Evaluation of polyaromatic hydrocarbons in soil from crude oil spilled sites in Ogbia Local Government Area of Bayelsa State, Nigeria

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ABSTRACT

***Background*:** As a result of the illegal oil refining activities within the oil producing area of the Niger Delta Area the environment is highly degraded. In the course of this activities a lot of pollutants among them polyaromatic hydrocarbons are released into the soil. This then creates a serious impact: destroying the wildlife habitat. This study was carried out within Ibalabiri Community in Ogbia LGA of Bayelsa State to ascertain the variation of these PAHs in and around the affected area of study.

***Methods*:** Sampling were done at four different selected sites within Ibalabiri community during the dry season. The pre-prepared samples were extracted for PAHs using Hexane: Dichloromethane solvent mixture with the aid of a soxhlet apparatus. The extract was further fractionated with the aid of a gradient column chromatography into aliphatic and aromatic fractions. The aromatic fraction was subjected to GC-MS and evaluated for PAHs constituents.

***Result*:** The low molecular weight PAHs identified included: naphthalene, acenaphylene, acenaphthalene, fluorine, phenantrene, anthracene while the high molecular weight PAHs were fluoranthene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene in all the 4 samples. Pyrene was only detected in samples 2 and 3. The total concentrations of the PAHs ranged from 452.00 mg/kg in sample 1 to 456. 6 mg/kg in sample 2.

***Conclusion*:** The presence of these PAHs is due to petrogenic source. Considering the toxicity of PAHs the result of the present study would be useful and also creates a better understanding of the source of PAHs pollution and control.

***Keywords*:** Ibalabiri, PAHs, soil pollution, illegal oil refining

1.0 INTRODUCTION

Crude Oil production in the Nigeria's Niger Delta area date back to 1958 with Oloibiri, an area in Ogbia Local Government area of Bayelsa state in the spotlight. The exploration of oil in this area had led to environmental pollution due to oil spillage. One of the major pollutants commonly associated with petroleum related activities [1] is polyaromatic hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAHs) are fused or condensed aromatic organic compounds with reported negative impact on the environment and are widely distributed in the ecosystem. [2, 3, 4, 5, 6]. According to Honda and Suzuki [7] the toxicities due to PAHs and their bioaccumulation in the terrestrial organisms is creating a serious effect on the human health - the final consumers of the animals. Ezekwe, and Oshionye [1] reported that the in Kolo Creek, the concentration of naphthalene was found to be between 0.01 - 0.1 mg/L. Lead, [8] also reported that oil pollution has untold consequences on food production and discouraging fishing activities within the area too. PAHs generally in this aquatic environment can mainly be considered to be of four types: petrogenic (derived from fuels), pyrogenic (from an incomplete combustion process), biogenic (being generated by organic metabolism) and diagenetic (generated by the transformation process in sediment) [9]. It is important to note that, of these four types of sources, petrogenic and pyrogenic sources are mainly artificial and are important contributors of environmental PAH pollution in the aquatic environment (Honda and Suzuki, 2020). Oil spills is the direct cause of PAH pollution which seriously impact on the environment toxicologically [7]. PAH toxicities and related bioaccumulation properties in aquatic animals has created a lot of concern in recent time. Studies have revealed the toxicity of PAHs, including endocrine disruption and tissue-specific toxicity including carcinogenic toxicity of PAHs [7]. This study was carried out within Ibalabiri Community in Ogbia LGA of Bayelsa State to determine the the variations of these PAHs in and around the affected area of study.

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2.0 MATERIALS AND METHODS

2.1 Material

2.1.1 The Study Area

Ibalabiri is one of the rural communities in Ogbia Local Government of Bayelsa State. A lot of illegal crude oil activities take place in this village such as the operation of illegal oil refining or medulla refining of the crude oil. The subject of the research was to assess the concentration of polyaromatic hydrocarbons as a contaminant in the soil in the locality where these activities are taking place.

2.1.2 Standards and reagents

All chemicals used were of Analar grade and were doubling distilled with highest purity. Reagents used included Hexane, dichloromethane, alumina (GC grade) as desiccant, conc. H_2SO_4, anhydrous sodium sulphate and organic free reagent water.

