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Pedological and Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Farmlands of a Tropical Oil Producing Region in Akwa Ibom State, Nigeria

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Abstract: The distribution and accumulation of PAHs especially in arable farmlands is problematic as these contaminants are toxic to humans who consume edible crops and vegetables grown on such contaminated soils unknowingly. Consequently, regular and intensive monitoring of these ecosystem should be prioritized to avoid further contamination and pollution. To this end, this study carried out a pedological and risk assessment of Polycyclic Aromatic Hydrocarbons in farmlands of a tropical oil producing region in Akwa Ibom State. Two sampling sites (non-flare and flare sites) were chosen where farming activities are predominant. Soil samples (twenty four in all) were collected at 6 different points from the flare and non-flare sites using a soil auger at two different rooting depths (0 – 15 cm and 15 – 30 cm) and analyzed for 17 PAHs using recommended standard methods. From the results, total polycyclic aromatic hydrocarbons were much higher in the flare site (15.97 mg/kg) than in the non-flare site (3.38 mg/kg). The 5-ring PAHs were the most dominant among other aromatic rings in terms of percentage composition in the non-flare (31.66%) and flare site (27.11%) while the 2-ring PAHs were the least dominant with percentage composition of 8.58% and 7.51% in the non-flare and flare sites, respectively. The diagnostic ratio computed revealed that the apportionment of the PAHs in the ecosystem was primarily from pyrogenic/petrogenic/grass, coal or wood combustion/heavy fuel composition/petroleum sources. The ecological risk assessment revealed a mean ERM quotient value of 0.34 indicating a 30% toxicity probability in soils of both study sites. This poses a serious hazard to public health as these pollutants are carcinogenic and also calls for immediate remediation and intervention plans to salvage and protect this ecosystem as well as the lives of these farmers cultivating and consuming edible crops and vegetables ignorantly.

Keywords: Pedology, Ecological Risk Assessment, Polycyclic Aromatic Hydrocarbon, Farmland, Oil Producing Region, Diagnostic Ratio

1. Introduction

Hydrocarbons are quantitatively the most important constituents of petroleum from natural and anthropogenic sources [19]. Anthropogenic sources of these hydrocarbons include offshore oil production, marine transportation, atmospheric or aerial depositions from combustion of coal and gas flaring, direct ocean dumping, coastal, municipal and industrial wastes, and run-off. However, among the anthropogenic sources, point discharges, contamination by urban run-offs, refineries and other coastal effluents are in aggregate substantial and are important in causing local, chronic pollution in the vicinity of estuaries, creeks, harbours and coastal settlements [19].

Polycyclic Aromatic Hydrocarbons (PAHs) consist of hazardous pollutants that are widely distributed, persistent and toxic with bioaccumulation potentials in the environment. They are made up of two or more conjugated aromatic rings ranging from a simple two-ring compound to more complex six-ring compounds. They are considered to be composed of the most toxic part of the chemicals found in fossil fuels such

as oil, natural gas and coal [7]. The US Environmental Protection Agency (USEPA) had indicated 17 PAHs as priority pollutants for carcinogenic risk (Agency for Toxic Substances and Disease Registry, ATSDR). The identified pollutants include; acenaphthene, acenaphthylene, anthracene, benz (a) anthracene, benzo (*a*) pyrene, benzo(e)pyrene, benzo (*b*) fluoranthene, benzo(g,h,i)perylene, benzo(j)fluoranthene, benzo(k)fluoranthene, chrysene, coronene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, phenanthrene, pyrene. The two major sources of direct PAH pollution into the marine environment are from the inshore smelter industry and offshore oil and gas production activities [7]. But also spills of crude oil may contribute to the total PAH input in marine ecosystems. PAHs are degraded both through chemical and biological processes in the water. The lighter PAHs are more water soluble than the heavier ones and are therefore more bio available [7] while the larger ones are considered the most toxic. PAHs are taken up by the aquatic organisms either directly from water or through diet.

