



World Scientific News

An International Scientific Journal

WSN 187 (2024) 31-46

EISSN 2392-2192

Levels, Profiles, and Sources of Total Petroleum Hydrocarbons (TPHs) in Sediments of the Aba River at Ogbor-Hill Region, South-Eastern, Nigeria

Augustine Avwerosuo Chokor

Department of Chemistry, Faculty of Science, Federal University Otuoke, Bayelsa State, Nigeria

E-mail address: chokoraa@fuotuoke.edu.ng

ABSTRACT

The levels and sources of total petroleum hydrocarbons in sediments of the Aba River at Ogbor Hill Region, South-Eastern Nigeria, were assessed in this study. Five (5) composite samples taken at different stations viz: ST-A, ST-B, ST-C, ST-D, and ST-E were extracted with dichloromethane (DCM) using Soxhlet extractor. This was followed by a silica gel clean up and n-hexane elution from a chromatographic column, to obtain the aliphatic fraction of hydrocarbons. Analyses of the aliphatic fractions were done with gas chromatography-flame ionization detector (GC-FID). The total concentrations of n-alkanes (ranging from C₈ – C₄₀) and the unresolved complex mixture (UCM) gave the total petroleum hydrocarbons (TPHs) concentrations that ranged from 41.5378 - 183.798 mg/Kg, with an average value of 85.877±60.41 mg/Kg. The average value was slightly higher than the 50 mg/Kg target value established by the Nigerian Department of Petroleum Resources (DPR) but was much lower than the intervention value (5,000 mg/Kg) set by the same body. Most of the stations also had their C₉ – C₁₈, and C₁₉ – C₃₆ fractions lower than the sediment benchmark values recommended by the Massachusetts Department of Environmental Protection (MADEP) for aliphatic fractions. Some source diagnostic ratios revealed that large portion of the hydrocarbons were from biogenic sources that were predominantly terrestrial. The carbon preference index (CPI) and the even to odd numbered alkanes ratio (E/O) however, gave much credence to contributions from anthropogenic petroleum inputs; enacting the mixed origin nature of the hydrocarbons source. Precautionary measures that will mitigate these anthropogenic inputs are necessary to sustain benthic lives and preserve human health.

Keywords: ecological risk, hydrocarbons pollution, Aba River, Sediment' benchmark, source diagnostic ratio, biogenic, anthropogenic

1. INTRODUCTION

The release of hydrocarbons contaminants into the environment of the oil bearing States of Nigeria has been a serious problem since the discovery of oil in these regions. Petroleum hydrocarbons have often accumulated in river sediments due to industrial, automobile and oil related activities; and have posed serious risks to the environment and public health. Oil related industrial development and operations including leakages from oil exploratory activities, refinery, tank farms, and pipelines constitute major source of oil pollution in the coastal environment [1]. Leakages from vessels and ships as well as indiscriminate dumping of petroleum products on water ways also contribute to pollution of water bodies. Other anthropogenic source of petroleum hydrocarbons in water bodies include: sewage, municipal and industrial discharges, automobile wastes and vehicular emission arising from incomplete combustion brought down by rain, carried by runoff and brought down to water bodies [2-3]. Oil spills often results in ecosystem damage and threat to public health. The effect which is usually a function of time, place, toxicity and concentrations of the spilled oil could lead to reduced reproduction, decreased growth rate, impairment of feeding mechanisms, diminished defence capacity against diseases and eventual death of various organisms [1-2, 4]. The ingestions of contaminated foods arising from bioaccumulation through the food chain is one major way that higher organisms and humans can get exposed to contaminated sediments. Exposure to petroleum hydrocarbons can lead to variety of problems including: infertility, birth defects, impaired development, disruptions in activities of various body organs, damage to the immune system, disruptions of hormonal functions and cancer [2-3, 5-9]. Sea foods consumption might constitute a pathway to hydrocarbons contaminations of human due to pollutions of water bodies. Therefore, to protect public health, the monitoring and assessment of these contaminants in water and sediments are necessary.

Aliphatic hydrocarbons include straight chain alkanes, branched chain alkanes, cycloalkanes and isoprenoids compounds. It is because of the large inclusiveness - being made up several hundreds of compounds that are difficult to measure separately - that the term Total Petroleum Hydrocarbons (TPHs) is used as a gross parameter for their measurement and quantifications [3]. Their presence in sediments could originate from petrogenic or natural source. Natural sources include inputs from: terrestrial plant waxes, marine phytoplankton, volcanic eruptions, biomass combustion, and natural oil seeps [10]. Though hydrocarbons are found naturally in the environment, large amount of it in a contaminated environment comes from anthropogenic processes such as petroleum exploration, refining, usage, and related activities [3]. The concentrations levels and source apportionment of aliphatic hydrocarbons in sediments is a common and effective means of understanding the level of oil pollution in sediments [1]. Various diagnostic indices are being use for source apportionment [2, 11-16]. Among them are: the n-C16 index, the ratio of even to odd numbered alkanes, ratio of low molecular weight to high molecular weight hydrocarbons ($\Sigma LMH/\Sigma HMH$), nC31/nC19 ratio, carbon preference index (CPI), long chain to short chain hydrocarbon ratio (LHC/SHC), pristane to phytane (Pr/Ph) ratio, average carbon length (ACL), etc. Appropriate use of these

indices has often elucidated the hydrocarbon source in the environmental medium. Thus, anthropogenic petroleum source are easily differentiated from biogenic (natural) sources; and terrestrial biogenic sources from marine inputs. Though some pollution studies have been carried out on the Aba River, works on hydrocarbons pollution loads are scanty hence this works seeks to determine the levels and source of aliphatic hydrocarbons in the sediments of the Aba River at Ogor-Hill axis.

