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ASSESSMENT OF HEAVY METALS AND HYDROCARBONS IN RHIZOPHORA MANGLE CALLINECTES SAPIDUS, & SEDIMENT IN QUA-IBOE RIVER, AKWA IBOM STATE NIGERIA

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ABSTRACT
The assessment of heavy metals and hydrocarbon contents in mangrove swamp flora and fauna in Qua-Iboe River was investigated. The sediment, *Callinectes Sapidus* and *Rhizophora mangle* in the study area were analysed for Pb, Cd, Hg, total petroleum hydrocarbon (TPH) and total hydrocarbon content (THC) in wet and dry season. Results showed that, among the metals investigated, Pb had the highest concentration in all the samples for both wet and dry seasons, ranging from 0.002 – 2.344mg/kg. THC showed a higher concentration than TPH in all the samples, ranging from 492.41 to 794,931.81 mg/kg while TPH ranged from 175.97 – 129204.54 mg/kg. Generally, pollutant concentrations were higher in the dry season than wet season and the bioaccumulative behavior of HM in the samples followed the order: sediment > *Rhizophora mangle* > *callinectes sapidus* while hydrocarbon bioaccumulation followed the order: *Rhizophora mangle* > *callinectes sapidus* > sediment. The concentration of Pb and hydrocarbon in the samples analysed were found to exceed the WHO and FEnv permissible limit, posing an environmental risk to aquatic flora and fauna.

KEYWORDS: Heavy metals, Total petroleum hydrocarbon, total hydrocarbon content, sediment, Callinectes Sapidus and Rhizophora mangle.

INTRODUCTION
The contamination of marine environment from Petroleum Hydrocarbons, Heavy metals and other pollutant has become a cause for concern in the last few decades. Several domestic, industrial, mining, agricultural, oil exploitation and exploration, solid waste, garbage disposal, municipal sewage, atmospheric fallout and so on introduces metals into environment, thereby causing pollution (Udofia et al., 2016). Large amount of Heavy metals are also discharge into various aquatic ecosystem from Agricultural drainage water which contain fertilizer and pesticides and from effluent of industrial activities and sewage effluents (ECD, 2002). Heavy metals and petroleum hydrocarbons can also be introduce from various harbor activities like docking vessel paints, vessel repair facilities antifouling petroleum exploitation (Tim et al., 1998; Chaerum et al., 2014). However, Okuo & Okolo (2006) described heavy metals to be of ecological significance today due to their toxic & accumulative nature. An outstanding incidence of metal pollution is the minamata mercury and Itai-itai cadmium poisoning in Japan, where many humans were infected, from the consumption of seafood contaminated with cadmium and mercury. Consequently it has been reported that petroleum products from crude oil contaminate the environment during production and this poses health hazard. Total petroleum Hydrocarbon (TPH) can originate from petroleum product ranging from oil to highly refined products and often contain heterocyclic (Riser-Robert, 1998). The presence of petroleum hydrocarbons in form of crude oil and grease in domestic and river water is concern to the public. Biologically, they have deleterious impact on aquatic life (Edema et al., 2008). There are many sources of TPH contaminants in our environment which include petroleum extraction, transportation, refining and consumption (MADEP, 2007). The amount and types of compounds in a petroleum hydrocarbon release differ widely depending on the product spilled and how it weathered oil spills devastate soil and aquatic systems and cause alteration in important microbial process (Adewuji et al., 2011). It is estimated that over ten million tons of crude oil enters the environment each year from accidental spills, associated with major sources of total petroleum hydrocarbons in our environment. The aim of this study is to assess the accumulation level of heavy metals in Callinectes Sapidus (blue crab) and Rhizophora mangle in Qua-Iboe River, Akwa Ibom State. These samples would serve as an indicator to ascertain the pollution status of the area, in-order to forestall future health risk.

MATERIALS AND METHODS

Sampling Location and Physiography

The Qua-Iboe River is in Ibeno Local Government Area of Akwa Ibom State. It is a major fine psammitic beaches, fringed with tidal mudflats and mangrove swamps. The river is located within latitude $4^0 30^' - 4^0 45^'$N and longitude $7^0 30^' - 8^0 45^'$ on the South – East Coastline of Nigeria (Edu *et al.*, 2012). However, Qua-Iboe River and adjoining Creeks are subjected to petroleum exploration and exploitation activities.

