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Total Hydrocarbon Concentrations (THC) in surface water, sediments and biota from Otamiri River, Rivers State, Nigeria

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Abstract
Etche local government is one of the major local areas in rivers state with rich natural resources. The rich environment has attracted some companies in the extractive sector and the indigene believed that their environment particularly the water bodies had been negatively impacted. This study was necessitated to actually verify the claim. Therefore, water, sediments and biota samples were collected from five locations in the rich Otamiri river for total hydrocarbon determination. The collected samples were prepared and analyzed using uv spectrometer. The results of the THC in surface water ranged from 1.51 to 19.38mg/l while the WHO recommended limit is 10mg/l, in sediments it ranged from 16.01 to 136.04mg/kg and the WHO recommended limit is 30mg/kg. The concentrations of THC in biota ranged from 3.29mg/kg to 16.20mg/kg with the WHO recommended limit of 0.001ųg/g. In the surface water, the concentrations of THC obtained were within the limit recommended except for one location, in sediments, the concentrations obtained from two locations were within the WHO recommended limit while the rest three were above the limit and in biota all the locations were more than the WHO recommended limit. The increase in the concentrations recorded for the sediments and biota may be attributed to sedimentation and bioaccumulation respectively over a period of time. It is our utmost view that the consumption of aquatic organisms from the river be discontinued forthwith pending when proper remediation exercise is carried out.

Keywords: hydrocarbon, concentration, local, government, determination, analysis, surface water, sediments, biota, gas, chromatography, detector etc.

Introduction
In aquatic environments, studies on hydrocarbon contamination have been based on the analysis of organisms, pelagic column and sediments, moreover total hydrocarbon concentration (THC) studies have received much attention due to enhanced bio-accumulative potential of hydrocarbon components in colloidal surface of sediments which allows for spatial and temporal distribution of hydrocarbons to be determined relative to their sources.
Abiodun *et al.* (2017) [1] reported a work on petroleum hydrocarbon profiles of water and sediment using liquid-liquid and Soxhlet extraction techniques and Gas chromatography equipped with flame ionization detector (GC-FID). The total petroleum hydrocarbon (TPHC) obtained in sediments ranged from 45.07 to 307mg/kg while in water it ranged from 0.72 to 27.03mg/l. Nsikak, *et al.*, (2007) [11] carried out work on petroleum hydrocarbon accumulation potential of shell fishes from littoral waters of the Bight of Bonny using standard methods. Their results show higher levels of total hydrocarbon in dry season than in wet season.
Wokoma (2014) [19] reported on total hydrocarbon concentrations in the Kua/Kinabere Creek in Ogoni land, an estuary of the Bonny River, sub-surface seawater and surface sediment using Soxhlet extraction techniques and gas chromatography with flame ionization detector (GC-FID). His results shows that concentrations of total hydrocarbon in water and sediments varied from 1.86±2.55mg/l and 1.403±8.031mg/kg respectively. The observed concentrations of THC are within the established permissible levels of 10mg/l in water and 30mg/kg in sediment. Cheraghi *et al.* (2015) [5], reported a work on biochemical and physical characteristics of petroleum hydrocarbon in contaminated soils in Tehran using soxhlet extraction procedures with same proportion from n-hexane and dichloromethane. For PAH analysis, high pressure Liquid chromatography (HPLC) and for TPH analysis, Gas chromatography (GC) was used.

Their results shows that total petroleum hydrocarbon TPH and polyaromatic hydrocarbon (PAH) concentrations varies from 10.1334.0-10.1367.1 and 2.58766 mg/Kg respectively.

Imaobong *et al.* (2017) carried out work on total petroleum hydrocarbon (TPH) concentration in surface water of cross river estuary, Niger Delta Nigeria using Gas. Chromatography equipped with flame ionization detector. Their results shows that the surface water was contaminated with total petroleum hydrocarbon with mean concentration ranging from 13.16181 ±1.485mg/l to 24.85462+ 8.058 mg/l compared to the control sample with concentration of 9.68200± 0.233mg/l. It was further observed that the level of TPH in their study was high relative to Nigerian permissible limit of 10mg/l in water. The level of TPH obtained from the study potent a serious risk to the survival of aquatic organisms and also affects the quality of water from the river that may be used for various purposes.

