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Concentration Distribution and Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbon in Kolo Creek Niger-Delta Nigeria

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Abstract

The ecological risk assessment of 16 USEPA priority polycyclic aromatic hydrocarbon (PAHs) in water and sediments of Kolo creek, Niger Delta Nigeria was assessed the samples were collected from November, 2018 to June, 2019 from seven locations (A-G) along the creek. The samples were extracted using standard methods and analyzed using gas chromatography (model: HP5890 S). The concentrations of the PAHs in the water and sediment samples ranged between $0.000 - 9.239 \ \mu/L$ and $.002 - 374.35 \ \mu/Kg$ respectively. All the compounds analyzed were detected in all the sampling places, even area far from the flow stations. Hence, the urban runoffs, sewage discharges, and agricultural activities are implicated. Four rings hydrocarbon were present in higher concentration when compared to other PAHs in all sampling sites, with benz (a)anthracene having the highest values in both matrixes. Similarly, lower molecular weight (LMW) PAHs were present in lower concentrations in all sampling sites and they are known to exhibit higher lethal toxicity than the larger PAHs. HMW were present in high concentrations than LMW and are persistent in the environment as a result of their increase resistance to oxidation, reduction and vaporization as molecular weight increases. Similarly, The PAFs of the investigated creek is less than 5%, suggesting existences of minor ecological risks that are insignificance. However, the TEQs detected in high molecular weight showed that there is possibility of cancer to those who may be exposed to the bottom sediment. The indices measured in this habitat may put more pressures to the aquatic organisms and cause drastic changes to their ecosystem which may lead to species extinction.

Keywords: Polycyclic aromatic hydrocarbon; Kolo creek; Risk assessment; Benzo (a) anthracene; Water; Sediments.

1. Introduction

Crude oil has been the major source of revenue in Nigeria and recently gas potential is being harnessed. These operations are in Niger Delta region of Nigeria of which Bayelsa is the hub [1]. Consequently, oil spills, gas flaring and other forms of pollution are common in this region. There is evidence of pollution in the environment by polycyclic aromatic hydrogen arising from oil and gas production in Niger Delta [2, 3]. Although most PAHS enter the environment via the atmosphere, soil and water sediments are the primary repository [4]. Crude oil production effluent contains significant amount of PAHS, organic acids, phenols, radioactive materials etc. it is believe that 'hydrocarbon' are likely contributor to produce water toxicity, and their toxicity is additive [5]. Higher values of PAHS have been recorded in estuaries and coastal areas as well as area with intense vessels transport and oil treatment [4]. Other sources of PAHS to the water body include processes such as the combustion of organic matters (pyrolytic origin), the slow transformation of organic matter in geothermal scale, degradation of biogenic material [5] Oil and gas production activities including gas flaring has shown to contribute particular PAHS compounds to Niger Delta environment [1]. There are also produced when wood, coal, garbage and tobacco are burnt. PAHS generated from these sources can bind to or form small particles in the air [6].

Concern on the levels and distribution of these ubiquitous compounds is due to their persistent in the environment and lipophilic nature [7]. After the deposition, PAHS may accumulate further in vegetation and other biota and be transferred to humans via food chain [8]. The mechanism of toxicity to human is through interference with the functions of the cellular membranes as well as enzyme systems which are associated with membrane.

PAHS has carcinogenic and mutagenic effects and they are potent immune suppressants [9-11]. Other health hazards of PAHS include embryotoxic effects to experiment animals [12] and genotoxicity [13].

Interest in the study of Kolo creek is because it is where one of oldest Shell Petroleum Development Company (SPDC) flow station is located and it traverses through several important communities in Ogbia local Area of Bayelsa State, namely: Imiringi, Kolo 1, Kolo 2, Emeyal 1, Emeyal 2, Otuasega and Oruma). PAHs normally accumulate in different environmental compartments especially the sediments, which release into water a basic

source, which harmful to aquatic organisms, and may be detrimental to human health, so measuring PAHs in the sediments become imperative as its present is a potential threat to aquatic ecosystems. Kolo creek serves as the major source of water to the rural dwellers, therefore, ecological risk assessment of PAHs in sediments is very important to protect human health and for ecological environment safety

2. Materials and Methods

2.1. Study Area

Kolo Creek is a non-tidal fresh water environment located in Ogbia Local Government Area of Bayelsa State. The creek lies within latitude $06^{\circ}19'16.68"N$ and longitude $04^{\circ}41'49.82"E$ and transverses several communities (Fig.1). Its climate is characterized by the dry and wet season's periods with temperatures reaching about $35^{\circ}C$ all through the year [14]. Surface waters and sediments were collected at points within and around the crude oil flow station at Imiringi community, with a view to identifying the contribution of oil and gas activities and fixed oil installations on the PAHs levels in water, as well as its overall impact on the sediment habitat.

