Variations of Polycyclic Aromatic Hydrocarbons in Two Major Rivers of the Soku Oil Field, Rivers State, Nigeria

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Abstract: The Polycyclic Aromatic Hydrocarbons (PAHs) have been shown from previous studies to be present in Crude oil and available records indicate that a total of 6,817 incident crude oil spills occurred between 1976 and 2001 in the study area with a loss of approximately three million barrels of oil, thus there is a need to examine PAHs in the Soku Oil Field. The variations of PAHs in two major rivers (San Bartholomew and Sombrero) of the Soku Oil Field area of Rivers State, Nigeria was determined by sampling surface waters and sediment in four stations (two stations per river) from July 2017 to May 2018. These samples were collected upstream and downstream of the two rivers bimonthly and in duplicates. Temperature °C, Dissolved Oxygen, salinity and pH were measured according to standard methods. PAHs in the surface water and sediment were analyzed by the use of High Pressure Liquid Chromatography-Fluorescence Detection (HPLC-FLD). The PAHs concentrations were grouped intoindividual PAHs, total low molecular weight PAHs (LMWPAHs) and total high molecular weight PAHs (HMWPAHs). The LMWPAHs in water were Acenaphthylene, Acenaphthene, Anthracene and Phenanthrene (from Below Detectable Limit (BDL) - 0.002 mg/l) while the HMWPAHs were Flouranthene, Benz(a)anthracene, Chrysene and Indenol[1,2,3-cd]pyrene (from BDL - 0.004 mg/l). 12 PAHs were found in sediment compared to the 8 found in water. Sediment PAH concentrations were higher than those in water (low mol. wt 17.68 mg/l and high mol wt PAH 7.793 mg/l) with the sediment acting as a sink. The high PAH concentration in sediment may be from accidental spill, discharges from illegal refineries, degeneration of bitumen coated wooden boats and other industrial activities in the area. This study will help other researchers uncover the critical areas of methods of remediation of the study area as well as investigate the health risks from consumption of available aquatic organisms.

Keywords:Niger -Delta, Polycyclic Aromatic Hydrocarbon, San Bartholomew, Sediment Sombrero, Surface water.

Date of Submission: 08-05-2019 2019

Date of acceptance: 23-05-

I. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are highly hydrophobic and organic lipophilic compounds with fused aromatic rings mainly of hydrogen and carbon atoms^{1,2} and has been shown from previous studies^{3,4} to be present in crude oil. Furthermore they are formed from incomplete combustion of coal, diesel oil and gasoline, garbage or other organic substances like tobacco from where they are distributed to the atmosphere, surface waters, soils and sediments^{5,1,6}. These compounds are semi- or non- volatile in nature, non-biodegradable, environmentally persistent and variably structured toxic compounds^{7,8,9}. Anthropogenic sources of PAHs vary widely and are present in a range of environments (e.g. sediment and marine waters) and concentrations depend on past or current industrial operations and thus petroleum, electric power generation, refuse incineration, home heating, production of coke, carbon black, coal tar and asphalt, internal combustion engines, discharges from industrial and waste water treatment plants and oil spills has been implicated as sources¹⁰. However, the fate and transport of PAHs in their environment are controlled by the PAH's hydrophobicity, rate of dissolution, physicochemical properties of the soil or water and the source phase¹¹.

Most studies ^{12,13,14,15,16} have divided PAHs into low – and high – molecular weight compounds. The word 'weight' may however be inappropriate since PAHs are analytically separated by their differential masses, thus the term low and high molecular mass shall be adopted. Generally the two and three benzene ring compounds have low molecular mass while those with four and more aromatic ring compounds have high molecular Mass PAHs (LMWPAHs) occur predominantly in the atmosphere in the vapour phase, where as multi-ringed PAHs are largely bound to particles. Intermediate – Molecular Mass PAHs (IMMPAHs) - four rings- are partitioned between the vapour and particulate phases, depending on the

atmospheric temperature¹⁷. The particle – bound PAHs are considered to be very hazardous to human health. Benzo (a) pyrene is often used as a marker for total exposure to carcinogenic PAHs¹⁸. PAHs with benzene rings less than four are widely distributed and extremely volatile, while those with more than four aromatic rings are less volatile, adsorbed on other combustion particles like soot¹⁵.

