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Geochemical characterization of n-alkanes and polycyclic aromatic hydrocarbons in water and sediment from new calabar river

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Abstract: Geochemical characterization of polycyclic aromatic hydrocarbon and n-alkanes in sediment and water from New Calabar Rivers was carried out using gas chromatography – Flame Ionization Detector (FID). A total of twenty-six (26) n-alkanes were quantified and identified for water sample whereas the sediment sample recorded a total of twenty-five (25) n-alkanes. The n-alkane concentrations varied between 0.48-43.80 for sediment samples and 0.27-22.0 for water sample. The study involves the use of some geochemical parameters such as CPI, C_{max}, Paq LHC/SHC for characterization of n-alkanes. The n-alkane in sediment and water from the study area ranged from $C_9 - C_{26}$ with C_{max} at C_{26} suggesting mixed contribution of terrestrial plant wax and petroleum/microbial sources of organic matter. $C_{max} < 25$ are indicative of petroleum and microbial source input while $C_{max} > 25$ reflects the incorporation of higher plant wax. The PAHs detected and quantified in the samples are the regular PAHs found in the ecosystem and are formed from anthropogenic sources. Based on the study, it was discovered that water and sediment from the study area had variable contributions to n-alkanes and PAHs predominantly petroleum inputs as the secondary source (allochthonous) continental inputs and microbial inputs from organic matter such as macrophytes and phytoplanktonic derived organic matter as its primary source (autochthonous) planktonic inputs.

Key words: Polycyclic Aromatic Hydrocarbon, n-alkanes, Geochemical Characterization, New Calabar River, *amongst others.*

INTRODUCTION

Hydrocarbons are ubiquitous elements of organic matter released into the waters of the world's marine and open sites. Via both atmospheric (dry/wet deposition, gas exchange across the air-water interface) and aquatic routes (direct discharges, continental run-offs, off-shelf exports), they join the marine system, the relative importance of which depends entirely on the geographical setting of the region. Although they can be extracted from both aquatic and terrestrial natural sources, a significant proportion of hydrocarbons are associated with various anthropogenic practices contributing to the formation and release of harmful organic pollutants. (1997, Bouloubassi et al.; Gogou et al., 2000; Tolosa *et al.*, 1996; Yunker *et al.*, 2002). Hydrocarbons in the aquatic environment appear to be associated with particles because of their hydrophobic nature, resulting in their downward transport across the water column and eventual deposition in sediments (Deyme et al., 2011; Parinos et al., 2013; Tsapakis et al., 2006).

In general, the coined term "PAH" refers to chemical compounds which consist only of atoms of carbon and hydrogen. Cluster, linear, or angular structures composed of two (2) or more benzene rings are commonly bonded (Menzie, et al., 1992;

Arey, and Atkinson 2003). While there were many polycyclic aromatic hydrocarbons but many data reporting, a small number of PAHs were reported through regulations and studies, specifically between 14 (fourteen) and 20 (twenty) compounds of human PAH. They are toxic by different behavior of living beings. The interference with the enzyme systems are as well as with the function of cellular membranes which are associated with the membrane is referred to as the mechanism of toxicity. Practically, the mutagenic, carcinogenic and potent immune-suppressants nature of PAHs has been investigated and proved.

The understanding of the nature of soil contamination by hydrocarbons and the significant of bioremediation techniques, comprehending the behavior and fate of aliphatic hydrocarbons is imperative, especially the microbe-contamination interactions. The key elimination action of hydrocarbons in the soil is by biodegradation (microbes) which is preferentially manipulated by certain factors; including hydrocarbon physiochemistry, bioavailability, environmental conditions, and the presence of active catalysts (microbes). Data produced by the GC system are used as a diagnostic tool to classify and source petroleum contamination, decide the degree of contamination, differentiate between hydrocarbon sources such as biogenic (biological), petrogenic (petroleum) or pyrogenic (combustion), assign hydrocarbon mixtures to multiple sources, and evaluate the level of degradation of hydrocarbons released (Ramsey et al., 2014; Suneel et al., 2013; Oros et al., 2007; Burns et al., 1997). Examination of these ratios allows to explain whether the environmental source of hydrocarbons is petrogenic,