2. MATERIALS AND METHODS

2. 1. Study area

The Aba River also known as the Waterside River has it root from Okpu-Umuobu town, some kilometers from Aba town and flows North-South direction before joining the Imo River. It is recharged by groundwater and precipitation. Five composite sediments samples were taken at five different stations (ST) at some kilometres apart downstream commencing from ST-A to ST-E. The coordinates of these stations were properly recorded viz: ST-A (N05°06'50.155'' E07°22'51.200''), ST-B (N05°06'31.716'' E07°22'57.713''), ST-C (N05°06'18.824'' E07°23'03.581''), ST-D (N05°06'09.432'' E07°23'11.166'') and ST-E (N05°05'57.084'' E07°23'22.016''). The major activities taking place at the river's sides include: commercial shipping, and regular vehicular transportation, as well as indiscriminate dumping of waste on the river, hide and skin burning (using vehicular tyres as fuel), commercial shipping, and regular vehicular transportation, as well as indiscriminate dumping of waste on the river. Factories (such as International Glass industry, Nigerian Breweries, 7UP Bottling Company PLC, Soap and Detergent factories etc), artesian workshops (like auto-mechanic workshops, iron welding and fabrications workshops), auto-refueling stations, abattoirs, and dumpsites also occupy portions of the river banks. Effluents from these factories as well as run-off from the town also find their way into the river.

2. 2. Sample collection

Composite samples of sediments taken at the different stations along the river bed were placed in pre-cleaned wide-mouth amber bottles; and kept in an ice-chest for onward transfer to the laboratory for analysis.

2. 3. Extraction of aliphatic hydrocarbons

Air dried sediment samples were homogenized and sieved through 0.5 mm mesh. Aliquot (10g) of it was mixed with sufficient quantity of anhydrous sodium sulfate (Na_2SO_4) (about 5g) to remove moisture, the mix was spike with surrogate standard (10 $\mu\text{g}/\text{mL}$ of 1-chlorooctadecane), wrapped in a filter paper, and then placed in a thimble afterward loaded into the main chamber of the soxhlet extractor. Extraction was performed with dichloromethane (DCM) for 24 hr. Extracts were dried by passing through column of anhydrous sodium sulfate; and reduced to 2mL with a rotator evaporator.

2. 4. Sample clean-up and separation

A chromatographic column (10 mm i.d. X 30 cm) packed with 10g activated silica gel slurry, with about 2cm anhydrous Na_2SO_4 layer on top was used to fractionate and separate the

aliphatic hydrocarbons portion. The sample was placed in the column and eluted with 30 mL of n-hexane to obtain the aliphatic hydrocarbons fraction. The eluates were concentrated to approximately 2 mL with rotator evaporator at 30 °C; 1.5 mL of it was transferred into chromatographic vial and stored at 4 °C prior to gas chromatographic analysis. A blank sample given the same treatment was used for quality assurance [11, 17-18].

2. 5. Gas chromatography analysis

Analysis of aliphatic hydrocarbons were performed using gas chromatography, with a flame ionization detector (GC-FID); Agilent 6890N system equipped with DB-5 capillary column with dimension of 30 m X 0.32 mm X 0.25 µm. The injected volume of sample was 1 µL. Helium at a flow rate of 1mL/min was used as the carrier gas. Samples injection was in split less mode. The column temperature was initially set at 50 °C for 5 minutes. It was then steadily increased at rate of 10 °C /min. for 15 minutes to 150 °C; after which it was ramped at 16 °C/min to 280 °C and held for 5 minutes. The injector and detector temperatures were set at 200 and 300 °C respectively. The sum of concentrations of the aliphatic that eluted from nC8 – nC40 and the unresolved hydrocarbons (UCM) measured by the GC-FID provides a measure of total petroleum hydrocarbons (TPH) concentration.

2. 6. Identification and quantification

Individual n-alkanes were identified by comparing their retention time to that shown by nC8 – nC40 standards, and quantifications were done by integrating peak areas of fractionated sample extracts and comparing their response factors to that of calibrated standards. The response factor of nC15 was used for the quantification of the unresolved peaks as prescribed by Luan and Szelewski [19]. Internal standard solutions, and surrogate standard solutions (1 chlorooctadecane) were used to quantify procedural recovery.

2. 7. Determination of Physicochemical Parameters

The pH, organic matter, and particle size analyses were determined in accordance with standard methods [20-22].

3. RESULTS AND DISCUSSION

3. 1. Levels of TPHs in the sediments

The total petroleum hydrocarbons (TPHs) found in this study for the different stations and the average value for all stations are as displayed in Fig. 1. The values ranged from 41.5378 mg/Kg in station B to 183.798 mg/Kg in station A, with an average value of 85.877±60.41 mg/Kg. The values in other stations were: C (54.585 mg/Kg), D (44.596 mg/Kg), and E (104.873 mg/Kg). The range of values categorized the river sediments as slightly to moderately polluted on the basis of the Massoud *et al* [23] classification.

Massoud *et al* [23] recommended four levels of hydrocarbons pollution for the assessment of marine sediments viz: unpolluted (10 – 15 mg/Kg); slightly polluted (15 - 50 mg/Kg), moderately polluted (50 – 200 mg/Kg), and heavily polluted (>200 mg/Kg). The Nigerian Department of Petroleum Resources (DPR) [24] set target and intervention guideline values for

soil and sediment's TPHs are 50 mg/Kg and 5,000 mg/Kg respectively. The values for three stations (ST- A, ST-C, & ST-E) and the mean value for five (5) stations in this study were higher than the target value indicating that there were anthropogenic accumulations of TPHs in these sediments. However, the values were still much below the intervention value.

