

Concentrations and Distribution of Total Petroleum Hydrocarbons in Surface Water and Sediment within Tombia Creek, Degema Local Government Area, Rivers State, Nigeria

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Abstract

As a result of anthropogenic activities water bodies of the Niger Delta area of Nigeria have been degenerated and tainted in quality and this study was therefore carried out to assess the concentration and distribution of total petroleum hydrocarbons in surface water and sediment within Tombia Creek, Degema Local Government Area, Rivers State, Nigeria. Water and sediment samples were collected from the creek at three designated locations to evaluate the concentrations of total petroleum hydrocarbons (TPH). After necessary laboratory pretreatment, sample extraction for TPH was performed using solvent extraction by means of dichloromethane which was followed by column chromatography clean up. Gas chromatography-flame ionization detector (GC-FID) was employed in the determination of the concentrations of TPH in surface water and sediments of the creek. The mean concentration of total TPH in water ranged from 35.695 ± 3.876 to 100.250 ± 19.194 mg/L, and in the sediments, it ranged from 143.577 ± 18.001 to 302.416 ± 29.364 mg/Kg. Values recorded for TPH in surface water was above the DPR and WHO requirements for surface water, and that of the sediments were within the range of moderate pollution. The partition coefficient calculated for the water and sediment phases indicated that TPH fractions prefer the sediment phase when compared to the water phase. The results recorded showed that the creek was contaminated due to anthropogenic activities that take place along the coast of the creek and thus necessitate serious attention, regulation and suitable control measures of activities which has brought about this present condition of the creek.

Keywords: Partition coefficient, Pollution, Total petroleum hydrocarbons, Tombia Creek, Gas chromatography-flame ionization

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 [28]. 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 have 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 [10]. 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 [24].

Water plays a central role in the lives of all organisms. However, the quality water and its conservation is particularly precarious for human survival. Over 71% of earth's surface is covered by water. Thus, water is unevenly distributed among aquatic environments. The majority of this is seawater. The ocean contain over 97% of water that make up the biosphere and the polar ice caps and glaciers contain an additional 2% and 1% is fresh water in rivers, stream and creeks, which actively exchanged ground water from waste generated such as agriculture, domestic, industrial and natural sources. All these forms are very important in life cycle [6,27,44].

The natural ecosystem is adversely affected by many human activities such as road construction, mining, discharged of waste and garbage from domestic and industrial effluents. These wastes may contain substances that can bioaccumulate in the tissue of plants and animals above desired levels. Wastewaters emanate from four primary sources including municipal sewage, industrial,

agricultural runoff, storm-water and urban runoffs. These sources of waste terminate in the surface and ground water and pollute the water with organic, toxic materials, heavy metals, and plant nutrients such as nitrogen and phosphorus from farmland. The industrial effluent also changes the color, temperature, pH, alkalinity, salinity of the affected water body [30].

The uninterrupted oil exploration, exploitation, maintenance and intense agricultural activities have been identified to be the major contributory factors of the observed pollution and contamination of its ecosystem and water bodies [60, 50]. Human's incapability to checkmate and maintain the natural environment has caused several indescribable adversity and endangered his coexistence with nature [58,14]. This situation is occasioned by industrialization and urban renewal programme initiatives [35].

The petroleum industry is the major contributor in the generated waste in the State. Thus, exposing rivers and creeks in these areas to risk of contamination from petroleum and associated pollutants. Marcus & Etori [37] also identified incidences of oil spillages and seepages in addition to gas flaring as potential sources of heavy metals and mineral hydrocarbons (polyaromatic hydrocarbons, PAHs) to aquatic and terrestrial environments, which ultimately settle into sediment matrices. More so, there are air-borne particulates derived from fossil fuel combustion which contains hydrocarbons. These pollutants are potentially deleterious to fauna and flora as well as devalue the integrity of water bodies [37].

The adulteration of surface water could also be attributed to the nature of its surrounding water bodies [16]. The measure of quality water does not solely lie on its intake by human alone, but rather, suitable for other important anthropogenic and recreational activities [27]. The basic purpose for monitoring the quality of water is imperative, both as a medium to check its current state and as an instrument for managing good policy implementation. Hence, a comprehensive

evaluation or investigation of water imply the examination of all the required constituents such as biological, chemical and physical properties of the said surface water in comparison to set standards, which could be natural or man-made for a specific purpose [16].

