

Aliphatic Hydrocarbons in Recent Dated Sediment Cores of Imo River, SE Nigeria: Environmental/Historical Implications

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Abstract

Four recent sediment cores (0-30 cm long) from Afam (AF), Mangrove (MG), Estuary (ES) and illegal Petroleum refinery (PT) sites of the Imo River, Southeastern Nigeria were analyzed to characterize the sources and distribution of organic matter (OM), as well as examine their historical trends of deposition and assess human-induced changes in the last ca. 5 decades using biomarker approach. Radionuclides ²¹⁰Pb and ¹³⁷Cs were used to assign approximate dates to each section of the cores. Evaluation of proxy parameters such as carbon preference index (CPI, 2.01 - 2.19), carbon number maximum (C_{max}, 29, 31) and atomic C/N (16.51-31.32) for the most recent top layers (0-5 cm) revealed greater wash-in of land-derived organic matter (OM), attributable to the recent rise in water height. The bottom layer (PT1, 25-30 cm,) of the PT core deposited ca. 1964-1972 exhibited a CPI of 0.97 and pristane/phytane (Pr/Ph, 3.75), suggesting that oil bunkering/illegal refinery activity had begun in the region ca. 8 years after the first commercial discovery of oil in Nigeria in 1956. The occurrence in high abundance of heptadecane in the middle layer (ES4, 10-15 cm) of the ES almost corresponded with the period of eutrophication that blocked the waterway in the late 1980s. Measurement of a marked unresolved complex mixture at the near-top layer (AF5, 5-10 cm) of the AF indicated that the heaviest contamination by petroleum hydrocarbons occurred at ca. 1997-2005. This time frame coincided with the period of intensive bunkering and oil pipeline vandalism by Niger Delta militant groups.

Keywords: biomarker, aliphatic hydrocarbons, historical trend, source, Imo River

1. Introduction

Allochthonous and autochthonous organic matter (OM) are deposited in the ocean margins and shelves rivers at a rapid rate (Saliot et al. 2001). Several studies showed that OM transported by tropical rivers/estuaries are mainly degraded terrestrial materials (Ittekkot 1988). Recently, the understanding of OM sources, distribution and fate in aquatic environment have received significance scientific attentions (Jaffé et al. 2005).

Particularly, aliphatic hydrocarbons are biomarkers substantially used to classified OM origins from terrestrial to marine environment (Camacho-Ibar et al. 2003; Oyo-Ita et al. 2010, 2016). As a major contributor to OM flux, tracing the sources of aliphatic hydrocarbons in the study area will help in the understanding of global dynamics of OM delivery.

The present study is part of the regional project aimed at understanding the sources, transport and fate of lipid biomarkers in the Niger Delta drainage basin.

As time has progressed, the deposition of hydrocarbons led to changes in the quality and quantity of OM influx at different sediment depths. Previous studies indicate that the contamination characteristics of certain organic contaminants in sediments are clearly diverse in different years due to industrial development and changes in the

energy condition of the environment (Guo et al. 2010; Oyo-Ita et al. 2017). Therefore, it is important to examine the historical trends in aliphatic hydrocarbons deposition in sediment cores. Extensive studies of temporal trends in aromatic hydrocarbons deposition in sediment cores have been documented worldwide (eg. Guo et al. 2010; Zhang et al. 2013; Oyo-Ita et al. 2017) and most reveal a good correlation between these trends and their vertical distributions. However, knowledge of such a correspondence in the case of aliphatic hydrocarbons is scarce, particularly for the tropical sub-saharan African sedimentary environment. The present study is the first investigation of historical trends in aliphatic hydrocarbons deposition in dated sediments from the Imo River aimed at identifying the effect of human activity/climate change on the study area over the last few decades. Previous organic geochemical studies of the river sediment focused mainly on the surface sediment samples including the distributions and sources of petroleum hydrocarbons (Oyo-Ita et al. 2016), polycyclic aromatic hydrocarbons (PAHs) in sediments and soils from oil exploration areas (Sojino et al. 2010), distribution of fossil fuel biomarkers (Ekpo et al. 2012) and fatty acids and alkanols distribution and sources (Oyo-Ita and Oyo-Ita 2013) as well as toxicological assessment of PAHs (Oyo-Ita et al. 2017). The present report was intended to chronicle the natural and humans-induced events that occurred after the period of oil discovery in commercial quantity in Nigeria in 1956 to ca. 2014 after the offer of amnesty to the Niger Delta Militant groups by the Nigerian government using aliphatic hydrocarbon biomarkers.

The main objectives of the present study were to: (i) determine the age of the sediment interval under study, (ii) characterize the sources and distribution of aliphatic hydrocarbons in the sediment, (iii) evaluate the historical trends in their deposition and (iv) identify the effects of humans-induced/climate changes in the study area.

