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Original paper

Hydrocarbons Distribution of Total Petroleum in the Surface Water of Kolo Creek, Ogbia Axis, Bayelsa State Nigeria

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ABSTRACT: This study investigated the total petroleum hydrocarbons level in surface water of the Kolo Creek, Ogbia, Bayelsa State, Nigeria. The study was carried out to assess the level of occurrence total petroleum hydrocarbons in the creek. Water samples were collected from four designated points along the creek. The water samples were extracted using dichloromethane (DCM) through the liquid-liquid extraction technique which was subsequently followed by clean-up of the chromatographic column. The samples were then analyzed using Gas Chromatography-flame ionization detector (GC-FID) for the determination of total petroleum hydrocarbons (TPH). The results of the analysis revealed that the mean concentrations of total petroleum hydrocarbons in the surface water within the months of study ranged from 42.3126±4.6438 to 89.4409±13.620 mg/L in surface water. The average amount of TPH in the surface water samples collected from all the four different sampling stations were generally higher than the maximum permissible limits by WHO which is 10mg/Kg in water. The level of occurrence in the stations were in the 2 > 1 > 4 > 3.Theresults recorded have indicated that the Kolo Creek is under severe pollution threat by total petroleum hydrocarbons and therefore underscores the essence for urgent remediation to advert serious health complication and adequate steps should be taken to forestall any impending danger that could pose severe threat to the aquatic ecosystem and the human dweller along the shores of the creek.

Keywords: Kolo creek, total petroleum hydrocarbons, pollution, surface water, oil bunkering
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INTRODUCTION

The significance of water and its usefulness cannot be overstressed in the life of humans and his various activities. Water (surface and underground) is beneficial in agricultural, industrial, social, economic and even in political improvement of human and his environment. But as a result of unrestrained and selfish behaviour of man, this natural resource has now been perturbed. The perturbation created due to usage of the natural water forms like rivers, lakes, creeks, estuaries, sea and also groundwater has resulted into the contaminations being introduced on daily basis into the water ecosystem (Edori et al., 2020).As a result of increase in population growth, technology, industrialization, oil exploration, production and exploitation, agriculture, domestic wastes (Emongere et al., 2005, Lima et al., 2008) and greed and selfishness on the part of man has greatly affected and have contributed immensely to the poor water quality observed in the Niger Delta Region of Nigeria. The contamination of surface water can be ascribed to the nature of its adjoining environment. Water of high quality is solely for the sake its consumption by humans, but its appropriateness for other vital anthropogenic and

recreational undertakings (Arimieari et al, 2014).Consequently, the overall reason for constant monitoring of the creek is important, both as a medium of checking its current status and as an instrument for effective management policy implementation.

Even though petroleum is a naturally occurring organic compound found deep under the earth's crust and hazardous to almost all life forms. One of the key environmental challenges today is oil pollution. It has brought considerable scientific attention resulted from the activities related to the petrochemical industry. Hydrocarbon pollution may originate from several sources: municipal and industrial wastes, runoff, accidental spillage of oil and shipping. The yearly global oil-seepage rate (NAS, 2003) is projected to be between 0.2 and 2.0 Mt (60 and 600 million gallons), with a best approximation of 0.6 Mt (180 million gallons) (Kvenvolden and Cooper 2003). These hydrocarbon components have been known to belong to the family of carcinogens and neurotoxic organic pollutants (Nilanjana and Preethy 2011).

TPHs can enter aquatic systems either as components of unburnt petroleum and petroleum products such as fuel, lubricating oils, or as products of incomplete combustion from exhaust emissions. Oil and oily discharges from ships symbolize a notable risk to marine ecosystems (Nageswar-Rao et al., 2016). Oil which floats in water, as a thin layer when spilled or discharged into it. This thin surface layer tends to split into droplets by wave action and these droplets become dispersed in the volume of sea water underneath (Veerasingam et al. 2011). Such occurrence set pressures on marine habitats and leads to accumulation in the tissues of mollusks, mussels, fish and marine mammals (Bernem et al. 2008). Although a significant portion of petroleum hydrocarbons entering the marine environment is removed by evaporation, a portion gets disseminated in water, accumulated in sediment and transferred to biota (Chouksey et al. 2004). The aquatic organisms consume hydrocarbons through the food chain and over a period of time bio-accumulate in their tissues. These components could be carcinogenic and mutagenic when they are involved in biological processes.