2.2. Samples Collection

Sediments and water samples were collected in November 2018 to June 2019 from seven locations (A-G) along Kolo Creek (Fig.1). Triplicate samples were collected at spatially different locations; upstream sample A was collected at 500 metres distance from the flow station at Imiringi, while samples B to F which represented the midstream locations within proximity of flow station clusters. Also, sample G was taken 500 metres downstream of Imiringi community. Water samples were collected separately in pre-washed 100 ml plastic vials. Sediment samples were collected in Ziploc bags and sealed. Samples were stored in ice-packed coolers before been transported to the laboratory.



Fig-1. Map of major roads and waterways in Bayelsa state Nigeria within which is the Kolo creek showing sampling stations

2.2.1. Sediment Sample Extraction

2g of samples was weighed into a clean extraction container. 10ml of extraction solvent (hexane) was added into the sample, mixed thoroughly and allowed to settle. The mixture was carefully filtered using filter paper fitted into Buchner funnels. The extracts were concentrated to 2ml and then transferred for cleanup/separation.

2.2.2. Clean-up Separation

1 cm of moderately packed glass wool was placed at the bottom of 10mm I.D. (internal diameter) x250mm long chromatographic column. Slurry of 2g activated silica in 10ml dichloromethane was prepared and placed into the chromatographic column. To the top of the column was added 0.5cm of sodium sulphate. The column was rinsed with additional 10ml of dichloromethane.

The column was pre-eluted with 20ml of hexane. This was allowed to flow through the sodium sulphate layer. Immediately, 1ml of the extracted sample was transferred into the column. The extraction bottle was rinsed with 1ml of hexane and the dissolved extracted was added to the column as well. The stop cork of the column was opened and the eluent was collected in a graduated measuring cylinder.

Just prior to exposure, the sodium sulphate layer air, hexane was added to the column in 1-2ml increments. Accurately measured volume of 8-10ml of the eluent was collected and was labelled poly aromatics (PAH).

2.2.3. Sample Analysis Using Gas Chromatography

The concentrated aromatic fractions were transferred into labeled gas vials with Teflon or rubber crimp caps for GC analysis.

1µl of the concentrated sample was injected by means of a hypodermic syringe through a rubber septum into the column by the FID detector whose response in dependent upon the composition of the vapor.

2.2.4. Water Sample Extraction

250ml of water samples was transferred into a separation funnel, the measuring cylinder used for transferring the solution into the separation funnel was rinsed with 25ml of dichloromethane. The organic solvent and the sample were mixed, so as to have all available organic material extracted into the solvent. The measuring cylinder was further rinsed with a 25ml dichloromethane so that no trace of organic materials left.

2.2.5. Sample Clean-Up and Separation

The organic extract is collected into receiving container (sample vial), passing the organic extract through an extraction column packed with glass-wool, silica-gel, and anhydrous sodium sulphate. The silica-gel aids the cleanup of the extracted by disallowing the passage of debris and impurities of other compounds that are not PAH (poly cyclic aromatic hydrocarbons). Anhydrous sodium sulphate acts as a dehydrating agent rid the organic extract of every form of moisture/water container on the sample(s).

1 cm of moderately packed glass wool was placed at the bottom of a 10mm I.D. (internal diameter) x250mm long chromatographic column. Slurry of 2g activated silica in 10ml methylene chloride was prepared and placed into the chromatographic column. To the top the column was added 0.5cm of sodium sulphate. The column was rinsed with additional 10ml of methylene chloride.

The column was pre-eluted with 20ml of hexane. This was allowed to flow through the column at a rate of about 2minutes until liquid in the column was just above the sodium sulphate layer.

Immediately, 1ml of the extracted sample was transferred into the column. The extraction bottle (sample vial) was rinsed with 1ml of dichloromethane and added to the receiving end of the column as well. The stop cork of the column was opened and the eluent was collected in graduated measuring cylinder.

Just prior to exposure the sodium sulphate layer to air, hexane was added to the column in 1-2ml increments. Accurately measured volume of 8-10ml of the eluent was collected and was labelled poly aromatics (PAH).

2.2.6. Water Sample Analysis Using Gas Chromatography

The concentrated aromatic fractions were transferred into labelled glass vials with Teflon or rubber crimp caps for GC analysis. 1µl of the concentrated sample was injected by means of an hypodermic syringe through septum into the column separation occurs as it emerges from the column (at a constant flow rate) by the FID (flame ionization detector) whose response is dependent upon the composition of the vapor.

