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SOURCES AND SEASONAL DISTRIBUTION OF *N*-ALKANES IN SEDIMENTS FROM CROSS RIVER ESTUARY, SOUTH-SOUTH NIGERIA.

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Abstract

The Cross river estuary located in South-East Nigeria, has great economic importance due to the numerous commercial activities taking place there. In the study, n-alkane concentrations, composition profiles and sources were assessed in surface sediments. Results revealed total n-alkane concentrations ranged between 140.75ng/g to 2437.67ng/g. Long /short chain hydrocarbons values ranged from 2.09 to 10.12, attributed to higher plant and/or macrophytes waxes. The extent of anthropogenic pressure on the estuary reflected in the variation in unresolved complex mixture with season. Highest carbon preference index in the month of February and results of most distribution ratios like proxy aquatic ratio and n-alkanes/C_{16} ratio implied major contribution from terrestrial plants/macrophyte waxes and a predominance of biogenic OM inputs with the highest biogenic flux recorded in the wet season. Dissimilarities in hydrological factors such as suspended sediment concentration, temperature and salinity as well as anthropogenic pressure influenced the behaviour of *n*-alkanes in the estuary.

Keywords: *n*-alkanes, anthropogenic, biogenic, macrophytes, sediments.

1. Introduction

Hydrocarbon pollution in coastal areas has become a subject of global interest, due to its widespread use as a source of energy which has led to its distribution in the environment (Lors et al., 2009). The principal sources of hydrocarbons in the marine environment are biogenic, diagenetic, pyrolytic and petrogenic. These hydrocarbons which are fed into the environment by way of spills, accidents or leaks from industrial discharges, or by products from commercial or household uses, originates from crude oil and found to contain a extensive array of chemical products such as gasoline, fuel oil, kerosene, heavy oil and lubricating oils, (Mille et al., 2007). Hydrocarbons in aquatic environment have a tendency to

combine with particulate organic matter owing to their hydrophobic tendency and they are then dumped in core sediments, not only recognized as an excellent sink for such pollutants, but the main nursing area of fisheries and other aquatic habitats (Commendatore et al., 2012).

Aliphatic hydrocarbons widely used as biomarkers for source correlation purposes and in differentiating between autochthonous and allochthonous organic matter (OM) includes n-alkanes, pristine, phytane, styrene, and hopanes. Over the years, lipid biomarkers have been confirmed as the most consistent method for source assessment of OM in coastal areas due to their resistance towards diagenesis and preservation during sediment deposition. The origin of n-alkanes in organic matter can be identified using diagnostic concentration ratios together with molecular markers and multivariate methods (Kavouras *et al*., 2001). Some of the indices which have been used over the years to identity and estimate the sources of n-alkanes in the environment are; Carbon preference index (CPI), which is the ratio of the concentrations of odd to even carbon n-alkanes (Maioli *et al*., 2010). CPI ratios close to 1 indicates greater input from petroleum, values less than 1 indicates input from reprocessed organic matter, and/or microorganisms whereas those greater than 1 are suggestive of inputs from vascular plants (Kennicutt *et al.*, 1987). Ficken *et al.* (2000) proposed an n-alkane proxy (Paq) in order to assess organic matter input from diverse sources, it indicates that Paq values ranging between 0.01 and 0.23 are attributed to terrestrial plant waxes, while values ranging between 0.48 and 0.94 are suggestive of immersed/floating species of macrophytes. This was to distinguish between immersed/floating macrophytes and emergent terrestrial plants. The proxy seeks to explain the point that underwater/floating sources have abundant mid-chain n-alkanes compared to terrestrial higher plants vegetation enhanced in long-chain n-alkanes. $C_{27,}$ C_{29} and C_{31}n-alkanes in samples represents influence from land plants waxes, while C_{15}, C_{17} and C_{19} n-alkanes indicates input from algae (Choudhary *et al.*, 2010). SHC (C_{15},C_{17},C_{19}) resulting from algae are more sensitive to biodegradation than the LHC (Meyers, 2003). Others are low/high molecular weight hydrocarbons (L/H); Σn-alkanes/n-C16; unresolved carbon mixture(UCM); Average Carbon Chain (ACL); n-C17pristane; and % plant wax contribution (Wax Cn) amongst others (Zhu *et al*., 2005).

Estuarine waters are found to be biologically more productive than the oceanic waters. This explains why there are considered locations for human development with over 69% of the largest cities in the world located around them (Wolanski *et al*., 2004). Estuaries are exceptional sites for community living as they provide water for drinking and other uses and also help the development of trade and communication. The water level and salinity increases and decreases with the tides and the seasons. In the wet seasons, the estuary may be flooded by fresh water from the rivers and in the dry season, the outflow from rivers may be reduced, this makes the estuaries to shrink and become saltier.

