HEALTH RISK ASSESSMENT AND SEASONAL CHANGES OF POLYCYCLIC AROMATIC HYDROCARBONS AND n-ALKANES IN WATER AND SUSPENDED PARTICULATE MATTER FROM CROSS RIVER ESTUARY, SOUTH-EAST NIGERIA

BY

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CERTIFICATION

I, NKOM, PATIENCE YAKE, with Registration Number: CHM/PhD/14/003 hereby certify that this thesis on "HEALTH RISK ASSESSMENT AND SEASONAL CHANGES OF POLYCYCLIC AROMATIC HYDROCARBONS AND n-ALKANES IN WATER AND SUSPENDED PARTICULATE MATTER FROM CROSS RIVER ESTUARY, SOUTH-EAST NIGERIA" is original and has been written by me. It is a record of my research work and has not been presented in any previous publication.

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Student/Candidate

Signature:……………………………

Date: 19/03/2021

DECLARATION

We declare that this thesis entitled "HEALTH RISK ASSESSMENT AND SEASONAL CHANGES OF POLYCYCLIC AROMATIC HYDROCARBONS AND *n*-ALKANES IN WATER AND SUSPENDED PARTICULATE MATTER FROM CROSS RIVER ESTUARY, SOUTH-EAST NIGERIA" by NKOM PATIENCE YAKE with Registration Number CHM/PhD/14/003, carried out under our supervision, has been examined and found to have met the regulations of the University of Calabar. We therefore recommend the work for the award of Doctor of Philosophy (PhD) in Organic Chemistry.

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ABSTRACT

Investigation of the behavior of the 16 priority Polycyclic aromatic hydrocarbons (PAHs) and n-alkanes in water and suspended particulate matter from the Cross River Estuary, South-East Nigeria was undertaken using gas chromatography-flame ionization detector (GC-FID) in order to characterize their sources, distribution and assess their risk potentials. Total Polycyclic Aromatic Hydrocarbon (TPAH) concentrations in water was in the range 0.23 ng/L in April sample (AprW4; 6 m) to 3.98 ng/L in December sample (DW4; 6 m; mean = 0.97±0.65 ng/L), with higher concentrations found in the dry season. Heavy precipitation (dilution effect) coupled with the hydrophobic nature of PAHs was thought to be responsible for the low concentrations of PAHs in the wet season. On the other hand, TPAH concentrations in suspended particulate matter (SPM) ranged between 5.16 ng/g dry weight (dw) in February sample (FSP3; 4 m) and 40.52 ng/g dw in June sample (JSP3; 4 m; mean = 17.77±8.48 ng/g). Higher concentrations of PAHs in SPM recorded in the wet season were linked to greater wash-in carrying higher amount of terrigenous materials associated with intense rainfall events to the estuary. Low molecular weights PAHs (LPAH) (2-3 rings) were predominant, accounting for about 80 % of TPAH. Utilization of some PAH isomeric indices such as: ΣLPAH/HPAH, Ant/(Ant+Phe), ΣPAH_{CARC}, Flu/Flu + Pyr, and Σ COMB/PAH indicated a scenario dominated by petrogenic PAH with minor pyrogenic inputs. Total n-alkane concentrations in water ranged between 0.04 ng/L in April sample (AprW3; 4 m) and 7.20 ng/L in June samples (JW4W; 6 m and AW1; surface; mean= 2.99±1.97 ng/L), whereas concentrations of n-alkanes in SPM with a minimum value of 41.32 ng/g in April sample (AprSP3; 4 m) and a maximum value of 2502.91ng/g in August sample (ASP2; 2 m) exhibited a mean value of 960.12±644.08 ng/g, dominated by long chain analogues. Mean concentrations of n-alkanes in water and SPM were higher in the wet season than the dry season, this may be linked to the effect of dilution. Examination of n-alkane diagnostic indices such as Natural n-Alkanes ratio (NAR), Terrestrial Aquatic Ratio (TAR), Carbon Preference Index (CPI), Proxy Aquatic Ratio (Paq), ratio of Low Molecular Weight/High Molecular Weight n-alkanes (LMW/HMW) and Σn-alkanes/C_{16} revealed the samples were predominated by vascular plant waxes with minor-to-moderate inputs from macrophytes and micro-organisms. **(Word count**: 375).

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LIST OF ABBREVIATIONS

COMB: Major Combustion Specific Compounds

CPI: Carbon Preference Index

ERM: Effect Range-Medium

ERM: Effect Range-Low

HMW: High Molecular Weight

LHC: Long Chain Carbon

LMW: Low Molecular Weight

PAH: Polycyclic Aromatic Hydrocarbon

Paq: Proxy Aquatic Ratio

SHC: Short Chain Carbon

SPM: Suspension Particulate Matter

SSC: Suspended Sediment Concentration

TAR: Terrigenous/Aquatic Ratio

TEFs: Toxic Equivalent Factor

TEQs: Toxic Equivalents

TMD: Terrestrial Marine Discriminate

UCM: Unresolved Complex Mixture

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Hydrocarbon contamination has become a matter of genuine environmental concern all over the world because of its broad use as vitality source in generally industrial and creating nations. These hydrocarbons which are generated from human activities as well as industrial procedures is widespread and are known to cause extreme environmental problems because of their ingenuity, lethal, mutagenic, bioaccumulation, carcinogenic properties (Sakari *et al*., 2008). They have been seen as the most notable organic contaminants in organic waste (Commendatore and Estevez, 2004). These wastes, which incorporate large quantities of sewage, dug ruins, storm water, and spilled oils, industrial as well as city waste discharged to water bodies within thje coast with next to zero treatment measures, mostly regarding creating nations (Wu *et al*., 2001, Muthukumar *et al*., 2013). Hydrocarbons were usually transported into the coastal areas as arrangements, but just a small bit eventually remains in arrangement. Its bulk is released within water segments towards the bottom residue by coagulation, sedimentation, flocculation, and offering ascend to conc. regarding silt higher than that in the water section (Hatze *et al*., 2003; Oliver, 2008). Residue therefore remains the potential sink for hydrocarbons and other organic conterminants (Farrington and Takada, 2014).

1.2 Polycyclic Aromatic Hydrocarbons (PAHs)

Among various hydrocarbons, the polycyclic aromatic hydrocarbons (PAHs) have gotten genuine attention since they have been perceived as hazardous environmental chemicals. Polycyclic aromatic hydrocarbons are a class of combined ring aromatic and ubiquitous contaminants in various environmental media which have been recorded by the US Environmental Assurance Agency (US EPA) as need contaminants because of their carcinogenicity, mutagenicity and ingenuity (Christensen and Arora, 2007; Tsang *et al.*, 2011; Oyo-Ita *et al.*, 2016). There are a thousand of PAHs in the earth but just a couple, for the most part 16 of them are regarded as need mixes (for example "Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenzo[a,h]anthrcene and Benzo[ghi]perylene, see FIG.1). Pyrogenic PAHs from natural sources such as volcanic eruption and timberland shoot do not contribute significantly to the overall PAH outflow" (Ogunfowokan *et al.*, 2003). These pollutants generally happen in coal, raw petroleum and refined oil based commodities (Readman *et al.*, 2002), can equally be shaped from inadequate burning of non-renewable energy sources, wood and other organic substances (El-Shahawi *et al.*, 2010). Introduction to PAHs have been accounted for to have adverse health impacts, which incorporate "DNA mutations, leukemia, cancer of the lungs, bladder, bone, brain, and scrotal and regenerative deformities" (Nadal *et al.*, 2004; Tune *et al.*, 2006).

These were usually gotten from land which is subsequently put away in worldwide oceans where riverine run-off is the significant pathway of their emptying into oceans (Zhang *et al.*, 2012). PAHs are generally more resistant to biodegradation than other absorbed biomarkers and continue barometrical particulate matter, contaminated water, sediments and marine organisms (Countway *et al.*, 2003; Guo *et al.*, 2007).

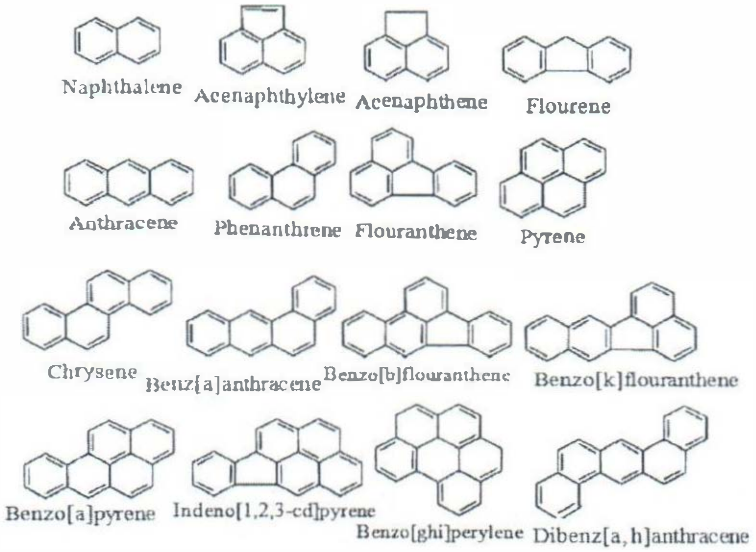

FIG. 1: The Chemical Structures of 16 Priority PAHs

PAHs could connect with particulate matter as well as sediments in perspective on their low watery dissolvability and hydrophobic nature (Tolosa *et al.*, 2005). Due to the aforementioned qualities, many examinations utilizes PAHs to diffrenciated between wellsprings of contaminants and their level of natural effect (Maioli *et al.*, 2010). Influx of PAHs in the ocean side environment has been on the increase in the earlier decades necessitating the identification of their occurrence, transportation and destiny (Van Meter *et al.*, 2000; Aichner *et al.*, 2007).

Generally, anthropogenic wellsprings of PAHs can be named either "petrogenic or pyrogenic using individual PAH proportions" dependent on eccentricity in PAH distribution and composition as a function of their emission sources (Zhang *et al.*, 2004). A portion of the PAH isomeric proportions which are utilized to differentiate between petrogenic and pyrogenic inputs includes Ant/(Ant + Phen), Influenza/(Flu+Phen), Influenza/(Influenza + Pyr), BaA/(BaA + Phen) and InP/Inp + BghiP amongst others.

1.3 Aliphatic Hydrocarbons (n-Alkanes)

Aliphatic hydrocarbons, for example, n-alkanes, isoprenoid hydrocarbons example pristine and phytane, styrene and hopanes have been broadly utilized as biomarkers for source correlation purposes, in differentiating between autochthonous and allochthonous organic matter (OM). Lipid biomarkers have throughout the years proven to be the most solid strategy for source assessment of OM in waterfront

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The origin of n-alkanes in organic matter can likewise be identified using diagnostic concentration proportions together with sub-atomic markers and multivariate strategies (Kavouras *et al*., 2001). A portion of the indices which have been utilized throughout the years to identity and measure the wellsprings of n-alkanes in the environment are; the significant hydrocarbons (MHs); low/high atomic weight hydrocarbons (L/H); Σn-alkanes/n-C16; unresolved carbon mixture(UCM); Normal Carbon Chain (leg tendon); n-C17pristane; and % plant wax contribution (Wax Cn) amongst others (Zhu *et al*., 2005). In rundown, n-alkanes from vascular plants origin display a predominance of odd/even carbon markers, higher CPI worth and MH generally around C27, C29, C31, in contrast with those from oil sources (Simmoneit *et al*., 1991).

1.4 Hydrology and Hydrogeology

The Cross River estuary which has an expected region of 54,000 square kilometers is shaped by the Calabar, Cross Waterway, Extraordinary Kwa and different tributaries which structure flood plains and wetlands that void into it. The hydrogeology of the waterway basin includes the Pre-Cambrian Oban Massif, Cretaceous sediments of the Calabar flank and the recent Niger Delta sedimentary basin (Eze and Effiong., 2010). Drainage is poor, hence liable to flooding, landslides and chasm erosion.

Wolanski *et al.* (2004) defined an estuary as a zone of transition within salinity, sediment attributes, turbidity, and substance composition including nutrients, separated gases and follow metals and in decent variety and profitability of plants and animal species. Estuarine waters are found to be commonly more organically beneficial than the oceanic waters. This explains why they are vital locations for human development with over 69% of the biggest urban areas on the planet situated around them (Wolanski *et al.*, 2004). An estuary is never static however continuously evolving, hence movement is constrained by tides, waves and stream inflows. The resultant physical and organic highlights of an estuary and its environment wellbeing are determined when sizes of the different techniques controlling the movements of water and sediments and the natural systems in the water and at the base.

The water level and salinity rise and fall with the tides and the seasons. During the wet seasons, waterways may flood the estuary with new water and during the dry season, the outpouring from streams perhaps moderate, this makes the estuaries to shrink and become progressively saline. Estuaries are excellent locales for community living they offer freshwater to drinking and different uses and likewise help the development of exchange and communication. The wetland and flood plains around the estuaries give rich wellspring of wild game and takes into account the development of irrigation and farming.

1.5 Human Activities

Estuaries are a portion of the coastal areas which are mostly in danger because of human activities. Development around the estuaries and the increasing population growth has affected these special areas in so many manners. Two significant problems which affect estuaries are sedimentation and pollution from run-off. Sedimentation happens when rains, streams and rivers wash sediments off the land into estuaries. This smothers the seabed killing mud-dwellers that cannot obtain up. This leads to loss of aquatic life (Kennish, 2002).

Pollution from industrial and agricultural run-off represents another difficult problem in estuarine environments (Kennish, 2002). Heavy metals and PAHs from industrial and urban waste tend to stress the ecosystem. Nutrients are essential in supporting the productivity of the estuaries, but when in abundance it can lead to algal bloom or exorbitant growth of plants such as mangrove. Other human impacts affecting the estuarine environment include oil spills from ships, exorbitant harvesting of fish, reclaiming land by drainage, building spans, sand extraction for construction, rubbish dumping, aquaculture, etc. These impacts on estuaries contribute to the reduction of habitats for plants and animals just as spoiling the recreational activities and the beauty of the estuaries.

Calabar Municipality and Calabar South which are located around the Cross river estuary with a population of more than 400,000, have no squander treatment workplaces. Squander from humans and those around "bungalow industries are dumped in surface regions or into open drains, the torrential rains wash most bit of these losses into the estuary (Akpan *et al.*, 2006), studies have shown that urban pollution and oil exploration practices in the zone both threaten the environment of the estuary, along these lines reducing the numbers and assorted variety of the species that offer nourishment to shrimps and fish" (Ekwu and Sikoki, 2005).

1.6 Study Area

The Cross River estuary (FIG. 2) which lies between latitude $4^{0}45$'N and $4^{0}55$'N and longitudes $8^{0}15$'E and $8^{0}25$'E, is one of the estuaries in the south-eastern bit of Niger-Delta, Nigeria. It covers a region of 53,000 km^2, of which 4,000km^2 of the all out territory lies in Cameroon and 49,000km^2 in Nigeria. The estuary is made out of numerous tributaries which rise up out of the western slants of the Cameroon mountains and streams south-westbound into the Atlantic ocean with a release of between 880-2533m^3 sec-1 (Lowenberg and Kunzel, 1992). The structure is presented to transitory flooding which depends on the tides and the seasons (wet/dry). The region has a rainy season between April and October, which accounts for 80 % of the annual rainfalls, with tops between June and September. Normal temperature ranges from 24 ^{0}C in August to 30 ^{0}C in February and relative dampness is high at 80-100 % (Eze *et al*., 2010). Changes in the season and tides are the central point that influence the hydrology of the Cross stream estuary (Oyo-Ita *et al*., 2010). The waterway basin which is wealthy in mud materials is situated within the tropical rainforest region. The territory rich in mineral in addition to dense vegetation as well as torrential rainfall qualities of the zone expect a tremendous activity in the biogeochemical control of organic as well as inorganic nutrients within estuary (Asuquo *et al*., 1998).

1.7 Significance and Justification of Study

Estuaries are known as the transition territories between land and oceans and they assume an important job in the transportation as well as future of hydrocarbons (Liu *et al*., 2014). These were influenced by both river area as well as oceanic dynamics and are found to be sensitive to hydrological forms. Rivers have been found to show seasonal fluctuation with hydrological forms, which brings about seasonal variations in OM (Gao and Chen, 2008).

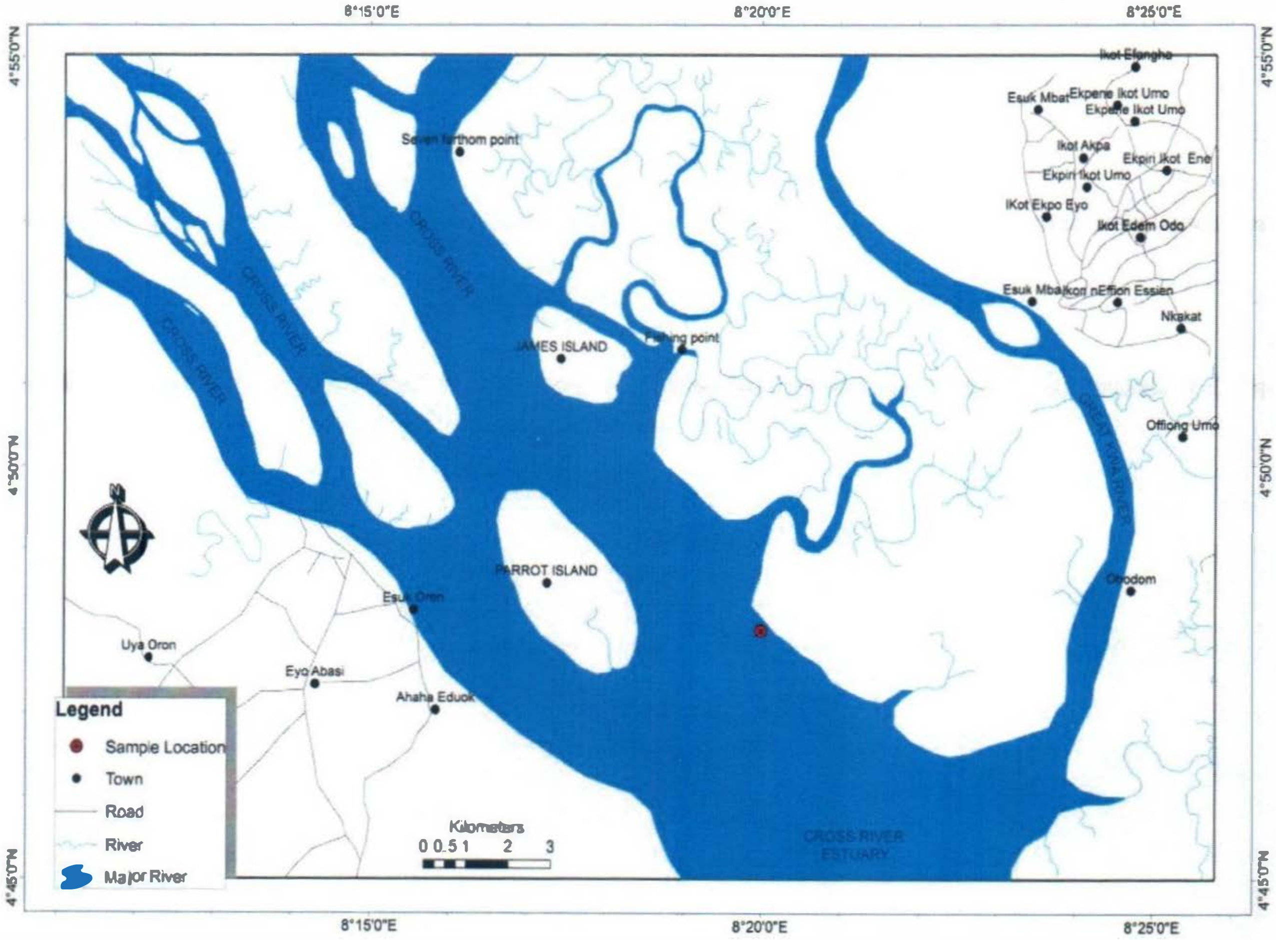

FIG. 2: Map of the Cross River Estuary Showing the Study Area

Environmental factors in the estuary like suspended particulate matter (SPM), temperature and salinity influence the distribution and destiny of hydrocarbons within oceanic environment (Tremblay *et al.*, 2005). Human exercises like burning of wood and coal, vehicular and transport emissions and dumping of industrial and household squander likewise show seasonal pattern (Liu *et al.*, 2009) which can influence the composition and environmental conduct of hydrocarbons in the estuary.

High density in population as well as quick urbanization in addition industrialization in the Cross River estuary has come about to the abundant hydrocarbons discharged into the estuary. Parrot Island, where sampling was completed, is situated in the central estuary and was so chosen because of the way that the hydrographic conditions now represent a midpoint between the ocean water and the crisp water (Lowenberg and Kunzel, 1992). In spite of the fact that there are reports of concentrates on the sources, occurrence and distribution of hydrocarbons, ketones and acetic acid derivations in sediments (Oyo-Ita *et al.*, 2010; Oyo-Ita *et al.*, 2013) just as substantial metals in water of the Cross River estuary (Asuquo *et al.*, 1998), examines on the seasonal changes of hydrocarbons in the estuary in response to hydrology and human activities are scarce and the assessment of the potential dangers presented by these hydrocarbons has not been accounted for. This work therefore, seeks to bridge the gap. In this work along these lines, a one-year field work regarding variations in hydrocarbons within Cross River estuary were completed from 2016-2017 in both wet as well as dry seasons.

1.8 Aim/Objectives

The aim of this study was to assess the response of hydrocarbons (PAHs and n-alkanes) in the Cross River estuary to changes in hydrology and human activities.

The main objectives of the study include the following:

i. To determine the concentrations and compositions of hydrocarbons in water and suspended particulate matter from the Cross river estuary.
ii. To identify the various sources of hydrocarbons in the estuary
iii. To assess the combined impacts of hydrology and human activities on the concentrations and compositions of these hydrocarbons in the estuary.
iv. To assess the potential risks posed by the hydrocarbons in the estuary.
v. To utilize statistical models to understand the relationships that exists amongst variables in the estuary.

CHAPTER TWO

LITERATURE REVIEW

Studies regarding effects of hydrology and human activities in the distribution of hydrocarbons in water as well as surface sediments have been undertaken worldwide.

2.1 Distribution, Delivery and Wellsprings of Polycyclic Aromatic Hydrocarbons

De Luca *et al.* (2005) examined the nature, distribution as well as origin of polycyclic aromatic hydrocarbons (PAHs) within sediments at Olbia harbor (Northern Sardinia, Italy). The results obtained showed PAH concentrations within sediments ranged from 0.16 to 0.77µgg-1, showing a reduced level of pollution, a prevalence of low molecular weight PAHs, including naphthalene, was found. Carcinogenic PAHs were present but in truly negligible amount. The main wellspring of PAHs was petrogenic because of oil spill from shipping.

Oyo-Ita *et al.* (2011) investigated "the sources and distribution of polycyclic aromatic hydrocarbons in post flooded soil near Afam power station, South-East Niger Delta, Nigeria, they reported a blended source scenario with predominance of petroleum hydrocarbons input within top soil while at the lower soil horizons, PAHs of combustion origin were predominant".

Yunker and Mcdonald, (2003) investigated petroleum biomarker sources in suspended particulate matter and sediments from the Fraser River basin and Strait of Georgia, Canada. They found out that the absence of structurally rearranged hopanes rules out contamination from California oils, while the presence of the enhanced

Oleanane in samples from the lower Fraser River suggest a source in coal dust lost during railroad transportation to the Coast.

Also. source characterization and historical trend of sedimentary PAHs from Refome Lake. South-South Nigeria was investigated by Oyo-Ita *et al.* (2017) in request to evaluate the sources and historical trends of deposition in the course of the last century. The total PAH concentrations ranged from 66.99ng/g dry weight to 182.24ng/g dry weight at the near bottom layer of R.S Center with a mean of 102.21 24.32 ng/g.

Distribution and ecological hazard assessment of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River estuary and the adjacent area, China was done by Zheng *et al.* (2016). The result shows that the PAH pollution was identified as blended combustion and petroleum sources. In view of species sensitivity distribution (SSD). it was revealed that the hazard in suspended particulate matter was higher than in water.

Charriau et al. (2013) examined the contaminations levels and apportioned wellsprings of "polycyclic aromatic hydrocarbons and n-alkanes in sediments of the upper Scheldt river basin. the result obtained showed that total n-alkane and PAH concentrations in the sample centers ranged between 2,8 to 29mgkg-1 and 49 to 96mgkg-1 respectively. the prevalence of combustion-inferred PAHs was indicated by the high concentration" of 4; 5-and 6-rings compounds. the authors explained that this could be as a result of a significant historical contamination from urban and industrial emissions.

2.2 Seasonal Variations of PAHs in Response to Hydrology and Human Activities

Seasonal changes of PAHs in response towards hydrology as well as human activities in the Pearl River estuary, China; was evaluated by Liu *et al.* (2017). The study "was completed to investigate the abundance of 16 priority PAHs and their response to the seasonal dynamics of hydrological cycles and human activities, the result obtained showed the mean monthly concentrations of Σ16 PAHs in water and suspended particulate matter (SPM) as 88.31ng/L and 2521ng/g, respectively". The PAHs shifted widely with reference to wet to dry season having LMW PAHs dominating. Higher concentrations of PAHs in the wet season were attributed to higher precipitation and strong washout effect of surface water. The biogeochemical procedures of organic matter within estuaries were sensitive to alteration with regards to hydrological cycles as well as human activities.

2.3 Distribution, Delivery and Wellsprings of Aliphatic Hydrocarbons (n-Alkanes)

Maioli *et al.* (2011) investigated the distribution and wellsprings of aliphatic hydrocarbons in suspended particulate matter in water from two Brazilian estuarine systems which are affected by sugarcane farming and urbanization. The total hydrocarbon concentration ranged between 12.40-257.50ng/g. The n-alkane characteristics dependent on CPI values suggested wellsprings of higher plants for surface sediments which could be associated with the sugarcane effluent. However, n-alkanes and petroleum biomarkers in the study areas were relatively low.

Assuncão *et al.* (2017) surveyed the aliphatic and polycyclic aromatic hydrocarbons in surface sediments collected from mangroves with different levels of urbanization in southern Brazil. In the results, the n-alkane concentration ranged from 1.9µg/g to 55.6µg/g (dry wt). CPI ranged from 2.1 to 7.9 which indicated the predominance of sediment of terrestrial origin mainly higher plants. Levels of n-alkanes in the mangroves were relatively low typical of uncontaminated surface sediments.

Ekpo *et al.* (2005) studied the even n-alkane/alkene predominance within sediments atb surfaces gotten at Calabar River, South-East Niger-Delta, and Nigeria. The results obtained showed a special gathering of organic compound which were prevalent in the study area with several distinctive features that includes a high abundance of even numbered n-alkanes, n-alk-l-enes, giving ascent to Carbon Preference Indices (CPI) between 0.15 and 0.82. A Complex Mixture (UCM) that is not assessed range was n-C18-n-C35, and the presence of hopanes indicated petroleum contamination.

Oyo-Ita *et al.* (2016) investigated the distribution and wellsprings of hydrocarbons in recent sediments of the Imo River, South-East Nigeria to determine the sources and fate of the hydrocarbons. The results obtained showed that "the aliphatic fraction was characterized by a far reaching contribution of highly weathered biodegraded hydrocarbon buildup reflected in the absence of prominent n-alkane tops coupled with the presence of 17 (H), 21 (H)- 25 norhopane" which is an indicator of heavy hydrocarbon biodegradation of Nigerian rough oils.

Gogou *et al.* (1999) studied the Marine Organic Geochemistry of the eastern Mediterranean aliphatic in Cretan Ocean surficial sediments. The result indicated that the total concentration of aliphatic hydrocarbon was low (562-5697 ng/g) with respect to other coastal sediments worldwide. The composition of aliphatic hydrocarbons was dominated by Unresolved Complex Mixture (UCM) indicating the presence of petroleum-related hydrocarbon inputs as confirmed by the detection of explicit, -hopanes.

Oyo-Ita *et al.* (2010) evaluated the distribution and wellsprings of aliphatic hydrocarbons and ketones in surface sediments from the Cross River estuary, South-East Niger-Delta, Nigeria. The result obtained indicates that the concentration of hydrocarbons (including pristine and phytane) range was 0.02-16.84 mg/kg and, CPI fluctuated from 0.81 to 4.0 indicating both biogenic and residual petroleum origins. A portion of the samples exhibited odd-to-even carbon number predominance indicating an input from terrestrial plant waxes and/or macrophytes.

2.4 Hydrology

Kouadio-Guy *et al.* (2018) studied the Hydrology and Eutrophication state of Sassandra River estuary in Ivory Coast (Gulf of Guinea). The result obtained indicated that the dynamics of the Sassandra River greatly influenced the variations in the chemical and physio-chemical parameters of the Sassandra estuarine zone. The estuarine is found to be heavily loaded during the wet season and salinity was found to be very low or zero during the flood but increased slightly to 0.1 to 2.93 % in the dry season. The physico-chemical parameters and those of the nutrient salts are characteristics of water of good quality.

The Hydrology of a well-mixed estuary at the semi-arid Northeastern Brazilian coast was investigated by Dias *et al.* (2009). The result obtained showed that the average velocity of flood and ebb tides varied from 0.11 to 0.24ms-1 (flood) and 0.11 to 0.28ms-1 (ebb). The estuary is an importer system of marine biogeochemical processes in the estuary.

Montagana *et al.* (2018) studied the effect of hydrological variability on the biogeochemistry of estuaries across a regional climatic gradient. The results obtained revealed that hydrological changes over spatial gradients are subject to climate change over time, which implies that climate change forecasts of higher temperatures and decreased precipitation can make the biogeochemistry of fresh estuaries change to the patterns of saltier estuaries.

A classification of U.S. estuaries based on physical and hydrologic attributes was investigated by Eagle *et al.* (2007). The result obtained showed that the ability of an estuary to dilute or flush pollutants can be estimated using physical and hydrologic properties like volume, bathymetry, freshwater inflow and rate of tidal exchange.

2.5 Human Activities

Yang, *et al.* (2004) studied the "effects of human activities on the Yangtze River suspended sediments flux into the estuary in the last century, the result obtained showed that the erosion of the surface area in the Yangtze River basin increased from 364 x 103km2 in the 1950s to 707 x 103 km2 in 2001 due to an increase in population, it also revealed that the annual suspended sediment flux into the estuary had increased drastically due to rapid increase in population and land use, human activities have gradually increased the suspended sediment flux into the estuary, Mollusk's response to anthropogenic impacts, An example from Cross River estuary South-Eastern Nigeria was investigated by Asuquo *et al.* (2018), the mollusks of the Cross River estuary were sampled monthly during the wet season and the dry season, the results obtained showed that the level of alteration of the ecosystem from anthropogenic activities could be deduced using variations in numerical strength and compositions of the sample in the environment". Low numerical strength was recorded which was attributed to the impacts from silt sedimentation caused by dredging activities in the estuary.

Day Jr. *et al.* (2012) studied the human impact and management of coastal and estuaries ecosystem. In his result, he identified four general categories of impacts on estuaries to include (a) enrichment with excessive levels of organic material, (b) inorganic nutrients of heat; physical alterations which includes channelization of streams, dredging, drainage, and navigation, (c) introduction of toxic materials like heavy metals, pesticides, etc. and (d) direct changes in community structure through harvesting, or introduction of exotic species.

Wu *et al.* (2016) evaluated the impact of human activities in the subaqueous topographic change in Lingding Bay of the Pearl River estuary, China, during 1955-2013. The results obtained showed that the subaqueous topography of Lending Bay was strongly affected by human activities as a result of land reclamation, which decreased the area covered by water from 1010 km2 to 833 km2, and the area of total flat area decreased from 215 km2 to 159 km2. It also showed that the water volume from 1955-2010 decreased by 615 x 106 m3.

Liu *et al.* (2012) studied the impact of human activities on nutrient transports in the Huanghe (Yellow River) estuary. The result obtained showed that the concentrations of nutrients in the Huanghe are characterized by high concentrations of nitrate and dissolved silicate but low phosphate and DOP levels, and also seasonal variations with high DiN/PO43- ratios, which results in nutrient imbalance, affecting phytoplankton production and composition.

2.6 Risk assessment

Aly Salem *et al.* (2014) examined "the monitoring and risk assessment of aliphatic and aromatic hydrocarbons in sediments of the Red Sea, Egypt, he observed that the concentration levels of PAHs in the study, as compared to the Effect Range Low (ERL) and Effect Range Medium (ERM) values were below the ERL except for El-Quseir station which was higher than the ERL but lower than the ERM, this reveals that PAHs in the surface sediments of the studied area have no adverse effects except at El-Quseir which may cause mild adverse effects, to assess the potential health risk factor, the BaP Equivalent (BaPE) and the Toxicity Equivalent Factors were applied". The result obtained indicated that values ranged between 0-72.27 ng/g, with the highest value at El-Quseir, showing high toxicity.

Source and ecological risk characteristics of PAHs in sediments from Qinhuai River and Xuanwu Lake, Nanjing, China were examined by Zhao *et al.* (2017). The ERL and ERM values from the study were compared with the sediments quality guidelines, and results obtained revealed that the low molecular weight PAHs were in the intermediate range (≥ERL and <ERM) indicating that occasional adverse effect were likely to occur. TEQ values varied from 54.6 to 558.6 ng/g which suggest that winter had larger impact on the ecological health and maximum potential toxicity. The ecological risk assessment suggested that the highest benzo[a]pyrene-equivalent was observed at the site of sewage disposal and heavy traffic.

2.7 Statistical analysis

2.7.1 Principal Component Analysis (PCA)

Principal component analysis "is a statistical tool that uses an orthogonal transformation to convert a set of observations of possibly correlated variables (entities each of which takes on various numerical values) into a set of values of linearly uncorrelated variables called principal components. Mohamed *et al*, (2016) investigated a new record for aliphatic and polycyclic aromatic hydrocarbon accumulation in the surficial sediments of El Mex Bay, Alexandria, Egypt after 19 years from the first one, principal component analysis (PCA) was used to differentiate between the origins of aliphatic hydrocarbons and PAHs". Results obtained reveals that after the rotation, Principal Component 1(PC1) accounted for 26.27 % of the total variance, which indicates moderate-to-long chain n-alkanes (C17-C26), PC2 displayed 21.04 % of the total variance and had high loading of C19, while PC3 had a covariance of 16.53 % and a high loading of C29.

