# Source Identification and Characterization of Organic Contaminants in Sediment and Periwinkle (*Littorina Littorea*) From Okujagu River

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Abstract: The research identifies the sources and characterizes the concentrations of n-alkanes and polycyclic aromatic hydrocarbons (PAHs) in sediment and Littorina Littorea from Okujagu River. Samples were evaluatedutilizing n-alkanes, 14 PAHs and Gas chromatography Mass spectrometer (GC-MS) ranging from C<sub>17</sub> to C<sub>32</sub> were identified and quantified. Total PAH and n-alkane dosage for both samples ranged from 2.38 to 2.48mg/kg and 0.36 to 3.127mg/kg respectively. The sources were examinedutilizing PAH diagnostic ratios and n-alkane indexes. n-alkanes were characterized by carbon preference index (CPI), n-alkane proxy (Paq), Carbon maximum (C<sub>max</sub>), and the ratio of long chain hydrocarbons to short chain hydrocarbons (LHC/SHC). PAH diagnostic ratios such as Phenanthrene to Anthracene (Ph/An), Fluoranthene to Pyrene (Fl/Pv). Ant/(Ant+Ph), Fl/(Fl+Py) and the ratio of lower molecular weight (LMW) PAHs to higher molecular weight (HMW) PAHs (LMW/HMW) were calculated to evaluate both petrogenic and pyrogenic (pyrolytic) PAHs. From the results, the diagnostic ratio of (FI/Py) for sediment was 40 (>1) indicating PAHs origin from pyrolytic source while Fl/Py ratio of the Littorina Littorea sample was 0.25(<1) indicating petrogenic source. The (Ph/An) ratio for sediment and Littorina Littorea were 3.5(<10) and 0.008(<1) respectively implying that the PAHs are source from combustion processes (pyrolytic). Also, the ratio of Ant/(Ant+Ph) was 0.22 (>0.1) for sediment and 0.99 (>0.1) for Litorina Littorea indicating PAHs origin from pyrogenic(pyrolytic) sources. While the ratio of Fl/(Fl+Py) was 0.98 (>0.4) for sediment suggesting PAH origin from pyrogenic(pyrolytic) source and 0.2 (<0.4) for Littorina Littorea indicating PAHs origin from petrogenic sources. The ratio of (LMW/HMW) PAHs was calculated to be 2.42 (>1) for sediment and 24.608 (>1) for Littorina Littorea indicating PAHs origin from petrogenic sources. According to the diagnostic ratios used in this study, the PAHs in the sediment and Littorina Littorea samples originate from both pyrolytic and petrogenic sources. The study recommends that the disposal of waste, effluent discharges from industries and chemical release through agricultural activities into the marine ecosystem should be regulated as to control the contaminants in the system.

*Keywords:* Concentration, Terrestrial, Biogenic, Macrophyte, Phytoplankton, Petrogenic, Pyrolytic, Organic Matter.

#### I. INTRODUCTION

Organic contaminants are various sources of plant and animal origin which alters the state of the ecosystem. They are carbon based chemicals which affects the life cycle of aquatic life and could be sourced from mechanical actions that coincidentally drain synthetic spillover into surface waters (Moustafa*et al.*, 2016).

Introduction to carbon-based contaminants, for example, polycyclic aromatic hydrocarbons (PAHs) and n-alkanes has been related with a scope of unfavorable wellbeing impacts, including malignant growth, resistant inadequacies and sensory system troubles. Development of carbon-based contaminants into water and soil occur through removals of waste, emanating releases from ventures and synthetic compounds discharge through agrarian actions. This contamination speaks to an expanding danger to the marine biological system and a likely danger to human wellbeing through utilization of items from the natural way of life (Rozita et al., 2010).

Polycyclic fragrant hydrocarbons (PAHs) and n-alkanes are marine environment interminable constituents and their dosages have impressively expanded because of anthropogenic actions. This engenders unwanted impacts, particularly in beach front zones adjoining to populated metropolitan zones. n-Alkanes comprise of saturated and straight carbon chains of C6–C40 which contain even and odd carbon numbers that demonstrate anthropogenic and natural wellsprings of hydrocarbon. (Ahmed et al., 2016).

Wellsprings of PAHs can be either petrogenic, from oil related actions (oil and its subsidiary) or pyrogenic (pyrolytic), from the deficient ignition of diesel fuel and motor oil, wood, coal, biomass of backwoods, grass fires, squander incinerators, and non-renewable energy sources that are utilized in mechanical processes and power plants (Ruchaya et al., 2006). PAHs, for example, naphthalene, fluorine, pyrene, acenaphthene, phenanthrene and so forth are broadly utilized in manufacturing products, for example, intermediates in drugs, horticultural items, photographic items, thermosetting plastics, and greasing up materials. Pyrogenic PAHs are described by the event of PAHs that convey a pudgy of sub-atomic loads, while oil hydrocarbons are overwhelmed by PAHs of the least sub-atomic weight (Neff et al., 2005). They are broadly scattered in the marine condition, especially in harbors, dockyards, marinas, estuaries and other shallow beach front regions with anthropogenic data sources (El Nemr, 2014). In marine environment, the contaminants caused by PAHs could be traceable to natural seepage or land-based sources such as river discharges, urban runoff. refineries and other industrial wastewater. Environmental distribution of PAHs is mostly associated with anthropogenic activities such as fossil fuel combustion, waste incineration, coal gasification, liquefaction processes, petroleum cracking, and production of coke, black carbon, coal tar, pitch and asphalt (Yunkeret al., 2002). This study seeks to identify and characterize the sources of organic contaminants in sediment and Littorina Littorea from the study area using some geochemical parameters.

