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Source Identification and Distribution of n-Alkanes and Polycyclic Aromatic Compounds in Suspended Particulate Matter from Great Kwa River, Southeast Nigeria

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Abstract The source identification and distribution of normal alkanes and polycyclic aromatic compounds in suspended particulate matter from Great Kwa River obtained during low and high tide was carried out using gas chromatography-mass spectrometry (GC-MS) technique. The study involves the use of geochemical parameters (ratios) such as unresolved complex mixture (UCM), Carbon preference index (CPI), Dominant carbon maximum (Cmax), n-alkane proxy ratio (Paq) and LHS/SHC to determine the sources of n-alkanes in the study sample. The occurrence of UCM in the Gas chromatogram of the sample shows petroleum contamination. The alkane proxy (Paq) was used to evaluate the origin of long chain alkane and the result shows its source as an indication of submerged/ floating species of microphyte. The LHC/SHC ratio shows microbial/ petroleum source. The PAHs detected and quantified in the samples were not the regular PAHs and were found from diagenetic products of organic matter transformation as well as the biosynthesis of microbes and plants. The results shows that the n-alkanes were predominantly petroleum inputs as the secondary source (allochthonous) continental inputs and microbes inputs from organic matter such as macrophytes, terrestrial plant wax and phytoplanktonic derived organic matter as its primary sources (autochthonous) planktonic inputs. Low tide influences the accumulation and distribution of persistent n-alkanes and PAHs than high tide due to sedimentation.

Keywords n-Alkanes, Polycyclic Aromatic Compounds,

Introduction

The occurrence of biogenic and anthropogenic organic matter varies from season to season and their concentrations in the ecosystem therefore reflect the natural background, human and biological activities. n-alkanes and PAHs have been used as molecular tracers to understand origin and reactivity of organic matter in the marine ecosystem [1-2]. Geochemical characterization of organic detritus in suspended particulate matter can provide an insight into the sources and early digenetic processes modulating the type, quality and quantity of organic matter within the water column prior to sedimentation [3]. Hydrocarbons are widespread organic compounds that are part of the carbon cycle in the environment. Both natural and anthropogenic hydrocarbons are widely distributed in the ecosystem. While natural hydrocarbons produced by marine and terrestrial plants are generally encountered at trace amounts, anthropogenic hydrocarbons are distributed widely and originate from diverse sources, including untreated domestic sewage and waste water as well as boat pollution [4]. Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants (POPs) produced by incomplete combustion of organic material. Their principal source in the environment is of anthropogenic origin, namely combustion of fossil fuels, such as petroleum and coal containing considerable amounts of PAH [5-6]. Three major types of hydrocarbons are generally found in the environment [7]. Petrogenic hydrocarbon whose sources are crude oil and its refined products. These are characterized by the distribution of alkylated homologous of naphthalene, fluorine, phenanthrene and chrysene.

Pyrogenic hydrocarbons which are generated in combustion processes. Biogenic hydrocarbons are generated by biological processes or in the early stages of diagenesis in marine sediments. For instance, in subtidal sediments, bacterial modification of recent inputs of organic matter yields perylene, an unsubstituted PAH produced by a process known as early diagenesis. Other biological sources include land plants, phytoplanktons, animals, bacteria, macroalgae and microalgae [8].

The characterization and identification of the molecular composition of the organic matter in suspended particulate matter, sediments and aquatic systems are important for understanding the nature of the components and assessing their potential toxic effects to human health. This is important because certain compound classes such as polycyclic aromatic hydrocarbon (PAHs), Oxygenated PAHS and nito-PAHs produce detrimental health effects and can be found in water, food as well as soil. Also, characterization of anthropogenic organic residues such as PAHs and n-alkanes may serve to further define and elucidate the spatial variation and geographical sources of organic burdens in urban versus rural areas [2]. Thus, the determination of the identities of organic compounds, their amounts, sources and the compound classes is essential for environmental assessment processes. The characterization of organic constituents in suspended particulate matter with respect to their natural and anthropogenic sources will facilitate an understanding of their local and regional impacts as well as providing an insight into the sources early diagenetic processes modulating the type, quality and quantity of organic matter within the water column prior to sedimentation. In this present study, the focus is on the;