The water – soluble LMMPAHs are rapidly degraded in water however, the continuous release of PAHs by wastewater into the aquatic environment can result in elevated concentrations in bivalves and shell fishes grown close to industrial areas and once PAHs reach the sediments, they become somewhat immobile⁴because their non polar structures inhibit them from dissolving in water. PAHs of higher molecular weight are not completely insoluble as some amount of PAH dissolves and becomes included in the pore water where they are bio-available⁴. These in turn are easily transported through the pore spaces of the sediment¹⁹.

Available records^{20,21} show that a total of 6,817 crude oil spills occurred between 1976 and 2001 with a loss of approximately three million barrels of crude oil in the Soku Oil Field area, hence an urgent need to investigate the levels of PAH in the pelagic and benthic systems of this field. Previous studies in the Niger Delta have focused on freshwater systems^{13,22}, surface water and sediment^{12,23,22}, PAHs in biota^{24,25,26,16}, and PAHs in coastal sediment²⁷. However, the common denominator in all these studies is the use of Gas Chromatography to determine PAHs as the nature of these study sites is unlike Soku Oil Field area with over 41 oil wells. The aim of this study was to determine the levels of PAHs in surface water and sediments of the major estuaries / riverswithin the Soku Oil Field, to define whether their concentrations are within acceptable limits and estimate their ecological risk nevertheless, it is hoped that this investigation provides baseline information for scientific research and propositions for environmental safety

II. Materials And Methods

2.1.Study Area

Soku Oil Field is situated between the co-ordinates of 04°61'21.9" E and 07°28'58.08"N and 04°63'52.21"E and 07°20'48.34" in Soku, Akuku Toru Local Government Area, Rivers State, Nigeria.It is characterized by heavy rainfall occurring between April to October ranging from 2000 to 2500 mm and the relief is lowland with an average elevation of not more than 5 m above sea level²⁷. The Soku Oil Fieldhas several oil and gas industrial facilities, these include gas and oil wells, flow stations, gas plant, gas flaring sites, andthe area is also ladened with condemned oil and gas pipelines. Some settlements around the oil field are Elem-Sangama, Etukukiri, Russiakiri, Ijawkiri, Ekulama which are separated by smaller creeks. Two major estuaries/rivers transcend this field –namely, San Bartholomew and Sombrero. The Soku Oil Field and associated Gas Plant is one of the major oil field facilities discovered and exploited after Oloibiri Oil Field in Rivers State, Niger Delta, Nigeria. The facility supplies the bulk of the gas to Nigeria Liquified Natural Gas (NLNG) at Finima, Bonny²⁰. The area has suffered long term accidental discharges and spillages of hazardous substances (industrial wastes/effluents, raw materials, chemicals, crude oil and refined petroleum products). Other activities include dredging, and transportation by outboard engine boats. The vegetation is typically a mangrove intertidal forest and the major occupation of the rural dwellers is fishing.

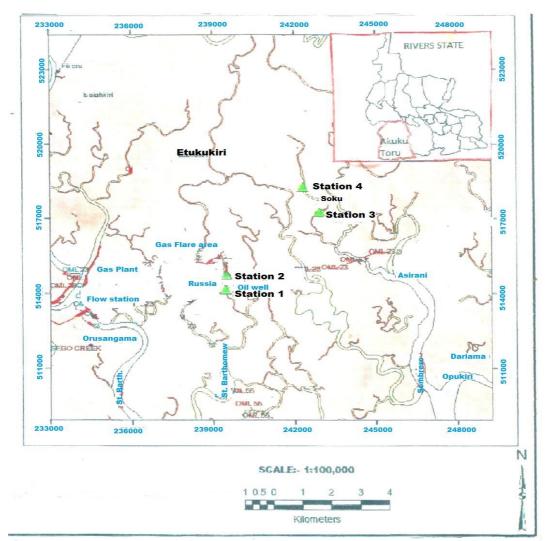


Fig. 1. Map of Study area showing Sampling Stations 1-4(Green triangles in the Map)Source: Office of Surveyor General, Port Harcourt, Rivers State