2.2.7. Ecological Risk Assessment of Pollutants in the Creek

Three parameters were used to assess ecological risk assessment of pollutants in Kolo Creek; species-sensitivity distribution, toxic equivalent quotient and sediments quality guideline

The species-sensitivity distribution: The species-sensitivity distribution (SSD) proposed by Kooijman [15], with further modification as proposed by Yanan, *et al.* [16] was used in the ecological risk assessment of pollutants in Kolo Creek, Niger Delta Nigeria. It is a statistical distribution that describes the variations in toxicity of a certain compound or multiple congeners to aquatic organisms [17]. In this investigation BurrIII and ReWeibull distribution functions are two

flexible distributions and well-fitting to species sensitivity data. BurrIII distribution functions state that:

 $F(x) = 1/[1 + (b/x)^{c}]^{k}$ Equation (ii)

where x = toxicity value (ug/L) and b, c, and k parameters.

However, when k tends to infinity, BurrIII distribution will convert to ReWeibull distribution with the relationship:

 $F(x) = \exp(-\alpha/x\beta)$ Equation (ii)

where $x = \text{toxicity data (ug/L) and } \alpha$ and β are parameters.

To ascertain the proportion of potentially affected aquatic organisms by a compound or multiple congeners to aquatic organisms, potential affected fractions (PAFs) of the SSD model are usually used to assess the ecological risks of individual and multiple congeners of PAHs in the water and sediment for each sampling site as described by Yanan, *et al.* [16]. However, in this investigation a congener of PAHs according to the number of rings was chosen to determine PAFs of the SSD models except the 6 rings (where the sediment quality guidelines not available). 2 rings (Naphthalene); Burr III: PAF = 1/[1+(b/x)c]k (fitting curves(fc),where b = 1560.085, c = 0.979,and k = 2.708;3 rings (Acenaphthene): ReWeibull: PAF = $exp(-\alpha/x\beta)$ (FC);where $\alpha = 254.220$, $\beta = 0.790$, b = 5652.548; 4 rings (Fluoranthene): Burr III:PAF = 1/[1+(b/x)c]k(FC); where c = 1.292, k = 0.445b = 492.867,5rings (Benzo(a)pyrene): ReWeibull: PAF = $exp(-\alpha/x\beta)$ (FC);where $\alpha = 4.120$, $\beta = 0.437$

2.3. Toxicity and Biological Effects of PAH's

Many PAHs and their degradation products are carcinogenic, while benzo[a]pyrene is the only PAH with sufficient toxicological data for derivation of a carcinogenic potency factor. Therefore, the toxic equivalency factor (TEF) was used to quantify the carcinogenicity of other PAHs relative to benzo[a]pyrene [18].

The toxic equivalent quotient (TEQ) is the carcinogenic potential of the high molecular weight PAHs and calculated by multiplying PAHs congeners by the toxic equivalent factor (TEF) as shown in equation 1.

 $TEQ = \Sigma Ci * TEFi$ Equation (i)

Where Ci is the concentration of PAHs congener and TEFi is the toxic equivalent factor relative to benzo(a)pyrene.

2.4. Assessing the Aquatic Health Using Sediments Quality Guidelines (SQGs)

A sediments quality guideline is the total concentration of the substance in surficial sediments on a dry weight basis, and is necessary for a better protection of aquatic biodiversity and in particular sediment dwelling organisms. It is important to note that sediments serve as home for benchic and epibenthic organisms and are an essential part of aquatic habitat.

In toxicity assessment, sediments determine the environmental fate of many toxic substances, bioaccumulative materials in aquatic environment, and the longevity of toxicants in the ecosystem [19]. Similarly, sediments represent a complex and dynamic matrix of living and non-living components that may determine the bioavailability of sediment-associated chemicals, especially when enough information is available to define the influence of any factor on the toxicity of a specific substance [20]

The following SQDs indices; effects range-low (ERL), effects range-median (ERM), threshold effects levels (TELs) and probable effects levels (PELs) were used to ascertain the health status of Kolo Creek, Niger- Delta Nigeria. Three ranges can be deduced from these indices; low range (the concentrations at which adverse biological effects are unlikely to occur: below the TEL or ERL values), middle range (the concentrations within which adverse biological effects are possible: between the TEL or ERL), and upper range (a concentrations within which adverse biological effects are likely to occur: above the PEL or ERM values) [21, 22].

2.5. Statistical Analysis

One way analysis of variance (ANOVA) was used to assess the variation in PAHs in different locations. Means were compared using the Bonferroni multiple comparison test, and the significant level was P < 0.05. All the calculations were done using statistical software, SPSS student version 10.

3. Results

3.1. PAHs Concentrations in Water

All of the 16 congeners of PAHs analyzed were detected at all the sampling places of water from Kolo Creek, Niger- Delta Nigeria (Table 1). Benz (a) anthracene was the highest PAHs congener reported $(31.70\pm0.054\mu g/L)$, followed by Benzo(k)fluoranthene $(3.00\pm0.915 \ \mu g/L)$, while acenaphthene $(0.01\pm0.323 \ \mu g/L)$, fluorine $(0.01\pm0.045 \ \mu g/L)$, phenanthrene $(0.01\pm0.036 \ \mu g/L)$, anthracene $(0.01\pm0.003 \ \mu g/L)$ were the least detected.