(i) Evaluate of the allochthonous continental and autochthonous planktonic inputs to n-alkane distribution in suspended particulate matter in the study area.
(ii) Determination of the source distribution of PAHs in the study area.
(iii) Investigation of the influence of tidal and seasonal variation on the accumulation and distribution of n-alkanes in SPM.

Study Area

The Great Kwa River is one of the tributaries of the cross rivers (Fig 1). It originates from the mountains of north-eastern cross rivers state and flows through some villages and farm settlements in the rainforest belt. It is located between latitude $4^{0}53^{1}$ and $4^{0}50^{1}$ N and longitude $8^{0}20^{1}$ and $8^{0}30^{1}$E. Its shallow depth (1.0-5.5M at flood tide) is navigable throughout the year by small boats. The soils are mainly composed of sandy-clay to clayed sand. The boundary between the sediments and crystalline rocks are masked by sandstone. The area experiences two major climatic seasons, the wet season dominated by southwest trade wind (April-October) and dry season which is dominated by North east trade wind (Nov-March). Along the river banks, sparsely populated fishing and farming settlements are found. Municipal surface runoff water from the city of Calabar reaches the Great Kwa River estuary after drainage through fresh water and mangrove swamps.

Experimental Method

Sample Collection

Eight (8) surface water samples were collected at hourly interval from a boat anchored at one location in the middle of the river (Fig 1) once a month from April –July, 2015. The sampling periods for water covered both ebb and flood tidal phases between the hours of 8:30am and 4:15pm. This station was chosen so that homogeneous water sample could be obtained due to turbulent mixing [9]. A 4 litre Nansen-type water sampler (made of plastic materials was used after thorough rinsing with the water. Water samples were filtered under pressure (3 bar, purified N_2) through a thin polycarbonate membrane filter (Nuclepore) with a 0.4∞m pore size. Total suspended-matter concentrations were determined gravimetrically. Samples of total suspended matter collected on Nuclepore filters, were weighed on a Cahn Modes 4700 Electrobalance before and after filtration. The reliability of the analytical methods was assessed by carrying out three replicate determinations in the water samples and the recovery range between 95-100%. Extraction of the SPM samples for SOM was carried out using a soxhlet apparatus (EPA method 3540). The thimbles and the glass wool used in the extraction were soxhlet-extracted with dichloromethane for 20 minutes on a water bath. 50g of SPM was placed in the soxhlet-extracted thimble with glass wool and then filled with

dichloromethane and extracted for 18 hours. Extracts were desulphurised by addition of 30g activated copper (Copper inversed in 20ml of 0.1M concentrated hydrochloric acid for 10mins), into the round-bottom flask during extraction. Extracts obtained were evaporated to near dryness using vacuum evaporator. The weights of extracts were determined as a measure of the amount of extractable or soluble organic matter (SOM) made up of asphaltenes and maltenes. Precipitation of asphaltenes from the SOM was carried out following the procedure described by schoell et al [10] in Nna and Nwineewii, [3]. 20ml of a mixture of dichloromethane/Petroleum ether was added to 10ml of the extract and centrifuged at 3000 rpm for about 20minutes. The asphaltenes precipitated from SOM were discarded after weighing. The maltenes obtained from the extract were further separated by liquid chromatography (column 30x1.2cm) into aliphatic, aromatic and hetero-fractions.