2.2. Sampling Stations and Design

Four sampling stations (Fig 1) - station 1 and 2 from the tributaries of San Bartholomew and stations 3 and 4 from Sombrero River - were established on the basis of up and downstreams of the point source. Station 1 situated at the co-ordinates of 4.6529°N and 6.66648°E was behind a multi-national Company's platform (oil well No. 015 and 037) withoil and gas pipe lines. Theleaks from pump valves on the oil wells and precipitation of flared gases were main sources of anthropogenic pollutants on the downstream flow. Station 2 with co-ordinates (4.6633°N and 6.65979°E) was 1.0 km away from Station 1 on the up stream direction, is at a rural settlement called Russiakiri where sources of pollutants include runoffs from surrounding oil wells, domestic and human wastes, and the precipitation from flared gases. Station 3 with co-ordinate (4.68135°N and 6.68059°E) which is 1.5 km away from station 1 is by Soku Community sand fill with dredging activities, domestic wastes, and untreated sewage from human and out board engine boat transportation activities as sources of pollution. Station 4 with co-ordinates (4.7014°N and 6.67727°E) was before Soku Community, a distance of 2 km away from the community with minimal human activities which served as control.

2.3 Collection of Surface Water

500ml amber glass bottles with fitted screw caps were used to collect water for laboratory analysis in replicates from each station. The sample containers were washed and rinsed twice with the water at specific sampling spots before collection of the samples. Generally, the water samples were collected by lowering the containers by hand to about 20cm below the water surface level and the bottles/containers were completely immersed before opening, allowed to fill and corked under water²⁸. Physico-chemimical parameters such as pH, conductivity, salinity and turbidity were measured in situ using Hanna multi-parameter (HI 9829 model) probe,

Mercury in – glass thermometer was used for temperature readings and Oxygen meter(YSI 54A) was used for the measurement of dissolved oxygen and biochemical oxygen Demand.

2.4. Laboratory Analysis of PAH inSurface Water

PAHs of the surface water were analyzed by the use of High Pressure Liquid Chromatography-Fluorescence Detection (HPLC-FLD). All glass wares used were thoroughly washed with hot water, rinsed with distilled water and dried for 60minutes at 180°C. 50ml of the water sample was filtered and passed through extraction column with flow rate of 2ml/min. Suspended PAHs were eluted off extraction column using Dichloro –methane solvent. The concentrated sample was collected in a small dark isolated glass container, kept in the refrigerator at 4°C and taken to the laboratory for analysis using a HPLC-FLD and recorded in mg/l.

2.5 Collection and Analysis of PAH from Littoral Sediment.

Sediments samples were collected randomly from three spots per location at low tide. The sediments were excavated to a depth of 4-5cm into plastic buckets. The sample was thoroughly mixed forming a 1:1 sediment to water slurrywhere pH, temperature and conductivity were measured and some representative quantities sub sampled into labeled 500ml amber bottles and taken to the laboratory. The sediment samples were air dried at room temperature in the laboratory, crushed to fine texture in a porcelain mortar, repackaged in labeled aluminium foils for PAHs analysis. 10 gof the homogenized sample was mixed with anhydrous 20g of Na₂SO₄and 20 mls of Di-chloromethane was added. The sample extraction was with Na₂SO₄ and Di-chloromethane solvent and the supernatant was used for PAHs analysis on HPLC-FLD²⁹. Replicate analysis was done from each of the samples and values recorded in mg/kg.

2.6Statistical Analysisand Ecological Risk Assessment

Statistical analysis to interpret the results include descriptive statistics, comparison of means using ANOVA, Separation of means, Piecharts and line graphs using EXCEL computer package and JMP statistical software. Confidence interval was 95%. The Risk Quotient (RQ) of PAH in surface water and sediment was used as a tool to characterise PAH risk to the ecosystem^{30,31}. A formula originally proposed by Kalf³² and applied by $Li^{33,34,35}$ was adopted. The formulae were:

$RQ = C_{PAH}/C_{OV}$ (Generalized Equation) —	
$RQ_{NCs} = C_{PAH}/C_{OV(NCs)}$	(2)
$RQ_{MPCs} = C_{PAH}/C_{OV(MPCs)}$	(3)
Where:	

 RQ_{NCs} = Risk Quotient of Negligible Concentrations in the medium, C_{PAH} = Concentration of individual PAHs. $C_{QV(NCs)}$ = Quality Values of the Negligible Concentration in the medium, RQ_{MPCs} = Risk Quotient of Maximum Permissible Concentration in the medium. $C_{QV(MPCs)}$ = Quality Value of the Maximum Permissible Concentration.