3.2. PAHs Concentrations in Bottom Sediment

Among the 16 priority PAHs compounds detected in the sediments of the creek, acenaphthene levels were found to be the lowest (0.01±0.698 μ g/gdw), while Benzo(a)anthracene (4-ring PAH) was the highest (702± 8.323 μ g/gdw).

Four rings PAHs apart from being abundant shows consistency in their concentrations; benz(a)anthracene (702± 8.323 μ g/gdw), pyrene (40.0±8.356 μ g/gdw), fluoranthene (23.0±4.363 μ g/gdw) and anthracene(8.0±1.415 μ g/gdw) than the 6 rings; dibenz(a,h)anthracene (44.0±14.099 μ g/gdw), indeno(1,2,3)-(d)pyrene (6.0±1.016 μ g/gdw), 5 rings; benzo(a)pyrene (29.0±9.318 μ g/gdw),benzo(k)fluoranthene (8.0±1.562 μ g/gdw), benzo(b)fluoranthene(6.0±1.175 μ g/gdw), 3 rings; acenaphthylene (7.0±0.961 μ g/gdw), fluorine (7.01±1.712 μ g/gdw), 2-methylnaphtalene (1.0±0.118 μ g/gdw), acenaphthene (0.01±0.698 μ g/gdw) and the 2 ring; naphthalene (7.0±2.263 μ g/gdw) (Table 2)

3.3. PAHs Toxicity of and Assessment of the Aquatic Health

The toxic equivalent quotient of the high molecular weight PAHs of investigated creek (Anthracene, Fluoranthene, Benzo[b] fluoranthene and Benzo[a] pyrene) were used for computing the TEQ in this study (Figure 2), with further illustration in Table 3. Benzo[a] pyrene was the most toxic (29.00) PAHs, followed by benzo[b]fluoranthene (4.80), fluoranthene (1.84) and anthracene (0.08). Thy contributed roughly 37% of the total PAHs in the samples analyzed.



The values of PAFs for individual PAHs in water and sediment from seven sampling stations are shown in figure 3. If values of PAFs the aquatic ecosystem is greater than 5%, there is threat of ecological risks, while PAF values less than 5% indicates existences of slight ecological risks.

Comparison of the concentration of different PAHs compounds of the Kolo creek with the Sediment Quality Guidelines revealed that the level of some of the PAHs congeners was less than SQG indices (effects range-low, effects range-median and threshold effects levels but higher than probable effects levels) (Table 4). Breakdown of each congener with SAGs showed that: Naphthalene (7.0±2.263 µg/Kg) was higher than ERL (1.60 µg/Kg), PEL (0.391 µg/Kg), TEL (0.346 µg/Kg), less than ERM (21.00 µg/Kg), Acenaphthylene (7.0±0.961 µg/Kg) > TEL (0.587), PEL (1.28), ERL (0.44), and ERM (6.40), phenanthrene (3.02±2.824) > TEL (0.867), ERL (0.19 $\mu g/Kg$, <PEL (5.44 $\mu g/Kg$) and < ERM (5.40 $\mu g/Kg$), anthracene (8.0 ±1.415 $\mu g/Kg$) > TEL> (4.69 $\mu g/Kg$)> PEL $(2.45 \ \mu g/Kg \ \mu g/Kg) > ERL \ (2.40), < ERM \ (15.00 \ \mu g/Kg), fluoranthene \ (23.0\pm4.363 \ \mu g/Kg) > TEL \ (1.13 \ \mu g/Kg),$ PEL (14.94 µg/Kg), ERL (6.00 µg/Kg), < ERM (51.00 µg/Kg), chrysene (12.0±0.493 µg/Kg) > TEL (1.08 µg/Kg), PEL (8.46 μ g/Kg), ERL (3.84) but < ERM (28.00), benzo(b)fluoranthene (8.0 ±1.562)> ERL (7.63)> PEL (4.30) μ g/Kg), < TEL (8.88 μ g/Kg) < ERM (16.00 μ g/Kg) While pyrene (40.0±8.356 μ g/Kg) and benz(a)anthracene (702± $8.323 \mu g/Kg$) were greater than all the SQG indices.



Fig-3. Potentially affected aquatic organism in surface water and sediment from seven Stations of Kolo- creeks, Niger Delta

4. Discussion

Kolo creek transverses within the SPDC flow station and no doubt the PAHs loads in the creeks could be attributed to the flow station. However, other factors such as urban runoffs, sewage discharges, and agricultural activities on PAHs level may not be misconstrued. Considering individual PAH composition in water and sediments, all of the compounds analyzed were detected at all the sampling places, even area far from flow stations. Hence, the urban runoffs, sewage discharges, and agricultural activities are implicated, hence supported the first submission. Similarly, incessant dredging activities using dredger that discharges black smokes throughout their movement; hence there are many nonpoint sources in the creek, contributing to the wide variations of PAH concentrations recorded.