Even with a deep insight to the fact that water pollution or contamination is a global pandemic, yet the nature of water pollution varies, depending on the developmental stage of the place under investigation. Likewise, countries or regions with fast growing population without good waste management are prone to generate much more waste product that will constitute nuisance within its environment than those countries with smaller population growth rate, that are practicing good waste management skills [59]. Thus, anthropogenic activities is constantly doing two things, polluting or degrading the earth's surface. As a result, these changes pose untold danger to streams, creeks and rivers and aquatic organisms that dwell in them.

However, quantification of contaminants in natural waters often faces difficulties. Apart from variations with time owing to certain natural and anthropogenic factors, there is the lack of useful connection between the concentrations of contaminants in the system and their bioavailability [37]. Nevertheless, the use of water, sediment and biota as indices has been key in evaluating environmental problems. As a result, these segments are periodically analyzed to assess, monitor and control aquatic pollution [42]. The greatest advantage of the use organisms to monitor pollution lies in the ability of such organisms to accumulate and sequester contaminants in such manner that they can be used as biomonitors without recourse to assumptions employed in water and sediment analyses [37].

Materials and Methods

Description of study area and location

Tombia Kingdom is a community under Degema Local Government in Rivers State, South-South

Nigeria. It is made up of sub communities under it. Tombia is one of the chief communities in Degema LGA of the Niger Delta Region and the Centre of the Nigerian oil economy and as such has become rapidly urbanized and modernized, becoming a Centre for social and economic life and a rapid growing commercial community in the Niger Delta Region. Tombia is situated along the Bonny River and the community is crisscrossed with several rivers, streams and estuaries. The estimated population of the Community as of 2015 was kept at 900,000 inhabitants [8]. The city is full of multinational oil firms and other industries especially those related to oil and gas business.

Tombia Creek is a creek surrounding the good people of Tombia Kingdom, Degema LGA in Rivers State that is link through River Sombrero. Majority of residents from this area are fishermen, whose lives depend on aquatic organism (biota), it is pertinent to note that the numerous anthropogenic activities has eliminated or diminished the life span of the aquatic organism in the sea to zero level for survival in the creek.

The study was centered on three points estuary of Tombia Creek, Station 1 is at Tombia Jetty and lies within latitude 4°47'41.24" north and longitude 6°54'50.40" east. Station 2 is approximately 600m at Oboko Polo and its geographical positioning is within latitude 4°47'32" north and longitude 6°53'40" east. Station 3 is at Ngia Poku its latitude is within 4°47'31" north and longitude 6°53'25" east. Oil bunkering and other associated activities are present in the Tombia Creek. Map showing sample points within Tombia Creek are shown in Figure 1.



Figure 1: Map showing sample points or stations of the Tombia Creek.

The geographic positions of sample locations along the Tombia Creek is provided in Table 1.

Table 1: The geographic positions of sample locations along Tombia Creek

Sample Identity	Geographic Position (Coordinates)	Location
1	4°47'41.24" N, 6°54'50.40"E	Tombia Jetty
2	4°47'32" N, 6°53'25" E	Oboko polo
3	4°47'31" N, 6°53'25" E	Ngia Poku

Human activities which take place within the estuary include ship and boat transportation, abattoirs close to the creeks, open defecation, dredging of sand, illegal oil business, timber markets, open dumping of domestic wastes, effluents from drainages. These have negatively impacted and perturbed the original state of the estuaries by creating environmental pollution in the creeks and thereby affecting normal human activities that had existed before now.

Collection of water sample for total petroleum hydrocarbons analysis

Water samples were collected from three designated stations in Tombia Creek in Degema Local Government Area, Rivers State, using

initially washed glass bottles. The glass bottles were previously rinsed with dichloromethane (DCM) to avoid being contaminated with the water samples. Water samples were collected at three points in each station at a depth of 30-40cm and thoroughly mixed together to obtain a representative samples. A 2ml of 0.2 M H_2SO_4 was added to the water samples to get a pH of about 2 to ensure the water sample was well preserved. Prevention of contamination or harm, was achieved by covering the bottles with sterile pieces of aluminum foils, followed by tightly covering the bottles a wooden screw. The bottles were stored in an ice packed cooler at 4°C and transported to the laboratory for pre-treatment and analysis [25]

Collection of sediment sample for total petroleum hydrocarbons analysis

Sediment samples were collected at the three different stations in Tombia Creek from the top few centimeters deep. Bulk representative samples were formed by mixing three points sediments together. The samples were collected using a hand held, van veen grab and transferred to glass bottles then transported to the laboratory.