1.1 Study Area

Details about the study area was described by Oyo-Ita and Oyo-Ita (2013). Briefly, the Imo River is a major river found in the southeastern Niger Delta, Nigeria (Fig. 1), located between 5° 55'N and 7° 1'E. The depth of the river is less than 20 m character by flood and ebb tides. The topography of the river is sloping and flooded (Ezeayim and Okereke 1996), especially during intensive rainfall. In March 2012, the Nigerian hydrological service announced an impending rise in water height to about 5 m occasioned by global climate change that subsequently caused devastating consequences to life and properties of coastal communities who ignored an early warning of evacuation from the region to the hinterland. The vegetation of the river bank includes grasses, mangroves and other terrestrial higher plants. A few industrial activities are also found along the river (Afam Power Station). However, illegal oil refinery and bunkering activity can be seen along the river bank resulting in oil spillage.

2. Materials and Methods

2.1 Materials and Quality Control/Assurance

n-Hexane, methanol (MeOH) and acetone (Me₂CO) were analytical grade solvents provided by Dr. Ehrenstofer GmbH (Augsburg, Germany) and Merck (Hohenbrunn, Germany). Alumina (Al₂O₃; active neutral 0.063-0.200 mm), silica gel (SiO₂; 0.063-0.200 mm) and anhydrous sodium sulfate (Na₂SO₄) were also from Merck. The external standard (perdeuterotetracosane) used for quantification: was from Cambridge Isotope Laboratory; Ambovar, USA.

All glassware used was cleaned initially with Me₂CO. It was heated at 300 °C overnight to decompose any trace of OM and finally rinsed with Me₂CO. One procedural blank was analyzed accompanying every batch of 2-5 samples to correct for background contamination during the preliminary steps of purification and extraction. Analysis of the samples was repeatedly carried out in triplicate and relative standard deviation values were calculated. Blanks were processed together with samples. Limits of quantification (LOQ) and limits of detection (LOD) values were calculated as the mean signal of the blanks plus 10x the standard deviation of the blank signals and mean signal of the blanks plus 3x the standard deviation of the blank signals, respectively.

2.2 Samples

The Imo River was divided into four different sampling sites on the basis of its characteristic features (Fig. 1). Each core (30 cm) was designed to cover the period of the first commercial oil discovery in Nigeria in 1956 to a time after the Federal government offered an amnesty to the Niger Delta militant groups in 2009.

Samples were collected after the devastating flood episode of 2012. Site I corresponded to a core obtained near thick mangrove vegetation (MG), Site II corresponded to a core collected near the Afam power station (AF) where natural gas combustion for power generation takes place. Site III corresponded to a core collected upstream near an illegal local petroleum refinery (PT) and Site IV to a core collected towards the estuary (ES) where fishery activity takes place. For each coring site, an additional core was collected for radiometric dating

using a box corer and carefully sealed in plastic bags to preserve the mud-line. For sediment characterization, each core was cut into 6 sections of 5 cm intervals, wrapped with pre-cleaned Al foil, labeled, kept in a cooler containing ice and brought to the laboratory and stored at -20°C in a deep freeze until further processing.

2.3 Grain Size, Bulk Density and Elemental Analysis

Sediment grain sizes were analyzed as reported by Strauss et al. (2015) ‘using a laser particle sizer (LS 200, Beckmann-Coulter) with a mesh range of $0.375\text{-}1000\ \mu\text{m}$ ’. Bulk density (BD) measurements were performed by determining the volume of frozen samples with the Archimedes Principle that involved quantifying the water displaced in a water-filled glass beaker using a balance (FCB 8K0.1, Kern; Arnaud et al., 2006). BD was calculated using the following equation:

$$\text{BD} [10^3 \text{ kgm}^{-3}] = \text{sample dry weight} [10^3 \text{ kg}] / \text{sample volume} [\text{m}^3].$$

More so, Total organic carbon (TOC) and total nitrogen (TN) were determined as previously reported by Oyo-Ita et al. (2016) ‘using flash combustion at 1024°C and thermal conductivity detection in triplicate with a CHNS Elemental Analyser (Carlo Erba 1108;). Pre-weighed freeze-dried samples were de-carbonated in 87% syrupy H_3PO_4 repeatedly until bubbling stopped and were rinsed in de-ionized water until neutral. The samples were dried in an oven and reweighed. The difference between the initial and final weights multiplied by 100 was taken as the total inorganic carbon (TIC) content.