Therefore, from the distribution of PAHs in these matrixes, it is difficult to differentiate the different sources of input; nonetheless, the data collected from different stations can act as an indication of the potential impacts of such high levels of PAHs on the local aquatic habitat.

With the exception of benz(a)anthracene, the concentrations of all the PAHs detected in water and sediments were below the WHO maximum permissible limit of $10\mu g/l$ in water and 0.01 $\mu g/gdw$ in the sediments [23]. The high concentrations detected in benz(a)anthracene ($31.70\pm0.054 \mu g/l$), could be attributed to the high volume of oil seepage from industrial activities, exhaust, road tars, coal tar pitch and coal combustion that are common occurrence in the vicinities of the investigated creek. The total PAHs concentrations found in this creek was lower than most studies around the world [24]. Though, PAHs do not show extremely high acute toxicity to aquatic organisms, the lower molecular mass compounds tend to exhibit higher lethal toxicity than the larger PAHs [13].

Four rings hydrocarbon were present in higher concentration when compared to other PAHs in all sampling sites, with Benz (a)anthracene having the highest values for both matrixes. Similarly, lower molecular weight (LMW) PAHs were present in lower concentrations in all sampling sites. Coincidentally the dominance of four rings PAHs was also reported by Pereira, *et al.* [25] and Dhananjayan, *et al.* [24] in PAHs distributions in sediments from San Francisco Bay, United State of America and distribution of PAHs in water and sediment collected along the harbour line, Mumbai, India respectively. Similar observation was reported by Nekhavhambe, *et al.* [26] in some rivers and sediments in Vhembe District of South Africa. High molecular weight were present in high concentrations with Dibenz(a,h)anthracene > Benzo(a)pyrene > Benzo(k)fluoranthene > Indeno(1,2,3)-(d)pyrene > Benzo(b)fluoranthene. They are more persistent than LMW PAHs in the environment as a result of their increase resistance to note that HMW PAHs such as benzo[a]pyrene and benzo[b] fluoranthene are carcinogenic and mutagenic to both aquatic and terrestrial organisms including mammals and birds [27].

The hydrophobic nature of PAHs showed that sediments had higher concentrations than the water. Corroborating this finding was the work of Kannan, *et al.* [28], where he reported higher sediments level of PAHs in sediments from Michigan Inland lakes in United State of America.

Considering the health hazard, TEQs observed for benzo[a]pyrene, fluoranthene Benzo[b]fluoranthene and anthracine in this investigation signified a possible cancer risk to those who may be exposed to the bottom sediment Salem, *et al.* [29] and Hussein, *et al.* [30].

The PAFs of the investigated creek is less than 5%, suggesting existences of minor ecological risks that are insignificance. According to Yanan, *et al.* [16] If values of PAFs in the aquatic ecosystem is greater than 5%, there is threat of ecological risks, while PAF values less than 5% indicates existences of slight ecological risks

The TEQs (35.72) observed HMW PAHs in this study showed that there is possibility cancer to those who may be exposed to the bottom sediment [30], since the inhabitants along the creeks depend solely on the water from the creeks for washing and other domestic purposes.

Considering the SQGs, the concentrations of the congeners showed that their concentrations is within the concentrations which adverse biological effects are possible [21], except benzo(b) fluoranthene which is between PEL or ERM values, a concentration that may cause adverse biological effects.

5. Conclusion

The creek is where one of oldest Shell Petroleum Development Company (SPDC) flow station is located and it traverses through several important rural communities. Most of the inhabitants depend on the water from the creek for irrigation purposes, bathing and other domestic activities. In this investigation, we assessed the risk of PAHs in the water and sediments beside oil spills, gas flaring and other forms of pollution are common in this region. The data collected from different stations along the creek indicates potential impacts of high levels of PAHs on the local aquatic ecosystem. The concentrations of all the PAHs detected in water and sediments were below the WHO maximum permissible limit, but all the PAHs examined were detected, most of which are of low molecular weight. The low molecular mass compounds tend to exhibit higher lethal toxicity than the larger PAHs. HMW were present in high concentrations than LMW and are persistent in the environment as a result of their increase resistance to oxidation, reduction and vaporization as molecular weight increases

The PAFs of the investigated creek is less than 5%, suggesting existences of minor ecological risks that are insignificance. The TEQs observed HMW PAHs in this study showed that there is possibility of cancer to those who may be exposed to the bottom sediment.