Statement of the Problem

Water is one of the oldest public health challenges and is tied to a variety of health-related concerns. Microbial and chemical toxins that have harmful effects on humans and the atmosphere arise from these issues. Special attention is given to chemical contaminants, especially xenobiotic compounds such as aliphatic hydrocarbons (AHCs) and polycyclic aromatic hydrocarbons (PAHs). PAHs and AHCs are truly multimedia pollutants which occur in all parts of the environment: atmosphere, inland and sea water, sediments, soils and vegetation (Edokpayi et al., 2016). This research is therefore aimed at evaluating the amount of PAHs and other hydrocarbon concentrations in sediment and water of new Calabar River.

Aim and Objectives

The aim of this work is to carry out geochemical characterization of n-alkanes and polycyclic aromatic hydrocarbons in sediments and water from new Calabar River.

The specific objectives of the study are to;

i. Evaluate the autochthonous and allochthonous planktonic inputs to n-alkanes and polycyclic aromatic hydrocarbon (PAHs) distribution in sediment and water of new Calabar River.
ii. Investigate the influence of tidal and seasonal variation on the physiochemical parameters of the study area.
iii. Determine the influence of tidal variations on the accumulation and distribution of n-alkanes and PAHs in sediments and water of new Calabar River.
iv. Establish the sources and transport route of organic components in sediment and water of new Calabar River.

MATERIALS AND METHOD

Apparatus and Reagents

Apparatus

The following apparatus were used in this study are; GC-FID machine, Oven, Rotary evaporator, Pestle and mortar, Soxhlet apparatus and Analytical sieve.

Reagents

The following reagents were used during the study are; Acetone, Acetonitrile, Dichloromethane, Hexane, Benzene, Anhydrous sodium sulphate and Sodium chloride

Sample Collection

Surface water sample was collected from three locations within the New Calabar River at a depth of about 3 to 4cm, prior to sample collection, glass bottles will be washed and sun-dried; before collection, then during collection of the water samples, the glass bottles will be rinsed twice with the same water samples they are to contain, after collection the sample will be stored in an ice-chest and maintained at $4^{o}C$ while being to the laboratory for analysis.

At the same or closer sites where the water samples were taken, the sediment samples were obtained with the aid of a soil auger and stored in polyethylene plastic bags and transferred to the laboratory in a manner identical to the water sample.

Extraction of sediment samples for PAHs determination

Sediment samples were air-dried, homogenized, gently ground with an agate pestle and mortar in the laboratory and sewn with a 500 micrometer analytical sieve (Edokpayi et al., 2016).

Approximately 20 g of each homogenized sediment sample was thoroughly mixed to capture moisture with anhydrous 10 g of Na2SO4 chloride. The sediment sample was collected in a 4 hou soxhlet apparatus With 150mL dichloromethane for 4 hours (CH2Cl2). The dichloromethane extract was washed to eliminate all moisture by going through a column filled with anhydrous Na2SO4 salt. The resulting extract was condensed to give an oily residue on a rotary evaporator; it was dissolved again in 1mL CH2Cl2 and 1µL was injected into the GC for analysis (Amos-Tautua et al., 2013).

Extraction and Analyses of PAHs and AHCs in water

For the extraction of PAHs in water samples, liquid-liquid extraction by partitioning was introduced. In the splitting funnel, 80 g of NaCl was applied to 550 mL of the sample. About 100 mL of hexane was combined with the above solution and shook for 3 minutes or so. The solution in the separatory funnel was permitted to rest for 2 minutes after which the upper layer containing AHCs was collected. This was replicated again and the blended extract was dehydrated with anhydrous sodium sulphate and condensed over the rotary evaporator to 5 mL and 1 µL was injected for analysis into the GC. Using a combination of dichloromethane and n-hexane, the PAHs in the sample were removed three times. Using anhydrous sodium sulfate, the extract was dehydrated after intense shaking and condensed to 5 mL with a 35-40 oC rotary evaporator and 1 µL was injected into the GC for examination (Edokpayi et al., 2016).