#### **II. MATERIALS AND METHODS**

#### The Study Area

The research was performed at Okujaguriver in Okujagu-Ama,Okrika Local government, Rivers State, Nigeria. The locality is situated in an island and is home to assessed 700 people. It is located on the eastern aspect of the Bonny estuary in southern Nigeria inside Longitude 7° 3' 11.37" E and Latitude 4° 48' 23" N. The Okujagu River and related water frameworks is one of the most significant oceanic environments in the Niger Delta uncommonly inclined to contamination from various human actions inside and outside the zone. Among the various human actions, fishing, drifting route, clothing, removal of squanders, swimming, etc go on in and around the territory unregulated. This amphibian body likewise gets gushing releases from numerous enterprises, private structures and the fundamental Port Harcourt abattoir sited along the bank at Trans-Amadi industrial layout.

#### Sample Collection

Surface sediment samples were collected utilizing Ekman Dredge sampler at appropriate depths of 10m from the Okujagu River. The samples were transferred into a clean aluminum foil and then placed on ice. Mature periwinkles (*Littorina Littorea*) were harvested at the sample station, where they were reared until they reach certain sizes before the harvest. The samples were collected and stored in isothermic boxes containing dry ice. The samples were thoroughly scrubbed and washed and were processed by boiling at 100°C for 5mins and the meat was aseptically extracted.

Samples were dried at room temperature, grinded and sieved before transporting to the laboratory for further analysis.

## Extraction of Soluble Organic Matter

of Extraction the sediment sample was conductedutilizingsoxhlet device (EPA 3540). strategy Soxhlet was processed with dichloromethane for 20 minutes i n a water shower for the thimbles and the glass fleece used in t he extraction. In the soxhlet extricated thimble, 50 g of the sed iment test was positioned with glass fleece and then filled wit h dichloromethane and isolated for 18 hours. By expansion of 30 g initiated (copper drenched in 20ml of 0.1 M condensed h ydrochloric corrosive for 10mins) into the round base carafe d

uring extraction, concentrate was desulphurised. In order to ap proach dryness using a vacuum evaporator, focus was lost. Co ncentrate heaviness was overcome as a proportion of the extra ctable or dissolvable carbon based matter (SOM) quantity con sisting of asphaltenes and maltenes.

#### Deasphaltation of the Extract

Precipitation of asphaltenes from the dissolvable carbon-based matter (SOM) was done utilizing the methodology depicted by Schoell et al; (1983). 20ml of a blend (1:30) of dichloromethane/oil ether was added to 10ml of the concentrate and centrifuged at 3000rpm for about 20mins. The asphaltenes hastened from solvent carbon-based matter were disposed of subsequent to washing. The maltenes acquired from the concentrate were additionally isolated by fluid chromatography (section 30 x 1.2cm) into aliphatic, fragrant and hetero-divisions.

#### Liquid Chromatographic Separation of Maltenes

#### The detachment of maltene

fluid chromatography has been completed into aliphatic, arom atic and hetero parts. A barrel-shaped column (30 x 1.2 cm) co mposed of glass was pushed above the silica gel with enacted silica gel (20 g actuated by oven heating for 2 hours at 400 ° C) and alumina (neutral, 10 g initiated by oven heating for 2 ho urs at 500 ° C). The condensed extract (2ml) was cautiously a pplied to the head of the column that had previously been cinc hed into place. The immersed (aliphatic) component was elute d with 50ml hexane; for the elution of the aromatic section, 20 0ml of 1:1 dichloromethane / hexane blend was used (Nna and Kpee, 2017). Eventually, to remove the hetero-division a mix ture (1:2, 60ml) of methanol / dichloromethane was used.

# Analysis by Gas Chromatography-Mass Spectrometry (GC-MS)

Using a Hewlett-Packard Model 6890 structure mass chromat ograph (GC) coupled to a Hewlett-Packard Model 5973 Quadr upole Mass Selective Detector (MSD), the gas chromatograph y mass spectrometry (GC-MS) study of the aromatic and aliph atic divisions of the maltenes extricates was carried out. On a DB5-MS fragment (60 m x 0.25 mm i.d, 0.25 µm film thicknes s), the GC detachment was achieved. The working conditions of the GC were as follows; the temperature was set from 50  $^{\circ}$ C (isothermal for 1 minute) to 120 ° C at a rate of 20 ° C / min and then to 300 ° C at a rate of 3 ° C / min, with a final tempe rature of 45 minutes. The carrier gas used was helium. Under electronic tension monitoring, measurements were passed into the cold onsegment injector. The outlet of the GC section was clearly connected to the mass spectrometer's particle wellspri ng. The GC-MS interface was held separately at 280 ° C, whil e the particle source and quadrupole evaluator were at 230 ° C and 150 ° C. In the electron sway mode (EI) at 70eV ionizatio n vitality, the mass spectrometer was run. 45-550 daltons (0-4 0mins) and 50 700 daltons (above 40mins) were reported as m ass spectra. Measurement was accomplished by acquiring mas s chromatograms at sub-atomic concentrations and, using the

HP-MSD chemstation integrator, selected m / z values of diffe rent PAH and biomarker compounds separately. Singular com pounds are characterized by mass spectrum association with writing information and explanation of mass spectrometric discontinuity designs

#### Statistical Analysis of Data

Statistical analysis of the data generated in the study was based on mean.