An RQ_{NCs} < 1 indicates that the single PAH might be of negligible concernwhile an RQ_{NCs} > 1 indicates that the contamination of the single PAH was of moderate riskand an RQ_{MPCs} < 1 showed that contamination was of moderate level, nevertheless RQ_{MPCs} >1 indicates that contamination of that single PAH might pose a high risk.

III.Results

3.1 PAHs in Surface Water .

Table 1 shows the mean individuals PAHs in surface water and their quality values and RQ. The LMWPAHs in surface water were Acenaphthylene, Acenaphthene, Anthracene and Phenanthrene with a mean concentration of 0.001 ± 0.0003 mg/L and range from Below Detectable Limit (BDL) – 0.002 mg/L (Table 1). Only four HMWPAHs (Fluoranthene, Benz[a] anthracene, Chrysene and Indeno[1,2,3-cd]pyrene) were detected with a mean concentration of 0.004 ± 0.0005 mg/L. The concentrations of both the low and high molecular PAHs were generally higher in the wet season (Figs 2 and 3). The mean concentration of individual PAHs are presented in Table 1 with their estimated RQ. Acenaphthylene and Indeno (1,2,3-cd) pyrene had RQ > 1, the others were <1.

PAH Compounds	SurfaceWater (mg/l)	*Recommended NC (mg/l).	*Recommended MPC (mg/l)	Calculated RQ(NC)	Calculated RQ(MPC)
Acenaphthylene	0.001	0.0007	0.07	1.43	0.014
Acenaphthene	0.00013	0.0007	0.07	0.19	0.002
Phenanthrene	0.0002	0.003	0.30	0.07	0.001
Anthracene	0.00044	0.0007	0.07	0.63	0.006
Fluoranthene	0.00052	0.003	0.30	0.17	0.002
Chrysene	0.00027	0.0034	0.34	0.08	0.001
Benz (a) anthracene	0.00009	0.0001	0.01	0.9	0.009
Indeno (1,2,3-cd) pyrene	0.003	0.0004	0.04	7.5	0.080
ΣLMMPAH	0.00177			1.43	
ΣΗΜΜΡΑΗ	0.00388			7.50	
Ratio of LMMPAH/HMMPAH	0.25				

 Table 1. Concentrations of PAHs in water and their Risk Quotients(RQ)

 $\Sigma LMMPAH = Summation Low molecular mass PAH, \Sigma HMMPAH = Summation High molecular mass PAH. Only <math>RQ_{NCs}$ and $RQ_{MPCs} \ge 1$ were summed for $\Sigma LPAH$ and $\Sigma HPAH$ respectively NC = Negligible concentration, MPC = Mean permissible concentration * **Cao et al., 2010**

Fig. 2 shows the seasonal variation of mean Low Molecular Mass PAHs (LMMPAHs) in the study area. PAHs found in both seasons were Acenapthylene, Acenapthhene, Phenanthrene, and Anthracene, however PAHs were higher in wet season than in dry season. The concentration of Acenapthylene was the highest in wet season than in dry season. A similar trend was observed with the other PAHs.

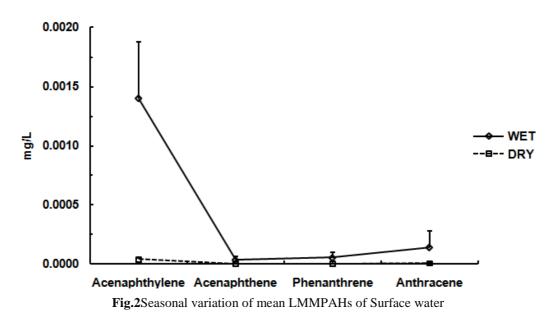


Fig. 3 shows the seasonal variation of High Molecular Mass PAHs (LMMPAHs) in the study area. PAHs found in both seasons were Fluoranthene, Benz[a]anthracene, Chrysene, and Indeno[1,2,3-cd]pyrene, however PAHs were also higher in wet season than in dry season. The concentration of Indeno[1,2,3-cd]pyrene was the highest in wet season than in dry season. A similar trend was observed with the other PAHs.

