at 0.043 mg/kg. According to the data shown in Table 1, the Obite area exhibited the lowest concentration of ncPAHs, while the Obagi study zone demonstrated the highest concentration. Among the non-carcinogenic polycyclic aromatic hydrocarbons (PAHs) examined, benzo (g,h,I)perylene exhibited the highest concentration across all locations, whereas acenaphthylene displayed the lowest concentration. However, none of the three study locations had any ncPAHs that above the detection limit.

The Table 2 shows remarkably low value of RQ_{NCs} of all the detected ncPAHs across Obagi, Obite and Ibewa clusters areas of Egi community. This clearly indicated that the ecological risk posed by these ncPAHs are negligible and never of any major concern, being less than 1.0.

Similarly, Table 3 shows very remarkably low value of RQ_{MPCs} of all the detected ncPAHs across Obagi, Obite and Ibewa clusters areas of Egi community. This clearly indicated that the ecological risk posed by these ncPAHs are negligible and never of any significance, being less than 1.0 and no remediation is needed. Comparing the ncPAHs results with that of cPAHs as can be seen in Fig. 2, it indicates that ncPAHs concentration in this study are very low and it's also low relative to other PAHs sediments' concentrations in other Niger-Delta communities. [12,13,14].

Table 1. Mean Concentration (mg/kg) of non-carcinogenic polycyclic Aromatic Hydrocarbons (ncPAHs) across the three cluster areas

PAHs	Obagi	Obite	Ibewa
Naphthalene	0.0530	0.033	0.090
Acenaphthylene	0.050	0.020	0.053
Acenaphthene	0.070	0.103	0.080
Fluorene	0.177	0.273	0.240
Anthracene	0.183	0.187	0.193
Phenanthrene	0.147	0.053	0.233
Fluoranthene	0.057	0.077	0.047
Pyrene	0.053	0.047	0.043
Benzo (g,h,I)perylene	0.783	0.710	0.593
tPAHs	**1.573**	**1.503**	**1.572**

Table 2. Ecological Risk of Non-Carcinogenic PAHs using RQ_{NCs}

PAHs	Obagi	Obite	Ibewa
Naphthalene	0.038	0.024	0.064
Acenaphthylene	0.044	0.017	0.044
Acenaphthene	0.058	0.086	0.067
Fluorene	0.148	0.228	0.200
Anthracene	0.153	0.156	0.161
Phenanthrene	0.029	0.010	0.046
Fluoranthene	0.002	0.003	0.002
Pyrene	0.044	0.039	0.036
Benzo (g,h,I)perylene	0.010	0.009	0.008

Table 3. Ecological risk of non-carcinogenic PAHs using RQ_{MPCs}

PAHs	Obagi	Obite	Ibewa
Naphthalene	0.001	0.001	0.001
Acenaphthylene	0.001	0.001	0.001
Acenaphthene	0.001	0.001	0.001
Fluorene	0.001	0.002	0.002
Anthracene	0.001	0.002	0.001
Phenanthrene	0.000	0.001	0.001
Fluoranthene	0.000	0.001	0.000
Pyrene	0.001	0.001	0.001
Benzo (g,h,I)perylene	0.001	0.001	0.000

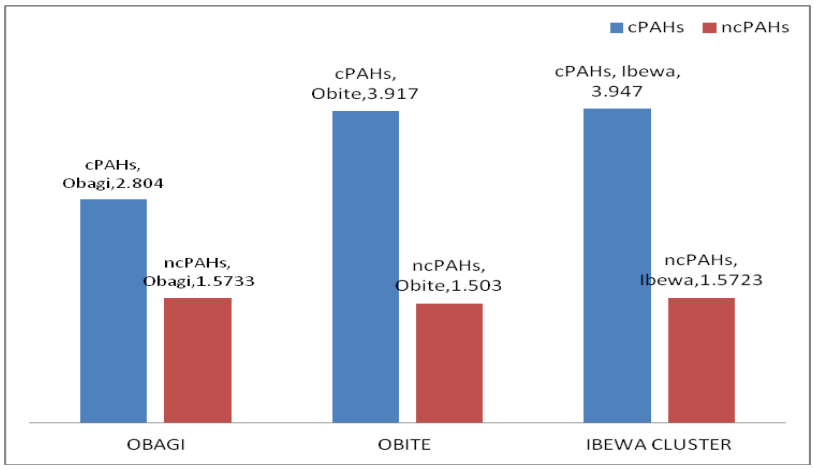

Fig. 2. Relationship between carcinogenic (PAHs) and non-carcinogenic PAHs (ncPAHs)

