CHARACTERIZATION AND SOURCE EVALUATION OF N-ALKANES IN SURFACE SEDIMENTS FROM THE NIGER DELTA COASTAL AREAS, NIGERIA

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Abstract

Surface sediments from coastal areas of four rivers in the Niger Delta region of Nigeria were characterized for n- alkane compositions using gas chromatography-mass spectrometry (GC-MS) technique. The total n-alkane concentrations in the entire study area ranged from 1.65 - 61.34mg/kg dry weight, with overall average of 21.52 ± 22.00. The mean n-alkane C^{16} - C^{31} concentrations for the sediments in the upper, middle and lower zones of the study area were in the ranges of 0.04 - 5.44mg/kg, 0.04 - 4.91mg/kg and 0.11- 10.31mg/kg, respectively. CPI values ranged from 0.31 - 13.32 for the entire stations, and the total organic carbon (TOC) contents for the sediments ranged from 0.44 to 4.26% (mean 2.36 ± 1.03). A predominance of odd/even carbon n-alkanes and UCM with different shapes and ranges were observed. Factor analyses reduced the data set into three principal components (PCs) confirming inputs from biogenic, anthropogenic and microbial/bacterial sources.

Keywords: *Characterization, n-alkanes, sources, principal components, factor analysis, Niger Delta*

Introduction

Sediments provide a dynamic and long-term reservoir for organic species. These organic species include lipids (solvent-soluble organic matter), such as hydrocarbons, fatty acids, alcohols and macromolecular organic matter. All these are derived from natural

biogenic, geologic and industrial sources (Simoneit, 1978; Mazurek and Simoneit, 1983;Aboul-Kassim andSimoneit, 1996). Lipid classes have been used as molecular tracers to understand the origin and reactivity of organic matter in marine ecosystem. Predominant lipid classes may reflect the nature of source organisms and the conditions in the immediate environment such as limiting nutrient supply. The magnitude and rates of change in the molecular characteristics of various lipid classes and individual compounds at various depths (and in surface sediments) can therefore be used to apportion and track the overall transfer of primary producers from the euphotic zone to the benthic sediments (Camacho-Ibar*et al.*, 2003). In the coastal and marine environment, these aliphatic hydrocarbons are sequestered and preserved in surficial sediments. Their sources are either natural from photosynthesis by marine biota inhabiting the surface waters or anthropogenic from land run-off, fallout, and/or industrial inputs (Aboul-Kassim andSimoneit, 1996).

Hydrocarbon contaminants have been released, over the years, into the Niger Delta coastal environment from different sources such as untreated effluents, domestic sewages, animal droppings, bush/wood burning, atmospheric fallout, traffic boat engines and crude oil spills. Understanding contaminant hydrocarbon sources, transport and fate in estuaries is important as these are regions of both high pollution input and resource use. In spite of anthropogenic pressure, estuaries remain dynamic and productive ecosystem of immense ecological, environmental and economic value (Dickhut*et al.*, 2003).In order to distinguish and evaluate the different anthropogenic versus biogenic sources of organic matter in sediments, the aliphatic hydrocarbon composition of surficial sediments from various sources must be determined and the proportion of each identified in the samples.Study on the distributions and sources of aliphatic hydrocarbons and ketones in surface sediments from the Cross River estuary, Southeastern Niger Delta has been reported (Oyo-lta *et al.*, 2010). Fubara *et al.* (2012) have reported the predominances and source implications of even n-alkenes in surface sediments from coastal areas of the Niger Delta region.Even n-alkane/alkene predominances (Ekpo *et al.*,2005) and predominance of n-docosane/docosene (Oyo-lta *et al.*,2006) have

been reported for surface sediments from the Calabar River estuary, with the presence of unresolved complex mixture (UCM) indicating petroleum contamination at two stations along the estuary.

Information on the geochemical characterization, distribution, transport and fate of n-alkanes in Niger Delta coastal sediments is rather scanty and fragmentary. This is highly regrettable, especially given the maze of rivers, creeks, estuaries and streams in the Niger Delta region.The present study is the first systematic investigation of a selected group of organic constituents, mainly n-alkanes in sediments from coastal areas of Bonny, Imo, Qua Iboe and Warri rivers in the South-western and eastern parts of the Niger Delta region of Nigeria. The objectives were to: (a) quantitatively characterise n-alkanes in the solvent extractable lipids of sediments from the Niger Delta coastal areas, (b) use the multivariate statistical approach and compositional indices to assess the different n-alkane sources, and (c) provide additional insight into the prospective sources and processes that modulate the flux of anthropogenic versus biogenic hydrocarbons ultimately accumulating in the Niger Delta coastal environment.

2.   Study area

The fan-shaped Niger Delta, which is the third largest in the world after the Mississippi (USA) and Pantanal (South-West Brazil), lies between latitudes (4 and 6)^0 north of the equator and longitudes (5 and 9)^0 east of the Greenwich Meridian. The North-South extension, north of the equator, is expressly defined by the Great Atlantic Ocean in the South to Aboh (Delta State) in the North where River Niger forks in Rivers Nun and Forcados at a village called Obotor(Tamuno, 2008). The East-West extension is from the boundary of the Bonny River to River Sapele, Delta State. According toTamuno(2008), the geographical Niger Delta is just about 25,640km^2 in size; made up of 7,400km^2 low land area, 11,700km^2 fresh water swamp, and 1,140km^2 salt barrier islands as ecological zones.

A simplified subdivision of the Niger Delta as fresh water zone, the mangrove and the coastal sand ridges was given by Mmom (2003). The Northern part of the fresh water zone is often regarded

as an extension of the lower Niger flood plain (Udo, 1975), and it is very susceptible to the annual floods during the rainy season. The southern part of the fresh water zone and most of the mangrove are swampy and hardly rise above 10m above mean sea level. This sub-zone covers a greater percentage of the Niger Delta. The strip of sand ridges and beaches lies close to the open sea and is bordered landwards by swamp areas with many creeks (Tamuno, 2008). The Niger Delta region displays a typical dendritic drainage pattern. This is because most of the tributaries join their main rivers at oblique angles. For example, Taylor Creek joins the main River Nun at Polaku, and the Epie Creek joins the River Nun/Ekole at Yenagoa. This also implies that there are many confluence towns in the Niger Delta. There is also a near parallel type of drainage, for example, New Calabar/Bonny River, Brass/Nun River, Forcados/Escravos River, Taylor Creek/Epie Creek and Orashi River.