2.4 Radiometric Analysis

Detailed method of radiometric analyses is given in Appleby et al. (1992) and Pinglot and Pourchet (1995). As described by these authors, ‘radiometric measurements were performed in a very low background P-type germanium well detector (Canberra Industries), which offered a relative efficiency of 40% and a $4\ \pi$ counting geometry. The counting device was placed in a low-level background laboratory, in order to ensure a very low detection threshold for environmental radioactivity. Such a precaution was particularly necessary for the isotopes of interest here (^{210}Pb , ^{214}Pb , ^{137}Cs and ^{241}Am)’. Furthermore, Arnaud et al. (2006) explained that ‘this analytical process allowed the measurement of ^{137}Cs and ^{210}Pb isotopes with detection limits of below 6 mBq/g. The experimental errors for this measurement, taking into account the different sources of error due to the sampling and analytical procedures, was approximately $\pm 20\%$ for ^{137}Cs and ^{210}Pb and $\pm 50\%$ for ^{241}Am . Counts were carried out on individual samples for time periods ranging from 10^5 to 3×10^5 s. For every 10 samples analyzed, the background level was measured over periods of 2×10^5 to 3×10^5 s. Sample specific activity A, and total uncertainties of calculated specific activity values, $\%A$, were expressed in Becquerel per kilogram of dry weight (Bq/kg dry wt). The standard deviation expressed the 95% confidence level’.

2.5 Extraction and Clean-Up

Prior to extraction, a standard solution containing the target compounds were spiked onto the samples. An aliquot (1 g) each of sediment was extracted 3x using ultrasonic bath for 30 min with 15 ml (Me_2CO : *n*-hexane; 1:1 v/v). All extracts were combined and concentrated to near-dryness with rotary evaporator. The total extract were re-dissolved in hexane and separated into non-polar and polar fractions with *n*-hexane and DCM:MeOH (1:1 v/v) respectively using a short glass column packed with Al_2O_3 prior to gas chromatography-mass spectrometry (GC-MS).

2.6 Instrumental Analysis

Analysis of the non-polar fraction was conducted as earlier reported by Oyo-Ita et al. (2010). ‘GC-MS Thermo-Finnigan TRACE (Manchester, UK) in the electron impact (EI) mode at 70 eV. A 30-m, 0.25-mm-id column coated with $0.25\ \mu\text{m}$ of ZB-5MS stationary phase (Phenomenex Zebron; USA) was used. The carrier gas was He at a constant 1.2 ml/min. The injector temperature, in ‘splitless’ mode, was 280°C and the purge valve was activated 50 s after injection. Column temperature program was 60°C (for 1 min) to 200°C at $10^{\circ}\text{C}/\text{min}$ and finally to 320°C (held 10 min) at $4.8^{\circ}\text{C}/\text{min}$. Transfer line and ion source were at 250°C and 200°C , respectively. Data were processed with the X-calibur Thermo Finnigan software (San Jose, California, USA) and acquired in the full scan and selected ion monitoring (SIM) modes with 6 min of solvent delay. Compounds assignment was on the basis of retention time and ion fragmentation pattern comparison with biomarker standards. Quantification was performed from SIM peak area conversion to compound mass using peak area of the external standard: perdeuterotetracosane for alkanes and hopanes. Surrogate data were used to calculate loss during the analysis (ie. for recovery purposes). The recovery study ($n = 3$) was carried out by spiking a standard solution containing the target compounds onto a silica matrix to determine their loss during the analytical procedure. The average recovery was $85 \pm 0.98\%$ (60–130%).

3. Results and Discussion

3.1 Sediment Bulk Characteristics

As presented in S1-1 and Fig. 2, results of sediment bulk properties including pH, grain size distribution, bulk density, TOC and TN did not vary significantly within each core and among the four cores. However, the three coring sites still provided evidence of sedimentary and historical events. These events were characterized by a change in grain size/bulk density at the top layers (SI-1) and inundation of the lower layers by petroleum hydrocarbons/algal OM in the last few decades, respectively.

The cores were dominated by gray-dark sandy silt and a minor clay deposits at depths between 5 and 30 cm, whereas a relatively higher silt/clay fraction were found at the top layers (0-5 cm). The fairly constant bulk density values recorded for the lower layers (SI-1) suggest that a steady sedimentation rates prevailed at the three coring sites. However, the slight drop in bulk density values at the top layers (0-5 cm) was linked to the flood episode of 2012, leading to a slight change in the sedimentation rates at the top layers.

