Introduction

Hydrophobic organic contaminants (HOCs) are a class of ubiquitous compounds, which have posed high risk to the human health and ecological systems [1]. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in urban atmospheres [2]. PAHs enter the environment via incomplete combustion of fossil fuels and accidental leakage of petroleum products, and as components of products such as creosote [3]. Due to PAHs carcinogenic activity, they have been included in the European Union (EU) and the Environmental Protection Agency (EPA) priority pollutant lists. Benzo (a) pyrene (BaP) as a marker of the carcinogenic potency of the polycyclic aromatic Hydrocarbons (PAH) mixture [4].

Crude oil is a naturally occurring, unrefined petroleum product composed of hydrocarbon deposits and other organic materials. A type of fossil fuel, crude oil can be refined to produce usable products such as gasoline, diesel and various forms of petrochemicals. It is a non-renewable resource which means that it can't be replaced naturally at the rate we consume it and is therefore a limited resource.

Contamination of soil and ground water by the accidental release of petroleum hydrocarbons (Figure1) is a common problem for drinking water supplies. Soils surrounding crude-oil refineries, fuel storage depots, and wood preservation are some of the more common sites where industrial scale PAH pollution has been detected. The zone where PHC are found as a free phase is designated as the source area revealed that at petroleum spill sites. Marine pollution due to oil spills is one of the most prevalent environmental and economic concerns worldwide.

Transport and distribution of PAHs in the environment are mainly governed by their physicochemical properties. 2 or 4- ringed PAHs are more soluble in water than members with higher molecular weight PAHs (more than rings) and distributed in soil and groundwater more readily. These low molecular weight PAHs may occur in the atmosphere mainly as vapor due to greater values of Henry’s law constant. They are prone to degradation process.
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in the environment. High molecular weight PAHs, due to less water soluble and high lipophilic characters, they mainly adsorb to particles in the environmental compartments [6].

Figure 1. Natural oil seeps, oil spills from boats or platforms, and produced water discharge from oil and gas producing installations as predominantly sources of PAHs in marine environment offshore. (Source: Pampanin and Sydnes [5])

Health Impact of PAHs

PAHs have been recognized as a potential health risk due to their essential chemical stability, high recalcitrance to different types of degradation (Figure 2) and high toxicity to living organisms [7]. PAHs can enter into the interior of cell through fat dissolution, resulting in toxicity and mutation of living things [8].

Figure 2. Metabolism of PAH leading to protein and DNA adducts [9]

Xenobiotics are released into the biosphere, posing significant risk to human health due to their toxicity. Polycyclic aromatic hydrocarbons (PAHs) from natural and/or anthropogenic sources are characterized by their teratogenic (agents that causes malfunctioning of embryo), mutagenic and carcinogenic properties [10, 11]. The United States Environmental Protection Agency (USEPA) lists 16 kinds of PAHs as priority pollutants [12]. Ogoko [13], evaluated PAH levels, total petroleum hydrocarbons and some toxic metals in soils of petroleum cooperation depot in Aba Metropolis, Nigeria. Results of analysis of PAH sand TPH ranged from 6.30 to 7.40 mg/kg and 5120.50 to 24902.23 mg/kg respectively. Investigating PAHs in obviously contaminated water and soil samples around the Nigerian oil rich regions is ongoing [13, 14, 15, 16, 17]

This present research is aimed at the analysis of polycyclic aromatic hydrocarbons (PAHs) in water samples from regions around the derricks of Ese-odo crude oil offshore. Compilation of a baseline data on PAHs in water samples in Ese-odo area of Ondo state as part of Niger Delta region in Nigeria, for the knowledge of the pre-exploitation and the use of local refineries status of the PAHs in the area which will thus provide reference data that are essential in monitoring the extent of contamination by toxic substances.