#### **III. RESULTS AND DISCUSSION**

Compound Name	Molecular Weight	Molecular Formular	Littorina Littorea	Sediment	Mean	SD
Octadecane	256	C <sub>17</sub> H <sub>37</sub>	0.18	0.09	0.07	0.09
Nonadecane	270	$C_{18}H_{40}$	0.08	0.31	0.10	0.15
n-Heneicosane	296	C <sub>21</sub> H <sub>44</sub>	0.06	0.35	0.12	0.23
Tricosane	324	C <sub>23</sub> H <sub>48</sub>	0.28	0.22	0.39	0.18
Tetracosane	338	C24H50	0.26	0.14	0.33	0.19
Pentacosane	352	C <sub>25</sub> H <sub>52</sub>	0.03	0.21	0.14	0.25
Hexacosane	366	C <sub>26</sub> H <sub>54</sub>	0.11	0.11	0.11	0.16
Heptacosane	380	C <sub>27</sub> H <sub>56</sub>	0.14	0.14	0.14	0.17
Octacosane	394	C <sub>28</sub> H <sub>58</sub>	0.48	0.21	0.59	0.19
Nonacosane	408	C <sub>29</sub> H <sub>60</sub>	0.53	0.23	0.65	0.19
Traicontane	422	C <sub>30</sub> H <sub>62</sub>	0.18	0.19	0.28	0.15
Dotriacontane	450	C <sub>32</sub> H <sub>66</sub>	0.05	0.25	0.15	0.14
Total Concentration			2.38	2.48	Mean	

Table 1: Concentration of n-Alkanes in sediment and Littorina Littorea (mg/kg)

Table 2: Characteristics	Organic Geochemical	Parameters	and Diagnostic
	Ratios from n-Alkan	es	

Samples	C <sub>max</sub> n-alkanes	CPI n-alkanes	$\mathbf{P}_{_{\mathrm{aq}}}$	LHC/SHC
Littorina Littorea	C29	1.1	0.37	3.0
Sediment	C	1.5	0.65	1.40

 $C_{max} = n$ -Carbon maximum

CPI = Carbon Preference Index

Paq = n- alkane Proxy

LHC/SHC = Ratio of long chain hydrocarbon to short chain hydrocarbon

$$P_{aq} = (\underline{C_{23} + C_{25}})$$
$$(C_{23} + C_{25} + C_{29})$$

 $CPI = \underline{C_{23} + C_{25} + C_{27} + C_{29}} \\ C_{24} + C_{26} + C_{28} + C_{32}$ 

LHC/SHC =  $\underline{C_{27}+C_{29}+C_{32}}$  $C_{17}+C_{21}$ 

Table 3: Concentration of PAHs in sediment and Littorina Littorea (mg/kg)

Compound Name	No. of Rings	Molec ular weight	Molecular Formula	Littorina Littorea	Sedim ent	Mean
Xylene	3	106.2	$C_8H_{10}$	ND	ND	ND
Naphthalene	2	128.2	$C_{10}H_{8}$	0.324	0.236	0.44
Acenapthene	3	152.2	$C_{12}H_8$	0.81	0.021	0.82
Acenaphthylene	3	152.2	$C_{12}H_8$	0.002	0.001	0.003
Fluorene	3	166.2	C13H10	0.024	0.02	0.01
Phenanthrene	3	178.2	$C_{14}H_{10}$	0.016	0.07	0.008
Anthracene	3	178.2	$C_{14}H_{10}$	1.90	0.020	1.91
Fluoranthene	4	202.2	$C_{16}H_{10}$	0.005	0.04	0.002 5
Pyrene	4	202.2	$C_{16}H_{10}$	0.02	0.001	0.021
1,2 Benzanthracene	5	228.3	C18H12	0.002	0.002	0.002
Benzo(a)pyrene	5	252.3	$C_{20}H_{12}$	0.022	0.015	0.03
Benzo b fluoranthene	5	252.3	$C_{20}H_{12}$	0.05	0.023	0.012
Benzo(k)fluoranthene	5	252.3	C20H12	0.001	0.05	0.001
Benzo(g_h_i)perylene	6	276.3	C22H12	0.014	0.009	0.019
Dibenzyl(a_h) anthracene	5	278.3	C <sub>22</sub> H <sub>14</sub>	0.011	0.012	0.02
Total Concentration				3.174	0.52	

Ratios	Littorina Littorea	Sediment	
Fl/Py	0.25	40	
Ph/An	0.008	3.5	
Ant/(Ant+Ph)	0.99	0.22	
Fl/(Fl+Py)	0.2	0.98	
ΣLMW/ΣΗMW	24.608	2.42	

Table 4: PAHs Diagnostic Ratios

Where:

Fl = Fluoranthene Py = Pyrene

Ph = Phenanthrene

An = Anthracene

 $\Sigma$ LMW = Sum of Lower Molecular Weight PAHs (2 or 3 ring PAHs)  $\Sigma$ HMW = Sum of Higher Molecular Weight PAHs (4 to 6 ring PAHs)

Fl/Py ratios greater than 10 (>10) come from pyrolytic origins while ratios less than 10 (<10) come from petrogenic sources.

# $Ph/An = \frac{Phenanthrene}{Anthracene}$

Ph/An ratios greater than 10 (>10) come from petrogenic origins while ratios less than 10 (<10) come from pyrolytic sources(Qiu, *et al*; 2009)

#### Distribution of n-alkane series

Sediment and *Littorina Littorea* from Okujagu River recorded n-alkane distributions ranging from  $C_{17}$  -  $C_{32}$  carbon chain length (Table 1). The n-alkane mean concentration varied from 0.03-0.53mg/kg for Littorina Littorea sample and 0.09-0.35mg/kg for sediment samples (Table 1). The total concentrations of n-alkanes in *Littorina Littorea* and sediment were 2.38 and 2.48mg/kg respectively.

The CPI, a measure of organically blended n-alkanes (Simoneit, et al., 2002) shows the overall commitments of nalkanes from regular (biogenic/earthbound, i.e; CPI >1) contrasted with anthropogenic (oil/petrochemical i.e; CPI <1) sources. In this investigation, the CPI was determined by Nna, (2014) and was found to have trademark esteems somewhere in the range of 1.1 and 1.5. This shows the presence of biogenic/earthbound contribution at all stations.

The ascertainment of carbon maximum (Cmax) for the two examples additionally give a sign of the relative source input, where Cmax > 25 for n-alkanes mirrors the consolidation of higher plant wax and Cmax < 25 shows a significant contribution of microbial/oil sources (Mazurel and Simoneit, 1997). By and large, the predominant Cmax decided for the nalkane biota and sediment gathered from Okujagu River were C21 and C29. This proposes a blended commitment of earthbound and oil/microbial wellsprings of carbon-based matter in the stream.