PCA was also performed on the PAHs matrix in sediments, and the results indicated that PC1 was responsible for 26.27 % of the total variance revealing dominance of 4,5 and 6 rings PAHs; BkF, BaP and B(ghi)P related to petroleum combustion and refined products. PC2 accounted for 21.07 % of the total variance and was dominated by Phenanthrene, Anthracene, Fluoranthene, Fluorene and Chrysene which are related to mixed sources of PAHs like incomplete combustion and petroleum pollution. PC3 explained 16.53 % of the total variance, related to PAHs with 5 rings associated with both gas and diesel engine emissions.

2.7.2 Cluster Analysis (CA)

Cluster analysis is concerned with the grouping of a set of objects in such a way that objects in the same group (called a cluster) are more similar to each other than to those in other groups (clusters).

Occurrence and transport of polycyclic aromatic hydrocarbons in the water bodies of the Baltic Sea was examined by Witt (2002). Cluster analysis was employed as pattern recognition technique and result obtained revealed four main clusters associated with four different water bodies identified in the month of February (Mecklemburg Bight (MB), Pomeranian Bight (PB), the eastern (EZOS) and western central Baltic Sea (WZOS). Two hot spots were found that were characterized by high naphthalene concentrations and a high LMW/HMW values. This dominance might be due to the petroleum origin of the PAHs in both samples.

2.6.3 Analysis of Variance (ANOVA)

The major work of ANOVA is to analyze differences among the means of the populations by evaluating the level of variation in each of these samples, relative to the amount of variation between the samples.

Mzoughi *et al.* (2010) studied the "distribution and partitioning of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons between water, suspended particulate matter, and sediments in harbours of the West coastal of the Gulf of Tunis (Tunisia)". Results obtained showed that PAH concentrations for water and SPM samples were higher in winter than in summer and differed significantly (ANOVA, $p < 0.05$). PAH group profile showed the predominance of compounds with 2-3 rings in SPM as well as water, in addition to compounds having 5-6 rings within sediments during summer and winter.

CHAPTER THREE

MATERIALS AND METHODS

This chapter examines the general procedure adopted in carrying out this work.

3.1 Sample collection, preparation and preservation

Sampling is an essential step in any research and it involves the collection of a representative portion of the material being examined. Sampling was carried out around Edik Ekpu area on Parrot Island (FIG. 2) within a period of 1year, from June 2016 to April 2017, covering the wet (April, June, August) and the dry seasons (October, December, and February).

3.1.1 Water

The water samples was gotten from flood tide within five alternative levels or depths in the water column; that is, surface, 2 m, 4 m, 6 m and 8 m represented as W_1, W_2, W_3, W_4 and W_5 respectively, using a stainless steel Nansen sampler fitted with a thermometer. 3 litres of water sample were collected at each depth, poured into a brown bottle of glass, ice cooled as well as being taking to laboratory, stored in deep-freezer at -4 ^{0}C pending another analysis.

3.1.2 SPM

The water samples collected per month was filtered with a glass fiber filter (Whatmann Grade GF/C: 47mm diameter and 1.2μm porosity), which were previously pre-combusted at 450 ^{0}C for 6 hours, pre-weighed, kept in a desiccator and post-weighed towards determining the total SPM and stored in a dessicator until further analysis.

3.2 Physicochemical properties determination

Temperature readings were taken *in situ*, salinity was measured using a conductivity meter (Iwouha *et al.*, 2012), while the pH was measured using a pH meter (Model: METTLER TOLEDO MP 220).

3.3 Extraction of sample as well as clean-up

3.3.1 Water

1000ml (1L) of the filtered water sample was transferred into a separating funnel and 60 ml of redistilled dichloromethane was added to it. The mixture was shaken vigorously with periodic venting for 2mins to release vapor pressure, and then allowed to stand for 10 mins. The lower layer was collected and the aqueous layer re-extracted twice. The extracts were air-dried and subsequently, fractionated by open column adsorption chromatography using silica gel activated at 450 ^{0}C, and alumina activated at 550 ^{0}C as adsorbents, and eluted with 10ml of hexane to obtain the aliphatic fraction and hexane/dichloromethane (4:1 v/v) to obtain the aromatic fraction (Silver *et al.*, 2007). The fractions were air-dried, and then subjected to gas chromatography-flame ionization detector (GC-FID) analysis.

3.3.2 SPM

The dried filters with their contents were extracted 3 times by ultrasonification using 50 ml dichloromethane for 15 minutes each. The extracts were stored in beakers which were pre-washed and heated in an oven. The extracts were concentrated in-vacuo and subsequently fractionated by open column adsorption chromatography using silica gel activated at 450 ^{0}C, and alumina activated at 550 ^{0}C as adsorbent, and eluted with 10ml of hexane to obtain the aliphatic fraction and hexane/dichloromethane (4:1 v/v) to obtain the aromatic fraction (Silver *et al.*, 2007).

3.4 Instrumental analysis

A "Hewlett Packard model 5890 II series in a 30 m, 0,25mm fused silica capillary column (Ultra 2, 5% diphenyl-dimethyl-polysiloxane) connected with a flame ionisation detector (FID) was used for analysis of individual alkanes and PAH, a splitless injection mode was used. Nitrogen was used as the carrier gas with a flow rate of 1 mL min^{-1}, the injector was maintained at 290 ^{0}C, all injection volumes were 1mL in the split less mode, the column temperature was initially held at 60 ^{0}C for 2min, ramped to 290 ^{0}C at a rate of 3^{0}C min^{-1} and then the temperature was held at 300 ^{0}C for 10 min, identification and quantification were performed by using respectively external and internal standards, respectively a standard mixture provided by International Atomic Energy Agency (IAEA) containing aliphatic (n-C10 to n-C34) and polycyclic aromatic hydrocarbons (PAHs) (naphthalene, 1-methylnaphthalene, ethylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, 2-methylphenanthrene, 1-methylphenanthrene, 3,6-dimethylphenanthrene, fluoranthene, pyrene, 1-methylpyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-cd)pyrene) was used as external standard for the identification of each alkane and PAH peak in the samples, the internal standards (9,10-dihydroanthracene, n-octadecene (C18,1) and n-dotriacontane (C32) were used to calculate the concentration of each individual compound in the sample confirmation analysis was performed by gas chromatography coupled with a high resolution mass spectrometer (GC-HRMS) Varian 4000) equipped with a CP-8400 auto sampler, a CP-8410 auto injector and a 30 m, 0,25mm i.d. DB-5ms fused silica capillary column, helium was used as the carrier gas with a flow rate of 1mL min $^{-1}$, the injector and transfer lines were maintained at 290^{0}C and 250^{0}C, respectively, injection volumes were 1mL in the splitless mode, the same temperature program used by GC-FID was maintained. the mass Spectrometer were employed within electron ionization mode as well as all spectra" was gotten with mass range of m/z 50–400.

3.5 Statistical analysis

The statistical analysis were undertaking with SPSS 21.0 and Excel windows 10. Multivariate analysis which includes Principal component analysis (PCA), Cluster analysis (CA), and Pearson correlation analysis were employed in the identification of the different components of samples and the interpretation of complex data sets.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Seasonal variations in PAH concentrations

The following USA EPA 16 priority listed PAH compounds were detected and quantified in water and SPM: Naphthalene (Naph), acenaphthylene (Acthy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), Benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo[a,h]anthracene (DBA), indeno(1,2,3)pyrene (InP), benzo(ghi)perylene (Bghi)P.

4.1.1 Water

The total PAH (TPAH) concentrations in water for the month of June ranged from 1.22 ng/L to 1.50 ng/L, minimizing at 2 m in JW2 and maximizing at 8 m in JW5 with a mean of 1.36±0.10 ng/L and 0.69 ng/L to 0.91 ng/L in the month of August, minimizing at the surface in AW1 with a maximum at 8 m in AW5 (mean= 0.80±0.09 ng/L) for the month of August. TPAH levels for the month of october ranged from 0.59 ng/L at 4 m in OW3 to 0.93 ng/L at 6 m in OW4 with a mean of 0.79±0.15 ng/L and 0.51 ng/L to 3.98 ng/L in December, minimizing at 2 m in DW2 and maximizing at 6 m in DW4 (mean =1.45±1.45 ng/L). In the case of February, a range from 0.66 ng/L at 2 m in FW2 to 1.01 ng/L at 8 m in FW5 was found with a mean of 0.81±0.13 ng/L, whereas a range of 0.23 - 1.21 ng/L was recorded for the month of April with a minimum at 6 m in AprW4 and a maximum at 8 m in AprW5 (mean = 0.62±0.38 ng/L; FIG. 3 a, Appendix 1). TPAH levels (0.23-3.98 ng/L) in water from Cross River estuary were lower than other estuaries around the world such as the Pearl River estuary, China (1.80 - 162.87 ng/L; Yang *et al.*, 2008), Gulf of

Tunis, Tunisia (378.4 - 703.1 ng/L; Mzoughi *et al.*, 2010) and the Yellow River estuary, China (144.3 - 2361 ng/L; Sun *et al.*, 2009).

The mean PAHs concentrations in water in the wet and dry seasons exhibited a remarkable seasonal variation (FIG. 3 b), reflected in the t-test analysis ($p > 0.05$) supporting the significant difference in the concentrations of PAHs in the two seasons (Appendix). This difference may be associated with the effect of dilution occasioned by wet precipitation. Correlation analysis (FIG.5) revealed a weak positive relationship between wet and dry season concentrations ($r^2 = 0.094$), suggesting that PAHs in water in the two seasons were mainly from different source(s).

Among the individual PAHs, Naph exhibited the highest concentration level consisting of 63.42 % (FIG. 4) relative to TPAH for the entire study, with low molecular weight congeners dominating over their high molecular weight counterparts, minimizing in Chr (0.034 %).

4.1.2 Suspended Particulate Matter (SPM)

The TPAH concentrations in SPM ranged from 20.35 ng/g dry weight (dw) at the surface in JSP1 to 40.52 ng/g at 4 m in JSP3 in the month of June with a mean of 29.68±8.56 ng/g, whereas 5.60 ng/g at 8 m in ASP5 to 16.52 ng/g at 4 m in ASP3 were found for the month of August with a mean of 10.96±5.22 ng/g. Also, the minimum of 11.97 ng/g at the surface in OSP1 to a maximum of 21.06 ng/g at 6 m in OSP4 in the month of October were found (mean = 15.88±3.47 ng/g). Furthermore, TPAH levels ranged from 11.71 ng/g at 8 m in DSP5 to 25.74 ng/g at 3 m in DSP2 in the month of December (mean = 18.27±5.24 ng/g), whereas a range of 5.16 - 21.67 ng/g was recorded for the month of february, minimizing at 2 m FSP2 and maximizing at 6 m in FSP4 with a mean of 13.33±6.08 ng/g and 9.32 ng/g at 4 m in AprSP3 to 32.26 ng/g at 6 m in AprSP4 in the month of April (mean = 18.47±8.81

ng/g; FIG. 6 a). The highest mean concentration in SPM was recorded in the month of June (29.68 ng/g), while the lowest mean concentration was recorded in the month of February (13.33 ng/g; FIG. 6 b). SPM in the wet season recorded a mean concentration of 18.47±42.96 ng/g, higher than that for the dry season (14.84±37.97 ng/g). Also, there was a remarkable seasonal variation in PAHs concentrations in SPM in the two seasons (t-test, $p>0.05$) with again low molecular weight species dominating (e.g Naph 62.69 % relative to TPAH) among the individual PAHs, while high molecular weight congeners such as BaA and Chr were not detected (FIG. 7). Correlation analysis of the concentration of PAHs in SPM in the wet and dry seasons revealed a poor positive relationship between these two variables ($r^2= 0.2361$, suggesting different PAHs source inputs in the two seasons. This seasonal variation in the mean concentrations in SPM in the wet and dry seasons could be attributed to surface run-off carrying terrigenous materials from domestic and commercial waste as well as wet precipitation associated with fall-out from fish roasting activities and vehicular exhaust emissions. In the present study, TPAHs levels (5.16-40.53 ng/g) in SPM were low compared to other estuaries around the world. For instance, the El Max Bay, Egypt (1123 - 8654 ng/g dw; Mohamed *et al.*, 2016) and two Brazilian estuarine systems: the Paraiba do Sul and Mundai-Manguaba estuaries (228 - 1814 ng/g dw and 221 – 1243 ng/g dw, respectively; Mailo *et al.*, 2011). The considerably higher PAHs concentrations in SPM relative to water may be attributed to the high adsorption capacity of PAH towards solid matrix associated with their hydrophobicity (Oyo-Ita and Oyo-Ita, 2012).

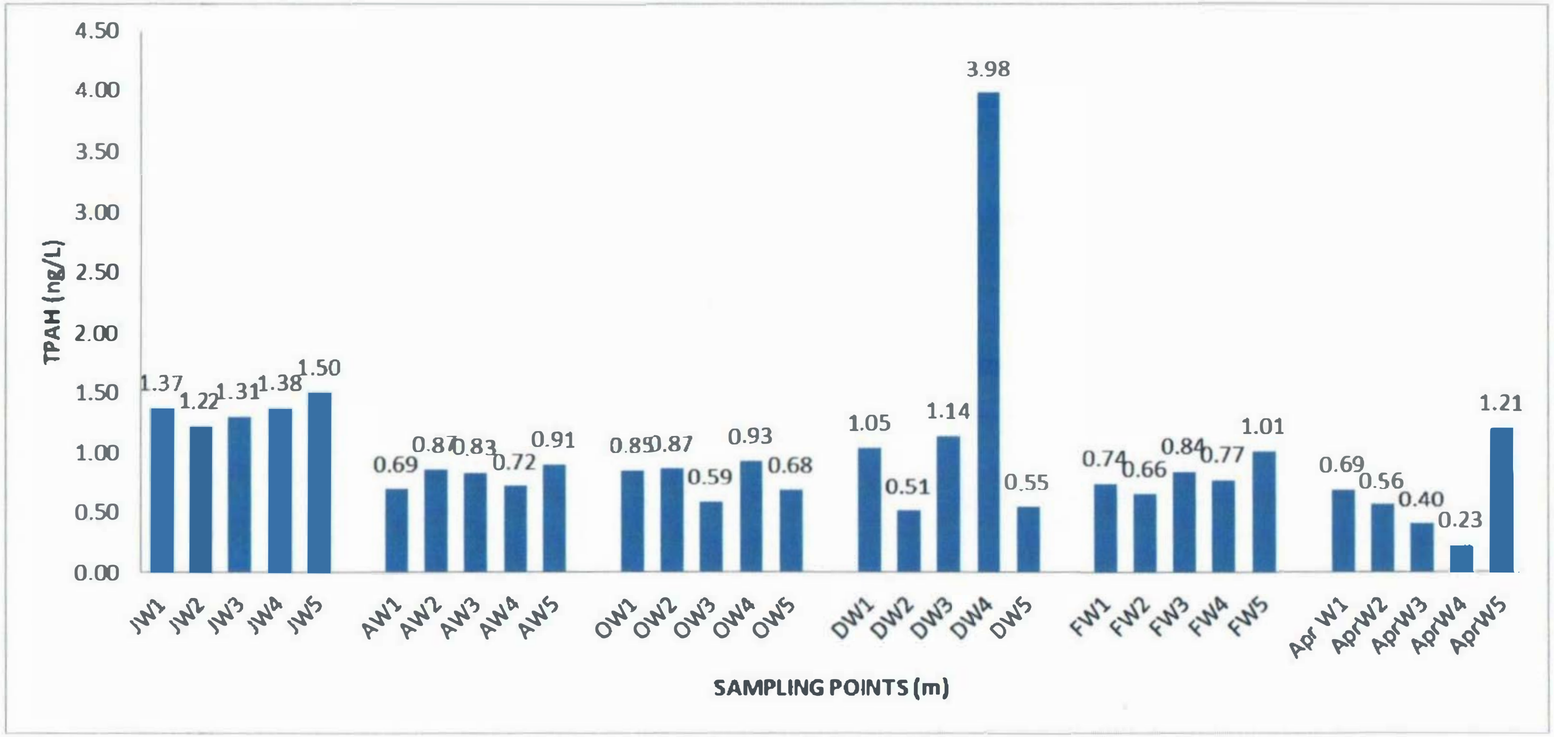

FIG. 3a: Total concentrations of PAHs in water

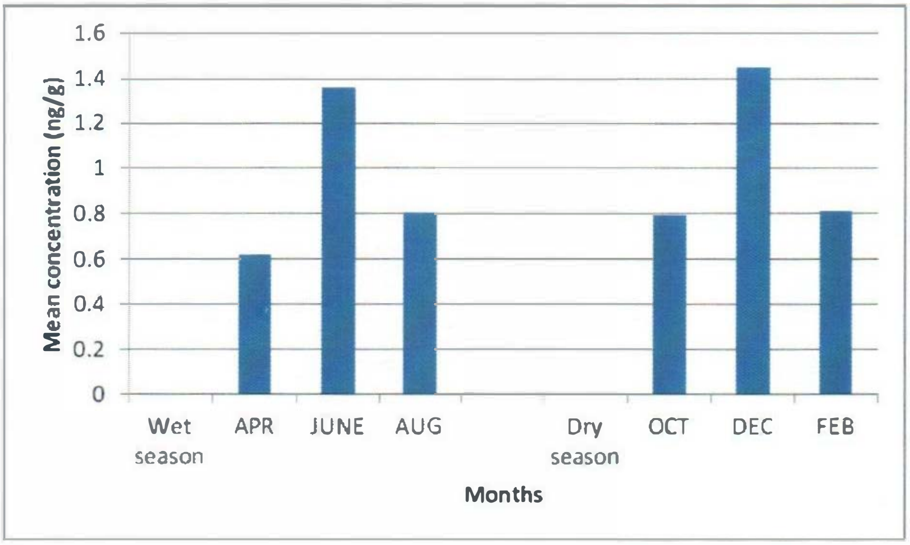

FIG. 3b: Monthly mean concentrations of TPAH in water

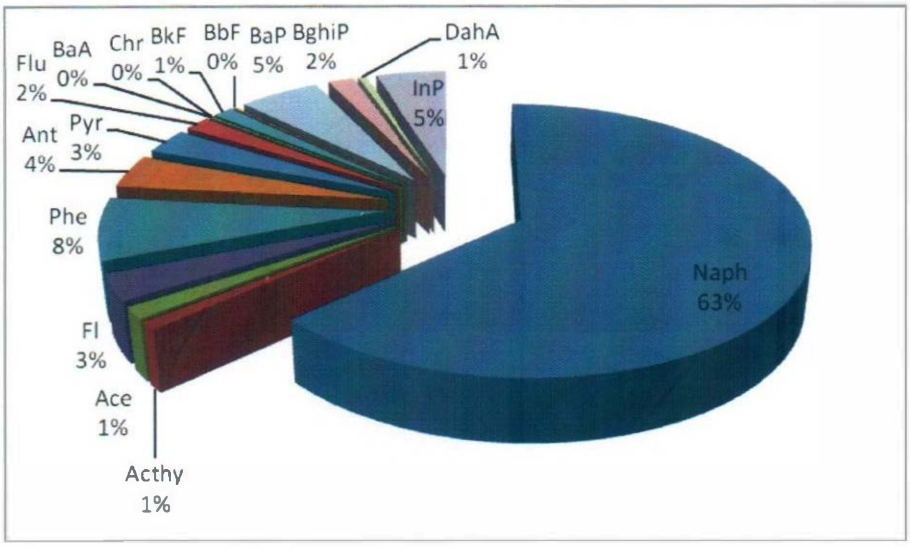

FIG. 4: Percentage composition of individual PAH relative to TPAH in water

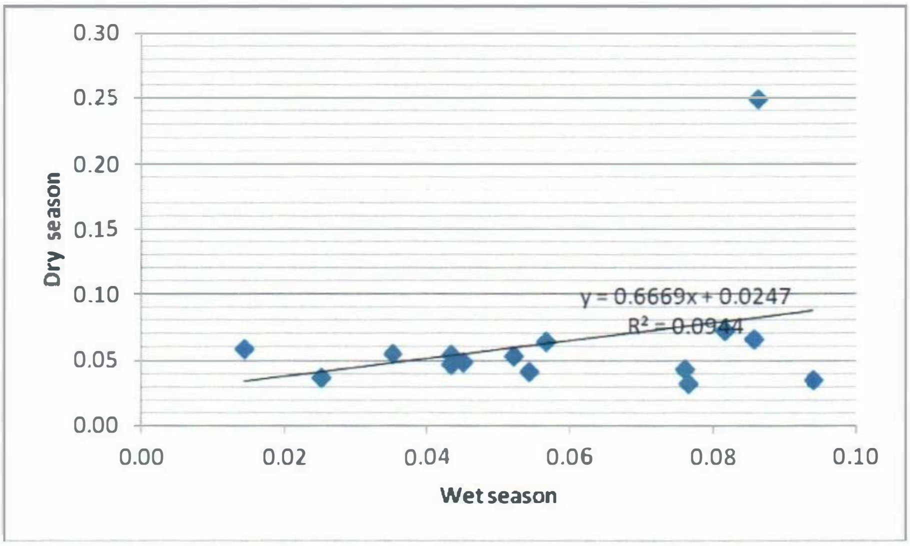

FIG. 5: Correlation between concentrations in PAH (water) in the wet and dry season

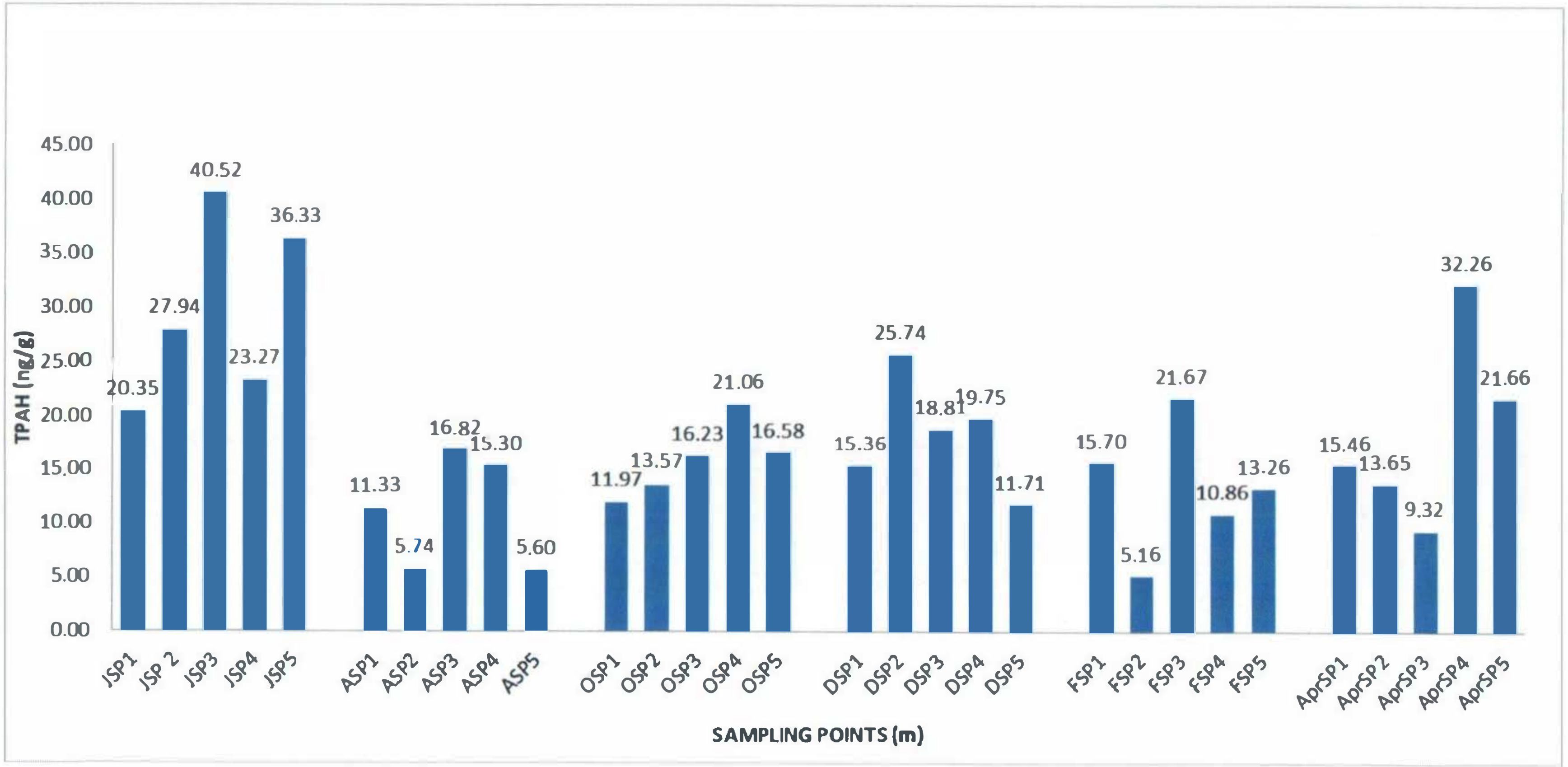

FIG. 6a: Total concentration of PAH in SPM

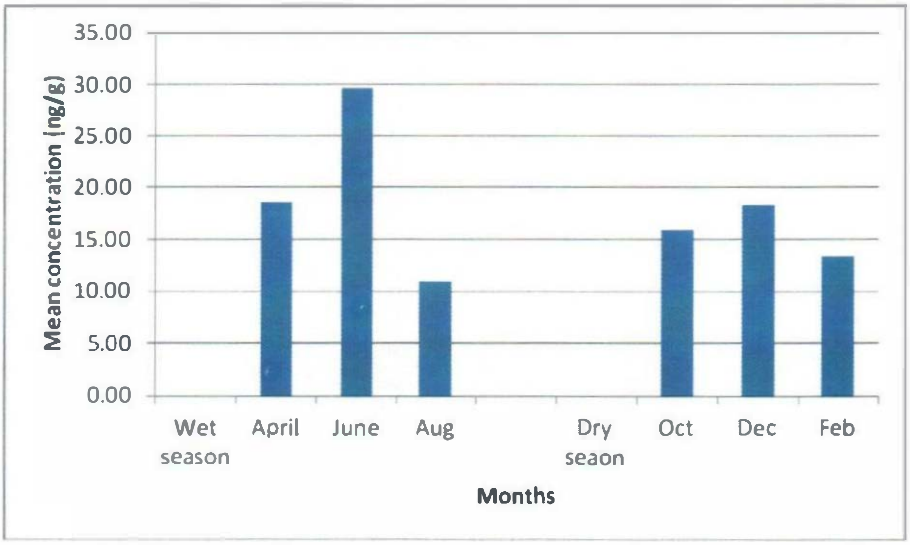

FIG. 6b: Monthly mean concentrations of PAHs in SPM

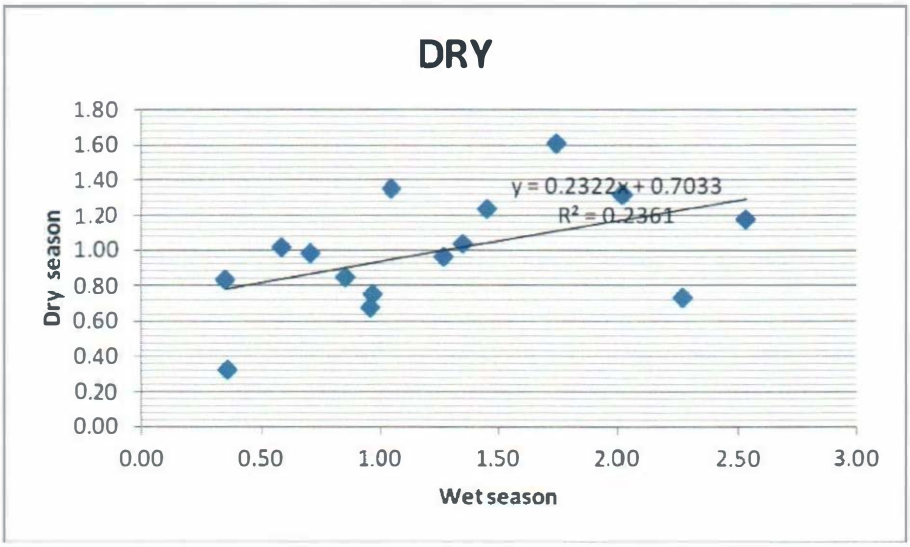

FIG. 8: Correlation between concentrations of PAH (SPM) in the wet and dry seasons

4.2 Seasonal variations in PAH compositions by ring size

4.2.1 Water

FIG. 9 shows the monthly ring-size variation in water PAH, with the LPAH, 2-3 rings dominating and accounting for 81.07% of TPAH, followed by HPAH (5-6 rings) accounting for 16.10 %, and the medium molecular weight (MPAH 4-rings) which accounted for 7.24 %. The 2 and 3 rings PAHs were relatively higher in the dry season (October, December and February) than the wet season (April, June and August), while the HPAH was greater at rainy season than dry season. TPAH composition by ring size followed the sequence 2>3>5>4>6. The distribution of the different PAH rings was suggestive of different PAH source inputs, dominated by petrogenic sources (eg. Petroleum and gasoline/diesel spill and a minor pyrolytic input (vehicular exhaust emission and wood burning; (Kannan *et al*., 2005).

4.2.2 SPM

FIG. 10 shows the monthly variation in PAH compositions by ring size in SPM. The LPAH were predominant throughout the period of study accounting for 85.58 %, followed by HPAH which accounted for 8.73 %, and lastly, MPAH accounting for 8.69 %. The TPAH composition by ring size followed the sequence 2>3>4>5>6. The LPAH were the dominant specie (83.20 %) which was slightly greater than that of dry season with 82 % probably due to surface run-off.

4.3 Source identification of PAHs by isomeric ratios

The major PAH inputs in aquatic environment originate within pyrelytic or petregenic (Zakaria *et al*, 2002; Stuut *et al*., 2004). In order to characterize PAHs sources, some diagnostic ratios were considered. According to De Luca *et al*., (2005), values of LPAH/HPAH less than 1 are indicative of pyrogenic sources, while values greater than 1 are petrogenic. Other PAH ratios such as Flu/(Flu+Pyr) and Ant/(Ant + Phen) were also used to distinguish between petrogenic and pyrogenic sources and to discriminate amongst pyrogenic sources (Shi *et al*., 2007). According to Yunker *et al*., (2002), Flu/(Flu+Pyr) values less than 0.40 signify inputs from petrogenic source and values between 0.40-0.50 imply vehicular exhaust emission (gasoline or diesel combustion), whereas values greater than 0.50 indicates a pyrogenic source from the combustion of grass, wood or coal. Brandhi *et al*., (2007), stated that Ant/(Ant+Phen) ratios less than 0.1 indicates petrogenic sources, while ratios greater than 0.1indicates pyrogenic sources.

Another important ratio which was considered in the source identification was the "ratio of the sum of major combustion specific compounds (ΣComb = BaA, BbF, BkF, BaP, Chr, Flu, Pyr, InP and Bghi P) to the sum of PAH" (Σ_{16} PAH), which can be expressed as (ΣComb/ΣPAH). High values of the ratio indicate extensive combustion activities of PAHs while low values indicate low combustion activities (El Nemr *et al*., 2013). However, in the present study, some level of consistency was found using four isomeric ratios.

4.3.1 Water

LPAH/ HPAH ratio as shown in TABLE 1 revealed that the PAHs in water were mainly of petrogenic source as all the stations recorded values greater than 1 minimizing at 3.02 in the month of June and maximizing at 11.11 in the month of February (De Luca *et al*., 2005). Ant/(Ant+Phen) ratios in all the stations were less than 0.10 implying extensive petroleum inputs (Brandhi *et al*., 2007).

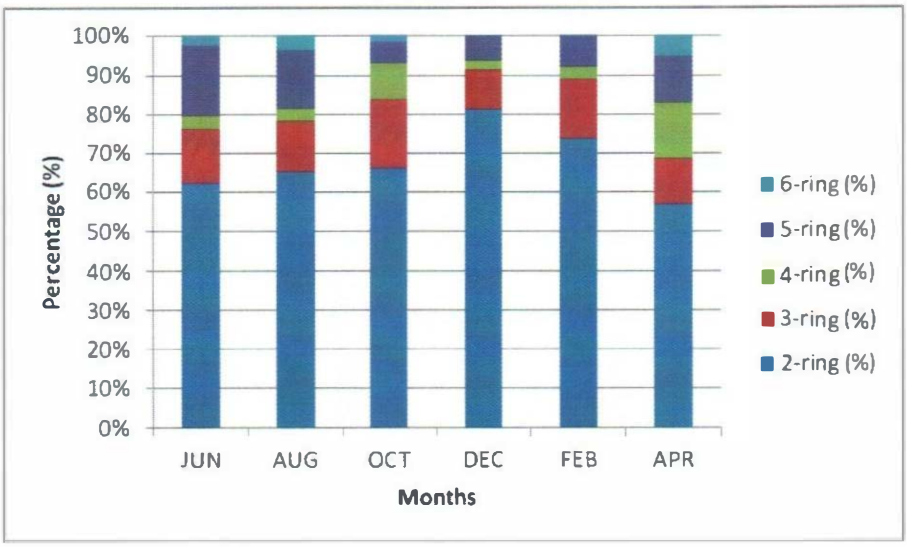

FIG. 9: Monthly variation in PAH composition by ring size in water

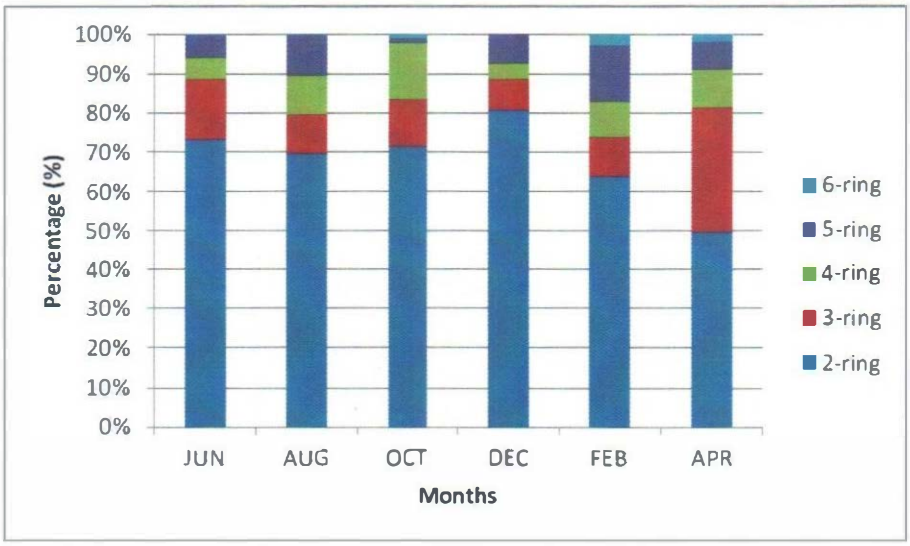

FIG.10: Monthly variation in PAH composition by ring size in SPM

Also, Flu/(Flu+Pyr) mean ratios ranged between 0.31 and 0.48 revealing a dominance of petrogenic input with a minor pyrogenic input. Furthermore, ΣCOMB/Σ16PAHs values obtained minimizes at 1.85 (February) and maximizes at 6.21 (June). This may be attributed to the enhanced fish roasting activity involving burning of wood, and also the fact that April being the beginning of the raining season, the rains may have washed all the waste from different point sources into the estuary. Nonetheless, the value is quite insignificant compared to other estuaries.