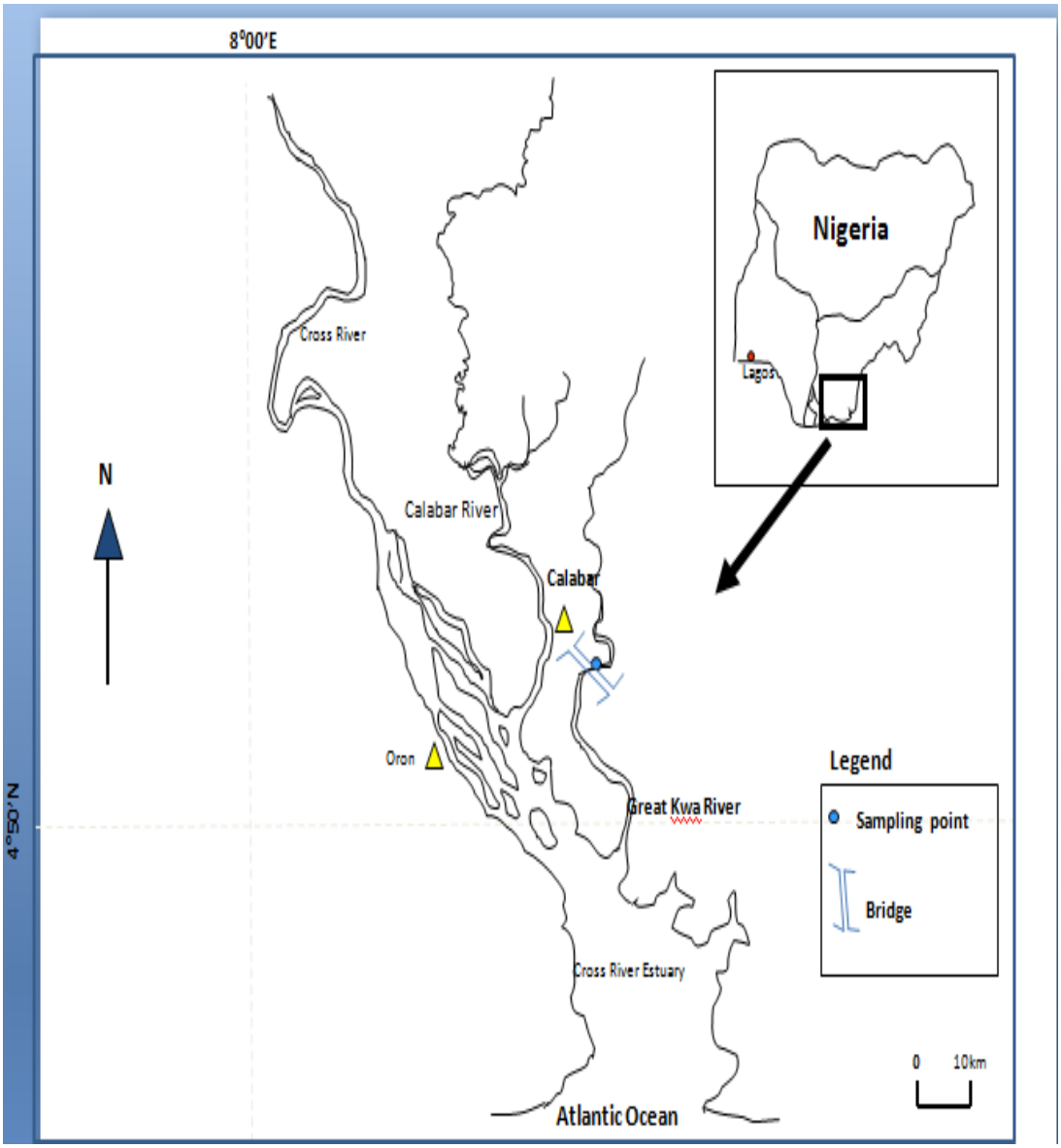


Figure 1

Instrumental Analysis

Gas chromatography-mass spectrometry (GC-MS) analyses of isolated fractions were performed on a Hewlett-Packard model 6890 GC coupled to a Hewlett-Packard Model 5973 quadrapole MSD. Separation was achieved on a