Preparation of water samples for TPHs analysis

Samples of water were meticulously filtered and then extraction using separatory funnel. Water samples were extracted using 130ml dichloromethane extractant and put into a two-litre glass separatory funnel. In order to enable the organic layer to be thoroughly separated from the organic layer, the separatory funnel was agitated for five minutes. Water was removed from the extract by mixing it with 5g of anhydrous sodium sulphate. The sample was poured into a filter papers placed in a filter funnel in a beaker. The filtrate collected into the beaker was allowed to dry in a fume cupboard at room temperature, and concentrated to 3ml before analysis. The extraction process was done three times for each sample [33].

Analysis of water and sediment samples for TPH determination

The determination of total petroleum hydrocarbons in water and sediment samples were analyzed with Agilent 5890N gas chromatography flame ionization detector (GC-FID). About 3ml of the concentrated sample was carefully injected into the gas chromatography vial to clean the syringe. Injected in to the micro syringe of the gas chromatograph was the blank dichloromethane the syringe was cleaned three times before the sample was analyzed. After rinsing the micro syringe with the sample, then the injection of the sample into the gas chromatograph was done for complete separation of the various petroleum hydrocarbons available in the sample after separating the component

compounds present in the samples the quality of total petroleum hydrocarbons content was resolved with a particular pack chromatography and was quantified in mg/L and mg/Kg for the samples of water and sediments respectively.

Partition coefficient for total petroleum hydrocarbons in the Tombia Creek.

Total petroleum hydrocarbon bio availability in sediment of the rivers solely depends on its distribution between the sediment and the surface water. It lies on the level of total petroleum hydrocarbon in the sediment phase and surface water phase. The spread of the distribution is measured by partition coefficient. The partition coefficient is mathematically represented as

$$K_d = \frac{\text{concentration of TPH in Sediment}}{\text{concentration of TPH in water}}$$

This is done to ascertain which of the phases that total petroleum hydrocarbon prefers.

Results and Discussion

Total petroleum hydrocarbons in surface water from Tombia Creek

The mean concentrations of total petroleum hydrocarbons in surface water from Tombia Creek as at the time of study are provided in Table 2 while the mean concentrations of total petroleum hydrocarbons within the stations during the time of investigation is illustrated in Figure 2. The extent to which the river was contaminated is a factor of the quantity of total petroleum existing per litre of water. The table indicated the concentrations of the diverse components of total petroleum hydrocarbons (TPH) and also the sum of total petroleum hydrocarbons present in the surface water from the three designated sample stations in Tombia Creek.

Table 2: Concentrations (mg/L) of total petroleum hydrocarbons in surface water from different stations of Tombia Creek

Carbon Length (ml/L)	Stations		
	1	2	3
C8	ND	0.350±0.084	ND
C9	ND	ND	ND
C10	ND	ND	ND
C11	ND	0.067±0.003	ND
C12	ND	0.079±0.005	ND
C13	ND	0.361±0.011	ND
C14	1.288±0.118	0.721±0.013	2.858±0.264
C15	2.047±0.252	1.684±0.100	2.095±0.202
C16	1.859±0.110	3.113±0.514	5.843±1.251
C17	3.118±0.316	4.843±1.101	3.516±0.415
C18	5.056±1.105	5.485±1.108	1.715±0.106
C19	5.991±1.401	10.208±2.110	3.682±0.403
C20	1.409±0.102	11.848±2.088	2.202±0.224
C21	1.352±0.106	ND	ND
C22	ND	5.359±1.097	3.321±0.208
C23	0.864±0.010	ND	ND
C24	2.654±0.300	5.203±1.131	3.007±0.332
C25	1.101±0.164	ND	ND
C26	1.989±0.189	10.168±2.168	2.945±0.109
C27	2.005±0.191	ND	ND
C28	3.110±0.254	12.111±2.956	2.594±0.252
C29	2.119±0.100	ND	ND
C30	2.516±0.102	18.253±2.810	1.917±0.110
C31	1.344±0.091	ND	ND
C32	1.234±0.086	4.421±1.014	ND
C33	ND	ND	ND
C34	ND	5.284±1.162	ND
C35	ND	ND	ND
C36	ND	0.684±0.012	ND
C37	ND	ND	ND
C38	ND	0.002±0.000	ND
C39	ND	ND	ND
C40	ND	0.006±0.000	ND
Total	41.056±4.997	100.250±19.194	35.695±3.876