The sediment cores were dated by the application of ^{210}Pb -derived model and validated by ^{137}Cs -derived model. The $^{210}\text{Pb}_{\text{xs}}$ specific activity profiles were relatively homogeneous for depths of between 5 and 30 cm (3.06-3.24 Bq/kg) and differed at 0-5 cm ((4.24-4.35 Bq/kg; SI- 1). The $^{137}\text{Cs}_{\text{xs}}$ specific activity reached maximum at 0-5 cm (5.08-5.12 Bq/kg) and then similarly became relatively homogenous in the underlying sample layers (5-30 cm; 3.09-3.28 Bq/kg; SI-1). The depths at which $^{210}\text{Pb}_{\text{xs}}$ and $^{137}\text{Cs}_{\text{xs}}$ specific activities were homogenous coincided with the depths 5-30 cm and differed from depth 0-5 cm in which the relatively higher silt/clay content and slight decrease in bulk density was found (SI-1). Consequently, the sediment deposits scenario did not meet the conditions for applying the CFCS model (Arnaud et al. 2006). Therefore, CFCS could not be used to calculate mean sedimentation rates for the cores. The calculated ages based on CRS model assumed the constant sedimentation rates for the whole cores. These sedimentation rates were derived from the mean slope of ^{210}Pb and ^{137}Cs specific activities plotted on a logarithmic scale. Mean sedimentation rates for AF, PT and MG cores were ca. 0.60, 0.58 and 0.62 cm/yr, respectively, with an overall mean of ca. 0.60 ± 0.07 cm/yr. This overall mean value was subsequently used to evaluate the historical variations of aliphatic hydrocarbons in the river sediment.

Ages of specific layers were determined by dividing their depths by the corresponding sedimentation rates. Age resolution of the cores represents an average provisional record of ca. 50 yr. of sedimentation history. Sedimentary records for the river date from ca. 1964 (ca. 8 yr after first commercial discovery of oil in Nigeria in 1956) to ca. 2014 (ca. 5 yr after an amnesty offer to Niger Delta militant groups by the Nigerian government in 2009).

Low TOC values were found in all layers of the cores (Fig. 2 a). The TOC content of AF was in the range 0.56 - 1.02%, maximizing in the near-top layer (AF5, 5-10 cm, ca. 1997-2005) and a minimum at the middle layer (AF3, 15-20 cm, ca. 1989-1997, Fig. 2 a). A TOC range of 0.33-0.42% was found for the MG, maximizing in the near-top layer (MG5, 5-10 cm, 1997-2005) and minimizing in the top layer (MG6, 0-5 cm, 2005-2013). ES exhibited a TOC content ranging from 0.31% at the top layer (ES6, 0-5 cm) to 0.49% at the near-top layer (ES5, 20- 25 cm). In the case of PT, TOC ranged from 0.10% to 0.22% with a maximum at the middle layer (PT3, 15-20 cm, ca. 1981-1989) and a minimum at the top layer (PT6, 0 - 5 cm, ca. 2005-2013). The fact that TOC maximized at the near-top layers of the cores, except PT, partly suggested that anthropogenic pressure on the river was heaviest in the period ca. 1997-2005. The prevalence of low TOC in the cores may be linked to poor adsorption capacity of organic carbon (OC) towards the coarse solid matrix characteristic of the sheltered basin morphology of the Niger Delta dominated by the sand fraction (SI-1: Oyo-Ita et al. 2016) and low primary productivity (Camachor-Ibar et al. 2003; Dominguez et al. 2009; Oyo-Ita and Oyo-Ita 2013).

TN content in sediments is an indication of the contribution of aquatic flora (Gonzalez-Vila et al. 2003). The values for the cores were low $< 0.05\%$, suggesting a minor contribution from aquatic flora to the OM composition in the sediment (Fig. 2 b). Atomic C/N profiles for the four cores revealed a wider range of 7.81-31.32 for AF and ES than for PT and MG (3.25-16.51), all maximizing in the top layers (Fig. 2 c). Oyo-Ita and Oyo-Ita (2012) reported a similar high C/N value for the top layer of Ukwa Ibom lake sediment, SE Nigeria and attributed the elevated level to greater wash-in of land-derived OM following pave-road extension exercise that involved tree logging/forest clearing. The elevated C/N scenario at the top layers here most likely reflected the effect of flood associated with the recent intense rainfall occasioned by global climate change, carrying larger amounts of land-derived debris to the river.

3.2 Vertical Distribution, Sources and Historical Trends of *N*-Alkanes

The aliphatic fractions of the cores comprised of *n*-alkanes in the range C_{12} - C_{37} , generally suggesting different

contributions from both biogenic (terrestrial/microbial) and petroleum sources. The *n*-alkanes concentrations for the four cores ranged from 12.51 ng/g dry weight (dw) in ES core for C₁₂ at the top layer (ES6, 0-5 cm) to 426.72 ng/g dw for heptadecane (C₁₇) at the near-top layer (AF5, 5-10 cm, ca. 1997-2005) of the AF core, with an overall mean of 174.11±12.25 ng/g dw (SI-1). Marked concentration levels (406.01 ng/g dw and 401.87 ng/g dw) were also measured for C₁₇ at the middle layers (ES3 and ES4, 10-15 cm and 15-20 cm) of the ES.