DB5-Ms column (30m x 0.25mm i.d; 0.25mm film thickness). The GC operating conditions were as follows: temperature holds at 65^0C for 2 minutes, increases from 65 to 300 ^{0}C at a rate of 6 ^{0}C min^{-1}, and with final isothermal holds at 300^0C for 20minutes. Helium was used as carrier gas. The sample was injected in the splitless mode with the injector temperature at 300^0C. The mass spectrometer was operated in the electron impact mode at 70eV ionization energy and scanned from 50 to 650 dalton. Data were acquired and processed using chemstation software. Compounds were identified by comparison with literature data and interpretation of mass spectrometric fragmentation patterns.

Results

The n-alkanes detected were heptadecane, octadeane, nonadecane, eicosane, heneicosane, docosane, tricosane, tetracosane, pentacosane, hexacosane, haptacosane, octacosane, nonasane, triacontane, hentriaontane, and dotriacontane.

SPM from Great kwa River recorded n-alkane distributions ranging from C_{17}–C_{32} carbon chain length (Table 2). The n-alkane mean concentrations varied from 0.03 to 0.38mg/kg for samples collected at low tide while the mean concentrations for n-alkanes in high tide samples ranged from 0.03 to 0.20 mg/kg (Table 2). Representative gas chromatograms showing the distribution of n-alkanes in aliphatic fraction of extract from spm collected at low and high tides. (Fig 2). A high unresolved complex mixture (UCM) of n-alkanes was observed in the low tide sample between $C_{20} – C_{31}$ in their total ion chromatograms (FIG 2).

The Carbon preference index (CPI) was calculated according to Zhu et al; [11] using the same odd-carbon and even-carbon number n-alkane concentrations in the respective samples at different tidal phases as follows:

$$CPI= (C_{23} + C_{25} + C_{27} + C_{29} + C_{31}) / (C_{24} + C_{26} + C_{28} + C_{30}).$$

The CPI values were in the range of 1.2-1.5 for SPM samples collected at high tide and 1.2-1.4 was recorded for sample at low tide. The dominant carbon maximum (C_{max}) determined for n-alkanes in high tide samples were $C_{22,}$ C_{27}, C_{28}, and C_{29} while C_{max} C_{24} and C_{28} were observed for low tide samples. To evaluate the origin of long-chain n-alkanes in the Spm sample i.e. whether the long-chain n-alkanes are derived from either higher plant waxes or macrophytes, the parameter n-alkane proxy (Paq) was calculated according to Ficken et al; [12] in Nna [13].

$$Paq= (C_{23} + C_{25}) / (C_{23}+ C_{25} + C_{29} + C_{31}).$$

Values of Paq (Table 1) ranged from 0.4-0.67 for high tide samples and 0.38-0.63 for low tide samples. To determine the dominant higher plant and / or macrophyte-derived and phytoplankton-derived organic matter (OM) in the SPM, LHC / SHC ratios were calculated using LHC / SHC = $(C_{27} + C_{29} +C_{31}) / (C_{17} + C_{19})$. The values ranged from 0.34 - 2.46 for SPM at high tide and 0.19 – 1.84 SPM samples at low tide (Table1).

Source Identification

UCM is a diagnostic parameter that is interpreted to be derived from the utilization of petroleum products. The n-alkane envelops depicted unimodal distribution for Spm samples (Fig 2) with evidence of petroleum contamination (presence of ucm). Spm samples collected at high tide showed a depletion or absence of UCM. This might be due to heavy microbial biodegradation enhanced by petroleum contamination during this tidal phase. Depletion of n-alkanes due to microbial biodegradation enhance by the presence of petroleum residues in SPM at high tide has been reported [14]. The Paq values is an indication of terrestrial plant waxes as well as submerged / floating species of macrophyte.