The vegetation of the Niger Delta coastal areas is characterized by extensive fresh water and mangrove swamps. The fresh water swamps consist of stilt rooted trees and shrubs. The main vegetation of the mangrove swamps of the Niger Delta according to Nwilo and Badejo, (2008) is dominated by the red mangrove which forms more than nineteen percent (19%) of the saline swamps. The white mangroves occur scattered among the red mangroves and thrive in less water- logged places. Ferns, Nipa palms and herbs are found in areas where their salt content is not too high. The Niger Delta has provided the best conditions for the thriving of vegetation on the Nigerian coast. By some estimates, over sixty percent (60%) of fishes caught between the Gulf of Guinea and Angola breed in the mangrove belt of the Niger Delta. According to Tamuno (2008), the vegetation of the Niger Delta region is arranged in the form of storey/ strata or layers. There is the upper stratum occupied by very tall trees of heights 30m and above; followed by the middle tier trees with heights of 15-20m, while the lower layer has trees and shrubs with heights below 12m. The upper layer is normally occupied by tall trees like the Iroko (*Chlorophoraexcelsa*), Mahogany (*Khayaivorensis*), and Abura (*Mitragyramacrophylla*) according to Nyanayo (2007).Palm trees (*Elaeisguineensis*) and others occupy the middle layer. The availability of sunlight is also partly responsible

for the growth of the tall plants as it provides them with the necessary solar energy for the photosynthetic process.

3. Materials and Methods

Sampling

Samples of surface sediments were collected at different stations each along the coastal areas of Bonny, Qua Iboe, Warri and Imo rivers as depicted in the map of the study area (Fig.1) using a modified grab sampler ($0.1m^2$). Samples were removed from the middle of the grab to avoid contact with the inner metallic surface of the grab sampler, wrapped in aluminium foil and stored frozen at - 4 ^{0}C. The sampling was carried out based on the nature of potential anthropogenic inputs (Table1). Prior to extraction, the samples were freeze-dried, crushed and sieved through a 230 mesh (< 63mm) sieve.

Extraction and fractionation

To minimize contamination, all glassware were cleaned with detergent solution, rinsed with distilled water, heated in an oven at 550^0C for eight hours to combust traces of surface organic matter, and finally rinsed with ANALAR grade dichloromethane. The total organic carbon (TOC) contents were determined using a LECO CNS analyzer. Extraction of the crushed and sieved (< 63mm) sediment samples for extractable organic matter (EOM) was carried out using a soxhlet apparatus(EPA-3540 Method, 1986). The thimbles and the glass wool used in the extraction were soxhlet-extracted with dichloromethane for 20 minutes on a water bath. Powdered sediment sample (50g) was then placed in the extracted thimble. The thimble with glass wool was filled with dichloromethane and extracted for 18hrs. Extracts were desulphurized by addition of 30g activated copper (copper immersed in 20ml of 0.1M concentrated hydrochloric acid for ten minutes) into the round-bottom flask during extraction. Extracts obtained were evaporated to near dryness using a vacuum evaporator. The weight of extracts was determined as a measure of the amount of extractable organic matter (EOM), made up of asphaltenes and maltenes. Precipitation of asphaltenes from the extractable organic matter (EOM) was carried out following the

procedure described by Schoellet al.(1983) and Meniconi andBarbanti (2007). Finally, a mixture (1: 2, 60ml) of methanol /dichloromethane was used to remove the heterofractions.

Gas chromatography-mass spectrometry (GC-MS) analysis

The gas chromatography-massspectrometry (GC-MS) analyses of the aliphatic and aromatic fractions from the sediment extracts were performed using an Agilent 6890 Series gas chromatograph (GC) interfaced to an Agilent 5973 Network Mass Selective Detector (MSD) and Agilent 7683 Series Injector. The GC Separation was achieved on a fused silica capillary column coated with DB 35 (60m x 0.25mm i.d., 0.25ìm film thickness). The GC oven temperature was programmed from 50^0C (isothermal for 1 minute) to 120^0C at a rate of 20^0C/ min, then to 300^0C at a rate of 3^0C/ min. The final temperature was held for 45 minutes. Helium was used as the carrier gas. Samples were introduced into the cool on-column injector under electronic pressure control. The GC column outlet was connected directly to the ion source of the mass spectrometer. The GC-MS interface was kept at 280 ^0C, while the ion source and quadrupole analyzer were at 230 and 150^0C, respectively. The mass spectrometer was operated in the electron impact(EI)mode at 70eV ionization energy. Mass spectra were recorded from 45- 550 dalton (0 - 40min) and 50 – 700 dalton (above 40 min). Data were acquired using the HP-MSD Chemstation Integrator. Individual compounds were identified by comparison of mass spectra with literature and library data.

Results and Discussion

The sampling stations, extractable organic matter (EOM), percentage total organic carbon (% TOC) contents, different n-alkane concentrations, total n-alkane (TNA) concentrations as well as some source diagnostic indices derived from n-alkane compositions are presented in Table 2. The average concentration for each n-alkane in every zone of the Niger Delta study area is given in Table 3.

Geochemical parameters

Variations in extractable organic matter (EOM) are depicted in Fig.2a with a maximum of 6346 mg/kg dry sediment weight for station WR3 and a minimum value of 212mg/kg for station BN13 (Table 2).Most stations at the middle zone (e.g. stations IM04, QIR22, BN02 and WR3 in Fig.2a) recorded high EOM values, while some stations (e.g. BN13, WR8 and QIR25) at the lower zone recorded relatively low EOM values. Stations at the upper zone of the study area recorded intermediate EOM values. EOM compositional variations in our samples may be attributed to differences in oxidative conditions at the water-sediment interface, salinity of the depositional environment, quantity and quality of organic matter sources. The percentage total organic carbon (%TOC) contents for the sediments ranged from 0.44 to 4.26% (mean 2.36 ± 1.03), maximizing for station IM04 (Table 2).