The study location, Cross river estuary (Fig. 1) which lies between latitudes $4^{O}45'$N and $4^{O}55'$N and longitudes $8^{O}15'$E

and 8^{O}25'E, is known to be one of the estuaries in the south-eastern part of Niger-Delta, Nigeria. It covers an area of 53,000 km^2, of which 4,000km^2 of the total area lies in Cameroon and 49,000km^2 in Nigeria. The estuary is composed of numerous tributaries which begins from the western slopes of the Cameroon mountains and runs south-westward emptying into the Atlantic Ocean with a release of between 880-2533m^3 sec^{-1}(Lowenberg & Kunzel, 1992). The system is open to temporary flooding which depends on the waves and the seasons (wet/dry). The region has a rainy season between April and October, which accounts for 80 % of the yearly rainfalls, with peaks between June and September. Mean temperature begins from 24^{O}C in August to 30^{O}C in February and relative humidity is high at 80-100% (Eze *et al*., 2010). Variations in the tides and seasons are the major features that affect the hydrology of the Cross river estuary (Oyo-Ita *et al*., 2010). The waterway basin which is endowed with clay resources is situated inside the tropical rainforest region. The area, rich in mineral coupled with the thick flora and heavy rainfall characteristics of the area plays a great part in the biogeochemical regulation of organic and inorganic nutrients in the estuary (Asuquo *et al*., 1998).

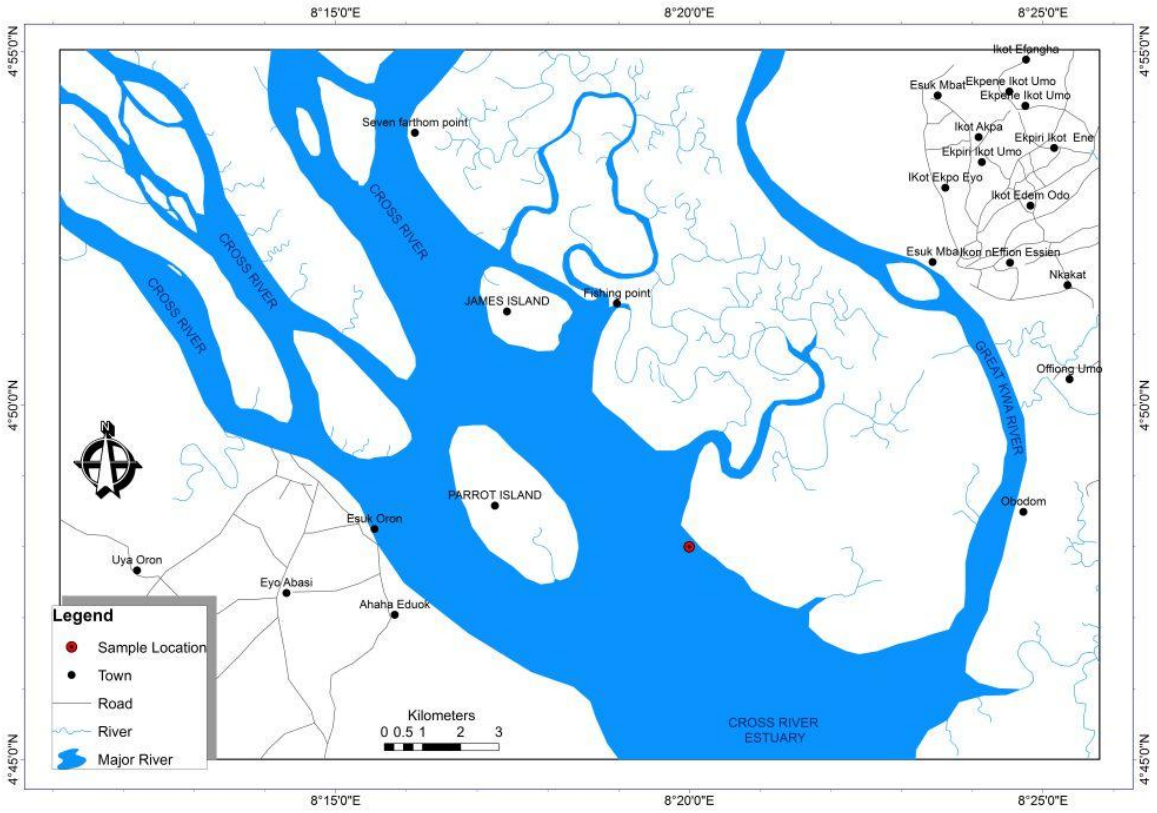

Fig. 1: Map of the Cross River Estuary Showing the Study Area

Environmental factors in the estuary such as suspended particulate matter (SPM), salinity and temperature affects the distribution and fate of hydrocarbons in the marine environment. Also, human factors such as wood and coal burning, vehicular and ship releases and dumping of waste from industrial and household

