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Research Article

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Total Hydrocarbon Content in Water and Sediment at Effluent Discharge Points into the New Calabar River, Rivers State, Niger Delta, Nigeria

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Abstract The role of hydrocarbons and its occurrence in the wetlands of the riverine environments of the Niger Delta States is very important for both individuals and cooperate bodies. Samples of water and sediments were collected between January to June from areas where drainages are let out into the New Calabar River. The Samples were examined for Total hydrocarbon content (THC) within the period. The results obtained showed that in water, the order was Minipiti>Iwofe Jetty > Police Post. Monthly variations and concentrations showed that the order was April (62.11±4.18) > March (52.59±7.50) > June (49.76±1.28) > February (49.20±12.91) > May (48.33±8.09) > January (48.30±5.89). In the sediments, the monthly variations and concentrations were in the order; April (107.02±10.33) > June (94.27±2.33) > March (91.87±9.13) > May (90.09±7.82) > February (81.01±9.57) > January (87.78±7.57). The portioning of the hydrocarbons in both sediment and water matrices showed that the hydrocarbons prefer the sediment phase to the water phase. The observed results showed that the concentrations of total hydrocarbons in both water and sediments were above the legal limit set by DPR, Nigeria. Furthermore, it has revealed the sediment to be the natural sink for aquatic pollutants. The high values of THC and their nature of occurrence in the aquatic media examined in this study implicated anthropogenic influence. Therefore, legal, cooperate and individual efforts should be put together to remedy this problem and also forestall further input through effective monitoring.

Keywords Total hydrocarbon content, Effluent Discharge Points, riverine environments

Introduction

The quality of water for both industrial and domestic use has become an issue of common concern in countries where crude oil mining activities are present [1]. The rising quest for petrochemicals all over the globe has led to discharge of petroleum-based chemicals into the already overburdened ecosystems. In most climes, there are accusations of governments taking sides with industries to put in place very flexible environmental guidelines, which has led to many social problems between the host communities and the mining industries. The mining and application of petroleum sources of energy all over the sphere has given rise to extensive pollution of the environment. Millions of barrels of crude oil go into the water bodies annually [2-3]. To control and manage pollution complications associated with discharges of petroleum in water environments is actually challenging. This is due to the enormous quantity of input sources and their geographical spread [4].

Experts and ecologists are confronted with the task of overcoming the harmful effects associated with the contamination of the environment with petroleum products and other pollutants globally. Far-reaching spills of crude oil on the environment, leaks from pipes, out flows from concealed and surface fuel storage tanks, unselective spills and insensitive disposal and mishandling of waste and petroleum associated products in the public are some of the main routes of environmental petroleum contamination. The effect of petroleum products in the environment has attracted worldwide interest among researchers because of the perceived health effects which are either carcinogenic, mutagenic or toxic [5]. Elevated levels of hydrocarbons prevailing in soiled sites may possibly pose health threat to both flora and fauna within the surroundings.

The hazard to several ecologies and their resources has been amplified because of increased environmental ruin. It has been documented that the different activities of man are the major causes of the deterioration of the environment and in few cases may be the result of natural occurrence [6].

Nigeria is the sixth largest producer of crude oil in the world. Nigeria practice a monoeconomic system that relies greatly on the oil rich region of the Niger Delta where the main stream oil industries are situated. The incessant and indiscriminate discharge of crude oil and its allied products in the Niger Delta has badly affected fishing communities along the coastal regions. Oil released unwittingly, intentionally from allowable limits and petroleum products constitute the key anthropogenic basis of hydrocarbons in the environment [7]. Spillage of oil is a consistent incidence in Nigeria. This occurrence frequently results due to deterioration of pipelines and reservoirs, disruption, mishaps, mismanagement, oil prospecting and production processes [8]. Equally, the aliphatic and polycyclic aromatic hydrocarbons components of dissolved petroleum are freely absorbed by most finfish and shellfish due to their high solubility in lipids and are bioaccumulated in their tissues [9].

This study therefore investigated the total hydrocarbon contents in surface water and sediments at effluents discharge points into the new Calabar River.