Continuous oil pollution and gas flaring in oil producing regions like Ibeno in Akwa Ibom State have significantly altered the ecology of the affected areas. Soils in such environment act as sinks for PAHs. According to [22], more than 90% of the total mass of PAHs in the environment is deposited and stored in soils. Polycyclic Aromatic Hydrocarbons in soils may accumulate in vegetables or other biota and passed along in the food chain [12]. This is detrimental to environmental and human health due to their high degree of mutagenicity and carcinogenicity [24]. PAHs deposited in soils can further cause the contamination of groundwater through leaching [2].

The health implications of the locals in this region cultivating farm produce in such contaminated and polluted soils in ignorance is thoughtful and calls for a serious concern and immediate response as these hydrocarbons are highly toxic and lethal when they bio-accumulate and bio-magnify in flora and fauna. It is upon this premise that this present study is carried out.

2. Materials and Methods

2.1. Study Area

This study was carried out in Lower Stubbs Creek, Ibeno, Akwa Ibom State. Lower Stubbs Creek is a perennial rainforest tributary of Qua Iboe River Estuary located in the coastal ridges of the Niger Delta of Akwa Ibom State, Nigeria. The Creek is located between latitudes 4°3'N and 4°8'N and longitudes 6°45'E and 7°55'E. The climate of this region is typical of the equatorial region with rainfall through the year. Two seasons, (dry and wet) are however discernible in the area. The dry season ranges between November and February with peak in January. The wet season extends from March to October with peak in August. The surface water of the aquatic systems is basically warm with temperatures generally greater than 24°C. The sea surface temperature

shows double peaked cycles which corresponds quantitatively to the cycle of the solar heights. Between October and May, sea surface temperature range from 27°C to 28°C while during the rainy season of June to October the range is between 24°C and 25°C. This variation and decline has been ascribed to an expression of the overall cooling of the South Atlantic Ocean during this period of the year [5]. The natives are engaged primarily in farming and fishing which constitute their dependable source of income and livelihood.

2.2. Soil Sampling

Soil samples were collected at 6 different points from the flare and non-flare sites using a soil auger at two different rooting depths (0 – 15 cm and 15 – 30 cm). Soil samples from the flare sites were obtained 20 m from where gas flaring activities were predominant. Soil samples obtained from both sites were then stored and preserved in well labeled Ziploc bags for laboratory analyses of the PAHs. Altogether, a total of 24 soil samples were collected from the study sites.

Figure 1. *Gas Flaring impacted site at Ibeno L.G.A.*

2.3. Determination of Polycyclic Aromatic Hydrocabons (PAHs) in Soil Samples

A gas chromatograph (GC, Hewlett- Packard HP 6890) coupled to a mass spectrometer (MS, Model 5971, Hewlett-Hackard) was used to quantify extractable organic PAHs. Aliquots of each sample were injected using 30:1 split ratio onto 30 ml, 0.25mm inner diameter, and HP-SMS 5% phenyl methyl siloxane capillary column. The operational conditions were as follows: 40-280°C at 6°C /min: scan rate 1.53 scans/s; and source temperature of 320°C. Helium was used as the carier gas (at 1.5ml/min). The PAHs were determined in selective ion-monitoring mode with ionization energy of 70 eV. The m/z peaks corresponding to the molecular masses of the individual PAH were used for identification and quantification. Concentrations of PAHs were calculated relative to the pre-deuterated internal standard. The PAHs analysed were Naphthalene, 2-Methylnaphthalene, Acenaphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene,

Dibenzo(a,h)anthracene, Benzo(g,h,i)perylene and Indeno(1,2,3-d)pyrene.

2.4. Statistical Analyses

The means of the analyzed PAHs were determined using Statistical Package for Social Sciences (SPSS 20.0).