Normal alkanes

Normal alkaneswere present in all stations from the lower zone, but were not detected in stations WR14 in the upper zone, WR7 and WR3 in the middle zone.Most stations in the study area recorded n-alkanes in the range of $C_{21}$to C_{31}. The total n-alkane concentrations in the entire study area varied between 1.65 – 61.34mg/kg dry weight (Table 2), with overall average of 21.52 ± 22.00. Variations in the total n-alkane (TNA) concentrations are presented in Fig. 2b. The mean n-alkane concentrations for the sediments in the upper, middle and lower zones of the study area ranged from 0.04 – 5.44mg/kg, 0.04 – 4.91mg/kg and 0.11-10.31mg/kg, respectively (Table 3). Examples of n-alkane distribution patterns in some stations from the study area indicating different contributions from anthropogenic and biogenic/terrestrial sources to sedimentary organic matter are depicted in Fig. 3.The n-alkane envelopes depicted unimodal distribution for sediments from Bonny coastal areas with evidence of petroleum contamination (presence of UCM, example Fig. 3b). The C_{16} – C_{18} n-alkanes, maximizing at C_{17} detectedin stations along the Bonny coastal areas possibly originated from both terrestrial/biogenic and anthropogenic sources, with a stronger biogenic signal. Higher-plant n-alkanes in

the range $C_{27} - C_{31}$ were barely present in samples fromBonnycoastal areasgiving supportive evidence to otherpossible biogenic organic matter inputs such as submerged/floating macrophytes. The n-alkane distributions in stations from Imo (e.g. Fig.3a) and Qua Iboecoastal areas, in the range C_{21}-C_{31} and maximizing at C_{29} at most stations, are comparable and reflect predominant terrestrial/biogenic source input from higher plants which dominate the coastal vegetation of these rivers. Normal n-alkanes in the range $C_{16} - C_{31}$ were not detected in stations WR3, WR7, and WR14 from coastal areas of the Warri river in Southwestern part of the Niger Delta region (Table 2). The GC traces (e.g. Fig. 3c) of these stations are erratic and compare closely with that reported for source input from sewage (Aboul-Kassim andSimoneit, 1996).

An odd/even predominance (OEP) in the n-alkanes $> C_{23}$ has often been used as a marker for a direct input of terrestrial plant waxes into geological and environmental samples (Simoneit*et al.*, 1987). Conversely, an even/odd predominance has been reported to be associated with recent sediments having organic matter input from phytoplanktonic organisms such as diatoms and some bacteria (Ekpo *et al.*, 2005; Elias *et al.*, 1997). Even-numbered n-alkane predominances are less common. Slight even carbon number n-alkane predominances or smooth distributions in the n-C_{20}–C_{30} range have been ascribed to reductive processes or bacterial inputs (Elias *et al.*, 1997). Our results, however, differ slightly from the even/odd predominance of n-alkanes ($C_{14} - C_{22}$) reported by Pearson and Obaje (1999) for Cretaceous sediments from the upper Benue Trough, Nigeria which was tentatively attributed to hyper salinity. In this study, the odd/even predominances in the n-$C_{17} - C_{31}$ range (Table 2) observed for most stations could be traced to mixed origin of terrestrial/biogenic, bacterial/microbial and anthropogenic organic source inputs, with stronger terrestrial/biogenic signal in stations from Imo, Qua Iboe and Bonny than Warri coastal areas.

The identification of the homologous n- alkanes in the hydrocarbon fractions allowed the determination of the carbon preference index (CPI) and Carbon maximum (C_{max}) for each sample set, which give supportive evidence for the relative incorporation of the different n-alkane sources. The CPI, a measure

of biologically synthesized n-alkanes (Simoneit, 1978; Simoneit*et al.*, 1991), indicates the relative contributions of n-alkanes from natural (biogenic/terrestrial; CPI > 1) compared to anthropogenic (CPI< 1) sources.The carbon preference index (CPI) was calculated according toZhu *et al.*(2005) using the same odd-carbon and even-carbon number n-alkane concentrations in the respective samples as follows:

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

Values of CPI ranged from 0.31 – 13.32 for the entire stations, with maximum value for station IM04(Table 2).Stations from Imo and Qua Iboe coastal areas recorded CPI values greater than one, suggesting terrigenous/biogenic sedimentary sources of n-alkanes. Conversely, the calculated CPI values for stations BN02, BN08, BN15 and WR8 were less than one, indicating a relatively higher proportion of n-alkanes from anthropogenic (mostly petroleum) sources. These results corroborate earlier reports by Oyo-lta*et al.* (2010); Ficken *et al.* (2000).In order to evaluate the origin of long-chain n-alkanes(i.e. whether the long-chain n-alkanes are derived from either higher plant waxes or macrophytes) in our coastalsediments,the parameter, Alkane Proxy (P_{aq}) was calculated according to [23] as follows:

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

Values of P_{aq} (Table 2) ranged from 0.12 – 1.00 for the entire sample suite. According to Ficken*et al.* (2000), values of P_{aq}ranging from 0.01 to 0.23 are linked to terrestrial plant waxes whereas those in the range of 0.48 to 0.94 are associated with submerged/floating species of macrophytes. Results of this study showed the importance of higher plant contribution to long-chain n-alkanes in almost all stations from Imo river coastal areas. Most stations from Bonny, Qua Iboe and Station WR2 from Warri coastal areas appeared to have more biogenic contributions to long-chain sedimentary n-alkanes from submerged/floating species of macrophytes.

Multivariate statistics (Factor analysis)

For a better understanding of the principal sources and biogeochemical processes responsible for the sedimentary n-alkanes in coastal sediments from Niger Delta of South eastern Nigeria, varimax rotated factor analyses using Statistica version 7.0 were carried out for the data suites. The varimax rotated factor analyses were calculated using eigen values greater than 1.0 and sorted by results having values greater than 0.6 being considered significant influences towards the principal sources. The results of sorted rotated factor analyses along with eigen values and percentages of variation are presented in Table 4. Three factors or principal components (PCs)explained 86.96%, 93.16%, 90.99% and 91.31% for the n-alkanes in stations from Warri, Imo, Bonny and Qua Iboe coastal areas, respectivelywith different percentages of total variance for the entire data structure.