References

- [1] Uzoekwe, S. A. and Ikpesu, T. O., 2019. "Assessment of polycyclic aromatic hydrocarbons (pahs) in ambient air of oil producing communities in Yenagoa and its environs." *J. Chem Soc. Nigeria*, vol. 44, pp. 359-371.
- [2] Leizou, K. E. and Mohammad, A. A., 2019. "Distribution, compositional pattern and potentials to human exposure of PAHS in water, Amassoma axis, Nun River, Bayelsa State." *Acta. Chemical Malaysia*, vol. 3, pp. 16-20.
- [3] Nwaichi, E. O., Agbam, P., and Iwu, P. I., 2017. "Polycyclic Aromatic Hydrocarbon (PAHS) and some trace merab in yam, cassava, orange and papaya from two oil and gas flaring impacted communities in southern Nigeria." *J. Applied Scien. Environment Manag.*, vol. 21, pp. 1057-1062.
- [4] Haeseler, F. D., Blanchet, V., and Vandecasteele, J. P., 2001. *Ecotoxicological handbook of environmental chemistry: PAHs and related compounds*. New York, NY: Springer.
- [5] Rey-Salgueiro, L., García-Falcón, M. S., Martínez-Carballo, E., and Simal-Gándara, J., 2008. "Effects of toasting procedures on the levels of polycyclic aromatic hydrocarbons in toasted bread." *Food Chemistry*, vol. 108, pp. 607–615.
- [6] Bruschweiler, E. D., Danuser, B., Huynh, C. K., Wild, P., Schupter, P., Vemez, D., Boiteux, P., and Hopf, N. B., 2012. "Generation of polycyclic aromatic hydrocarbon (pahs) during wood working operations front oncol." Available: <u>Http://doi.Org/10.3389/func.2012.00148</u>
- [7] Zhang, J. and Fan, S. K., 2019. "Influence of PAHS Speciation in soil on Vegetation Uptake of PAHS using successive extraction,." *J. Hazard Mater*, vol. 320, pp. 114-122.
- [8] Inengite, A. K., Oforka, N. C., and Osuji, L. C., 2017. "Evaluation of polycyclic aromatic hydrocarbons in sediments of Kolo Creek in the Niger delta." *Int. Jour. of Applied Sciences*, vol. 5, pp. 127-143.
- [9] Armstrong, B. G., Hutchinson, E., Unwin, J., and Fletches, T., 2004. "Lung Cancer risk after exposure to polycyclic aromatic hydrocarbon: A review and in eta- analysis." *Environment Health Perspect*, vol. 112, pp. 970-978.
- [10] Canadian Council of Minister of the Environment, 2010. *Canadian soil quality guideline for potential carcigiogenic and other pahs, scientific criteriaclocument.* Winnipeg: CCME.
- [11] International Programmed on Chemical Safety, 2010. "Polycyclic aromatic hydrocarbons selected nonheterocyclic." Available: <u>http://www.unicem.org./document/ehc/ehi/ehc202.htin</u>
- [12] Wassenburg, D. M. and Ana Di-Guilio, R. T., 2004. "Synergistic embryo toxicity of polycyclic hydrocarbon receptor against with cytochrome P450 A inhibitors in Fundulus neteroclitus." *Environment Health Perspect*, vol. 112, pp. 1658-1664.
- [13] Arey, J. and Atkinson, R., 2003. *Photochemical reactions of PAH in the atmosphere.p* 47-63. *In P.E.T. Douben (Ed.) PAHs: An ecotoxicological perspective*. New York: John Wiley and Sons Ltd.
- [14] Ogamba, E. N. and Nwabueze, E., 2017. "Assessment of physicochemical quality of sediment from Kolo Creek, Niger Delta." *Greener Journal of Biological Sciences*, vol. 7, pp. 020-024.
- [15] Kooijman, S., 1987. "A safety factor for LC50 values allowing for differences in sensitivity among species." *Water Res.*, vol. 21, p. 269.
- [16] Yanan, C., Caiyun, S., Jiquan, Z., and Feng, Z., 2018. "Assessing 16 polycyclic aromatic hydrocarbons (pahs) in river basin water and sediment regarding spatial-temporal distribution." *Partitioning, and Ecological Risks Pol. J. Environ. Studies,* vol. 27, pp. 579-589.
- [17] Wheeler, J. R., Grist, E. P. M., Leung, K. M. Y., Morritt, D., and Crane, M., 2002. "Species sensitivity distributions: data and model choice." *Marine Pollution Bulletin*, vol. 45, p. 192.
- [18] MacDonald, D. D., Ingersoll, C. G., Smorong, D. E., Lindskoog, R. A., Sloane, G., and Biernacki, T., 2003. *Development and evaluation of numerical sediment quality assessment guidelines for Florida inland waters*. Florida: Florida Department of Environmental Protection.
- [19] Loring, D. H. and Rantala, R. T., 1992. "Manual for the geochemical analysis of marine sediments and suspended particulate matter." *Earth-Sci. Rev.*, vol. 32, p. 235.
- [20] Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Carlson, A. R., and T., A. G., 1992. "Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments." *Environ. Sci. Technol.*, vol. 26, pp. 96–101.
- [21] Cao, Z. J., Liu, Y., and Luan, E. T., 2010. "Distribution and ecosystem risk assessment of polycyclic aromatic hydrocarbons in the Luan River, China." *Ecotoxicology*, vol. 19, pp. 827–837.
- [22] Macdonald, D. D., Carr, R. S., Calder, F. D., Long, E. R., and Ingersoll, C. G., 1996. "Development and evaluation of sediment quality guidelines for Florida coastal waters." *Ecotoxicology*, vol. 5, pp. 253–278.
- [23] Abolanle, S. A., John, A. O., Oluwaseyi, S. O., Nobanathi, W. M., Godwin, O., and Olaoluwa, S. A., 2017. "Determination of polycyclic aromatic hydrocarbon levels of groundwater in Ife north local government area of Osun state, Nigeria." *Toxicology Reports*, vol. 4, pp. 39-48.
- [24] Dhananjayan, V., Muralidharan, S., and Vinny, R., 2012. "Occurrence and distribution of polycyclic aromatic hydrocarbons inwater and sediment collected along the harbour line, Mumbai, India." *International Journal of Oceanography,* Available: <u>http://doi:10.1155/2012/403615</u>
- [25] Pereira, W. E., Hostettler, F. D., and Rapp, J. B., 1996. "Distributions and fate of chlorinated pesticides, biomarkers and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco Bay, California." *Marine Environmental Research*, vol. 41, pp. 299–314.