The polycyclic aromatic hydrocarbons (PAHs) are one of the major categories of pollutants entering the marine environment and accumulating in SPM prior to sedimentation. PAHs accumulation in SPM is both due to anthropogenic factors, petrogenic and pyrolytic sources are the most important. Whereas, pyrolytic sources include combustion processes (e.g. fossil fuel combustion, forest fire, shrub and grass fires), the petrogenic input is closely related to petroleum products (e.g. oil spills, road construction materials). PAHs from pyrolytic processes are more strongly associated to sediments and much more resistant to microbial degradation than PAHs of petrogenic origin [15]. The fate and behavior of PAHs in aquatic systems is influenced by a number of physical, chemical and biological processes. While some of these processes, such as photo oxidation, hydrolysis, biotransformation,

biodegradation and mineralization result in the transformation of PAHs into other substances. The results suggest that PAHs in the samples, generated from biogenic organic matter that has been transformed in the water column. Hence, the PAHs are sourced from diagenetic alteration of organic products and not anthropogenic and pyrogenic sources.

Conclusion

The n-alkane envelops depicted unimodal distribution from SPM collected at low tide from the study area is an evidence of petroleum contamination (presence of UCM), hence, one of the major sources of the makers is petroleum. The alkane proxy (Paq) calculated showed that most of the long-chain alkane samples were contributed by submerged/floating species of macrophytes in the river system. The result also showed that the dominant higher plant and / or macrophyte-derived and phytoplankton derived OM in the SPM from the study at SL1, SL2, SL4 as well as SH2 and SH3 are dominated by both input sources with no particular trend except for sample SH2 which is traceable to macrophyte waxes dominant.

PAHs were showed to be from biogenic organic matter transformed in the water column due to diagenetic products alteration as well as direct biosynthesis by microbes and plants due to domestic waste waters, urban runoff, discharge originating from landfills in the study area and not anthropogenic source which is due to incomplete combustion of organic matter at high temperature. We concorminatly confirmed that SPM from the study area had variable contributions of n-alkanes from predominantly petroleum source (secondary / allochthonous source) while vascular plant inputs and microbial inputs from organic matter such as macrophytes and phytoplankton derived organic matter are seen as primary (autochthonous) sources, low tide influences the accumulation and distribution of n-alkanes and PAHs than high tide.

Table 1: Concentration of n-alkanes in SPM at low and high tides from GKR Sample Stations/Concentrations