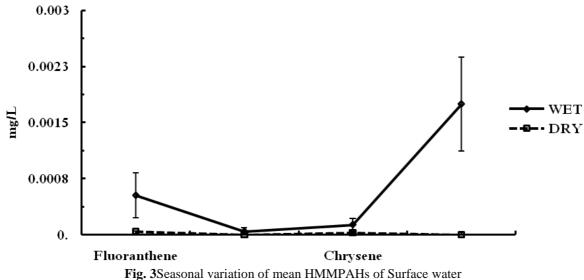


Fig. 3Seasonal variation of mean HMMPAHs of

3.2 PAHs in Sediment

Table 2 shows the mean concentration of individual PAHs, their respective quality values and Risk Quotients (RQ). The total concentration of LMWPAHwas9.17 mg/kg andHMWPAH was 3.51 mg/kg. Only six PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Flourene, Pyrene and anthracene) were above recommended Minimum Permissible Concentration (MPC) with $RQ_{MPC} > 1$, while all the detected 12 PAHs had $RQ_{NC} > 1$.

PAH Compounds	Sediment (mg/Kg)	*Recommended NC (mg/Kg)	*Recommended MPC (mg/Kg)	Calculated RQ _{NC}	Calculated RQ _{MPC}
Naphthalene	2.57	0.0014	0.14	1,835.71	18.36
Acenaphthylene	1.84	0.0012	0.12	1,533.33	15.33
Acenaphthene	1.47	0.0012	0.12	1,225	12.25
Fluorene	0.94	0.0012	0.12	783.33	7.83
Phenanthrene	0.38	0.0051	0.51	74.51	0.75
Anthracene	1.97	0.0012	0.12	1,641.67	16.42
Fluoranthene	0.53	0.0260	2.6	20.38	0.20
Pyrene	0.19	0.0012	0.12	158.33	1.58
Chrysene	0.76	0.1070	10.7	7.10	0.07
Benz (a) anthracene	0.30	0.0036	0.36	83.33	0.83
Dibenz (a,h) anthracene	0.17	0.0270	2.70	6.30	0.06
Indeno (1,2,3-cd) pyrene	1.56	0.0590	5.90	26.44	0.26
ΣLMMPAH	9.17			7093.55	70.19
ΣΗΜΜΡΑΗ	3.51			301.88	1.53

 Table 2 Concentration of PAHs in Sediment, their Quality values and Risk Quotients(RQ)

 $\Sigma LMMPAH = Summation Low molecular mass PAH, \Sigma HMMPAH = Summation High molecular mass PAH. Only <math>RQ_{NCs}$ and $RQ_{MPCs} \ge 1$ were summed for $\Sigma LPAH$ and $\Sigma HPAH$ respectively NC = Negligible concentration, MPC = Mean permissible concentration. * Cao et al. (2010)

Fig. 4 shows the percentage concentration of low and high molecular mass PAHs in sediments. 72 % of PAHs in the sediment consisted of High Molecular Mass PAHs while 28% consisted of Low Molecular Mass PAHs.

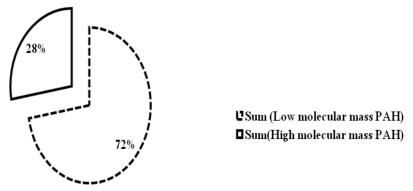


Fig. 4. Percentage concentration of Low and High Molecular Mass PAHs in sediment

Fig. 5 shows the seasonal variations in low molecular mass PAHs in the sediment, which was observed to be Naphthalene, Acenaphthylene, Acenaphthene, Flourene, Anthracene and Phenanthrene. Their concentrations in dry season were higher than in wet season except for Acenaphthylene.