2.1.3 Sample collection

The sampling points were chosen in order to have an overall overview on PAHs contamination in the Ibalabiri village. The sampling areas were selected with the assumption that they might be polluted with PAHs as a result of illegal oil activities which is the major sources of PAHs. The sampling was done during the dry season. Soil samples were collected at four different points within the study area in three sets with stainless hand-held auger. One set which was the top layer was between 0 and 10 cm deep from the surface, second set which was the middle layer was collected between 10 and 20 cm deep below the surface and the third set which was the bottom layer was collected below the surface at depth of 20–30 cm. The replicate samples collected at each point were thoroughly mixed to form a composite sample. Each of these composite samples was then wrapped in aluminum foil and properly preserved until extraction and analysis.

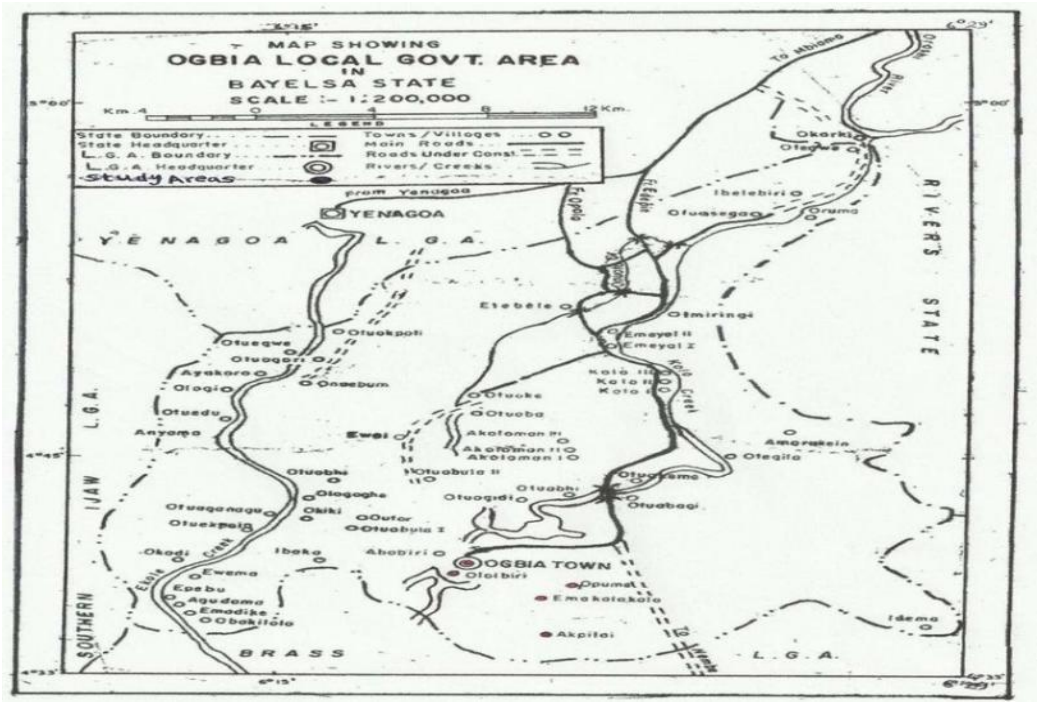

Fig 1: Map of Ogbia Local Government Area

2.2 Methods

2.2.1 Sample preparation and treatment

2.2.1.1 Extraction

Each of the soil samples prior to the extraction for PAHs analysis were air dried in a dust free environment at room temperature. The samples were the powered with a porcelain mortar and pestle and sieved using a 2 mm mesh sized sieve (10). The reference method employed in the extraction of PAHs in soil was US EPA 3540C (Soxhlet extraction). 10 grams of the composite soil sample was blended thoroughly with 10 g of anhydrous sodium sulfate and placed in an extraction thimble. 200 ml of the extraction solvent mixture (Hexane: Dichloromethane in the ratio of 300:100 ml) was poured into a 500 ml round bottom flask

containing one boiling chips. The flask was then attached to the extractor and the sample extracted for 16–24 h at 4–6 cycles/hour depending on the sample. The extract was then allowed to cool after complete extraction [11]

2.2.1.2 Separation and concentration of the fractions

The soluble organic matters were fractionated into aliphatic and aromatic fractions using a glass column packed with neutral alumina. 10 g of the alumina was packed into the column and properly cleaned with redistilled hexane. The extract was poured onto the alumina and was allowed to elute using the redistilled hexane to remove the aliphatic fractions into a precleaned 25 ml glass container. The aromatic fraction was recovered by using the mixture of hexane and dichloromethane in ratio of 3:1. The aromatic fraction was concentrated to approximately 1.0 ml using rotary evaporator. The obtained extract was stored in an organic free precleaned glass vials with screw caps for analysis. It was refrigerated at − 4 °C until it was analyzed.