So as to assess the source of long-chain n-alkanes in the examples (i.e, regardless of whether the long chain n-alkanes are gotten from either higher plant waxes or macrophytes), the boundary, n-alkane intermediary (Paq) was determined. Estimations of Paq (Table 3) extended from 0.37 to 0.65 for the whole example suite. Ficken et al. (2000) reported that estimations of Paq running from 0.01 to 0.23 are connected to earthbound plant waxes, while those in the scope of 0.48 to 0.94 are related with lowered/skimming types of macrophytes. Aftereffects of this investigation propose more commitment from lowered/skimming types of macrophytes to long chain n-alkanes in sediment from Okujagu River.

To decide the predominant higher plants and/or macrophyteinferred or potentially phytoplankton-determined matter, LHC/SHC proportions were determined and had values going from 1.40 to 3.00 (Table 2). As indicated by Commendatore, *et al.* (2012). High estimations of LHC/SHC are overwhelmed by higher plant as well as macrophyte waxes, while low qualities are overwhelmed by phytoplankton-determined carbon-based matter. Results of this study suggest more contribution from phytoplankton-derived organic matter.

## Distribution of PAHs

A total of Fourteen (14) PAHs were quantified, identified and detected in both sediment and *Littorina Littorea* samples obtained from Okujagu River (Table 3). As can be seen in the *Littorina Littorea* sample, Anthracene and Acenaphthene recorded the highest concentration followed by Naphthalene. The lowest PAHs concentration recorded in *Littorina Littorea* was Benzo(k)Fluoranthene, Acenaphthylene and 1,2 Benzanthracene. The sediments recorded Naphthalene as the most concentrated PAHs whereas Pyrene and Acenaphthylene were low in their concentrations (Table 3).

## Source Identification

The significant wellsprings of anthropogenic PAHs are nonrenewable energy source burning (Pyrolytic) and oil spillage (Petrogenic). PAH unique mark proportions, for example, Phenanthrene to Anthracene (Ph/A), Fluoranthene to Pyrene (Fl/Py), Ant/(Ant+Ph), Fl/(Fl+Py) and the proportion of LMW PAHs to HMW PAHs (LMW/HMW) have been determined to assess both petrogenic and pyrogenic (pyrolytic) PAHs (Magi et al., 2002). Petrogenic PAHs are regularly portrayed by Ph/A qualities > 10 though ignition measures that bring about the creation of pyrolytic PAHs are determined by low Ph/A proportions (<10). For the most part, Fl/Py proportions more noteworthy than 1 (>1) originate from pyrolytic birthplaces while proportions of under 1 (<1) appear to be petrogenic source (Qiu, et al., 2009). The Origin of PAHs in the sediment could be discernible to petroleum derivative burning (pyrolytic) because of the presence of phenanthrene. Anthracene, fluoranthene, pyrene and benzo(a)anthracene (Qiuet al., 2009). The xylene is another proof to discover the

#### pyrolytic wellspring of PAHs. The demonstrative proportion of fluoranthene/pyrene indicated that Fl/Py proportion for sediment was 40 (>1) showing PAHs inception from pyrolytic source while Fl/Py proportion of the periwinkle test was determined and the worth was 0.25(<1) demonstrating petrogenic source. This outcome was in accordance with the report by Que, et al.,2009. The Phenanthrene/Anthracene proportion was determined and for sediment, an estimation of 3.5 which was under 10 inferring that the PAHs are source from burning cycles (pyrolytic) and that of Littorina Littorea was 0.008 which was additionally under 10, a sign of petroleum product ignition (pyrolytic) sources. This is in agreement with the report by Fickenet al., (2000). The analytic proportions of Ant/(Ant+Ph) and Fl/(Fl+Py) were additionally used to recognize petrogenic and pyrolytic PAHs. Petrogenic PAHs are frequently portrayed by Ant/(Ant+Ph) values <0.1 while burning cycles that bring about the creation of pyrolytic PAHs are indicated by Ant/(Ant+Ph) values >0.1 (Pies, et al., 2008). Likewise, Fl/(Fl+Py) proportions more noteworthy than 0.4 (>0.4) originate from pyrolytic causes while proportions of under 0.4 (<0.4) appear to be petrogenic source (De La Torre-Roche et al., 2009). From the outcomes (Table 4), the proportion of Ant/(Ant+Ph) was determined to be 0.22 (>0.1) for sediment and 0.99 (>0.1) for Littorina Littorea demonstrating PAHs birthplace from pyrogenic(pyrolytic) sources. While the proportion of Fl/(Fl+Py) was determined to be 0.98 (>0.4) for sediment recommending PAH birthplace from pyrogenic(pyrolytic) source and 0.2 (<0.4) for Littorina Littorea showing PAHs starting point from petrogenic sources. This result is also in agreement with the report by Flemminget al., (2008). The circulation of various PAH rings likewise demonstrates various wellsprings of the PAHs from petrogenic and pyrogenic beginnings. This is on the grounds that PAHs from a petrogenic source prevalently comprise of lower atomic loads (two and three rings), while the pyrogenic birthplace PAHs by and large have higher sub-atomic loads, for example, four-and five-ring PAH species (Kannan et al., 2005). From the outcomes, The all-out centralization of lower sub-atomic weight (LMW) PAHs for sediment and Littorina Littoreawas 0.368 and 24.608 separately while the absolute convergences of higher sub-atomic weight (HMW) PAHs for sediment and *Littorina Littorea* was 0.152 and 0.125 individually. From the outcomes, the centralizations of the lower atomic weight PAHs are discovered to be higher than the higher sub-atomic weight PAHs (Table 3) showing PAHs beginning from petrogenic sources. The proportion of LMW PAHs to HMW PAHs (LMW/HMW) has accordingly been utilized to recognize petrogenic (>1 values) and pyrolytic (<1 values) sources. From the outcomes (Table 4), the proportion of Lower atomic weight PAHs and Higher sub-atomic weight PAHs was calculated to be 2.42 (>1) for sediment and 24.608 (>1) for Littorina Littoreaindicating PAHs origin from petrogenic sources.