Materials and Methods

Materials used and methods applied in this work are in line with current research standard. Commercial PAHs standard containing the 15 out of 16 US EPA PAHs including: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo [b] fluoranthene, benzo [a] pyrene and benzo [ghi] perylene among others were supplied by Sigma Aldrich, USA and delivered by Bristol Scientific, Lagos.
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Sites Description and Sampling

Ese – Odo Local Government Area of Ondo state, blessed with crude oil, hence, Niger Delta Region in Nigeria lies along the Atlantic coaster of Nigeria with geographical coordinated, longitudes 4°85’0” East and 5° 95’0” East and latitude 6° 30’0”North and 6°60’0” North) Population; 187,000, occupation; farming. Minimum temperature is 24 °C and the maximum around 33 °C. Major treat is lack of portable water as linked to peculiarity of the crude oil exploration. Sampling was carried out during rainy season in accordance with methods described by elsewhere[15,18]. Collection of water samples was made at around derricks (frameworks constructed over oil wells for purpose of borring and lowering pipes) of petroleum extraction in NNPC/CHEVRON Opuekeba utility platform in Awoye (Figure 3). Focus for sample collection was at the surface of the water; under, upstream and downstream of the derricks at a distance of about 100 m, 200 m, 300 m apart, using sterilized 2.5 L reagent bottles. The sites geo-location was conducted with Global Positioning System (GPS) and presented in Table 1.

Table 1. Description of Sample and Sample Locations

<table>
<thead>
<tr>
<th>S/N</th>
<th>Geographical Coordinates</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.003644, 5.042882</td>
<td>Water sample from under the oil derrick</td>
</tr>
<tr>
<td>2</td>
<td>6.004025, 5.043333</td>
<td>100 m upstream of the derrick</td>
</tr>
<tr>
<td>3</td>
<td>6.021338, 5.048928</td>
<td>200 m upstream of the derrick</td>
</tr>
<tr>
<td>4</td>
<td>5.914700, 4.977753</td>
<td>300 m upstream of the derrick</td>
</tr>
<tr>
<td>5</td>
<td>6.007336, 5.466737</td>
<td>100 m downstream of the derrick</td>
</tr>
<tr>
<td>6</td>
<td>6.045267, 5.051112</td>
<td>200 m downstream of the derrick</td>
</tr>
<tr>
<td>7</td>
<td>5.887900, 4.887798</td>
<td>300 m downstream of the derrick</td>
</tr>
</tbody>
</table>

Samples Treatment

Samples were preserved with 2 mL of hydrochloric acid and the amber reagent bottles, to render inactive any microorganism that may cause biodegradation of the samples. Bottles containing samples were wrapped with aluminum foil to prevent contamination and transported to the laboratory and stored at 4 °C [18].
Preparation of Water Samples

The standard PAHs (1000 ppm) were run on the GC-MS to calibrate the instrument prior to GC-MS quantification. The GC-MS chromatogram of the standard was presented as Figure 4.

Figure 4. GC-MS Chromatogram of PAHs Standards

Extraction

The preserved water samples were homogenized, extracted by liquid-liquid extraction method [17,19] and concentrated. A 150-mL water sample was transferred to a 250-mL separating funnel, and 9 mL of dichloromethane was added. The separating funnel was shaken for a period of 2 min, and the organic layer was separated and collected in a 50-mL flat-bottomed flask containing 2 g of anhydrous sodium sulfate. The extraction step was repeated twice, and the resulting extracts were combined. The combined extract was concentrated to near dryness using rotary evaporator, transferred into amber vial and kept in the refrigerator analyses [19].

Clean up

The water extracts containing the organic (PAH) layer was purified by silica gel column chromatography. Each extract was loaded onto the column and eluted with dichloromethane. The first 1.0 mL of eluate was discarded and then 5.0 mL of eluate was collected into amber vial and kept in the refrigerator for analyses [16,17,20].

GC-MS Conditioning

An Agilent Technologies GC-MS comprises of 7890A gas chromatography and MS 5975C mass spectrometer detector was used in this study. The instrument comprises a column thickness of 0.25 µm and Helium as carrier gas at the rate of 1 mL/min. temperature programme of initial temperature at 60 ºC hold for 0.5 mins then ramp to 240 ºC at the rate of 10 ºC/min to final temperature at 300 ºC hold for 6 mins [16,17].