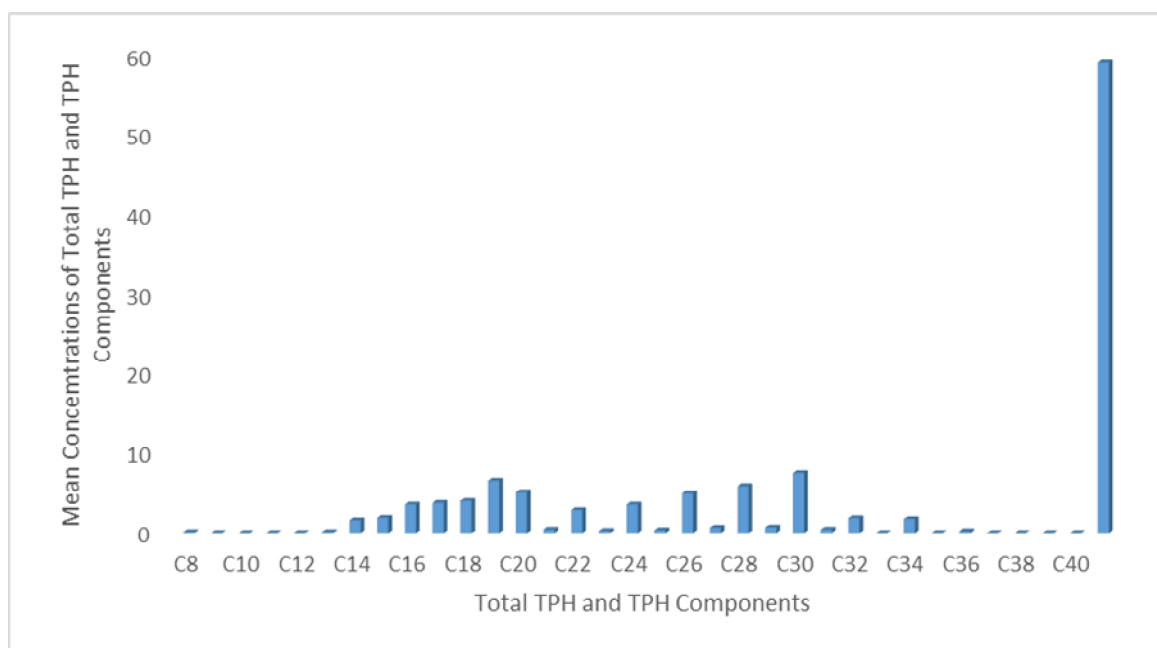


Figure 2: Mean concentrations of total TPH and TPH components in surface water within the stations of the Tombia Creek during the time of study.

The results obtained for the mean concentrations of total petroleum hydrocarbons in the surface water in the stations of Tombia Creek within the period of study ranged from 35.695 ± 3.876 to 100.250 ± 19.194 mg/L. The order of occurrence of total petroleum hydrocarbons in the stations was $2 > 1 > 3$. The mean concentration of total petroleum hydrocarbons fractions within the period under investigation varied from not detected to 18.253 ± 2.810 mg/L. The mean value of total petroleum hydrocarbons obtained for the stations within the period under study was 59.000 ± 9.356 mg/L. The individual concentrations of total petroleum hydrocarbons fractions as at the time under investigation ranged from not detected to 5.061 ± 1.260 mg/L in the creek. C9, C10, C33, C35, C37 and C39 were not recorded in any of the stations during the period of this investigation while C30 in Station 2 had the highest concentrations in all stations of the creek used in the study.

The mean concentration of total petroleum hydrocarbons obtained in this investigation in the Tombia Creek in the different stations used in this study were far above the national acceptable limit of 10.00mg/L in surface and groundwater set by

DPR [9], FEPA [21] and also that of EUEPA [19] acceptable limit of 300 g/L in river water.