4.3.2 SPM

Results obtained for PAH distribution ratios in SPM (TABLE 2) revealed that the mean values for ΣLPAH/HPAH in all the stations were greater than 1 with the lowest value of 3.64 recorded in the month of April while December had the highest value of 11.93. This indicated that the PAHs SPM were mainly of petrogenic origin. Also, the result of Ant/(Ant+Phe) indicated that this samples was predominantly of petrogenic origin as all the values recorded were mostly less than 0.1. Flu/(Flu+Pyr) ratios for almost all the sampling points were less than 0.4, implying dominant influence by petrogenic PAHs, except August which had a value of 0.46 (>0.50) indicating inputs from vehicular exhaust or wood/grass burning emission inputs (Yunker *et al*., 2002). The ΣCOMB/ΣPAH mean ratios in SPM ranged between 2.31 in December and 4.24 in June. The values, although higher than those of water were considerably smaller than combustion input in SPM from other regions of the world. From Tables 1 and 2, it was observed that the SPM held on better to HPAH than water, this could be attributed to the hydrophobic nature of PAH and also the strong affinity of PAH to solid matrix.

TABLE 1

Distribution ratios of PAHs in water from the Cross River estuary

Months	ΣPAHs	ΣLPAH	ΣHPAH	ΣLPAH/HPAH	Ant/(Ant+Phen)	Flu/Flu+Pyr	ΣCOMB	% ΣCOMB/ΣPAH	TEQ_{CARC}	BaPE
APR	0.62	0.43	0.19	3.91	0.04	0.48	0.19	3.47	0.06	0.18
JUN	1.36	1.01	0.35	3.02	0.04	0.36	0.35	6.21	0.10	0.10
AUG	0.80	0.61	0.19	4.85	0.07	0.38	0.19	3.42	0.11	0.20
OCT	0.74	0.63	0.11	6.21	0.02	0.36	0.11	2.52	0.04	0.08
DEC	1.45	1.30	0.14	10.41	0.04	0.36	0.14	2.52	0.03	0.03
FEB	0.81	0.70	0.10	11.11	0.08	0.31	0.10	1.85	0.06	0.07
Petrogenic	-	-	-	> 1	< 0.10	< 0.40	-			
Pyrogenic	-	-	-	< 1	> 0.10	> 0.40	-			

TABLE 2

Distribution ratios of PAH in SPM from the Cross River estuary

Months	ΣPAHs	ΣLPAH	ΣHPAH	ΣLPAH/HPAH	Ant/(Ant+Phen)	Flu/(Flu+Pyr)	ΣCOMB	% ΣCOMB/ΣPAH	TEQ	BaPE
APR	18.47	14.40	4.07	3.64	0.05	0.35	4.07	4.12	0.66	0.62
JUN	29.68	25.50	4.19	6.41	0.06	0.32	4.19	4.24	0.99	0.98
AUG	10.96	8.49	2.47	5.36	0.05	0.46	2.47	2.50	0.83	0.60
OCT	15.88	12.85	3.03	4.84	0.08	0.35	3.03	3.07	0.17	0.12
DEC	18.27	15.99	2.28	11.93	0.05	0.21	2.28	2.31	1.07	0.96
FEB	13.33	9.60	3.73	3.77	0.07	0.39	3.73	3.77	1.41	0.84
Petrogenic	-	-	-	> 1	< 0.10	< 0.40	-	-	-	-
Pyrogenic	-	-	-	< 1	> 0.10	> 0.40	-	-	-	-

4.4 Source identification by Principal component analysis (PCA)

The results from principal component analysis (PCA), as far as PAH source identification is concerned are more robust and reliable than those of molecular ratios. PCA of PAH concentrations in water and SPM were expected to identify those compounds that co-vary.

4.4.1 Water

The first "principal components (PC1, PC2 and PC3) (TABLE 3) were identified through the use of eigenvalue >1, which accounted for 63 % of the total variance. PC1 accounted for 36 % of the total variance and was heavily weighted by LPAHs (FIG. 11 a, b), including fluorene, acenaphthylene, phenanthrene as well as pyrene and fluoranthene, according to Tolosa *et al* (2005), petroleum derived residues contains relatively greater amount of LPAHs". Therefore, PC1 can be said to originate mainly from petroleum sources. PC2 made up 14.53 % of total fifference as well as highly weighted by HPAHs including benzo (k)fluoranthene and benzo(a)anthracene which are linked with vehicular exhaust emissions (Larser and Barker 2003). PC3 was weighted with HPAHs which included chrysene and benzo(b)fluoranthene and accounted for 12.46 % of the total variance. These were attributed to admixture of vehicular exhaust and wood combustion sources (Simcik *et al*., 1999; Larsen and Baker, 2003).

4.4.2 SPM

For PAHs in SPM, the first three principal components "(PC1, PC2 and PC3)" made up 65.38 % of general difference (TABLE 6). PC1 (FIG. 12 a, b) which accounted for 35.80 % of the total variance was heavily weighted by LPAH including fluorene, pyrene, fluoranthene, anthracene, acenaphthylene, naphthalene and phenanthrene which are attributed to petrogenic sources. PC2 was heavily weighted by HPAH which includes "benzo(b)fluoranthene and benzo(ghi)perylene", as well as accounted for 17.38 % of the total variance. These compounds are markers for vehicular exhaust emissions (Larser and Baker, 2003). PC3 accounted for 12.20 % with a moderate loading of benzo(a)pyrene, acenaphthene and phenanthrene which were mixed source regarding petrogenic as well as combustion sources.

4.5 Relationship amongst sampling stations using cluster analysis of PAHs

Analysis using hierarchical cluster has to do with tool which complements other diagnostic indices towards identification of hydrocarbon sources. In the study, cluster analysis was employed to water and SPM samples to classify the study area into specific regions with defined characteristics.

4.5.1 Water

The result of cluster analysis of water PAHs, as represented in the dendogram (FIG. 13) showed two distinguishable clusters (a) OW3, OW5, DW5, AW1, FW2, FW4, AprW1, OW2, AW3, AW2, FW1, OW4, FW3, DW1, AW5, FW5, OW1, AprW5, JW2, DW3, JW3, JW4, JW5, JW1, Aprw3, AprW4, DW2, AprW2, AW4 and (b) JW4 and DW4. The first cluster (a) showed great similarity between them indicating a common source characteristic of hydrocarbons of petrogenic origin, while the second cluster (b) showed great dissimilarity to the first group indicating that the media was impacted much through inputs from combustion sources in addition to the petroleum sources.

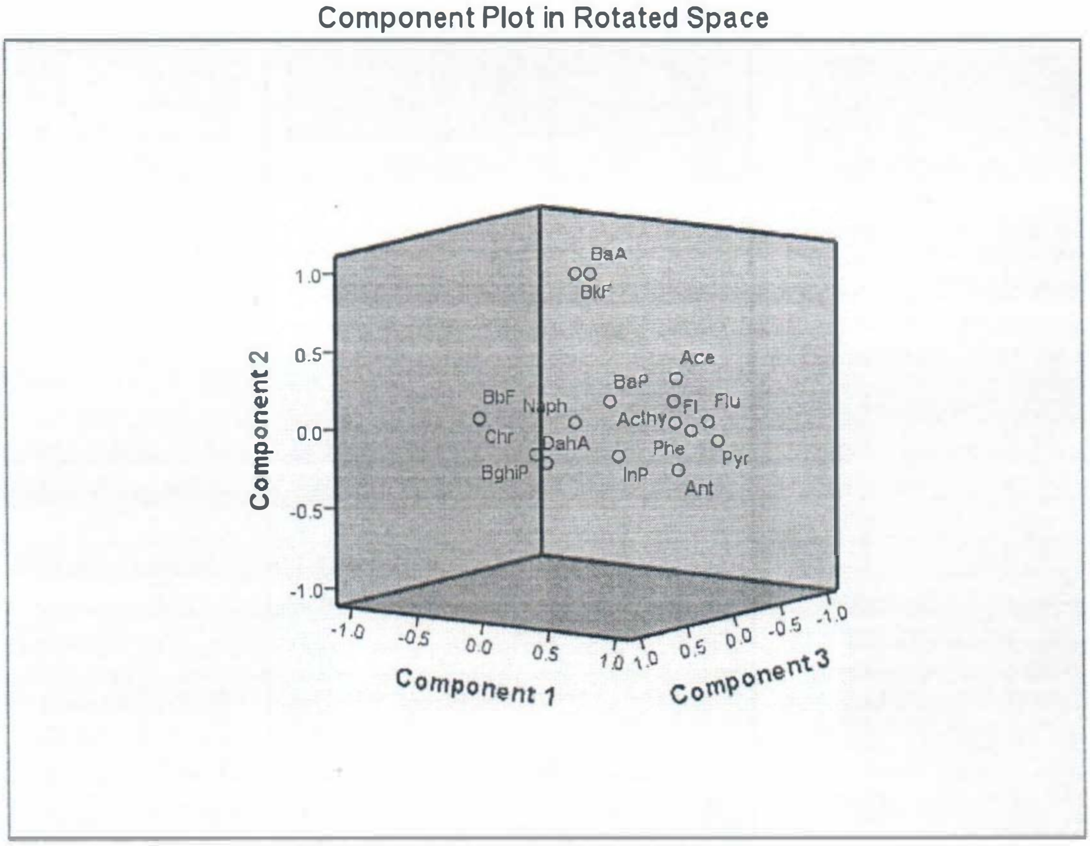

FIG.11a: Principal component analysis plots (a) all PAHs

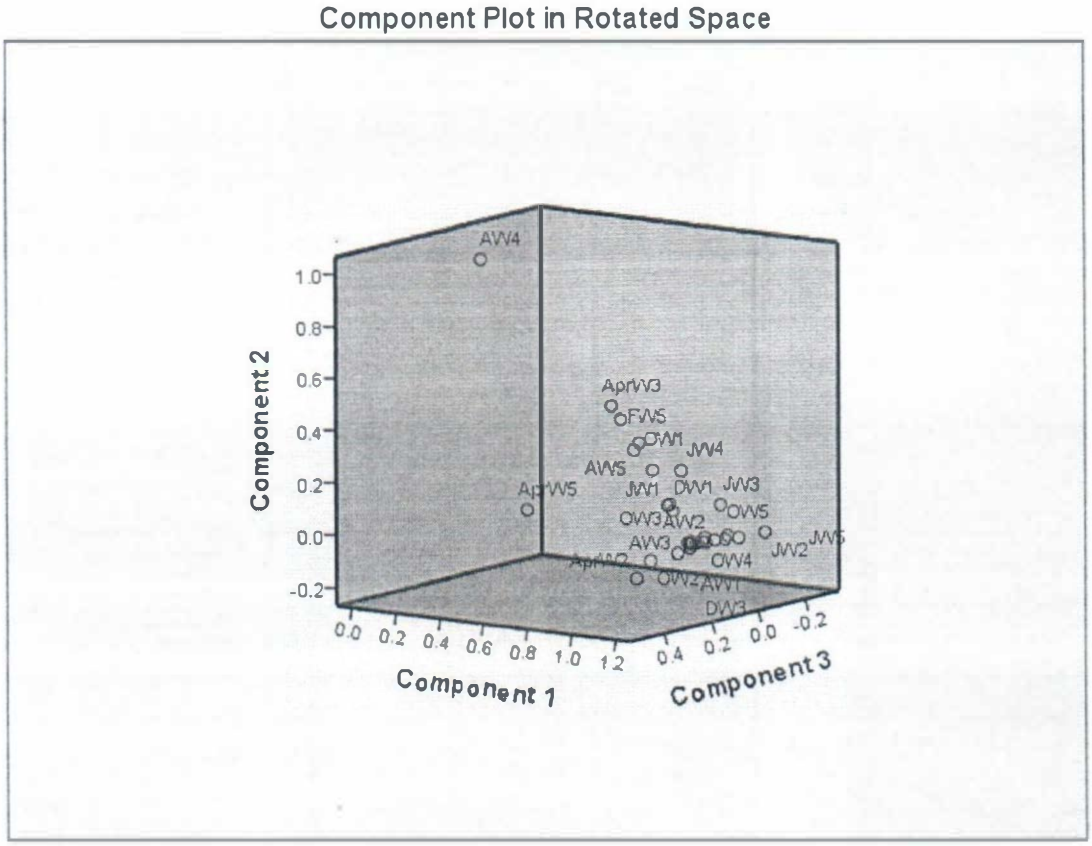

FIG. 11b: Principal component analysis plots all variables in water

TABLE 3

Eigenvalue, total variance and factorial weight matrix explained by PCA for PAHs in water

	Components		
	PC 1	**PC 2**	**PC 3**
Eigenvalue	5.76	2.32	1.99
Variance %	36.03	14.53	12.46
Sources	Petroleum Sources	Vehicular emissions	Vehicular emissions/wood combustion
Pyr	**.875**	.012	.133
Fl	**.861**	-.127	.217
Acthy	**.831**	.096	.222
Flu	**.806**	.221	.140
Phe	**.783**	-.038	.169
Ant	.689	-.147	.293
Ace	.655	.285	-.080
InP	.541	-.476	.408
BaP	.294	.266	-.025
BkF	.174	**.902**	-.001
BaA	.255	**.876**	-.106
Naph	.270	-.387	.202
Chr	-.546	.221	**.730**
BbF	-.546	.221	**.730**
BghiP	-.263	.105	.503
DahA	-.433	.096	.449

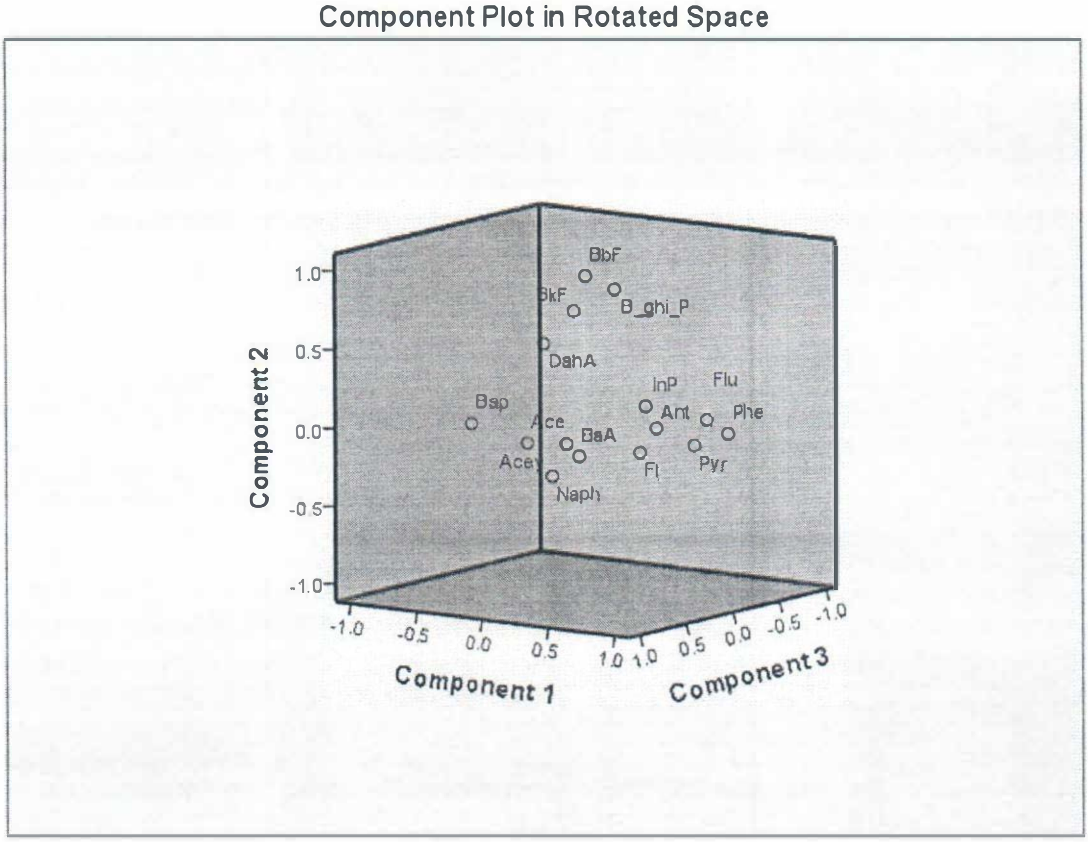

FIG. 12 a: Principal component analysis plots PAHs in SPM

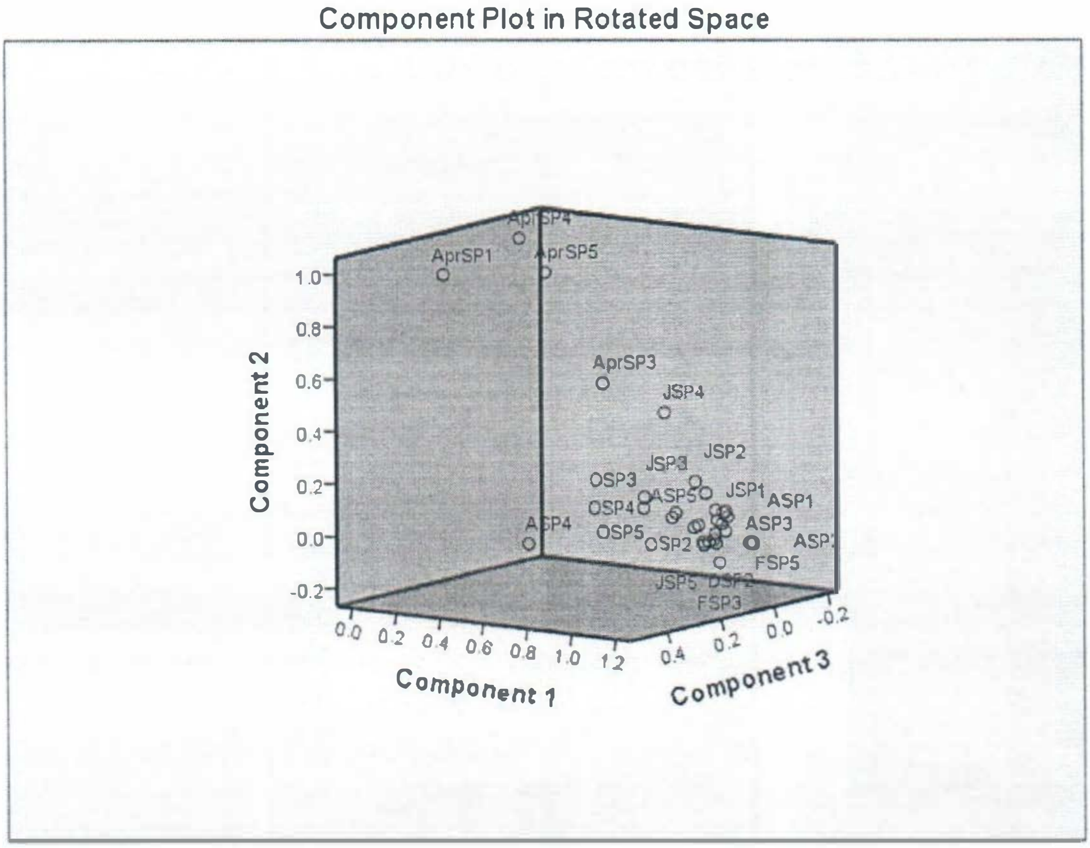

FIG.12 b: Principal component analysis plot variables in SPM

TABLE 4

Eigenvalues, total variance and factorial weight matrix explained by PCA for PAHs in SPM

	Components		
	PC 1	**PC 2**	**PC 3**
Eigenvalue	5.37	2.61	1.83
Variance %	35.80	17.38	12.20
Sources	Petroleum sources	Vehicular emission	Petroleum/ combustion sources
Fl	**.958**	-.092	.057
Pyr	**.941**	.041	-.252
Flu	**.864**	.204	-.321
Ant	**.769**	.103	-.068
Acey	**.758**	-.143	.416
Naph	**.738**	-.421	.400
Phe	**.726**	.166	**-.525**
Ace	.580	-.198	**.566**
InP	.412	.372	-.051
BaA	-.179	-.053	-.016
BbF	.051	**.878**	.269
B_ghi_P	.128	**.856**	.114
DahA	-.056	.586	.451
BkF	-.157	.510	.108
Bap	-.020	-.185	**.651**

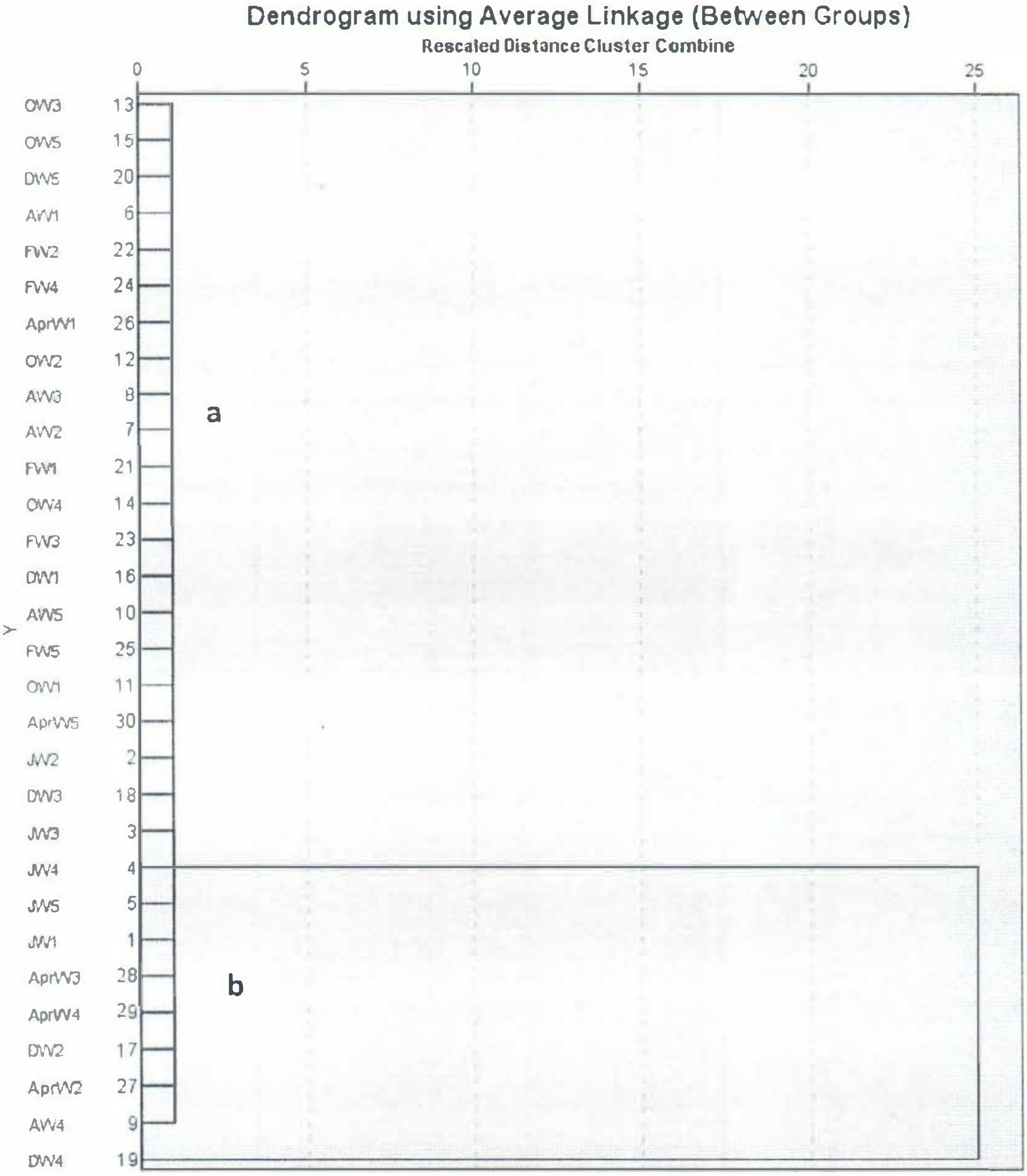

FIG. 13: Dendogram plot of water samples showing relationship amongst stations

4.5.2 SPM

Result of cluster analysis for SPM is as shown on the dendogram plot (FIG.14) showed three main clusters. The first cluster (a) with stations DSP1, FSP1, OSP2, OSP3, OSP4, OSP5, OSP1, DSP5, FSP5, FSP4, ASP1, and AprSP2 had the shortest distance between them and possible similar source characteristics most likely of petroleum origin, the distance increased slightly to ASP4 and FSP3. The second major cluster (b) with short distance (great similarity) was observed between ASP5, FSP2, ASP2, AprSP3 and AprSP1, also JSP4 and AprSP5 indicating 5-6 rings PAHs related to vehicular exhaust emission, and the third cluster (c) which had stations DSP3, DSP4, JSP1, ASP3, DSP2 and JSP2 with the shortest distance and great similarity indicated 2 and 5 rings PAH related to mixed sources of petroleum and wood combustion inputs.

4.6 Effects of hydrological cycles on PAH distributions

Hydrological cycles could be enhanced when dealin with changes within estuarine ecosyatem, such as SSC, salinity as well as temperature (Liu *et al.*, 2017). In the study, the estuarine parameters showed remarkable seasonal variation (FIG. 15). The monthly mean suspended sediment concentration (SSC) in the wet season ranged from 0.12 ng/L to 0.33 ng/L having .21±0.07 ng/L as value mean, and 0.01 ng/L to 0.14 ng/L in the dry season with a mean value of 0.14±0.21 ng/L. Salinity ranged between 5.50 % to 23.50% with a mean of 13.43±6.23 % minimizing in the month of June and maximizing in the month of February. Temperature varied significantly with values ranging from 20 ^{0}C to 36 ^{0}C with a mean value of 27.25±6.11^{0}C, and was found to be higher in the wet season than in the dry season, several studies in the past on the "seasonal variation of PAHs in coastal environments such as the Gao-ping River, Taiwan (Doong and Lin, 2004), and the Yellow River, China (Sun *et al*, 2009) have attributed the seasonal variation in PAHs to changes in riverine discharges and rainfall, and have reported a relatively lower PAH concentration in the wet season (Doong and Lin, 2004, Zhang *et al*., 2012), in the present study, PAHs recorded a significant difference each month with the total concentrations in SPM being higher in the wet season than in the dry season, this could be attributed to the heavy rainfall and surface run-off which discharges all its waste from vehicular emissions, domestic and industrial sites into the estuary, and also due to the hydrophobic nature of PAHs which tends to adsorb onto SPM. estuaries which are known as transition zones are mixing zones for fresh water delivered by rivers and saline water from oceans, the distribution, partition and mobility of PAHs derived from land will differ due to changes in the physico-chemical properties of the estuaries". Pearson correlation analysis was carried out to determine the seasonal impacts of hydrological parameters on PAHs. The result showed that for water (FIG.16 a-c), temperature revealed a weak negative correlation with concentration (r^2= -0.0069), and a strong negative correlation with salinity (r^2= -0.6797), also concentration showed a negative correlation with salinity (r^2=0.0172). Furthermore, SPM (FIG.17 a -c) indicated that temperature showed a weak positive correlation with concentration (r^2= 0.0145), and a strong negative correlation with salinity (r^2= -0.6797). Salinity showed a strong negative correlation with concentration (r^2=0.3288). These seasonal variations in hydrological parameters greatly influenced the behavior of PAHs in the estuary.