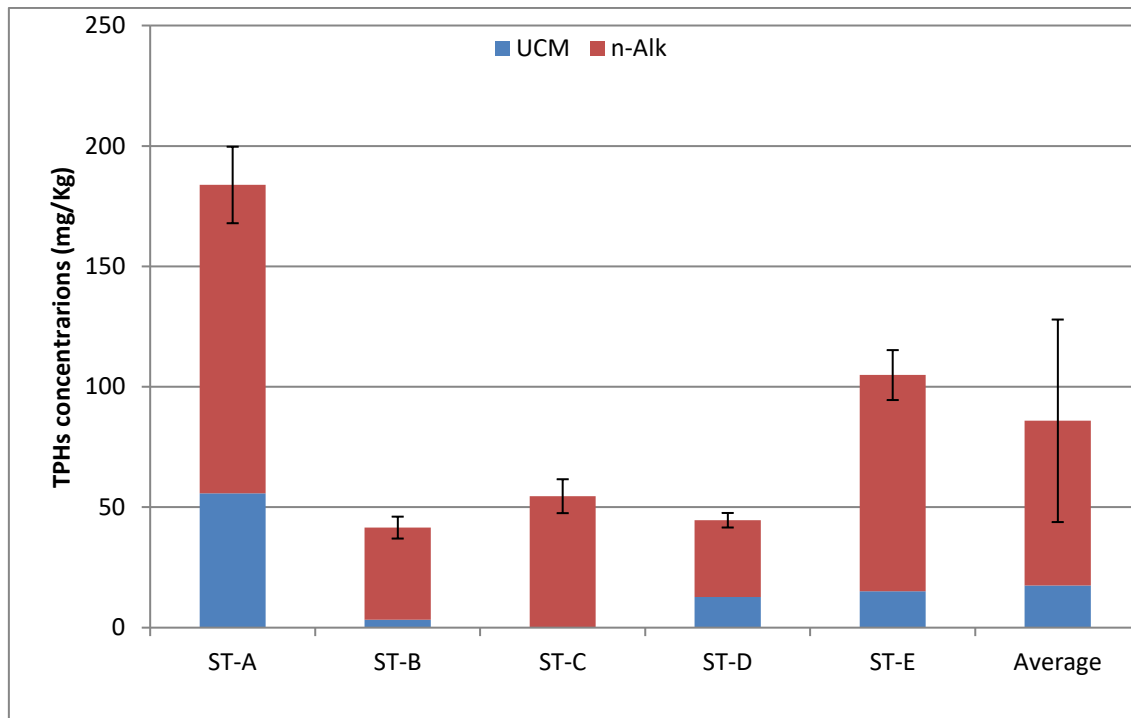


Fig. 1. Levels of TPHs (mg/Kg) in sediments at the different stations

The range of values obtained in this study, were higher than the 3.162 – 8.758mg/Kg reported by [25] for the Woji Creek, Niger Delta Estuary of River State, Nigeria. It was also larger than the 25.46 – 69.35 mg/Kg recorded for the Onyima Creek, in the same Niger Delta, Nigeria [26]. Elsewhere across the Globe, the values are higher than those of: Algoa Bay, Eastern Cape, South Africa (0.72 – 27.03 mg/Kg) [11], Bizerte Lagoon, Tunisia (0.05 - 20.0 mg/Kg) [27], Mediterranean Sea, Damelta harbor (0.16 – 4.16 mg/Kg) [28], Candarli Gulf, Turkey (3.88 – 24.7 mg/Kg) [29], and Papar and Putatan both in Sabah, Malaysia (0.52 – 4.59; & 0.26 – 1.64 mg/Kg) [30]. The range of values were however comparably lower than: the 270 – 830 mg/Kg reported for the Qua-Iboe River, Akwa-Ibom State, Nigeria [17], the 54.72 – 2,002 mg/Kg observed for River Oluwa, Western Nigeria [13], and the 112.30 – 657.30 mg/Kg recorded for the New Calabar River, South-Southern Nigeria [31]. The range of values were much less significant than the 400 – 6,205 mg/Kg recorded for the sediment from the Upper Reaches of Sombreiro River, Niger Delta, Nigeria [32], and the 1,403 – 3,755 mg/kg reported for sediments of polluted tidal Creek in Bonny River, Nigeria [33]. Around the world, the range is much lower than the 496 – 8,972 mg/Kg recorded for the sediment of Ceuta harbor, North of Africa, Spain [34], and the 1,166.3 – 2,137.4 mg/Kg reported for the sediments along discharged Basin Suez Oil Refinery Company, South West of Suez Gulf [14].

The mean of this study (85.87 ± 60.41 mg/Kg) was much higher than those reported for Ugbo Water Ways, South Western Nigeria (0.131 mg/Kg) [35], and the Onyima Creek, Niger Delta (41.214 mg/Kg) [26]. The mean was also much higher than those reported for the coastal sediments of Askar, East of Bahrain (10.46 ± 6.85 mg/Kg) [36] and Candarli Gulf, Turkey (8.695 mg/Kg) [29]. The mean TPHs (85.877 ± 60.41 mg/Kg) of this study, was however comparably lower than the 184.89 mg/Kg reported for the sediment of the New Calabar River, South Southern Nigeria [37]. It was also lower than the 339.2 mg/Kg recorded by [38] for the sediment of oil polluted coastal areas in South-Eastern Nigeria. The mean values reported for sediments of some other Nigerian Rivers were: the River Niger at Okpu and Iyiowa-Odekpe axes (440.023 ± 54.78 mg/Kg) [3], the Qua-Iboe River (606.83 ± 229.48 mg/Kg) [17], Upper Bonny River (528.25 mg/Kg) [39], Ubeji River ($1,602.4 \pm 8.9$ mg/Kg) [40], the Benin River, Adjacent a lubricating oil production factory ($41,900$ mg/Kg) [41], and the Odidi and Eqwa Rivers ($215,730 \pm 81$ & $215,700 \pm 77$ mg/Kg) [42]. These values were much higher than that reported in this study. Elsewhere around the world, the value is comparably lower than the 779 mg/Kg observed in Bapco Oil Coastline, near a refinery In Bahrain [10], and the $1,638.683$ mg/Kg recorded along the Discharged Basin of Suez Oil Refinery Company, South West of the Suez Gulf [14].

The TPHs levels in the sediments did not follow any specific order up or downstream; reflecting the diversity of TPHs sources rather than discharge from a single point source. The order of TPHs loads in the sediments was: ST-A > ST-E > ST-C > ST-D > ST-B. Organic carbons (OC) in sediments bind to petroleum hydrocarbons making them less available to benthic organisms, thus, reducing their toxicity. It is therefore necessary to consider the organic carbon content in sediments in the assessment hydrocarbons toxicity. It is usual to normalized hydrocarbons at 1% organic carbon sediment concentration in order to account for their difference in bio-availabilities. The organic carbon (OC) concentrations for the different locations viz: ST-A (1.76%), ST- B (3.21%), ST- C (1.02%), ST- D (1.11%), and ST-E (1.46%) were used to normalized TPHs values at 1% organic carbon. The values obtained for the normalized TPHs were: ST-A (1.0443×10^4 mg/Kg OC.), ST-B (1.2940×10^3 mg/Kg OC.), ST-C (5.3519×10^3 mg/Kg OC.), ST-D (4.0176×10^3 mg/Kg OC.), and ST-E (7.1831×10^3 mg/Kg OC.). The order of the normalized TPHs loads in the sediments was not different from that of the un-normalized one, probably due to the low carbon contents and very less variation in carbon content in the sediments.