2.4.1. Diagnostic Ratio

Diagnostic ratio is a useful tool which helps in identifying and apportioning the origin of PAHs present in various environmental media (Yunker *et al*., 2002 and Bucheli *et al*., 2004). In this study, the diagnostic ratios used were Baa / Baa + Chr, Ant / Ant + Phe, Fla / Fla + Pyr, Phe/Ant, Ind/Ind + Bghip, Bap/(Bap + Chr) and LMW/HMW ratio (Table 2). Baa / Baa + Chr ratio of 0.2 to 0.35 indicate mixed petrogenic and pyrogenic origin and > 0.35 indicate pyrogenic origin (Zhang, 2004). Ant / Ant + Phe ratio of > 0.1 indicate dominance of heavy fuel composition, while < 0.1 indicate petroleum source, Fla/Fla+Pyr ratio of < 0.4 indicate petroleum source, 0.4 – 0.5 indicate liquid fossil fuel combustion while > 0.5 indicate coal, wood or grass combustion (Yunker *et al*., 2002). Phe/Ant ratio of < 10 and < 15 indicate pyrogenic and petrogenic sources. Ind/Ind + Bghip ratio of < 0.2 indicate petrogenic source, 0.2 – 0.5 indicate fuel combustion (Vehicle and crude oil) while > 0.5 indicate grass, coal or wood combustion (Mannino and Orecchio, 2008). Bap/(Bap + Chr) ratio of < 0.2 indicate petroleum source, 0.2 – 0.35 indicate coal, wood or grass combustion while > 0.35 indicate vehicular emission (Essumang *et al*., 2011). HMW/LMW ratios of > 1 and < 1 indicate pyrogenic (Soclo *et al*., 2000) and petrogenic sources (Zakaria *et al*., 2002).

2.4.2. Health Risk Assessment Ecological Risk Assessment

The mean Effect Range Medium (ERM) quotient approach was used to evaluate the possible ecotoxicity of PAHs in the soils. The mean ERM quotient values was calculated using the method described by [13] as follows:

$$m - ERM - q = \sum \left(\frac{C_i}{ERM_i}\right)/n$$

where C_i is the concentration of PAH, ERM_i is the ERM value for the same target PAH and *n* is the number of PAH.

According to [14], m-ERM-q are categorized according to their possibility of toxicity. Values ≤ 0.1 indicates an 11 percent probability of toxicity, 0.1 to 0.5 indicates a 30% probability of toxicity and 0.5 to 1.5 indicates a 46% probability of toxicity and > 1.5 indicates a 75% probability of toxicity [18].

3. Results

3.1. Characterization of PAHs in Soils of Non-flare and Flare Sites

Table 1 represents the mean concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) obtained from the soils of flare and non-flare sites of Lower Stubbs Creek Mangrove Ecosystem. The analyzed PAHs in this study were divided into 5 groups: 2-ring, 3-ring, 4-ring, 5-ring and 6-ring. The results showed that both the low molecular weight polycyclic aromatic hydrocarbons, (Naphthalene, Acenaphthalene; Acenaphthene; Fluorene; Phenanthene and Anthracene), and the higher molecular weight PAHs (Fluoranthene, Pyrene, Benzo(a) anthracene, Chrysene, Benzo(k)fluoranthene, Benzo(h)fluoranthene, 2-Methylnaphthalene, Benzo(a)pyrene Dibenzo(a,h)anthracene, Benzo(g,h,i)perylene and Indeno(1,2,3-d)pyrene) were higher in concentrations in the flare than in the non-flare sites. In terms of their aromatic rings, the relative abundance were as follows in the non-flare sites: 2-ring (8.58%), 3-ring (25.44%), 4-ring (22.49%), 5-ring (31.66%) and 6-ring (11.83%) while that of the flare sites were as follows: 2-ring (7.51%), 3-ring (26.42%), 4-ring (19.16%), 5-ring (27.11%) and 6-ring (19.80%) (Figure 2) Total polycyclic aromatic hydrocarbons were much higher in the flare site with a value of 15.97 mg/kg as against 3.38 mg/kg recorded in the non-flare site. Comparative representation of the PAHs values recorded in the flare and non-flare sites is presented in Figure 3.