Nwineewii, & Marcus, (2015) [12] conducted a research on polyaromatic hydrocarbon in surface water and their toxicological effects in some creeks of south East Rivers State using L-L partition with CH_2Cl_2 and Gas chromatography equipped with flame ionization detector (GC-FID), results obtained showed that the concentrations of PAH ranged between 0.008 and 0.24mg/l. From the results, it was observed that the concentrations of the pollutants were within the USEPA recommended limits of between 0.20 and 400ppm for drinking water and 10mg/l by WHO.

Olaji *et al.* (2014) reported work on assessment of total hydrocarbon concentrations in four fish species of Degele community in Nigeria and their dietary intake in the populace using gas chromatography equipped with flame ionization detector (GC-FID) for the evaluation of total petroleum hydrocarbon. Their results showed that the mean concentrations of aliphatic hydrocarbon were as follows C*larias gariepinus* (46.7±16.7mg/kg), *Heterobranchus longifilis* (42.7±17.4mg/kg), *and Oreochromis niloticus (1123.70±52.10mg/kg and Liza falicipinis (29.0±1.4mg/kg)* The highest level of aliphatic hydrocarbon concentration was obtained in *Oreochronsniloticus*. According to their studies, carcinogenic polyaromatic hydrocarbon of lower molecular weight (LMW PAHs) was detected with clearly observed naphthalene and its substituents in all the studied fish species.

Enetimi *et al.* (2017) [7] reported on assessment of hydrocarbon level in surface water Aligning Imirigi oil field facilities in the Niger Delta using standard procedures. Their results shows total hydrocarbon (TH) content ranged from 2.06mg/l (upstream) to 2.32mg/l (downstream) and control being 0.08mg/l.

Ibigoni, *et al.* (2009) [8, 9] reported work on evaluation of total hydrocarbon levels in some aquatic media in an oil polluted mangrove wetland in the Niger Delta using standard analytical procedures. Their result showed elevated THC mean levels in water (23.6±4.3mg/l), sediment (286.44±50.28mg/g) and biota (*Tympanotonus fuscatus*) periwinkle (449.30 ± 55.42mg/g). From their results petroleum hydrocarbon content (PHC) levels in water at the wellhead stations were above 10mg/l being the maximum recommended limit by the Federal Ministry of Environment (FMENV) Nigeria.

Epipellic and benthic sediments are known to act as principal sinks for hydrocarbons in aquatic environments. It is likely that a route of exposure for sediment dwelling organisms is through ingestion from interstitial water and biota's such as fishes also appear to absorb most hydrocarbons directly from the water phase (NRC, 1983). Contamination of aquatic ecosystem by natural and anthropogenic hydrocarbon inputs is attributable to industrial and maritime activities. Coastal ecosystems are episodically exposed to this challenge owing to their proximity to the sources of pollution. Organic chemicals such as hydrocarbons are major constituents of petroleum (Tissot and Welte, 1978; Philip, 1985) and can enter marine environments through oil spills riverine discharges; offshore oil production and transportation, land derived organic matter, sewage disposal as well as biomas burning. Although certain hydrocarbons could be produced biogenically from bacteria and chemical degradation of naturally occurring lipids, petrogenic sources constitute the major hydrocarbon inputs to littoral water pollution cases.

Study Area

The study was conducted in Etche local government, one of the major local government areas in rivers state. Etche is bordered on the north by Omuma and on the west Ikwere local government. The people of Etche are predominantly farmers while a harmful of them are involved in government paid job. There have been oil exploration and exploitation in the place for a long time. The inhabitants of the local government felt that their environment may have been impacted due to the activities of the oil companies in the place. The study covered part of Otamiri River as shown in Figure 2 which cuts across different communities like Isu, Opiro, Umuechem, Chokocho and Igboh etc.