The estimation of ecological risk of petroleum hydrocarbons in sediments and groundwater based only on Total Petroleum Hydrocarbons (TPHs) values is oversimplification, and often results in large errors in the risk assessment. This is because; TPHs measure hundreds to thousands of hydrocarbons and related organic compounds that vary widely in persistence in the environment and toxicity [43]. However, to determine risk based on the concentrations of tens and possibly thousands of individual hydrocarbons in contaminated sites would be too complex and costly. Therefore, the proposed methodology that divides the hydrocarbons into classes or groups (fractions) with similar chemical and toxicological properties as given by Massachusetts Department of Environmental Protection (MADEP) [43] was used to further assess the impact of the hydrocarbons in this study. The sediment benchmarks recommended by [43] for aliphatic petroleum hydrocarbons fractions in mg/Kg OC are: C₅ – C₈ (1591), C₉ – C₁₈ (3167), and C₁₉ – C₃₆ (9883). Since the analytical method used in this study, did not cater for volatile hydrocarbons in the range of C₅ – C₇, we rely on the other two fractions for the assessment. The obtained values for C₉ – C₁₈ hydrocarbons were: ST-A (3218.42 mg/Kg OC),

ST-B (397.47 mg/Kg OC), ST-C (2173.52 mg/Kg OC), ST-D (899.65 mg/Kg OC), and ST-E (4722.33 mg/Kg OC). These values except for stations A and E were lower than the benchmark value (3167.00 mg/Kg OC). The average value (2282.28 mg/Kg OC) was also lower than the sediment benchmark value. The C₁₉ – C₃₆ fractions for the sediments were: ST-A (3873.18 mg/Kg OC), ST-B (662.67 mg/Kg OC), ST-C (1086.13 mg/Kg OC), ST-D (1819.50 mg/Kg OC), and ST-E (1372.96 mg/Kg OC) with overall average for the stations been 1767.89 mg/Kg OC. These values were all below the sediment benchmark value of 9883.00 mg/Kg OC for the C₁₉ - C₃₆ fractions of aliphatic hydrocarbons. The implication is that though there were evidences of petroleum hydrocarbons accumulations in the sediments, the values obtained did not represent threat to sediments' biota and human health.

Table 1. Some Physicochemical characteristics of the sediments

Stations characteristics	pH	% OM	% Sand	% Clay	% Silt
A	5.73	3.043	71.53	16.42	12.05
B	5.87	5.550	84.36	3.44	12.20
C	5.83	1.763	81.03	5.10	13.87
D	6.03	1.919	78.57	6.38	15.05
E	5.91	2.524	67.75	14.87	17.38
Mean+SD	5.87±0.11	2.959 ±1.53	76.65 ±6.85	9.24 ±5.96	14.11 ±2.21

Table 2. Correlation coefficients between TPHs and some physicochemical parameters

	pH	% OM	% Sand	% Clay	% Silt
TPHs	-0.6891*	-0.09321	-0.7421*	0.9125**	-0.1614

** Significant at 1% level, *Significant at 5% level

3. 2. The relationship between TPHs and physicochemical characteristics of the sediments

Some basic physicochemical characteristics of the sediments are as shown in Table 1. Table 2 gives their relationships with TPHs. The sediments pH ranges from 5.83 – 6.03, with a mean of 5.84 ±0.11. The organic matter range was from 1.76 – 5.55%, particle size analysis shows that the sediments were largely made up of sand fractions. Highly significant positive correlation between TPHs and sediment physicochemical characteristics (Table 2) was seen only for clay content. No correlation was observed for the organic matter content, the closeness of these values to one another perhaps, is responsible for this observation. Clay sized particles

have been implicated as sorption media for contaminants, thus playing active roles in accumulations and release of TPHs in sediments [3]. The negative correlation between percent sand and TPHs indicate that TPHs accumulations are lessened by increasing the proportions of sand fractions in the sediments. Also, the slight negative correlation between pH and TPHs reflect the ability of TPHs pollutants to contribute to sediments acidity [3]. Thus, the more the TPHs in the sediments, the more acidic (lesser pH) the sediments becomes. Chemical pollutants are well known to affect pH levels and impacts toxicity of the medium.

3. 3. Aliphatic hydrocarbons profiles and identifications of source.

The mean distributions of aliphatic hydrocarbons in sediments of the different stations are as shown in Table 3. The most dominant hydrocarbons were in the range of C₁₃ – C₁₈. This was followed by those in the ranges of C₃₂ – C₃₃, and C₂₆ – C₂₇ respectively. The C₈ – C₁₂ hydrocarbons were present in slight amount, except in station C where they were largely dominant. The C₁₉ – C₂₅ hydrocarbons were present in moderate amount whereas C₃₆ and above were scantily present. Pristane and phytane – the isoprenoid hydrocarbons were also present in all stations. Based on transport and fate in the environment, TPHs are grouped into three viz: Gasoline Range Organic (GRO) (C₆ – C₁₀), Diesel Range Organic (DRO) (C₁₀ – C₂₈), and Oil Range Organic (ORO) (> C₂₈) [44].

However, based on similarities in chemical and toxicological properties, aliphatic hydrocarbons are grouped into: C₅ - C₈, C₉ – C₁₈, and C₁₉ – C₃₆ [43]. On the basis of the basis of the first classification, it can be said that hydrocarbons in the sediments were largely in the Diesel Range Organic. This did not however exclude the presence Oil and Gasoline Range organics. Based on the MADEP [43] classification, we can deduced that both C₉ - C₁₈ and C₁₉ – C₃₆ hydrocarbons fractions were visibly present. The method used in this study did not allow for complete determination of the C₅ – C₈ group and drawing inference on its presence. The presence of these hydrocarbons could have come from: spilled oil, fumes and leakages from trucks and generators, leachates from auto-mobile and power engines servicing sites, and hydrocarbons washed down the drains by rains. The relatively large proportions of low molecular weight hydrocarbons present in the stations particularly, C₁₀ – C₂₀ tended to portray a recent contaminations of these stations.