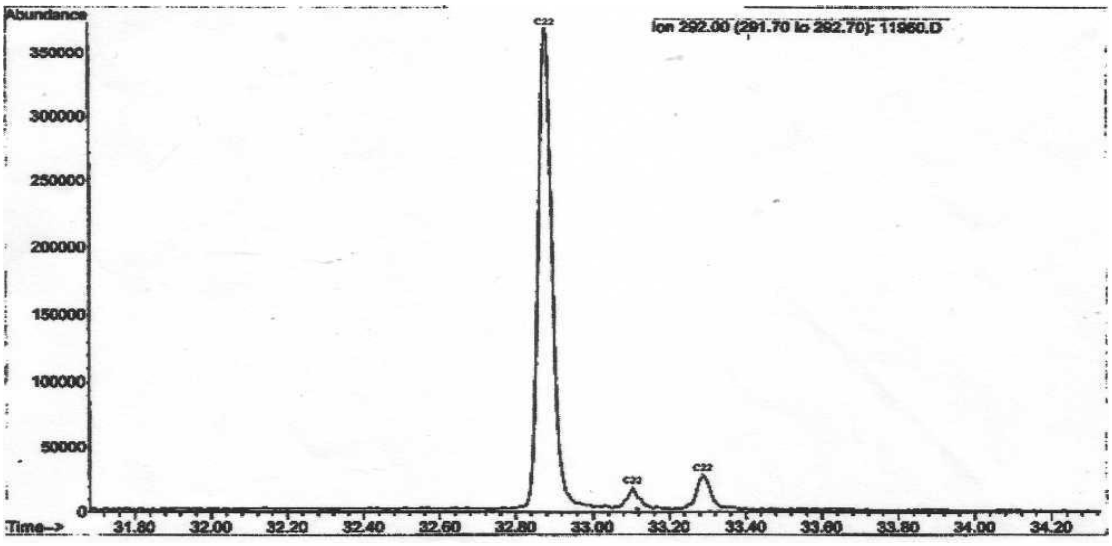
Compound			LOW TIDE						HIGH TIDE					
Name	**MW**	**MF**	**SL1**	**SL2**	**SL3**	**SL4**	**Mean**	**SD**	**SL1**	**SL2**	**SL3**	**SL4**	**Mean**	**SD**
Pristane	268	$C_{19}H_{40}$	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd
Phytane	282	$C_{20}H_{42}$	nd	nd	nd	nd	nd		nd	nd	nd	nd	nd	nd
n-heptadecane	240	$C_{17}H_{36}$	nd	nd	0.38	nd	0.38		nd	nd	nd	0.11	0.03	0.06
n-octadecane	256	$C_{18}H_{38}$	nd	nd	0.31	nd	0.31		nd	nd	nd	0.1	0.03	0.05
n-Eicosane	270	$C_{19}H_{40}$	nd	nd	0.3	nd	0.3		nd	0.15	nd	nd	0.05	0.09
n-Heneicosane	282	$C_{20}H_{42}$	nd	nd	0.28	nd	0.28		nd	0.18	nd	0.09	0.07	0.09
n-Docosane	296	$C_{21}H_{44}$	0.07	nd	nd	nd	0.03	0.05	0.11	0.21	nd	0.12	0.11	0.09
n-Tricosane	310	$C_{22}H_{46}$	0.05	nd	0.26	0.28	0.2	0.13	0.11	0.36	0.2	0.1	0.19	0.12
n-Tetracosane	324	$C_{23}H_{48}$	0.01	0.5	0.29	0.34	0.29	0.21	0.09	0.21	0.21	0.11	0.15	0.07
n-Pentacosane	338	$C_{24}H_{50}$	0.05	0.33	0.45	0.31	0.28	0.17	0.09	0.17	0.2	0.12	0.14	0.05
n-Hexacosane	352	$C_{25}H_{52}$	0.05	0.28	0.32	0.36	0.25	0.14	0.09	0.23	0.21	0.12	0.16	0.07
n-Heptacosane	366	$C_{26}H_{54}$	0.05	0.28	0.34	0.28	0.24	0.13	0.08	0.31	0.19	0.1	0.17	0.11
n-Octacosane	380	$C_{27}H_{56}$	0.09	0.27	0.43	0.34	0.28	0.15	0.14	0.34	0.21	0.11	0.2	0.1
n-Nonacosane	394	$C_{28}H_{58}$	0.05	0.45	0.42	0.46	0.35	0.19	0.11	0.21	0.33	0.11	0.19	0.11
n-traicontane	408	$C_{29}H_{60}$	0.05	0.34	0.41	0.41	0.3	0.17	0.11	0.34	0.21	0.16	0.2	0.09
Hentriaontane	422	$C_{30}H_{62}$	0.06	0.29	0.35	nd	0.23	0.16	0.07	0.17	nd	nd	0.06	0.08
Dotriacontane	436	$C_{31}H_{64}$	0.05	0.32	0.41	nd	0.26	0.18	0.08	0.31	nd	nd	0.10	0.15
	450	$C_{32}H_{66}$	0.05	nd	0.25	nd	0.15	0.14	0.11	0.34	nd	0.12	0.14	0.14

Nd = not detected

Table 2: Concentration of PAHs in SPM collected at high and low tides from GKR Sample Stations/Concentrations (mg/kg)