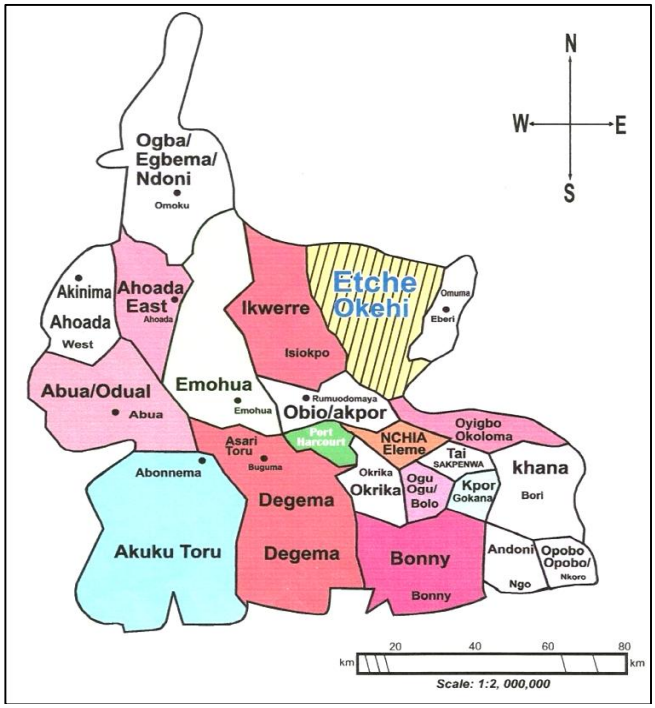

Fig 1: map of rivers State showing the study Area

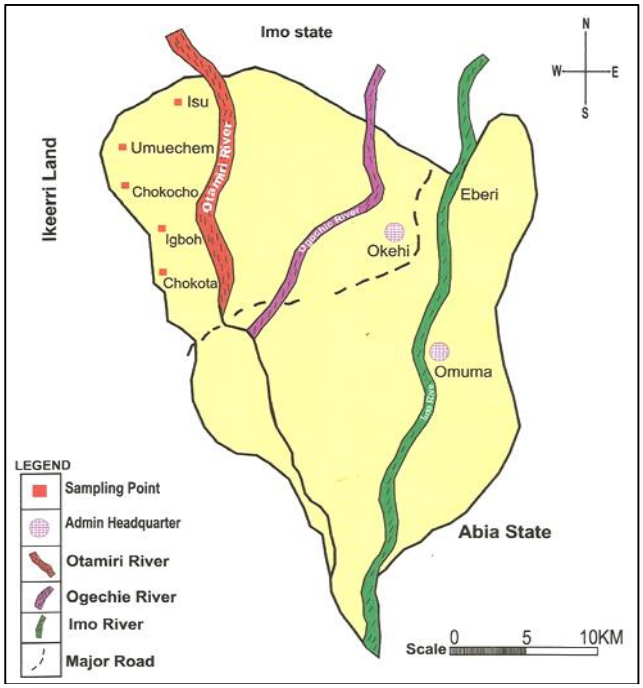

Fig 2: Map of Etche Local Government Area Showing Various Sampling Point

Collection of sediment samples

The sediment samples were collected from five different communities (Isu, Opiro, Umuechem, Nchokocho and Igboh) within Otamiri River from the month of November, 2017 to February 2018. With the use of a scooper, the sediment was excavated to a depth of 2-4cm and rapped with aluminum foil after collection. The collected sediment samples were preserved in cool box containing ice pack and taken to the laboratory for proper storage until time of analysis.

Collection of biota: Cat fish (*Clarias gariepinus*)

The fish samples were collected using gillnets and castnets at night with the help of local fishermen. After the fish samples were collected, they were preserved in cool boxes and taken to the laboratory for storage in the refrigerator until analysis was carried out.

Determination of Total Hydrocarbon Concentration (THC) in Biota (Catfish)

Total hydrocarbon concentration in catfish was determined following the method by Odu *et al.* (1985) [13] and Dambo (2000) [6]. Five grams (5g) of each sample were weighed and duplicated into 100ml conical flasks arranged serially. Then 10ml of toluene was added to each flask (to extract the hydrocarbons) and mixed thoroughly, for hydrocarbon (oil and grease) to exude. It was then filtered through a No. 1 Whatman filter paper and the absorbance of the filtrate measured using a spectrophotometer (Spectronic 21-D model). The total hydrocarbon concentrations in the tissue were calculated after duly reading the concentration of the oil in the extractant from the spectrometer. The total hydrocarbon concentration was calculated with due reference to the standard and multiplication by the appropriate dilution factor.

Determination of Total Hydrocarbon Concentration (THC) in Sediment

The collected sediment sample was dried to a constant weight in a hot-air oven for 24 hours at 100^0C. They were ground and sieved to remove coarse particles using 1mm pores sieves. 10ml of toluene was measured and added to 5 grams of sediment sample.

The mixture was shaken thoroughly for 10 minutes and allowed to settle. Thereafter, toluene was decanted (Supernatant) and measured at 420nm using Spectronic 21D. Hydrocarbon concentrations in the sediment samples were then calculated after reading the concentration of the hydrocarbon in the extract with reference to a standard curve and multiplied by the appropriate dilution factor to give total hydrocarbon (Odu *et al.*, 1985; Dambo, 2000) [13, 6].