Materials and Methods

Study Area

The study area is at three different point where effluents are discharged into the New Calabar River. These points were built by the Rivers State Government for drainage purposes, so that during the rainy seasons, water can easily be drained off from residential areas and the highways. The areas were at the Rumuolumeni axis of Port Harcourt, which houses many multinational and local industries that deal with petroleum and allied products. Effluents from these industries and homes are directly connected to the drainage system which runs into the New Calabar River. The point wher samples were taken include the Police Post area (4^o 48’ 52.1” N, 6^o 56’ 21.4” E), Minipiti (4^o 41’ 31.8” N, 6^{o}56’ 8.4” E), both of which drains into the mangrove wetland of the river and the Iwofe Jetty area (4^o 48’ 32.4” N, 6^o 55” 42.7” E) which drains directly into the river. The map of the area is shown in Figure 1.

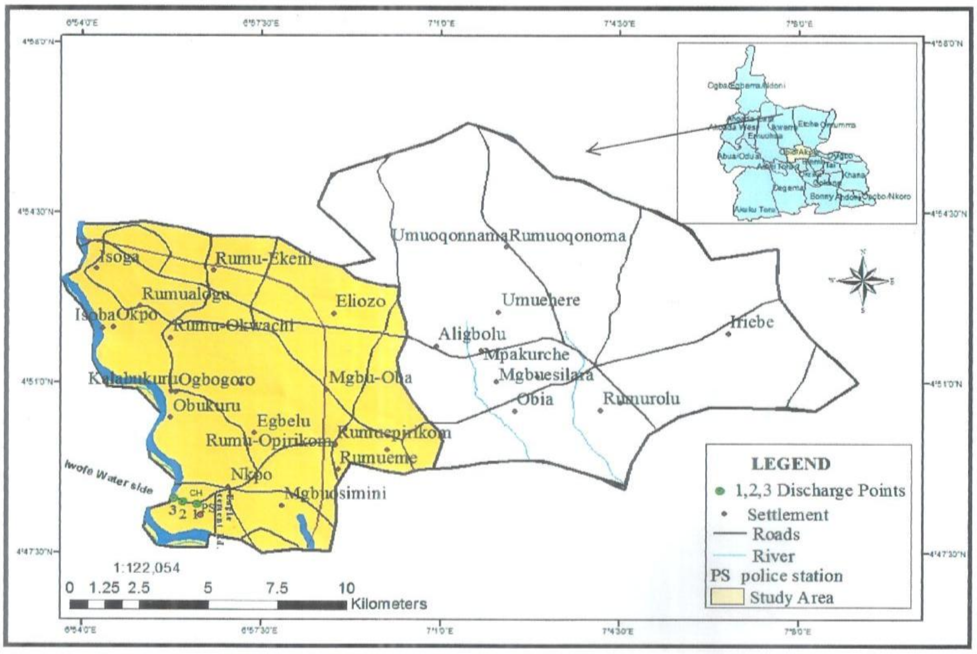

Figure 1: Rumuolumini South West showing Drainage Discharge Points

Collection and Preparation of Samples

Water sample were collected from the surface at a depth of 25 cm with glass bottles and corked under water. Sediment samples were collected from the upper layer at a depth of 5-10cm. The sediment samples were put into glass containers and covered immediately. Both water and sediment samples were placed in ice cold chest containers and transported to the laboratory. The water samples were stored at a temperature of 4^o C in a refrigerator in the laboratory pending time for further treatment and analysis.

The sediment samples were brought out of the glass containers and placed in an aluminum foil. They were allowed to dry freely without exposure to the sun or any form of contact with sunlight. Thereafter, the samples were pound to powder and sieved with 1µm mesh.

Extraction and Determination of THC

Both water and sediment samples were extracted according to standard methods [4, 10]. The filtration method was used to transfer the extracts into 50.0ml flasks and then topped up to the 50.0ml mark with the extraction solvent, toluene. Triple extractions were performed on all the samples. The concentrations of total hydrocarbon in both water and sediments samples were determined spectrphotometrically at a wavelength of 420 nm using spectrometer model HACHDR3900. The concentrations of the hydrocarbon content were obtained from a standardized calibration curve initially prepared and the values compared with those obtained from blank solutions using the same measurement procedures [4].