Table 4 shows some diagnostic indices of hydrocarbons source. The n₁₆ indexes tend to suggest that the source of hydrocarbons in station E was petrogenic while that of station A was of mixed origin. The others showed evidence of biogenic inputs. The nC₁₆ index is computed by the division of total n-alkanes concentrations by the concentration of nC₁₆. For oil contaminated samples, nC₁₆ index is small (<16); it is larger (>50) when the contamination is of biological origin [10]. Also the sums of low molecular weight to high molecular hydrocarbons ($\sum\text{LMH}/\sum\text{HMH}$) were lower than one (1) in all stations except station E which had value of 2.19. This indicates that majority of the stations (except ST-E) had their hydrocarbons source largely from biogenic origin. The $\sum\text{LMH}/\sum\text{HMH}$ index is used to characterize hydrocarbons source. Hydrocarbons sourced from higher plants, marine animals and sedimentary bacterial often have values less than unity (1), whereas, those from petroleum and plankton origin have values that are typically close to or greater than unity [3,14-15].

The Even/ odd numbered alkanes (E/O) ratios however, showed slight evidence of anthropogenic inputs in stations A and C, having values that are slightly higher than one (1). The other stations viz: B (0.60), D (0.80), and E (0.77) were less than unity; an indication of biogenic inputs.

Table 3. Mean aliphatic profiles of hydrocarbons in sediments at the different stations

Components Concentrations (mg/Kg)	ST-A	ST-B	ST-C	ST-D	ST-E
C8	2.39	2.06	19.84	1.27	0.68
C9	0.47	1.00	15.63	0.73	0.55
C10	0.85	1.07	0.92	0.64	0.69
C11	1.38	2.61	1.92	0.17	0.32
C12	2.90	2.42	0.93	1.85	6.10
C13	4.52	2.82	0.86	0.51	7.47
C14	5.75	0.31	1.03	0.68	8.67
C15	6.41	0.91	0.16	1.51	8.92
C16	5.79	0.35	0.16	0.51	6.61
C17	4.37	0.22	0.08	0.80	5.18
Pr	10.80	0.36	0.35	0.93	13.74
C18	5.17	0.34	Bd	0.87	4.29
Ph	8.24	0.33	0.12	0.78	6.40
C19	3.39	0.16	0.02	0.62	3.37
C20	4.79	0.10	0.12	0.96	2.57
C21	3.87	0.12	0.17	0.68	0.88
C22	4.39	0.02	0.05	0.38	0.87
C23	3.23	0.05	0.07	0.65	0.86
C24	3.51	0.02	1.05	1.00	0.50
C25	4.65	0.24	0.01	1.04	1.22
C26	6.69	1.74	0.11	1.33	0.17
C27	8.84	0.85	0.07	0.76	0.62
C28	2.50	2.48	0.22	1.83	1.05
C29	1.95	3.54	0.46	2.06	1.41

C30	1.54	2.93	0.65	1.46	1.77
C31	2.79	0.89	0.71	1.70	1.06
C32	4.17	3.11	1.81	2.86	0.63
C33	6.49	0.75	3.27	1.17	1.26
C34	2.02	1.34	0.92	1.18	0.99
C35	2.24	0.93	1.19	0.37	0.82
C36	1.12	2.01	0.18	0.14	0.01
C37	0.54	0.74	0.64	0.27	0.01
C38	0.18	0.64	0.29	0.09	Bd
C39	0.06	0.57	0.25	Bd	0.03
C40	Bd	0.19	0.05	Bd	Bd
Σ C9 – C18	56.64	12.76	22.17	9.99	68.95
Σ C19 – C36	68.17	21.27	11.08	20.20	20.05
TAH	127.98	38.22	54.31	31.81	89.72
UCM	55.82	3.32	0.28	12.79	15.16
TPH	183.80	41.54	54.58	44.60	104.87

*TAH: Total Aliphatic Hydrocarbons, UCM: Unresolved complex mixtures, TPH: Total Petroleum Hydrocarbons, Bd: Below detection

Table 4. Calculated aliphatic hydrocarbons source diagnostic ratios in different stations

Diagnostic indices	Stations						
	ST-A	ST-B	ST-C	ST-D	ST-E	Range	Average
Σ LMW/ Σ HMW	0.51	0.11	0.05	0.29	2.19	0.05 – 2.19	0.63
CPI	1.40	0.58	1.20	0.78	1.28	0.58 – 1.40	1.05
E/O	1.11	0.60	1.06	0.80	0.77	0.60 – 1.11	0.87
nC ₁₆ index	22.12	110.74	331.29	62.84	13.56	13.56 – 331.29	108.11
nC ₃₁ /nC ₁₉	0.82	5.39	29.28	2.74	0.32	0.32 – 29.28	7.71

LHC/SHC	0.96	4.07	4.53	1.54	0.18	0.18 – 4.53	2.26
Pr/Ph	1.31	1.10	2.95	1.19	2.15	1.10 – 2.95	1.74
U/R	0.436	0.0867	0.0051	0.402	0.1689	0.005 – 0.436	0.22

* \sum LMW/ \sum HMW: sum of low molecular weight hydrocarbon to sum of high molecular weight hydrocarbon, CPI: carbon preference index, E/O: even to odd hydrocarbons ratio, LHC/SHC: long chain to short chain hydrocarbons, Pr/Ph: pristane over phytane ratio, U/R: ratio of unresolved to resolved hydrocarbons.

The dominance of odd numbered alkanes (nC_{15} , nC_{17} , nC_{19}) over even numbered ones (nC_{16} , nC_{18} , nC_{20}), as reflected in the even numbered to odd numbered alkanes ratio (E/O) is often used to distinguished the source of the hydrocarbons [45-46]. The carbon preference index (CPI) values for the different stations were A (1.40), B (0.58), C (1.20), D (0.78), and E (1.28).

These values tend to suggest that the sources of aliphatic hydrocarbons in stations A, C and E were from crude oil, while those of stations B and D portray evidence of degraded crude oil. According to Chokor [3], Maioli et al [18], and Onyema et al [47] CPI values in the neighbourhood of one (1) suggest crude oil sources; whereas values below unity evidence degraded crude oils. The value that is higher than one (1) especially in the range of 3 – 10 represents biogenic inputs [48]. The CPI also measures the ratio of odd to even numbered hydrocarbons but its calculated in a different way as shown in Eq. 1

$$CPI_{25-33} = 0.5 \times [(C_{25} - C_{33}) / (C_{24} - C_{32})] + [(C_{25} - C_{33}) / (C_{26} - C_{34})] \quad (1)$$

It is a useful index for assessing the predominance of natural hydrocarbons over anthropogenic ones or otherwise [49-50].