2.3 Statistical analysis

Results obtained were presented as the mean of three determinations and standard deviation of PAHs in (µg/kg). Test of significance was carried out using Chi square and the levels of significance were accepted at $p<0.05$ using Statistical Package for Social Sciences (SPSS version 16) program.

3.0 RESULTS AND DISCUSSIONS

The results of the analysis of the four (4) samples from the different soils locations are presented in Tables 1, 2 and 3. Table 1 (Figure 2) displays the low molecular weight poly-aromatic hydrocarbons, (LMW PAHs). These are napphthalene, acnaphylene. Acephthalene, fluorene and phenantrene. Table 2 shows the concentrations of the low molecular weight poly-aromatic hydrocarbons, LMW PAHs namely fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo]b]fluoranthene, benzo[k]fluorenethene, bnzo[a]pyrene, indeno(1,2,3-ed)pyrene, dibenzo(a,h)anthracene and benzo(ghi)pyrene. Table 3 is made up of the 2-, 3-, 4-, 5- and the 6-ring members of the poly-aromatic hydrocarbons. These are generally carcinogenic in nature. Certain PAHs were however not detected during these analysis: in Table 2 indeno(1,2,3-ed)pyrene, dibenzo(a,h)anthracene and benzo(ghi)pyrene were not detected while in Table 3 the 6-ring PAHs were not detected. The non-detection of these PAHs may either be as a result of the detection limits of the instrument or the substances were actually not present in the analysed samples. For each of the samples, the mean levels and standard deviation were also calculated for individual and for the total PAHs.

Table 1: Concentrations of low molecular weight PAHs

PAHs	SAMPLE 1 (µg/kg)	SAMPLE 2 (µg/kg)	SAMPLE 3 (µg/kg)	SAMPLE 4 (µg/kg)
Naphthalene	2.00 ±0.2	3.00 ±0.1	2.00 ±0.5	2.50 ±0.3
Acenaphylene	6.00 ±0.5	5.20 ±0.3	5.80 ±0.8	6.20 ±1.5
Acenaphthalene	8.00 ±1.0	7.50 ±0.2	8.10 ±0.4	8.00 ±2.0
Fluorene	2.00 ±0.1	2.10 ±0.4	1.80 ±0.1	2.30 ±0.3
Phenantrene	2.00 ±0.1	2.20 ±0.4	2.10 ±0.4	2.20 ±0.2
Anthracene	2.00 ±0.2	2.00 ±0.2	2.20 ±0.2	1.80 ±0.5
LMW PAHs	22.00 ±0.4	22.00 ±2.5	22.00 ±2.0	23.00 ±3.0

(n = 3; p < 0.05)

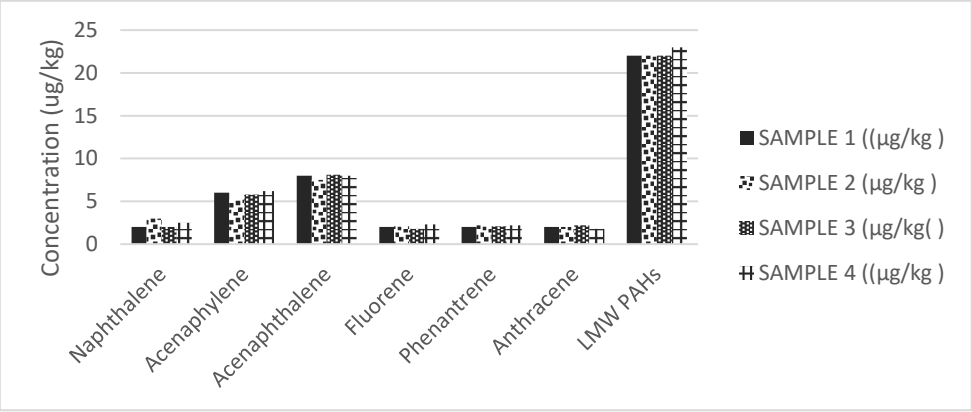

Figure 2: Level of the distribution of the Low Molecular Weight Hydrocarbon;