Table 1. Mean Concentrations of Polycyclic Aromatic Hydrocarbons from soils of Lower Stubbs Creek Mangrove Ecosystem.

PAH Types	Non Flare site (mg/kg)	Flare site (mg/kg)	Number of rings	Carcinogenicity Classification
2-Methylnaphthalene	0.10	0.20	2	Nc
Acenaphthylene	0.11	1.05	3	Nc
Acenaphthene	0.10	0.90	3	Nc
Anthracene	0.15	0.70	3	Nc
Benzo(a)anthracene	0.13	0.53	4	B
Benzo(a)pyrene	0.20	0.80	5	B
Benzo(b)fluoranthene	0.48	1.79	5	2B
Benzo(g,h,i)perylene	0.20	1.36	6	Nc
Benzo(k)fluoranthene	0.20	1.27	5	2B
Chrysene	0.30	1.19	4	2B
Dibenzo(a,h)anthracene	0.19	.47	5	B
Fluoranthene	0.13	0.48	4	Nc
Fluorene	0.30	0.70	3	Nc
Indeno(1,2,3-d)pyrene	0.20	1.80	6	2B
Naphthalene	0.19	1.00	2	2B

PAH Types	Non Flare site (mg/kg)	Flare site (mg/kg)	Number of rings	Carcinogenicity Classification
Phenanthrene	0.20	0.87	3	Nc
Pyrene	0.20	0.86	4	Nc
$\sum$ 17PAHs	3.38	15.97		