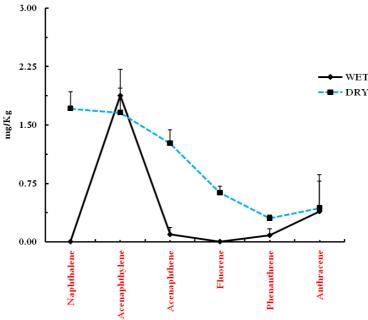


Fig. 5Seasonal variation of LMMPAHs in sediment

Fig. 6 shows the seasonal variations of the high molecular mass PAHs in sediment, and those detected were Flouranthene, Pyrene, Chrysene, Benz[a]anthracene, Dibenz[a,h]anthracene and Indeno[1,2,3,cd]pyrene. These PAHs were higher in wet season except for Pyrene while Benz[a]anthracene and Dibenz[a,h]anthracene had similar concentrations in both seasons.

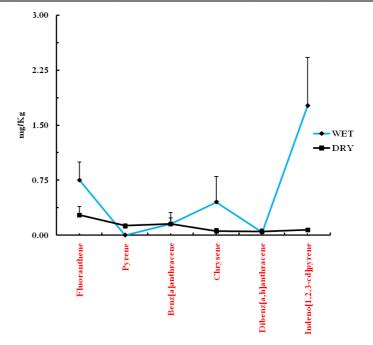


Fig.6Seasonal variation of HMMPAHs in sediment

Fig. 7 confirms the spatial variation of the 12 PAH compounds detected in the sediments of the various stations, they include Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Anthracene, Phenanthrene, Fluoranthene, Pyrene, Chrysene, Benz[a]anthracene, Dibenz[a,h]anthracene and Indeno[1,2,3-cd]pyrene. However, in station 1, ten PAHs were detected, in Station 2, eleven PAHs were detected while in station 3 and 4, nine and eleven PAHs were detected respectively.

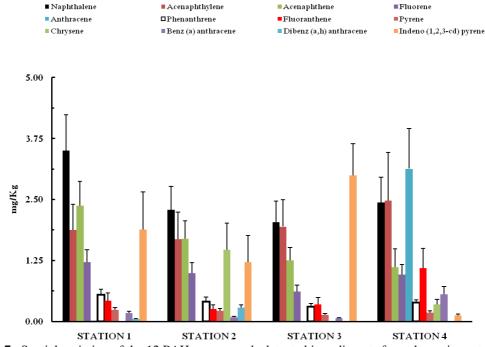


Fig. 7. Spatial variation of the 12 PAHs compounds detected in sediments from the various stations.

Fig. 8 shows the seasonal variations of the 12 PAH compounds detected in the sediments. The following PAH compounds were detected during the dry season - Naphthalene, Fluorene, and Pyrene, with Naphthalene having the highest concentration and Pyrene the lowest. Other PAHs were detected in dry and wet seasons but occurring at different concentrations, for instance, Acenaphthylene, Acenaphthene and Dibenz[a,h]anthracene, amongst others, were detected in both seasons with Acenaphthylene having high

concentrations and Dibenz[a,h]anthracene having the least concentration. Similar pattern may be used to understand other PAH variations in both seasons.

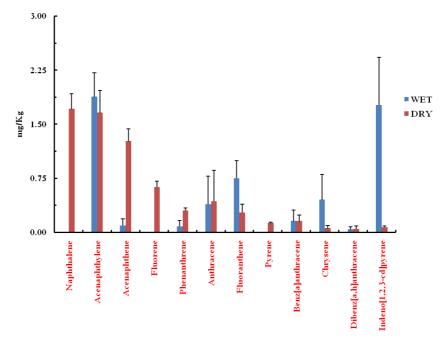


Fig. 8 Seasonal variation of the 12 PAHs compounds detected in sediment from the study area

IV. Discussion

PAHs in soot and atmospheric particles can settle on the surface of lakes, streams, rivers and oceans by dry or wet deposition. They are thereby dispersed by currents and eventually become integrated with the sediment. Eight out of the 16 PAHs investigated in the study were detected in surface water. The low molecular weight compounds were four (Acenaphthylene, Acenaphthene, Anthracene and Phenanthrene) as well as the high molecular mass compounds (Fluoranthene, Benz[a]anthracene, Chrysene and Indeno[1,2,3-cd]pyrene). The mean concentration of total PAHs in surface water was 1.38E-03 mg/L much higher than 3.4E-05 mg/L reported for Ubeji, Warri River by Asagbra¹⁶. The results are not in agreement with the lower values expected of high molecular weight compounds in the surface water due to their relatively high affinity to sorb to particulate matter as reported by^{36 & 37}. The high molecular mass congeners are lipophilic and are not easily soluble to be proportionally available as the low molecular weight congeners. Hence their availability in the surface water as high as 69% may be as a result of frequent strong turbulence or mixing of surface water by commercial outboard engine operators and tidal flow. The source of PAH in Soku Oil Field could be attributed to the waste from the use of bitumen in wooden boat constructions and engine exhaust, atmospheric deposition and surface runoff from domestic waste. A ratio of LMMPAH to HMMPAH of less than one (< 1) indicates a pollution source of pyrogenic origin and greater than one (> 1) suggests a pollution source from petrogenic origin^{38,39,40}. The result of this study (0.25) showed pollution sources for surface water were from pyrogenic origin.