sources also show seasonal variation (Liu *et al*., 2009) which can impact on the configuration and environmental behavior of hydrocarbons in the estuary. Parrot Island, where sampling was done, is located in the central estuary and was so selected as a result of the hydrographic settings at this point representing a borderline between the ocean water and the fresh water (Lowenberg and Kunzel, 1992). Although there are reports of studies on the sources, occurrence and distribution of hydrocarbons, ketones and acetates in sediments (Oyo-Ita *et al*., 2010; Oyo-Ita *et al.,* 2013) as well as heavy metals in water of the Cross River estuary (Asuquo *et al.,* 1998), studies on the seasonal changes of hydrocarbons in the estuary in response to human activities and hydrology are scarce and the assessment of the potential risks posed by these hydrocarbons has not been reported. This work therefore, seeks to bridge the research gap. A six-months field study on the disparities in hydrocarbons in the Cross River estuary was carried out in the wet and dry seasons.

This study aims at determining the sources and distribution of hydrocarbons (n-alkanes) in the Cross River estuary, and the objectives of the study includes:

i. Determining the concentrations and compositions of n-alkanes in sediments from the Cross River estuary.
ii. Identifying the various sources of n-alkanes in the estuary
iii. Assessing the combined impacts of hydrology on the concentrations and compositions of n-alkanes in the estuary.

2. Materials and methods

2.1 Sample collection, preparation and preservation

Sampling was carried out around Edik Ekpu area on Parrot Island (Fig.1) within a period of 6 months, covering the wet (April, June, August) and the dry seasons (October, December, and February).

Sediments samples were collected using a Vaan veer grab sampler and wrapped in aluminum foil, transported to the laboratory and air-dried. Small portions of the already dried samples were finely crushed with the help of a washed and dried mortar and pestle and stored until further analysis. 2g of the air-dried and crushed sediment samples were extracted by ultra-sonification technique using 10ml mixture of acetone and hexane (1:1 v/v) in triplicate. The extracts were separated using a centrifuge, decanted carefully into a beaker and vacuum evaporated to near dryness.

3. Resultsand Discussion

3.1 Seasonal variation in n-alkanes concentrations

ΣC_8-C_{40} levels of *n*-alkanes in sediments (Fig 2) ranged between 140.75 ng/g (4 %) and 2437.67 ng/g(60 %) with a minimum in the month of February and a maximum in June (mean = 1026.23±1234.74ng/g). Highest mean *n*-alkanes concentration in sediments (73.87 ng/g) was found in the month of June (wet season), while the lowest mean concentration of 4.27 ng/g was recorded in February (dry season) (Fig 3). The mean *n*-alkanes concentrations in the wet and dry seasons revealed a significant seasonal disparity ($p< 0.05$). Also, correlation analysis showed a moderate positive relationship existing between the wet and the dry seasons *n*-

alkane concentrations (r= 0.38), signifying changes in the amount and quality of OM inputs in the two seasons.

Total *n*-alkane levels (140.75 to 2437.87 ng/g) in sediments in the present study were comparatively higher than Gulf of Tunis, Tunisia which ranged from 701.00 to 741.70 ng/L (Mzoughi and Chouba, 2011) and Shatt Al-Arab River, Iraq (8.81 to 35.58 µg/L; Al-Hejuje et al. 2015). This could be attributed to high anthropogenic activities around the sampling area, as well as high urbanization.