Soluble water fractions of hydrocarbons are toxic and are known for causing severe harm to plants and animals in aquatic environment. Diving birds may be rendered flightless when oiled; thereby, resulting into loss of insulating properties against cold that would certainly cause death. They also end up taking in some amount of oil in an attempt to clean themselves by preening and thus causing enteritis (Boyle 1969; Jinadu, 1989). Contamination of surface water is detrimental to human and plants, it creates severe disorder to our environment if not properly managed or controlled (Mishra and Patel, 2015).

An overwhelming chronic input of chemical contaminants like hydrocarbons from focal points and non-focal points within and in the vicinity of coastlines along a water body may greatly affect natural resources. This could cause large-scale and chronic impacts, modification of habitats by influencing the health of benthic organisms, and the overall quality of the marine ecosystem with potential long term risks for human health and the environment (Zaghden et al., 2005; Marchand et al., 2006). The effects of hydrocarbons, alone or in combination with other pollutants depend on factors such as volume released, chemical properties, proximity to other sources of pollution and their interaction with local and natural environmental variables (Ye et al., 2007; Pinedo et al., 2014).

Thus, an anthropogenic action is continually responsible for two things, contaminating or degrading the earth's surface. These combined with the concurrent rise of flood water annually across all low land, rivers and streams of the Niger Delta region of Nigeria, there is the likelihood of the area being disposed to drift of organisms out to the sea if not appropriately checked. As a result, these changes pose untold danger to streams, creeks and rivers and aquatic organisms that dwell in them. In addition to these is the unceasing oil exploitation and maintenance undertakings that is regularly taking place at Imiringi sub-station and its vicinities which could possibly increase wastes that would later on affect the area (Edori et al., 2021).

MATERIALS AND METHODS

Study area

The Kolo Creek lie between latitude $4^{o}23$ and $4^{o}36$ north and longitude $6^{o}14$ and $6^{o}16$ east. It is a non-tidal fresh water in Ogbia Local Government Area in Bayelsa State, Nigeria. This creek is connected by several small lakes which are either artificial or natural, including ponds; borrow pits and tributaries that run into it. This region is known for its large fresh water swamps and tropical rain forest. There are so many oil fields that are connected to the Kolo Creek flow station along the creek (Figure 1). There existed unapproved oil businesses along the shores of the creek, which also show that a lot of operations release their effluents into the creek. This creek also serves as the main source of drinking water to the inhabitants before the advent of borehole water. The Creek was very useful to the inhabitants for farm irrigations, and also beneficial for animals and other forms of aquatic lives production for the rural dwellers (Edori et al., 2021).

The research work was carried out using four designated locations namely; Oruma; Station 1, Imiringi; Station 2, Kolo 1; Station 3 and Akoloman; Station 4. Originally. These people were known for farming and fishing and host to two oil fields known as Oloibiri and