The ratio of pristane (Pr) to phytane (Ph) is a useful diagnostic tool. Biogenic hydrocarbons are characterized by the abundance of pristane over phytane, and the resultant high values reliably indicate the absence of petroleum, and clear signal of biological inputs [2, 49]. The Pr/Ph values of the different stations shown in Table 4 have values ranging from 1.10 – 2.95 with a mean of 1.74. The values in the stations B and C were typically close to one (1); the others have values that are larger than one. These suggest that the hydrocarbons contaminations were largely from the contributions of biogenic source. The slight presences of unresolved complex mixtures (UCM) in these stations however, are indications that petrogenic inputs to hydrocarbons contaminations cannot be ruled out. One of the more convincing indicators of petroleum contaminations in water or sediment samples is the presence of an unresolved complex mixture (UCM) [18].

Long chain to short chain hydrocarbons (LHC/ SHC) ratio is important in the determination of hydrocarbons source – whether it is from phytoplankton marine origin or terrestrial vascular plants. LHC/SHC ratio is computed using the relation shown in Eq. 2

$$LHC/SHC = [\sum(nC_{27} + nC_{29} + nC_{31}) / \sum(nC_{15} + nC_{17} + nC_{19})] \quad (2)$$

Higher ratio greater than 4 is indicative of terrestrial plant waxes whereas ratios in the range of 0.21 – 0.80 connotes phytoplankton (marine) origin.

Ratios within 2.38 – 4.33 however, represent a mixture of both sources [2-3, 11, 13]. The values obtained in this study viz: A (0.98), B (4.07), C (4.53), D (1.54), and E (0.18) tended to portray that station B and C were from terrestrial vascular plants whereas, stations A and E showed evidence of phytoplankton marine origin. Station C is likely a mixture of both origins – terrestrial and marine.

The nC_{31}/nC_{19} ratios however, gave more credence to non-marine (terrestrial) inputs as evidenced in nC_{31}/nC_{19} ratios that were greater than 0.4 except for ST-E that was slightly lower (0.32). The C_{31}/C_{19} ratio has been used to index source of aliphatic hydrocarbons in sediments. Strong nC_{31} presence usually indicates terrestrial biogenic inputs. Marine biogenic source is implicated by large presence of nC_{19} . The ratio therefore, indicates the dominance of either source.

Ratio higher than 0.4 implied non-marine or terrestrial sourced hydrocarbons, whereas values lower than it connote marine source [2-3, 13, 26, 45, 51]. The relative low levels of aliphatic hydrocarbons in sediments with much of it diagnosed to have originated from natural sources did not constitute much threat to the benthic fauna and human health. Exposure of the benthic fauna to petroleum hydrocarbons above the sediment benchmark may result in developmental malformations, loss of reproductive capacity and several diseases in the sediment dwelling organisms and fishes [3].

4. CONCLUSION

The study was conducted to determine the levels, profiles and sources petroleum hydrocarbons in sediments of the Aba River at Ogbor-Hill region, South-Eastern Nigeria. The result revealed a range of 41.5378 – 183.798 mg/Kg with a mean of 85.8774 ± 60.41 mg/Kg.

The mean value was slightly higher than the 50mg/Kg target value established by the Nigerian Department of Petroleum Resources (DPR), but was much lower than the 5,000 mg/Kg intervention value established by the same body. The aliphatic fractions (C9 – C18, and C19 – C36) in the sediments at most stations were also lower than the recommended sediment benchmark values. Aliphatic profiles and diagnostic indices revealed that large proportion of hydrocarbons were from biological/ natural origin. However, values obtained from the carbon preference index (CPI) and the even to odd numbered alkanes (E/O) indices showed much evidence of petrogenic contribution; indicating the mixed origin nature of the hydrocarbons.

The levels aliphatic hydrocarbons in these sediments did not constitute much threat to benthic organisms and human health. However, due to possibility of accumulations of these petroleum hydrocarbons in the sediments, it is recommended that effort be made to curb further rise in anthropogenic inputs of petroleum hydrocarbons in the sediments in order to protect benthic organisms and human health in general.

References

- [1] Nasim, T., H. Z. Nasser, and B. Pardis. Concentrations and Sources of Aliphatic and Aromatic Hydrocarbons in Babolsar Coastal Sediments in the Caspian Sea. *Pollution*, 7(2) (2021) 469-479

- [2] Chokor, A. A. Total petroleum and aliphatic hydrocarbons profile of the River Niger surface water at Okpu and Iyiowa-Odekpe regions in South-Eastern, Nigeria, *Chemistry International*, 7(3) (2021) 188 – 196
- [3] Chokor, A. A. Distribution and Source Fingerprinting of Total Petroleum Hydrocarbons in Sediments of the River Niger at Okpu and Iyiowa-Odekpe Axes in South-Eastern, Nigeria, *World News of Natural Sciences*, 42 (2022) 151-168
- [4] Law, R. J. and J. Klungsoyr. The analysis of polycyclic aromatic hydrocarbons in marine samples. *Int J Environ Pollut*, 13 (2000) 262–283
- [5] Al-Shwafi, N. A. A. Total petroleum hydrocarbon carcinogens in commercial fish in the red sea and Gulf of Aden-Yemen. *JKAU: Marine Science* 19 (2008) 15–28
- [6] Enuneku, A. A., M. Ainerua, N. O. Erhunmwunse, and O. E. Osakue. Total petroleum hydrocarbons in organs of commercially available fish; *Trachurus Treciae* (Cadenat, 1949) from Oliha Market, Benin City, Nigeria. *Ife Journal of Science*, 17(2) (2015) 383-393
- [7] Ite, A.E., T. A. Harry, C. O. Obadimu, E. R. Asuaiko, and I. J. Inim. Petroleum Hydrocarbons Contamination of Surface Water and Groundwater in the Niger Delta Region of Nigeria, *Journal of Environment Pollution and Human Health*, 6(2) (2018) 51-61. doi: 10.12691/jephh-6-2-2
- [8] Kponee, K. Z., A. Chiger, I. I. Kakulu, D. Vorhees, and W. Heiger-Bernays. Petroleum contaminated water and health symptoms: a cross-sectional pilot study in a rural Nigerian community, *Environmental Health*, (2015) 14: 86, DOI:10.1186/s12940-015-0073-0
- [9] Oyibo, J. N., M. O. Wegwu, A. A. Uwakwe, J. O. Osuoh, et al., Analysis of total petroleum hydrocarbons, polycyclic aromatic hydrocarbons and risk assessment of heavy metals in some selected finfishes at Forcados Terminal, Delta State, Nigeria. *Environ. Nanotechnol. Monit. Manag.* 9 (2018) 128–135
- [10] Tolosa, I., S. De Mora, M. R. Sheikholeslami, J. Villeneuve, J. Bartocci, and C. Cattini. 2004. Aliphatic and aromatic hydrocarbons in coastal Caspian Sea sediments, *Marine Pollution Bulletin*, 48: 44-60
- [11] Adeniji, A. O., O. O. Okoh, and A. I. Okoh. Petroleum hydrocarbon profiles of water and sediment of Algoa Bay, Eastern Cape, South Africa, *International Journal of Environmental Research and Public Health* 14 (2017a) 1263, doi 10.3390/ijerph14101263
- [12] Ahmed O. E., S. A. Mahmoud, and A. E. Mousa. Aliphatic and poly-aromatic hydrocarbons pollution at the drainage basin of Suez Oil Refinery Company. *Current Science International* 4(1) (2015) 27-44
- [13] Fagbote, O. E. and E. O. Olanipekun. Characterization and sources of aliphatic hydrocarbons of the sediments of River Oluwa at Agbabu Bitumen deposit area, Western Nigeria, *Journal of Scientific Research and Reports*, 2(1) (2013) 228–248