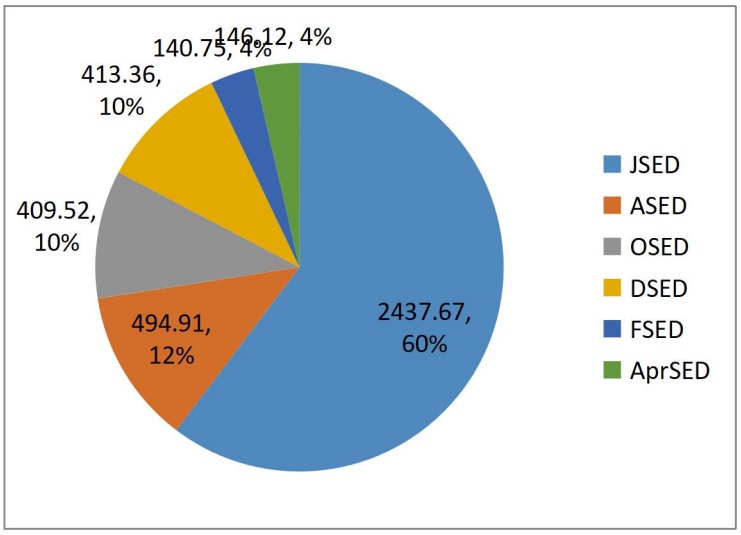

Fig. 2: Total concentrationand percentage of n-alkanes in sediments

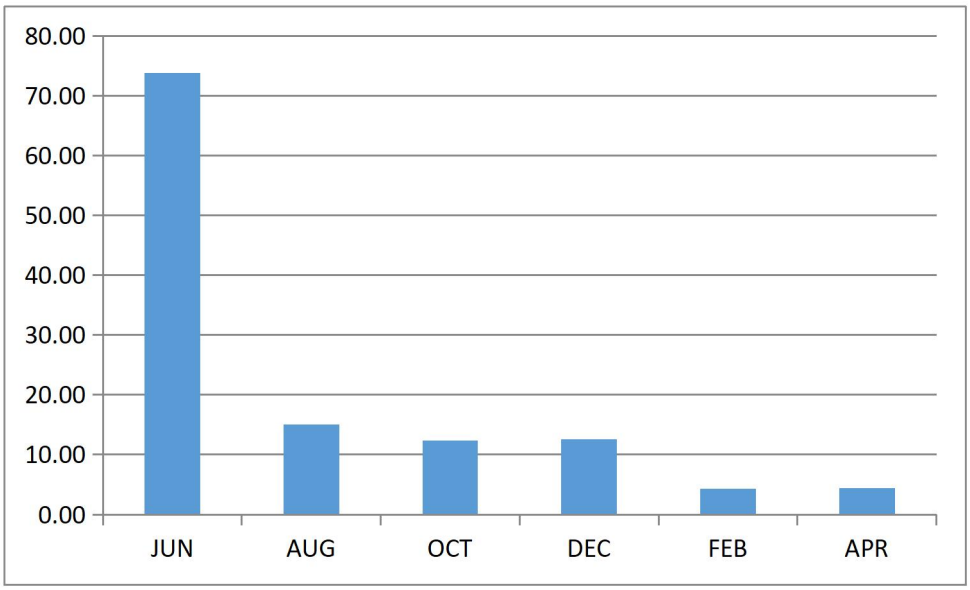

Fig. 3: Monthly mean concentrations of n-alkanes in sediments

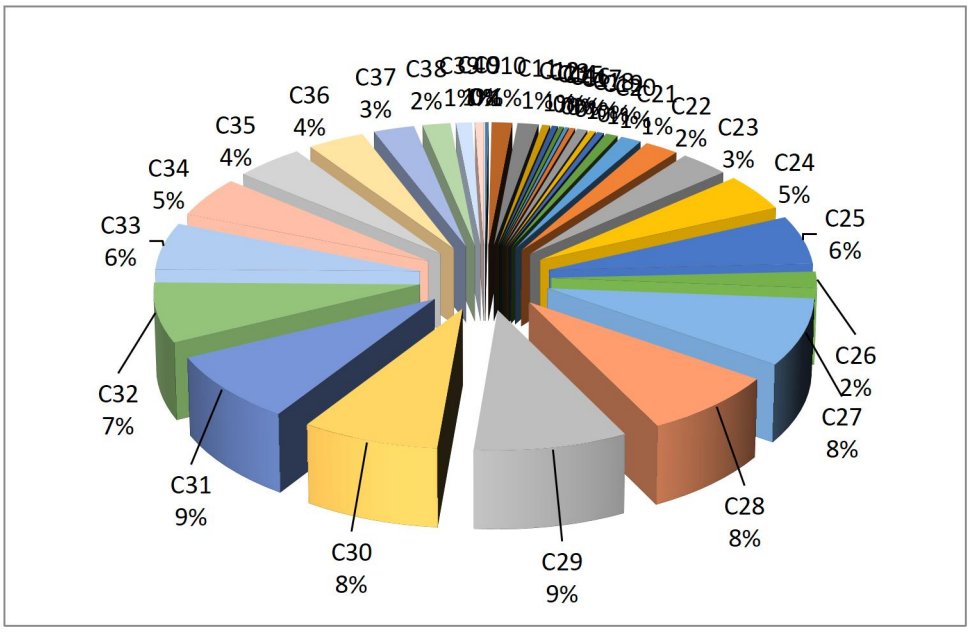

Fig. 4: Total concentration of n-alkanes in the wet season

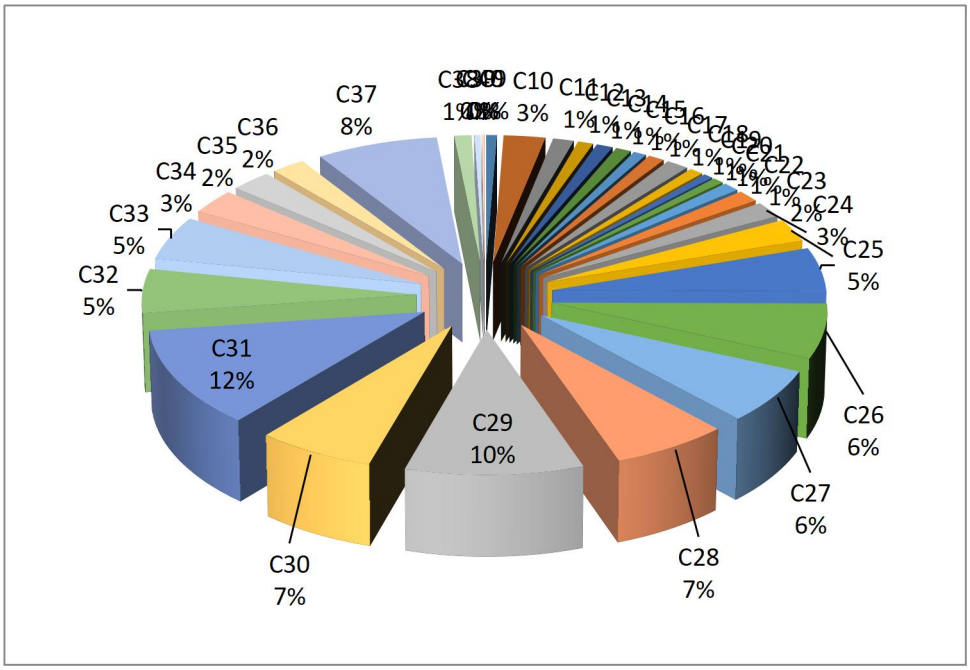

Fig. 5: Total concentration of n-alkanes in the dry season

3.2 Source analysis of n-alkanes by calculated distribution indices

n-Alkanes derive their sources from mutually biogenic and anthropogenic inputs (Aboul-Kassim and Simoneit, 1995), and found to be useful parameters in assessing not only the sources, but also fate of OM in the aquatic environments (Sikes *et al*., 2009). SHC originate from algae or plankton, whereas LHC originate from vascular plants (Meyers, 1997). The source analysis of n-alkanes for sediment samples were calculated using various distribution indices as indicated below (Table 1).

Result obtained indicated that SHC values ranged between 31.87 at FSED to 253.42 at JSED, with a mean value of 82.85±89.24, while LHC values varied between 97.61 at AprSED to 2096.11 at

JSED with a mean of 571.60±81.47. LHC/SHC ratios showed values ranging from 2.09 to 10.12 with a mean value of 6.90±8.76, which is suggestive of a dominance of higher plant and/or macrophytes waxes. TAR ratio had values ranging between 5.35 to 39.81 with a mean of 15.31±16.15 reflecting dominance of higher plantin puts of terrestrial origin.

The anthropogenic sources of n-alkanes in the study area were reflected in the distribution of Carbon Preference Index (CPI) and unresolved complex mixture (UCM). CPI is the ratio of odd to even carbon, and values around unity are indicative of inputs from petroleum, while values <1 are indicative of inputs from microorganisms and >1 imply contribution from