Factor 1, which was positively loaded with CPI, accounted for 75.14%, 71.48%and 71.07% of the total variance for n-alkanes in stations from coastal areas of Imo, Bonny and Qua Iboe rivers, respectively. This factor was attributed to biogenic/terrestrial sources. On the other hand, Factor 1 accounted for only 45.38% of the total variance for n-alkanes in stations from coastal areas ofWarri river with negative loading on CPI, thus indicating relatively weak terrestrial/biogenic contributions to sedimentary n-alkanes in stations from these areas.The second factor obtained using n-alkanes and compositional indices explained 13.95%, 11.61%, 29.36% and15.36% of the total variance for n-alkanes in stations from coastal areas ofImo, Bonny, Warri and Qua Iboe rivers, respectively;and was found to be negatively associated with compositional indices (CPI, OEP, Paq) in the entire data structure. This factor was attributed to petrochemical sources. The third factor contributed 4.08%, 7.90%, 12.22% and 4.88% of the total variance for n-alkanes in stations from coastal areas ofImo, Bonny, Warri and Qua Iboe rivers, respectively. This factor, which was negatively loaded with CPI, OEP and Paq,was attributed to microbial/bacterial source inputs to sedimentary organic matter.

Conclusion

Hydrocarbons are present in worldwide environmental ecosystems. Numerous studies for apportioning sources of hydrocarbons, especially n-alkanes, in the environment that apply diagnostic indices based on chemical finger printing have been made mainly in temperate climate countries. In the present study, the sources of n-alkanes in sediments from coastal areas of four rivers in south-eastern and western parts of an industrialized and urban Niger Delta region of Nigeria are being reported. The analyses presented here of n-alkanes show that these compounds, when combined with other measures such as the UCM, provide additional insight into the prospective sources and processes that modulate the flux of terrestrial/biogenic and anthropogenic hydrocarbons ultimately accumulating in Niger Delta coastal environment. Based on the n-alkane distribution patterns, compositional indices and results of multivariate statistical analysis (factor analysis), sedimentary n-alkanes in all the samples analysed were found to originate from mixed terrestrial/biogenic, anthropogenic and microbial/bacterial sources.

Acknowledgements

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(a)   Station

Concentration (mg/kg)
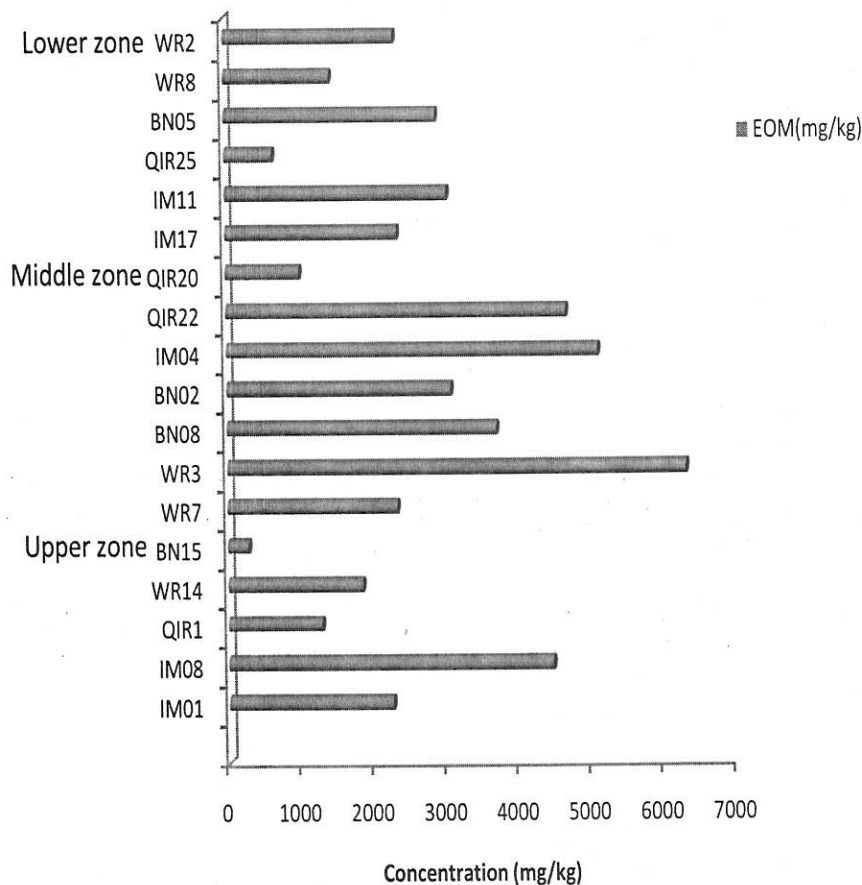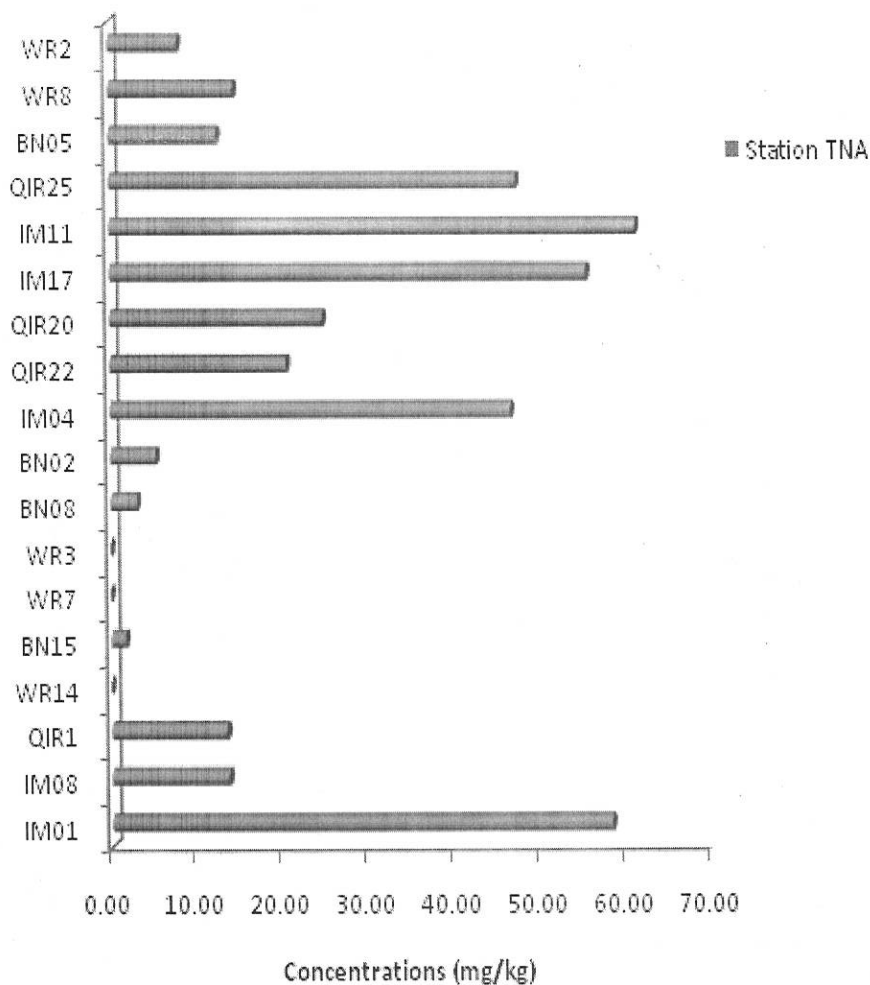
Fig.2 Variations in (a) Extractable organic matter (EOM); (b) Total n-alkane (TNA)in the study area.