Sample Characterization

Among the fifteen out of sixteen US Environmental Protection Agency (USEPA) priority PAHs analyzed are Naphthalene (NAP), Acenaphthene (ACE), Fluorene (FLR), Phenanthrene (PHE), Fluoranthene (FLT), Pyrene (PYR), Benzo [a] anthracene (BaA), Benzo [b] fluoranthene (BbFA), Benzo [a] pyrene (BaP), Dibenz [a,h] anthracene (DBahA), Benzo [g,h,i] perylene (BghiP), and Indenol [1,2,3-cd]pyrene (IP). The water extract was analyzed for the listed PAHs using gas chromatography coupled with mass spectroscopy (GC-MS) for both qualitative and quantitative analyses. Similar instrumentation was earlier documented [21].

RESULTS AND DISCUSSION

Figure 4 is the GC-MS chromatogram of the water extract showing detected PAHs. Quantitative data revealed the result for each of the available PAHs as presented in Table 2. The results show the mean concentrations, sum of concentration, percent abundance and ratios of PAHs in water sample during wet season (July, 2018). Results of analysis showed values of PAHs in the ppm or mg/kg range. This agrees
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with the early findings [13], wherein the evaluated PAH levels in soils of petroleum cooperation depot in Aba metropolis, Nigeria, ranged from 6.30 to 7.40 mg/kg. Higher range estimated in this study could be linked to mixed origin of the PAHs, combining oil wells as well as anthropogenic and petrogenic activities. Overall, water sample from Ese-Odo offshore area as at the time of the research was evidently contaminated and could drift to household water bodies if not properly managed.

From Table 2, The ring-wise trend of PAHs prevalence is evident. It is observed that the $\Sigma_4$ ring PAHs are the most dominant PAH compounds with concentration of 174.55 ppm (45.81%). Pyrene (3.695%) and Benz[a]anthracene (0.488%) are least in the group. Next in the frequency trend is the two membered ring with values of $\Sigma_2$ ring PAHs = 106.79 ppm followed by $\Sigma_3$ ring PAHs; 74.45 ppm (19.54%) > $\Sigma_5$ ring PAHs; 22.53 ppm (5.91%) and the least dominant is the six membered rings reported as $\Sigma_6$ ring PAHs; 2.74 ppm (0.72%). The low values obtained for the six membered ring corroborates with similar report [5], wherein the data obtained from offshore oil production platforms in the north sea have showed that the major aromatic compounds are benzene, toluene, ethylbenzene and xylene (97%), 2- and 3-ring PAHs (3%) while naphthalenes, phenanthrenes and dibenzothiophenes and larger PAHs (<0.2%).

From Figures 6 and 7, the estimated concentrations of the $\Sigma_{LP}$PAHs; 355.79 ppm (93.35%) is more than 14 times the values for $\Sigma_{HP}$PAHs; 25.27 ppm (6.65%). This further supports documented opinion [6], which stated...
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that the 2 or 4- ringed LPAHs are more soluble in water than members with higher molecular weight HPAHs (4 or more rings) and distributed in soil and groundwater more readily. By implication, dominance of LPAHs over HPAHs could be linked to low level of high density of diesel and biomass combustion that are responsible for HPAHs [22,23].

Figure 6. Levels of PAHs (ppm) in Ese-Odo Offshore Crude oil Contaminated water

PAH prevalence was presented as percent abundance in Figure 6. It is evidence that higher values obtained are predominantly for low molecular weight (LMW) PAHs. The 4-ring structures PAHs are dominant while the five membered ring Benzo[a]pyrene (0.54%), to the six membered ring, Benzo [ghi] perylene (0.55%) to Indeno[1,2,3-ed]pyrene (0.17%) of high molecular weight (HMW) presented low values that are also within contamination level.