Table 2: Concentrations of high molecular weight PAHs

PAHs	SAMPLE 1 ((µg/kg)	SAMPLE 2 (µg/kg)	SAMPLE 3 (µg/kg( )	SAMPLE 4 ((µg/kg)
Fluoranthene	2.00 ±0.1	1.80 ±0.1	1.60 ±0.1	2.10 ±0.5
Pyrene	ND	0.20 ±0.1	0.10 ±0.0	ND
Chrysene	6.00 ±0.1	6.50 ±0.3	6.40 ±0.5	6.80 ±1.8
Benzo[a]anthracene	4.00 ±0.1	5.10 ±0.2	4.80 ±0.1	3.80 ±1.5
Benzo[b]fluoranthene	92.00 ±0.1	89.6 ±13.2	91.20 ±0.6	92.10 ±10.5
Benzo[k]fluoranthene	42.00 ±0.1	43.00 ±2.1	41.80 ±0.6	41.70 ±0.8
Benzo[a]pyrene	58.00 ±0.1	60.10 ±3.1	59.20 ±5.2	58.20 ±2.5
Indeno(I,2,3-cd)pyrene	ND	ND	ND	ND
Dibenzo(a,h)anthracene	ND	ND	ND	ND
Benzo(ghi)pyrene	ND	ND	ND	ND
HMW PAHs	204.00 ±0.1	206.20 ±12.4	205.10 ±4.8	204.70 ±7.5
ΣPAHs	226.00 ±0.1	228.20 ±4.1	227.10 ±4.4	227.70 ±7.2

(ND = not detected; n = 3; p < 0.05)

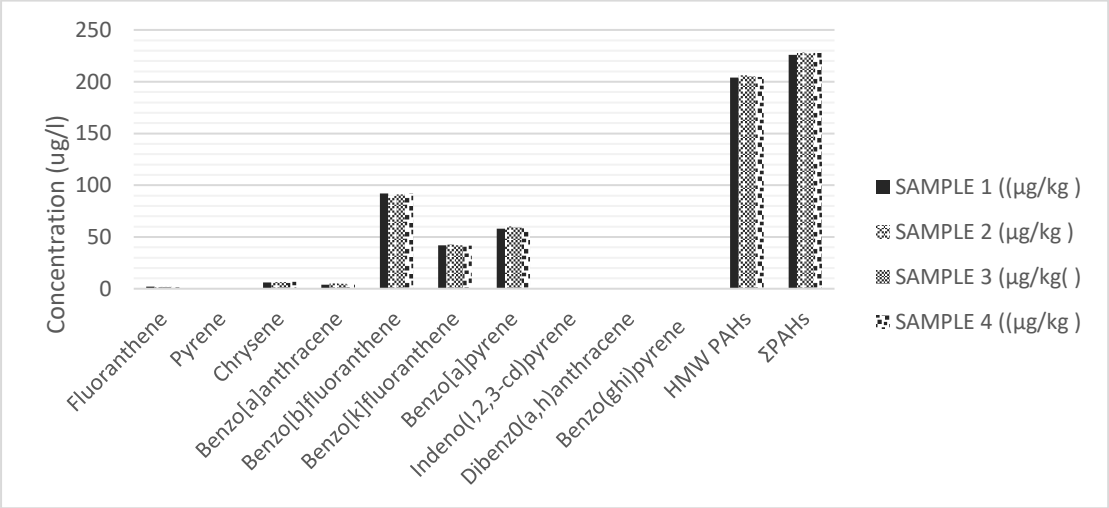

Figure 3: Level of the distribution of the High Molecular Weight Hydrocarbon

Table 3: Concentrations of carcinogenic PAHs

PAHs	SAMPLE 1 ((*µg/kg*)	SAMPLE 2 (*µg/kg*)	SAMPLE 3 (*µg/kg*)	SAMPLE 4 ((*µg*/kg)
Σ2-ring PAHs	2.00 ±0.1	2.10 ±0.1	1.90 ±0.4	2.10 ±0.8
Σ3-ring PAHs	20.00 ±0.5	21.20 ±0.6	20.90 ±2.2	20.60 ±0.4
Σ4-ring PAHs	12.00 ±0.4	13.10 ±1.2	12.80 ±1.6	12.10 ±2.1
Σ5-ring PAHs	192.00 ±2.0	191.80 ±4.2	192.20 ±1.4	192.10 ±4.2
Σ6-ring PAHs	ND	ND	ND	ND
Σc PAHs	226.00 ±2.0	228.20 ±4.4	227.80 ±1.2	226.90 ±4.0