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- [26] Nekhavhambe, T. J., Van Ree, T., and Fatoki, O. S., 2014. "Determination and distribution of polycyclic aromatic hydrocarbons in rivers, surface runoff, and sediments in and around Thohoyandou, Limpopo Province, South Africa." *Water. SA.*, vol. 40, pp. 415–424.
- [27] Joshua, N. E., John, O. O., Oluwaseun, E. P., and Titus, A. M., 2016. "Determination and distribution of polycyclic aromatic hydrocarbons in rivers, sediments and wastewater effluents in vhembe district, South Africa." *Int. J. Environ. Res. Public Health*, vol. 13, p. 387.
- [28] Kannan, K., Johnson-Restrepo, Y., Yohn, S., Giesy, J., and Long, D., 2005. "Spatial and temporal distribution of polycyclic aromatic hydrocarbons in sediments from Michigan Inland lakes." *Environ. Sci. Technol.*, vol. 39, pp. 4700-4706.
- [29] Salem, D., Morsy, F., El-Nemr, A., El-Sikaily, A., and Khaled, D., 2014. "The monitoring and risk assessment of aliphatic and aromatic hydrocarbons in sediments of the Red Sea, Egypt." *E. J. A. R.*, vol. 40, pp. 333-348.
- [30] Hussein, R. A., Al-Ghanim, K. A., Abd-El-Atty, M. M., and Mohamed, L. A., 2016. "Contamination of Red Sea Shrimp (Palaemon serratus) with polycyclic aromatic hydrocarbons: a health risk assessment study." *Polish. J. Environ Studies*, vol. 25, pp. 615-620.

Table-1. Distribution of PAHs in the surface water $(\mu g/L)$ of Kolo creek, Niger Delta Nigeria

Sampling Locations Along Kolo Creek								
PAHs	WA	WB	WC	WD	WE	WF	WG	Mean ± SE
Naphthalene	0.002	0.060	0.438	0.008	0.051	0.075	0.001	1.00±0.151
2-methylnaphtalene	0.003	0.007	0.000	0.006	0.000	0.004	0.001	0.10±0.002
Acenaphthylene	0.020	0.217	0.039	0.122	0.255	0.016	0.015	1.01±0.104
Acenaphthene	0.003	0.004	0.090	0.002	0.008	0.002	0.004	0.01±0.323
Fluorine	0.002	0.011	0.102	0.002	0.012	0.018	0.005	0.01±0.045
Phenanthrene	0.011	0.056	0.028	0.023	0.012	0.005	0.002	0.01±0.036
Anthracene	0.003	0.011	0.006	0.005	0.001	0.004	0.001	0.01±0.003
Fluoranthene	0.055	0.044	0.030	0.022	0.053	0.004	0.003	0.01±0.021
Pyrene	0.015	0.023	0.017	0.013	0.018	0.028	0.009	0.01±0.087
Benz(a)anthracene	9.239	2.238	1.762	1.984	0.373	0.798	1.000	31.70±0.054
Chrysene	0.188	0.119	0.008	0.038	0.008	0.087	0.004	0.01±0.041
Benzo(b)fluoranthene	0.030	1.102	0.164	0.054	0.056	0.020	0.002	1.00±0.368
Benzo(k)fluoranthene	0.049	2.508	0.267	0.115	0.065	0.084	0.005	3.00±0.915
Benzo(a)pyrene	0.084	1.126	0.599	0.042	0.226	0.035	0.007	2.00±0.147
Indeno(1,2,3)-(d)pyrene	0.212	0.539	0.272	0.085	0.106	0.427	0.008	2.00±0.183
Dibenz(a,h)anthracene	0.060	0.779	0.190	0.109	0.066	0.072	0.014	1.00±0.314