Determination of Partition Coefficient of THC between the Sediment and Water Phases

The distribution of the total hydrocarbon content between the sediment and water matrixes was calculated from the formula;

$$\text{Kd} = \frac{Distribution\ of\ THC\ in\ Sediment\ Phase}{Distribution\ of\ THC\ in\ the\ Water\ Phase}$$

Where Kd is the partition coefficient or distribution ratio. The principle behind the portioning of the hydrocarbons lies in the preference that possibly will allow more of the hydrocarbons to exist. It also explains the hydrophobicity and hydrophilicity of the hydrocarbons.

Results

The results of the total hydrocarbon content in water at the different drainage discharge points into the New Calabar River are shown in Table 1. The results showed slight variations between the months and the stations. In the water, the values of THC were highest at the Minipiti station which was followed by the values observed at the Iwofe Jetty station and then the Police Post Station. At the Iwofe Jetty station, the values ranged from 45.74±7.37 - 65.42±10.76 mg/L. The highest value was observed in the month of April and the lowest in February. At the Minipiti station, the values varied from 49.06±7.10 - 66.46±8.41 mg/L. The values observed in the different months showed that it was highest in February and lowest in June. The concentrations of THC at the Police Post station varied from 35.40±4.82 - 56.21±4.63 mg/L. The highest value was observed in April and the lowest in February. The highest and lowest values within the period of experimentation were observed at the Minipiti and PolicePost stations in February, which were 66.46±8.41and 35.40±4.82 mg/L respectively. The general stations trend in the concentrations of THC in water within the period was Minipiti > Iwofe Jetty > Police Post, while monthly variation was in the order April > March > June > February > may > January.

Table 1: Total Hydrocarbon Content (mg/L) in Surface Water of New Calabar River at Effluents Discharge Points

Months of Analysis	Stations			Monthly Mean
	Iwofe Jetty	Minipiti	Police Post	
January	47.65±6.48	55.82±7.32	41.43±5.91	48.30±5.89
February	45.74±7.37	66.46±8.41	35.40±4.82	49.20±12.91
March	50.92± 4.29	62.49±11.03	44.36±5.66	52.59±7.50
April	65.42±10.76	64.71±7.02	56.21±4.63	62.11±4.18
May	48.33±5.92	58.26±3.26	38.44±9.26	48.33±8.09
June	51.55±6.42	49.06±7.10	48.67±7.14	49.76±1.28

The results of the total hydrocarbon content in sediment at the different drainage discharge points into the New Calabar River are shown in Table 2. The results showed slight variations between the months and the stations. In the sediment, the values of THC were highest at the Iwofe Jetty station which was followed by the values observed at the Minipitistation and then the Police Post Station. At the Iwofe Jetty station, the values ranged from 92.49±10.45 - 120.42±15.64 mg/L. The highest value was observed in the month of April and the lowest in January. At the Minipiti station, the values varied from 81.49±8.72 - 105.36±7.62 mg/L. The values observed in the different months showed that it was highest in April and lowest in January. The concentrations of THC at the Police Post station varied from69.05±9.11 - 95.29±10.25 mg/L. The highest value was observed in April and the lowest in January. The highest and lowest values within the period of experimentation were observed at the Iwofe Jettystation in April and Police Post stations in January, which were 120.42±15.64 and 69.05±9.11 mg/L respectively. In All the stations, highest values of THC were observed in the month of April. The variations of THC observed in sediment samples in the stations were in the order; Iwofe Jetty >Minipiti> Police Post, while monthly variation were in the order; April > June > March > May >February > January.