- [14] Farid, N. A., S. A. Mahmoud, and O. E. Ahmed. Assessment of Contamination by Petroleum Hydrocarbons in Sediments along Discharge Basin of Suez Oil Refinery Company, Southwest of the Suez Gulf, *Egypt. J. Chem.* 57(2) (2014) 75-96
- [15] Kanzari, F., A. D. Syakti, L. Asia, L. Malleret, A. Piram, G. Mille, and P. Doumenq. Distributions and sources of persistent organic pollutants (aliphatic hydrocarbons, PAHs, PCBs and pesticides) in surface sediments, of an industrialized urban river (Huveaune), France. *Science of the Total Environment*, 478 (2014) 141–151
- [16] Riccardia, C., P. D. Filippoa, D. Pomataa, F. Incoronatoa, M. D. Basilioa, M. P. Papinib, S. Spicagliaa. Characterization and distribution of petroleum hydrocarbons and heavy metals in groundwater from three Italian tanks farms, *Sci. Total Environ.* 393 (2008) 50–63
- [17] Iyang, S. E., A. B. Aliyu, and A. O. Oyewale. Total petroleum Hydrocarbons content in Surface Water and Sediment of Qua-Iboe River, Ibeno, Akwa-Ibom State, Nigeria, *J. Appl. Sci. Environ. Manage.*, 22(12) (2018) 1953-1959
- [18] Maioli, O. L. G., K. C. Rodrigues, B. A. Knoppers, D. A. Azevedo. Distribution and sources of aliphatic and polycyclic aromatic hydrocarbons in suspended particulate matter in water from two Brazilian estuarine systems, *Continental Shelf Research*, 31 (2011) 1116–1127
- [19] Luan, W.; M. Szelewski. Ultra-fast total petroleum hydrocarbons (TPH) analysis with agilent low thermal mass (LTM) GC and simultaneous dual-tower injection. In Agilent Technologies Application Note (2008) 1–8. Agilent: Santa Clara, CA, USA.
- [20] Folsom, B. L., C. R. Lee, and D. J. Basta.. Influence of disposal environment on availability and plant uptake of heavy metals in dredged material. U.S. Army, Washington. *Tech. Rep. El*, (1981) 81-12
- [21] Gee, G. N. and D. Or. Particles size analysis. In: methods of soil analysis, Part 4. Physical methods, Dane, J.H. and G. C. D. Topp (eds.). *American Society of Agronomy*, Madison, WI, (2002) 255 – 293.
- [22] Nelson, D. W; and L. E. Sommers. Total carbon and matter. In Page, A.Z. et al. (Ed) *Methods of soil analysis*. Part 2; 2nd ed. ASA, SSSA, (1982) Pp 539 -579
- [23] Massoud, M. S., F. Al-Abdali, A. N. Al-Ghadban, and M. Al-Sarawi. Bottom sediments of the Arabian Gulf-II. TPH and TOC contents as indicators of oil pollution and implications for the effect and fate of the Kuwait oil slick, *Environ. Pollut.* 93 (1996) 271–284
- [24] DPR. EGASPIN Soil/Sediment Target and Intervention Values for Mineral Oil (or TPH), Department of Petroleum Resources, Environmental Guidelines and Standards for the Petroleum Industry in Nigeria, Revised ed., The Petroleum Regulatory Agency of Nigeria: Lagos, Nigeria,(2002) pp. 1–415.
- [25] Ihunwo, O. C., M. O. Onyema, V. O. Wekpe, C. Okocha, A. R. Shahabnia, L. Emmanuel, V.N. Okwe, C. B. Lawson, P. C. Mmom, A. N. Dibofori-Orji, and E. Bonnail. Ecological and human health risk assessment of total petroleum hydrocarbons in surface water and sediment from Woji Creek in the Niger Delta Estuary of Rivers State, Nigeria, *Heliyon*, 7(8) (2021) e07689 dio: 10.1016/j.heliyon.2021.e07689