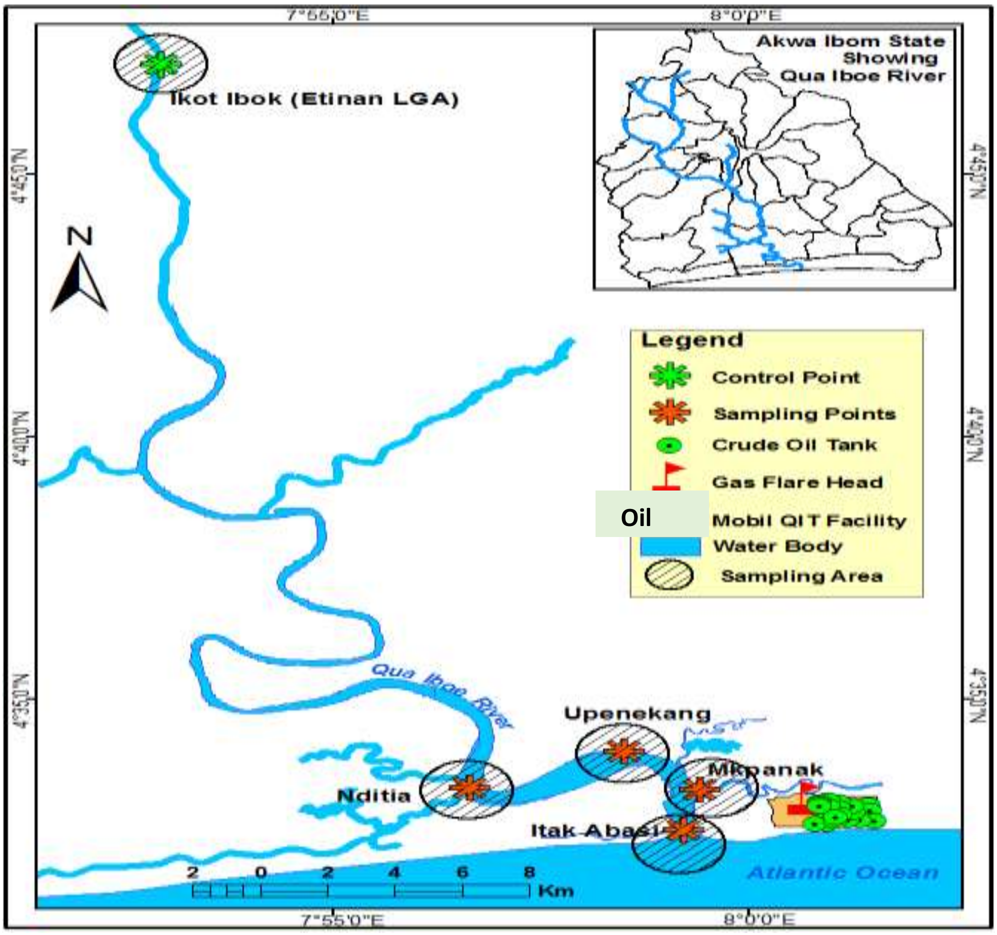

Fig 1: ***Location of Sampling Points along Qua-Iboe River***

Sample Collection and Treatment

Five sampling locations were chosen from Qua-Iboe River with a control site inclusive (as shown in fig 1), in Ibeno Local Government Area of Akwa Ibom State in the mouth of December 2016, January – February 2017 (dry season) and July – September 2017 (wet season).

Callinectes Sapidus (blue Crab)

A hundred (100) fresh and mature samples of *Callinectes sapidus* were obtained through the assistance of local fishermen, using Quadrat sampling method described by Clapcott *et al*. (2011). The samples were collected into an amber glass container prewashed with 6% nitric acid (for hydrocarbon analysis) and a black polythene bag (heavy metal analysis) to avoid contamination and photo degradation. It was immediately transferred into an ice cooler before being transported to the laboratory to keep the samples fresh.

Rhizophora mangle

About twenty stands of *Rhizophora mangle* plant were collected in five (5) study locations, with the use of stainless steel knife into a 6% HNO_3 pre-washed amber glass container and a polythene bag. The samples were immediately transferred into an ice cooler to maintain its freshness, before taken to the laboratory for analysis (Oteri, 2012).

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Sediment

The sediment samples were collected in triplicate from the five (5) study locations, using a clean van Veen grab sampler. The collected sediment samples were placed in a two litre amber glass container and polythene bags previously acid washed as stated above. It was placed in an ice cooler before transporting to the laboratory.