Table 2: Total Hydrocarbon Content (mg/Kg) in Surface Sediments of New Calabar River at Effluents Discharge Points

Months of Analysis	Stations			Monthly Mean
	Iwofe Jetty	Minipiti	Police Post	
January	92.49±10.45	81.49±8.72	69.05±9.11	81.01±9.57
February	95.68±10.33	90.10±12.15	77.57±8.45	87.78±7.57
March	102.37±11.19	93.12± 3.48	80.12±9.17	91.87±9.13
April	120.42±15.64	105.36±7.62	95.29±10.25	107.02±10.33
May	100.38±10.21	88.47±8.85	81.42±6.89	90.09±7.82
June	97.46±13.33	93.41±3.10	91.94±1.56	94.27±2.33

The partition/distribution ration of total hydrocarbons between sediment and water at the effluents discharge points is shown in Table 3. The partitioning of the hydrocarbons varied from 1.46 – 1.94 in January, 1.37 – 2.19 in February, 1.49 – 2.01 in March, 1.63 – 1.84 in April, 1.52 -2.12 in May and 1.89 - 1.90 in June. The highest partition ratio was observed in February at the Police Post Station, which was followed by the value observed in May at the same station. The lowest portion value was observed at the Minipiti station in the month of February.

Table 3: Partition Coefficient of Total Hydrocarbons Contents between Sediment and Surface Water at the Effluents Discharge Points

Months	Stations		
	Iwofe Jetty	Minipiti	Police Post
January	1.94	1.46	1.67
February	2.09	1.37	2.19
March	2.01	1.49	1.81
April	1.84	1.63	1.70
May	2.08	1.52	2.12
June	1.89	1.90	1.89

Discussion

Total Hydrocarbons Content in Water

The concentrations of THC in the different stations within the months in the surface water were varied. This variation in concentration in the river during the time under consideration can be ascribed to the disparity in the nature and volume of human imposed discharges into the river (the study area). The total hydrocarbon content in observed in the present work is higher than the values observed in other studies in surface water [4, 10-12]. The observation of the present study which implicated human interference in the content of THC in the surface water is in disagreement with the observation of Charles *et al* [12], who concluded that the presence of THC in the Ovia River, Delta State, Nigeria was as a result of natural causes, but agrees with the observations of *Howard et al*., [4] and Wokoma [10], that implicated human activities within the area to be the cause of the high level of THC in surface water.

Fundamentally, the interest on the presence of hydrocarbon in the environmental is borne on the nature of its toxicity to human, plants and animals exposed to it at high levels for long time. Alongside crude oil search, hydrocarbon may possibly leak into the environment as a result of poor control of wastes containing oil [7], release of crude oil products through conveyance in the domestic and international water ways and legally allowable level of discharge [13]. Other sources of hydrocarbon pollution of water are runoffs from soils laden with hydrocarbon contamination such as mechanic workshops and power generating stations, impoundments and wastes from homes which comprise of hydrocarbons [12], illegal and agricultural discharges, accidental discharges and reinjection wells [14].

The concentrations of THC in water within the period of sampling in the various stations were higher than the allowable limit of 10mg/L in surface water recommended by DPR [15]. High concentration of THC in water has negative impact on the oxygen content of the water. This reduction is due to the prevention of oxygen from mixing well with the water [16]. The implications of reduced oxygen in water are reduction in growth of aquatic plants and animals, death of aquatic plants and animals [17] and stinking of the water especially when stagnant. The presence of elevated levels of THC in water affects feeding habits of aquatic organism, through alteration of the food chain [16, 18], sticks to the leaves of water weeds, distorts the breathing mechanisms of aquatic animals through the blockade of gills and renders the water not fit for human consumption [19].

Total Hydrocarbons Content in Sediment

The concentrations of THC in the sediment in this present work were lower than those of Howard *et al* [4], in sediments from mangrove marshland situated in the Niger Delta Nigeria, that experienced oil spill and also the values observed in sediments from a tidal Creek, Bonny River, Niger Delta, Nigeria [10]. Although most hydrocarbon components are hydrophobic and insoluble in water, which is the reason for floating on top of water yet the concentrations of sediments THC in this present work are higher than those of the surface water. This observation is in agreement with the observation of other authors in similar environment [4, 10]. This observation suggests that there are some underlying mechanisms that precipitates hydrocarbons in surface water to the bottom sediment. Firstly, it may be that heavier constituents of hydrocarbons are easily pulled through the water column by gravitation to the bottom sediment [20]. Secondly, the remaining fraction then mixes with water and suspended particulate matter which then passed down to the sediment [21]. Thirdly, other solid particles that are freely floating on the surface of water such as leaves and sticks are easily adhered to by hydrocarbons, which eventually after having taken enough water sink to the bottom sediment, thereby increasing the sediment content. Fourthly, petroleum hydrocarbons easily adhere to shoreline plants and lead to early mortality, which eventually sink to the bottom to increase its value above that of the water. Fifthly, the lighter fraction floating on the surface of water are easily volatilized in the presence of high wind and high temperature [21].