- [26] Edori, E. S. and O. S. Edori. Fingerprints of Total Petroleum Hydrocarbons in the Water and Sediments of Onyima Creek (Ede Onyima), EngenniAhoada West, Rivers State, Nigeria, *Global Journal of Science Frontier Research: (H) Environment & Earth Science*, 21(2) (2021) version 1
- [27] Mzoughi, N., M. Dachraoui, and J. P. Villeneuve. Evaluation of aromatic hydrocarbons by spectrofluorometric in marine sediments and biological matrix: what reference should be considered? *Compete. Rend. Chem.* 8(1) (2005) 97-102
- [28] Shereet, S. M. Pollution of petroleum hydrocarbon in the new Damietta harbour, Egypt, *Emirates Journal for Engineering Research*, 14(1) (2009) 65-71
- [29] Kucuksezgin, F., I. Pazil, and L. T. Gonul. Marine organic pollutants of the Eastern Aegean: Aliphatic and polycyclic aromatic hydrocarbons in Candarli Gulf sacrificial sediments. *Marine Pollution Bulletin*, 64 (2012) 2569–2575
- [30] Siti Aishah, M. A., T. Rohana, Z. Y. Soon, and M. A. Masni. Petroleum Hydrocarbon in Surface Sediment from Coastal Area of Putatan and Papar, Sabah, *The Malaysian Journal of Analytical Sciences* 17(2) (2013) 286-290
- [31] Ibigoni, C. H., U. U. Gabriel-Snr, and M. Horsfall-Jnr. Evaluation of total hydrocarbon levels in some aquatic media in an oil polluted mangrove wetland in the Niger Delta. *Applied Ecology and Environmental Research*, 7(2) (2009) 111-120
- [32] Howard, L. C., A. O. Briggs, J. O. Nduka, and N. I. Uzomba. Total Hydrocarbon levels of surface sediment and water from the Upper reaches of Sombreiro River, Niger Delta, Nigeria. *Journal of Nigerian Environmental Society*, 7(3) (2012) 16-22
- [33] Wokoma, O. A. F. Levels of total hydrocarbon in water and sediment of a polluted tidal creek, Bonny River, Niger Delta Nigeria, *International Journal of Scientific & Technology Research*, 3(12) (2014) 351–354
- [34] Guerra-Garcia, J. M., J. C. Garcia-Gomez. Assessing pollution levels in sediments of a harbor with two opposing entrances, Environmental implications. *J. Environ. Manag.*, 77 (2005) 1–11
- [35] Ashiru, O.R. and M.O. Ogundare. An assessment of total petroleum hydrocarbon and trace metal concentration in the sediments of Ugbo water way, south western Nigeria, *African Journal of Environmental Science and Technology*, 13(1) (2019) 13-21
- [36] Al-Khatlan, A.F., T.S. Ali, A.A. Abuhussain. Distribution of petroleum hydrocarbons in coastal sediments of Asker, East of Bahrain. *Biol. Appl. Environ. Res.* 3(1) (2019) 82-92
- [37] Horsfall (Jr), M., F. E. Ogban, and, A. I. Spiff. Petroleum hydrocarbon pollution: the distribution in sediment and water of the New Calabar River, Port Harcourt, Nigeria. *The Science of the Total Environment* 141 (1994) 217-221
- [38] Eja, M. E. and O. R. Ogri. Evaluation of total hydrocarbon (THC) levels in oil polluted coastal areas of South Eastern Nigeria, *Global J. Environ. Sci.* 2(1) (2003) 8-10
- [39] Ideriah, T. J. K., A. S. Braide, and A. O. Briggs. Distribution of lead and total hydrocarbon in tissues of periwinkles (*Tympanotomus fuscatus* and *Pachymelania aurita*) in the Upper Bonny River, Nigeria, *J. Appl. Sci. Environ. Mgt.* 10(2) (2006) 145-150

- [40] Adewuyi, G. O., O. T. Etchie, and O. T. Ademoyegun. Determination of total petroleum hydrocarbons and heavy metals in surface water and sediment of Ubeji River, Warri, Nigeria, *Bioremediation, Biodiversity and Bioavailability*, 5(1) (2011) 46-51
- [41] Akporido, S.O. and A. R. Ipeaiyeda. An assessment of the oil and toxic heavy metal profiles of sediments of the Benin River adjacent to a lubricating oil producing factory, Delta State, Nigeria, *International Research Journal of Public and Environmental Health*, 1(2) (2014) 40-53
- [42] Ogeleka, D. F., O. Edjere, A. Nwudu, and F. E. Okieimen. Ecological effects of oil spill on pelagic and bottom dwelling organisms in the riverine areas of Odidi and Egwa in Warri, Delta State. *Journal of Ecology and the Natural Environment*, 8(12) (2016) 201-211
- [43] MADEP. Sediment toxicity of petroleum hydrocarbons fractions, Massachusetts Department of Environmental Protection, Office of Research and Standards (2007).
- [44] TPHCWG. Selection of Representative TPH Fractions Based on Fate and Transport Considerations, Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Series, (John B. Gustafson, Ph.D.; Joan Griffith Tell, Ph.D. and Doug Orem). (1997) vol. 3, (<http://www.aehs.com/>)
- [45] Adeniji, A. O., O. O. Okoh, and A. I. Okoh. Petroleum hydrocarbon fingerprints of water and sediment samples of Buffalo River Estuary in the Eastern Cape province, South Africa, *Hindawi J. Anal. Methods Chem.* (2017b) <https://doi.org/10.1155/2017/2629365>
- [46] Sakari, M., M. P. Zakaria, N. H. Lajis, C. A. R. Mohamed, and M. H. Abdullah. Reconstruction of aliphatic hydrocarbon history and sources from sedimentary record of the Johor Strait, Malaysia. *Coast. Mar. Sci.* 35(2012) 142-152
- [47] Onyema, M., L. Osuji, and S. Ofodile. Geochemical fingerprinting of an oil-impacted site, Niger Delta: source and weathering profile of aliphatic hydrocarbons. *Researcher* 5 (2013) 16-21
- [48] Jeanneau, L., P. Faure, E. Montarges-Pelletier, and M. Ramelli. Impact of a highly contaminated river on a more important hydrologic system: changes in organic markers. *Sci. Total Environ.* 372 (2006) 183–192
- [49] Abdallah, R. I., N. M. Khalil, and M. I. Roushdie. Monitoring of pollution in Egyptian Red Sea. *Egyptian Journal of Petroleum* 24 (2015) 59-70
- [50] Omayma, E. A., A. M. Sawsan, and M. Abd El Rahman. Monitoring and Assessment of Petroleum Hydrocarbons in Surface Seawater along Alexandria Coasts, Egypt, *International Journal of Environment*, 4 (2015) 70-86
- [51] Yusuff, H. B., Z. B. Assim, S. B. Mohamad. Aliphatic hydrocarbons in surface sediments from South China Sea of Kuching Division, Sarawak, *The Malaysia Journal of Analytical Sciences* 16(1) (2012) 1-11