(a)

Abundance

TIC: BN15AL.D

(b)

UCM

Time-->
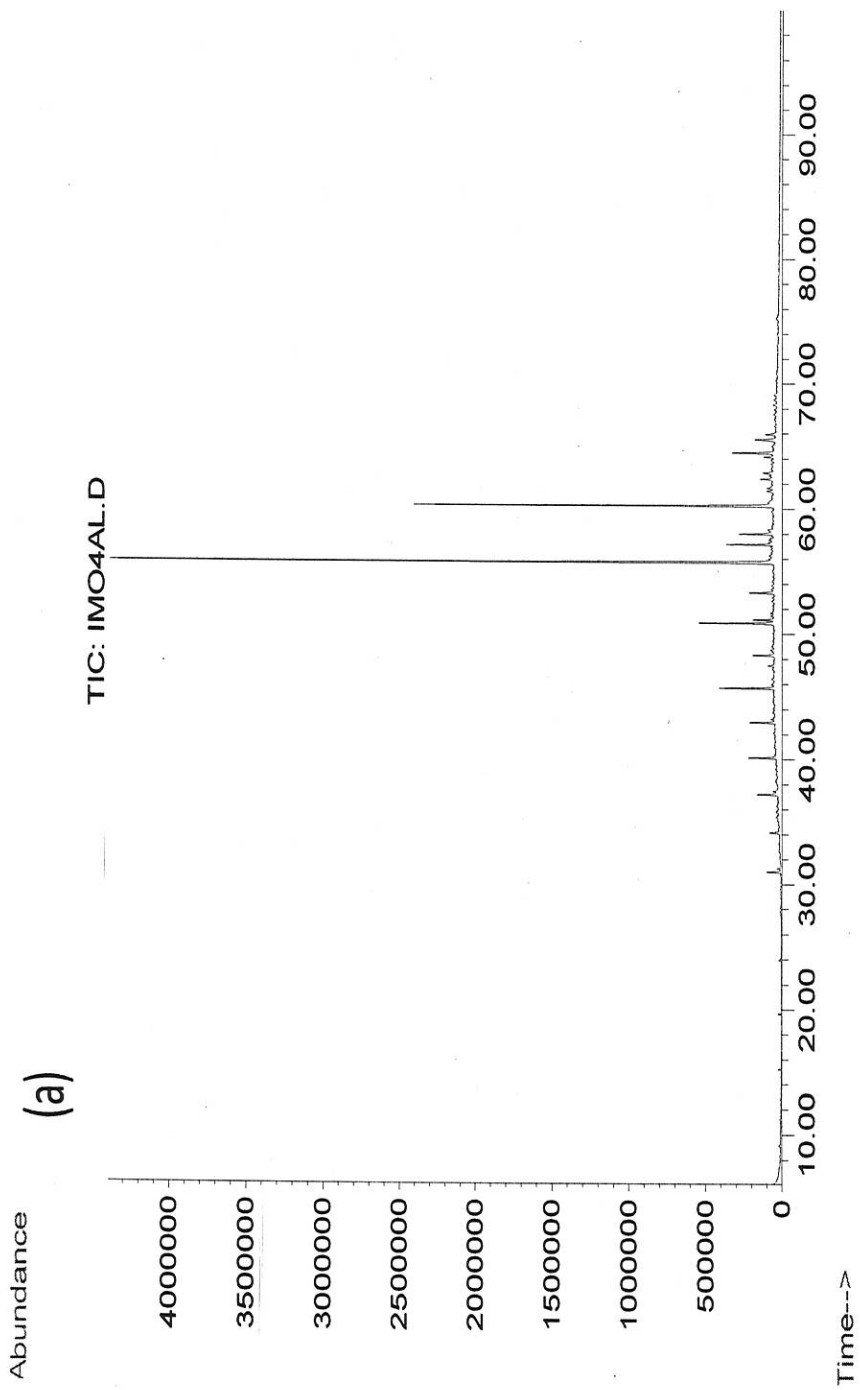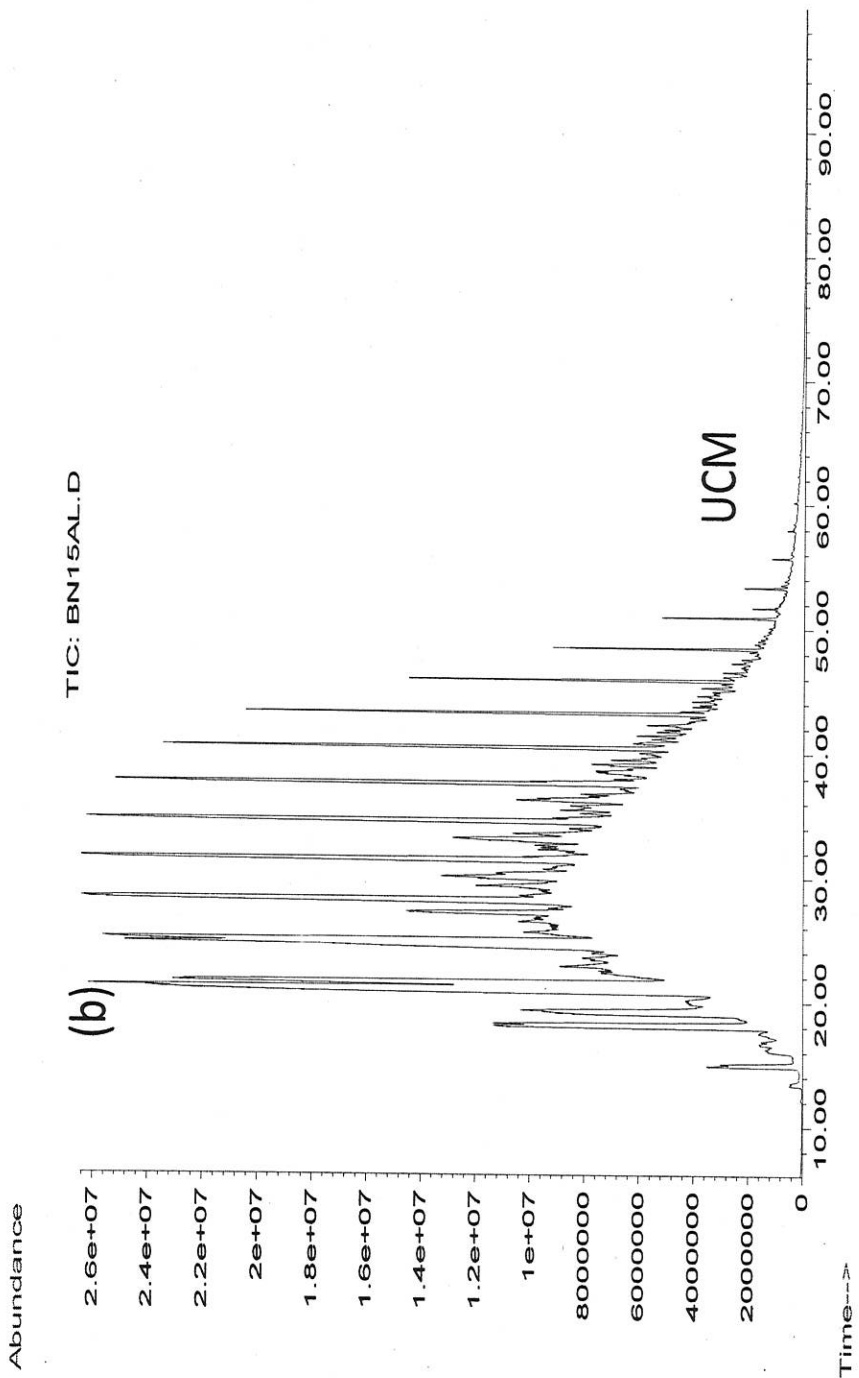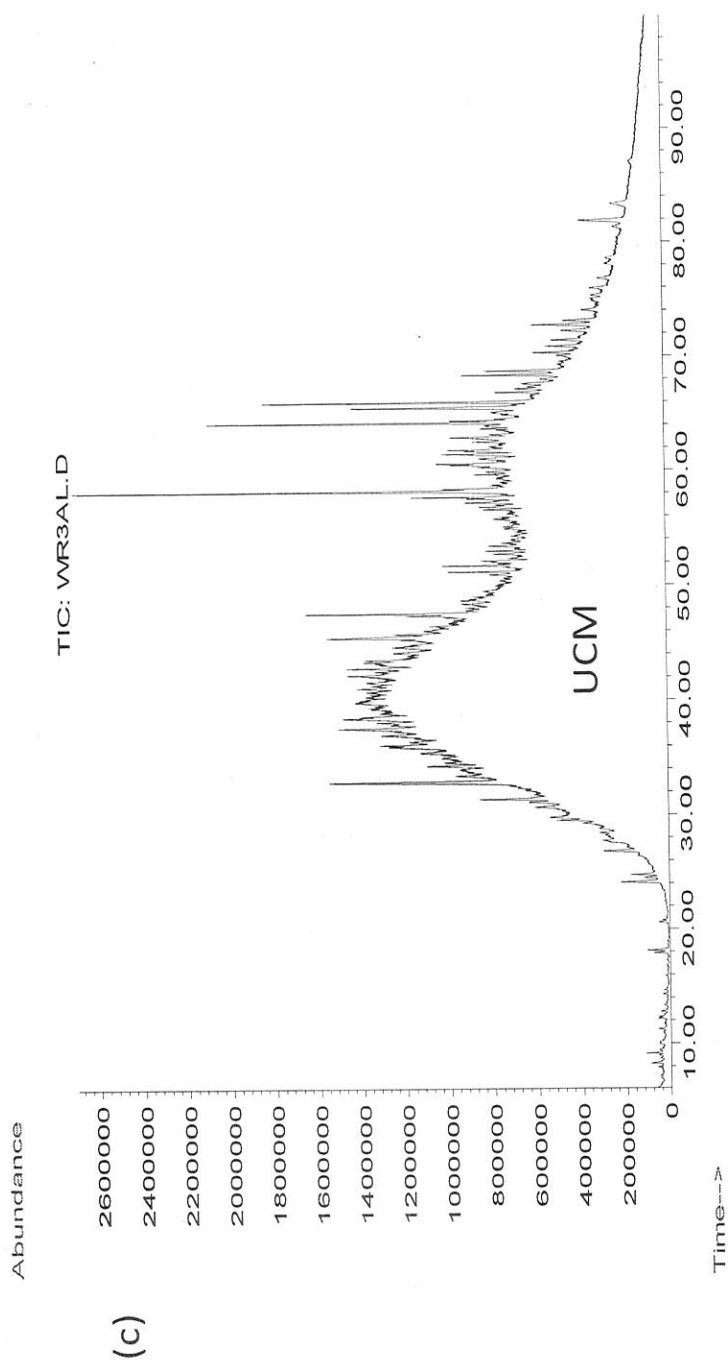
Fig.3. Examples of Gas Chromatograms (TIC) of n-alkane distributions for surface sediments from Niger Delta coastal areas showing (a) terrestrial, (b) petroleum and (c) sewage input sources, for stations IM04 (in middle zone), WR3 and BN15 (in upper zone), respectively.