#### **IV. CONCLUSION**

The study was centered on identifying and characterizing the sources of organic contaminants concentration in sediment and Periwinkle (Littorina Littorea) from Okujaguriver. The organic contaminants considered in this study were n-alkanes and Polycyclic aromatic hydrocarbons. Sources of n-alkanes from the study area was traceable to natural or anthropogenic sources. The sources for LMW to HMW PAHs was traceable to petrogenic and pyrolytic sources for sediments. However, there were considerably traces of PAHs sources from petrogenic in the Littorina Littorea. A number of indices were used to identify hydrocarbon sources of n-alkanes found in sediment and Littorina Littorea and from the findings, the sources of n-alkanes found were from submerged floating of macrophytes, biogenic/terrestrial input, species petroleum/microbial sources of organic matter and phytoplankton derived organic matter. Sources of PAHs could be petrogenic or pyrolytic. The sources of PAHs were obtained through diagnostic ratios such as Phenanthrene to Anthracene (Ph/An), Fluoranthene to Pyrene (Fl/Pv), Ant/(Ant+Ph), Fl/(Fl+Py) and the ratio of lower molecular weight (LMW) PAHs to higher molecular weight (HMW) PAHs (LMW/HMW). From the diagnostic ratios used in this work, the PAHs in sediment and Littorina Littoreaoriginate from both petrogenic and pyrolytic sources.

#### V. RECOMMENDATIONS

The study recommends the following measures as to curtail the menace of organic contaminants in aquatic environments.

- Measures should be put in place to regulate the disposal of waste, effluent discharges from industries and chemical release through agricultural activities into the marine ecosystem.
- Illegal refining should be stopped as they are the major source of petrogenic PAHs.
- Industries that generate waste should always pre-treat the wastewater coming from the industries and abattoir before final disposal into the river.
- Further studies should be carried out in the same area to identify the sources of more organic contaminants with a view to combat the menace associated with it and for making decisions concerning site remediation.

#### REFERENCES

- Ahmed, E. N., Abeer, A., Moneer, S. R., &Amany, E. S. (2016). Distribution and sources of n-alkanes and polycyclic aromatic hydrocarbons in shellfish of the Egyptian Red Sea coast: *Egyptian Journal of Aquatic Research*. National Institute of Oceanography and Fisheries, KayetBey, Elanfoushy, Alexandria, Egypt.
- [2] Arens, M. J., &Depree, C. V. (2010). A source mixing model to apportion PAHs from coal tar and asphalt binders in street pavements and urban aquatic sediments. *Chemosphere*, 81, 1526-1535.
- [3] Barakat, A.O., Mostafa, A., Wade, T.L., Sweet, S.T., & El Sayed, N.B. (2010). Spatial distribution and temporal trends of polycyclic aromatic hydrocarbons in sediments from Lake Maryut,

Alexandria, Egypt: Water, Air and Soil Pollution. doi:10.1007/s11270-010-0624-5.

- [4] Bellas, J., Saco-Álvarez, L., Nieto, O., &Beiras, R. (2008). Ecotoxicological evaluation of polycyclic aromatic hydrocarbons utilizing marine invertebrate embryo–larval bioassays: *Marine Pollution Bulletin*, 57, 493-502.
- [5] Bray, E. E., & Evans, E. D. (1961). Distribution of n-paraffins as a clue to recognition of source beds: *Geochim. Cosmochim. Acta*, 22, 2–15.
- [6] Charriau, A., Bodineau, L., Ouddane, B, & Fischer, J. C. (2013). Polycyclic Aromatic Hydrocarbons and n-alkanes in sediments of the Upper Scheldt River Basin: contamination levels and source apportionment. HAL Id: hal-00922199.
- [7] Choudhary, P., Routh, J., & Chakrapani, G.J. (2010). Organic geochemical record of increased productivity in akeNaukuchiyatal, Kumaun Himalayas, India: *Environmental Earth Science*, 60, 837–843.
- [8] Commendatore, M.G., Nievas, M.L., Amin, O., & Esteves, J. L. (2012). Sources and distribution aliphatic and polyaromatic in coastal sediments from the Ushuaia Bay (Tierra del Fuego, Patagonia, Argentina): *Marine Environmental Research*, 74, 20–31.
- [9] Countway, R. E., Dickhut, R. M., &Canuel, E. A. (2003). Polycyclic aromatic hydrocarbon (PAH) distributions and associations with organic matter in surface waters of the York River, VA Estuary: *Organic Geochemistry*, 34, 209–224.
- [10] Da Silva, D.A., &Bicego, M.C. (2010). Polycyclic aromatic hydrocarbons and petroleum biomarkers in Sao Sebastiao Channel, Brazil, assessment of petroleum contamination: *Marine Environmental Research*, 69, 277-286.
- [11] De La Torre-Roche, R.J., Lee, W.Y., & Campos-Díaz, S.I. (2009). Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas, analysis of a potential problem in the United States/Mexico border region: *Journal of Hazardous Materials*, 163, 946-958.
- [12] El Nemr, A., El-Sadaawy, M. M., Khaled, A., & El-Sikaily, A. (2014). Distribution patterns and risks posed of polycyclic aromatic hydrocarbons contaminated in surface sediment of the Red Sea coast, Egypt: *Desalination Water Treat.* 52, 7964– 7982.
- [13] El Nemr, A., El-Sadaawy, M. M., Khaled, A., &Draz, S.O. (2013). Aliphatic and polycyclic aromatic hydrocarbons in the surface sediments of the Mediterranean: assessment and source recognition of petroleum hydrocarbons: *Environ. Monit. Assess.185*, 4571–4589.
- [14] El Nemr, A., Said, T.O., Khaled, A., El-Sikaily, A., & Abd-Allah, A.M. (2007). The distribution and sources of polycyclic aromatic hydrocarbons in surface sediments along the Egyptian Mediterranean coast: *Environ. Monit. Assess.* 124, 343–359.
- [15] Ficken, K. J., Li, B., Swain, D. L., & Eglinton, G. (2000). An nalkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes: *Organic Geochemistry*, 31, 745–749.
- [16] Flemming, A.T., Weinstein, J. E., &Lewitus, A. J. (2008). Survey of PAH in low density residential stormwater ponds in coastal South Carolina, false dark mussels as potential biomonitors: *Marine Pollution Bulletin*, 56, 1598-1608.
- [17] Fubara, E. P. (2011): Organic Geochemical Characterization and hydrocarbon source identification of Niger Delta Coastal Sediments, South Eastern Nigeria. Unpublished ph.Dthesis. Department of chemistry, University of Calabar, Calabar, Nigeria.
- [18] Hussein, I., Abdel, S., & Mansour, M. S. (2016). A review on polycyclic aromatic hydrocarbons: source, environmentalimpact, effect on human healthandremediation: *Egyptian Journal Petrol*, 25, 107–123.
- [19] Hwang, H. M., & Foster, G. D. (2006). Characterization of polycyclic aromatic hydrocarbons in urban stormwater runoff flowing into the tidal Anacostia River, Washington, DC, USA: *Environmental Pollution*, 140, 416-426.
- [20] Hwang, H. M. Wade, T. L., & Sericano, J. L. (2003). Concentrations and source characterization polycyclic aromatic