PAHs profile in the sediment was dominated by the low molecular weight congeners. The sum of all the individual congeners of the low molecular mass was 17.689mg/kg while the high molecular mass recorded a sum total of 7.793mg/kg. The ratio of low to high molecular weight of PAH was 2.27 suggesting that the pollution source for sediment was petrogenic. Indeno[1,2,3-cd]pyrene made up 47% of the high molecular mass PAHs while Acenaphthylene was 42% of the low molecular weight PAHs. This high value could be attributed to accidental discharge by illegal refining of crude oil and other oil related industrial activities. The result of total PAH in sediment is comparable with the records of 27.10-55.93mg/kg reported by⁴¹ in Vhembe, South Africa. Twelve PAHs compounds were detected in the sediment as against the eight in the surface water confirming sediment as a sink in an aquatic environment.

The ecological risk assessment of PAHs in surface water indicated that contamination of Acenaphthylene and Indeno[1,2,3-cd]pyrene were individually of moderate risk while all other PAHs compounds detected in the study might be of negligible concern. In the sediment, all the low molecular weight PAHs recorded $RQ_{(NCs)}$ > 1 and $RQ_{(MPCs)}$ > 1 with the exception of phenanthrene. These however indicated that the

contamination of each PAH in all the low molecular weight PAHs compounds except Phenanthrene might pose a high risk while Phenanthrene indicated a moderate risk level. All the HMMPAHs in sediment recorded $RQ_{(NCs)}>1$ while the $RQ_{(MPCs)}$ were <1 except for Pyrene. This is indicative of the contamination level of PAHs in the sediment ranging from moderate to high risk. Baumard⁴²has classified PAH pollution levels in terms of total PAH concentration as follows; Low(0- 0.1mg/kg), Moderate(0.1-1.0mg/kg), High(1.0-5.0mg/kg) and Very High(>5.0mg/kg). Based on this classification, the current study showed a PAH pollution of low to very high and could be comparable with the report from ^{35,43}. The total PAH concentration in sediment was higher than those reported by Dosunmu⁴⁴ from Imo river sediment of the Niger Delta area. However, the surface water PAHs was lower than that reported by⁴⁵.

V. Conclusion

The Soku Oil Field has a host of influences from illegal refining of crude oil, outboard engine spills from petroleum oil and exhaust releases, industrial and human activities. The following were conclusions from the investigations; PAHs compounds were divided into low and high molecular mass of which eight and twelve congeners were detected in surface water and sediments respectively. In surface water there were 4 LMMPAH and 4 HMMPAH. Based on their ratio the origin of the PAH could be said to be pyrogenic. Acenaphthylene and Indeno[1,2,3-cd]pyrene indicated moderate risk as others were of negligible concern. Ecological risk assessment showed high contamination levelin the sediment with $RQ_{(NCs)}$ and $RQ_{(MPCs)} > 1$. The origin of sediment PAH was petrogenic probably from spills from the illegal refineries and other oil related activities in the area. This study discovered a moderate to high concentration of PAHs in the surface water and sediment of Soku Oil Field that could pose a threat or health risk to benthos and humans through food chain as they may ingest and bio-accumulate these chemicals from the environment. This study will help other researchers uncover the critical areas of methods of remediation of the study area as well as investigate the health risks from consumption of pelagic and benthic aquatic organisms.

Author's contribution: APU and EIKE wrote the protocol, OU did the field work, analysis and interpretation of data, BKNO, OU and APU wrote the first and final draft of the manuscript.

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