Quantification of homologous *n*-alkane series in the sediment cores allowed the calculations of both carbon maximum (C_{max}) and carbon preference index (CPI). Generally, CPI less and greater than 1 shows *n*-alkanes from biogenic sources of microbial and terrestrial respectively (Simoneit et al. 1991), compared to petrochemical/petroleum (CPI - around 1) sources (Pies et al. 2008).

CPIs calculated for cores AF, MG, PT and ES showed a trend in which the most recent top layers exhibited the highest values (>1). For instance, the observed variation in CPI values for PT in the range 0.90 - 1.20 and a maximum at the surface layer (PT6, 0-5 cm, ca. 2005-2013; Fig. 2 d) indicated microbial alteration of fresh plant matter/oil in the lower layers and greater wash-in of terrestrially-derived OM onto the top layer earlier linked to the recent rise in water height following intense rainfall occasioned by climate change, respectively. The near-bottom and bottom layers of PT and MG were largely inundated by microbial input, having CPIs of 0.04. Generally, the irregularity in CPI patterns down cores reflected changes in energy structure/anthropogenic pressure, enabling deposition of different types and amounts of OM to the river sediment over the last ca. 5 decades.

Besides CPI, a more specific diagnostic parameter that gives indication for the source input of biogenic OM is C_{max}. C_{max} > 25 for *n*-alkanes indicates higher plant wax incorporation and < 25 reflects a strong microbial source input (Mazuerk and Simoneit 1983). Here, *n*-alkanes distributions indicated C_{max} at 22 at the bottom layer (MG1, 25-30 cm) of MG, revealing a significant proportion of microbial OM thriving at ca. 1964-1972 (Fig. 3 a, Table 1, Ekpo et al. 2005). In support of this source contribution, Oyo-Ita et al. (2006) and Elias et al. (1997) recorded a predominance of C₂₂ in sediments surface of Cross River estuary, Southeastern Nigeria and in the Amazon shelf and Pacific hydrothermal system, respectively. These authors attributed such occurrence to bacterial alteration of algal detritus. The emergence of land-derived OM thereafter became enhanced at the top most layer (MG6, 0-5 cm).

In the case of ES, C_{max} at 14, 22, 24 and odd/even predominance in the range C₂₅ - C₃₅ was apparent at the bottom layer (ES1, 25-30 cm). This distribution reflected a mixed source of a higher proportion of aquatic microbial over land-derived OM input (Fig. 3 b). The trend persisted thereafter until ES4, 15-20 cm when emergence of C₁₇, a marker indicative of algal growth (Pastor et al. 2001) became apparent (Fig. 3 c). Although radiometric analysis was not possible for the ES core, going by the data obtained for other cores, this sediment interval almost coincided with the period of occurrence of eutrophication (excessive growth of macro-algal e-water hyacinth) towards the estuarine portion of the river, a consequence of effluents discharges from a fertilizer plant ca. 4 km from the Afam power station (Guardian Newspaper, 12th July 1989). However, a dramatic change occurred in the OM fluxes at the most recent top layer (ES6, 0-5 cm) where C_{max} 27, 29 and 31 prevailed (Fig. 3 d). This later pattern is characteristic of higher proportion of vascular plant wax influx to the top layer (Elias et al., 1997; Oyo-Ita et al. 2010). An additional OM input to the top layer reflected in C_{max} at 19, pointed to a bacterial source (Ittekkot, 1988).

In comparison, biogenic OM flux to the AF did not vary remarkably down core (C_{max} - 14, 20, 27, 29 and 31), revealing a fairly constant OM input from both microorganisms and vascular higher plant, except at the near-top layer (AF5, 5-10 cm; Fig. 4 a) deposited ca. 1997-2005. At this near-top layer, additional OM sources (C_{max} at 17, 19, 21) occurred, characteristic of algal and bacterial OM inputs (Aboul-Kassim and Simoneit, 1996). Field observation revealed that the near-top layer (AF5; 5-10 cm) of AF had the smell of oil, supported by the occurrence of a marked unresolved complex mixture (UCM) in the layer (Fig. 4 a). The presence of UCM in aquatic sediment is an indication of relative contribution of petroleum hydrocarbon and/or biodegraded mixture of hydrocarbon. The heavy impact by petroleum hydrocarbons in the period ca. 1997-2005 was linked to frequent and intensive oil bunkering activity and/or oil pipeline vandalism by the Niger Delta militia groups. According to Okpo and Eze, (2012), 'in June 1998, a 16-inch underground Shell pipeline burst, discharging ca. 800,000 barrels of oil into the area'. As in our case study, the pronounced UCM in sediment cores revealed variations in local histories of petroleum hydrocarbons delivery to the study area (Meyers, 2003).