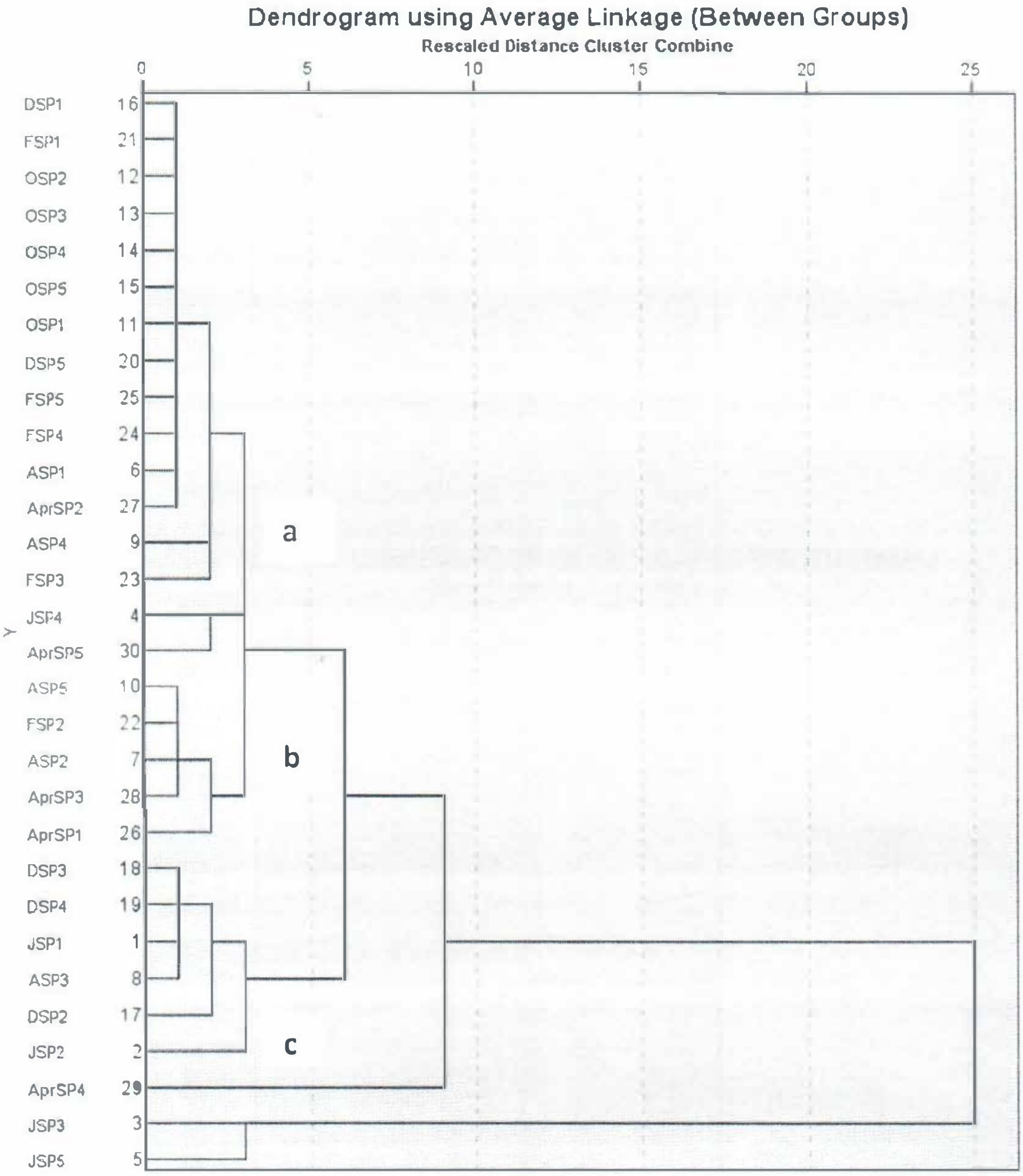

FIG. 14: Dendogram plot of SPM samples showing relationship amongst stations

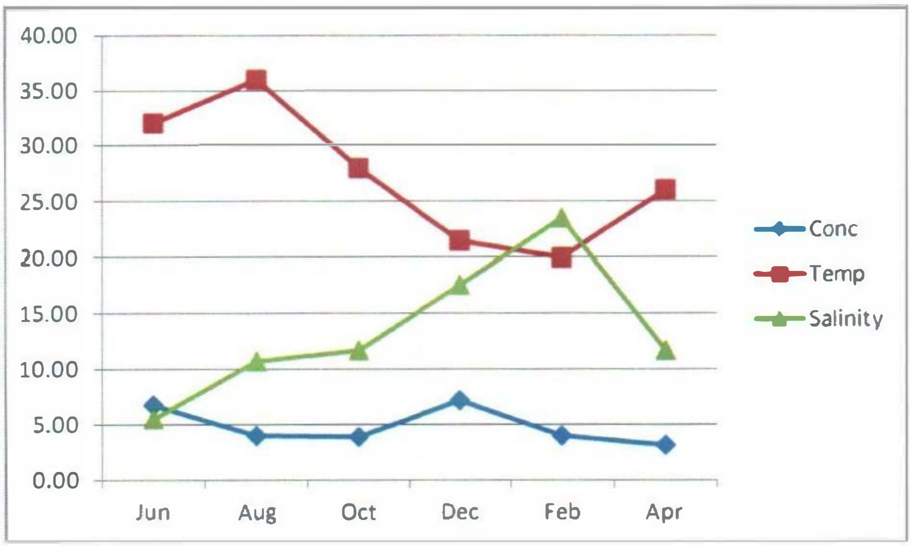

FIG. 15: Seasonal variation in PAH temperature (0C), salinity and SSC (g/L)

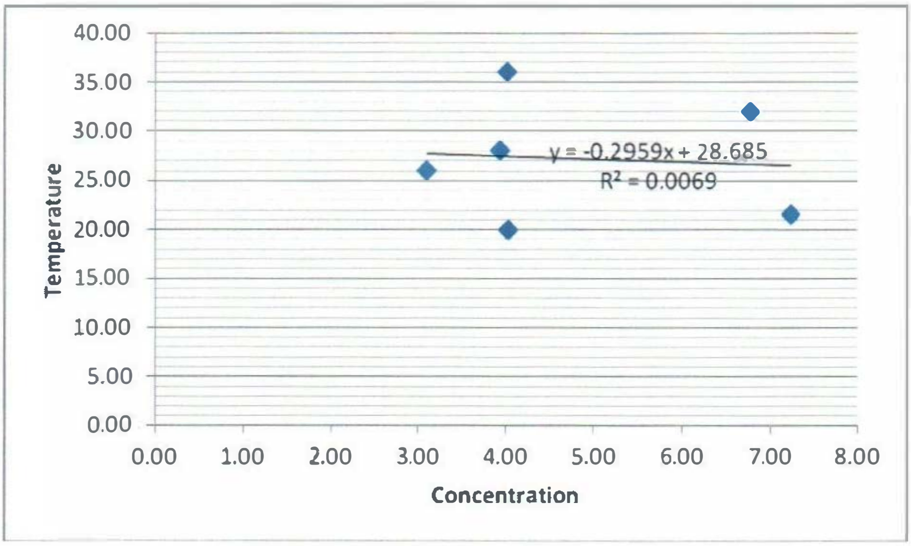

FIG. 16a: Correlation between concentration and temperature of water

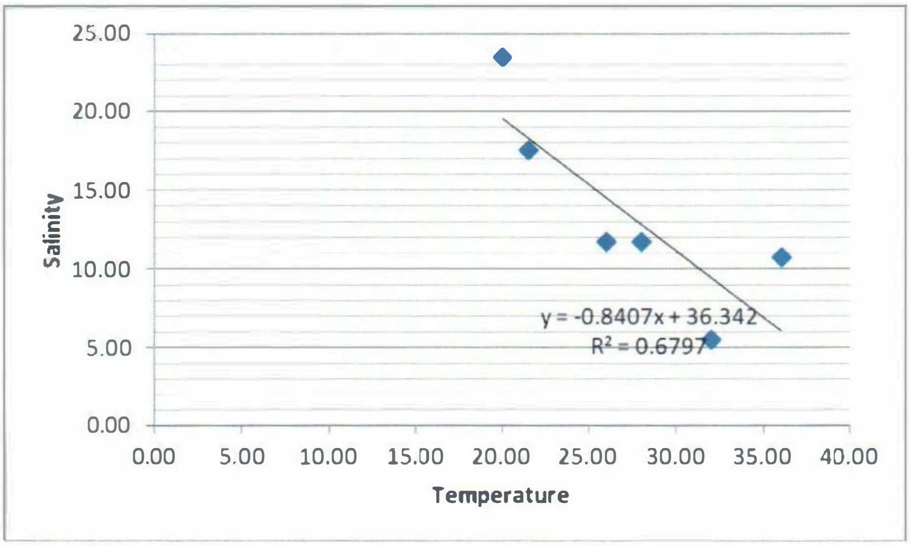

FIG. 16 b: Correlation between salinity and temperature of water

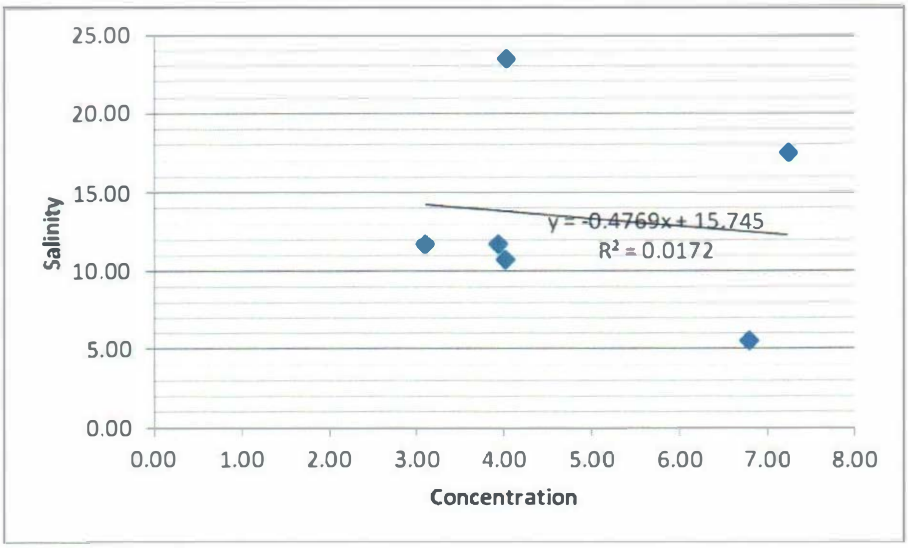

FIG.16 c: Correlation between salinity and concentration of water

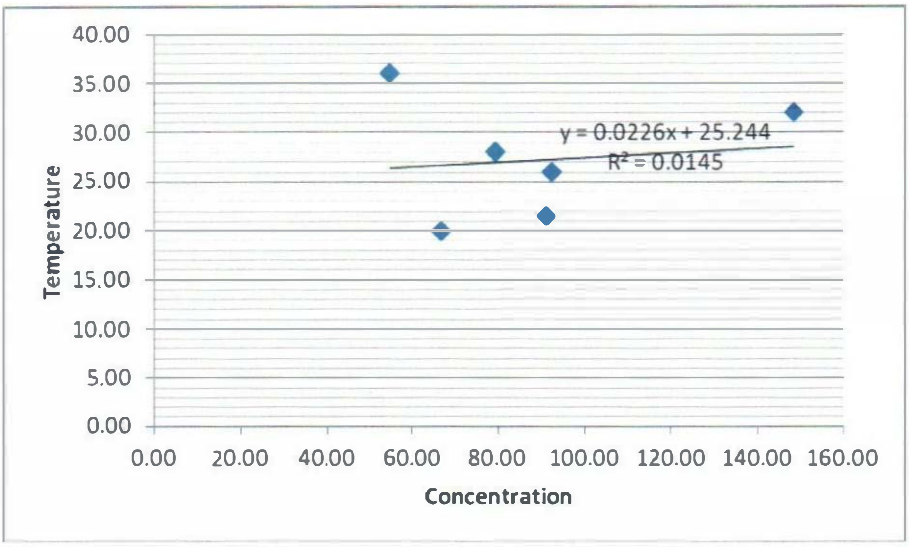

FIG. 17a: Correlation between concentration and temperature of SPM

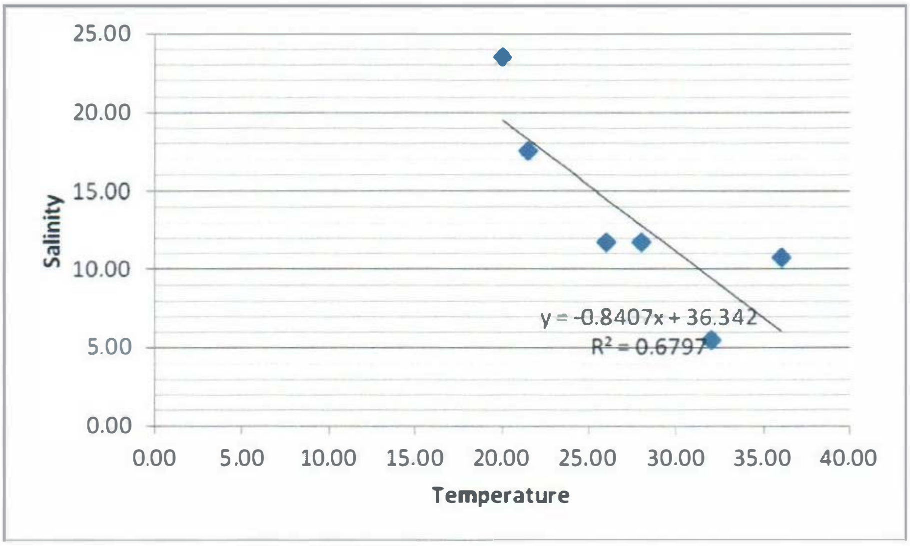

FIG. 17 b: Correlation between temperature and salinity of SPM

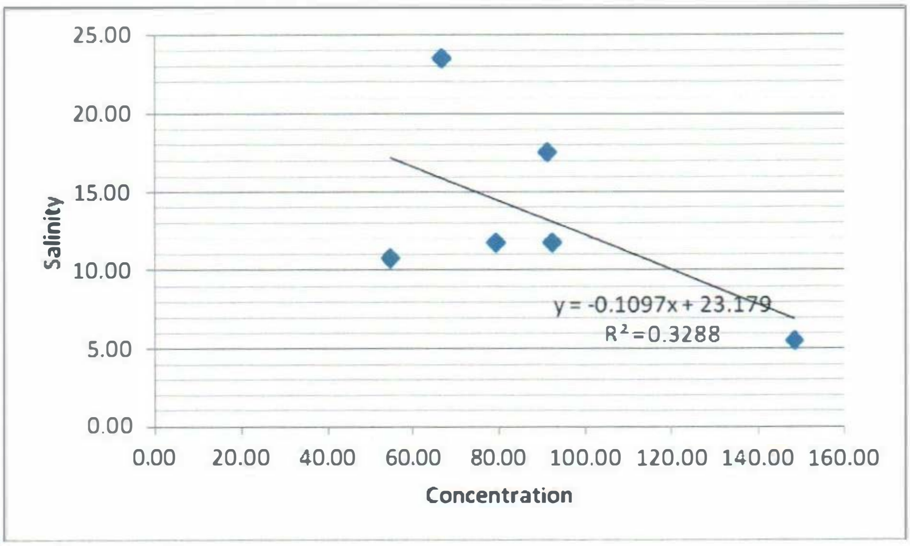

FIG.17c: Correlation between concentration and salinity of SPM

4.7 Effects of anthropogenic activities on PAH distribution

Previous studies have revealed that emissions have remained the major source of PAHs in cities due to the influx of people and vehicles (Li *et al*, 2006). These could be the cause of high vehicular emission regarding PAHs within samples analyzed. Particle-bound PAHs from vehicular emissions and other petroleum sources may have been delivered into the estuary as a result of strong wash-out within urban wet season city run off, which would result in higher concentrations in the wet season in SPM, Coal consumption has also been found to be another important source of energy supply in some cities around the world like Guangzhou city, China where "coal powered stations provided about 70 % of the city power within the city" (Li *et al*, 2006). However, in the present study, ships/ boats activities and off-shore oil spill may be responsible for the levels of petrogenic PAHs in the estuary. Wood burning by communities around the estuary for roasting of fish which is the predominant occupation of the catchments, may be the major contributors of pyrolytic PAHs in the estuary. Also, the dredging of the Calabar River which is one of the tributaries of the estuary and ploughing of land for farming by communities around the estuary are other possible sources of PAHs in the estuary.

4.8 Assessment of health risk

The three main routes of PAH with regards to being exposed to humans were ingestion, breathing it in as well as contact to dermal part of the body (Edokpayi *et al*., 2016). The health risk assessment was calculated using three parameters namely: BaPE, TEQ_{carc}, and the Effect Range Low (ERL) and Effect Range Medium (ERM). Results for water and SPM PAHs are recorded in TABLES 3 and 4, respectively.

4.8.1 BaP equivalent (BaPE)

The 16 priority PAHs are of great "concern because of their carcinogenicity (Qiao *et al*. 2006), the BaP equivalent (BaPE) was used in the study to quantitatively assess the PAH potential health risk" and this was obtained using the following equation (Liu *et al*., 2009):

BaPE = BaA x 0.06 + BbF x 0.07 + BkF x 0.07 + BaP + DahA x 0.06 + Icdp x 0.08. BaA = Benzo(a)anthracene. BbF = Benzo(b)fluoranthene, B(k)F = Benzo(k)fluoranthene, BaP = Benzo(a)pyrene, DahA = Dibenzo[a,h]anthracene and Icdp= Indeno[1,2,3-cd]pyrene.

BaPE calculated for water in the study ranged from 0.00 to 0.43 with a mean value of 0.11±0.12 and SPM ranged from 0.00 to 4.61 with a mean of 0.69±1.15. The values recorded were low compared to other estuaries around the world like the Red sea with a value of 45.27ng/g (Aly Salem *et al*., 2014).

4.8.2 Toxic equivalent factors (TEFs)

The Toxic equivalent factors (TEFs) "of the seven carcinogenic PAHs (BaA, BaP. BkF, BbF, Chr, DahP and InP), were used to quantitatively assess their toxicological significance to human health, Toxicty is often expressed relative to benzo[a]pyrene (BaP), the reference standard. The toxic equivalents (TEQ_{carc}) can then be calculated thus, $TEQ_{carc} = \Sigma(C_i \times TEF_i)$, where C_i is the concentration of individual PAH and TEF_i is the corresponding TEF, according to the USEPA, the TEFs for Chr. BaA. BbF, BkF, BaP. InP and DahP" are 0.001, 0.1, 0.1, 0.1, 1, 0.1 and 1respectively (Guo *et al*., 2011). The TEQ_{carc} for water and SPM were7.21 ng TEQ g^{-1} and 25.67ng TEQ g^{-1} with mean values of 0.06 ng TEQ g^{-1} and 0.86 ng TEQ g^{-1}, respectively. The result obtained shows higher toxicity factor in SPM which may pose some threat to biota.

4.8.3 Effect range-low and effect range-medium

To study the biological effects of PAHs of Cross River estuary, the effects range-low (ERL) and effect range-medium (ERM) were used, (TABLE 5). PAH values above the recommended ERM indicates the occurrence of increased toxic affects within the zone, moderate conterminated effects were recorded when PAH concentration were within ERL and ERM level, and no adverse influence were required regarding PAH concentrations smaller than ERL level (Long *et al.*, 1995). The result obtained in this study indicated that the concentrations of PAHs in SPM were below the ERL and ERM values except for Naphthalene which recorded a value greater than ERL but smaller than ERM, showing that PAHs within SPM do not pose serious threats to resident flora and fauna, except Naphthalene which would require more public concern in terms of its remediation.

4.9 Seasonal variation in n-alkane concentrations

4.9.1 Water

The total concentrations (ΣC_8 - C_{40}) of n-alkanes in water (FIG.18 a) ranged between 1.60 ng/L (JW5 = 8 m) and 7.20 ng/L(JW4 = 6 m) in the month of June, with a mean value of 4.78±2.02 ng/L, and 3.76 ng/L to 7.20 ng/L in the month of August, minimizing at 6m in AW4 and maximizing at the surface in AW1with a mean value of 4.81±1.37 ng/L. Total n-alkane concentration level for the month of October ranged from 1.54 ng/L at 8 m in OW5 to 3.80 ng/L at the surface (OW1) in the month of October with a mean value of 2.56±0.99 ng/L,and 1.72 ng/L at 4 m (DW3) to 5.99 ng/L at 6 m (DW4) in December with a mean value of 3.14±1.75 ng/L. Furthermore, values for February ranged between 0.74 ng/L at 4 m (FW3) and 3.35 ng/L at 8 m (FW5) with a mean value of 1.91±1.05 ng/L, whereas a range of 0.04 ng/L to 1.90

ng/L was recorded in the month of April with a minimum at 4 m in AprW3 and a maximum at the surface (Apr W1) with a mean value of 0.72±0.83 ng/L (FIG. 18 a). The highest mean concentration of n-alkanes in water was recorded in the month of August with a value of 4.81 ng/L, which could be said to be most polluted, while the lowest mean concentration of 0.72 ng/L was recorded in April.

The mean concentration of total n-alkanes in the wet and dry seasons exhibited a remarkable seasonal variation (FIG.18 b) as the concentration was higher in the wet season than the dry season with the LHC dominating. Also, the correlation analysis (FIG. 20) revealed a positive correlation between the wet and the dry seasons (r^2= 0.0777). Choudhary *et al.* (2010) stated that aquatic algae (both micro and macro-algae) and photosynthetic bacteria are found to be dominated by C_{15}, C_{17} and C_{19} n-alkanes, whereas vascular plants are found to be dominated by C_{27}, C_{29} and C_{31} n-alkanes. The abundance of n-alkanes in them is a reflection of the source of organic matter. Among the individual n-alkanes, C_{27}, C_{29} and C_{31} exhibited higher percentage composition consisting of 8 %, 7 % and 6 %, respectively (Fig.19) relative to C_{15}, C_{17} and C_{19} with 0.23 %, 0.48 % and 0.31 %, respectively, which is suggestive of the predominance of terrestrial vascular plants input.

TABLE 5

PAHs in SPM Concentration (ng/g) and ERL and ERM toxicity guidelines (Long *et al.*, 1995; Mai *et al.*, 2002; Liu *et al.*, 2009)

			This study		
PAH	**ERL**	**ERM**	**SPM**	**ERL**	**ERM**
Naph	160.00	2100.00	332.52	>	<
Acey	16.00	500.00	4.86	<	<
Ace	44.00	640.00	10.49	<	<
Fl	19.00	540.00	17.64	<	<
Phe	240.00	1500.00	49.01	<	<
Ant	853.00	1100.00	19.64	<	<
Pyr	665.00	2600.00	25.41	<	<
Flu	600.00	5100.00	12.59	<	<
BaA	261.00	1600.00	1.32	<	<
Chr	384.00	2800.00	0.00	<	<
BkF	280.00	1620.00	12.74	<	<
BbF	320.00	1800.00	3.82	<	<
BaP	430.00	1620.00	17.93	<	<
BghiP	430.00	1600.00	5.49	<	<
DahA	63.40	260.00	4.44	<	<
InP	-	-	15.10	<	<

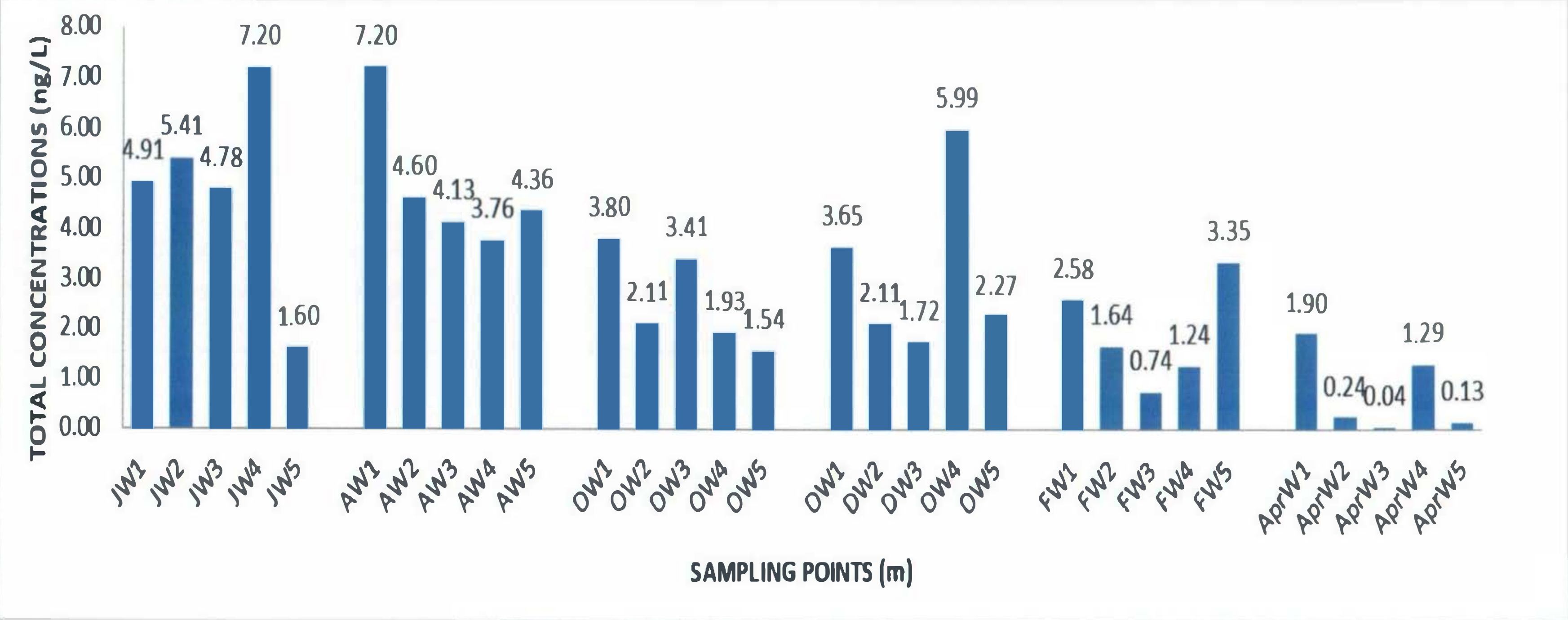

FIG. 18 a: Total n-alkane concentrations in water

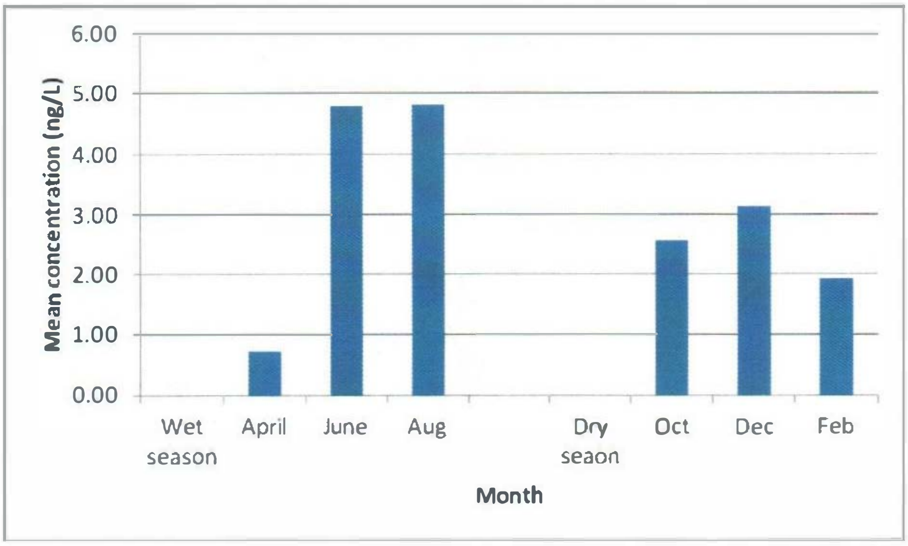

FIG.18 b: Monthly mean concentrations of n-alkanes in water

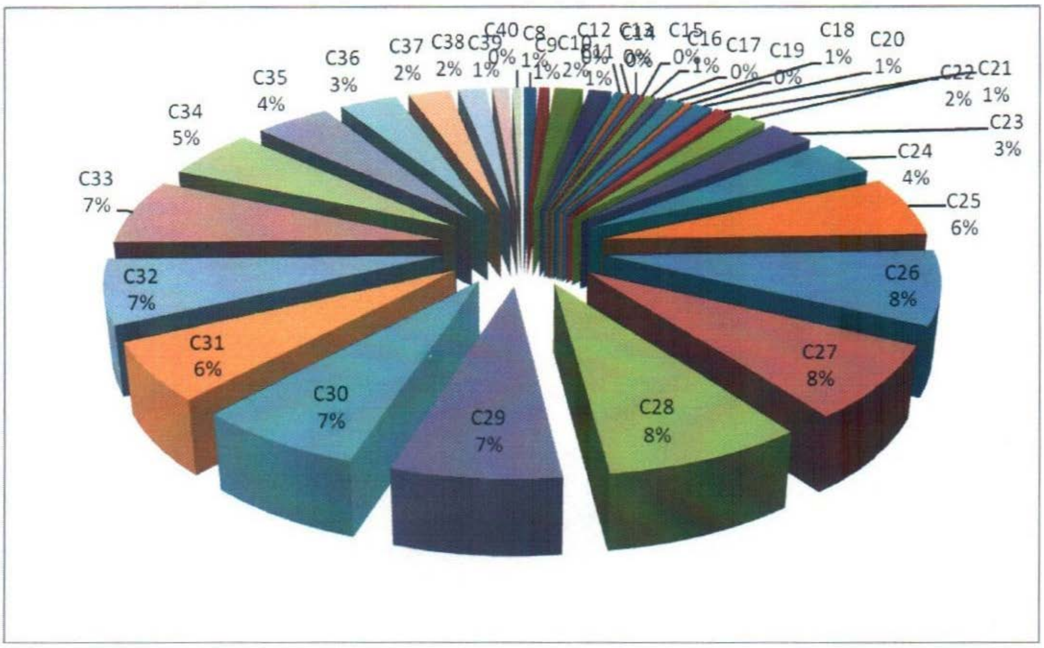

FIG.19: Percentage composition of individual n-alkanes relative to total n-alkane in water

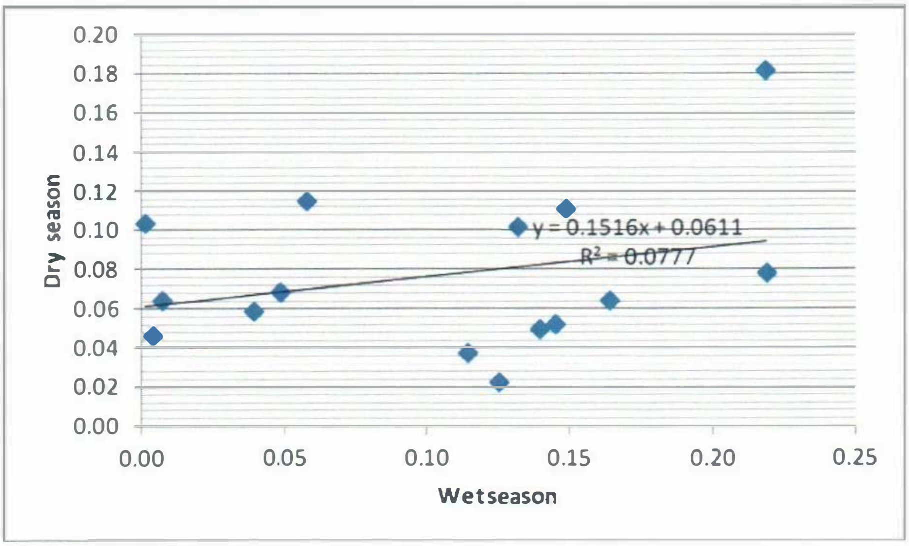

FIG. 20: Correlation between concentrations of n-alkanes (water) in the wet and dry seasons

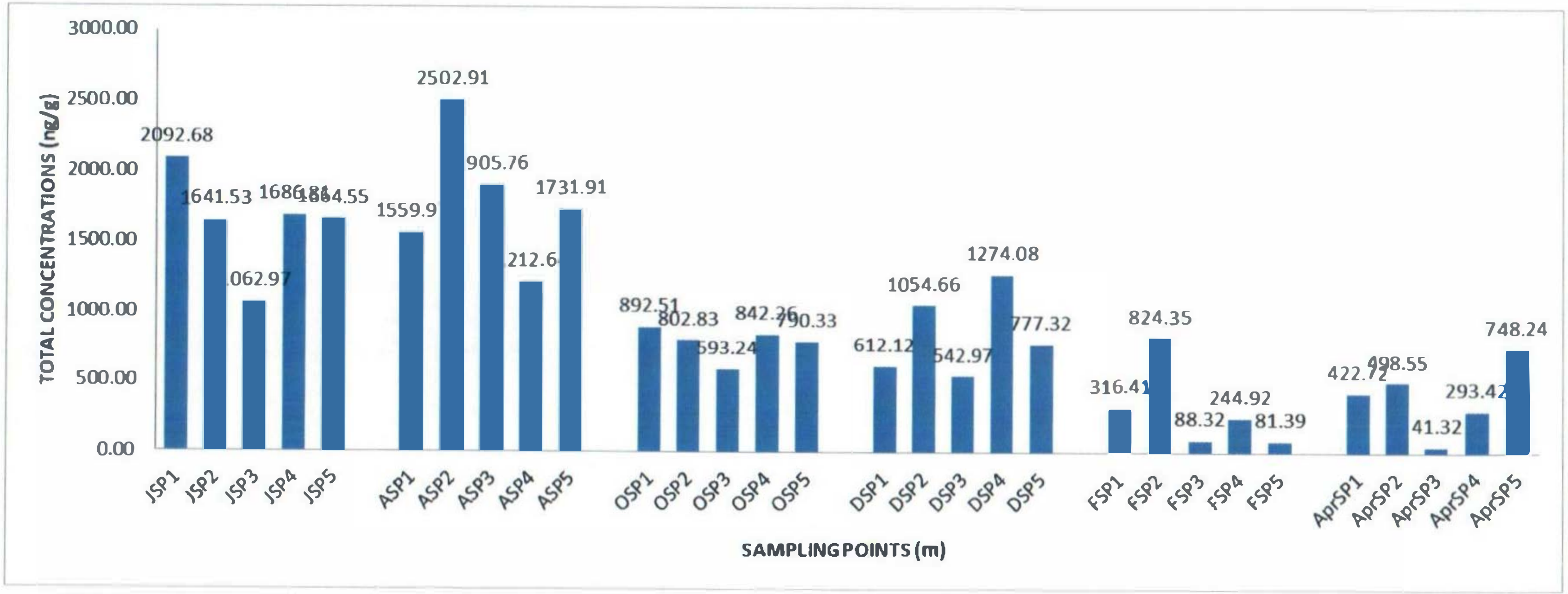

FIG. 21 a: Total concentration of n-alkanes in SPM

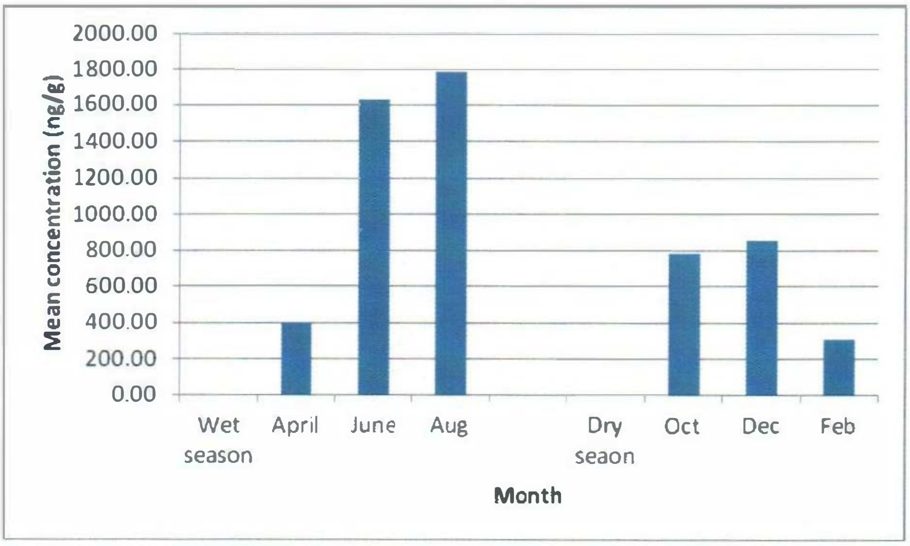

FIG. 21 b: Monthly mean concentrations of n-alkanes in SPM

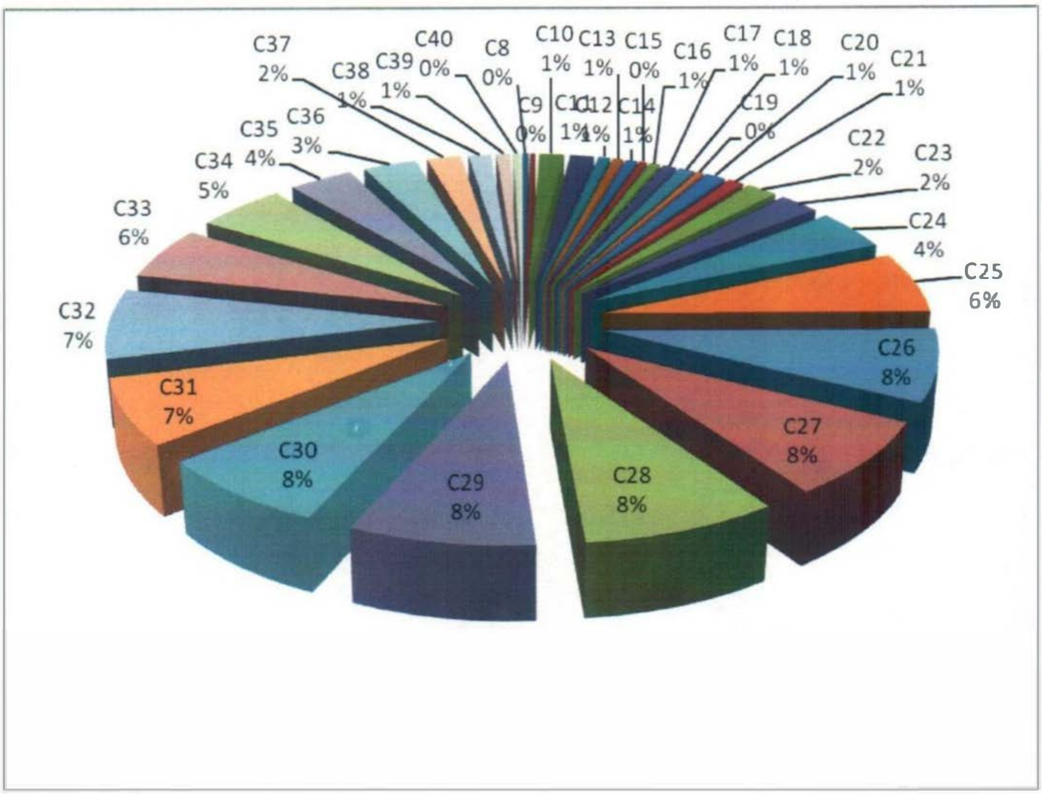

FIG. 22: Percentage composition of individual n-alkanes relative to total n-alkanes in SPM

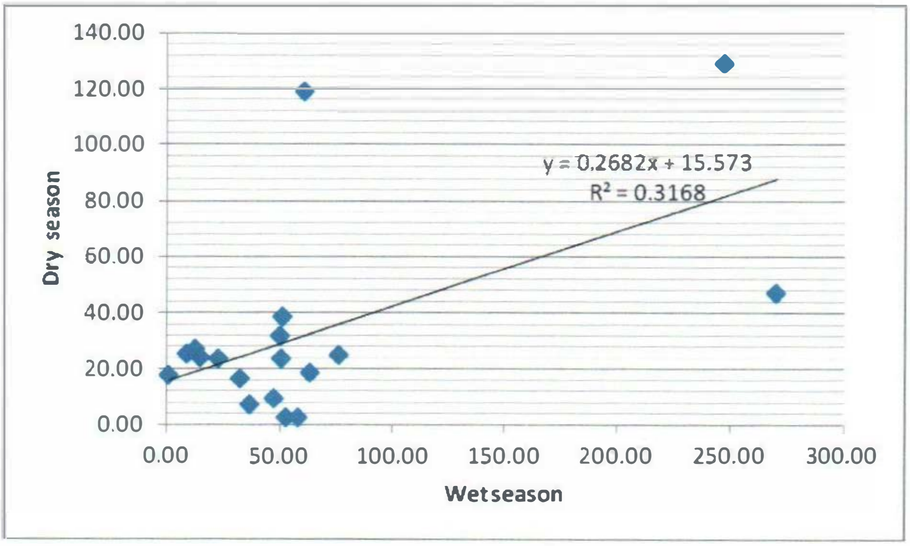

FIG. 23: Correlation between concentrations of n-alkanes (SPM) in the wet and dry seasons

4.10 Source analysis of n-alkanes by calculated distribution indices

n-Alkanes derive their sources within biogenic as well as anthropogenic source (Aboul-Kasim & Simomeit, 1995), in addition to being useful tools in assessing not only the sources, but also transport as well as safe storage of organic matter in the aquatic environments (Sikes *et al*, 2009). Short-chain n-alkanes comes up within algae or plankton, whereas long chain n-alkanes originate from vascular plants (Meyers, 1997). The source analysis of n-alkanes for water and SPM samples were calculated using various distribution indices as indicated below.