(ND = not detected; n = 3; p < 0.05)

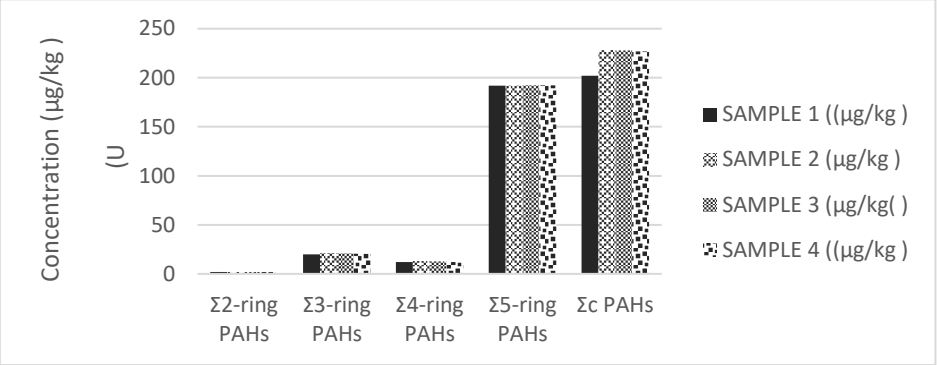

Figure 4: Level of the distribution of the Carcinogenic Hydrocarbon;

Table 4 shows the concentrations the PAHs in each of the samples that was analysed. The was no significant difference in the total amount of the PAHs concentration in each of the four samples analysed. This is also presented in the bar chart in Fig 5.

Table 4: Concentrations of the Polyaromatic Hydrocarbons in each of the soil samples

PAHs	SAMPLE 1 ((µg/kg)	SAMPLE 2 (µg/kg)	SAMPLE 3 (µg/kg)	SAMPLE 4 ((µg/kg)
LMW PAHs	22.00 ±0.2	22.00 ±0.9	22.00 ±0.8	23.00 ±0.4
HMW PAHs	204.00 ±0.8	206.20 ±4.6	205.10 ±5.2	204.70 ±9.7
Σc PAHs	226.00 ±1.2	228.20 ±7.2	227.80 ±5.4	226.90 ±3.2
ΣPAHs	452.00 ±4.0	456.6 ±2.5	454.9 ±3.6	454.6 ±7.5

(n = 3; p < 0.05)