2B = Group of PAHs which are possibly carcinogenic to humans (International Agency for Research on Cancer, 2002); B = group of PAHs that are probably carcinogenic to human (International Agency for Research on Cancer, 2002); All other PAHs compounds designated 'nc' are currently regarded as 'not classifiable [15].
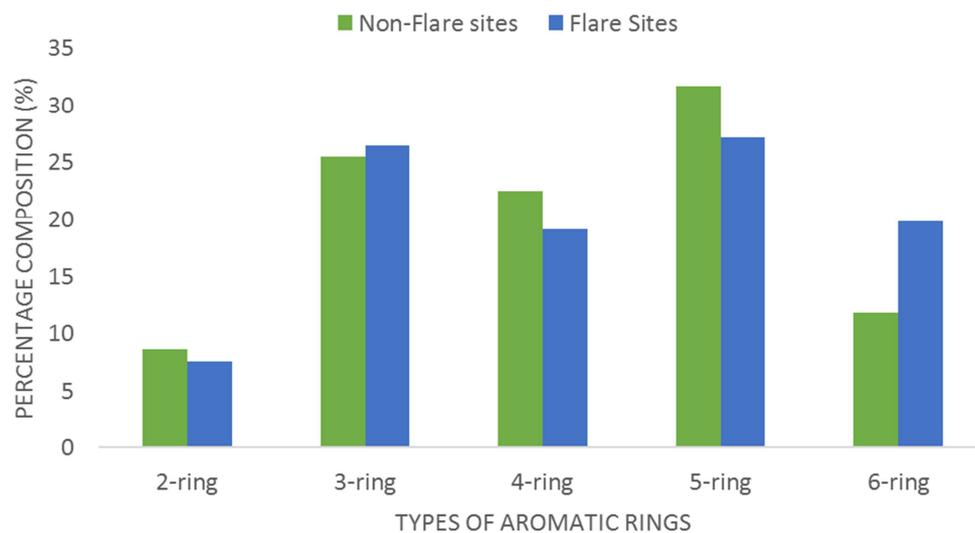
Figure 2. *Percentage composition of aromatic rings in non-flare and flare sites.*
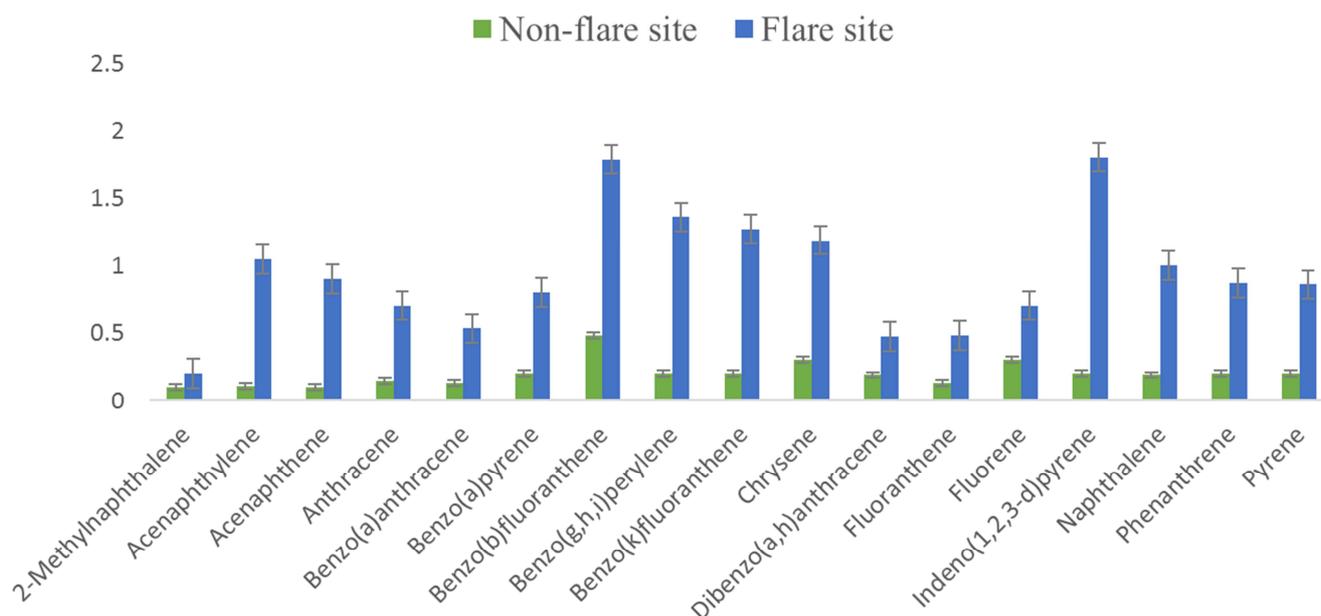
Figure 3. *Comparative representation of the PAHs concentration recorded in the flare and non-flare sites.*

3.2. Identification of PAH sources

3.2.1. Diagnostic Ratio

The diagnostic ratio as presented in Table 2 shows that for the non-flare and flare sites, the ratio of Baa/Baa + Chr ranged from 0.30 to 0.31 with mean value of 0.305, Ant/Ant+ Phe values ranged between 0.43 and 0.45 with mean value of 0.44, Fla/Fla+ Pyr ratio ranged between 0.36 and 0.39 with mean value of 0.375, Phe/Ant ranged from 1.24 to 1.33 with mean of 1.285, Ind/(Ind + Bghip) had values ranging from 0.50 – 0.57 with mean of 0.535, Bap/(Bap + Chr) ranged between 0.27 – 0.40 with mean of 0.335 while HMW/LMW ranged from 1.94 – 1.95 with a mean value of 1.945. The diagnostic ratios calculated showed that the PAHs in the studied areas followed this order; HMW/LMW > Phe/Ant > Ind/(Ind + Bghip) > Ant/Ant+Phe > Fla/Fla+Pyr > Bap/(Bap + Chr) > Baa/Baa+Chr.