Table 1: Sample Location and Types of Potential Anthropogenic Inputs

Sample locations*	Zone	Potential anthropogenic inputs
IM01	Upper	Domestic sewage as a result of nucleated settlements and engine boat pollution
IM08 QIR1 WR14 BN15		
WR7 WR3 BN02 IM04 QIR22 QIR20 BN08	Middle	Agricultural waste, engine boat pollution and fishing activities
IM17 IM11 QIR25 BN05 WR8 WR2	Lower	Oil spills, oil pollution from ships and engine boats, and untreated sewage

*IM=Imo; BN=Bonny; QIR=Qua Iboe; WR=Warri Rivers,respectively.
1, 2,3, etc refer to sampling stations

Table 2 Geochemical parameters, n-alkane concentrations and compositional indices of surface sediments from coastal areas of Niger Delta

Zone	Station	TOC (%)	EOM (mg/kg)	C_{16}	C_{17}	C_{18}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{31}	TNA	C_{range}	C_{max}	CPI	OEP	P_{aq}
Upper	IM01	3.18	2259.00	nd	nd	nd	0.64	2.01	2.06	1.96	3.32	1.99	4.50	1.92	23.81	11.07	58.28	21-31	C_{29}	8.16	1.52	0.16
	IM08	2.76	4489.00	nd	nd	nd	0.34	0.95	0.93	1.45	1.80	1.83	2.16	1.56	1.61	1.04	13.71	21-31	C_{29}	1.22	1.30	0.62
	QIR1	3.36	1296.00	nd	nd	nd	0.58	1.12	1.87	2.03	1.93	1.67	1.52	nd	1.76	1.02	13.50	21-31	C_{24}	1.68	1.40	0.68
	WR14	1.26	1860.00	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
	BN15	0.97	295.00	nd	0.16	nd	0.68	0.26	0.21	0.21	0.08	0.04	nd	0.01	nd	nd	1.65	17-28	C_{22}	0.31	0.78	1.00
Middle	WR7	3.27	2345.00	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	WR3	2.98	6346.00	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
	BN08	1.43	3725.00	0.08	0.82	0.76	0.46	0.17	0.47	0.15	0.08	0.01	nd	0.05	nd	nd	3.05	16-28	C_{17}	0.50	3.16	1.00
	BN02	1.45	3094.00	0.20	1.32	0.41	0.37	0.88	0.96	0.29	0.37	0.45	nd	0.12	nd	nd	5.32	16-28	C_{29}	0.90	1.18	1.00
	IMO4	4.26	5144.00	nd	nd	nd	0.43	0.92	1.07	1.03	2.11	1.00	2.98	1.06	23.68	12.40	46.68	21-31	C_{29}	13.32	1.85	0.12
	QIR22	3.12	4707.00	nd	nd	nd	0.43	0.80	1.27	1.35	2.19	1.18	2.19	1.37	2.74	7.12	20.64	21-31	C_{31}	3.65	1.81	0.56
	QIR20	3.48	1024.00	nd	nd	nd	0.65	1.70	1.62	1.64	2.59	1.24	2.81	nd	7.96	4.68	24.89	21-31	C_{29}	6.26	1.46	0.35
Lower	IM17	1.76	2373.00	nd	nd	nd	0.62	1.11	1.95	1.47	3.05	1.09	4.00	1.44	23.21	17.63	55.57	21-31	C_{29}	11.97	2.18	0.18
	IM11	1.96	3066.00	nd	nd	nd	0.78	1.47	2.08	1.70	3.10	1.51	3.84	1.73	28.11	17.02	61.34	21-31	C_{29}	10.54	1.88	0.16
	QIR25	0.44	672.70	nd	nd	nd	1.23	4.49	4.40	5.65	5.57	5.07	4.90	3.55	7.69	4.85	47.40	21-31	C_{29}	1.61	1.10	0.55
	BNO5	1.67	2923.00	0.67	2.76	nd	0.75	3.25	2.34	1.45	0.83	0.46	nd	0.10	0.05	nd	12.66	16-29	C_{17}	1.60	0.83	0.70
	WR8	2.71	1468.00	nd	nd	nd	0.82	1.29	nd	0.74	nd	6.75	1.05	nd	2.11	1.84	14.60	21-31	C_{26}	0.67	0.40	
	WR2	2.37	2354.00	nd	nd	nd	1.49	1.20	1.59	1.06	0.69	0.49	nd	nd	0.71	0.87	8.10	21-31	C_{26}	1.46	1.67	0.76

TNA = Total n-alkanes, CPI = Carbon preference index : calculated according to [22] as $(C_{23} + C_{25} + C_{27} + C_{29} + C_{31})/(C_{24} + C_{26} + C_{28} + C_{30})$, P_{aq} = n-alkane proxy : calculated according to [23] as $(C_{23} + C_{25})/(C_{23} + C_{25} + C_{29} + C_{31})$, OEP = Odd even predominance $(C_{21} - C_{25})$, Cmax = Carbon maximum (n-alkane with maximum concentration), TOC = Total organic carbon, EOM = Extractable organic matter

Table 3: Mean n-alkane concentrations for the sediments in the different zones of the study area

Compound Name	MW	Molecular Formula	Average concentration (mg/kg) Zone		
			Upper	Middle	Lower
n-Hexadecane	226	$C_{16}H_{34}$	nd	0.04	0.11
n-Heptadecane	240	$C_{17}H_{36}$	0.04	0.31	0.46
n-Octadecane	254	$C_{18}H_{38}$	nd	0.17	nd
n-Heneicosane	296	$C_{21}H_{44}$	0.46	0.33	0.95
n-Docosane	310	$C_{22}H_{46}$	0.87	0.63	2.14
n-Tricosane	324	$C_{23}H_{48}$	1.01	0.77	2.06
n-Tetracosane	338	$C_{24}H_{50}$	1.13	0.64	2.01
n-Pentacosane	352	$C_{25}H_{52}$	1.43	1.05	2.21
n-Hexacosane	366	$C_{26}H_{54}$	1.11	0.55	2.56
n-Heptacosane	380	$C_{27}H_{56}$	1.64	1.14	2.3
n-Octacosane	394	$C_{28}H_{58}$	0.7	0.37	1.14
n-Nonacosane	408	$C_{29}H_{60}$	5.44	4.91	10.31
n-Hentiracontane	436	$C_{31}H_{61}$	2.63	3.46	6.37

Table 4 Varimax rotated factor analyses of n-alkanes and compositional indices for