The recorded mean concentration of total petroleum hydrocarbons in the Tombia Creek was observed to be lower than that reported in the work of Ogeleka, et al. [41] in the Odidi and Egwa riverine areas of Warri Delta State which gave the value of 97592 ± 46 and 91590 ± 51 mg/L. In the investigation of Howard, et al. [24], the mean concentration of hydrocarbon was found to be 33076.00 g/L, which is higher than the level obtained in this study

Daniel and Nna [7], recorded TPH concentration between 9.6820 ± 0.233 to 24.85462 ± 8.058 mg/L and that of Inyang, et al. (2018), recorded a range of 63.52 to 183 g/L were all lower than what was obtained in this work. The result obtained in this work was observed to be also higher than that reported by Alinnor and Nwachukwu [4], the concentration obtained ranged within 23.6 ± 4.3 mg/L, while investigating the level of total petroleum hydrocarbons and also higher than the average concentration of total petroleum hydrocarbons recorded in the Orashi River, in the stations in an investigation carried out by Edori et

al. (2021) which ranged from 7.645 ± 2.683 to 12.212 ± 3.303 mg/L

Again, the observed mean concentration value of total petroleum hydrocarbons recorded in the Tombia Creek were observed to be above that recorded by Edori and Kpee [11], on a work carried out in the Taylor Creek, which recorded as low as 2.461 ± 2.687 to 10.009 ± 4.145 mg/L in the stations. In the investigation undertaken by Ikpe, et al. [25] on total petroleum hydrocarbons in Ethiopie River, Oghara Community revealed that mean concentration that was as low as 0.004 ± 0.003 and 0.008 ± 0.008 mg/L which was far lower than that obtained from this work.

In other parts of the world, total petroleum hydrocarbons concentration in surface water have been reported, such include the work of Suratman [51], in the Johor Peninsular, Malaysia which reported a level of 25 to 2795 g/L, also the work of Sammarco et al. [48] on the Deepwater Horizon Gulf of Mexico which recorded a range of 60,000-260,000 g/L of total petroleum hydrocarbons, and petroleum hydrocarbons pollution level recorded by Sari et al. [49], in Wonocolo oil field was 211,025.73 g/L were either higher or lower than that recorded from this study.

The resultant effect of hydrocarbons in the surface water affects the level of oxygen availability in the water, activities of micro-organisms are reduced, fish breeding and spawning grounds are reduced and even the roots of trees in the mangrove are affected [53,52].

The implication of high quantity of oil films present in the surface water is the reduction of the gaseous diffusion (oxygen deterioration) to the plants and animals that inhabit the aquatic

environment [45,24]. Total petroleum hydrocarbons contamination in the surface water of any river causes damage to the ecological setting of the environment due to the carcinogenic, mutagenic and toxic nature of total petroleum hydrocarbons [56,34,49]. The presence of the diesel range organics in the surface water of the creek can lead to changes in the structure of species due to the high level of its toxicity [32], since long term exposure of organisms accumulates and transfers in the food chain processes thereby giving negative implications on aquatic organisms [12].

The presence of total petroleum hydrocarbons in Tombia Creek varied from station to station. This observation was also reported in the Orashi River where the concentration of TPH was not uniform within the stations in which there were noticeable clear variations from station to station [16]. This is a clear indication that the source of pollution was anthropogenic [6,7,12].

Total petroleum hydrocarbons in sediments of Tombia Creek

The mean concentrations of total petroleum hydrocarbons in sediments from Tombia Creek as at the time of study are provided in Table 3 while the mean concentrations of total petroleum hydrocarbons within the stations during the time of investigation is illustrated in Figure 3. The extent to which the creek was contaminated or polluted is a factor of the quantity of total petroleum existing per kilogram of sediment. The table showed the concentrations of the different fractions of total petroleum hydrocarbons (TPH) and also the sum of total petroleum hydrocarbons present in the sediment from the three designated stations sampled from the Tombia Creek.

Table 3: Concentrations (mg/Kg) of total petroleum hydrocarbons in sediments different stations of Tombia Creek

Carbon Length (mg/Kg)	Stations		
	1	2	3
C8	25.052 ± 2.941	ND	0.229 ± 0.051
C9	ND	ND	1.050 ± 0.112
C10	ND	ND	2.625 ± 0.168
C11	ND	ND	3.642 ± 0.291
C12	ND	ND	7.332 ± 1.433