Table 2. *Diagnostic PAHs ratio in soils of the non-flare and flare sites.*

PAHs	Diagnostic ratio		Mean values	Sources
	Non-flare site	Flare site		
Baa/Baa+Chr	0.30	0.31	0.305	Petrogenic and Pyrogenic
Ant/Ant+Phe	0.43	0.45	0.44	Heavy fuel composition
Fla/Fla+Pyr	0.39	0.36	0.375	Petroleum
Phe/Ant	1.33	1.24	1.285	Pyrogenic and petrogenic
Ind/(Ind + Bghip)	0.50	0.57	0.535	Grass, coal or wood combustion
Bap/(Bap + Chr)	0.40	0.27	0.335	coal, wood or grass combustion
HMW/LMW PAHs	1.94	1.95	1.945	Pyrogenic

Baa = Benzo(a)anthracene, Chr = Chrysene, Ant = Anthracene, Phe = Phenanthrene, Fla = Fluoranthene, Pyr = Pyrene, Ind = Indeno(1,2,3-d)pyrene, Bghip = Benzo(g,h,i)perylene, Bap = Benzo(a)pyrene.

3.2.2. Ecological Risk Assessment

Table 3 shows the calculated Effect Range Medium (ERM) of individual PAHs and the mean ERM quotient of PAHs for study sites. The m-ERM-q values ranged from 0.19 to 0.48 with a mean value of 0.34.

Table 3. *ERM quotients of PAHs in the study sites.*

PAH Types	ERM SSG	Non Flare site (mg/kg)	Flare site (mg/kg)
2-Methylnaphthalene	670	0.00015	0.00029
Acenaphthylene	640	0.00017	0.0016
Acenaphthene	500	0.0002	0.0018
Anthracene	1100	0.00014	0.00064
Benzo(a)anthracene	1600	0.000081	0.00033
Benzo(a)pyrene	1600	0.00013	0.0005
Benzo(b)fluoranthene	-	-	-
Benzo(g,h,i)perylene	330	0.00061	0.0041
Benzo(k)fluoranthene	-	-	-
Chrysene	2800	0.00011	0.00043
Dibenzo(a,h)anthracene	1	0.19	0.47
Fluoranthene	5100	0.000025	0.000094
Fluorene	540	0.000555556	0.0013
Indeno(1,2,3-d)pyrene	950	0.000210526	0.0019
Naphthalene	2100	0.000090	0.00048
Phenanthrene	1500	0.000133333	0.00058
Pyrene	2600	0.000077	0.00033
m-ERM-q		0.19	0.48

4. Discussion

The pedological assessment of Polycyclic Aromatic Hydrocarbons revealed variations in their concentrations in the flare and non-flare sites. While higher concentrations of PAHs were recorded in the flare sites, lower concentrations were obtained in the non-flare sites. This disparity in concentrations may be attributed to the varying levels of petrogenic, pyrogenic and industrial activities predominating these areas. For instance, the non-flare site was characterized by less anthropogenic and industrial activities while offshore oil production, burning of fossil fuels, gas flaring, emission of hazardous wastes from automobiles and engine boats and effluent discharges were prevalent in the flare sites. Similar observations were made by [19]. The mean values obtained for PAHs concentrations in the soil was low when compared with those reported by [1] and [11]. These differences in PAHs concentrations may be explained by the severity of activities contributing these contaminants into the soil. The type of soils and their retention abilities for PAHs may further expound their different concentrations in soils. For instance, soils with abundant clay and silt substrates will retain more PAHs than sandy soils. This had been alluded by [23]. These scholars reported that the extent of soil pollution by PAHs depends on factors such as the cultivation and use of the soil, its porosity, its lipophilic surface cover, and its content of humic substances. The dilution of these contaminants by rain water and tidal influxes around these study sites may also accentuate their observed low values when compared with other studies. The high accumulation and uptake by the plants, phytodegradation, phytovolatilization and leaching may further substantiate the low concentrations of PAHs obtained in this study. Several field studies have demonstrated the accumulation of PAHs in vegetables and other food crops [27], [12]. Also, accumulation of various PAHs in the soil in varying proportions may justify the soil as being a major sink or reservoir for hydrocarbon products and contaminants. This is consistent with the reports of [22]. These scholars affirmed that more than 90% of the total mass of PAHs in the environment is stored in soils. In line with this, [4] reported that soil can contribute substantial amounts of PAHs to the atmosphere in warmer climates. Additionally, the occurrences of PAHs in these soils may provide valuable information concerning their various sources of emission and subsequent evaluation of the environmental and health risks associated with PAHs [17], [20].