Identification and Quantification by GC-FID

Sample fractionation was done using a glass chromatographic column (15 cm x 1 cm) stocked at the lower end with glass wool and lined with activated silica gel (100-200 mesh) topped with 0.5 g of anhydrous sodium sulphate to extract water. Saturated hydrocarbons were eluted with n-hexane and aromatic hydrocarbons were eluted with hexane/dichloromethane (1:1 v/v. PAH and AHC fraction analysis of each sample extract was conducted with AGILENT 6890 gas chromatography (GC) equipped with a flame ionization detector (FID) and fitted with a 25.0 m long capillary column, 320 µm diameter, stationary phase; phenyl methyl siloxane, phenyl methyl siloxane, In splitless mode, one microlitre (1µl) of each sample extract was injected with Helium used as the carrier gas and operating conditions were as follows: flow rate (H2 35ml/min, air 350ml/min, N2 10ml/min); injection temperature (initial 100oC, final 325oC). At a rate of 6oC/min, the GC oven temperature was programmed from 40oC to 320oC and kept for 15 minutes at 350oC. The detection and quantification of PAHs and AHCs was based on a distinction between the peak retention periods and those obtained from the normal PAH mixture

(standards supplied by instrument manufacturer).
). External calibration curves prepared from the normal solution of each of the PAHs is centered on quantification (Amos-Tautua et al., 2013; Illechukwu et al., 2016).

Validation Studies and Preparation of Calibration Standards

For confirmation tests for both the water and sediment samples, the Spiked recovery process was used. Samples were spiked with a normal mixture of 1 L of 100 mg/L composed of 16 PAHs to 500 mL of pre-extracted samples of water. Second, double-distilled water (500 mL) was pre-extracted as a blank sample in triplicate with 30 mL dichloromethane. After that, the spiked samples were collected and analyzed. The standards of the PAHs were used to calibrate the instrument. Serial dilution from stock solution was used to prepare the calibration levels (Edokpayi et al., 2016).

RESULTS AND DISCUSSION

Table 1: Concentration of n-alkanes in sediment and water from New Calabar River

Name of Compounds	MF	Sediment Concentration	Water (µg/l)	Mean	SD
Nonane	C_9H_{20}	10.87	8.67	9.77	1.10
Decane	$C_{10}H_{22}$	15.85	13.20	14.53	1.33
Undecane	$C_{11}H_{24}$	43.80	14.23	29.02	14.79
Dodecane	$C_{12}H_{26}$	7.823	2.01	4.92	2. 91
Tridecane	$C_{13}H_{23}$	1.09	0.46	0.78	0 .32
Tetradecane	$C_{14}H_{30}$	20.64	2.11	11.38	6. 57
Pentadecane	$C_{15}H_{32}$	10.71	4.83	7.77	2. 94
Hexadecane	$C_{16}H_{34}$		2.31	1.16	1.16
Heptadecane	$C_{17}H$	1.32	3.48	2.40	1.08
Nonadecane	$C_{19}H$	0.87	2.62	1.75	0.88
Edcosane	$C_{20}H_{42}$	2.08	10.63	6.36	1.28
Henicosane	$C_{21}H$	12.31	13.07	12.69	0.38
Docosane	C_{22}	6.43	3.08	4.76	1.68
Trieicosane	C_{23}	2.80	8.02	5.41	2.46
Tetracosane	$C_{24}H$	6.03	5.03	5.53	0.50
Pentacosane	C_{25}	4.03	0.27	2.15	1.88
Hexacosane	$C_{26}H_{54}$	17.69	22.0	19.85	2.16
Heptacosane	$C_{27}H$	3.86	8.62	6.24	2.38
Octacosane	C_{28}	4.86	2.62	3.74	1.12
Nonacosane	$C_{29}H$	1.86	3.02	2.44	0.58
Neo-nonacosane	$C_{29}H$	0.48	2.08	1.28	0.80
Triacontane	$C_{30}H_{62}$	2.45	14.02	8.24	5.79
Hentriacontane	C_{31}	2.40	1.42	1.91	0.49
Dotriacontane	$C_{32}H_{66}$	12.55	2.23	7.44	5.13
Tritriacontane	$C_{33}H_{68}$	11.57	8.43	10.00	1.57
Tetratriacontane	$C_{34}H_{70}$	1.27	3.03	2.15	0.88