Compound Name			High Tide						Low Tide					
	MW	MF	SH1	SH2	SH3	SH4	Mean	SD	SL1	SL2	SL3	SL4	Mean	SD
Des A-26,27-dinor Oleana-5,7,9,11,13,-pentaene	292	$C_{22}H_{28}$	0.12	0.16	nd	nd	0.07	0.08	nd	nd	nd	nd	nd	nd
Des A-25,26-dinor ursana 5,7,9,11,13-pentaene	292	$C_{22}H_{28}$	Nd	1.14	nd	nd	0.04	0.07	nd	nd	nd	nd	nd	nd
Des A-25,26,-dinor lupana-5,7,9,11,13-pentaene	292	$C_{22}H_{28}$	0.13	0.19	nd	nd	0.08	0.09	nd	0.36	nd	nd	0.12	0.21
1-methyl-7,8-(3-iso propy) cyclopeneophenanthrene	274	$C_{21}H_{22}$	0.21	0.029	nd	nd	0.13	0.15	nd	nd	nd	nd	nd	nd
3,4,7,-trimethyl-1,2,3,4-tetrahydrochrysene	274	$C_{21}H_{22}$	0.09	0.11	nd	nd	0.05	0.06	nd	nd	0.38	nd	nd	0.23
3,3,7,-trimethyl-1,2,3,4-tetrahydrochrysene	274	$C_{21}H_{22}$	0.12	0.19	nd	nd	0.08	0.09	nd	0.45	0.33	nd	nd	0.23
23,35-Dinoroleana-1,3,5 (10), 12-tetraene	274	$C_{28}H_{40}$	0.14	0.16	nd	nd	0.08	0.09	nd	nd	0.38	nd	nd	0.22
Octahydro-1,2,4a,9-tetramethylpicene	367	$C_{26}H_{30}$	Nd	0.25	nd	nd	0.06	0.13	0.15	nd	0.29	nd	0.07	0.14
Octahydro-1,2,4a,9, tetramethylpicene	342	$C_{26}H_{30}$	0.17	0.33	nd	nd	0.13	0.16	0.08	nd	0.56	nd	0.04	0.3
23,25,26,27-tetranorlypha-1,3,5,7,9,11,13-heptaene	342	$C_{26}H_{30}$	Nd	0.34	nd	nd	0.08	0.17	nd	nd	nd	nd	nd	nd

Nd = not detected



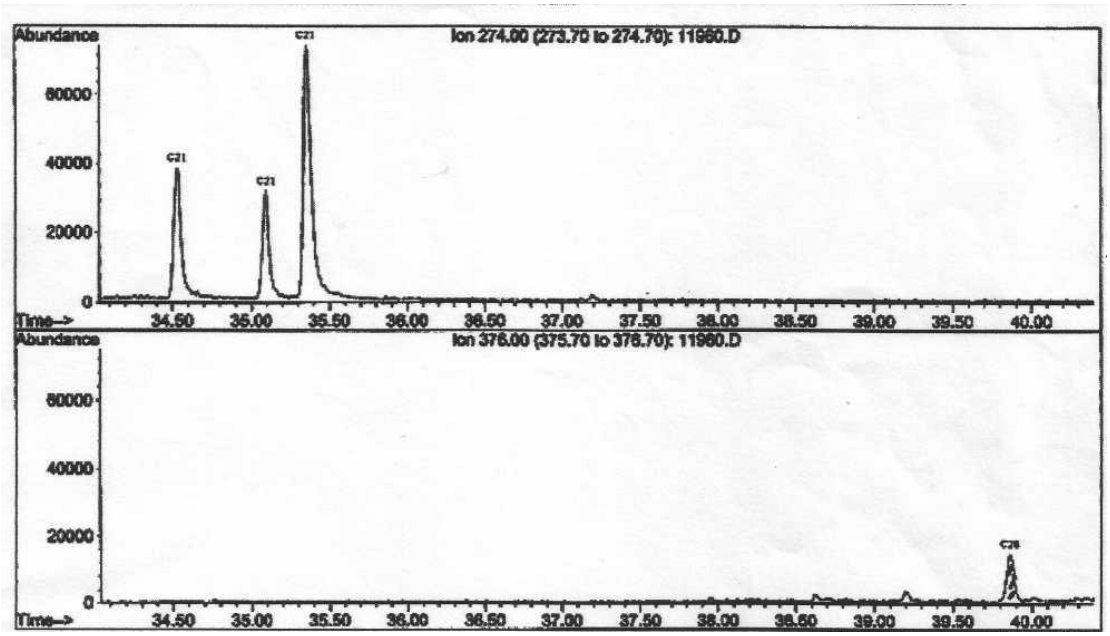


Figure 2: Representative Gas Chromatograms of PAHs in aromatic fraction of SPM from Great Kwa River