Determination of Total Hydrocarbon Concentration (THC) in Surface Water

100ml of water sample was mixed with 5ml of toluene (both in separate funnel), and swirled for 30 minutes. The mixture was allowed to stand for about 5 minutes and then filtered. The filtered extract was read directly at 420nm using specronic 21D. The THC in the water was calculated as shown below:

$$\text{THC} = \frac{\text{Absorbance value}}{\text{Vol of water sample-Vol of Toluene used for extraction}} \text{ x2678.8}$$

Where 2678.8 is dilution factor

Results and Discussions

Results

Total hydrocarbons Concentration (THC) in Sediments

The table 1 below shows the results of the concentrations of total hydrocarbons in sediments from Otamiri River and fig. 3 is the component bar chart of the monthly distribution of THC from one location to another.

Table 1: Total hydrocarbon concentrations mg/kg (THC) in sediments

S/N	Location	Month of Sampling					
		Nov 2017	Dec. 2017	Jan. 2018	Feb. 2018	$\bar{X}$ S.D.	WHO
1	Umuechem	121.05	128.49	136.04	110.01	123.80 ± 8.01	30mg/kg
2	Chokocho	96.48	104.69	98.31	91.34	97.71 ± 3.67	30mg/kg
3	Opiro	21.36	27.85	23.09	20.49	23.19 ± 3.28	30mg/kg
4	Igboh	20.02	24.72	22.10	18.33	21.29 ± 2.75	30mg/kg
5	Isu	18.41	21.44	19.07	16.01	18.73 ± 2.23	30mg/kg

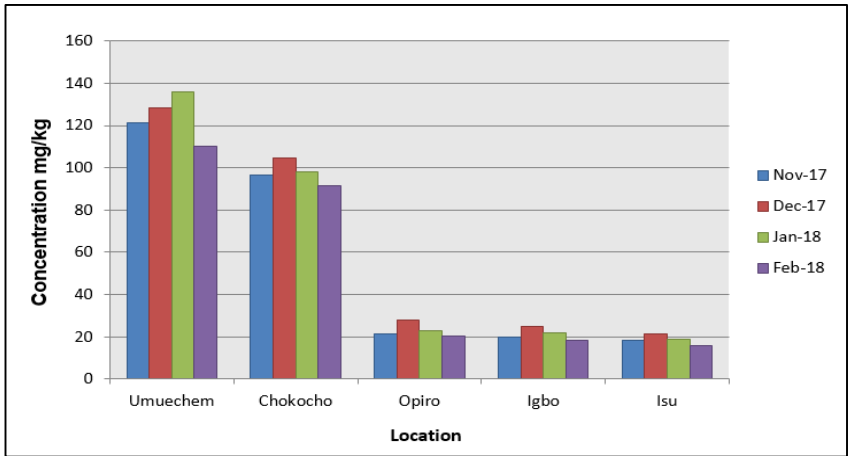

Fig 3: Component bar chart showing total hydrocarbon concentrations (THC) in sediments

At the Umuechem location, the THC recorded ranged from 110.1 to 136.04mg/kg with the mean concentration of 123.80±8.01 while from chokocho, the THC obtained ranged from 91.34 to 104.69mg/kg and the mean was 97.71±3.67mg/kg. From the opiro location, the THC obtained ranged from 20.49mg/kg to 27.85mg/kg and the mean was 23.17±3.28. Also, from the Igboh location, the concentration of total hydrocarbon observed ranged between 18.41mg/kg and 24.72mg/kg with the mean concentration of 21.29±2.27mg/kg. Sediments collected from Isu location recorded the THC ranging from 16.01 to 21.44mg/kg while the mean was 18.73±2.23 mg/kg. The mean THC obtained from Umuechem, and Chokocho were higher than the permissible limit of 30mg/kg set by the World Health Organisation but Opiro, Igboh and Isu locations recorded THC mean concentrations that were within set limits for THC. However, the mean concentrations obtained in the study were higher than those reported by Abiodun *et al.* (2017) [1], who recorded concentration range of 0.72 to 27.03mg/kg, Ali *et al.* (2014) in their study recorded concentrations range of 0.24 to 20.65 mg/kg in the coastal area of papar totuaran, Sabah Malaysia.. The results showed that lower concentrations of total hydrocarbon were obtained in the month of February while December had the highest concentration across the sample locations. This could be as a result of variation in month with regard to rainfall as February has a higher rainfall when compared to other months in the study. The higher rain fall results in higher volume of water thereby reducing the THC level. It is noted that the river current tends to be higher in the month of February because of the volume of water giving the Hydrocarbon less residence time in the water around such periods.