Table 2: Characteristics of organic geochemical parameters and diagnostic ratios for sediment and water from New Calabar River

Parameters	C_{max} n-alkane	CPI n-alkanes	P_{aq}	LHC/SHC
Sediment	C_{10}, C_{11}, C_{14}	0.44	0.58	3.70
Water	C_{26}	0.47	0.35	1.99

Table 3: The abbreviation, source, molecular formula, molecular weight, and carcinogenicity index of polycyclic aromatic hydrocarbon (PAHs)

Compound name,	No of rings,	Sources	Abbreviation,	MF	MW	Carcinogenicity
Naphthalene	2	petro	Naph	$C_{10}H_8$	128.2	0
Acenaphthylene	3	petro	Acy	$C_{12}H_8$	152.2	0
Acenaphthene	3	petro	Ace	$C_{13}H_8$	152.2	0
Fluorene	3	petro	Fl	$C_{14}H_{10}$	166.2	0
Phenanthrene	3	petro	Phe	$C_{14}H_{10}$	178.2	0

Anthracene	3	$C_{16}H_{10}$	178.2	petro	0	Ant
Fluoranthene	4	$C_{16}H_{10}$	202.2	petro	0	Flu
Pyrene	4	$C_{18}H_{12}$	202.2	petro	++	pyr
Benzo(a)anthracene	4	$C_{18}H_{12}$	228.3	petro	++	BaA
Chrysene	4	$C_{20}H_{12}$	228.3	Petro	++	Chry
Banzo(b)Flouranthene	5	$C_{20}H_{12}$	252.3	pyro	++	BbF
Bebzo(k)Flouranthene	5	$C_{20}H_{12}$	252.3	pyro	++	BkF
Benzo(a)Pyrene	5	$C_{22}H_{12}$	252.3	pyro	+++	BaP
Dibenzo(ah)anthracene	5	$C_{22}H_{14}$	278.3	pyro	+++	DahA
Benzo(ghi)perylene	6	$C_{22}H_{12}$	276.3	pyro	0	BghiP
Indeno(1,2,3-c,d)pyrene	6	$C_{22}H_{12}$	276.3	pyro	+++	InP

According to United State Environmental Protection Agency (USEPA) 0 = non carcinogenic, ++ = carcinogenic, +++ = strongly carcinogenic, petro = petrogenic, pyro = pyrolytic

Table 4: Concentration of PAHs in sediment and water from New Calabar River

Name of Compounds (mglkg)	Water	Sediment	Mean	SD
Fluorene	0.0036	0.004	0.0038	$2x10^{-4}$
Naphthalene	0.083	0.038	0.061	0.02
Fluoranthene	0.0015	0.072	0.037	0.03
1,2-Benzanthracene	0.35	0.43	0.39	0.04
BenzO(a)pyrene	0.086	0.007	0.05	0.04
Xylene	0.0379	0.043	0.04	2.59
Benzo(ghi)perylene	0.0175	0.038	0.03	0.01
Benzo(k) fluoranthene	0.009	0.03	0.02	0.01
Phenanthrene	0.0284	0.06	0.04	0.02
Di benzxl (a, b) anthyracene	0.33	0.22	0.20	0.06
Acenaphthylene	0.48	0.40	0.44	0.04
Anthracene	0.083	0.063	0.07	0.01
Benzo (b) fluoranthene	0.46	0.37	0.42	0.05

Sediment from New Calabar River recorded n-alkane distributions ranging from C_9-C_{34}. Carbon chain length (Table 1). The n-alkane mean concentrations varied from 0-78-29.02 mg/kg for water and sediment samples. The concentrated 8 n-alkanes for sediment sample ranged from 0-48 – 43.80 mg/kg while n-alkane concentration in water sample ranged from 0-27 – 22.0 mg/kg (Table 1). The total concentrations of n-alkanes in sediment and water were 205.64 and 161.58 respectively.