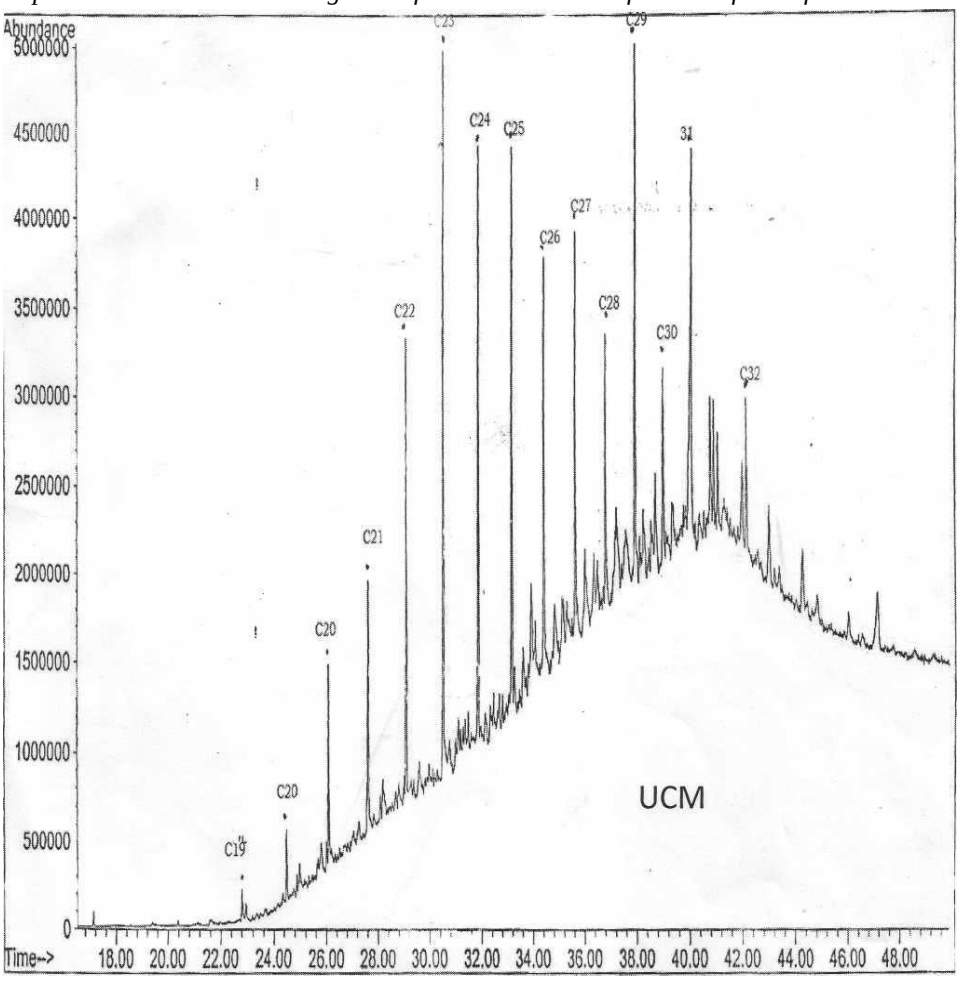


Figure 3: Gas chromatogram showing presence of UCM and unimodal distribution of n-alkanes from aliphatic fraction of SPM samples from Great Kwa River collected at low tide.

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