Table 1: Sample Location, Geography Coordinate and Site Description

Site	Site Code	Co-ordinate	Site Description
1.	N_1	N04^0 34' 56.74'' E07^0 54' 50.96''	**Nditia:** This site is located in the dredging area of the river. Fishing, cattle rearing and dumping of domestic waste into the river is prevalent.
2.	U_2	N04^0 34' 02.6'' E007^0 58' 25.9''	**Ukpenekang:** this site experiences lot of human activities such as welding, farming, fabrication of boats engines, washing of cars and lumbering work. There is also presence of local fish market.
3.	M_3	N04^0 33' 04.3'' E008^0 00' 50.96''	**Nkpanak:** A multinational oil company is situated here. Human activities such as welding, fishing, faming and trading are prevalent. The effluent and discharge unit of the company is also located in this area. There is gas flaring ongoing in this area
4.	I_4	N04^0 32' 49.8'' E007^0 59' .21.0''	**Itak Abasi:** This area is closer to the Atlantic Ocean. A lot of fishing activities, fabrication of engine boats takes place here. Abandoned boats, used tyres and other waste were noticeable in this site. This site serves as boat berthing activity.
5.	I_5	N04^0 47' 0.50'' E07^0 52' 55.80''	**Itak Abasi:** This site is devoid of any human activity. It serves as the control site.

Preparation of Hydrocarbon (TPH & THC)

TPH extraction mixture was prepared using acetone and dichloromethane (I:IV/V). 250ml of acetone $(CH_3)_2CO$ and 250ml of dichloromethane $(CH_3 (CI)_2)$ was measured into a 1000ml volumetric flask and properly mixed by gently swirling the mixture (Schwab *et al*., 1999).

Determination of TPH & THC from *Callinectes sapidus* and *Rhizophora Mangle*

Total Petroleum Hydrocarbon (TPH) and Total Hydrocarbon Content (THC) were determined from *callinectes sapidus* and *Rhizophora mangle* during dry & wet season using gas chromatography fitted with frame ionization Detector (GC - FID) as described by MERLL (2004). Each of the *callinectes sapidus* and *Rhizophora mangle* were cut into pieces using stainless steel knife and then crushed with the help of porcelain mortar & pestle. 10g of each of the crush samples were weighed into 100ml beakers and extracted with 60ml of the extraction mixture as described by Schwab *et al.*, 1999. The extract were reconcentrated using rotary evaporator to about 2ml and stored at a temperature of – 4^{0}C until GC analysis.

Determination of TPH & THC from Sediment

The sediment were dried at ambient temperature in an open container, covered lightly with clean papers and then stored in clean amber glass bottles. The samples were ground with a porcelain mortar and then passed through a series of graduated strainers to remove stones and vegetable matter. 10g of the sample was weighed into a 100ml beaker and the above extraction method outlined in the preceding section was repeated for sediment samples using acetone/dichloromethane mixture as extraction solvent.

Determination of Heavy Metals

All reagent used were of analytical grade and deionized water was used in all preparation except otherwise stated. The modified method reported by Adewuyi *et al*., 2010 was used for sample digestions. Samples were over-dried at temperature of 105^{0}C for 24hrs in an oven.

The samples (1 g) were accurately weighed into different digestion flask and digested with 10ml of 10:1 mixture of Nitric acid (HNO_3) and Perchloric ($HClO_4$) acid. At the end of digestion, 50ml of deionized water was added to the digest, filtered (using Whatman filter paper No. 2) and made up to 100ml mark in a volumetric flask with deionized water. The digest were corked, labeled and refrigerated until AAS analysis.

RESULTS AND DISCUSSION

The results of the analysis carried out on *callinectes sapidus*, *Rhizophora mangle* and sediment samples in Qua-Iboe River are summarized in the table 2 – 4.

Table 2: Concentration of heavy metals and hydrocarbon contents in Callinectes Sapidus (blue crab)

Metals/ Hydrocarbons (mg/kg)	Pb		Cd		Hg		TPH		THC	
Site(n=3)Seasons	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
1.	1.398±0.30	0.754±0.33	0.000±0.00	0.000±0.00	0.078±0.01	0.038±0.02	801.54 ±12.55	628.90 ±2.16	2141.16 ±15.76	1939.58 ±2.05
2.	2.002± 0.00	0.765±0.33	0.001±0.00	0.007±0.00	0.098±0.00	0.043±0.26	959.11 ±0.63	66.09 ±0.73	2222.46 ±0.43	2049.1567 ±8.70
3.	2.050±0.01	0.70±0.33	0.004±0.00	0.002±0.00	0.024±0.01	0.023±0.00	4652.37 ±19.39	4030.46 ±0.15	11174.85 ±1.47	10642.03 ±1.35
4.	2.017±0.01	1. 697±0.33	0.003±0.00	0.001±0.00	0.017±0.00	0.021±0.00	1286.45 ±1.01	1054.87 ±8.33	3185.5300±1.01	1864.37 ±0.86
5.	0.002±0.000	0.001±0.00	0.00±0.00	0.000±0.00	0.001±0.00	0.001±0.00	149.20 ±0.62	121.33 ±0.2	390.95 ±0.03	232.87 ±12.52
WHO	0.1		0.01		0.002					
FMEnv	0.05		0.01		0.001					