In the case of core PT, no distinct UCMs were apparent in any of the layers (Fig. 4 b, c) probably due to the fact that the core was obtained upstream relative to the site where illegal petroleum refining takes place. This implies that contamination by petroleum hydrocarbons in the last ca. 5 decades was not widespread but rather was

localized or confined within small areas. In other words, long-range water current trajectory did not play a major role in the distribution of petroleum hydrocarbons in the river in the last ca. 5 decades. Hence, the effect of oil exploitation around the study area from the time of first discovery of commercial quantity of oil in Nigeria in 1956 was not widespread. The near-top layer (PT5, 5-10 cm) of PT exhibited C_{max} at C_{22} and C_{24} with an even/odd predominance in the range C_{12} - C_{26} , characteristic of microbial input (Table 1; Fig. 4 b). Sediment samples with specific predominance of organisms input including bacteria and diatoms have been reported (e.g. Simoneit et al. 1991; Elias et al. 1997; Ekpo et al. 2005).

Here again the recent rise in water level experienced in 2012 following intense rainfall resulted in greater wash-in of land-derived OM to the top layer (PT6, 0-5 cm, C_{max} at the 29; Fig. 4 c) of PT core. In specific terms, a predominance of C_{31} in sediments indicates that the watershed is populated by grasses, whereas C_{27} or C_{29} is more abundant in sediments in areas where trees dominate (Cranwell et al. 1987; Vogts et al. 2012). On the basis of this source assignment, the watersheds of AF and ES sites were populated by grasses and trees, those of the MG and PT sites were more populated by trees. However, recent study shows that most of the C_{max} applications have been based on a narrow set of data that cannot address intra- and inter-plant variability. A more widespread analysis of data on trees and grasses of different species from different locations of the world shows that C_{27} , C_{29} and C_{31} are highly variable among plants, causing the chemotaxonomic differentiation between woody plants and grasses challenging to determined based on *n*-alkane abundances (Bush and Mcinerney 2013).

To determine the proportion of higher plant-/macrophyte-derived OM relative to microbial (bacterial-/phytoplankton-derived) OM in the cores, long chain hydrocarbon (C_{25} - C_{35}) over short chain hydrocarbon (C_{14} - C_{24} ; LHC/SHC) ratios values were calculated and ranged from 1.01 to 1.84 for core MG, indicative of an admixture of almost equal proportion of higher plant/macrophyte and phytoplankton/bacteria in lower layers and a slightly higher proportion of higher plant/macrophyte vs. phytoplankton/bacteria in the upper layers (Table 1). The data support the earlier source assignment from CPI and C_{max} for these layers. On the other hand, a relatively higher proportion of land-/macrophyte-derived OM was generally found for core PT than for MG with LHC/SHC ranging from 1.1 to 2.3 (Table 1). PT5, for instance, with intermediate LHC/SHC value (1.1) also indicated a mixed source scenario of almost equal contributions from land-/macrophyte-derived and phytoplankton-/bacteria-derived OM.

The ES core exhibited LHC/SHC values ranging from 0.7 to 2.7 with a minimum at the middle layer (ES4, 15-20 cm), indicating a dominant microbial-derived OM input (e.g. algae). The result was in agreement with the C_{max} and CPI source data earlier assigned to the layer. Other layers of the ES core exhibited intermediate values, still supporting a mixed source scenario of almost equal contribution from land-/macrophyte-derived and microbial-derived OM, except at ES2 (20-25 cm, 2.3) and ES6 (0-5 cm, 2.7), which indicated a greater input from land-derived OM.

LHC/SHC values for the AF core were in the range 1.1 - 2.4 with terrestrially-derived OM dominating overall. However, evidence of a relatively enhanced input from microorganisms (e.g. petroleum inhabiting bacteria and algae) was apparent at the near-top layer (AF5, 5-10 cm) reflected in an intermediate LHC/SHC value of 1.1.