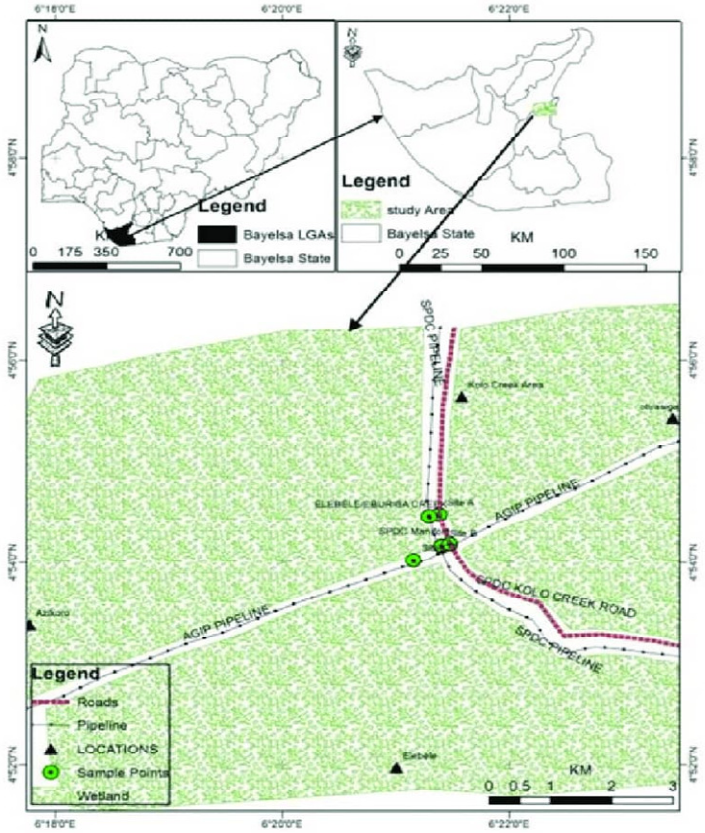

Figure 1: Map of Kolo Creek showing sampling points.

Kolo Creek oil fields (Eli, 2012; Amolo and Amolo, 2022).

Collection of water samples

The water samples for total petroleum hydrocarbons were collected with the aid of glass bottles. The glass bottles were first washed with dichloromethane so that the water sample could be prevented from contamination and was then preserved by adding 2ml of 0.2m H_2SO_4 so that the pH will be brought to about 2. The sample bottles were then covered with sterile aluminium foil pieces and was then screwed tightly using plastic screws. The collected samples were then stored at a temperature of -4^oC to prevent evaporation of TPH fractions before being conveyed to the laboratory for further laboratory pre-treatment, determination and analysis (Ikpe et al., 2016).

Extraction of water sample for TPH

Extraction of collected water sample was completed with the aid of a separatory funnel. One litre of the water sample was transferred into the separatory funnel. A glass stopper that contain about 40ml dichoromethane (DCM) as solvent of extraction, for complete separation of the organic phase from the aqueous phase. The separatory funnel was stirred constantly for a period of 6-10 minutes. The components were allowed to attain equilibrium in the separatory funnel and was then allowed for about 10 minutes to settle down. This methods was repeated for each of the samples for at least three times. Filtration method was adopted at a temperature of 40^oc to concentrate the sample extract. The extracts that were concentrated were then transferred to a pre-weighing bottle and then allowed to evaporate to dryness (Manahan, 2003; Lawson, 2011). The extracted water sample was then added into a chromatographic column which was packed with silica gel slurry and 3cm anhydrous sulphate layer on top to entirely remove any polar organic materials that could be found in the solvent. With 25ml n-hexane, the column of the chromatography was eluted to recover all the several components of TPH components. The eluted samples were concentrated to 3ml with rotary evaporator at 4^oC and then evaporated to dryness. The procedure used by Maioli et al, (2011) was employed in treating the samples. A prepared 4ml tetrachloroethylene was added to dissolve the extract and

an agilent 6890 gas chromatography with flame lionization detector (GC-FID) was employed in the determination and analysis of the concentrations of total petroleum hydrocarbon fractions. The detector was maintained at 350^{o}C. The GC/FID measured the total petroleum hydrocarbon by calculating up all the aliphatic and aromatic s used in the sample.

Sample clean up

Column preparation was done through the introduction of glass-wool into an already washed chromatographic column. Thereafter, into an already clean silica gel was introduced. Then addition of slurry was made into the chromatographic column. Anhydrous sodium sulphate was added into the column, thereafter the addition of pentane. Thus, in a previously cleaned beaker, the concentrated sample was mixed with cyclohexane and thereafter introduced into the column already prepared. The sample was eluted with pentane and then collected into the beaker below the column. Thereafter, the elution of sample was carried out by the introduction of more pentane, after which the column was then rinsed with dichloromethane. The sample was allowed to stand in a fume cupboard after elution at room temperature for evaporation to take place.