4.10.1 Water

TABLE 6 shows the mean diagnostic indices used in identifying the "sources of n-alkanes in water, generally, the concentration of the long chain n-alkanes (LHC>C23) were found to be higher than the short-chain n-alkanes (SHC <C23)". The LHC ranged between 0.01 ng/L at AprW3 to 6.02 ng/L at JW4 with a mean value of 2.56±1.65 ng/L, while the SHC values varied between 0.03 ng/L at AprW3 and 1.17ng/L at DW4, with a mean value of 0.35±0.30 ng/L. The LHC/SHC ratios was assesses towards determinining major grater plants/macrophyte as well as phytoplankton derived organic matter, and result obtained revealed values ranging from 3.57 in April to 12.69 in August indicating dominant inputs from higher plant waxes/macrophytes (Commendatore *et. al*., 2012; Oyo-Ita *et al*., 2010).

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 values which are around unity are indicative of inputs from petroleum, while values less than 1 are indicative of inputs from microorganisms and greater than 1 imply contribution from higher plants (Oyo-Ita *et al*., 2017). n-Alkanes which originates from land plant material indicated a constant odd-numbered carbon chain while even numbered carbon chain predominance is indicative of inputs from micro-organisms (Commedatore *et al.*, 2012; Kamzari *et al.*, 2014). Although contributions from petroleum sources were evident, the CPI values indicated a predominance of higher plants inputs.

In support of this source assignment, UCM values usually reflecting the contamination by petroleum hydrocarbon or extent of hydrocarbon biodegradation, were widespread in the water samples except at AprW3 (4 m) (FIG. 24 d) which was relatively pristine with little or no influence by anthropogenic pressure. UCM, also known as 'hump', is a feature frequently observed in gas chromatographic (GC) data of crude oils and extracts from organisms exposed to oils and is composed of unresolved cyclic and branched hydrocarbons. The observed bimodal UCM distributions found in JW2, DW4 and AW1 (FIG. 24 a-c, respectively) may indicate an additional source input from coal/wood utilization (Zhang *et al.*, 2004; Oyo-Ita *et al.*, 2017).

Other distribution indices which were calculated to identify the hydrocarbon sources in the samples included: Terrestrial/Aquatic Ratio (TAR), Terrestrial Marine Discriminant (TMD), Proxy Aquatic Ratio (P_{aq}) and n-alkane/C16.

TAR was used to investigate the terrigenous/aquatic mixture of hydrocarbons in a sample. In the study, TAR values were calculated using the expression:

$$TAR = [(C27+C29+C31)/(C15+C17+C19)$$

Values of these ratio greater than1 are suggestive of dominant inputs from terrestrial OM, while values less than1 imply major contribution from aquatic OM (Simoneit *et al.*, 2002). In the study, TAR values ranged between 15.66 in December to 34.64 in August, which is indicative of the predominance of terrestrial over aquatic OM inputs.

TMD is a powerful tool in differentiating between terrestrial and marine OM. and it was computed thus:

TMD = [(n-C25+ n-C27+n-C29+n-C31+n-C33)/(n-C15+n-C17+n-C19+n-C21+n-C23)

Value of TMD=1 indicates terrestrial plants inputs; < 0.5 shows marine plants input, and values between 0.5 and 1 for both terrestrial and marine inputs. The TMD values in water samples varied between 1.96 at AprW3 and 21.35 at FW1 with a mean value of 8.05±3.55 which supports the dominance of terrestrial OM.

The n-alkane proxy (P_{aq}) as proposed by Ficken *et al.* (2000) was calculated as follows:

[(C23+C25)/(C23+C25+C29+C31)]

According to these authors, "Paq values ranging between 0,01 and 0.23 are due to terrestrial plant waxes, while values ranging between 0,48 and 0.94 are due to submerged/floating species of macrophytes". The results revealed intermediate Paq mean values (0.27-0.48) implying an almost equal proportions of terrestrial and macrophytes contributions to the water samples.

The n-alkanes/C16 ratio was also calculated to determine the relative proportion of biogenic and anthropogenic sources of n-alkanes in the water sample. Syakti *et al.* (2013) stated that values of n-alkanes/C16 greater than 50 suggest biogenic origin, whereas values less than 15 indicate petrogenic origin. The result obtained in the present study showed mean values ranging from 90.40 to 637.18 which imply that the water samples were dominated by biogenic over anthropogenic inputs.

TABLE 6

Concentrations of n-alkanes (ng/L) and calculated distribution indices in water collected from the Cross River estuary

Components	Σ C8-C40	SHC	LHC	LHC/SHC	CPI	TAR	Paq	Σn-alkanes/C16
JUNE	4.78	0.59	4.04	7.42	1.05	21.60	0.48	503.08
AUG	4.81	0.45	4.23	12.69	1.15	34.64	0.39	637.18
OCT	2.56	0.27	2.23	8.54	1.09	16.86	0.33	90.40
DEC	3.14	0.46	2.60	6.75	1.12	15.66	0.38	151.32
FEB	1.91	0.24	1.64	7.52	1.21	17.28	0.38	165.69
APR	0.72	0.11	0.59	3.57	1.26	17.44	0.27	176.66

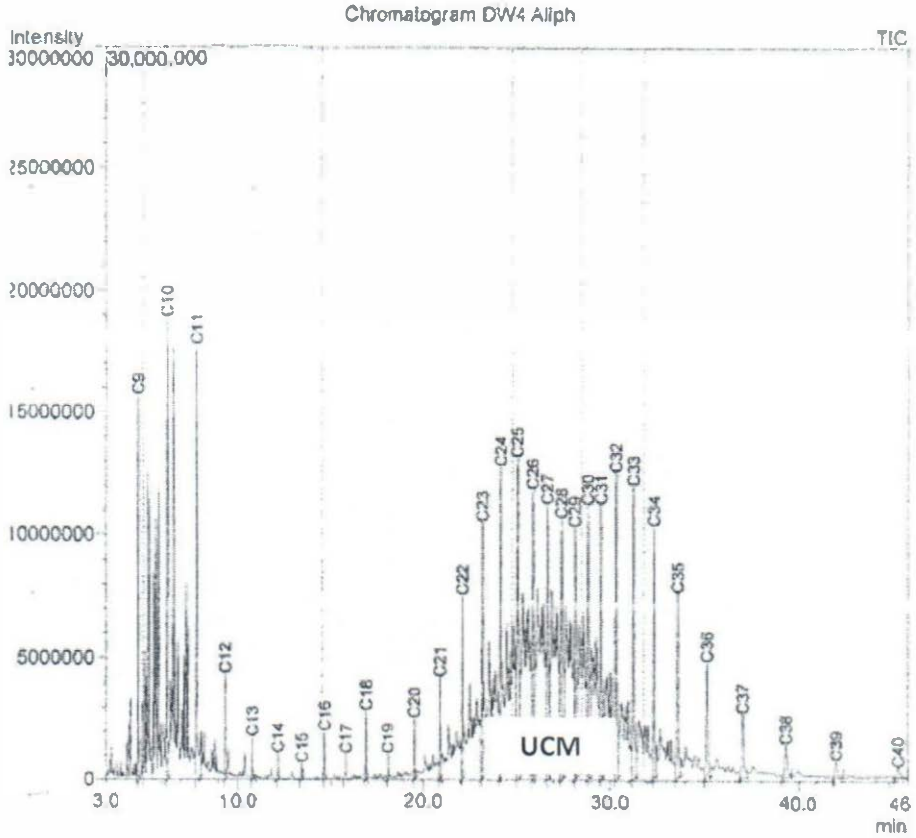

FIG. 24 a: Gas chromatograms of n-alkanes from the Cross River estuary

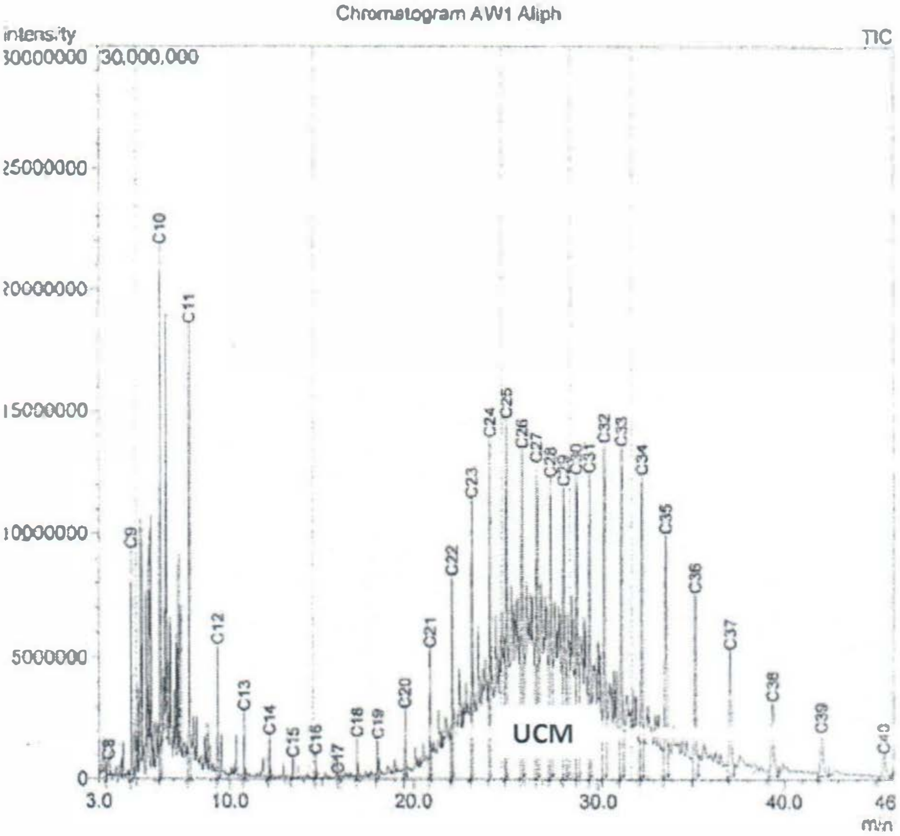

FIG. 24 b: Gas chromatograms of n-alkanes from the Cross River Estuary

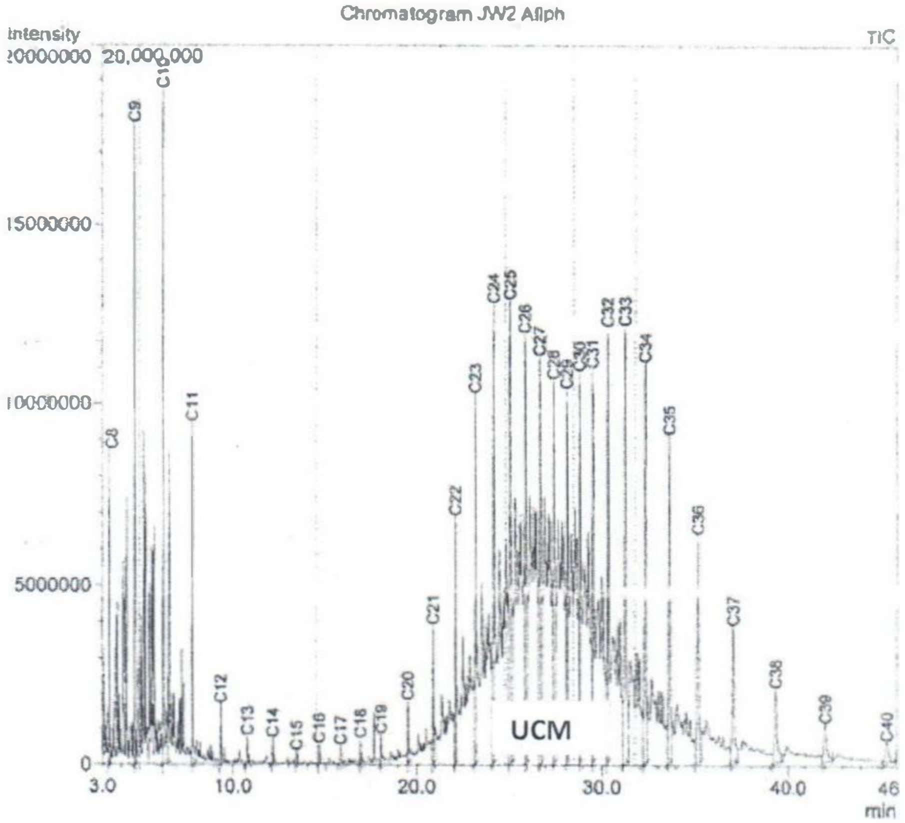

FIG. 24 c: Gas chromatograms of n-alkanes from the Cross River estuary

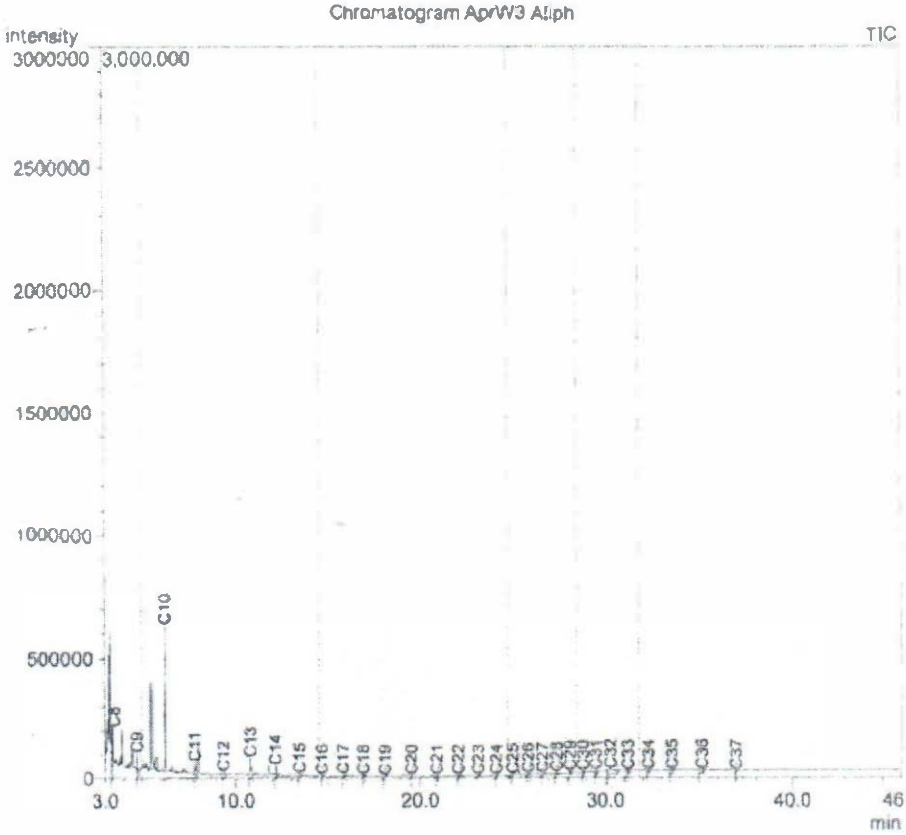

FIG. 24 d: Gas chromatograms of n-alkanes from the Cross River estuary

4.10.2 SPM

Result of n-alkane distribution indices as shown in TABLE 7 indicated LHC values ranging between 21.22 at AprSP3 to 2252.65 ng/g at ASP2 with a mean value of 822.00±633.15 ng/g, and the SHC values varied between 19.88 ng/g at AprSP3 to 479.18 ng/g at DSP4 with a mean value of 115.96±123.74 ng/g. LHC/SHC ratios ranged between 1.06 ng/g at AprSP3 to 22.67ng/g at ASP4 with a mean of 8.10±5.12. This shows that SPM n-alkanes at the stations were dominated by higher plants and macrophyte wax sources. CPI values in the study ranged between 0.23 at AprSP3 to 1.53 at JSP3 with a mean value of 1.11±1.10, which suggested a dominance of higher plants input. The TAR values ranged between 1.87 at AprSP1 and 80.89 at ASP4 with a mean of 20.79±10.53, since all the values are greater than1, it indicates that the n-alkanes may have originated from higher plants of terrestrial origin. The TMD values in SPM samples ranged between 1.76 at AprSP3 and 13.72 at FSP3 with a mean of 7.57±2.88 which indicated higher plants dominance. P_{aq} values from the Table ranged between 0.18 at FSP5 and 0.45ng/g at ASP2 with a mean of 0.33±0.42, suggestive of terrestrial plants input.

Ratio of Σn-alkanes/C_{16} was also determined for SPM, and results obtained indicated values ranging between 28.47 at FSP4 and 897.55 at ASP4 with a mean value of 284.15±150.27. The results revealed that the samples were dominated by biogenic inputs.

4.11 Source identification of n-alkanes by PCA

Source identification of n-alkanes was carried out using PCA as follows:

4.11.1 Water

The first principal components (PC1, PC2 and PC3) (TABLE 8) were identified through the use of eigenualue >1, that made up 84.23 % of general variance. PC1 accounted 65.23 % of general diference and hard much waight with reference to LHC n-alkanes and minor contribution from SHC (TABLE 20, FIG. 35 a), including C24, C23, C22, C34, C35, C26, C36, C37, C32, C28, C38, C21, C27, C39, C30, C25, C29, C40, C31, C19, C15, C12. Therefore, PC1 can be said to originate from a mixture of both input sources with the vascular plants input dominating. PC2 made up for 10.94 % of general variance and highly weighted by SHC including C18, C16, C17 which are associated with inputs from aquatic algae and photosynthetic bacteria (Choudhary *et al*., 2010). PC3 was moderately weighted with SHC which included C11, C12 and C8 and accounted for 8.07 % of the total variance which are associated with aquatic algae and bacteria.

4.11.2 SPM

The first three principal components (PC1, PC2 and PC3) were identified through the use of eigenvalue >1(TABLE 11, FIG. 26 a), which accounted for 84.42 % of the total variance. PC1 made up for 52.32 % of the total difference showing medium to long chain n-alkanes (C21-C39), while the second factor (PC2) accounted for 20.40 % of the total variance and had high loading of SHC (C15, C18, C19, C16, C14, C20 and C17). PC3 rep. a co-variance of 11.69 % of general diffenerence had a low loading of C20, C17 and C13. PC1, PC2 and PC3 revealed contribution of n-alkanes from mixed sources with inputs from vascular plants dominating.

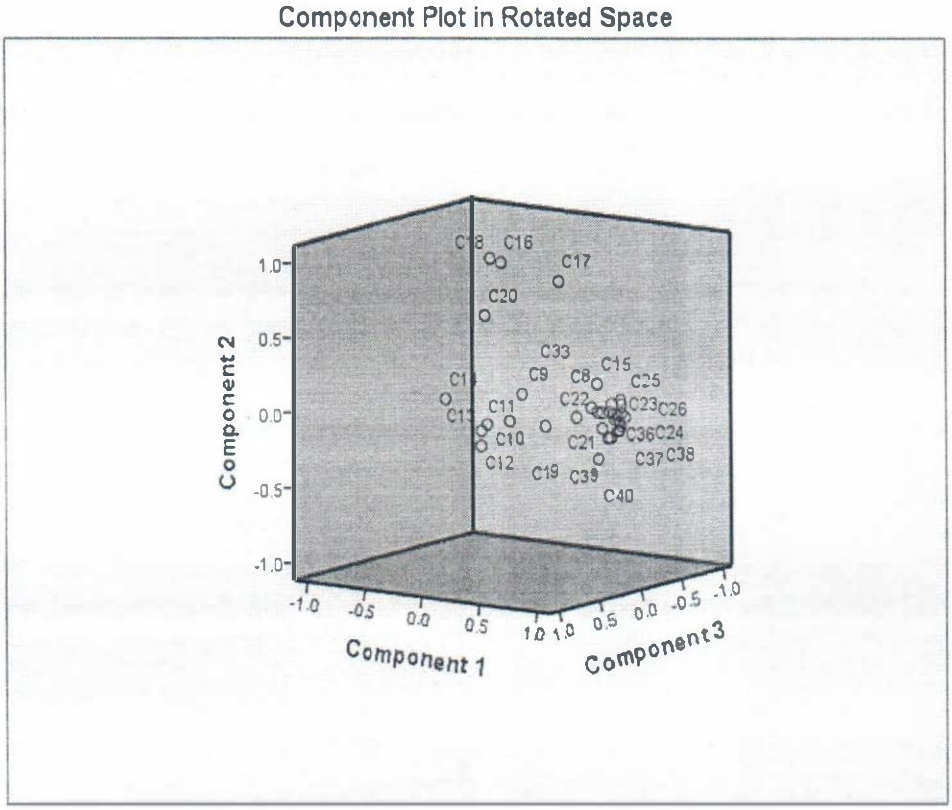

FIG. 25 a: Principal component analysis plots for all n-alkanes in water

TABLE 7

Concentrations of n-alkanes (ng/g dry wt) and calculated distribution indices in SPM from Cross River estuary

Components	ΣC8-C40	SHC	LHC	LHC/SHC	CPI	TAR	Paq	Σn-alkanes/C16
JUNE	1629.71	111.15	1475.37	13.28	1.28	30.99	0.37	413.29
AUG	1782.64	97.40	1641.27	18.19	1.13	50.15	0.39	714.29
OCT	784.24	121.38	647.39	5.71	1.02	11.84	0.32	139.66
DEC	852.23	180.26	655.18	5.25	1.12	12.58	0.33	184.34
FEB	311.08	76.79	228.49	3.11	1.16	13.12	0.27	141.98
APR	400.85	108.76	284.28	3.04	0.92	6.05	0.31	111.31

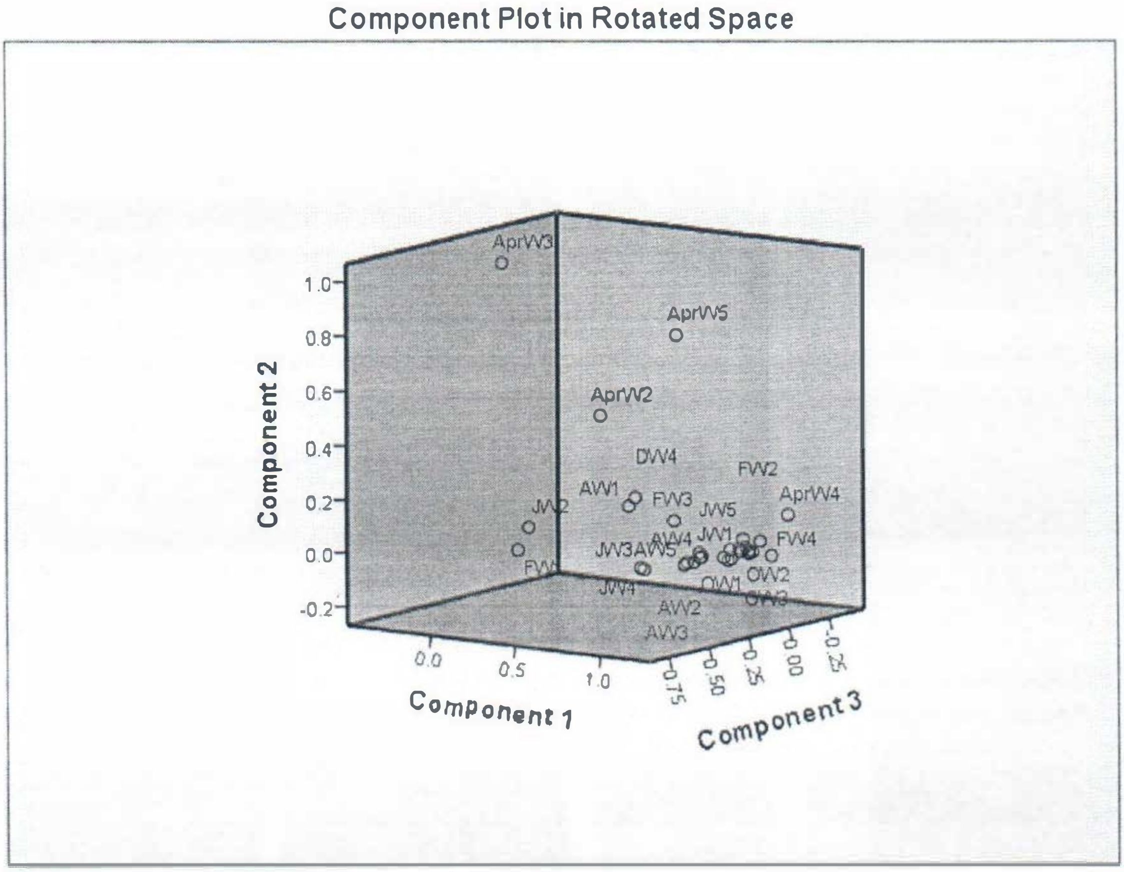

FIG. 25 b: Principal component analysis plots for variables in water

TABLE 8

Eigenvalues, total variance and factorial weight matrix explained by PCA for n-alkanes in water

	Components		
	PC 1	PC 2	PC 3
Eigenvalues	21.52	3.61	2.66
Variance %	65.22	10.94	8.07
Sources	Vascular plants	Aquatic algae/ Bacteria	Aquatic algae/ Bacteria
C24	**.984**	-.020	-.070
C23	**.980**	-.083	-.108
C22	**.978**	-.024	-.112
C34	**.977**	-.021	-.135
C35	**.971**	-.095	-.172
C26	**.969**	.047	-.164
C36	**.968**	-.116	-.178
C37	**.961**	-.118	-.190
C32	**.960**	.090	-.134
C28	**.959**	.151	-.077
C38	**.953**	-.157	-.176
C21	**.946**	-.138	-.123
C27	**.942**	.108	-.029
C39	**.942**	-.124	-.164
C30	**.924**	.187	-.120
C25	**.923**	-.035	.039
C29	**.921**	.215	-.058
C40	**.914**	-.267	-.083
C31	**.854**	.247	.096
C19	.784	.087	-.073
C15	.732	.284	-.035
C12	.703	-.185	**.627**
C10	.694	-.355	.511
C13	.681	.028	.587
C11	.655	-.263	**.639**
C9	.591	-.317	.428
C33	.538	-.064	.134
C18	.036	**.934**	.145
C16	.103	**.905**	.149
C17	.229	**.827**	-.098
C20	.436	.605	.150
C8	.503	-.114	**-.601**
C14	.487	.264	.553

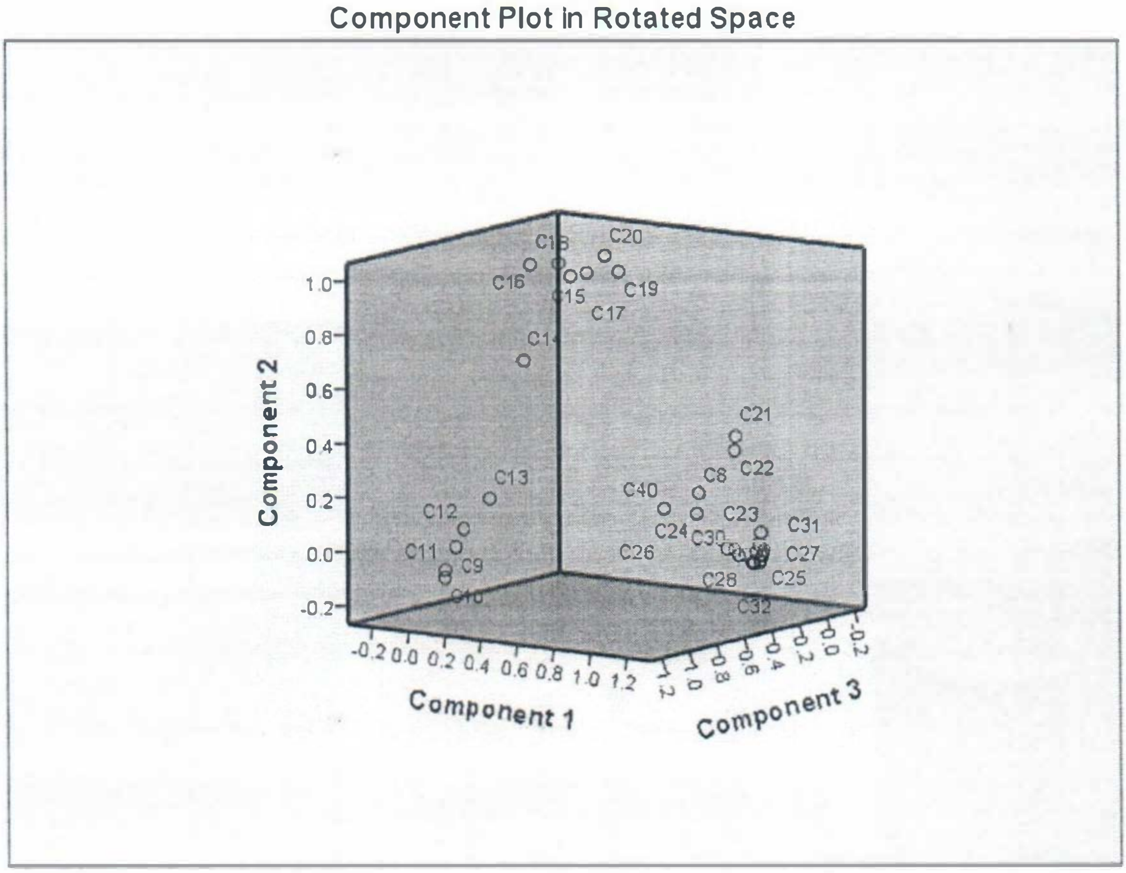

FIG. 26 a: Principal component analysis plots for n-alkanes in SPM

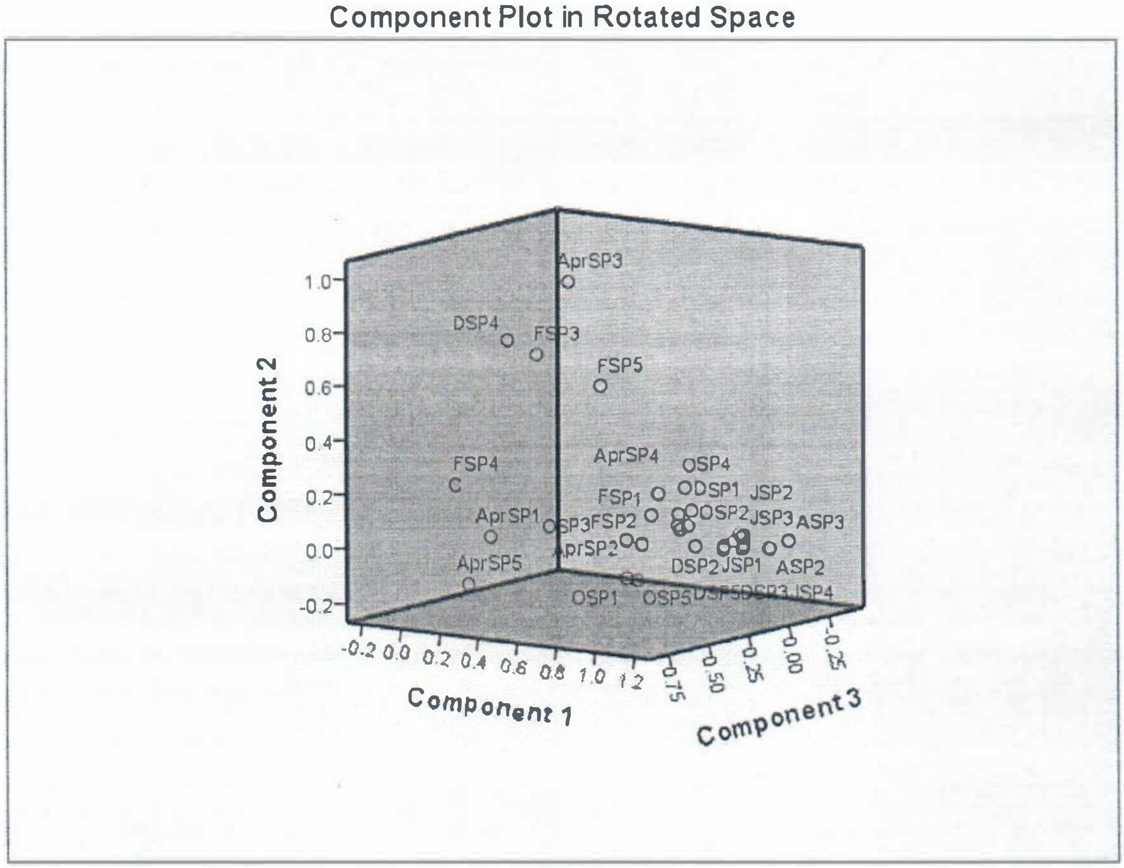

FIG. 26 b: Principal component analysis plots for variables in SPM

TABLE 9

Eigenvalues, total variance and factorial weight matrix explained by PCA for n-alkanes in SPM

	Components		
	PC 1	**PC 2**	**PC 3**
Eigenvalues	17.27	6.73	3.86
Variance %	52.32	20.40	11.69
Sources	Vascular plants	Algae/ bacteria/ macrophytes	Algae/ bacteria
C30	**.986**	-.041	.002
C32	**.986**	-.078	.030
C33	**.985**	-.072	-.020
C31	**.981**	-.015	-.035
C35	**.979**	-.064	.022
C27	**.977**	-.058	-.040
C23	**.977**	.006	-.065
C28	**.976**	-.087	-.011
C29	**.974**	-.048	-.056
C37	**.972**	-.070	.027
C39	**.969**	-.049	.085
C25	**.955**	-.089	-.036
C26	**.941**	-.037	.014
C38	**.911**	-.114	.062
C34	**.904**	-.149	.043
C36	**.876**	-.119	.071
C21	**.871**	.353	-.198
C22	.751	.227	-.264
C40	.654	.031	.138
C24	.563	.005	-.116
C8	.479	.076	-.242
C15	.153	**.924**	-.238
C18	-.191	**.872**	-.339
C19	.223	**.843**	-.432
C16	-.074	**.819**	-.378
C14	.113	**.777**	.108
C20	.016	**.773**	-.556
C17	-.082	**.722**	-.515
C13	.231	.624	.592
C11	.060	.559	**.776**
C10	.033	.519	**.769**
C9	.086	.605	**.707**
C12	.158	.631	**.705**

4.12 Relationship amongst sampling stations using cluster analysis of n-alkanes

The measurement regarding similarities and or differences within molecular composition in different samples by cluster analysis was employed in the identification of point sources of n-alkanes.