Table 4. Diagnostic ratio of LMW/HMW

PAHs	Obagi	Obite	Ibewa
LMW	0.11±0.014 (19%)	0.12±0.02 (18%)	0.13±0.02 (20%)
HMW	0.47±0.09 (81%)	0.54±0.10 (82%)	0.51±0.08 (80%)
Ratio	0.2340	0.2222	0.2549

LMW= low molecular weight, HMW = high molecular weight

Concentrations in mg/Kg from the study: Fig. 2 present the relationship between carcinogenic PAHs (cPAHs) and non-carcinogenic PAHs (ncPAHs) in Obagi, Obite and Ibewa cluster study areas. It was observed that, for the three study areas, the cPAHs was in higher concentration than the ncPAHs due to the industrial activities in study areas. The utilization of ANOVA to analyze the concentrations did not yield statistically significant changes in the levels of PAHs across the several research locations, regardless of their carcinogenic or non-carcinogenic nature ($p<0.05$). Nevertheless, a significant disparity was seen in the homologous composition and levels of the various polycyclic aromatic hydrocarbons (PAHs).

The diagnostic ratios of PAHs with low molecular weight (LMW) to those with high molecular weight (HMW) are displayed in Table 4. In all three regions examined, the research found that HMW PAHs were more concentrated than LMW PAHs. Obagi had an LMW/HMW ratio of 0.2340, Ibewa's was 0.2222, and Obite's was 0.2549. In Obagi, the proportion of Low Molecular Weight (LMW) PAHs compared to High Molecular Weight (HMW) PAHs was 19%, while in Obite it was 18%, and in the Ibewa cluster it was 20%. The ratios of sediment PAHs diagnoses for the three study sites are presented in Table 4. In order to distinguish between polycyclic aromatic hydrocarbons (PAHs) associated with petrogenic origins and those that are pyrogenic, the LMW/HMW ratio might be employed. A LMW/HMW ratio below 1 is indicative of sources associated with pyrogenic origins, while a ratio above 1 indicates sources associated with petrogenic origins. The sediments of the Obagi,

Obite, and Ibewa cluster sites exhibited a significant abundance of polycyclic aromatic hydrocarbons (PAHs) derived from pyrogenic sources, as evidenced by the presence of LMW/HWM ratios below 1. The concentration distribution pattern reported in this study can be attributed to various factors, including photooxidation, the molecular weight of polycyclic aromatic hydrocarbons (PAHs), and volatility. PAHs with low molecular weight are prone to degradation due to their inherent instability.

4. CONCLUSION

The long-term study showed that ncPAHs concentrations were highest at Obagi cluster area while Obite recorded the lowest concentrations of ncPAHs. Benzo (g,h,i) perylene concentrations amongst the ncPAHs has highest concentrations across the three cluster areas studied over the period, while Acenaphthylene had the least concentrations across the three cluster areas. Overall, the low ncPAHs concentration across the three cluster areas does not impact negatively on the ecosystem. Ecologically the risk posed by ncPAHs using the RQ_{NCS} and RQ_{MPCS} models respectively indicates considerably low ecological risk and low negligible remedial actions respectively, since both RQ_{NCs} and RQ_{MPCs} data are less than 1,ie., a single ncPAHs analyzed does not pose any significant ecological risk. Periodic and routine field re-evaluation should be done at intervals and using the results in this research work as baseline for long term monitoring for possible escalation of field data that might warrant remediation action. To mitigate accumulation of ncPAHs in the sediments overtime and its toxicological effect in human, oil and gas companies in the Niger-Delta area should re-inject their flays into the ground, bush burning should be reduced and government should outlaw combustion engines and replace them with environmentally friendly energy sources. In the event of need for remediation in future, I suggest the application of Detoxification by chemical reaction (DCR) technology, which is not only cost effective and efficient but is environmentally friendly.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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