Parameters	(a) Imo coastal sediments (Marked loadings are > .600000)			(b) Bonny coastal sediments			(c) Warri coastal sediments			(d) Qua Iboe coastal sediments		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
C_{MAX}	0.963	-0.139	0.066	0.935	0.149	0.228	0.208	-0.543	0.766	0.962	0.000	0.168
CPI	0.975	-0.054	0.018	0.939	0.147	0.215	0.208	-0.541	0.767	0.959	0.016	0.184
OEP	0.975	-0.043	0.016	0.937	0.145	0.226	0.172	-0.925	0.017	0.958	0.016	0.189
Paq	0.028	-0.047	0.018	0.936	0.144	0.229	0.101	0.232	0.944	0.958	0.015	0.188
$n-C_{16}$	-0.975	-0.047	0.018	0.621	-0.128	0.628	-0.959	0.028	0.110	0.958	0.015	0.188
C_{17}	-0.975	-0.047	0.018	0.621	0.153	0.228	-0.959	0.028	0.110	0.958	0.015	0.188
C_{18}	-0.975	-0.047	0.018	0.266	0.095	0.927	-0.959	0.028	0.110	0.958	0.015	0.188
C_{21}	0.975	-0.050	0.018	0.936	0.148	0.226	0.208	-0.544	0.765	0.957	0.012	0.193
C_{22}	0.975	-0.049	0.022	0.932	0.154	0.235	0.209	-0.547	0.762	0.954	0.000	0.208
C_{23}	0.975	-0.056	0.018	0.934	0.152	0.230	0.172	-0.925	0.017	0.954	0.006	0.206
C_{24}	0.975	-0.048	0.018	0.934	0.149	0.231	0.208	-0.925	0.764	0.953	0.002	0.213
C_{25}	0.975	-0.058	0.020	0.935	0.148	0.228	0.172	-0.925	0.017	0.955	-0.001	0.206
C_{26}	0.976	-0.042	0.018	0.936	0.147	0.227	0.210	-0.576	0.739	0.953	0.003	0.211
C_{27}	0.974	-0.062	0.025	-0.936	-0.146	-0.227	0.082	0.233	0.946	0.956	-0.003	0.201
C_{28}	0.975	-0.047	0.017	-0.936	0.146	0.226	-0.959	-0.028	-0.110	0.466	0.348	0.147
C_{29}	0.924	-0.283	0.123	0.492	-0.298	-0.339	0.209	-0.553	0.758	0.955	-0.030	0.204
C_{31}	0.955	-0.205	0.035	-0.936	-0.146	-0.227	0.209	-0.552	0.759	0.962	-0.011	0.166
	% total variance	Eigen values	% Cummul.	% total variance	Eigen values	% Cummul.	% total variance	Eigen values	% Cummul.	% total variance	Eigen values	% Cummul.
1	75.14	31.56	75.14	71.48	30.02	71.48	45.38	19.06	45.38	71.07	29.85	71.07
2	13.95	5.86	89.08	11.60	4.87	83.09	29.36	12.33	74.74	15.36	6.45	86.43
3	4.08	1.71	93.16	7.90	3.32	90.99	12.22	5.13	86.96	4.87	2.05	91.31

Extraction: Principal Components
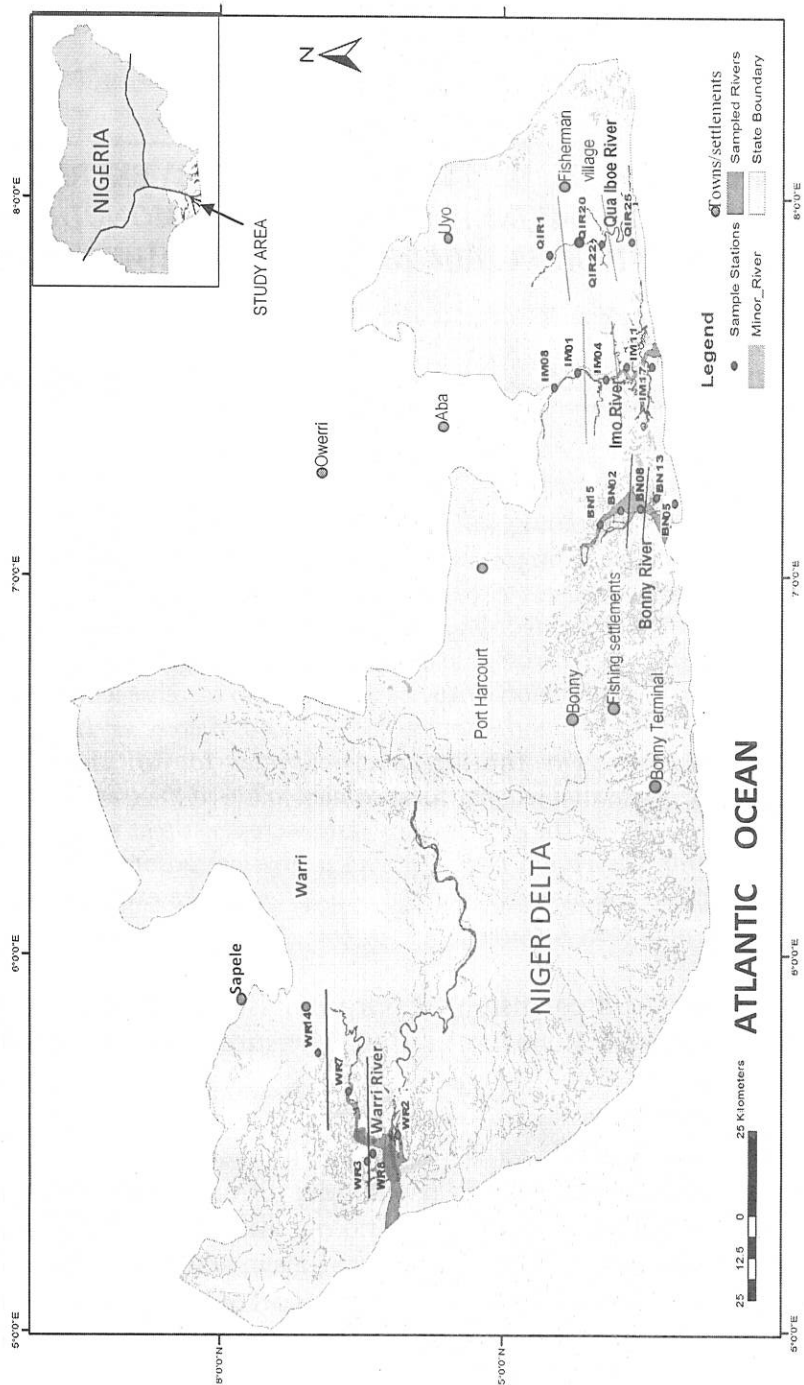
Factors 1,2 and 3 are terrestrial/biogenic, anthropogenic and microbial sources

Fig. 1 Map of study area showing sample stations