The dominance of the 5-ring PAHs in the non-flare and flare sites may invariably suggest that these PAHs have lower volatility, solubility and higher persistence in soils [10]. It may also be inferred that these contaminants belonging to this assemblage share a similar source apportionment. These sources may include pyrogenic, petrogenic, fuel combustion and petroleum sources. Their dominance may further highlight that these aromatic rings are the major contributors to $\sum$ 17PAHs composition in these ecosystem. The dominance of 5-ring PAHs in this study is in synchrony with the findings of [10] but deviates from that of [11]. The latter scholars reported the dominance of the 4-ring PAHs in the coastal and estuarine areas of the Northern Bohai and Yellow Seas, China. The lower percentage composition recorded for the 2-ring PAHs may be attributed to their high volatility in the soil [9], [29].

The diagnostic ratios calculated showed that the PAHs concentrations in the study areas were predominantly from pyrogenic/petrogenic/grass, coal or wood combustion/heavy fuel composition/petroleum sources. These are not unrelated to the consistent gas flaring and venting activities which are conspicuous in Lower Stubbs Creek. This corroborates with the findings of Ite *et al.* (2013).

The m-ERM-q values obtained ranged from 0.19 to 0.48 with a mean value of 0.34. This mean value was between the range of 0.1 and 0.5. This, according to [18] indicates a 30% probability of toxicity. This may further imply that there is a great tendency of plants grown on these soils to absorb and accumulate these PAHs contaminants in their tissues. If this trend should continue, the toxicity percentage may increase geometrically over time. This calls for a concern as these may endanger human health through consumption of edible crops and vegetables grown on such contaminated soils.

5. Conclusion

This study assessed the PAH concentrations in farmlands of an oil producing region in Akwa Ibom State. It revealed varying levels of PAHs in the soil owing to different anthropogenic and industrial activities discharging these toxic hydrocarbons into the soil. Of the aromatic rings encountered in this study, the 5-ring PAHs had the highest percentage composition in both the non-flare and flare sites while the 2-ring PAHs had the least percentage abundance. The higher molecular ring PAH (4 – 6 rings) also predominated these sites when compared with the lower molecular ring PAHs. (2 – 3 rings). The diagnostic ratio evaluation highlighted that these PAHs were mostly from pyrogenic, petrogenic, grass, coal and wood combustion, heavy fuel combustion and petroleum sources which are attributes of perpetual gas flaring and venting activities from oil producing companies in Lower Stubbs Creek. Ecological risk assessment revealed a 30% probability of toxicity of soils in these sites. This poses a serious health risk to the public as these contaminants are carcinogenic and also calls for immediate remediation and prevention plans to salvage the lives of the locals growing and consuming agricultural produce in ignorant and the ecosystem at large.

From this premise, the following recommendations are made:

i) Farmers should not cultivate crops on farmlands with proximity to gas flaring or petroleum contaminated sites as such crops are highly carcinogenic.

ii) Efficient and eco-friendly methods should be adopted by oil producing and servicing firms in the discharge of their wastes.

iii) Gas flaring apparatus should be sited far away from where people live as hazardous substances emitted from it can endanger human lives.

iv) Regular environmental monitoring and time series studies should be carried out to help checkmate the status of this ecosystem against pollution.

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