4.12.1 Water

The result of cluster analysis for water is as shown on the dendogram (FIG.27) with three distinguishable clusters observed. (a) Which comprises of stations Aprw3, AprW5, AprW2, and, FW3 combined first with the smallest distance, and increased to stations OW5, DW3, JW5, FW2, OW2, DW5, OW4, DW2 and AprW1, then finally to FW4 and AprW4, indicating moderate to long chain n-alkanes (C21-C40) related to mix sources of algae/bacteria and vascular plants inputs. The second cluster (b) as observed at AW3 and AW4 with the shortest distance which extended to OW3, FW5, OW1, and DW1, the distance further increased to JW1, AW2, AW5, and JW3. These, according to the PCA was indicative of SHC (C14- C20) related to inputs from aquatic algae and bacteria. Finally, the third cluster (c) comprised of AW1, DW4, JW2, with great similarity which increased to JW4 and FW1which were dominated by algae and bacteria source inputs.

4.12.2 SPM

Result of cluster analysis employed in the SPM classification of the various stations into specific regions with defined characteristics is as shown in the dendogram below (FIG. 28). The complete linkage method indicated that the first cluster (a) which comprised of stations FSP3, FSP5, AprSP3, FSP1, AprSP4, FSP4, and AprSP1were combined first with the smallest distance (or great similarity) between them and similar source characteristics indicating moderate to long chain n-alkanes (C21-C39) derived from vascular plants inputs with minor contribution from aquatic algae and bacteria. The combining distances increased to stations OSP1, DSP2, OSP2, DSP1, DSP3, AprSP2, OSP2, DSP3, AprSP2, OSP2, DSP5, OSP4, FSP2 and AprSP5. Stations OSP5 and DSP4 combined at a great distance to the first cluster showing great dissimilarity in source characteristics. The second cluster (b) comprised of JSP3, ASP4, JSP2, JSP5, JSP4, ASP5, ASP1, JSP1, ASP3 and ASP2 indicating SHC derived from aquatic microorganisms.

4.13 Effects of hydrological cycles and anthropogenic activities on n-alkane distribution

The mean concentrations of n-alkanes in water and SPM throughout the period of study was found to be higher in the wet season with mean values of 1.56±1.40 ng/L and 577.76±588.16 ng/g respectively, compared to values in the dry season which were 1.15±1.11 ng/L and 295.08±250.88 ng/g, respectively. Also, LHC "concentrations were higher in the wet season than in the dry season". Cmax showed seasonal changes in the two seasons with water having C10 and C25 in the wet season and C16, C18 and C27 in the dry season. SPM wet season showing Cmax at C10, C21 and C27, while Cmax in the dry season were C10, C18, C28 and C29 and Cmax for sediments wet season C8, C10 and C29, and dry season C10, C29 and C31 (APPENDIX 5). Yandav *et al.* (2013) stated that higher levels of C29 n-alkanes can be ascribed to increased frequency of dust storms since C29 is indicative of n-alkanes arising from road dust with surface deposited plant litter and accumulated vehicle/industrial emissions. The prevalence of C29 in the dry season in water, SPM and sediments is suggestive of inputs from harmattan dust carrying debris of terrestrial plants into the estuary. The seasonal variation of n-alkanes in the samples with the LHC showing a dominant trend could be attributed to input of terrigenous plant waxes due to large amounts of green leaves and also vegetation debris been washed off from the land into the estuary in the wet season.

Unresolved complex mixture (UCM) represents components resistant to weathering and bacterial breakdown and its presence in chromatograms has frequently been taken as strong evidence for petroleum pollution (Frysinger *et al.*, 2003). The anthropogenic contribution of n-alkanes is evident from the presence of UCM in most of the samples analysed (FIG. 29 a and b). CPI values of n-alkanes in water and SPM had values greater than1 dominating with the highest values of 1.75 (AprW3) and 1.53 (JSP3), respectively, in the wet season. This is indicative of greater inputs from higher plants sources entering the estuary via surface run-off from land. CPI values less than 1 and around unity was also observed indicating minor contribution from micro-organisms and petroleum sources indicating impact of anthropogenic activities resulting from boat/ship traffic, oil transportation and spillage etc. Kang *et al.* (2016) stated that low molecular n-alkanes are usually related to anthropogenic activities such as fossil fuel combustion. Biomass burning have also been found to generate large amounts of n-alkanes especially HMW alkanes (Yandav et al., 2013). The large amount of LHC n-alkanes in the samples may be as a result of the heavy roasting activity involving burning of wood around the Parrot Island, and also boat and shipping activities in the estuary.

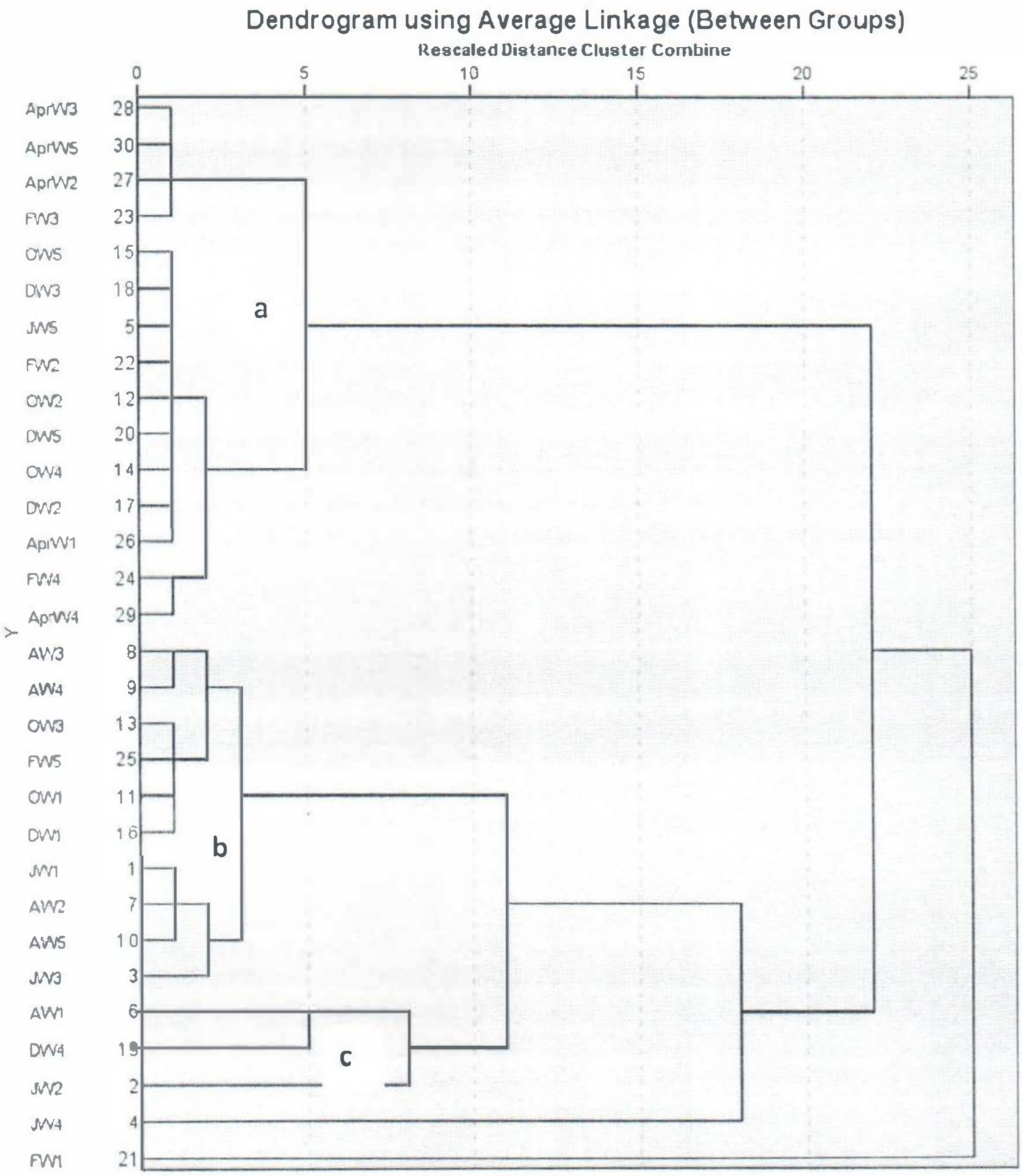

FIG. 27: Dendogram plot of n-alkanes in water

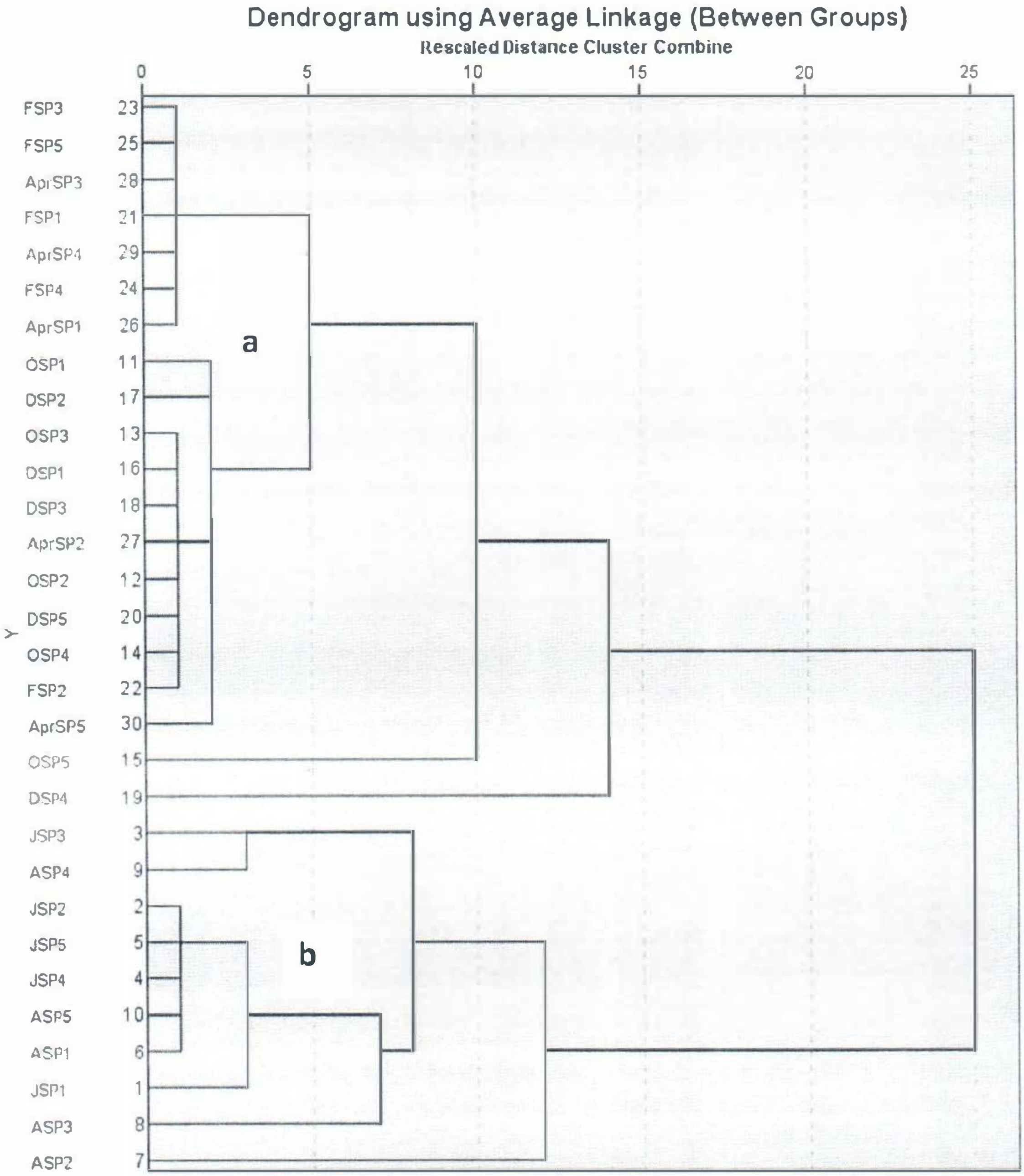

FIG. 28: Dendogram plot of n-alkanes in SPM

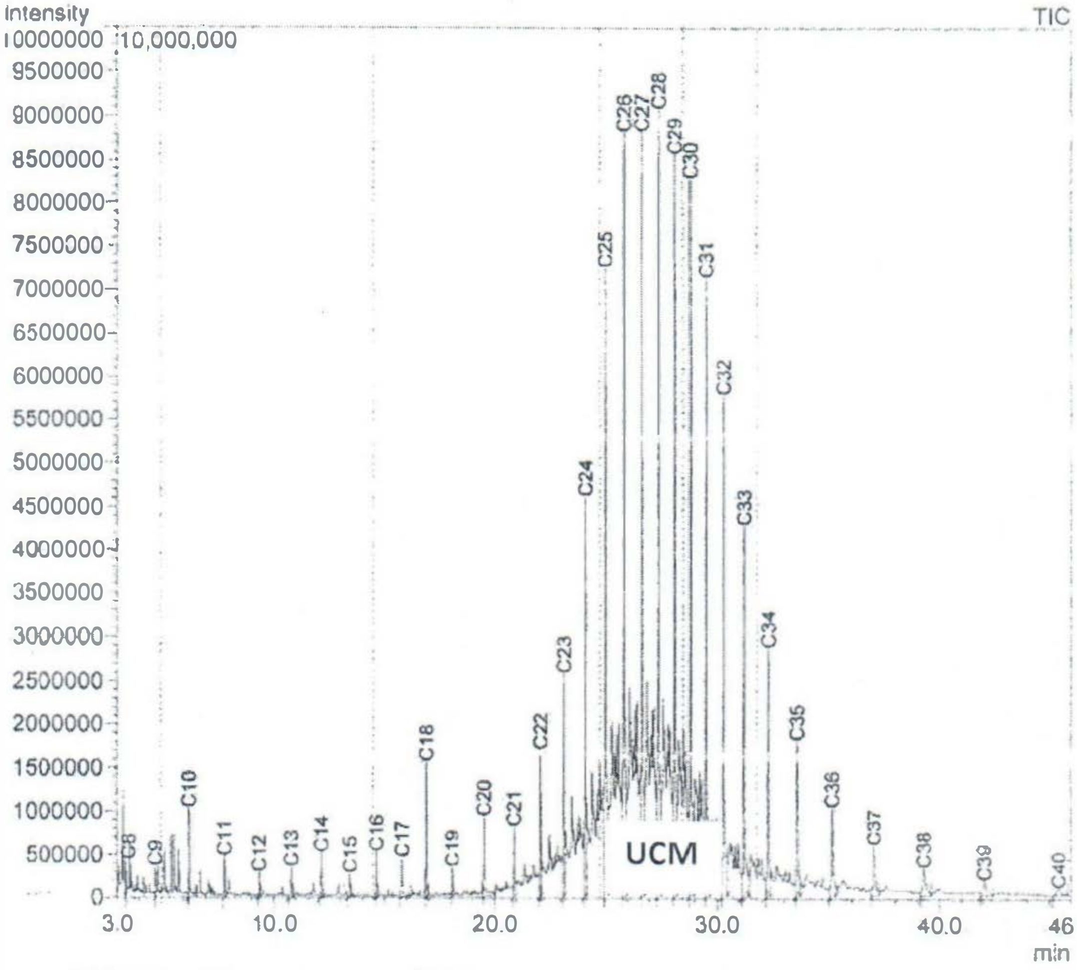

FIG. 29 a: Chromatogram of FW1

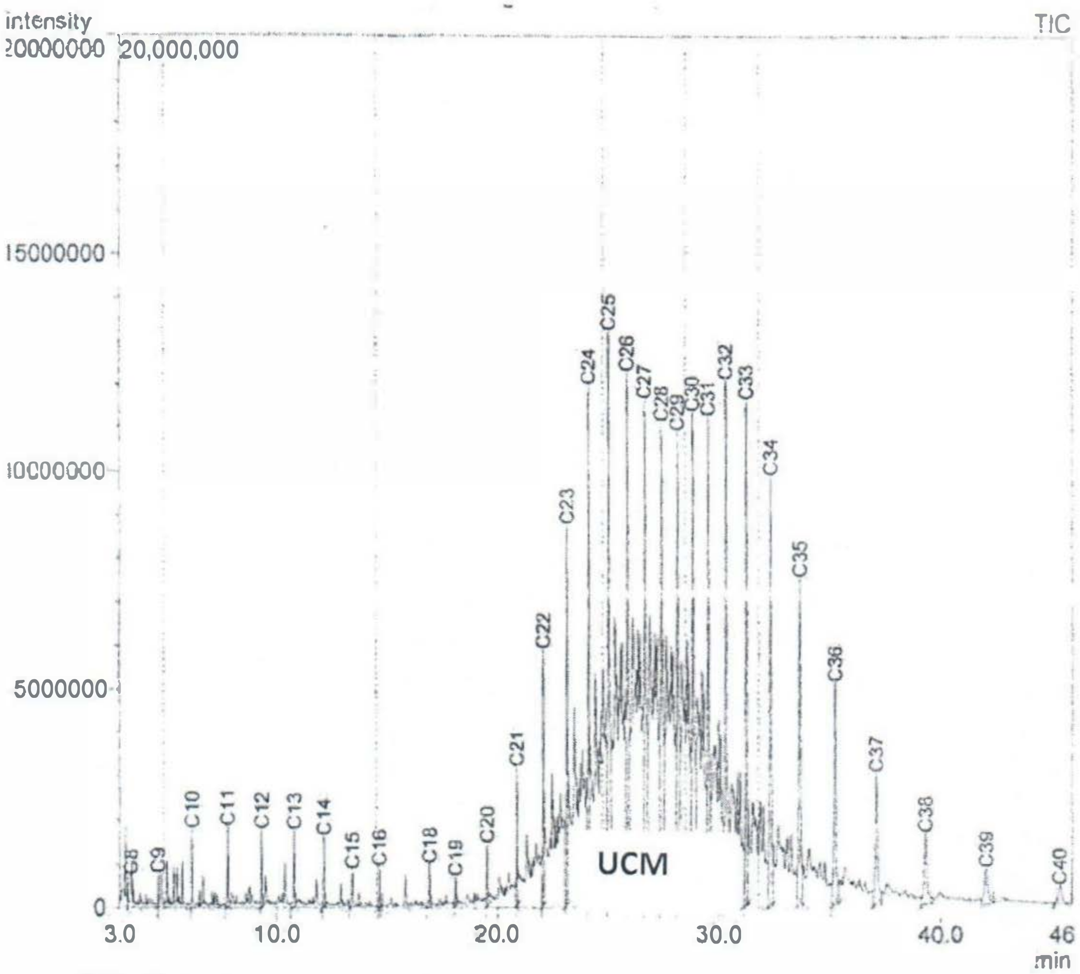

FIG. 29 b: Chromatogram of ASP2

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study investigated the estuarine behavior of U.S. EPA 16 priority PAHs and n-alkanes as well as their risk potentials and association with hydrological as well as anthro-pogenic actions from estuary within Cross River. There was a remarkable seasonal variation in PAH concentrations within wet as well as dry seasons, as the concentrations in the wet season were higher than that of the dry season during the sampling period. For instance, the TPAH concentrations for water were found to be higher in the dry season than in the wet season, which could be as a result of dilution effect. The TPAH concentrations in SPM were higher in the wet season than the dry season, most likely attributable to the increased input from domestic and industrial wastes entering the estuary through torrential rainfall and surface run-offs. PAH compositions in water and SPM revealed the following trends according to the number of rings: 2>3>5>4>6 rings and 2>3>4>5>6 rings, respectively. LPAH (2-3 rings) were predominant, accounting for over 80% of TPAH concentrations which is an indication of major inputs from petroleum products to the estuary. Furthermore, there were moderate levels of 5-ring PAHs in water and SPM, accounting for over 8 %, with BaP dominating. These levels could be attributed to wood burning as a result of roasting activities by the Edik-Ekpu community located around the Parrot Island, which is noted for roasted fish business, and also fumes from automobile exhaust, which were released into the environment from boat/ship transport. In terms of individual PAH species, Naph, usually found in coal tar and petroleum recorded the highest concentration in water and SPM throughout the period under study.

Some isomeric ratios such LPAH/HPAH, Flu/(Flu+Pyr), Ant/(Ant+Phe) and % ΣCOMB/ΣPAH were employed in source identification of PAHs. The results obtained indicated a predominance of petrogenic PAHs over Pyrogenic PAHs in the estuary. The low to moderate values of ΣCOMB/ΣPAH showed moderate combustion processes effected the PAHs concentration in the study area. Changes in environmental factors such as suspended sediments concentration, salinity as well as temperature greatly influenced the distribution of PAHs within estuary. The health risk assessments carried out on SPM using environmental thresholds such as BaPE and TEQs were considerably low, indicating no adverse effects on resident flora and fauna. Furthermore, values recorded for ERL and ERM revealed that all the PAHs values in SPM were less than ERL values except Naphthalene which had a value greater than ERL but less than ERM.

The total concentrations of n-alkanes in water and SPM were higher in the wet season than the dry season, with the inputs from vascular plants (Cmax C_{27}, C_{29} and C_{31}) dominating. Some n-alkane distribution indices such as: LHC/SHC, P_{aq}, TAR, Σn-alkanes/C16 and CPI, were calculated and the results obtained indicated that the n-alkanes originated from both marine and terrestrial origin with inputs from terrestrial sources dominating. UCM profiles (JW2, ASP2, AW1, DW4 and FW1) recorded in some samples were higher in the wet season samples, indicating the presence of petroleum inputs to the area, whereas samples with little or no UCM profiles (AprW3) are indicative of a pristine environment.

A more robust PCA for PAHs in water and SPM accounted for 63 % and 65.38 % of the total variance respectively, heavily weighted by 2-3 rings PAHs. PCA of n-alkanes in water and SPM explained 84.24 % and 84.42 % of the total variance, respectively, with high loading of LHC. Pearson correlation and t-test were used to determine the relationships between the concentrations of hydrocarbon in the wet and dry seasons. The results showed a significant difference between the 2 seasons.

Finally, seasonal variation in suspended sediment concentration (SSC) with temperature and salanity alterations, and also human activities example bush/wood burning, fish roasting and emissions from ships and boats, has been found to influence the concentrations of hydrocarbons in the estuary. The biogeochemical processes in the estuary has affinity towards changes within hydrology as well as activities of human, that could require another with reference to global climate change.

5.2 Recommendations

These recommendations below were made for further studies:

1. Research on impact of human activities and hydrology should be carried out on other areas of the estuary, especially locations around the banks where these activities are severe.
2. The study of biota from the estuary, to assess the risk potential posed by PAHs is highly recommended.
3. Government should step-up awareness campaigns through health and safety agencies on dangers of prolonged exposure to PAHs and possible means of remediating them.

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APPENDIX I

Total concentrations of PAHs (ng/L) in water from the Cross river estuary

Stations	Naph	Acthy	Ace	Fl	Phe	Ant	Pyr	Flu	BaA	Chr	BkF	BbF	BaP	BghiP	DahA	InP	Total (ng/L)
JW1	0.69	0.02	0.01	0.04	0.07	0.07	0.03	0.03	0.00	0.00	0.00	0.00	0.17	0.18	0.00	0.07	1.37
JW2	0.64	0.02	0.01	0.06	0.11	0.08	0.05	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.24	1.22
JW3	0.75	0.02	0.01	0.05	0.09	0.07	0.05	0.02	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.16	1.31
JW4	0.81	0.01	0.01	0.04	0.08	0.08	0.05	0.02	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.11	1.38
JW5	0.91	0.02	0.04	0.06	0.13	0.04	0.05	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	1.50
TOTAL	3.81	0.09	0.09	0.24	0.47	0.34	0.23	0.12	0.00	0.00	0.00	0.00	0.42	0.18	0.00	0.78	6.78
MEAN	0.76	0.02	0.02	0.05	0.09	0.07	0.05	0.02	0.00	0.00	0.00	0.00	0.08	0.04	0.00	0.16	1.36
AW1	0.46	0.01	0.01	0.02	0.05	0.05	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.69
AW2	0.62	0.01	0.02	0.03	0.05	0.06	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.87
AW3	0.54	0.00	0.01	0.02	0.03	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.10	0.05	0.01	0.83
AW4	0.19	0.01	0.02	0.03	0.05	0.04	0.03	0.02	0.00	0.00	0.00	0.00	0.26	0.05	0.00	0.03	0.72
AW5	0.56	0.01	0.02	0.03	0.04	0.05	0.02	0.01	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.91
TOTAL	2.36	0.04	0.08	0.14	0.22	0.22	0.12	0.08	0.00	0.00	0.00	0.00	0.43	0.15	0.10	0.08	4.02
MEAN	0.47	0.01	0.02	0.03	0.04	0.04	0.02	0.02	0.00	0.00	0.00	0.00	0.09	0.03	0.02	0.02	0.80
OW1	0.42	0.01	0.01	0.03	0.11	0.06	0.05	0.03	0.00	0.00	0.00	0.00	0.13	0.00	0.00	0.00	0.85
OW2	0.52	0.01	0.01	0.03	0.08	0.06	0.04	0.02	0.01	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.87
OW3	0.43	0.00	0.01	0.02	0.03	0.03	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.59
OW4	0.57	0.01	0.02	0.03	0.10	0.07	0.05	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.03	0.93
OW5	0.46	0.00	0.01	0.02	0.06	0.02	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.01	0.68
TOTAL	2.40	0.03	0.06	0.12	0.38	0.24	0.19	0.12	0.01	0.00	0.10	0.00	0.13	0.07	0.03	0.05	3.93
MEAN	0.48	0.01	0.01	0.02	0.08	0.05	0.04	0.02	0.00	0.00	0.02	0.00	0.03	0.01	0.01	0.01	0.79
DW1	0.67	0.01	0.02	0.04	0.11	0.05	0.04	0.02	0.00	0.00	0.00	0.00	0.08	0.02	0.00	0.00	1.05
DW2	0.33	0.00	0.01	0.02	0.08	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.51
DW3	0.66	0.02	0.02	0.04	0.17	0.04	0.05	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	1.14
DW4	3.54	0.01	0.01	0.04	0.08	0.04	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	3.98
DW5	0.39	0.01	0.01	0.02	0.05	0.03	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.55
TOTAL	5.60	0.05	0.07	0.16	0.49	0.16	0.15	0.09	0.00	0.00	0.00	0.00	0.11	0.02	0.00	0.34	7.23
MEAN	1.12	0.01	0.01	0.03	0.10	0.03	0.03	0.02	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.07	1.45
FW1	0.59	0.01	0.02	0.03	0.05	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.74
FW2	0.52	0.01	0.01	0.03	0.05	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.66
FW3	0.58	0.00	0.01	0.02	0.07	0.03	0.03	0.01	0.00	0.00	0.00	0.00	0.07	0.01	0.01	0.00	0.84
FW4	0.50	0.01	0.02	0.03	0.12	0.03	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.77
FW5	0.51	0.01	0.02	0.06	0.13	0.05	0.03	0.01	0.00	0.00	0.00	0.00	0.20	0.00	0.00	0.00	1.01
TOTAL	2.69	0.04	0.08	0.16	0.41	0.13	0.13	0.06	0.00	0.00	0.00	0.00	0.27	0.01	0.01	0.04	4.03
MEAN	0.54	0.01	0.02	0.03	0.08	0.03	0.03	0.01	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.01	0.81
Apr W1	0.48	0.01	0.00	0.03	0.05	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.69
AprW2	0.27	0.00	0.00	0.01	0.03	0.01	0.00	0.00	0.00	0.01	0.04	0.03	0.00	0.09	0.04	0.01	0.56
AprW3	0.18	0.01	0.01	0.02	0.05	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.40
AprW4	0.16	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.23
AprW5	0.50	0.02	0.03	0.04	0.09	0.03	0.04	0.03	0.03	0.00	0.26	0.00	0.14	0.00	0.00	0.00	1.21
TOTAL	1.59	0.04	0.05	0.12	0.23	0.09	0.07	0.05	0.03	0.01	0.31	0.03	0.22	0.09	0.04	0.12	3.10
MEAN	0.32	0.01	0.01	0.02	0.05	0.02	0.01	0.01	0.01	0.00	0.06	0.01	0.04	0.02	0.01	0.02	0.62

Total concentrations of PAHs (ng/L) in water in the wet season

ths	Apr W1	AprW2	AprW3	AprW4	AprW5	JW1	JW2	JW3	JW4	JW5	AW1	AW2	AW3	AW4	AW5	Total(ng/L)
Naph	0.48	0.27	0.18	0.16	0.50	0.69	0.64	0.75	0.81	0.91	0.46	0.62	0.54	0.19	0.56	7.76
Acthy	0.01	0.00	0.01	0.00	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.01	0.00	0.01	0.01	0.17
Ace	0.00	0.00	0.01	0.00	0.03	0.01	0.01	0.01	0.01	0.04	0.01	0.02	0.01	0.02	0.02	0.22
Fl	0.03	0.01	0.02	0.01	0.04	0.04	0.06	0.05	0.04	0.06	0.02	0.03	0.02	0.03	0.03	0.50
Phe	0.05	0.03	0.05	0.01	0.09	0.07	0.11	0.09	0.08	0.13	0.05	0.05	0.03	0.05	0.04	0.92
Ant	0.02	0.01	0.02	0.01	0.03	0.07	0.08	0.07	0.08	0.04	0.05	0.06	0.02	0.04	0.05	0.65
Pyr	0.02	0.00	0.01	0.00	0.04	0.03	0.05	0.05	0.05	0.05	0.03	0.03	0.02	0.03	0.02	0.43
Flu	0.01	0.00	0.01	0.00	0.03	0.03	0.02	0.02	0.02	0.03	0.02	0.02	0.01	0.02	0.01	0.25
BaA	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
Chr	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
BkF	0.00	0.04	0.00	0.00	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.31
BbF	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
BaP	0.00	0.00	0.08	0.00	0.14	0.17	0.00	0.08	0.18	0.00	0.00	0.00	0.00	0.26	0.17	1.08
BghiP	0.00	0.09	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.05	0.00	0.42
DahA	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.05	0.00	0.00	0.13
InP	0.08	0.01	0.00	0.02	0.00	0.07	0.24	0.16	0.11	0.21	0.00	0.03	0.01	0.03	0.00	0.98
Total(ng/L)	0.69	0.56	0.40	0.23	1.21	1.37	1.22	1.31	1.38	1.50	0.69	0.87	0.83	0.72	0.91	13.90
Mean (ng/L)	0.04	0.04	0.03	0.01	0.08	0.09	0.08	0.08	0.09	0.09	0.04	0.05	0.05	0.04	0.06	0.87
STD	0.12	0.07	0.05	0.04	0.13	0.17	0.16	0.18	0.20	0.23	0.11	0.15	0.13	0.07	0.14	1.87