To further characterize the sources of OM in the study area, the proxy parameter, P_{aq} , was calculated (Table 1). P_{aq} reported by Ficken et al. (2000) expresses the relative proportion of mid-chain (n - C_{23} , n - C_{25}) to long-chain length homologues (n - C_{29} , n - C_{31}). According to the interpretation, P_{aq} values between 0.4 and 1.0 are indicative of a high contribution from submerged/floating aquatic macrophytes, while between 0.1 and 0.4, they correspond to emergent terrestrial higher plant'. Here, P_{aq} values for core MG were in the range 0.25-1.0, maximizing in the bottom layer (MG1, 25-30 cm; 1964-1972), indicating a greater contribution from submerged/floating macrophytes to the bottom layer. On the other hand, a range of 0.35 -0.61 was calculated for core PT, minimizing at the near-top layer (PT5, 5-10 cm, 1997-2005), indicating higher contribution from higher plant vs. macrophyte to the near-top layer, and a maximum at PT3 indicative of higher contribution from macrophyte over higher plant to the middle layer. A P_{aq} range of 0.29 - 0.51 for core ES, with almost all the layers having about equal proportions of higher plant-derived and macrophyte-derived OM, except at ES3 (15-20 cm, 0.31) and ES6 (0-5 cm 0.29) apparently influenced more by higher plant wax input. A P_{aq} range of 0.30 - 0.44 for core AF indicated a greater contribution from higher plants at AF3, AF4 and AF6, while the other layers exhibited values characteristic of almost an equal proportion of macrophyte and higher plant input.

3.3 Vertical and Historical Distributions of Isoprenoid Hydrocarbons and Triterpanes

Pristane (Pr) and phytane (Ph) were detected in relatively high abundance in the aliphatic fractions of the four cores. The concentrations ranged from 0.46 ng/g dw at the near-bottom layer (PT2, 20-25 cm) of PT for Ph to 114.33 ng/g dw at the middle layer (ES3, 15-20 cm) for Pr, with an overall mean of 78.71 ± 43.22 ng/g (SI-3).

High Pr/Ph values (e.g. 8-11) have been reported to be characteristic of biogenic hydrocarbons source and low ranked coal, while low values are the result of oils (e.g. < 2) and high ranked coal (e.g. < 8; Pies et al. 2008). Pr/Ph for cores ES and AF ranged from 0.43 at the middle layer (AF3, 15-20 cm) of AF to 1.25 at the middle layer (ES4, 10-15 cm) of ES, reflecting varied inputs from oils to these sites in the last ca. 5 decades.

Pr/Ph for cores MG and PT was in the range 1.15 – 4.17, with minimum and maximum values at the near-bottom (MG2, 20-25 cm) and middle layers (MG4, 15-20 cm) of MG, respectively (Table 1). Although input from oil was evident, the relatively high Pr/Ph values at MG4 (4.17), PT1 (3.75) and PT5 (3.86) were suggestive of input from high ranked Nigerian coal utilization as an energy source to fuel the illegal petroleum refinery process at different time intervals in the remote regions. Field observation revealed debris of coaly material dispersed in the vicinity of the illegal activity site. This scenario implied that the illegal activity had begun ca. 8 yr after the discovery of oil in commercial quantity in Nigeria in 1956 and that the illegal activity was not concentrated at one location in the study area. This means that at certain geologic time-frame, these saboteurs relocated from one area to another, following occasional policing/patrolling of the waterway by the Nigerian Navy to stem the tide of oil bunkering.

To further evaluate the impact of humans-induced activity in the study area in the last ca. 5 decades, evaluation of the types and levels of triterpanes was carried out. Triterpanes such as hopanes, 18 α -oleanane (30O) and gammacerane (30G) are petroleum source marker due to their relatively resistant to environmental degradation in recent sediments (Bouloubassi et al. 2001). Also, Peters and Moldowan, (1993) reported that ‘hopanes are abundant in petroleum and sediments, because their precursor hapanoids are important membrane components in living cells and are resistant to degradation during diagenesis’. Thus, the presence of hopanes and other triterpanes such as 30O and 30G in contemporary sediments confirms fossil fuel contamination.

The following triterpanes were detected in the four cores; 18 α -22,29,30-trisnorneohopane (27TS), 17 α -22,29,30-trisnorhopane (27TM), 17 α ,21 β -25-norhopane (25NOR30AB), 15 α -Ethyl-17 α -27-norhopane (diahopane; 30D), 18 α -oleanane (30O), 17 α ,21 β -hopane (30AB), gammacerane (30G), 17 α ,21 β -22R-homohopane (31AB), 17 α ,21 β -22S-thomohopane (31ABS), 17 α ,21 β -22R-bishomohopane (32ABR), 17 α ,21 β -22S-bishomohopane (32ABS), 17 α ,21 β -22S-trishomohopane (33ABS) and 17 α ,21 β -22R-trishomohopane (33ABR). The concentrations of triterpanes ranged from 0.34 ng/g dw to 119.42 ng/g dw, minimizing in 25NOR30AB at the middle layer (PT4, 10-15 cm) of PT and maximizing in 30AB at the near-top layer (AF5, 5-10 cm) of AF with an overall mean of 37.31 \pm 12.64 ng/g (SI-3).