The high concentrations of Total Hydrocarbons obtained in sediments from Umuechem and Chokocho may be attributed to crude oil exploration around Umuechem location and operations of illegal refineries. This may also have arisen due to intermittent discharge from oil pipelines and installations around these locations. Also Fig.1 above illustrates the comparism of THC from the month of November to that of February in the five locations studied.

Total Hydrocarbons Concentrations in Surface Water (mg/l)

The Concentrations of Total Hydrocarbon in Surface Water from Otamiri River are shown in table 2 below.

Table 2: Total Hydrocarbon Concentrations mg/l (THC) in Surface Water (mg/l)

S/N	Location	Month of Sampling						
		Nov 2017	Dec. 2017	Jan. 2018	Feb. 2018	$\bar{X}$	S.D.	WHO
1	Umuechem	17.37	19.38	18.03	15.07	17.48 ± 11.09		10mg/l
2	Chokocho	9.49	11.23	10.31	7.33	9.59 ± 1.66		10mg/l
3	Opiro	5.81	7.32	6.06	3.49	5.67 ± 1.59		10mg/l
4	Igboh	3.04	5.85	4.21	1.51	3.65 ± 1.84		10mg/l
5	Isu	4.22	6.11	5.70	2.06	4.52 ± 1.83		10mg/l

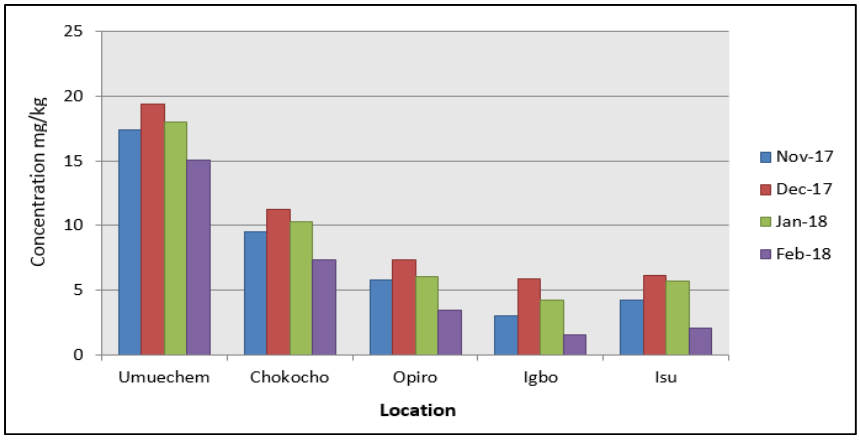

Fig 4: Component bar chart showing total hydrocarbon concentrations (THC) in Surface Water (mg/l)

The concentration of Total Hydrocarbon in surface water from the various locations ranged as follows Umuechem (15.07 to 19.03mg/l), Chokocho (7.33 to 11.23mg/l), Opiro (3.49 to 7.32mg/l), Igboh (1.51 to 5.85mg/l) and Isu (2.06 to 6.11mg/l). The mean concentrations for Umuechem, Chokocho, Opiro, Igboh and Isu were 17.48±11.09, 9.59±1.66, 5.67±1.59, 3.65±1.84 and 4.52 ±1.83 respectively. The highest concentration of total hydrocarbon was obtained from the Umuechem location in the month of December while the lowest was from Isu in the month of February. Umuechem is playing host a multinational oil company that is involved in exploration and drilling with pipeline crisscrossing the place. At times there are pipeline rupture and damages to pipeline due to sabotage bringing about oil spill. This of course, could be attributed to the high THC recorded in the place. The results obtained in this work for THC in surface water are within the limit of 10mg/l stipulated by the World Health Organization except for one location (Umuechen). The concentrations of THC in surface water from this study are in line with researches by some scholars on THC in surface water, amongst such includes works by Wokoma (2014) [19], on surface water around Kua/Kinabere Creek in Ogoni land, an estuary of Bonny River who recorded the concentration range of 1.86 to 2.55 mg/l and Enetimi *et al.* (2017) [7], that recorded a concentration range of 2.06 to 2.32 mg/l for THC in surface water around Imiringi Oil Field.

Total Hydrocarbon Concentration in Biota (Catfish *Clarias Gariepinus)* from Otamiri River.

The results of concentrations of Total Hydrocarbons in Biota across the sampled locations are presented in table 3 below. From the results, it was observed that the concentrations of THC varied from location to location across month.