Table 3: Concentration of heavy metals and hydrocarbon contents in Rhizophora Mangle Root

Metals/ Hydrocarbons (mg/kg)	Pb		Cd		Hg		TPH		THC	
Site(n=3)Seasons	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet

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1.	1.030±0.01	1.030±0.01	0.361±0.33	1.038±0.00	0.001±0.00	0.001±0.00	98554.3800±10.77	91771.08 ±2.27	177767.20±36.75	190894.70 ±4.41
2.	1.401± 0.30	1.056±0.01	0.036±0.03	0.150±0.12	0.07±0.01	0.0017± 0.00	103735.67 ±1.91	95798.67 ±3.33	151704.46 ±1.53	794,931. 87 ±7.01
3.	2.003±0.02	1.385±0.30	0.038±0.00	0.031±0.00	1.094±0.01	1.091±0.00	129204.54±10.21	101382.07 ±1.17	402694.1867 ±1.32	315291.4133 ±0.08
4.	1.699±0.30	1.084 ±0.007	0.045±0.00	0.029±0.00	1.088±0.00	1.065±0.00	81167.91± 0.29	97415.21 ±6.52	262318.96 ±0.29	315458.92 ±2.74
5.	0.037±0.00	0.034±0.00	0.00±0.00	0.000±0.00	0.003±0.00	0.002±0.00	199.51 ±1.27	175.24 ±0.16	232.85 ±85.17	200.44 ±0.48
WHO	0.1		0.01		0.001					
FMEnv	0.05		0.01		0.001					

Table 4: Concentration of heavy metals and hydrocarbon contents in Sediment

Metals/ Hydrocarbons (mg/kg)	**Pb**		**Cd**		**Hg**		**TPH**		**THC**	
Site(n=3)Seasons	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**
1.	1.732±0.63	1.399±0.30	0.052±0.00	0.041±0.01	1.019±0.01	0.060±0.02	264.51 ± 17.13	175.97 ±13.57	579.58 ±10.43	492.41 ±22.51
2.	2.344± 0.33	2.003±0.03	0.065±0.00	0.222±0.18	1.016± 0.012	0.0395± 0.30	263.71 ±0.52	186.32 ±0.14	631.88 ±0.16	536.66 ±0.02
3.	2.026±0.06	2.008±0.00	0.068±0.00	0.027±0.00	1.053±0.00	1.051±0.00	3143.91±39.31	2763.51 ±7.21	7186.25 ±8.09	6868.60 ±0.56
4.	2.015±0.004	1.697 ±0.30	0.028±0.00	0.026±0.00	1.054±0.00	1.050±0.00	3122.911± 16.21	1443.60 ±12.10	9859.95 ±1.11	1761.05 ±1.30

5.	0.056±0.00	0.00±0.00	0.00±0.00	0.000±0.00	0.001±0.00	0.001±0.00	607.80 ±1.33	504.45 ±0.17	855.37 ±36.10	813.74 ±0.85
WHO		0.1	0.01		0.001					
FMEnv		0.05	0.01		0.001					

Table 2 showed concentration (mg/kg) of metals (Pb, Cd, Hg) and hydrocarbons (TPH & THC) in *Callinectes Sapidus*. The three heavy metals investigated were quite high in the sample during dry than in wet season, when compare with the recommended standard of WHO/FEPA (2006) and control (I_5). All the heavy metals (Pd, Cd, Hg) and Hydrocarbons (TPH & THC) recorded a higher mean value in site 3 with the following ranges Pb: 0.0707 – 2.050 mg/kg, Cd: 0.000 – 0.004mg/kg, Hg: 0.038 – 1.024mg/kg, TPH: 1, 054.87 – 4,652.37mg/kg and THC: 1,864.37 – 11, 174.85mg/kg. These values corroborate the existing anthropogenic activities in Qua-Iboe River, especially in M_3 where oil exploration/exploitation, gas flaring and incessant dumping of household waste is prevalence. However, the seasonality variations could be attributed to decrease in water body during dry season as a result of evaporation, thereby increasing the concentration, whereas the decrease in concentration in wet season could be associated with dilution as corroborated in a similar study by Moses *et al.* (2015). The high presence of TPH/THC in the sample is as a result of accumulation of petroleum contaminant over time. This is in line with assertion of Jack *et al.* (2005) who confirmed that hydrocarbon takes longer time to sink to the river bed by gravity than spread by tidal waves.