C13	ND	ND	11.049±1.965
C14	3.034±0.332	ND	2.160±0.280
C15	8.411±1.796	ND	0.041±0.006
C16	13.168±1.911	8.426±1.626	0.013±0.001
C17	12.463±1.548	5.204±1.302	1.253±0.053
C18	12.315±1.352	11.498±1.727	3.857±0.306
C19	15.460±1.667	45.254±3.919	10.674±1.620
C20	15.341±1.808	26.852±2.885	10.839±1.514
C21	ND	ND	ND
C22	18.052±2.203	20.422±2.314	7.214±1.203
C23	ND	ND	ND
C24	2.533±0.220	21.800±2.286	13.308±1.694
C25	ND	ND	ND
C26	2.586±0.301	59.066±3.784	14.402±1.800
C27	ND	ND	ND
C28	2.533±0.218	49.030±3.315	32.117±3.104
C29	ND	ND	ND
C30	2.471±0.225	33.888±3.006	18.689±2.002
C31	ND	ND	ND
C32	6.232±1.165	16.799±2.102	2.880±0.224
C33	ND	ND	ND
C34	3.926±0.314	4.177±1.100	7.768±1.685
C35	ND	ND	ND
C36	ND	ND	0.241±0.019
C37	ND	ND	ND
C38	ND	ND	0.003±0.000
C39	ND	ND	ND
C40	ND	ND	0.056±0.002
Total	143.577±18.001	302.416±29.364	151.520±19.533

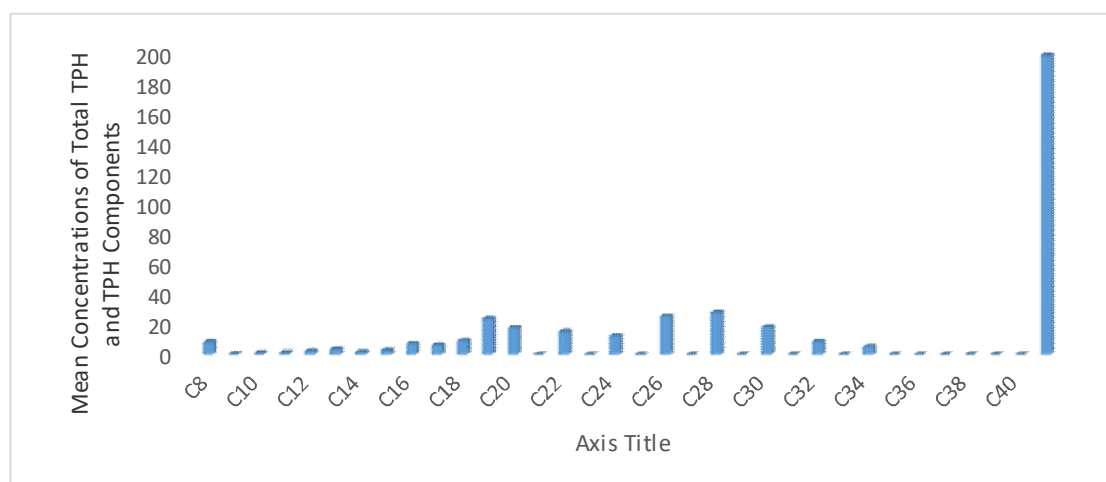


Figure 3: Mean concentrations of total TPH and TPH components in sediment within the stations of the Tombia Creek during the time of study.

The results obtained for the mean concentrations of total petroleum hydrocarbons in the sediments in the different stations of Tombia Creek within the period of study ranged from 143.577±18.001 to 302.416±29.364 mg/Kg. The order of occurrence of total petroleum hydrocarbons in the

stations was 2 > 3 > 1. The mean concentration of total petroleum hydrocarbons fractions within the period under investigation varied from not detected to 59.066±3.784 mg/Kg. The mean value of total petroleum hydrocarbons obtained for the stations within the period under study was

199.171±22.299 mg/Kg. The individual concentrations of total petroleum hydrocarbons fractions as at the time under investigation ranged from not detected to 59.066±3.784 mg/Kg in the creek. C21, C23, C25, C27, C29, C31, C33, C35, C37 and C39 were not recorded in any of the stations during the period of this investigation while C26 in Station 2 had the highest concentrations in all stations of the creek used in the study.

The mean values obtained for total petroleum hydrocarbons in the stations of the Tombia Creek were above the acceptable range given by the Federal Ministry of Environment of 30mg/Kg in water [22] but below the Directorate of petroleum Resources acceptable limit of 50mg/Kg and far below the 5000mg/Kg intervention limit set by DPR [9].