hydrocarbons in pine needles from Korea, Mexico, and United States: *Atmospheric Environment*, *37*, 2259-2267.

- [21] Keshavarzifard, M., Zakaria, M. P., Keshavarzifard, S., & Sharifi, R. (2018). Distribution and Sources of Aliphatic Hydrocarbons in Surface Sediments from two Major Rivers of Peninsular Malaysia: Agricultural Engineering Letters, 18–22.
- [22] Keshavarzifard, M., Zakaria, M. P., Keshavarzifard, S., & Sharifi, R. (2018). Distributions, Composition Patterns, Sources and Potential Toxicity of Polycyclic Aromatic Hydrocarbons (PAHs) Pollution in Surface Sediments from the Kim Kim River and Segget River, Peninsula Malaysia. Pertanika: *Journal of Science & Technology*, 26(1).
- [23] Kim, D., Kumfer, B.M., Anastasio, C., Kennedy, I.M., Young, T.M. (2009). Environmental ageing of polycyclic aromatic hydrocarbons on soot and its effect on source identification: *Chemosphere*, 76, 1075-1081.
- [24] Lapworth, D.J., &Gooddy, D.C. (2006). Sources and persistence of pesticides in a semi-confined chalk aquifer of southeast England: *Environmental Pollution*, 144, 1031-1044.
- [25] Lapworth, D.J., Gooddy, D.C., Allen, D., & Old, G.H. (2009). Understanding groundwater surface water and hyporheic zone biogeochemical processes in a Chalk catchment utilizingfluorescence properties of dissolved and colloidal organic matter: *Journal of GeophysicalResearch*, 114, G00F02. 10, pp. 10.1029/2009JG000921.
- [26] Latimer, J., & Zheng, J. (2003). The sources, transport, and fate of PAH in the marine environment, in: P.E.T Douben (Ed.), PAHs, An Ecotoxicological perspective: John Wiley and Sons Ltd, New York.
- [27] Liu, Y., Chen, L., Huang, Q. H., Li, W.Y., Tang, Y. J., & Zhao, J. F. (2009). Source apportionment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Huangpu River, Shanghai, China: Science of the TotalEnvironment,407,2931- 2938.
- [28] Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D.,Wirers, F., Balsaa, P., Gans, O.,Weiss, S., Blaha, L., Bolchi, M., &Gawlik, B.M. (2010a). Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water: *Water Research*, 44, 4115-4126.
- [29] Magi, E., Bianco, R., Ianni, C., & Di Carro, M. (2002). Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea: *Environmental Pollution*, 119, 91-98.
- [30] Manoli, E., Kouras, A., & Samara, C. (2004). Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece: *Chemosphere*, 56, 867-878.
- [31] Mark, B., Yunker, W., Macdonald, A., Roxanne V., Reginald, H., Mitchell, J., Darcy, G., & Stephanie, S. (2002): PAHs in the Fraser River basin, a critical appraisal of PAH ratios as indicators of PAH source and composition: *Organic Geochemistry*, 33, 489-515.
- [32] Masood, N., Zakaria, M. P., Ali, M. M., Magam, S. M., Alkhadher, S., Keshavarzifard, M., & Hussein, M. A. (2014). Distribution of petroleum hydrocarbons in surface sediments from selected locations in Kuala Selangor River, Malaysia: In From sources to solution. Springer, Singapore.
- [33] Mille, G., Asia, L., Guiliano, M., Malleret, L., &Doumenq, P. (2007). Hydrocarbons in coastal sediments from the editerranean sea, Gulf of Fos area, France: *Marine Pollut. Bull.* 54, 566–575.
- [34] Moustafa, G. S., Mahmoud, M. K., Thanaa, A. M., & El-Sayed, E. (2016). An Overview on the Organic Contaminants: SDRP Journal of Earth Sciences & Environmental Studies.
- [35] Neff, J. M., Scott, S. A., &Gunstert, D. G. (2005). Integr. Environ. Assess. Manage. 1, 22–33.
- [36] Nikolaou, A., Kostopoulau, M., Lofrano, G., &Meric, S. (2009). Determination of PAHs in marine sediments: Analytical Methods and Environmental Concerns: *Global NEST Journal*, 11(4), 391-405.
- [37] Nna, P.J., &Kpee, F. (2018). Source Identification and distribution of n-alkanes and Polycyclic Aromatic compounds in suspended

particulate matter from Great Kwa River, South East Nig: *The Pharmaceutical and Chemical Journal*, 5(2), 92-99.