The presence of very high values of THC in the sediment will affect the feeding pattern of bottom dwelling plants and animals [17], pose health risk to human consumers of such plants and animals harvested from the hydrocarbon polluted environment and the destruction of the natural vegetation of the marshland.

Trends of the concentration pattern of THC

The observed trend in concentrations showed that the concentrations of THC in both water and sediment were highest in April and lowest in January, while stations values showed highest values in Minipiti and the lowest in Police Post for surface water and highest in Iwofe Jetty but lowest in the Police Post in the sediment. The presence of more hydrocarbon content in either the Minipitior Iwofe Jetty stations is attributable to the different activities within these spots. At the Minipiti station, there is an abattoir cited close to the point of collection. At the abattoir, there is constant burning of animal bones, burning of cow skin to remove the hair and the drainage which discharges effluents from the nearby university, timber station (saw mill), mechanic workshop, filling stations and the clustered houses that directly discharge organic waste to the drainage course.

At the Iwofe Jetty, there is the trade on local products such as plantain, banana, foofoo, gari, oil palm and its allied produce, lifting of bunkered fuel, boat engines, dredgers, small ships, oil firm and other agro based industries and effluents from part of the nearby university that flows through the drainage. The wastes from sold products are directly discharge into the river. Added to this, is that the Iwofe Jetty is at the main stream of the river, where all the discharge materials are washed into during high tide.

Finally, the Police Post station has the least interference and lower human population around it, although there is the presence of a filling station along the course of the drainage flow. The nature of the place where the discharge first occur is flat and widespread and as such equally distributes any pollutant that may have accompanied discharged effluent and any other wastes.

The high value observed in the month of April may be connected with the beginning of heavy rains, which carries along its course pollutants by the roadside into the drainage system and finally discharged at the designated points. The very low values observed in January is because of the very low activities exhibited by the inhabitants being the beginning of the year. Normally, activities in Port Harcourt begins slowly in January due to the end of year break.

Partition Coefficient/Distribution Ratio of Total Hydrocarbon Content

Partition coefficient otherwise known as distribution ratio (Kd) is originally used to describe the amount of any compound that is present in a mixture of two solvents which cannot mix together at equilibrium. It may also be a comparative ration of how soluble a solute is in two different liquids mixed together. The partition coefficient observed in the present work showed values greater than one (> 1) in all the stations and months. The fact is that values greater than one is indicative of preference of the hydrocarbons for sediment than water.

The importance of the information given by the values of partition coefficient of environmental pollutants isa necessity for the control of pollution and also for establishment of excellent measures to contain and control the mobility and spreading of chemical contaminants in any medium [23]. As observed in the present study, the partitioning of the total hydrocarbons between the sediment-water phases were above 1, which indicated that the hydrocarbons prefer the sediment to the water phase. The portioning or distribution of pollutant or other chemical species between sediment and water phases is very vital in the manner of acceptance and buildup of organic chemicals in organisms present in aquatic medium and therefore affecting the food-chains [24]. The presence of high values of THC in the sediment compared to that of the water portends danger because a physical view of the surface water may not show any sign of pollution, but it has the potential to resuspend these particles back to the water phase at certain environmental conditions which may by biotic or abiotic which might be detrimental to aquatic organisms. So, the extent to which chemical partitions between sediment and water play and important part the development of sediment quality criteria [25].

Conclusion

The high concentrations and nature of occurrence of total hydrocarbon content observed in both water and sediments at the different discharge points into the new Calabar River showed that the majority of the input sources were purely anthropogenic. These high levels can be deleterious to benthic creatures. This is because bio-organisms (planktons, crustaceans, crabs, periwinkles and fish) can ingest or absorbed it into their system either through the skin, feeding or respiration, which will eventually be transferred to man the ultimate consumer. Therefore, effort should be put in place to curb any further input as to curtail incidence of mass mortality of aquatic plants and animals.

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