higher plants (Oyo-Ita *et al*., 2017). n-Alkanes which originates from terrestrial plant material showed a prevalence of odd-numbered carbon chain while even/odd carbon numbered predominance are indicative of inputs from micro-organisms (Commedatore *et al*., 2012; Kanzari *et al*., 2014).CPI recorded values ranging from 1.08 (AprSED) to 1.79 (FSED) with a mean of 1.55±1.49, indicating inputs from higher plants. The highest CPI value (1.79) was recorded in the month of February, suggesting a greater wash-in of higher plant waxes to the estuary in the month, while lowest value of 1.08 was recorded in the month of April indicative of petroleum inputs to the estuary. Unresolved complex mixture (UCM), also known as 'hump', is a component often found in gas chromatographic data of extracts from organisms exposed to oils and crude oils, and it consist of unresolved cyclic and branched hydrocarbons (Frysinger et al. 2003). The extent of anthropogenic pressure on the estuary reflected in the variation in UCMs with season as shown in the representative chromatogram (Fig. 6), supporting the earlier claim that petroleum/petrochemical contamination was heavy in the estuary.

Other distribution indices which were calculated to ascertain the hydrocarbon sources in the samples included: Terrestrial/Aquatic Ratio (TAR), Proxy aquatic ratio (P_{aq}), n-alkane/C16, n-C29/n-C17.

TAR used to investigate the terrigenous/aquatic mixture of hydrocarbons in the sample, was calculated using the expression: TAR = [(C27+C29+C31)/(C15+C17+C19).
Values>1 are suggestive of dominant inputs from terrestrial OM, while values <1 imply major contribution from aquatic OM (Simoneit *et al*., 2002).In the study, the bimonthly mean TAR values ranged between 5.35 in August to 39.81 in October (Table 1), indicative of higher terrestrial OM inputs in thed ry than in the wets eason.