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Table-2. Distribution of PAHs in the sediments	(µggdwL) of Kolo	creek, Niger Delta Nigeria
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Sampling Locations Along Kolo Creek								
PAHs	SA	SB	SC	SD	SE	SF	SG	Mean ± SE
Naphthalene	0.608	0.132	0.123	0.394	0.026	0.015	6.179	7.0±2.263
2-methylnaphtalene	0.058	0.049	0.158	0.066	0.003	0.006	0.339	1.0 ± 0.118
Acenaphthylene	0.769	1.000	1.541	2.759	0.222	0.031	0.228	7.0±0.961
Acenaphthene	0.148	0.092	0.176	0.024	0.009	0.002	0.042	0.01±0.698
Fluorine	0.183	1.030	0.615	0.319	0.041	4.842	0.196	7.01±1.712
Phenanthrene	0.104	1.775	3.197	0.301	0.005	7.762	0.3451	3.02±2.824
Anthracene	0.063	1.075	3.826	0.1932	0.004	2.348	0.188	8.0 ±1.415
Fluoranthene	1.210	1.499	7.637	0.089	0.036	11.30	1.652	23±4.363
Pyrene	2.427	24.775	4.278	4.033	0.102	3.822	0.821	40±8.356
Benz(a)anthracene	74.496	374.352	2.594	50.516	12.344	134.286	53.959	702±8.323
Chrysene	0.824	9.795	0.997	0.357	0.054	1.357	0.476	12.0±0.493
Benzo(b)fluoranthene	0.284	3.283	0.358	0.428	0.143	0.031	1.532	6.0 ±1.175
Benzo(k)fluoranthene	0.185	2.997	0.211	0.704	0.101	0.029	3.772	8.0 ±1.562
Benzo(a)pyrene	1.958	0.993	0.228	2.161	2.284	0.107	25.513	29.0±9.318
Indeno(1,2,3)-(d)pyrene	0.733	0.242	0.519	1.073	0.305	0.181	3.066	6.0±1.016
Dibenz(a,h)anthracene	0.513	1.481	1.182	2.445	0.229	0.244	38.269	44.0±14.099
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Table-3. Toxicity equivalent quotient of HMW PAHs in the sediment from Kolo -creek, Lower Niger Delta Nigeria

PAHs	TEF	TEQ
Anthracene	0.01	0.08
Fluoranthene	0.08	1.84
Benzo[b]fluoranthene	0.80	4.80
Benzo[a]pyrene	1.0	29.00
$\sum TEQ (\mu g/gdw)$	35.72	

Table-4. Comparison of the concentration of different PAHs compounds of the Kolo creek with the Sediment Quality Guidelines

PAHs	Number of	Concentration	ns(µg/Kg)	Sediment Quality		
	rings			Guidelines (µg/kg)		
		Mean ± SE	TEL	PEL	ERL	ERM
Naphthalene	2	7.0±2.263	0.346	0.391	1.60	21.00
2-methylnaphtalene	3	1.0 ± 0.118	-	-	-	-
Acenaphthylene	3	7.0±0.961	0.587	1.28	0.44	6.40
Acenaphthene	3	0.01±0.698	-	-	-	-
Fluorine	3	7.01±1.712	-	-	-	-
Phenanthrene	3	3.02±2.824	0.867	5.44	0.19	5.40
Anthracene	4	8.0 ±1.415	4.69	2.45	2.40	15.00
Fluoranthene	4	23.0±4.363	1.13	14.94	6.00	51.00
Pyrene	4	40.0±8.356	1.53	1.39	6.65	26.00
Benz(a)anthracene	4	702± 8.323	0.75	6.93	2.61	16.00
Chrysene	4	12.0±0.493	1.08	8.46	3.84	28.00
Benzo(b)fluoranthene	5	6.0 ±1.175	8.88	7.63	4.30	16.00
Benzo(k)fluoranthene	5	8.0 ±1.562	-	-	-	-
Benzo(a)pyrene	5	29.0±9.318	-	-	-	-
Indeno(1,2,3)-(d)pyrene	6	6.0±1.016	-	-	-	-
Dibenz(a,h)anthracene	6	44.0±14.099	-	-	-	-