Sample separation and detection

Agilent 5890 gas chromatography – flame ionization detector (GC-FID) was used for the detection of total petroleum hydrocarbons in the surface water samples at different stations of the Kolo Creek. 3ml of concentrated sample was injected into the gas chromatography vial for cleaning of syringe, the blank dichloromethane was injected into micro syringe of gas chromatography. Before the analysis of the sample, the cleaning of the syringe was carried out thrice. The micro-syringe was washed after with the sample, thereafter, the sample was injected into the gas chromatography for the total separation of the various components of the sample. Thus separation of components in the sample, the amount of total petroleum hydrocarbon content resolved at the particular chromatogram was then measured in mg/L for water sample.

RESULTS AND DISCUSSION

The results obtained (Tables 1-4) for total petroleum hydrocarbons in the surface water of the creek within the months of study in the various stations showed that in January, values recorded were 82.7305, 103.1961, 37.8704 and 40.2898mg/L for Stations 1, 2, 3 and 4 respectively. In March, values recorded were 95.9651, 110.4321, 45.7098 and 54.7111mg/L for Stations 1, 2, 3 and 4 respectively. In May, values recorded were 89.6271, 104.6310, 43.3577 and 47.8942mg/L for Stations 1, 2, 3 and 4 respectively. The mean concentrations of TPH within the months in the different stations were 89.4409±13.620, 106.0862±7.901, 42.3126±4.6438 and 47.046±6.698 for Stations 1, 2, 3 and 4 respectively. The order of occurrence of mean total petroleum hydrocarbons in the creek was Station 2 > 1 > 4 > 3. The order of occurrence in the months showed that March > May > January.

Table 1: Concentrations of total petroleum hydrocarbons in surface water samples from Kolo Creek in January.

Carbon Length	Stations			
	1	2	3	4
C8	-	-	-	-
C9	6.9669	-	-	-
C10	5.6439	12.8460	-	-
C11	3.4078		-	-
C12	-	-	-	-
C13	66.2473	10.1877	-	0.5890
C14	0.4646	-	-	-
C15	-	10.7240	1.3304	0.5986
C16	-	1.9116	0.4581	-
C17	-	2.8918	2.0655	21.0983
C18	-	-	4.6905	1.7187
C19	-	1.0366	0.6062	11.1675
C20	-	10.9042	0.0185	1.3659
C21	-	1.6279	1.4423	1.1444
C22	-	10.8887	0.2753	0.8942
C23	-	2.0041	-	1.1389
C24	-	-	-	0.5743
C25	-	2.8720	2.6017	-
C26	-	10.5724	1.5211	-
C27	-	-	-	-
C28	-	2.8923	4.3504	-
C29	-	1.4793	0.9704	-
C30	-	10.0017	0.4952	-
C31	-	10.3558	0.6210	-
C32	-	-	-	-
C33	-	-	-	-
C34	-	-	-	-
C35	-	-	-	-
C36	-	-	-	-
C37	-	-	16.4238	-
C38	-	-	-	-
C39	-	-	-	-
C40	-	-	-	-
Total	82.7305	103.1961	37.8704	40.2898

The average concentrations of total petroleum hydrocarbons obtained in the surface water of the Kolo Creek within the four different sampling stations were far higher than the maximum acceptable limits of 10.00mg/L for surface and groundwater set by DPR and FEPA (Tables 1-4). The recorded concentration of total petroleum hydrocarbons in this research was higher than that reported in the work of Edori et al., (2021) in the Orashi River in Engenni, Ahoada West, Rivers State

Table 2: Concentrations of total petroleum hydrocarbons in surface water samples from Kolo Creek in March.