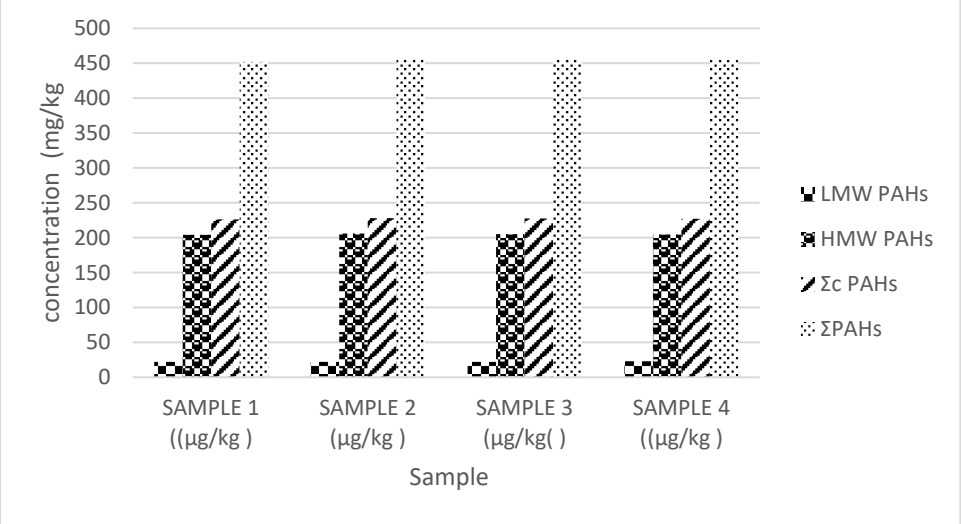

Fig 5: Level of the distribution of the Polyaromatic Hydrocarbons

5.0 DISCUSSION

The concentrations of the low molecular weight poly-aromatic hydrocarbon naphtalene, acenaphylene, acenaphthalene, fluorene and phenantrene in Sample 1 were found to be between the range of 2.00 µg/kg and 8.00 µg/kg. The highest concentrations were in acenaphylene and acenaphthalene with 6.00 µg/kg and 8.00 µg/kg respectively. In Sample 2, the same trend was also observed ranging between 2.00 µg/kg in anthracene and 7.50 µg/kg in acenaphthalene. The concentration of acenaphylene was however next to acenaphthalene with 5.20 µg/kg. In Sample 3 the last concentration was that of fluorene having 1.80 µg/kg and acenaphthalene with 8.10 µg/kg. Acenaphylene had a concentration of 5.80 µg/kg. In Sample 4, th PAH having the last concentration was anthracene with 1.80 µg/kg while acenaphylene and acenaphthalene had 6.20 µg/kg and 8.00 µg/kg respectively. In all the samples, the summations of the concentrations of each of the PAHs were the same, (22.00 µg/kg) except for Sample 4 with 23.00 µg/kg. Across the difference samples,

acenaphthalene maintained the lead with 8.00 µg/kg in all the samples followed by acenaphylene and ranging between 5.20 µg/kg and 6.20 µg/kg. The consistencies in the concentration of the different PAHs indicate that the sources of the crude oil pollution in these places are the same. The high molecular weight poly-aromatic hydrocarbons analysed in the samples show a significantly higher concentrations (Table 2) than as found in the case of low molecular weight poly-aromatic hydrocarbons. In sample 1, fluoranthene had the least concentration of 2.00 µg/kg while Benzo[b]fluoranthene had the highest concentration of 90.00 µg/kg. Others are Chrysene 6.00 µg/kg; Benzo[a]anthracene 4.00 µg/kg; Benzo[k]fluoranthene 42.00 µg/kg; Benzo[a]pyrene 58.00 µg/kg. Except for pyrene that that was not detected in only sample1 and sample 4, indeno(I,2,3-cd) pyrene, dibenzo(a,h)anthracene and benzo(ghi)pyrene were never detected in any of the four (4) samples analysed. The concentrations of the HMW PAHs in Sample 2 was similar to that of Sample 1 with pyrene having the least concentration of 0.20 µg/kg and Benzo[b]fluoranthene having 89.60 µg/kg. Also, in Sample 3 pyrene had the least concentration of 0.10 µg/kg with Benzo[b]fluoranthene having the highest concentration of 91.20 µg/kg. The high concentration of Benzo[b]fluoranthene in the samples is also noticed in Sample 4 having 92.10 µg/kg and fluoranthene having the least; 2.10 µg/kg. The total concentrations of the high molecular weight poly-aromatic hydrocarbons in each of the samples analysed were within the same range of 226.00 µg/kg and 228.20 µg/kg in Samples 1 and 2 respectively. Across the different samples, the concentrations of the HMW PAHs were maintained with little variations in all the samples analysed. PAHs are a group of ubiquitous persistent organic pollutants [12, 13] that are capable of accumulating in the soil for a long time [14]. PAHs are toxic, carcinogenic and mutagenic to all living organisms [12, 15, 16, 17]. The 2-ring, 3-ring, 4-ring, 5-ring and 6-ring polyarometic hydrocarbons are always associated with carcinogenic properties. [12,15,16, 17]. The concentrations of these group PAHs are shown in Table 3. Their concentrations ranged between 226.00 in sample 1 and 228.20 mg/kg in Sample 2. Samples 3 and 4 had 227.80 mg/kg and 226.90 mg/kg respectively. This is a clear indication that the source of pollution is the same and also the physicochemical properties, porosity and other properties of the soil affecting their absorption are the same within the area of study. This is also represented in the bar chart (Figure 3).

5.0 CONCLUSION

The level of destruction done to this natural habitat in Ibalabiri Community and livelihood has not received the deserved attention around Ogbia Local Government Area with residential areas, farmlands and water bodies. The adverse health effect of pollution due to the presence of trace metals and PAHs is of concern to researcher and the governments: Local, State and Federal governments should take serious steps not only in the remediation process but also in stopping the illegal activities.

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Conflict of interest

The author has no relevant financial or non-financial interests to disclose

Contribution of the Author

The work was designed by Dr. Richard A. Ukpe. The initial draft was also written by the author who also carried out the bench work.

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