Generally, the triterpanes exhibited similar distribution pattern in all layers of the four cores except at the bottom (MG1, 25-30 cm) and top (MG6, 0-5 cm) layers of MG and the near-bottom layer (PT2) of PT. For example, a *m/z* 191 chromatogram for the top layer of MG deposited ca. 2005-2013 shows absence of 30O and 25NOR30 (marker compounds characteristic of oils of continental origin - eg Niger Delta oil; Ekweozor et al. 1979; Oyo-Ita et al. 2016) and 27TM as well as the occurrence at low level of 30G (Fig. 5 a). The later (derived from *Genacilinae*, an algal species that thrives more on a hypersaline environment) are abundant in petroleum of lacustrine origin (Peter and Moldowan 1993). Its detection at the top layer of the core suggested an input from petroleum products utilization derived from a different source imported into the Nigerian economy. Triterpanes including 30O and 30G were not detected in the bottom layer (MG1, 25-30 cm) of the MG (SI-2). The scenario suggested that the impact of oil exploitation activity on the sediment deposited about the early 1960s in the MG area was negligible and that the activity became apparent from early 1970s.

A somewhat different triterpanes distribution pattern was found for most layers of ES, AF and PT cores with the detection of 27TS, 27M, 30O, 25NOR30 and 30G (Fig. 5 b c). This trend implied that an admixture of indigenous and imported oils pervasively impacted the portions of the river in the last ca.5 decades except at the near-bottom layer (PT2, 20-25 cm) of PT. Similar to MG1 profile, a *m/z* 191 chromatogram of PT2 shows absence of triterpanes (Fig. 5 d), revealing that a period of inactivity related to oil exploitation existed at ca. 1972-1981 in the area.

Another prove that Imo River sediments were impacted by hydrocarbons of petroleum origin was again illustrated in the ratio of homohopane index [22S/(22S + 22R)]. Homohopane ratio increases with increasing maturity. This imply that immature OM exhibit low homohopane ratios (Gulnay and Korkmaz 2008). Generally, the extended 17 α ,21 β -homohopane > C₃₁ in petroleum showed the epimers at C-22 at an equilibrium ratio 22S/(22S+22R) of ca. 0.6 as reported by Franco et al. (2006). Here, the calculated ratio ranged from 0.57-0.64 with a mean value of 0.60 \pm 0.03 (Table 1), confirming contamination by matured OM of petroleum hydrocarbons.

Finally, the total aliphatic hydrocarbon (TAH) concentrations for the study were less than those reported for

sediments from many rivers, estuaries, lakes and seas of the world, ranging from 1,962 ng/g dw at the middle layer (10-15 cm, ca. 1989-1997) of MG core to 10,234 ng/g dw at the near-bottom layer of PT core (25 cm, 1972-1981; Fig. 6 a, b, c). For instance, higher levels of TAH were recorded in sediments from Khniss Tunisian coast, Mediterranean sea (1020 - 2332 µg/g dw, Zrafi et al. 2013); Buffalo river estuary, South Africa (12.59 - 1100 µg/kg dw, Adeniji et al. 2017); Tropical Brazilian estuarine system (27.8 -139.5 µg/g dw, Thias et al. 2013); Lake Washinton, USA (11 - 900 µg/g dw, Stuart et al. 2004).

4. Conclusions

Vertical distribution, source and historical variations of aliphatic hydrocarbons in subsurface sediment cores collected from four locations (Mangrove, Afam, illegal petroleum refinery and Estuary) of Imo River, SE Nigeria in the last ca. 5 decades were determined. Evaluation of organic geochemical parameters such as C/N, CPI, C_{max} , LHC/SHC, P_{aq} , Pr/Ph, UCM and 22S/(22S+22R) homohopane as well as triterpanes distributions enabled OM source characterization and anthropogenic changes to be studied.

The results revealed inputs from biogenic (aquatic and/or terrestrial) and petrogenic OM in almost all layers of the four cores with greater wash-in of land-derived OM to the surface layers (0-5 cm, ca. 2005-2013). Sedimentological and radiometric measurements indicated that this time-frame corresponded with the recent rise in water height/flood associated with intense rainfall event of 2012 occasioned by climate change.

While the impact by petroleum hydrocarbons on the bottom layer of the illegal petroleum refinery core (deposited ca. 1964-1972) showed that oil contamination had begun ca. 8 years after the first commercial discovery of oil in Nigeria in 1956. However, the middle layer of the Estuary core was inundated by macro-algal OM. A relatively pristine depositional environment dominated by aquatic micro-organisms was recorded for the bottom layer of the Mangrove core, while a marked UCM measured at the near-top layer of the Afam core indicated that the heaviest contamination by petroleum hydrocarbons occurred at ca 1997-2005 coinciding with the period of intensive oil bunkering/pipeline vandalism of the Niger Delta militias in the area.

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