Proxy aquatic ratio (P_{aq} = $[(C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})]$ values which stretched between 0.01 and 0.23 are ascribed to higher plant leaf waxes, while ratios which stretched between 0.48 - 0.94 are linked to floating/submerged macrophytes (Ficken et al. 2000). Here, the bimonthly mean P_{aq} results revealed intermediate values (0.21-0.38; Table 1), implying an almost identical amount of terrestrial plant and macrophytes inputs to the water with higher input of macrophyte and terrestrial higher plant found in the month of June and April (wet season), respectively.

The n-alkanes/C_{16} ratio was also calculated to determine the comparative proportion of biogenic and anthropogenic sources of n-alkanes in the water sample. Syakti *et al*. (2013) stated that values of n-alkanes/C_{16}>50 suggest biogenic origin, whereas values <15 indicates petrogenic origin. In the study, results show all values greater than 50, with the highest value observed in the month of June (337.47), indicative of inputs from biogenic origin. The investigative factor that gives helpful proof of the occurrence of natural inputs to the aquatic environment is the carbon maximum (C_{max}). For example, C_{max} of 31 in sediments is an indication that the area is colonized with grasses whereas C_{27} and C_{29} are more rich in aquatic sediments where trees control the neighborhood of the lake. Generally, $C_{max}(C_8\text{-}C_{20})$ was predominated by C_8, C_{10} and C_{11} in most sediments samples in the wet season, whereas $C_{max}(C8\text{-}C_{20})$ at C_{10}, C_{11} and C_{17} or C_{18} predominated in most sediments in the dry season. The results indicated that seasonal changes did not only affect the quantity of OM flux but also the OM quality. On the other hand, $C_{max}(C_{21}\text{-}C_{40})$ was predominated by C_{29} in most sediments in the wet season except in JSED samples with C_{max} at C_{21}, C_{25}, C_{26}. APrSED and ASED exhibited C_{max} at C_{30} and C_{31} in addition, respectively, indicating that higher input of macrophyte occurred in the wet season. Besides the occurrence of C_{max} at C_{29} and C_{31} in all sediments in the dry season, $C_{max}(C_8\text{-}C_{20})$at C_{10} was found in all the sediments in the dry season. Result reveals predominance of grasses and higher plants inputs in the sediments.

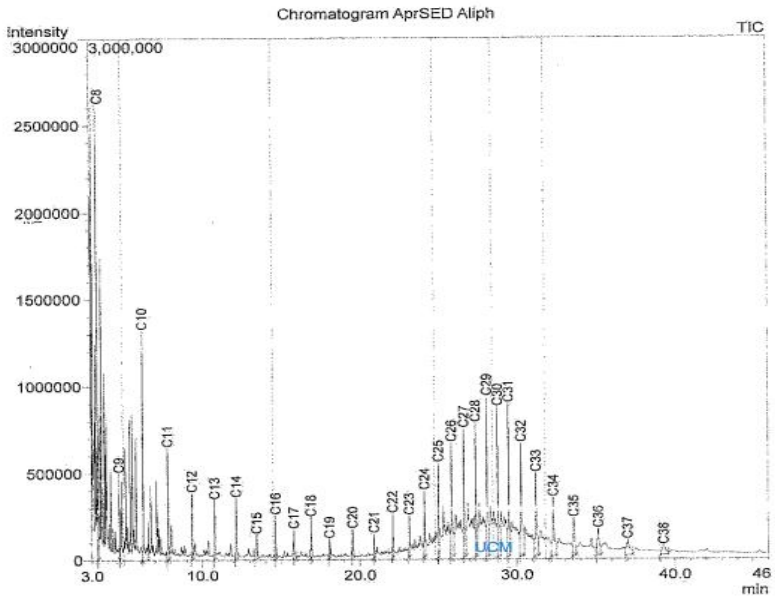

Fig. 6: Gas chromatogram of n-alkanes in sediments showing the UCM

Table 1: Concentrations of n-alkanes(ng/g) and calculated distribution indices in sediments

Months	ΣC8-C40	SHC (Σ<C23)	LHC (Σ>C23)	LHC/ SHC	CPI	TAR	Paq	Σn-alkanes/ C16

JSED	2437.67	253.42	2096.11	8.27	1.55	17.62	0.38	337.47
ASED	494.91	43.83	443.40	10.12	1.66	39.81	0.22	262.35
OSED	409.52	77.46	321.93	4.16	1.42	5.35	0.28	66.03
DSED	413.36	43.82	363.62	8.30	1.68	30.62	0.23	191.84
FSED	140.75	31.87	106.94	3.36	1.79	16.17	0.21	103.67
AprSED	146.12	46.73	97.61	2.09	1.08	6.36	0.25	80.60
TOTAL	4042.32	497.13	3429.61	36.29	9.17	115.94	1.57	1041.97
MEAN	673.72	82.85	571.60	6.90	1.55	15.31	0.32	297.70
STD	904.61	89.24	781.47	8.76	1.49	16.15	0.40	317.67
MAX	2437.67	253.42	2096.11	10.12	1.79	39.81	0.38	337.47
MIN	140.75	31.87	97.61	2.09	1.08	5.35	0.21	66.03