Rhizophora mangle root exhibited high presence of Pb in this pattern; $M_3 > I_4 > U_2 > N_1$. There were above WHO/FEPA standard of 0.1 and 0.05mg/kg respectively. The high concentration of lead particles from gasoline combustion which consequently settles on the sediment and taken by the plant root through uptake. (Abechi *et al.*, 2010). It could be link to increase in root uptake of these metals as permeability of the aging roots increases (Okuo *et al*. 2010).

The concentration of Cd and Hg in the sample were lower than that of Pb, but were all higher than the WHO/FEPA standards. The low level of Cd and Hg in the sample could be due to losses through excretion, leaching, autolysis and microbial decomposition (Okuo *et al.*, 2010). It is worthy of note that cadmium could be introduce in the Qua Iboe river through used tyres scattered at the bank of the river for boat berthing and run-off. According to WHO (1993), cadmium has a long biological life of 20 – 30 years in the kidney, and chronic exposure may eventually accumulate to toxic level which consequence may be "Itai – itai" bone disease.

TPH and THC in *Rhizophora* root fell within the ranges of 91, 771.08 – 129,204.54mg/kg and 190, 894.70 – 402, 694.1867mg/kg respectively, which is above the DPR (2002) recommended standard of 0.6mg/kg and control (200.44mg/kg). The high presence of TPH/THC could be attributed to incessant oil spillage from oil facility of the operating oil company overtime, oil exploration exploitation, introduction of gasoline, alkanes water soluble aromatics (BTEX, substitute benzene) and water insoluble poly aromatics hydrocarbon through anthropogenic sources (Edjere *et al.*, 2016). The TPH/TH data from the sample is higher than a similar study undertaken by Onwuka *et al*., 2012. Hence this is an indication of serious pollution threat to biota & human in Qua Iboe River, which calls for urgent remediation.

Sediment (Table 4) exhibited the high presence of all the heavy metals and hydrocarbons analysis in this study, there above WHO/FEPA (2006)/DPR (2007) standards. This agrees with studies that highlights sediment as the sink of pollutant or pollutant pool (Manaham *et al.*, 2000, Subodh and Abhiroop, 2013 and Ademoroti 1996).

Pb ranged from 1.732 (N_1) to 2.344mg/kg (U_2) in sediment and its accumulation can be attributed to atmospheric deposition from over loaded heavy duty vehicles, industrial emissions and refuse incineration (Ukpebor *et al.*, 2010). The major source of Pb in the atmosphere which affect our marine ecosystem in Nigeria is through the organometallic compound – $C_2H_3)_4$ Pb which is added to fuel as anti-knock.

Cd were found to be higher in wet than in dry season with a concentration of 0.222mg/kg, which was above the control (0.00mg/kg) and WHO/FEPA standard of 0.01mg/kg. This corroborated with the research undertaken by Moses *et al*. (2015) who recorded higher Cd value in wet than dry season. The finding in this study is consistent to other studies (Udosen *et al*., 2007). The presence of Cd could be linked to run-off during wet season through washing down lubricating oil or used tyres fillings from the tarred road (due to friction) to the river.

Hg were higher in the sediment when compound with the control (0.001mg/kg) and WHO/FMEnv (0.01mg/kg) standard it took this pattern; $M_3 > I_4 > U_2 > N_1$. Accumulation of Hg in the sediment could be as a result by the operating oil company (Onianwa *et al*., 2012). It could also be introduce into the river through washing down of Hg containing products such as batteries, thermometers, electrical switches and dental amalgam (for dental filling). Consequently, elemental and methyl mercury are toxic to the central and Peripheral nervous systems. The inhalation of mercury vapour can produce harmful effect on the nervous, digestive and immune systems, lungs, and kidneys and may be fatal (WHO 2018).

TPH/THC indicated a high concentration ranged; 175.97 – 3, 143.91mg/kg and 492.41 – 9, 859.95mg/kg respectively higher than the DPR (2002) recommended standard of 0.6mg/kg. From this study there is an indication of bioaccumulation, due to higher data obtained from biota and the sediment.

CONCLUSION

Several researches have proved that bioaccumulation initiates one pathway of heavy metals and hydrocarbon to the food chains; as such much attention should be given to this process. However this study has confirmed that Qua – Iboe River is under a serious pollution threat. Hence serious attention should be given such as remediation/clean-up forestalls future health risk.

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