Carbon Length	Stations			
	1	2	3	4
C8	-	-	-	-
C9	4.9884	-	-	-
C10	6.8395	13.2486	1.0013	-
C11	3.3910	-	-	-
C12	-	-	-	-
C13	60.4972	11.1087	0.8014	0.8994
C14	1.6358	-	-	-
C15	-	9.0702	1.5380	1.0391
C16	5.0036	2.3316	0.6881	-
C17	-	3.1819	3.0591	25.1016
C18	-	-	5.0691	1.0789
C19	4.5170	3.0139	1.0021	14.1130
C20	-	11.4269	0.1054	1.4101
C21	-	1.4886	1.4004	1.4005
C22	2.5531	10.7669	0.4962	1.6337
C23	-	2.8833	-	2.0304
C24	1.0342	-	-	1.8873
C25	-	2.3687	2.7018	-
C26	3.1637	12.0101	2.1581	-
C27	-	-	-	-
C28	-	3.0018	4.0346	0.9433
C29	-	3.2285	1.3075	-
C30	1.3482	8.8956	1.0311	-
C31	-	12.1053	0.5520	-
C32	-	-	-	-
C33	0.9934	0.3015	0.5453	1.1328
C34	-	-	-	-
C35	-	-	-	2.0410
C36	-	-	-	-
C37	-	-	18.2183	-
C38	-	-	-	-
C39	-	-	-	-
C40	-	-	-	-
Total	95.9651	110.4321	45.7098	54.7111

Table 3: Concentrations of total petroleum hydrocarbons in surface water samples from Kolo Creek in May.

Carbon Length	Stations			
	1	2	3	4
C8	-	-	-	-
C9	4.3245	-	-	-
C10	5.5871	12.1948	0.9068	-
C11	2.3910	-	-	-
C12	-	-	-	-
C13	61.0201	10.6483	0.7810	1.0381
C14	0.3456	-	-	-
C15	-	8.3907	1.3942	0.8943
C16	4.6842	2.5529	0.6983	-
C17	-	2.8873	3.0096	22.0109
C18	-	-	4.9940	0.7008
C19	3.9057	2.6489	0.9933	12.1001
C20	-	10.9104	0.1104	1.1107
C21	-	2.2266	1.3104	1.5032
C22	2.1849	10.9796	0.4652	1.4617
C23	-	2.6655	-	1.9330
C24	0.9551	-	-	1.6084
C25	-	2.1003	2.5098	-
C26	2.0675	10.6857	2.3164	-
C27	-	-	-	-
C28	-	2.6391	3.8172	0.8131
C29	-	3.9128	1.4000	-
C30	1.1689	7.9849	0.8593	-
C31	-	11.0034	0.4906	-
C32	-	-	-	-
C33	0.8941	0.1998	0.4869	1.0204
C34	-	-	-	-
C35	0.0984	-	-	1.6985
C36	-	-	-	-
C37	-	-	16.8143	-
C38	-	-	-	-
C39	-	-	-	-
C40	-	-	-	-
Total	89.6271	104.6310	43.3577	47.8942

which was between 10.913±2.2022 to 12.21±3.3034mg/L. The results recorded was also higher than that obtained by Isibor and Freeman (2016) whose total petroleum hydrocarbons concentration ranged from not detected to 3.69±0.19mg/L in a work done in Egboko River.Other studies that were lower than this work were that of Alinnor and Nwachukwu, (2013) with concentration ofs 23.6±4.3 mg/L and that obtained by Edori and Kpee (2019), in a work done in the Taylor Creek, which recorded figures ranging from 2.461±2.687 to 10.009±4.145 mg/L for the stations.

The presence of total petroleum hydrocarbons in Kolo Creek showed a clear variation from one station to another. This is a pointer to the fact that the source of contamination was anthropogenic. The rate of the flow of the creek and the kind of wind displayed in the creek should have prompted the concentrations of the lower total petroleum hydrocarbons fractions. The high degree of occurrence of total petroleum hydrocarbons components in the surface water of the creek was made possible due to the continuous operation of the oil bunkering business despite evaporation of the lower fractions at high temperature and strong wind. The low occurrence of the lower components of the total petroleum hydrocarbons components in the creek possibly might be due to the strong wind, high temperature and high rate of evaporation and other forms of disturbances that is associated with the creek. This observation corroborates that which was observed in the work of Daniel and Nna (2016) and that of Edori and Kpee (2019).

Chouksey et al., (2004) and Nageswar Rao et al., (2016) observed that at certain months of the year that total petroleum hydrocarbon fraction was low due to evaporation, high temperatures and low atmospheric pressures. The authors also observed that high TPHs values recorded in the surface water of the estuary

Table 4: Mean concentrations of total petroleum hydrocarbons in surface water from Kolo Creek within the period under investigation.