The mean concentrations of total petroleum hydrocarbons obtained in this investigation on carried out on the stations of Tombia Creek were below or lower than that obtained in the work of Ogeleka, et al. [41], in Egwa (215700±77 mg/Kg) and Odidi (215730±81mg/Kg). The work of Etchie, et al. [18], the result obtained for total petroleum hydrocarbons in sediment and soil ranged between 600 to 2300 mg/Kg, and in Adewuyi, et al. [3], the mean concentration level of total petroleum hydrocarbon recorded was 1602.4±115.3mg/Kg in the Ubeji River, Warri, Delta State, Nigeria, were all above that recorded in this study. Total petroleum hydrocarbon recorded in the sediment of Qua-Iboe River by Inyang, et al. [26] had a mean value of 606.83±229.48 mg/Kg, and in Ezekwe and Utong [20], the total hydrocarbon recorded in the Oturuba Creek ranged between 1546 to 3997.9mg/Kg in the dry season and between 1727.5 to 5118.5 mg/Kg in the wet season and in Adeniji, et al. [1], from sediment samples in the Buffalo River Estuary, Cape Province, South Africa was of the range of 1259 to 11,000 mg/Kg, were all higher than the result obtained from this study.

However, in the work of Edori and Marcus [13], in the sediments of Taylor Creek recorded an average value of 18.034 to 23.64 mg/Kg in the months of study were lower than this work and also that which was recorded in the sediments of Orashi River by Edori et al. [16] which varied from 22.3925±5.2104 to 50.4431±15.9916 mg/Kg. Also, in Ashiru and Ogundare [5], the concentration of the total petroleum hydrocarbon on the sediments of Ugbo water way recorded as low as 0.131mg/Kg, which is far lower than that recorded in this work. Other cases found to be lower than this work occur in the Northwest of the Persian Gulf with a total mean value of total petroleum hydrocarbons of 45.94 g/g, and that of Adeniji, et al. [1,2] in the sediments of Algoa Bay, South Africa with a range of 0.72 to 27.03mg/Kg.

The pollution level of total petroleum hydrocarbons in the sediments of rivers can be classified into four levels as in Massoud, et al. [39] and Ritchie, et al. [47]. The four levels are (10-15 mg/Kg) as unpolluted, (15-50 mg/Kg) as slightly polluted, (50-200 mg/Kg) as moderately polluted and (> 200 mg/Kg) as heavily polluted. The level of occurrence and contamination in this study averagely sum up within 50-200 mg/Kg which is for moderately polluted and > 200 which is for heavily polluted, it shows that activities such as crude refining, for self-sustenance prevalent in the area and the inability of the Nigerian government to make room for adequate clean-up and proper sensitization on the matter of oil activities has given rise to such high pollution level of total petroleum hydrocarbons as experienced in the Tombia Creek.

Sediment acts as natural sink to absorb the contaminants in the water ecological systems. When significant level of pollution due to contamination of the sediments occur, there is the possibility of loss of species and the biodiversity of the ecological frame are completely affected [38]. This situation affects the food chain of the lower (bottom) and upper levels of the ecosystem. The impact of the contamination might have

direct toxic effect on the bottom dwelling animals and can also negatively affect humans through consumption of fishes or water from such contaminated rivers. Therefore, there is need for proper sediment quality analysis in order to monitor the river ecological systems [27,54].

Petroleum hydrocarbons manifest toxic effects even at low concentration range of 10-2-1-5 mg/dm³ and affects aquatic creatures in their developmental stages [32]. The presence of total petroleum hydrocarbons in sediment bring about changes in the pattern of the naturally ecosystem, by altering the metabolic processes and reducing the species present and in general create instability in the ecosystem [31]. Petroleum hydrocarbons when present in the sediment can hinder and reduce the growth of phytoplanktons. Hydrocarbons when carried into the river, may take a long period before being flushed out of the system. The process involved include, dissolution, evaporation, dispersion, emulsification, biodegradation and sedimentation which finally deposits at the bottom of the river. This give severe impact on the aquatic life, as total petroleum hydrocarbons may be buried in the sediment for years without changes in the level of concentration [57,46].

The hydrocarbons in the sediments are of utmost importance because they are easily absorbed to matter and settle to the bottom which is the

reservoir for the accumulation of contaminants and pollutants. The information on the mode of contamination by the various categories of total petroleum hydrocarbons can be used to deduce the rate of anthropogenic influence and the source of contamination of the environment [40,36].

Partition coefficient of total petroleum hydrocarbons (TPH) in the Tombia Creek

The values obtained for partition coefficient of total petroleum hydrocarbons in the studied creek is shown in Tables 4. In the Tombia Creek, partition coefficients were not recorded for C8 to C13, odd hydrocarbon components of C21 to C33 and C35 to C40 in all the stations used for the study. C14 and C15 were not recorded in Stations 2, C22 was not recorded in Stations 1, C32 was not recorded in Stations 3 and C34 was not recorded in Station 1 and 3. All other TPH components' partition coefficients were recorded in all the stations used in the investigation. All values of partition coefficient of TPH recorded within the stations ranged from 0.002 in C16 in Station 3 to 12.381 in C28 in Station 3. Partition coefficients of TPH components not recorded were either not observed in water or sediment phases or in both.