- [38] Nudi, A.H., Wagener, A.L., Francioni, E., Sette, C. B., Sartori, A. V., & Scofield, A. L. (2010). Biomarkers of PAHs exposure in crabs Ucidescordatus: laboratory assay and field study: *Environ.Res.110*, 137–145.
- [39] Oyo-Ita, O. E., Ekpo, B. O., &Orosa, D. R. (2010). Distributions and sources of aliphatic hydrocarbons and ketones in surface sediments from the Cross River estuary, S.E. Niger Delta, Nigeria: J. Appl. Sci. Environ. Sanit. 5 (1), 1–11.
- [40] Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T. A., & Hofmann, T. (2008). Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils: *Chemosphere*, 72, 1594-1601.
- [41] Plachá, D., Raclavská, H., Matýsek, D., &Rümmeli, M. H. (2009). The polycyclic aromatic hydrocarbon concentrations in soils in the Region of ValasskeMezirici, the Czech Republic: *Geochemical Transactions*, 10, 12-33.
- [42] Qui, Y. W., Zhang, G., Liu, G. O., & Wai, O. (2009): Polyclyclicaromatichydrocarbons(PAHs) in the water column and sediment core of Deep Bay, South China. Estuariescoast: *Shelf Science*, 83(1), 60-66.
- [43] Ranjan, R. K., Routh, J., Ramanathan, A. L., &Klump, J. V. (2012).Polycyclic aromatic hydrocarbon fingerprints in the Pichavaram mangrove estuarine sediments, southeastern India: Organic Geochemistry, 53, 88–94.
- [44] Ratola, N., Alves, A., Lacorte, S., & Barceló, D. (2011). Distribution and sources of PAHs utilizing three pine species along the Ebro River: *Environmental Monitoring and Assessment*.doi:10.1007/s10661-011-2014-x.
- [45] Ratola, N., Amigo, J. M., & Alves, A. (2010). Levels and sources of PAHs in Selected sites from Portugal, biomonitoring with Pinuspinea and Pinuspinaster needles: *Archives of Environmental Contaminant Toxicology*, 58, 631-647.
- [46] Ravindra, K., Sokhi, R., & Van-Grieken, R. (2008a). Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation: *Atmospheric Environment*, 42, 2895-2921.
- [47] Ravindra, K., Wauters, E., & Van-Grieken, R. (2008b). Variation in particulate PAHs levels and their relation with the ransboundary movement of the air masses: *Science of the Total Environment*, 396, 100-110.
- [48] Rhead, M. M., & Hardy, S. A. (2003). The sources of polycyclic aromatic compounds in diesel engine emissions: *Fuel*, 82, 285-393.
- [49] Rodriguez-Mozaz, S., Lopez de Alda, M., & Barcelo, D. (2004). Monitoring of estrogens, pesticides and bisphenol A in natural waters and drinking water treatment plant by solid- phase extraction-liquid chromatography-mass spectrometry: *Journal of Chromatography A*, 1045, 85-92.
- [50] Rozita, O., Norashikin, S., &Pauzi, A. (2010). Organic Contaminants In Soil/Sediment As A Tracer For Pollution Sources: *Chemical Sciences Journal*, Volume 2010: CSJ-4.
- [51] Ruchaya, B., Gullaya, W., Ayako, T., &Hideshige, T. (2006). Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand: *Marine Pollution Bulletin*, 52, 942–956.
- [52] Saad, A. A., El Nemr, A., El-Sikaily, A. M., Mokhamer, E. H., & Khamis, M.A. (2015). Urinary metabolites and oxidative stress of polycyclic aromatic hydrocarbon as biomarker of exposure to environmental marine pollution: *Int. J. Chem. Environ. Eng.* 6 (2), 95–104.
- [53] Sakari, M., Zakaria, M. P., Junos, M. B., Annuar, N. A., Yun, H. Y., Heng, Y. S., Zainuddin, S. M., & Chai, K. L. (2008). Spatial distribution of petroleum hydrocarbon in sediments of major rivers from east coast of peninsular, Malaysia: *Marine Science*, 3 (1), 1–8.
- [54] Shilla, D. J. (2016). Distribution and Behavior of Polycyclic Aromatic Hydrocarbon (PAH) In Sub-tropical River-Estuary, Okinawa, Japan: *Chemical Ecology*, 32, 472–491.
- [55] Shilla, D. J., & Routh, J. (2017). Utilizing biochemical and isotopic tracers to characterize organic matter sources and their

incorporation into estuarine food webs, Rufiji delta, Tanzania: *Chemical Ecology*, *33*, 893–917.