Table 3: Total Hydrocarbon Concentrations,mg/kg inBiota (cat fish) from Otamiri River

S/N	Location	Period of Sampling of Biota (Fish)					
		Nov 2017	Dec. 2017	Jan. 2018	Feb. 2018	$\bar{X}$ S.D.	WHO
1	Umuechem	10.54	16.20	15.11	11.32	13.29± 2.78	0.001µg/g
2	Chokocho	8.67	10.89	10.99	7.63	9.55 ± 1.67	0.001µg/g
3	Opiro	6.73	9.55	10.10	5.49	7.97 ± 1.22	0.001µg/g
4	Igboh	4.99	6.74	7.52	5.10	6.09 ± 1.24	0.001µg/g
5	Isu	3.54	5.66	6.45	3.29	3.48 ± 2.13	0.001µg/g
Overall mean ($\bar{x}$) and Standard Deviation(S.D)						8.08 ± 058	

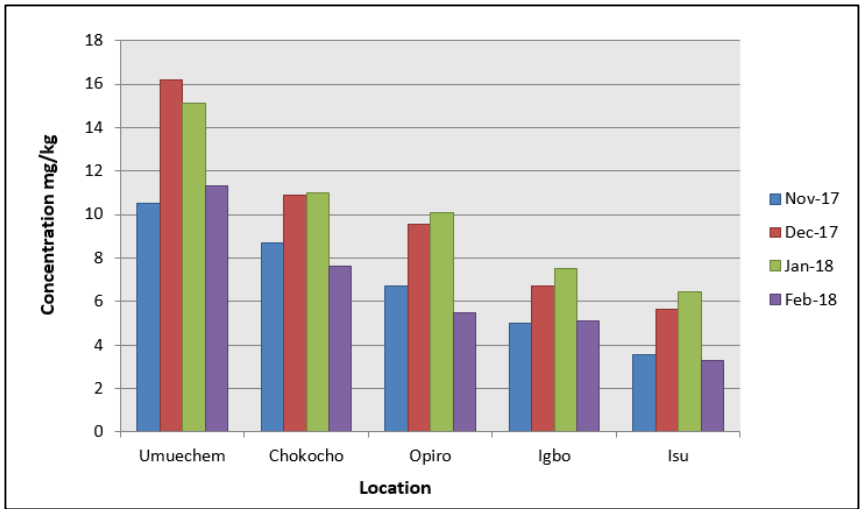

Fig 5: Component bar chart showing total hydrocarbon concentrations in biota (cat fish) from Otamiri River

The total hydrocarbon concentrations in biota from the various locations ranged as follows Umuechem (10.54-16.20mg/kg), Chokocho (7.63-10.99mg/kg), Opiro (5.49-10.10mg/kg), Igboh (4.99-7.52mg/kg), and Isu (3.29-6.45mg/kg). Considering the results, it was observed that the highest THC of 16.20mg/kg was obtained in the month of December from Umuechem while the least which was 3.54mg/kg was recorded from the Isu location in the month of November. Ibigoni, *et al.* (2009) [8, 9] works on the evaluation of total hydrocarbon levels in some aquatic media in an oil polluted mangrove wetland in the Niger Delta using standard analytical procedures. Their result showed an elevated THC mean levels in biota (*Tympanotonus fuscatus*) periwinkle 449.30 ± 55.42mg/g. The concentrations of total hydrocarbons obtained in the work are far above the recommended limit of 0.001µg/kg set by WHO. It was also noted that THC obtained in the biota were more than those for the surface water. The high concentrations in the biota compared to surface water could be ascribed to the bioaccumulative nature of the biota. The monthly distribution of THC across locations can be observed from the component bar chart in fig 5 above. This clearly illustrates the spatial distribution from one location to another.

Conclusion

The concentrations of total hydrocarbon in surface water, sediments and biota from Otamiri river in Etche local government area of river state were carried out to estimate the level of hydrocarbons pollution in the river. Findings from the study revealed that the THC in surface water from all the locations were within the limits stipulated by WHO except one. In sediments, it was discovered that the concentrations in two out of the five locations were more than the limit set by WHO whereas in the biota, all the locations recorded THC that were more than the set limit by WHO. The elevated concentrations of total hydrocarbons recorded in the samples

collected from the river could be attributed to illegal refining of crude along the river and the operational activities of the oil companies within the place. It is our view that the use of resource from the river for domestic purposes be suspended forthwith pending when proper remediation work is carried out.

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