Table 4: Partition coefficient of total petroleum hydrocarbons (TPH) between sediment and water phases in Tombia Creek

Carbon Length	Stations		
	1	2	3
C8	-	-	-
C9	-	-	-
C10	-	-	-
C11	-	-	-
C12	-	-	-
C13	-	-	-
C14	2.356	-	0.756
C15	4.109	-	0.020
C16	7.083	2.707	0.002
C17	3.997	1.075	0.435
C18	2.436	2.096	2.250
C19	2.581	4.433	2.900

C20	10.888	2.266	4.922
C21	-	-	-
C22	-	3.811	2.196
C23	-	-	-
C24	2.301	4.190	4.426
C25	-	-	-
C26	1.300	5.809	4.890
C27	-	-	-
C28	0.814	4.048	12.381
C29	-	-	-
C30	0.982	1.857	9.749
C31	-	-	-
C32	5.050	3.800	-
C33	-	-	-
C34	-	0.790	-
C35	-	-	-
C36	-	-	-
C37	-	-	-
C38	-	-	-
C39	-	-	-
C40	-	-	-

The dash (-) indicates the either the numerator or denominator was not detected or both were not detected during the analysis.

The partition coefficient is useful in explaining the preferred stable phase of petroleum hydrocarbon components in a water body. Results obtained from the Tombia Creek indicated that sediment is preferred phase when compared with the water phase, which could be due to the hydrophobic characteristic or nature exhibited by water to oil. The results obtained showed that values greater than one indicates preference for sediments while values that are lower than one indicated that the component is water loving. It was observed that certain hydrocarbon components were either more in the water phase or sediment phase. This could be as a result of the creek flow pattern and dynamics at the sampling station or disturbances that come from transportation activities, operators of illegal oil bunkering and associated businesses within the stations or the possibility of fresh discharge into the river during the sampling period. This observation is in agreement with Edori et al. [16]. The higher contamination experienced in the sediment as compared to the surface water may be due to the hydrophobic nature of total

petroleum hydrocarbons. Sediments acts as sink to hydrophobic compounds and this leads to accumulation. The rate at which these compounds decomposes will increase the concentration of the various compounds [17,23]. The total petroleum hydrocarbons components due to their hydrophobic nature have affinity for solid particles instead of water [29,43,44]. This removes the fractions from the water phase, thereby enhancing the higher concentration of total petroleum hydrocarbons on the sediment phase.

The propensity or inclination for total petroleum hydrocarbons to have higher presence or concentration in the sediments when compared to that of surface water also emanates from the point that complex components or fractions of the hydrocarbon residue are more in the sediment because they naturally sink and settle down to the bottom of the river bed and become part of the sediments [43]. This also stress the fact and confirm to the point that heavier fractions of crude oil (residue) are solids, and therefore have the tendency to settle to the bottom sediments of

the river [15]. Wakeman and Themelis [55] also observed that contaminants that are brought into the river from land base runoffs that enter into the water surface are quickly attached to by suspended particles or materials and thereby quickly making the contaminants to settle down to the bottom of the river bed which then increases the concentration. This further proves how the sediment is significant in the role of being a natural sink for the marine environment [52].

Conclusion

Water is a very vital natural resource. Its practicality to diverse forms of life in a well-known information. When once the emerging nature of water is altered and compromised, it spells serious unfavourable consequences to human beings and other biota. The scarcity of good water quality is a worldwide challenge. Water pollution/contamination has become a subject of great concern locally and globally.

This study has showed that total petroleum hydrocarbons (TPH) are potential and likely contaminants/pollutants of surface water. The study has also showed the sources of these contaminants/pollutions into water bodies.

This study revealed that the water and sediment in the creek were contaminated by total petroleum hydrocarbons. The high concentration of the TPH in the water has rendered the water unfit for use for cooking, bathing, washing and agricultural purpose of watering crops. The government should as a matter of urgency evolve effective remediation options to clean up the aquatic environment of TPH to the barest minimum and also in collaboration with non-governmental organizations should embark on sensitization programmes to educate the people on the proper means of waste disposal.

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