- [56] Shilla, D. J., Tsuchiya, M., & Abel, D. S. (2011). Terrigenous nutrient and organic matter in a subtropical river estuary, Okinawa, Japan: Origin, distribution and pattern across the estuarine salinity gradient: *Chemical Ecology*, 27, 523–554.
- [57] Soclo, H., Budzinski, H., Garrigues, P., & Matsuzawa, S. (2008). Biotaaccumulationofpolycyclic aromatic hydrocarbons in Benin coastal waters: *Polycyclic Aromatic Compounds*, 28, 112–127.
- [58] Soclo, H., Garrigues, P., & Ewald, M. (2000). Origin of polycyclic aromatichydrocarbons(PAHs) in coastal marine sediments: case studies in Cotonou, Benin and Aquitaine, France areas: *Marine Pollution Bulletin*, 40, 387–396.
- [59] Tolosa, I., de Mora. S.J., Fowler, S.W., Villeneuve, J.P., Bartocci, J., &Cattini, C. (2005). Aliphatic and aromatic hydrocarbons in marine biota and coastal sediments from the Gulf of Oman: *Marine Pollution Bulletin*, 50, 1619–1633.
- [60] Tsapakis, M., Stephanou, E.G., &Karakassis, I. (2003). Evaluation of atmospheric transport as a nonpoint source of polycyclic aromatic hydrocarbons in marine sediments of the Eastern Mediterranean: Marine Chemistry, 80 (4), 283–298.
- [61] Tsapakis, M., & Stephanou, E.G., (2005). Occurrence of gaseous and particulate polycyclic aromatic hydrocarbons in the urban atmosphere: study of sources and ambient temperature effect on the gas/particle concentration and distribution: *Environmental Pollution*, 133, 147-156.
- [62] Vinas, L., Franco, M.A., Soriano, J.A., Gonzalez, J.J., Pon, J., &Albaige, J. (2010). Sources and distribution of polycyclic aromatic hydrocarbons in sediments from the Spanish northern continental shelf. Assessment of spatial and temporal trends. *Environmental Pollution*, 158, 1551-1560.
- [63] Wagener, A., Hamacher, C., Farias, C., Godoy, J.M., & Scofield, A. (2010). Evaluation of tools to identify hydrocarbon sources in recent and historical sediments of a tropical bay: *Marine Chemistry*, 121, 67-79.
- [64] Wang, C. Sun, H. Chang, Y. Song, Z. & Qin, X. (2011). PAHs distributioninsedimentsassociated with gas hydrate and oil seepage from the Gulf of Mexico. *Marine Pollution Bulletin*, 62, 2714–2723.
- [65] Wang, D., Chen, J., Xu, Z., Qiao, X., & Huang, L. (2005). Disappearance of polycyclic aromatic hydrocarbons sorbed on surfaces of pine (*Pinusthunbergii*) needles under irradiation of sunlight. Volatilization and photolysis: *Atmospheric Environment*, 39, 4583-4591.
- [66] Wang, G., Huang, L., Zhao, X., Niu, H., & Dai, Z., (2006). Aliphatic and polycyclic aromatic hydrocarbons of atmospheric aerosols in five locations of Nanjing urban area, China: *Atmospheric Research*, 81, 54-66.
- [67] Wang, H. S., Cheng, Z., Liang, P., Shao, D. D., Kang, Y., Wu, S. C., Wong, C. K., & Wong, M.H. (2010c). Characterization of PAHs in surface sediments of aquaculture farms around the Pearl River, Delta. *Ecotoxicological and Environmental Safety*, 73, 900-906.
- [68] Wang, J. Z., Nie, Y. F., Luo, X. L., & Zeng, E.Y. (2008). Occurrence and phase distribution of polycyclic aromatic hydrocarbons in riverine runoff of the Pearl River, Delta: *Marine Pollution Bulletin*, 57, 767-774.
- [69] Wang, L., Yang, Z., Niu, J., & Wang, J. (2009b). Characterization, ecological risk assessment and source diagnostics of polycyclic aromatic hydrocarbons in water column of the Yellow River Delta: *Journal of Hazardous Materials*, 169, 460-465.
- [70] Wang, W., Simonich, S.L., Xue, M., Zhao, J., Zhang, N., Wang, R., Cao, J., & Tao, S. (2010b). Concentrations, sources and spatial distribution of polycyclic aromatic hydrocarbons in soils from Beijing, Tianjin and surrounding areas, North China: *Environmental Pollution*, 158, 1245-1251.
- [71] Wang, X. L., Tao, S., Dawson, R.W., &Xu, F.L. (2002). Characterizingand comparing risks of polycyclic aromatic hydrocarbons in a Tianjin wastewater-irrigatedarea. *Environ. Res.* 90, 201–206.

- [72] Wang, Z., Chen, J., Yang, P., Qiao, X., & Tian, F. (2007). Polycyclic aromatic hydrocarbons in Dalian soils, distribution and toxicity assessment: *Journal of Environmental Monitoring*, 9, 199-204.
- [73] Wang, Z., Chen, J., Yang, P., Tian, F., Qiao, X., Bian, H., & Ge, L. (2009). Distribution of PAHs in pine (*Pinusthunbergii*) needles and soils correlates with their gas particle partitioning: *Environmental Science and Technology*, 43, 1336-1341.
- [74] Wang, Y., Li, P., Li, H., Liu, X., & Wang, W. (2010). PAHs distribution in precipitation at Mount Taishan China. Identification of sources and meteorological influence: *Atmospheric Research*, 95, 1-7.
- [75] Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., &Sylvestre, S.
  (2002). PAHs in the Fraser River basin: a critical appraisal of PAH ratiosasindicatorsof PAH source and composition: *Organic Geochemistry*, 33, 489–515.
- [76] Zakaria, M. P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E., &Kumata, H. (2002). Distribution of polycyclic aromatic hydrocarbons (PAHs) inriversandestuaries in Malaysia: *Environmental science & technology*, 36(9), 1907-1918.

- [77] Zhang, W., Zhang, S., Wan, C., Yue, D., Ye, Y., & Wang, X., (2008). Source diagnostics of polycyclic aromatic hydrocarbons in urban road runoff, dust, rain and canopy through fall: *Environmental Pollution*, 153, 594-601.
- [78] Zhang, X.L., Tao, S., Liu, W.X., Yang, Y., Zuo, Q., & Liu, S.Z., (2005). Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios, a multimedia approach: *Environmental Science and Technology*, 39, 9109-9114.
- [79] Zhang, X.X., Cheng, S.P., Zhu, C.J., & Sun, S.L., (2006). Microbial PAH-Degradation in soil, degradation pathways and contributing factors: *Pedosphere 16*,555-565.
- [80] Zhao, J., Zhang, F., Chen, J., & Xu, Y., (2010). Characterization of polycyclic aromatic hydrocarbons and gas/particle partitioning in a coastal city, Xiamen, Southeast China: *Journal of Environmental Science*, 22, 1014-1022.
- [81] Zhao, S. M., Wang, D. W., Li, X. M., Huang, B., Hu, P., & Zhang, L.W.(2014).Distributions, sources and risk assessment of polycyclic aromatic hydrocarbons in surface sediments from Dianchi Lake, China: *Int. J. Environ. Res.* 8, 317–328.