Total concentrations of PAHs (ng/L) in water in the dry season

MONTHS	OW1	OW2	OW3	OW4	OW5	DW1	DW2	DW3	DW4	DW5	FW1	FW2	FW3	FW4	FW5	Total(ng/L)
Naph	0.42	0.52	0.43	0.57	0.46	0.67	0.33	0.66	3.54	0.39	0.59	0.52	0.58	0.50	0.51	10.69
Acthy	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.12
Ace	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.02	0.21
Fl	0.03	0.03	0.02	0.03	0.02	0.04	0.02	0.04	0.04	0.02	0.03	0.03	0.02	0.03	0.06	0.44
Phe	0.11	0.08	0.03	0.10	0.06	0.11	0.08	0.17	0.08	0.05	0.05	0.05	0.07	0.12	0.13	1.28
Ant	0.06	0.06	0.03	0.07	0.02	0.05	0.00	0.04	0.04	0.03	0.02	0.01	0.03	0.03	0.05	0.53
Pyr	0.05	0.04	0.02	0.05	0.03	0.04	0.02	0.05	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.47
Flu	0.03	0.02	0.01	0.03	0.02	0.02	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.26
BaA	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Chr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BkF	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10
BbF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaP	0.13	0.00	0.00	0.00	0.[illegible]0	0.08	0.03	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.20	0.51
BghiP	0.00	0.00	0.02	0.00	0.04	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.10
DahA	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.04
InP	0.00	0.00	0.01	0.03	0.01	0.00	0.00	0.11	0.22	0.00	0.00	0.01	0.00	0.03	0.00	0.43
Total(ng/L)	0.85	0.87	0.59	0.93	0.68	1.05	0.51	1.14	3.98	0.55	0.74	0.66	0.84	0.77	1.01	15.19
Mean (ng/L)	0.05	0.05	0.04	0.06	0.04	0.07	0.03	0.07	0.25	0.03	0.05	0.04	0.05	0.05	0.06	0.95
STD	0.11	0.13	0.11	0.14	0.11	0.16	0.08	0.16	0.88	0.10	0.15	0.13	0.14	0.12	0.13	2.62

APPENDIX 2

Concentrations of PAHs (ng/g) in SPM from the Cross River estuary

Stations	Naph	Acey	Ace	Fl	Phe	Ant	Pyr	Flu	BaA	Chr	BkF	BbF	BaP	B(ghi)P	DahA	InP	Total(ng/g)
JSP1	13.09	0.20	0.49	0.72	1.25	1.20	1.11	0.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.88	20.35
JSP2	19.72	0.24	0.48	0.85	2.47	1.18	1.61	0.79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.60	27.94
JSP3	28.58	0.58	0.39	1.51	4.25	1.48	2.12	1.10	0.00	0.00	0.00	0.00	0.00	0.52	0.00	0.00	40.52
JSP4	12.16	0.17	0.46	0.97	3.67	1.15	2.33	1.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.19	23.27
JSP5	26.34	0.29	0.56	0.70	1.27	1.05	1.04	0.48	0.00	0.00	0.00	0.00	4.61	0.00	0.00	0.00	36.33
TOTAL	99.89	1.48	2.37	4.76	12.92	6.06	8.21	3.94	0.00	0.00	0.00	0.00	4.61	0.52	0.00	3.67	148.41
MEAN	19.98	0.30	0.47	0.95	2.58	1.21	1.64	0.79	0.00	0.00	0.00	0.00	0.92	0.10	0.00	0.73	29.68
STD	7.47	0.16	0.06	0.33	1.37	0.16	0.58	0.34	0.00	0.00	0.00	0.00	2.06	0.23	0.00	0.81	8.56
ASP1	7.37	0.12	0.26	0.46	0.64	0.44	0.45	0.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.32	11.33
ASP2	3.57	0.06	0.02	0.22	0.32	0.38	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	1.03	0.09	5.74
ASP3	12.90	0.17	0.51	0.69	0.78	0.47	0.83	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	16.82
ASP4	7.05	0.08	0.21	0.35	0.43	0.25	0.33	0.34	0.00	0.00	3.13	0.00	2.53	0.00	0.00	0.60	15.30
ASP5	3.77	0.09	0.02	0.22	0.32	0.25	0.05	0.08	0.00	0.00	0.39	0.24	0.00	0.10	0.00	0.06	5.60
TOTAL	34.66	0.52	1.03	1.94	2.50	1.80	1.69	1.16	0.00	0.00	3.52	0.24	2.53	0.10	1.03	2.07	54.79
MEAN	6.93	0.10	0.21	0.39	0.50	0.36	0.34	0.23	0.00	0.00	0.70	0.05	0.51	0.02	0.21	0.41	10.96
OSP1	8.04	0.08	0.26	0.42	0.73	0.82	0.63	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.62	11.97
OSP2	9.98	0.07	0.31	0.44	0.51	0.32	0.60	0.27	0.00	0.00	0.63	0.00	0.00	0.42	0.00	0.00	13.57
OSP3	9.75	0.00	0.50	0.73	1.09	0.91	0.70	0.41	0.00	0.00	1.88	0.00	0.00	0.00	0.00	0.27	16.23
OSP4	12.13	0.16	0.45	0.57	1.06	1.10	0.94	0.58	0.00	0.00	2.37	1.18	0.00	0.49	0.00	0.02	21.06
OSP5	11.76	0.08	0.36	0.49	0.74	0.37	0.84	0.42	0.00	0.00	1.52	0.00	0.00	0.00	0.00	0.00	16.58
TOTAL	51.66	0.40	1.89	2.65	4.13	3.52	3.71	2.05	0.00	0.00	6.41	1.18	0.00	0.91	0.00	0.90	79.41
MEAN	10.33	0.08	0.38	0.53	0.83	0.70	0.74	0.41	0.00	0.00	1.28	0.24	0.00	0.18	0.00	0.18	15.88
DSP1	11.33	0.19	0.43	0.52	0.56	0.18	0.55	0.25	0.00	0.00	0.00	0.00	1.19	0.00	0.00	0.15	15.36
DSP2	16.44	0.29	0.71	0.69	0.55	0.64	0.82	0.16	0.00	0.00	0.00	0.00	3.45	0.00	0.57	1.41	25.74
DSP3	14.96	0.19	0.55	0.62	0.68	0.97	0.83	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	18.81
DSP4	15.54	0.41	0.83	0.76	1.11	0.00	0.77	0.34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	19.75
DSP5	8.54	0.10	0.30	0.45	0.77	0.64	0.66	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.71
TOTAL	66.81	1.19	2.83	3.04	3.67	2.43	3.64	0.99	0.00	0.00	0.00	0.00	4.64	0.00	0.57	1.56	91.36
MEAN	13.36	0.24	0.57	0.61	0.73	0.49	0.73	0.20	0.00	0.00	0.00	0.00	0.93	0.00	0.11	0.31	18.27
FSP1	11.02	0.15	0.32	0.54	0.76	0.40	0.43	0.20	0.26	0.00	0.00	0.00	1.14	0.00	0.12	0.35	15.70
FSP2	3.46	0.06	0.02	0.25	0.22	0.15	0.02	0.03	0.08	0.00	0.02	0.00	0.46	0.28	0.11	0.00	5.16
FSP3	7.53	0.27	0.57	0.74	1.20	0.97	1.03	0.64	0.00	0.00	1.13	1.39	1.06	1.41	1.86	1.88	21.67
FSP4	7.67	0.07	0.20	0.33	0.38	0.25	0.26	0.10	0.00	0.00	0.00	0.00	0.88	0.35	0.21	0.17	10.86
FSP5	8.59	0.09	0.27	0.45	0.49	0.57	0.38	0.26	0.98	0.00	0.00	0.00	0.00	0.00	0.54	0.64	13.26
TOTAL	3827	0.63	1.39	2.31	3.05	2.35	2.12	1.22	1.32	0.00	1.14	1.39	3.54	2.04	2.84	3.04	6666
MEAN	7.65	0.13	0.28	0.46	0.61	0.47	0.42	0.24	0.26	0.00	0.23	0.28	0.71	0.41	0.57	0.61	13.33
AprSP1	5.35	0.09	0.09	0.40	3.45	0.64	070	0.45	0.00	0.00	1.67	1.01	0.00	1.28	0.00	0.33	15.46
AprSP2	900	0.07	0.26	0.41	0.58	0.32	0.44	0.20	0.00	0.00	0.00	0.00	1.79	0.00	0.00	0.57	13.65
AprSP3	4.81	0.09	0.04	0.37	1.97	0.25	0.54	0.32	0.00	0.00	0.00	0.00	0.83	0.00	0.00	0.10	9.32
AprSP4	12.65	0.23	0.48	1.08	10.39	2.25	2.41	1.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.56	32.26
AprSP5	9.42	0.16	0.11	0.68	6.35	0.00	1.95	1.05	0.00	0.00	0.00	0.00	0.00	0.64	0.00	1.29	21.66
TOTAL	41.23	0.64	0.98	2.94	22.74	3.47	605	3.23	0.00	0.00	1.67	1.01	2.62	1.92	0.00	3.86	9236
MEAN	8.25	0.13	0.20	0.59	4.55	0.69	1.21	0.65	0.00	0.00	0.33	0.20	0.52	0.38	0.00	0.77	18.47

Total concentrations of PAHs (ng/g dw) in SPM in the wet season

Stations	AprSP1	AprSP2	AprSP3	AprSP4	AprSP5	JSP1	JSP2	JSP3	JSP4	JSP5	ASP1	ASP2	ASP3	ASP4	ASP5	Total(ng/g)
Naph	5.35	9.00	4.81	12.65	9.42	13.09	19.72	28.58	12.16	26.34	7.37	3.57	12.90	7.05	3.77	175.78
Acey	0.09	0.07	0.09	0.23	0.16	0.20	0.24	0.58	0.17	0.29	0.12	0.06	0.17	0.08	0.09	2.64
Ace	0.09	0.26	0.04	0.48	0.11	0.49	0.48	0.39	0.46	0.56	0.26	0.02	0.51	0.21	0.02	4.38
Fl	0.40	0.41	0.37	1.08	0.68	0.72	0.85	1.51	0.97	0.70	0.46	0.22	0.69	0.35	0.22	9.64
Phe	3.45	0.58	1.97	10.39	6.35	1.25	2.47	4.25	3.67	1.27	0.64	0.32	0.78	0.43	0.32	38.15
Ant	0.64	0.32	0.25	2.25	0.00	1.20	1.18	1.48	1.15	1.05	0.44	0.38	0.47	0.25	0.25	11.33
Pyr	0.70	0.44	0.54	2.41	1.95	1.11	1.61	2.12	2.33	1.04	0.45	0.02	0.83	0.33	0.05	15.95
Flu	0.45	0.20	0.32	1.20	1.05	0.41	0.79	1.10	1.15	0.48	0.25	0.02	0.46	0.34	0.08	8.32
BaA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BkF	1.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.13	0.39	5.19
BbF	1.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.24	1.25
BaP	0.00	1.79	0.83	0.00	0.00	0.00	0.00	0.00	0.00	4.61	0.00	0.00	0.00	2.53	0.00	9.76
B(ghi)P	1.28	0.00	0.00	0.00	0.64	0.00	0.00	0.52	0.00	0.00	0.00	0.00	0.00	0.00	0.10	2.54
DahA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.03	0.00	0.00	0.00	1.03
InP	0.33	0.57	0.10	1.56	1.29	1.88	0.60	0.00	1.19	0.00	1.32	0.09	0.00	0.60	0.06	9.59
Total(ng/g)	15.46	13.65	9.32	32.26	21.66	20.35	27.94	40.52	23.27	36.33	11.33	5.74	16.82	15.30	5.60	295.56
Mean(ng/g)	0.97	0.85	0.58	2.02	1.35	1.27	1.75	2.53	1.45	2.27	0.71	0.36	1.05	0.96	0.35	18.47
STD	1.47	2.22	1.24	3.82	2.67	3.21	4.84	7.04	3.03	6.52	1.81	0.90	3.18	1.87	0.92	42.96

Total concentrations of PAHs (ng/g dw) in SPM in the dry season

Stations	OSP1	OSP2	OSP3	OSP4	OSP5	DSP1	DSP2	DSP3	DSP4	DSP5	FSP1	FSP2	FSP3	FSP4	FSP5	Total (ng/g)
Naph	8.04	9.98	9.75	12.13	11.76	11.33	16.44	14.96	15.54	8.54	11.02	3.46	7.53	7.67	8.59	156.74
Acey	0.08	0.07	0.00	0.16	0.08	0.19	0.29	0.19	0.41	0.10	0.15	0.06	0.27	0.07	0.09	2.23
Ace	0.26	0.31	0.50	0.45	0.36	0.43	0.71	0.55	0.83	0.30	0.32	0.02	0.57	0.20	0.27	6.10
Fl	0.42	0.44	0.73	0.57	0.49	0.52	0.69	0.62	0.76	0.45	0.54	0.25	0.74	0.33	0.45	8.00
Phe	0.73	0.51	1.09	1.06	0.74	0.56	0.55	0.68	1.11	0.77	0.76	0.22	1.20	0.38	0.49	10.86
Ant	0.82	0.32	0.91	1.10	0.37	0.18	0.64	0.97	0.00	0.64	0.40	0.15	0.97	0.25	0.57	8.30
Pyr	0.63	0.60	0.70	0.94	0.84	0.55	0.82	0.83	0.77	0.66	0.43	0.02	1.03	0.26	0.38	9.46
Flu	0.37	0.27	0.41	0.58	0.42	0.25	0.16	0.00	0.34	0.24	0.20	0.03	0.64	0.10	0.26	4.26
BaA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.08	0.00	0.00	0.98	1.32
Chr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BkF	0.00	0.63	1.88	2.37	1.52	0.00	0.00	0.00	0.00	0.00	0.00	0.02	1.13	0.00	0.00	7.55
BbF	0.00	0.00	0.00	1.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.39	0.00	0.00	2.57
BaP	0.00	0.00	0.00	0.00	0.00	1.19	3.45	0.00	0.00	0.00	1.14	0.46	1.06	0.88	0.00	8.18
B(ghi)P	0.00	0.42	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	1.41	0.35	0.00	2.95
DahA	0.00	0.00	0.00	0.00	0.00	0.00	0.57	0.00	0.00	0.00	0.12	0.11	1.86	0.21	0.54	3.41
InP	0.62	0.00	0.27	0.02	0.00	0.15	1.41	0.00	0.00	0.00	0.35	0.00	1.88	0.17	0.64	5.50
Total(ng/g)	11.97	13.57	16.23	21.06	16.58	15.36	25.74	18.81	19.75	11.71	15.70	5.16	21.67	10.86	13.26	237.43
Mean(ng/g)	0.75	0.85	1.01	1.32	1.04	0.96	1.61	1.18	1.23	0.73	0.98	0.32	1.35	0.68	0.83	14.84
STD	1.97	2.45	2.39	2.95	2.89	2.78	4.05	3.69	3.83	2.10	2.69	0.85	1.74	1.88	2.09	37.97

APPENDIX 3

Relationship between concentrations of PAH in water in the wet and dry season

Wet	Dry
0.04	0.05
0.04	0.05
0.03	0.04
0.01	0.06
0.08	0.04
0.09	0.07
0.08	0.03
0.08	0.07
0.09	0.25
0.09	0.03
0.04	0.05
0.05	0.04
0.05	0.05
0.04	0.05
0.06	0.06

Relationship between Concentration, Temperature and Salinity of water from the Cross River estuary

Months	Conc	Temp	Salinity
Jun	6.78	32.00	5.50
Aug	4.02	36.00	10.70
Oct	3.93	28.00	11.70
Dec	7.23	21.50	17.50
Feb	4.03	20.00	23.50
Apr	3.10	26.00	11.70

Relationship between concentration of PAH in SPM in the wet and dry season

Wet	Dry
0.97	0.75
0.85	0.85
0.58	1.01
2.02	1.32
1.35	1.04
1.27	0.96
1.75	1.61
2.53	1.18
1.45	1.23
2.27	0.73
0.71	0.98
0.36	0.32
1.05	1.35
0.96	0.68
0.35	0.83

Relationship between Concentration, Temperature and Salinity of PAH in SPM from the Cross River estuary

Temp	Conc	Salinity
32.00	148.41	5.50
36.00	54.79	10.70
28.00	79.41	11.70
21.50	91.36	17.50
20.00	66.66	23.50
26.00	92.36	11.70

APPENDIX 4

Comparative analysis of the concentration of PAHs in water in the wet (April, June and August) and dry season (February, October and December) using t-test

Variable	T	Df	P-value	Wet	Dry
Wet-dry season	-0.452	239	0.652		
Mean concentration				0.0577	0.0633

Comparative analysis of the concentration of PAHs in SPM in the wet (April, June and August) and dry season (February, October and December) using t-test

Variable	T	Df	P-value	Wet	Dry
Wet-dry season	1.945	239	0.053		
Mean concentration				1.232	0.989

APPENDIX 5

Total concentrations of n-alkanes (ng/L) in water from the Cross River estuary

Stations	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	C33	C34	C35	C36	C37	C38	C39	C40	Tot (ng/l
JW1	0.03	0.01	0.06	0.04	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.03	0.06	0.10	0.15	0.21	0.30	0.42	0.38	0.41	0.34	0.37	0.32	0.34	0.26	0.25	0.22	0.18	0.13	0.09	0.05	0.03	4.9
JW2	0.06	0.16	0.26	0.13	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.06	0.11	0.17	0.23	0.46	0.37	0.39	0.38	0.18	0.17	0.19	0.23	0.44	0.36	0.30	0.24	0.17	0.12	0.07	0.04	5.4
JW3	0.05	0.02	0.07	0.04	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.06	0.11	0.16	0.22	0.33	0.39	0.39	0.39	0.26	0.27	0.21	0.29	0.27	0.30	0.26	0.21	0.15	0.10	0.06	0.03	4.7
JW4	0.32	0.03	0.08	0.04	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.06	0.11	0.18	0.24	0.30	0.37	0.58	0.40	0.51	0.44	0.48	0.23	0.53	0.27	0.46	0.44	0.36	0.28	0.20	0.12	0.06	7.2
JW5	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.03	0.04	0.06	0.10	0.15	0.12	0.13	0.13	0.14	0.12	0.12	0.08	0.06	0.05	0.04	0.03	0.02	0.01	0.01	1.6
TOTAL	0.47	0.23	0.48	0.26	0.08	0.06	0.05	0.04	0.05	0.07	0.06	0.08	0.16	0.31	0.53	0.77	1.03	1.55	1.90	1.68	1.83	1.35	1.44	1.06	1.52	1.32	1.43	1.27	1.03	0.76	0.52	0.32	0.17	23.8
MEAN	0.09	0.05	0.10	0.05	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.03	0.06	0.11	0.15	0.21	0.31	0.38	0.34	0.37	0.27	0.29	0.21	0.30	0.26	0.29	0.25	0.21	0.15	0.10	0.06	0.03	4.7
STD	0.13	0.07	0.09	0.04	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.02	0.03	0.05	0.07	0.09	0.13	0.15	0.12	0.14	0.12	0.14	0.07	0.15	0.13	0.15	0.14	0.11	0.09	0.06	0.04	0.02	2.0
AW1	0.01	0.07	0.29	0.29	0.09	0.04	0.03	0.01	0.01	0.00	0.02	0.03	0.05	0.08	0.14	0.19	0.27	0.34	0.50	0.44	0.48	0.46	0.43	0.38	0.46	0.46	0.39	0.36	0.30	0.23	0.17	0.11	0.06	7.2
AW2	0.01	0.00	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.08	0.13	0.19	0.28	0.35	0.39	0.40	0.34	0.36	0.30	0.35	0.33	0.26	0.22	0.17	0.12	0.08	0.05	0.03	4.6
AW3	0.01	0.01	0.03	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.05	0.08	0.12	0.16	0.25	0.34	0.33	0.33	0.30	0.28	0.27	0.29	0.23	0.22	0.19	0.16	0.13	0.09	0.06	0.04	4.1
AW4	0.00	0.00	0.02	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.03	0.06	0.10	0.15	0.23	0.30	0.31	0.35	0.31	0.29	0.27	0.28	0.27	0.21	0.16	0.13	0.09	0.06	0.04	0.02	3.7
AW5	0.01	0.00	0.02	0.03	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.03	0.07	0.11	0.17	0.36	0.32	0.37	0.34	0.33	0.33	0.30	0.32	0.31	0.24	0.20	0.15	0.10	0.07	0.04	0.02	4.3
TOTAL	0.03	0.09	0.38	0.39	0.14	0.10	0.07	0.05	0.04	0.05	0.05	0.06	0.12	0.23	0.42	0.65	0.94	1.46	1.81	1.85	1.91	1.74	1.68	1.53	1.69	1.60	1.33	1.13	0.90	0.67	0.47	0.30	0.17	24.0
MEAN	0.01	0.02	0.08	0.08	0.03	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.08	0.13	0.19	0.29	0.36	0.37	0.38	0.35	0.34	0.31	0.34	0.32	0.27	0.23	0.18	0.13	0.09	0.06	0.03	4.8
STD	0.00	0.03	0.12	0.12	0.03	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.05	0.06	0.06	0.06	0.05	0.07	0.09	0.08	0.08	0.07	0.06	0.05	0.03	0.02	1.3
OW1	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.03	0.04	0.08	0.01	0.06	0.03	0.07	0.09	0.15	0.21	0.28	0.32	0.34	0.29	0.29	0.27	0.27	0.25	0.19	0.15	0.11	0.08	0.05	0.03	0.02	3.8
OW2	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.02	0.02	0.04	0.01	0.02	0.01	0.03	0.04	0.07	0.12	0.21	0.19	0.20	0.18	0.16	0.17	0.15	0.13	0.11	0.07	0.05	0.03	0.02	0.00	0.00	2.1
OW3	0.00	0.00	0.02	0.01	0.01	0.01	0.01	0.01	0.06	0.05	0.09	0.01	0.05	0.03	0.07	0.08	0.13	0.20	0.25	0.26	0.31	0.26	0.26	0.22	0.23	0.21	0.19	0.12	0.10	0.07	0.04	0.03	0.01	3.4
OW4	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.03	0.02	0.04	0.01	0.02	0.01	0.03	0.04	0.07	0.13	0.17	0.17	0.18	0.18	0.17	0.15	0.14	0.12	0.08	0.06	0.04	0.03	0.02	0.00	0.00	1.9
OW5	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.00	0.02	0.01	0.02	0.03	0.05	0.09	0.14	0.14	0.16	0.13	0.14	0.12	0.11	0.09	0.07	0.05	0.04	0.03	0.02	0.00	0.00	1.5
TOTAL	0.02	0.02	0.07	0.04	0.02	0.03	0.04	0.03	0.16	0.13	0.28	0.04	0.17	0.09	0.22	0.28	0.48	0.74	1.04	1.08	1.19	1.05	1.02	0.93	0.90	0.79	0.63	0.45	0.35	0.24	0.16	0.06	0.03	12.7
MEAN	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.03	0.03	0.06	0.01	0.03	0.02	0.04	0.06	0.10	0.15	0.21	0.22	0.24	0.21	0.20	0.19	0.18	0.16	0.13	0.09	0.07	0.05	0.03	0.01	0.01	2.5
STD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.03	0.00	0.02	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.06	0.07	0.06	0.07	0.07	0.06	0.04	0.03	0.02	0.01	0.02	0.01	0.9
DW1	0.01	0.00	0.02	0.02	0.01	0.01	0.01	0.01	0.04	0.03	0.06	0.01	0.05	0.02	0.05	0.07	0.11	0.22	0.24	0.26	0.30	0.27	0.27	0.27	0.29	0.25	0.20	0.19	0.13	0.10	0.06	0.04	0.00	3.6
DW2	0.01	0.01	0.02	0.01	0.01	0.02	0.02	0.01	0.03	0.04	0.05	0.01	0.04	0.02	0.04	0.05	0.08	0.12	0.18	0.16	0.17	0.16	0.16	0.14	0.14	0.10	0.08	0.07	0.06	0.04	0.03	0.02	0.01	2.1
DW3	0.00	0.00	0.02	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.04	0.01	0.03	0.01	0.03	0.04	0.06	0.10	0.15	0.14	0.14	0.12	0.12	0.12	0.12	0.10	0.09	0.06	0.04	0.03	0.02	0.02	0.01	1.7
DW4	0.00	0.13	0.28	0.33	0.06	0.03	0.02	0.01	0.02	0.02	0.03	0.01	0.04	0.07	0.12	0.18	0.25	0.46	0.36	0.42	0.44	0.35	0.37	0.32	0.37	0.35	0.28	0.23	0.17	0.12	0.08	0.04	0.03	5.9
DW5	0.00	0.00	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.03	0.05	0.09	0.14	0.21	0.20	0.22	0.19	0.18	0.17	0.16	0.12	0.10	0.08	0.06	0.04	0.03	0.02	0.01	2.2
TOTAL	0.02	0.15	0.36	0.39	0.11	0.08	0.07	0.05	0.12	0.12	0.20	0.05	0.19	0.14	0.28	0.38	0.59	1.04	1.15	1.18	1.28	1.09	1.11	1.01	1.08	0.91	0.74	0.63	0.46	0.34	0.22	0.13	0.06	15.7
MEAN	0.00	0.03	0.07	0.08	0.02	0.02	0.01	0.01	0.02	0.02	0.04	0.01	0.04	0.03	0.06	0.08	0.12	0.21	0.23	0.24	0.26	0.22	0.22	0.20	0.22	0.18	0.15	0.13	0.09	0.07	0.04	0.03	0.01	3.1
STD	0.00	0.06	0.12	0.14	0.02	0.01	0.00	0.00	0.01	0.01	0.02	0.00	0.01	0.02	0.04	0.06	0.07	0.15	0.08	0.11	0.12	0.09	0.10	0.09	0.11	0.11	0.09	0.08	0.06	0.04	0.02	0.01	0.01	1.7
FW1	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.02	0.00	0.02	0.01	0.02	0.04	0.06	0.14	0.17	0.16	0.17	0.15	0.16	0.12	0.11	0.93	0.07	0.05	0.04	0.03	0.02	0.01	0.01	2.5
FW2	0.00	0.00	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.03	0.01	0.03	0.01	0.03	0.03	0.05	0.11	0.15	0.12	0.14	0.14	0.13	0.17	0.10	0.08	0.07	0.05	0.04	0.03	0.02	0.01	0.01	1.6
FW3	0.01	0.00	0.01	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.02	0.01	0.04	0.01	0.02	0.01	0.02	0.05	0.04	0.04	0.04	0.05	0.04	0.05	0.09	0.06	0.03	0.03	0.02	0.01	0.01	0.00	0.00	0.7
FW4	0.03	0.00	0.01	0.01	0.01	0.01	0.02	0.00	0.02	0.01	0.04	0.01	0.06	0.01	0.02	0.02	0.04	0.11	0.11	0.11	0.11	0.12	0.09	0.07	0.06	0.05	0.04	0.02	0.02	0.01	0.01	0.00	0.00	1.2
FW5	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.01	0.06	0.02	0.08	0.01	0.06	0.03	0.06	0.08	0.13	0.20	0.26	0.29	0.32	0.26	0.23	0.22	0.22	0.20	0.18	0.11	0.08	0.06	0.04	0.02	0.00	3.3
TOTAL	0.06	0.02	0.08	0.06	0.04	0.04	0.06	0.03	0.10	0.05	0.19	0.04	0.21	0.07	0.15	0.18	0.31	0.61	0.73	0.73	0.79	0.71	0.64	0.63	0.58	1.33	0.39	0.26	0.19	0.13	0.09	0.05	0.01	9.5
MEAN	0.01	0.00	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.04	0.01	0.04	0.01	0.03	0.04	0.06	0.12	0.15	0.15	0.16	0.14	0.13	0.13	0.12	0.27	0.08	0.05	0.04	0.03	0.02	0.01	0.00	1.9
STD	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.01	0.02	0.00	0.02	0.01	0.02	0.03	0.04	0.05	0.08	0.09	0.11	0.08	0.07	0.07	0.06	0.38	0.06	0.04	0.03	0.02	0.01	0.01	0.00	1.0
AprW1	0.03	0.00	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.02	0.01	0.03	0.02	0.04	0.05	0.09	0.15	0.19	0.18	0.18	0.17	0.13	0.13	0.11	0.06	0.07	0.08	0.03	0.02	0.01	0.00	0.00	1.9
AprW2	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.2
AprW3	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0
AprW4	0.01	0.00	0.01	0.01	0.01	0.01	0.02	0.00	0.02	0.00	0.02	0.01	0.05	0.01	0.01	0.01	0.02	0.03	0.05	0.07	0.15	0.16	0.14	0.14	0.12	0.08	0.06	0.02	0.02	0.01	0.01	0.00	0.00	1.2
AprW5	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.1
TOTAL	0.04	0.01	0.10	0.03	0.02	0.02	0.03	0.01	0.03	0.01	0.05	0.01	0.09	0.03	0.06	0.07	0.12	0.19	0.26	0.27	0.35	0.35	0.29	0.29	0.29	0.16	0.14	0.11	0.06	0.04	0.03	0.01	0.00	3.5
MEAN	0.01	0.00	0.02	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.01	0.01	0.01	0.02	0.04	0.05	0.05	0.07	0.07	0.06	0.06	0.06	0.03	0.03	0.02	0.01	0.01	0.01	0.00	0.00	0.7
STD	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.01	0.02	0.02	0.04	0.06	0.08	0.08	0.09	0.09	0.07	0.07	0.05	0.04	0.03	0.03	0.01	0.01	0.01	0.00	0.00	0.8

Total concentrations of n-akanes (ng/L) in water in the wet season

Stations	AprW1	AprW2	AprW3	AprW4	AprW5	JW1	JW2	JW3	JW4	JW5	AW1	AW2	AW3	AW4	AW5	Total(ng/L)
C8	0.03	0.00	0.00	0.01	0.00	0.03	0.06	0.05	0.32	0.01	0.01	0.01	0.01	0.00	0.01	0.55
C9	0.00	0.00	0.00	0.00	0.00	0.01	0.16	0.02	0.03	0.01	0.07	0.00	0.01	0.00	0.00	0.34
C10	0.02	0.02	0.02	0.01	0.02	0.06	0.26	0.07	0.08	0.02	0.29	0.02	0.03	0.02	0.02	0.96
C11	0.01	0.00	0.00	0.01	0.00	0.04	0.13	0.04	0.04	0.01	0.29	0.02	0.02	0.02	0.03	0.68
C12	0.01	0.00	0.00	0.01	0.00	0.02	0.02	0.02	0.01	0.01	0.09	0.01	0.02	0.01	0.02	0.24
C13	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.04	0.01	0.02	0.01	0.02	0.18
C14	0.01	0.00	0.00	0.02	0.00	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.02	0.01	0.01	0.16
C15	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.10
C16	0.01	0.00	0.00	0.02	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.13
C17	0.01	0.00	0.00	0.00	0.00	0.02	0.01	0.01	0.02	0.01	0.00	0.01	0.02	0.01	0.01	0.13
C18	0.02	0.00	0.00	0.02	0.00	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.16
C19	0.01	0.00	0.00	0.01	0.00	0.02	0.01	0.01	0.03	0.01	0.03	0.01	0.01	0.01	0.01	0.15
C20	0.03	0.01	0.00	0.05	0.00	0.03	0.03	0.03	0.06	0.01	0.05	0.02	0.02	0.01	0.02	0.37
C21	0.02	0.00	0.00	0.01	0.01	0.06	0.06	0.06	0.11	0.03	0.08	0.04	0.05	0.03	0.03	0.57
C22	0.04	0.00	0.00	0.01	0.00	0.10	0.11	0.11	0.18	0.03	0.14	0.08	0.08	0.06	0.07	1.00
C23	0.05	0.00	0.00	0.01	0.00	0.15	0.17	0.16	0.24	0.04	0.19	0.13	0.12	0.10	0.11	1.49
C24	0.09	0.01	0.00	0.02	0.00	0.21	0.23	0.22	0.30	0.06	0.27	0.19	0.16	0.15	0.17	2.08
C25	0.15	0.01	0.00	0.03	0.00	0.30	0.46	0.33	0.37	0.10	0.34	0.28	0.25	0.23	0.36	3.20
C26	0.19	0.01	0.00	0.05	0.01	0.42	0.37	0.39	0.58	0.15	0.50	0.35	0.34	0.30	0.32	3.97
C27	0.18	0.01	0.00	0.07	0.01	0.38	0.39	0.39	0.40	0.12	0.44	0.39	0.33	0.31	0.37	3.81
C28	0.18	0.01	0.00	0.15	0.01	0.41	0.38	0.39	0.51	0.13	0.48	0.40	0.33	0.35	0.34	4.08
C29	0.17	0.01	0.00	0.16	0.01	0.34	0.18	0.26	0.44	0.13	0.46	0.34	0.30	0.31	0.33	3.44
C30	0.13	0.01	0.00	0.14	0.01	0.37	0.17	0.27	0.48	0.14	0.43	0.36	0.28	0.29	0.33	3.41
C31	0.13	0.01	0.00	0.14	0.01	0.32	0.19	0.21	0.23	0.12	0.38	0.30	0.27	0.27	0.30	2.88
C32	0.11	0.05	0.00	0.12	0.01	0.34	0.23	0.29	0.53	0.12	0.46	0.35	0.29	0.28	0.32	3.50
C33	0.06	0.01	0.00	0.08	0.01	0.26	0.44	0.27	0.27	0.08	0.46	0.33	0.23	0.27	0.31	3.09
C34	0.07	0.01	0.00	0.06	0.00	0.25	0.36	0.30	0.46	0.06	0.39	0.26	0.22	0.21	0.24	2.9[illegible]
C35	0.08	0.01	0.00	0.02	0.00	0.22	0.30	0.26	0.44	0.05	0.36	0.22	0.19	0.16	0.20	2.51
C36	0.03	0.01	0.00	0.02	0.00	0.18	0.24	0.21	0.36	0.04	0.30	0.17	0.16	0.13	0.15	1.99
C37	0.02	0.01	0.00	0.01	0.00	0.13	0.17	0.15	0.28	0.03	0.23	0.12	0.13	0.09	0.10	1.48
C38	0.01	0.01	0.00	0.01	0.00	0.09	0.12	0.10	0.20	0.02	0.17	0.08	0.09	0.06	0.07	1.01
C39	0.00	0.00	0.00	0.00	0.00	0.05	0.07	0.06	0.12	0.01	0.11	0.05	0.06	0.04	0.04	0.62
C40	0.00	0.00	0.00	0.00	0.00	0.03	0.04	0.03	0.06	0.01	0.06	0.03	0.04	0.02	0.02	0.34
Total(ng/g)	1.90	0.24	0.04	1.29	0.13	4.91	5.41	4.78	7.20	1.60	7.20	4.60	4.13	3.76	4.36	51.54
Mean	0.06	0.01	0.00	0.04	0.00	0.15	0.16	0.14	0.22	0.05	0.22	0.14	0.13	0.11	0.13	1.56
STD	0.06	0.01	0.00	0.05	0.00	0.14	0.14	0.13	0.19	0.05	0.17	0.14	0.12	0.12	0.14	1.40