4. Conclusion

In conclusion, this study examined the concentrations as well as sources of hydrocarbons in the Cross river estuary in the wet and dry seasons. Results obtained revealed that there was a marked seasonal variation in the concentration of n-alkanes in the two seasons with the concentrations in the wet season been greater compared to that of the dry season. This can be ascribed to heavy washed-out effect of surface water and higher precipitation during the wet season. The LHC were found to dominate throughout the period of study and is suggestive of inputs from petrogenic sources and vascular plants. The biogeochemical processes in the estuary were sensitive to changes in hydrology and anthropogenic actions, which will require additional investigation in the context of total climate change.

References

Aboul-Kassim TAT, Simoneit BRT (1995) Petroleum hydrocarbon fingerprinting and sediment transport assessed by molecular biomarker and multivariate statistical analyses in the eastern harbor of Alexandria, Egypt. *Marine Pollution Bulletin* 30:63-73. http://doi.org/10.1016/0025-326X(94)00102-F

Al-Hejuje M. M., Hussain N. A., Al-saad H. T. (2015). Total petroleum hydrocarbons(TPHs), n-alkanes and polynuclear aromatic hydrocarbons (PAHs) in water of Shatt Al-Arab River-part 1. *Global Journal of Biology, Agriculture & Health Sciences*, 4(1):88-94.

Asuquo, F. E., Eja, M. E., Ekwu, A. O., Bassey, E. E. (1998). Post Impact Assessment (PIA)of Cross River Coastal areas affected by Mobil (Idoho) Oil spill. Report submitted to Cross River State Government, 68pp.

Choudhary, P, Routh. J., Chakrapani, G. J. (2010). Organic geochemical record of increased productivity in Lake Naukuchiyatal, Kumaun Himalayas. India. *Environmental Earth Sciences*. 60, 837-843.

Commendatore, M. G., Nievas, M. L., Amin, O., Estevez, J. L. (2012). Natural and anthropogenic hydrocarbons in sediments from the Chubut River (Patagonia, Argentina). *Marine Environment Res.,* 74, 20.

Ekpo, B. O., Oyo-Ita, O. E., Oros, D. R., Simoneit, B. R. T. (2011). Distributions and sources of polycyclic aromatic hydrocarbons in surface sediments from the Cross River estuary, S. E. Niger Delta, Nigeria. *Environmental Monitoring Assessment.*

El Nemr, A., El-Sadaawy, M. M., Khaled, A. Draz, S. O. (2013). Aliphatic and polycyclic aromatic hydrocarbons in the surface sediments of the Mediterranean: Assessment and Source recognition of petroleum hydrocarbons. *Environmental Monitoring Assessment*. 185, 4571-4589.

El Nemr, A., Moneer, A. A., Rogab, S., El Sikaily, A. (2016). Distribution and source s of n-alkanes and polycyclic aromatic hydrocarbons in shellfish of the Egyptian Red Sea Coast. *Egyptian Journal of Aquatic Research.* 42, 121-131.

Eze, E. B., Efiong, J. (2010). Morphometric parameters of the Calabar River Basin: Implication for Hydrologic processes. *Journal of Geography and Geology.* 2(1) 1916-9787.

Ficken KJ, Li B, Swain DL, Eglinton G (2000) An n-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. *Organic Geochemistry* 31: 745-749. https://doi.org/10.1016/S0146-6380(00)00081-4

Frysinger GS, Gaines RB, Xu L, Reddy CM (2003) Resolving the unresolved complex mixture in petroleum-contaminated sediments. *Environmental Science and Technology* 37:1653-1662. https//doi.org/10.1021/es020742n

Kanzari, F. Syakti, A. D. Asia, L., Malleret, L. Piran, A., Mille, G. Doumenq, P. (2014). Distributions and sources of persistent organic pollutants (aliphatic hydrocarbons, PAHs, PCBs and Pesticides) in surface sediments of an industrialized urban river (Huveaune), *France Science. Total Environment.* 478, 141-151.

Kavoures,I. G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E. G., Von

Baer D, Oyola, P (2001). Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. *Environmental Science and Technology,* 1;35(11):2288-94.

Kennicult, M. C., Barker, C., Books, J. M., Defreitas, D. A., Zhu, G. H. (1987). Selected organic matter source indicators in Orinoco, Nile and Changjiang deltas. *Organic Geochemistry,* 11, 41-51.