Carbon Length	Stations			
	1	2	3	4
C8	-	-	-	-
C9	5.4266±1.122	-	-	-
C10	6.0235±0.577	12.7631±0.434	0.6360±0.451	-
C11	3.0633±0.475	-	-	-
C12	-	-	-	-
C13	62.5882±2.596	10.6482±0.376	0.5275±0.373	0.8422±0.188
C14	0.8153±0.582	-	-	-
C15	-	9.3950±0.980	1.4209±0.087	0.8440±0.183
C16	3.2293±2.287	2.2654±0.266	0.6148±0.111	-
C17	-	2.9870±0.138	2.7114±0.457	22.7369±1.713
C18	-	-	4.9179±0.164	1.1661±0.420
C19	2.8076±2.001	2.2331±0.859	0.8672±0.185	12.4602±1.229
C20	-	11.0805±0.245	0.0781±0.042	1.2956±0.132
C21	-	1.7810±0.320	1.3844±0.055	1.3494±0.151
C22	1.5793±1.127	10.8784±0.087	0.4122±0.098	1.3299±0.316
C23	-	2.5176±0.374	-	1.7008±0.399
C24	0.6631±0.470	-	-	1.3567±0.565
C25	-	2.4470±0.320	2.6044±0.078	-
C26	1.7437±1.312	11.0894±0.653	1.9985±0.344	-
C27	-	-	-	-
C28	-	2.8444±0.152	4.0674±0.219	-
C29	-	2.8735±1.025	1.2260±0.185	-
C30	0.8390±0.598	8.9607±0.825	0.7952±0.223	-
C31	-	11.1548±0.722	0.5545±0.053	-
C32	-	-	-	-
C33	0.6292±0.447	0.1671±0.125	0.3441±0.244	0.7177±0.510
C34	-	-	-	-
C35	0.0328±0.026	-	-	1.2465±0.892
C36	-	-	-	-
C37	-	-	17.1521±0.771	-
C38	-	-	-	-
C39	-	-	-	-
C40	-	-	-	-
Total	89.4409±13.620	106.0862±7.901	42.3126±4.6438	47.046±6.698

studied could be ascribed to the increased land-based sources, such as industrial effluents originating from nearby industries; marine based sources and increased ship traffic. This observation is also true in this work whereby during the month of March there was an upsurge in the concentration of total petroleum hydrocarbons in the creek due to discharge from adjoining lands.

The subsequent outcome of hydrocarbon components in the surface water upsets the quantity of oxygen availability in the water, reduction in activities of micro-organisms, reduction in the breeding and spawning grounds of fish and also effect on the roots of trees within the affected area (Ugochukwu and Leton, 2004, Udoh and Akpan, 2010). The consequence of the high level or amount of oil films existing in the surface water is the decrease in gaseous diffusion (oxygen deterioration) to aquatic plants and animals inhabiting the environment that is polluted (Osuji et al., 2004, Howard et al., 2009). The existence of total petroleum hydrocarbons in the surface water of any river above the required limit can potentially damage to the environmental setting due to the carcinogenic, mutagenic and toxic nature of total petroleum hydrocarbons (Wang et al., 2011; Liu et al., 2012, Sari et al., 2018).

Conclusion

This investigation the distribution of TPHs in surface water of Kolo Creek, Ogbia axis, Bayelsa State, Nigeria. The level of TPH recorded in the surface water exceeded that which is acceptable by regulatory bodies such as the WHO for potable water and other usages. The high value of TPH observed in the surface water was connected to both land and water-based anthropogenic sources. Such activities include the operation of the Kolo Creek sub-

station at Imiringi, the illegal oil marketing and bunkering activities, transportation, effluents discharged from the adjoining illegal refining sites and leakages from tanks. The degree of occurrence of petroleum hydrocarbons in the surface water of the creek was an indication that there was severe crude oil contamination. This could result into dangerous health situation, imbalance in the water ecosystem and environmental deterioration of the area under study. There is therefore the necessity for continuous pollution monitoring of the creek in order to improve the water environment by relevant agencies of government to return the creek to its former nature that was useful to the inhabitants.

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