Figure 7. Abundance (%) of PAHs in Ese-Odo Offshore Crude oil Contaminated water

PAH Source Identification

By generalizations, The probable sources of environmental PAHs could be evaluated using ratio of different PAHs compounds [22] as presented in Table 3. Petrogenic contamination is characterized by the predominance of the lower-molecular-weight (LPAHs). 2-4 membered ring PAH have high volatility and are easily drifted from one point to another point of impact. They are non-point source pollutants. The risk from mobility of HPAHs is less owing to the heavier weight of such PAHs. This is
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linked to their low volatility and slow transport rate. It could be generalized rather than mere suggestion that contamination of Ese-Odo offshore waters by PAHs is of petrogenic origin. It is worth of note that Petrogenic sources of PAHs containing HPAHs resulted from geochemical alteration of organic matter from petroleum spills, bitumen seepages, coal fired plants and municipal sewage treatment facilities. Pyrolytic contribution generated mainly through incomplete combustion of organic matter at carbonation temperatures (within 400 degrees) characterized by high–molecular-weight PAHs 5-6 benzene ring is low in the study area.

Table 3. Diagnostic ratio of PAHs (Adopted [24,25] current study)

<table>
<thead>
<tr>
<th>PAHs Ratio</th>
<th>value</th>
<th>Origin (source)</th>
<th>PAH source of Study area</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHEn/ANth</td>
<td>&lt;10</td>
<td>Petrogenic</td>
<td>NA</td>
</tr>
<tr>
<td>PHEn/ANth</td>
<td>&gt;10</td>
<td>Pyrogenic</td>
<td>NA</td>
</tr>
<tr>
<td>LPAH/HPA</td>
<td>&lt;1</td>
<td>Pyrogenic</td>
<td>Petrogenic</td>
</tr>
<tr>
<td>LPAH/HPAH</td>
<td>&gt;1</td>
<td>Petrogenic</td>
<td>Petrogenic</td>
</tr>
<tr>
<td>Pyr&lt;Flth</td>
<td></td>
<td>Pyrogenic</td>
<td>Pyrogenic</td>
</tr>
<tr>
<td>FLth&gt;PYr</td>
<td></td>
<td>Pyrogenic</td>
<td>Pyrogenic</td>
</tr>
<tr>
<td>PYR&lt;FLth</td>
<td>&gt;1</td>
<td>Petrogenic</td>
<td>Pyrogenic</td>
</tr>
<tr>
<td>IPy/IPy+BPer</td>
<td>&gt;0.5</td>
<td>pyrogenic</td>
<td>Petrogenic</td>
</tr>
<tr>
<td>IPy/IPy+BPer</td>
<td>&lt;0.2</td>
<td>Petrogenic</td>
<td>Petrogenic</td>
</tr>
<tr>
<td>BaA/(BaA +Chry)</td>
<td>&lt;0.2</td>
<td>Petrogenic</td>
<td>NA</td>
</tr>
<tr>
<td>ΣLPAH</td>
<td>abundant</td>
<td>Petrogenic</td>
<td>Petrogenic</td>
</tr>
</tbody>
</table>

NA- Not Applicable since ANth and Chrysene ,Chr were not detected

Contrary to the source generalization on petrogenecity, the concentration of pyrene (14.08 ppm) is less compared to that of the fluoranthene (113.16 ppm). This characterizes pyrogenic sources. Hence, source identification could be specific owing to certain distinct parametersorder than generalizing. It could also be deduced that based on the contribution by 4 ringed member PAHs in this study, the source of contamination is pyrogenic. Fluoranthene/pyrene ratio (FLTH/PYR) is 7.18, with fluoranthene having the highest contribution. FLTH is less thermodynamically stable than PYR and a predominance of FLTH over PYR is characteristic of pyrogenic source [24]. Overall, the main (point) source for the PAHs in the area under study is petroleum derived. Values obtained are by implication a reason for concern since transport of these PAHs from regions within the derricks into domestic water could be high. USEPA standard values are as low as 0.0002 mg/L for Benzo[a] pyrene [26] as against 1.73 mg/L reported for BaP in this study. The USEPA Reference Dose (Rd) value for Anthracene is 0.3 mg/kg/day [26]

The high level of pollutants at near offshores is a wakeup call for remediation and other safe ecological measures to avert the contamination of domestic (household) water by these non-point source pollutants

REFERENCES

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