Representative gas chromatograms showing the distribution of n-alkanes in aliphatic fraction of extract from sediment, are given in Fig 1. As a way to identify the hydrocarbon source in the water and sediment of the study area (New Calabar River), some parameters has been carefully calculated; such are:

- ✓ n-alkane proxy ratio (p_{aq}) this represent the various plant types such as floating vs submerged plant types (Ficken et al, 2000)

n-alkane proxy ratio is given as $P_{aq} = (C_{23} + C_{25})/C_{23} + C_{25} + C_{29} + C_{31}$

Terrigenous aquatic ratio (TAR) this represent the in situ algae vs terrestrial organic matter (Bourbonnier and Meyers, 1996)

Terrigenous aquatic ratio is given as

$$\text{TAR} = \frac{C_{27} + C_{29} + C_{31}}{C_{15} + C_{17} + C_{19}}$$

The natural n-alkane ratio (NAR) this quantifies the proportion of natural n-alkane and petroleum n-alkane (Mille at al 2007),

This is given as $$\text{NAR} = \frac{\sum_{\text{n-alkane}}(C_{19} - C_{32}) - {}^{2}\sum_{\text{even numbers of n-alkanes}}(C_{20} - C_{32})}{\sum_{\text{n-alkanes}}(C_{19} - C_{32})}.$$

The diagnostic parameters used for the source identification of the n-alkanes as reported by Nna (2013) are as discussed below:

Using the same odd-carbon and even carbon number n-alkane concentration in the respective samples, the carbon preference index (CPI) was determined according to Zhu et al., (2005).

$$\textbf{CPI} = \frac{C_{23} + C_{25} + C_{27} + C_{29} + C_{31}}{C_{24} + C_{26} + C_{28} + C_{30}}$$

It was observed that the CPI values (Table 2) were 0.44 for sand and 0.47 for water, respectively. In the sediment sample, the dominant carbon limit (Cmax) calculated for n-alkanes was C10, C11, C14 and C26, while the dominant carbon maximum (Cmax) was C10, C11, C26 and C36 for the water sample. The parameter n-alkane proxy (Paq) was determined according to Ficken et al., (2000) in Nna to determine the origin of long-chain n-alkanes in the samples (whether the long-chain n-alkanes are extracted from either higher plant waxes or macrophytes) (2013).

$$\mathbf{P_{aq} = (C_{23} + C_{25})/C_{23} + C_{25} + C_{29} + C_{31}}$$

Paq (Table 2) values were found to be 0.58 for sand and 0.35 for water. LHC/SHC ratios were determined to determine the dominant higher plant and/or macrophyte derived and phytoplankton derived in sediment and water using:

$$\text{LHC/SHC} = \frac{C_{17} + C_{29} + C_{31}}{C_{17} + C_{19}}$$

The value ranged from 3.70 for sediment and 1.99 for water sample.

The distribution of n-alkane in sediment and water from New Calabar River was in the range $C_9 - C_{34}$ (Table 1). Biodegradation results in depletion of n-alkanes prior to significant altercation of any other compound class including phytoene (Peters and Moldowan, 1993). The systematic differences in n-alkane distributions that distinguish sediment from water could probably be a reflection of the variations in degree of biodegradation. High-plant n-alkanes in the range $C_{27} - C_{34}$ were present pointing to a probable biogenic organic matter input from a dominant phytoplankton in New Calabar River. In the sample area, the n-alkane distribution is in the C9-C34 range with Cmax at C10, C11, C14 and C26 Comparable and reflective feedback from higher plants and submerged macroptytes from the prevalent terrestrial biogenic source.

For all soil and water samples, the calculation of carbon limit (Cmax) also provides an impression of the relative source input, where Cmax> 25 for n-alkanes represents the incorporation of higher plant wax and Cmax< 25 reveals a major input of microbial/petroleum sources (Mazurek and Simoneit, 1997). C10, C11 C14 and C24 were, however, the dominant Cmax determined for n-alkanes in sediments from the Latest Calabar River. This indicates that terrestrial and petroleum/microbial origins of organic matter in the sediment make a mixed contribution. The Cmax¬of the water was determined to be C26 meaning the n-alkane is contributed by petroleum/microbial causes.