Liu, A. X., Lang, Y. H., Xue, L. D., Liu, J. (2009). Ecological risk analysis of polycyclic aromatic hydrocarbons (PAHs) in surface sediments from Laizhou Bay. *Environmental Monitoring Assess.* 159,429-436.

Lors, C., Perie, F., Grand, C., Damilot, D. (2009). Benefits of ecotoxicological bioassays in the evaluation of a filed biotreatment of PAHs polluted soils, *Global NEST Journal*, 11(3), 251-259.

Löwenberg, U. H., Kunzel, T. H. (1992). Investigation on the hydrology of the lower Cross River, Nigeria. *African Environmetal Pollution and Health.* 1, 76-87.

Maioli, O. L. G., Knoppers, B. A., Azevedo, D. A. (2009). Sources, distribution and variability of hydrocarbons in total atmospheric suspended particulates of two Brazilian areas influenced by sugar cane burning. *Journal of Atmospheric Chemistry,* 64, 159-178.

Maioli, O. L. G., Rodrigues, K. C., Knooppers, B. A., Azevedo, D. A. (2011). Distribution and sources of aliphatic and polycyclic hydrocarbons in suspended particulate matter in water from two Brazilian estuarine systems. *Journal of Continental Shelf Research*, 31, 1116-1127.

Meyers PA (1997) Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Organic Geochemistry* 27: 213-250. https://doi.org/10.1016/S0146-6380(97)00049-1

Mille, G., Asia, L., Guiliano, M., Malleret, L., Doumenq, P. (2007). Hydrocarbons in coastal sediments from the meditteranean sea (Gulf of Fos area, France). *Marine Pollution Bulletin*, 54: 566-575.

Mzoughi, N., Chouba, L. (2011). Distribution and partitioning of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons between water, suspended particulate matter and sediment in harbours of the West coastal of the Gulf of Tunis (Tunisia). *Journal of Environmental Monitoring*, 13, 689-698.

Oyo-Ita, O. E. Oyo-Ita, I. O. (2013). PAH depositional history and sources in recent sediments core from Ukwa Ibom Lake. S. E. Nigeria. *Journal Environmental Geochemistry* 35(2): 185-199.

Oyo-Ita, O. E., Ekpo, B. O., Oros, D. R., Simoneit, B. R. T. (2010). Distribution and sources of aliphatic hydrocarbons and ketones in surface sediments from the Cross River estuary, S. E. Niger Delta, Nigeria. *Journal of Applied Science in Environmental Sanitation*. 5, 1-11.

Oyo-Ita, O. E., Offem, J. O., Ekpo, B. O., Adie, P. A. (2013). Anthropogenic PAHs in mangrove sediments of Calabar River, SE, Niger Delta, Nigeria. *Applied Geochemistry*, 28, 212-219.

Sikes E L, Uhle ME, Nodder SD, Howard ME (2009) Sources of organic matter in a coastal marine environment: Evidence from n-alkanes and their ^{13}C distributions in the Hauraki Gulf, New Zealand.

Marine Chemistry 113:149-163. https://doi.org/10.1016/j.marchem.2008.12.003

Simoneit BRT (2002) Biomass burning-a review of organic tracers for smoke from incomplete combustion, Applied Geochemistry 17:129-162. https://doi.org/10.1016/S0883-2927(01)00061-0

Wolanski, E., Delhez, E., Andutta, F. P. (2013). *Estuary Hydrology*. Researchgate.

Yang, S. L., Shi, Z. Zhao, H. Y., Li, P., Dai, S. B., Gao, A. (2004). Research notes. Effects of human activities on the Yangtze River suspended sediment flux into the estuary in the last century. *Journal of Hydrology and Earth system sciences,* 6, 1210-1216.

Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., Sylvester, S. (2002). PAHs in the Fraser River Basin: A critical appraisal of PAH ratio as indicators of PAH source and composition. *Organic Geochemistry.* 33,489-515.

Yunker, M. B., MacDonlad, R. W. (2003). Petroleum biomarker sources in suspended particulate matter and sediments from the Fraser River Basin and strait of Georgia, Canada. *Organic Geochemistry,* 34, 1525-1541.

Zhao, Z., Qui, Z., Cao, J., Xia, L. (2017). Source and ecological risk characteristics of PAHs in sediments from Qinhuai River and Xuanwu Lake, Nanjing, China. *Journal of Chemistry,* 40, 1100-1118.

Zhu, Y., Liu, H., Cheng, H., Xi, Z., Liu, Xiufeng, Xu,, Xiaobai (2004). The distribution and source apportionment of aliphatic hydrocarbons in soils from the outskirts of Beijing. *Organic Geochemistry*, 36, 475-483.