Total concentrations of n-akanes (ng/L) in water in the dry season

Stations	OW1	OW2	OW3	OW4	OW5	DW1	DW2	DW3	DW4	DW5	FW1	FW2	FW3	FW4	FW5	Total(ng/L)
C8	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.01	0.10
C9	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.01	0.19
C10	0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.02	0.28	0.02	0.01	0.02	0.01	0.01	0.02	0.51
C11	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.33	0.01	0.01	0.01	0.02	0.01	0.02	0.48
C12	0.01	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.06	0.01	0.01	0.01	0.01	0.01	0.01	0.17
C13	0.01	0.00	0.01	0.01	0.00	0.01	0.02	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.15
C14	0.01	0.01	0.01	0.00	0.00	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.17
C15	0.01	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.10
C16	0.03	0.02	0.06	0.03	0.01	0.04	0.03	0.02	0.02	0.01	0.01	0.01	0.00	0.02	0.06	0.37
C17	0.04	0.02	0.05	0.02	0.01	0.03	0.04	0.02	0.02	0.02	0.01	0.01	0.00	0.01	0.02	0.30
C18	0.08	0.04	0.09	0.04	0.03	0.06	0.05	0.04	0.03	0.02	0.02	0.03	0.02	0.04	0.08	0.67
C19	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.13
C20	0.06	0.02	0.05	0.02	0.02	0.05	0.04	0.03	0.04	0.02	0.02	0.03	0.04	0.06	0.06	0.57
C21	0.03	0.01	0.03	0.01	0.01	0.02	0.02	0.01	0.07	0.02	0.01	0.01	0.01	0.01	0.03	0.30
C22	0.07	0.03	0.07	0.03	0.02	0.05	0.04	0.03	0.12	0.03	0.02	0.03	0.02	0.02	0.06	0.65
C23	0.09	0.04	0.08	0.04	0.03	0.07	0.05	0.04	0.18	0.05	0.04	0.03	0.01	0.02	0.08	0.84
C24	0.15	0.07	0.13	0.07	0.05	0.11	0.08	0.06	0.25	0.09	0.06	0.05	0.02	0.04	0.13	1.37
C25	0.21	0.12	0.20	0.13	0.09	0.22	0.12	0.10	0.46	0.14	0.14	0.11	0.05	0.11	0.20	2.39
C26	0.28	0.21	0.25	0.17	0.14	0.24	0.18	0.15	0.36	0.21	0.17	0.15	0.04	0.11	0.26	2.92
C27	0.32	0.19	0.26	0.17	0.14	0.26	0.16	0.14	0.42	0.20	0.16	0.12	0.04	0.11	0.29	2.99
C28	0.34	0.20	0.31	0.18	0.16	0.30	0.17	0.14	0.44	0.22	0.17	0.14	0.04	0.11	0.32	3.25
C29	0.29	0.18	0.26	0.18	0.13	0.27	0.16	0.12	0.35	0.19	0.15	0.14	0.05	0.12	0.26	2.85
C30	0.29	0.16	0.26	0.17	0.14	0.27	0.16	0.12	0.37	0.18	0.16	0.13	0.04	0.09	0.23	2.77
C31	0.27	0.17	0.22	0.15	0.12	0.27	0.14	0.12	0.32	0.17	0.12	0.17	0.05	0.07	0.22	2.58
C32	0.27	0.15	0.23	0.14	0.11	0.29	0.14	0.12	0.37	0.16	0.11	0.10	0.09	0.06	0.22	2.57
C33	0.25	0.13	0.21	0.12	0.09	0.25	0.10	0.10	0.35	0.12	0.93	0.08	0.06	0.05	0.20	3.03
C34	0.19	0.11	0.19	0.08	0.07	0.20	0.08	0.09	0.28	0.10	0.07	0.07	0.03	0.04	0.18	1.76
C35	0.15	0.07	0.12	0.06	0.05	0.19	0.07	0.06	0.23	0.08	0.05	0.05	0.03	0.02	0.11	1.35
C36	0.11	0.05	0.10	0.04	0.04	0.13	0.06	0.04	0.17	0.06	0.04	0.04	0.02	0.02	0.08	1.00
C37	0.08	0.03	0.07	0.03	0.03	0.10	0.04	0.03	0.12	0.04	0.03	0.03	0.01	0.01	0.06	0.71
C38	0.05	0.02	0.04	0.02	0.02	0.06	0.03	0.02	0.08	0.03	0.02	0.02	0.01	0.01	0.04	0.47
C39	0.03	0.00	0.03	0.00	0.00	0.04	0.02	0.02	0.04	0.02	0.01	0.01	0.00	0.00	0.02	0.24
C40	0.02	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.03	0.01	0.01	0.01	0.00	0.00	0.00	0.11
Total(ng/L)	3.80	2.11	3.41	1.93	1.54	3.65	2.11	1.72	5.99	2.27	2.58	1.64	0.74	1.24	3.35	38.05
Mean	0.12	0.06	0.10	0.06	0.05	0.11	0.06	0.05	0.18	0.07	0.08	0.05	0.02	0.04	0.10	1.15
STD	0.11	0.07	0.10	0.06	0.05	0.11	0.06	0.05	0.15	0.07	0.16	0.05	0.02	0.04	0.10	1.11

APPENDIX 6

Total n-alkane concentrations (ng/g dw) in suspended particulate matter from the Cross River estuary

tations	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	C33	C34	C35	C36	C37	C38	C39	C40	Totalng
JSP1	8.29	2.77	11.39	7.74	4.58	4.14	5.46	3.39	4.98	6.36	4.72	5.14	10.86	20.15	38.20	60.65	89.41	127.16	164.34	185.40	190.73	169.08	167.10	146.50	155.06	138.55	109.43	86.20	64.11	46.42	29.93	16.82	7.61	2092.6
JSP2	7.92	2.70	10.00	6.98	4.67	3.83	4.49	2.99	4.63	7.18	4.49	4.90	10.22	13.78	23.91	38.53	48.88	100.92	132.28	170.01	121.34	139.70	111.72	126.59	139.66	99.00	88.00	80.77	48.30	41.12	19.56	15.66	6.81	1641.5
JSP3	6.70	1.92	9.09	8.46	5.80	5.16	4.21	3.12	4.45	7.93	4.15	3.17	5.84	11.36	19.85	29.73	46.97	69.88	10.98	99.67	93.82	102.60	97.72	79.64	82.48	58.87	53.54	44.18	34.23	25.05	16.30	10.09	6.02	1062.9
JSP4	6.09	2.00	9.63	6.73	3.06	2.88	2.84	1.92	2.46	4.48	2.61	2.96	7.28	12.96	26.12	45.18	70.19	145.00	159.50	137.77	169.04	141.09	124.53	119.05	123.87	109.13	80.72	62.62	44.37	30.22	19.32	11.19	0.00	1686.8
JSP5	7.31	2.35	9.82	7.36	4.62	3.98	4.35	3.06	4.54	6.77	4.32	4.03	8.75	13.37	25.01	41.86	39.53	114.04	145.89	153.89	145.19	140.40	118.13	122.82	131.76	104.07	84.36	71.60	46.33	35.67	19.44	13.43	6.41	1664.5
OTAL	36.32	11.73	49.94	37.28	22.73	19.90	21.35	14.48	21.06	32.70	20.29	20.22	42.95	71.62	133.09	215.45	314.99	557.00	612.98	746.72	720.11	692.87	619.19	594.60	632.82	509.62	416.07	345.36	237.34	178.48	104.55	67.19	26.85	8148.5
MEAN	7.26	2.35	9.99	7.46	4.55	4.00	4.27	2.90	4.21	6.54	4.06	4.04	8.59	14.32	26.62	43.19	63.00	111.40	122.60	149.34	144.02	138.57	123.84	118.92	126.56	101.92	83.21	69.09	47.47	35.70	20.91	13.44	5.37	1629.7
ASP1	1.97	1.01	5.61	3.52	2.80	3.88	1.93	3.15	2.19	1.53	2.33	2.61	5.78	12.57	25.18	42.89	68.41	110.14	135.49	146.54	156.09	146.85	135.15	110.10	109.74	83.27	71.17	56.23	42.23	30.26	19.68	10.95	4.81	1559.9
ASP2	2.75	3.03	10.92	12.90	14.74	15.61	12.83	7.36	5.57	0.42	5.71	5.07	11.61	23.42	44.98	73.34	99.85	201.36	173.23	194.11	198.91	178.43	199.84	162.27	192.54	146.36	142.54	119.88	92.70	67.06	43.38	25.87	14.33	2502.9
ASP3	3.17	2.60	9.13	6.76	4.70	4.90	4.21	3.11	2.44	3.76	2.71	2.51	5.64	10.60	23.44	36.87	62.82	96.38	142.88	134.51	153.87	130.29	137.00	113.80	141.78	108.26	211.40	64.75	143.46	33.22	55.59	21.28	27.92	1905.7
ASP4	0.00	1.13	6.04	3.41	1.48	2.52	1.90	1.82	1.35	0.31	1.73	1.65	3.60	7.51	15.85	26.00	43.72	93.84	103.50	97.08	113.26	100.60	110.43	91.89	103.97	68.66	62.41	49.86	37.70	28.77	18.85	11.39	0.00	1212.6
ASP5	6.07	2.15	6.24	8.66	3.43	4.30	3.49	2.84	2.37	3.64	2.44	2.84	5.77	11.88	24.11	40.21	66.23	128.37	132.05	141.00	160.40	153.23	140.14	120.33	126.36	117.61	93.28	69.17	54.82	37.17	26.14	14.98	0.00	1731.9
OTAL	13.96	9.93	37.94	35.26	27.15	31.22	26.37	18.28	13.92	11.47	14.92	14.68	32.40	65.99	133.56	219.82	341.03	650.09	687.14	713.25	782.52	709.39	722.57	598.38	674.38	524.16	380.80	360.09	370.91	196.48	163.64	84.47	47.05	8913.1
MEAN	2.79	1.99	7.59	7.05	5.43	6.24	5.27	3.66	2.78	2.29	2.98	2.94	6.48	13.20	26.71	43.96	68.21	130.02	137.43	142.65	156.50	141.88	144.51	119.68	134.88	104.83	116.16	72.02	74.18	39.30	32.73	16.89	9.41	1782.6
DSP1	3.38	1.98	4.85	3.86	2.94	3.21	2.89	4.97	5.21	14.70	14.41	7.03	28.27	15.31	59.41	24.10	36.05	54.87	58.98	79.51	63.34	94.57	65.40	66.43	49.61	39.69	29.43	20.20	16.55	9.88	7.15	2.43	1.91	892.51
DSP2	5.87	3.79	14.11	12.40	6.30	6.30	4.43	3.41	7.35	7.92	15.44	2.96	9.64	5.07	15.62	15.27	27.58	41.90	66.28	61.14	70.34	68.73	61.25	57.26	60.27	37.65	33.60	26.71	19.87	15.00	9.69	6.46	3.22	802.83
DSP3	2.71	1.92	7.98	5.83	2.90	3.14	2.34	1.32	3.62	5.00	9.68	1.64	6.29	3.24	8.46	10.61	19.60	12.22	51.62	48.81	58.01	53.06	54.50	46.46	41.07	29.01	25.48	19.01	13.49	9.43	8.28	4.41	2.00	593.24
DSP4	1.71	1.82	8.49	29.33	22.68	15.05	11.08	4.72	5.53	7.08	8.47	2.69	7.11	5.03	9.55	13.91	24.20	30.38	69.28	61.24	73.30	67.77	61.90	57.20	78.94	43.68	37.62	23.97	18.03	13.14	8.40	5.73	2.65	842.26
DSP5	2.38	2.30	9.27	5.24	3.33	3.89	3.13	4.28	7.78	14.90	14.02	4.07	12.75	7.10	12.36	13.46	208.60	32.38	50.62	44.99	51.28	51.12	46.43	38.31	41.29	26.67	22.58	17.55	14.27	10.06	6.58	4.86	2.50	790.33
OTAL	16.04	11.79	44.70	56.65	38.15	31.59	24.48	18.69	29.49	49.68	62.02	18.39	64.06	35.75	105.40	77.34	316.03	201.75	296.78	295.70	316.27	335.26	289.47	265.67	271.18	176.70	148.71	102.45	82.21	57.51	40.10	23.90	12.27	3921.1
MEAN	3.21	2.36	8.94	11.33	7.63	6.32	4.90	3.74	5.90	9.94	12.40	3.68	12.81	7.15	21.08	15.47	63.21	40.35	59.36	59.14	63.25	67.05	57.89	53.13	54.24	35.34	29.74	21.49	16.44	11.50	8.02	4.78	2.45	784.24
DSP1	2.57	2.27	11.17	15.03	9.97	7.52	5.50	2.87	2.22	1.95	5.06	2.02	6.05	1.98	7.49	11.27	20.13	33.50	51.34	47.69	54.60	51.75	46.51	41.90	40.51	33.56	28.73	20.28	15.21	10.76	7.05	5.82	1.83	612.12
DSP2	2.80	2.92	11.12	6.35	5.52	6.66	11.41	8.45	13.68	11.89	17.27	7.04	21.97	14.48	20.61	26.53	39.26	57.47	79.69	81.31	78.33	79.83	82.19	69.11	72.58	63.60	36.35	39.99	30.82	22.57	15.74	10.70	6.44	1054.6
DSP3	1.94	1.72	7.51	4.23	5.03	6.67	5.89	2.81	2.18	3.58	4.63	1.80	5.77	3.29	6.10	9.75	16.29	36.93	45.57	42.27	49.11	43.22	41.38	55.90	34.00	27.86	26.20	16.21	14.16	8.57	6.78	3.52	2.11	542.97
DSP4	2.88	21.82	135.76	166.29	36.81	19.08	13.09	8.10	7.76	8.40	13.85	5.97	11.61	11.19	16.49	20.53	34.05	48.59	80.13	71.41	75.23	73.18	74.44	69.00	64.32	47.12	35.53	37.40	25.84	17.16	11.29	8.28	5.41	1274.0
DSP5	2.68	2.59	11.15	10.69	7.74	7.10	8.65	3.49	4.99	6.20	9.45	4.00	8.83	7.58	11.99	15.90	27.09	42.76	63.52	59.55	64.91	62.47	60.48	62.45	52.42	40.34	32.13	20.84	20.53	13.96	9.17	7.05	4.62	777.32
OTAL	12.87	31.32	176.71	202.59	65.07	47.03	44.54	27.72	30.83	34.08	50.26	20.84	54.23	40.51	62.68	83.47	136.82	219.24	322.27	302.23	322.17	310.45	305.01	298.37	263.83	212.47	158.94	134.72	106.55	73.03	50.03	35.37	22.40	4261.1
MEAN	2.57	6.26	35.34	40.52	13.01	9.41	8.91	5.54	6.17	6.82	10.05	4.17	10.85	8.10	12.54	16.70	27.36	43.85	64.45	60.45	64.43	62.09	61.00	59.67	52.77	42.49	31.79	27.44	21.31	14.61	10.01	7.07	4.48	852.23
FSP1	4.35	1.43	7.68	4.82	2.84	2.95	2.75	1.43	2.04	3.03	3.49	1.23	4.54	2.11	3.94	5.45	9.30	20.67	24.56	25.32	26.75	26.20	24.80	32.23	19.38	16.02	13.49	8.49	6.40	4.31	2.81	1.61	0.00	316.41
FSP2	5.07	3.37	12.49	8.49	9.61	7.59	20.77	10.73	25.13	12.52	24.04	7.37	23.20	10.96	16.82	18.18	25.95	41.47	52.55	58.60	56.33	61.34	58.91	53.79	51.63	43.97	25.65	27.33	19.15	12.81	9.19	5.66	3.68	824.35
FSP3	2.11	1.14	13.49	1.11	0.61	1.61	0.78	0.35	0.25	0.33	0.48	0.24	0.51	0.34	0.56	0.71	1.99	3.10	6.46	5.53	9.74	9.27	7.32	6.80	5.57	2.19	1.88	1.01	1.20	1.06	0.61	0.00	0.00	88.32
FSP4	5.84	2.36	9.39	5.92	5.62	4.79	9.53	1.84	8.60	2.25	10.75	2.27	16.27	1.99	4.91	3.38	6.14	11.00	13.80	13.02	13.66	16.60	14.00	14.22	12.22	9.82	8.82	4.92	4.93	2.85	1.96	0.86	0.37	244.92
FSP5	1.23	0.63	7.81	0.57	0.38	1.00	0.54	0.33	0.59	0.18	2.12	0.58	2.63	0.74	1.65	1.24	2.14	1.32	4.60	3.96	4.71	5.56	5.38	6.24	6.12	5.07	4.56	1.42	2.46	1.94	1.68	0.00	0.00	81.39
OTAL	18.59	8.93	50.87	20.91	19.07	17.93	34.36	14.68	36.61	18.30	40.88	11.68	47.15	16.14	27.88	28.97	45.52	77.57	101.97	106.42	111.19	118.98	110.41	113.29	94.92	77.07	54.39	45.16	34.15	22.98	16.26	8.13	4.05	1555.3
MEAN	3.72	1.79	10.17	4.18	3.81	3.59	6.87	2.94	7.32	3.66	8.18	2.34	9.43	3.23	5.58	5.79	9.10	15.51	20.39	21.28	22.24	23.80	22.08	22.66	18.98	15.41	10.88	9.03	6.83	4.60	3.25	1.63	0.81	311.08
prSP1	0.00	3.68	10.32	12.58	7.41	6.96	10.16	8.30	13.31	22.19	16.64	6.37	13.51	6.54	11.90	9.75	13.55	24.10	33.00	25.34	31.02	21.53	22.76	21.99	20.48	13.95	15.11	7.50	6.80	0.42	3.21	1.57	0.70	422.72
prSP2	1.51	0.87	5.72	1.85	1.44	2.55	6.01	3.38	9.24	3.95	10.81	2.99	12.73	4.06	7.49	8.34	14.67	36.44	37.43	40.45	42.23	44.53	43.95	42.37	32.09	26.82	19.25	12.55	9.72	5.89	4.53	2.08	0.00	498.55
prSP3	0.00	2.40	7.05	1.14	0.60	4.87	3.07	0.25	0.11	0.24	0.07	0.05	0.05	0.03	0.04	0.12	0.06	0.09	0.11	0.27	4.79	0.00	0.86	0.85	13.92	0.00	0.00	0.00	0.17	0.00	0.10	0.00	0.00	41.32
prSP4	2.01	0.97	6.05	3.41	3.37	4.05	4.00	1.98	4.23	1.68	5.22	1.24	4.91	1.80	3.73	4.70	8.80	14.43	23.11	9.27	29.26	25.48	24.17	24.18	22.12	17.12	12.45	9.42	7.48	5.57	3.78	2.49	0.95	293.42
prSP5	4.88	2.80	7.48	9.84	3.07	6.11	8.54	13.96	18.33	48.56	25.87	14.58	49.39	13.25	21.44	16.15	21.86	35.32	46.89	41.74	53.35	51.71	45.54	56.06	34.82	28.13	23.83	13.94	11.05	8.12	5.13	3.13	1.39	748.24
OTAL	8.40	10.71	36.63	28.82	17.89	24.55	31.78	27.87	45.23	76.62	58.61	25.22	80.60	26.27	44.59	39.05	58.92	110.39	140.55	117.06	160.66	143.24	137.27	145.44	123.42	86.02	70.66	43.49	35.22	19.99	16.75	9.28	3.04	2004.2
MEAN	1.68	2.14	7.33	5.76	3.58	4.91	6.36	5.57	9.05	15.32	11.72	5.04	16.12	5.25	8.92	7.81	11.78	22.08	28.11	23.41	32.13	28.65	27.45	29.09	24.68	17.20	14.13	8.70	7.04	4.00	3.35	1.86	0.61	400.85

Total concentrations of n-akanes (ng/g dry wt) in SPM in the wet season

Stations	AprSP1	AprSP2	AprSP3	AprSP4	AprSP5	JSP1	JSP2	JSP3	JSP4	JSP5	ASP1	ASP2	ASP3	ASP4	ASP5	Total(ng/g)
C8	0.00	1.51	0.00	2.01	4.88	8.29	7.92	6.70	6.09	7.31	1.97	2.75	3.17	0.00	6.07	58.68
C9	3.68	0.87	2.40	0.97	2.80	2.77	2.70	1.92	2.00	2.35	1.01	3.03	2.60	1.13	2.15	32.37
C10	10.32	5.72	7.05	6.05	7.48	11.39	10.00	9.09	9.63	9.82	5.61	10.92	9.13	6.04	6.24	124.51
C11	12.58	1.85	1.14	3.41	9.84	7.74	6.98	8.46	6.73	7.36	3.52	12.90	6.76	3.41	8.66	101.36
C12	7.41	1.44	0.60	1.37	5.07	4.58	4.67	5.80	3.06	4.62	2.80	14.74	4.70	1.48	3.43	67.77
C13	6.96	2.55	4.87	4.05	6.11	4.34	3.83	5.16	2.88	3.98	3.88	15.61	4.90	2.52	4.30	75.76
C14	10.16	6.01	3.07	4.00	8.54	5.46	4.49	4.21	2.84	4.35	3.93	12.83	4.21	1.90	3.49	79.51
C15	8.30	3.58	0.25	1.98	13.96	3.39	2.99	3.12	1.92	3.06	3.15	7.36	3.11	1.82	2.84	60.63
C16	13.34	9.24	0.11	4.23	18.33	4.08	4.63	4.45	2.46	4.54	2.19	5.57	2.44	1.35	2.37	80.20
C17	22.19	3.95	0.24	1.68	48.56	6.36	7.18	7.93	4.48	6.77	3.53	0.42	3.76	0.11	3.61	120.79
C18	16.64	10.81	0.07	5.22	25.87	4.72	4.49	4.15	2.61	4.32	2.33	5.71	2.71	1.73	2.44	93.82
C19	6.37	2.99	0.05	1.24	14.58	5.14	4.90	3.17	2.98	4.03	2.61	5.07	2.51	1.65	2.84	60.12
C20	13.51	12.73	0.05	4.91	49.39	10.86	10.22	5.84	7.28	8.75	5.78	11.61	5.64	3.60	5.77	155.94
C21	6.54	4.66	0.03	1.80	13.21	20.15	13.78	11.36	12.96	13.37	12.57	23.42	10.60	7.51	11.88	163.88
C22	11.90	7.49	0.04	3.73	21.44	38.20	23.91	19.85	26.12	25.01	25.18	44.98	23.44	15.85	24.11	311.24
C23	9.75	8.34	0.12	4.70	16.15	60.65	38.53	29.73	45.18	41.85	42.80	73.34	36.87	26.60	40.21	474.82
C24	13.55	14.67	0.06	8.80	21.85	89.41	48.88	46.97	70.19	59.53	68.41	99.85	62.82	43.72	66.23	714.94
C25	24.10	36.44	0.09	14.43	35.32	127.16	100.92	69.88	145.00	114.04	110.14	201.36	96.38	93.84	148.37	1317.48
C26	33.00	37.43	0.11	23.11	46.89	164.34	132.28	10.98	159.50	145.89	135.49	173.23	142.88	103.50	132.05	1440.67
C27	25.34	40.45	0.27	9.27	41.74	185.40	170.01	99.67	137.77	153.89	146.54	194.11	134.51	97.08	141.00	1577.03
C28	31.02	42.23	4.79	29.26	53.35	190.73	121.34	93.82	169.04	145.19	156.09	198.91	153.87	113.26	160.40	1663.29
C29	21.53	44.53	0.00	25.48	51.71	169.08	139.70	102.60	141.09	140.40	146.85	178.43	130.29	100.60	153.23	1545.50
C30	22.76	43.95	0.86	24.17	45.54	167.10	111.72	97.72	124.53	118.13	135.15	199.84	137.00	110.43	140.14	1479.04
C31	21.99	42.37	0.85	24.18	50.66	146.50	126.59	79.64	119.05	122.82	110.10	162.27	113.80	91.89	120.33	1338.43
C32	20.48	32.09	13.92	22.12	34.82	155.06	139.66	82.48	123.87	131.76	109.74	192.54	141.78	103.97	126.36	1430.63
C33	13.95	26.82	0.00	17.12	28.13	138.55	99.00	58.87	109.13	104.07	83.27	146.36	108.26	68.66	117.61	1119.79
C34	15.11	19.25	0.00	12.45	23.85	109.45	88.00	53.54	80.72	84.36	71.17	142.54	211.40	62.41	93.28	1067.54
C35	7.59	12.55	0.00	9.42	13.94	86.20	80.77	44.18	62.62	71.69	56.23	119.88	64.75	49.86	69.37	749.03
C36	6.80	9.72	0.17	7.48	11.05	64.11	48.30	34.23	44.37	46.33	42.23	92.70	143.46	37.70	54.82	643.46
C37	0.42	5.89	0.00	5.57	8.12	46.42	41.12	25.05	30.22	35.67	30.26	67.06	33.22	28.77	37.17	394.95
C38	3.21	4.53	0.10	3.78	5.13	29.93	19.56	16.30	19.32	19.44	19.68	43.38	55.59	18.85	26.14	284.94
C39	1.57	2.08	0.00	2.49	3.13	16.82	15.66	10.09	11.19	13.43	16.95	25.87	21.28	11.39	14.98	160.94
C40	0.70	0.00	0.00	0.95	1.39	7.61	6.81	6.02	0.00	6.41	4.81	14.33	27.92	0.00	0.00	76.94
Total(ng/g)	422.72	498.55	41.32	293.42	748.24	2092.68	1641.53	1062.97	1686.81	1664.55	1559.97	2502.91	1905.76	1212.64	1731.91	19066.00
Mean	12.81	15.11	1.25	8.89	22.67	63.41	49.74	32.21	51.12	50.44	47.27	75.85	57.75	36.75	52.48	577.76
STD	8.79	15.42	2.83	8.51	17.55	66.96	53.35	34.12	57.71	54.45	53.74	75.87	62.02	41.69	57.92	588.16

Total concentrations of n-akanes (ng/g dry wt) in SPM in the dry season

Stations	OSP1	OSP2	OSP3	OSP4	OSP5	DSP1	DSP2	DSP3	DSP4	DSP5	FSP1	FSP2	FSP3	FSP4	FSP5	TOTAL(ng/g)
C8	3.38	5.87	2.71	1.71	2.38	2.57	2.80	1.94	2.88	2.68	4.35	5.07	2.11	5.84	1.23	47.50
C9	1.98	3.79	1.92	1.82	2.30	2.27	2.92	1.72	21.82	2.59	1.43	3.37	1.14	2.36	0.63	52.04
C10	4.85	14.11	7.98	8.49	9.27	11.17	11.12	7.51	135.76	11.15	7.68	1249	13.49	9.39	7.81	272.28
C11	3.86	12.40	5.83	29.33	5.24	15.03	6.35	4.23	166.29	10.69	4.82	8.49	1.11	5.92	0.57	280.14
C12	2.94	6.30	2.90	22.68	3.33	9.97	5.52	5.03	36.81	7.74	2.84	9.61	0.61	5.62	0.38	122.29
C13	3.21	6.30	3.14	15.05	3.89	7.52	6.66	6.67	19.08	7.10	2.95	7.59	1.61	4.79	1.00	96.54
C14	2.89	4.43	2.34	11.68	3.13	5.50	11.41	5.89	13.09	8.65	2.75	20.77	0.78	9.53	0.54	103.38
C15	4.97	3.41	1.32	4.72	4.28	2.87	8.45	2.81	8.10	5.49	1.43	10.73	0.35	1.84	0.33	61.09
C16	5.21	7.35	3.62	5.53	7.78	2.22	13.68	2.18	7.76	4.99	2.04	25.13	0.25	8.60	0.59	96.93
C17	14.70	7.92	5.08	7.08	14.90	3.95	11.89	3.58	8.46	6.20	3.03	12.52	0.33	2.25	0.18	102.06
C18	14.41	15.44	9.68	8.47	14.02	5.06	17.27	4.63	13.85	9.45	3.49	24.04	0.48	10.75	2.12	153.15
C19	7.03	2.96	1.64	2.69	4.07	2.02	7.04	1.80	5.97	4.00	1.23	7.37	0.24	2.27	0.58	50.90
C20	28.27	9.64	6.29	7.11	12.75	6.05	21.97	5.77	11.61	8.83	4.54	23.20	0.51	16.27	2.63	165.45
C21	15.31	5.07	3.24	5.03	7.10	3.98	14.48	3.29	11.19	7.58	2.11	10.96	0.34	1.99	0.74	92.41
C22	59.41	15.62	8.46	9.55	12.36	7.49	2061	6.10	1649	11.99	3.94	16.82	0.56	4.91	1.65	195.97
C23	24.10	15.27	10.61	13.91	13.46	11.27	26.53	9.75	20.52	15.90	5.45	18.18	0.71	3.38	1.24	190.28
C24	36.05	27.58	19.60	24.20	208.60	20.13	39.26	16.29	34.05	27.09	9.30	25.95	1.99	6.14	2.14	498.37
C25	54.87	41.90	32.22	40.38	32.38	33.50	57.47	36.93	48.59	42.76	20.67	41.47	3.10	11.00	1.32	498.56
C26	58.98	66.28	51.62	69.28	50.62	51.34	7969	45.57	80.13	65.52	24.56	52.55	6.46	13.80	4.60	721.01
C27	79.51	61.14	48.81	61.24	44.99	47.69	81.31	42.27	71.41	59.55	25.32	58.60	5.53	13.02	3.96	704.36
C28	63.34	70.34	58.01	73.30	51.28	54.60	7833	49.11	75.23	64.91	26.75	56.33	9.74	13.66	4.71	749.63
C29	94.57	68.73	53.06	6777	51.12	51.75	79.83	43.22	73.18	62.47	26.20	61.34	9.27	16.60	5.56	764.68
C30	65.40	61.25	54.50	61.90	4643	46.51	82.19	41.38	74.44	60.48	24.80	58.91	7.32	14.00	5.38	704.89
C31	66.43	57.26	46.46	57.20	38.31	41.90	69.11	55.90	6900	62.45	3223	53.79	6.80	14.22	6.24	677.33
C32	4961	60.27	41.07	78.94	41.29	40.51	72.58	34.00	64.32	52.42	19.38	51.63	5.57	12.22	6.12	62993
C33	39.69	37.65	29.01	43.68	26.67	33.56	63.60	27.86	47.12	40.34	16.02	43.97	2.19	9.82	5.07	466.23
C34	29.43	33.60	25.48	37.62	22.58	28.73	36.35	26.20	35.53	32.13	13.49	25.65	1.88	8.82	4.56	362.05
C35	20.20	26.71	1901	23.97	17.55	20.28	3999	16.21	33.40	26.84	8.49	27.33	1.01	4.92	3.42	289.33
C36	16.55	19.87	13.49	18.03	14.27	15.21	30.82	14.16	25.84	20.53	640	19.15	1.20	4.93	2.46	222.90
C37	9.88	15.00	9.43	13.14	10.06	10.76	22.57	8.57	17.16	13.96	4.31	12.81	1.06	2.85	1.94	153.52
C38	7.15	9.69	8.28	8.40	6.58	7.05	15.74	6.78	11.29	9.17	2.81	9.19	0.61	1.96	1.68	106.38
C39	2.43	6.46	4.41	5.73	4.86	5.82	10.70	3.52	8.28	7.05	1.61	5.66	0.00	0.86	0.00	67.40
C40	1.91	3.22	2.00	2.65	2.50	3.83	6.44	2.11	5.41	4.62	0.00	3.68	0.00	0.37	0.00	38.72
Total(ng/g)	892.51	802.83	593.24	842.26	790.33	612.12	1054.66	542.97	1274.08	777.32	316.41	824.35	88.32	244.92	81.39	9737.72
Mean	27.05	24.33	17.98	25.52	23.95	18.55	31.96	16.45	38.61	23.56	9.59	24.98	2.68	7.42	2.47	295.08
STD	2687	23.01	18.97	24.64	37.05	17.64	2806	17.05	38.30	22.24	962	19.05	3.39	4.88	2.19	250.88

APPENDIX 7

Relationship between concentrations of n-alkanes in water in the wet and dry seasons

Wet	Dry
0.06	0.12
0.01	0.06
0.00	0.10
0.04	0.06
0.00	0.05
0.15	0.11
0.16	0.06
0.14	0.05
0.22	0.18
0.05	0.07
0.22	0.08
0.14	0.05
0.13	0.02
0.11	0.04
0.13	0.10

Relationship between Concentration, Temperature and Salinity of n-alkanes in SPM from the Cross River estuary

Months	Conc	Temp	Salinity
Jun	23.89	32.00	5.50
Aug	24.06	36.00	10.70
Oct	12.78	28.00	11.70
Dec	15.72	21.50	17.50
Feb	9.55	20.00	23.50
Apr	3.59	26.00	11.70

APPENDIX 8

Comparative analysis of the concentrations of n-alkanes (ng/L) in water in the wet season (April, June and August) and dry season (February, October and December)

Variable	T	Df	P-value	Wet	Dry
Wet-dry season	5.389	494	0.000		
Mean concentration				0.104	0.077

Comparative analysis of the concentrations of n-alkanes (ng/g dry wt) in SPM in the wet season (April, June and August) and dry season (February, October and December) using t-test

Variable	t	Df	P-value	Wet	Dry
Wet-dry season	9.020	239	0.652		
Mean concentration				0.0577	0.0633