Simoneit et al. (1991) indicated that CPI is a metric of biologically synthesized n-alkanes demonstrating their relative contributions from natural sources (biogenic/terrestrial i.e., CPI > 1) relative to anthropogenic sources (petroleum/petrochemical i.e., CPI < 1). In this analysis, the CPI was measured in Nna (2013) according to Brey and Evans (1961) and was found to range from 0.44 to 0.47 for both investigated sediment and water samples. This shows in the system the existence of petroleum inputs. This finding was consistent with Kassin and Simoneit (1996) who recorded CPI values of 0.42 to 0.86 in Alexandria (Egypt) bottom sediment. This may, however, be due to strong microbial biodegradation intensified during this process by petroleum pollution.

In other instances, the parameter alkane proxy (Paq) was determined to determine the origin of long-chain n-alkanes in our samples (whether long-chain n-alkanes) was extracted from either higher plant waxes or macrophytes. Paq (Table 2) values varied from 0.35 to 0.58 for both water and sediment. Paq values ranging from 0.01 to 0.23 are associated with terrestrial plant waxes, according to Ficken et al. (2000), while those in the range of 0.488 are associated with terrestrial plant waxes In tests from the New Calabar Channel, submerged/floating macryophthal species are associated with long-chain n-alkanes. LHC/SHC ratios were determined to assess the dominant higher plant and/or macrophyte-derived and/or phytoplankton-derived matter and had values of 3.70 for sediment and 1.99 for water (Table 2).

The polycyclic aromatic hydrocarbons (PAHs) described and observed in the samples were polycyclic aromatic compounds and their alkylated homologous compounds using their parent ions. In the sediment and water collected from the Latest Calabar Channels, 13 (13) parent and alkylated homologous PAHs were found and quantified. The overall amounts of PAHs from the sample in soil and water is 1.922 for water and 1.775 for sediment, respectively. Table 3 indicates the mean amounts of the PAHs observed and quantified in the samples.

One of the key categories of contaminants entering the marine environment and accumulating in sediment through sedimentation is polycyclic aromatic hydrocarbons (PAHs). Their occurrence poses considerable concern for human health, especially during coastal activities (bathing, waters, aquaculture, etc). Remobilization (e.g. dredging) can increase their bioavailability, leading to a danger to the marine environment (Nikolaou et al., 2009). The sediment deposition of PAHs is attributable both to anthropogenic and natural pollution. Within anthropogenic variables, the most important are petrogenic and pyrolytic sources.

CONCLUSION

In the worldwide natural ecosystem, organic matters are present and their ability to inflict harmful consequences is generally correlated with the accumulation of the different lasses of organic matter. Several studies have been undertaken primarily in temperate climate countries for the source allocation of organic matter such as PAHs and n-alkanes in the marine environment that apply diagnostic indices based on chemical fingerprinting. The origins of organic matter in the present analysis (n-alkanes and PAHs). Water and sediment from the New Calabar River were analyzed.

In the sample from the study field, petroleum pollution is obviously from conventional markers such as alkyl PAHs with anthropogenic influence. Via these conventional metrics, petroleum toxicity is clearly demonstrated, their lack of precision and vulnerability to losses attributable to volatilization or biodegradation is made unsuitable for quantitative source intensity estimates. More specific and stable markers such as diagenetically modified n-alkanes often suggest that the natural petroleum history is strong. The research indicated that organic matter (PAHs and n-alkanes) In this extraordinary hydrodynamic environment and microbial contributions from the organic matter in the sample region, the vector contribution from our study area was primarily from the source of petroleum, which is the sufficient marker of organic matter.

Therefore, we simultaneously verified that there were variable contributions of PAHs and n-alkanes from sediment and water from our sample region. Microbial contributions from organic matter such as macrophytes and phytoplankton derive organic matter from primarily petroleum sources (secondary/allochthonous sources).

RECOMMENDATIONS

The following recommendations were considered necessary for further studies in this area:

1. The Geochemical characterization of lipids in suspended particulate matter from the study area should be carried out during seasonal variation.
2. Distribution and transportation of lipids in the study area should be carried out.

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