DETERMINATION OF THE LEVEL OF PETROLEUM HYDROCARBON IN WATER, FISHES AND PLANTS FROM PART OF RIVER ETHIOPE, OGHARA IN DELTA STATE, NIGERIA

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Abstract

The occurrence of crude oil in the Niger Delta with its concomitant petroleum industrialization has resulted in generation of enormous waste products. Also spilled oil produces deleterious effect on both flora and fauna. As such human daily activities and means of survival are dependent on the environment in which they live; hence there is need for best environmental management practices. This research investigated the total petroleum hydrocarbons in plants, water and fish samples from and around River Ethiope, Oghara community in Delta State, Nigeria. Total petroleum hydrocarbon (TPH) in Plants, water and fish were extracted separately using standard analytical method and examined with the use of Gas Chromatography with Flame Ionization Detector (GC/FID) after purifying the extract through column packed with silica gel. The results of the analysis revealed that the levels of TPHs in water ranged between (0.004 $\pm$ 0.003 and 0.008 $\pm$ 0.008) mg/L while in fish ranged between (0.019 $\pm$ 0.001 and 0.034 $\pm$ 0.001) mg/L and in plant ranged between (0.004 $\pm$ 0.001 and 0.044 $\pm$ 0.001) mg/L. Moderately high molecular weight aromatic and high molecular weight aliphatic hydrocarbons were present.

INTRODUCTION

Total petroleum hydrocarbon (TPH) is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil. Crude oil is used to make petroleum products, which can contaminate the environment (ATSDR, 1999). TPH is a mixture of chemicals, but they are all made mainly from hydrogen and carbon, called hydrocarbons. Some chemicals that may be found in TPH are hexane, jet fuels, mineral oils,

benzene, toluene, xylenes, and naphthalene, as well as other petroleum products and gasoline components. However, it is likely that samples of TPH will contain only some, or a mixture, of these chemicals (ATSDR, 1999).

The presence of TPH in river water is of concern to the public. Many of these products or their metabolites have been known to be toxic to living organisms, and affect both aquatic and terrestrial environments. It is inevitable that sizeable quantities of these products will find way into the soil, water, plants and air by mishandling, spilling or leaking of underground storage tanks and oil pipes. Oil spills devastate soil and aquatic systems and cause alteration in important microbial process (Ijah, 1998). Biologically, they have deleterious impact on aquatic life (Edema, 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 petroleum hydrocarbon release differ widely depending on the product spilled and how it weathered.

The amount of Total Petroleum Hydrocarbon (TPH) found in environmental sample is useful as a general indicator of petroleum contamination at that site where the analyzed samples are taken. Soil and groundwater petroleum hydrocarbon contamination has long been of concern and has spurred various analytical and site remediation developments (Hites, 1976). Total Petroleum Hydrocarbon (TPH) affects human beings in different ways. Some of the Total Petroleum Hydrocarbon (TPH) compounds, particularly the smaller compounds such as benzene, toluene and xylene (which are present in gasoline), can affect human central nervous system (ATSDR, 1995).

This research work is aimed at determining the total petroleum hydrocarbons in water, fish and plant samples in Ethiope River. The information obtained could then be analyzed in order to provide data that could serve as background for levels of total petroleum hydrocarbons in water in this area.

2.1 Study Area

River Ethiope is found in Delta State of Nigeria .The River originates from a community called Umuaja and flow through several others before joining the sea at Sapele. Also Oghara in Ethiope West local Government Area of Delta State is among the area the River

traversed, which is the study area. However, the study area is situated between latitude 5'40'6''N and 6'00''N and longitude 5'39'5''E and 6'10'9''E.The River is about 50km long.

2.2 SAMPLE COLLECTION

2.2.1 Fish Sample

The fish samples from the river were randomly collected by local fishermen. The fish samples average 200gm were collected and wrapped in sterile aluminium foil and immediately stored in ice-packed cooler before being taken to the laboratory for pre-treatment and analysis.

2.2.2 Water Sample

Three water samples were collected each from the bank and at the centre of the river. The river used was about 100 meters from the community and about 50 meters from the community market. Each of the water sample collected was approximately 500ml. Samples were collected weekly.

All glass sample bottles used were thoroughly cleaned and rinsed with dichloromethane (DCM) prior to use. A piece of sterile aluminium foil was used immediately to cover each bottle so as to prevent any sort of contamination. No space was allowed between the foil and the water samples. The bottles were thereafter tightly covered with plastic screw cover. These were kept in ice-packed cooler and transferred to laboratory for pre-treatment and analysis. 2ml of 0.2M H_2SO_4 was added to the water to bring the pH to about 2.

2.2.3 Plant Sample

The most common plant around the river *(Nuphar Pumilum* (Timm) DC) were uprooted into a clean well-labelled black polyethene bag and transferred to laboratory for pre-treatment and analysis.

2.3 TPH Extraction from Fish Samples

TPH extraction mixture was prepared. The mixture contains acetone and dichloromethane (1:1 v/v). 250ml of acetone and 250ml of dichloromethane were measured into a 1000ml volumetric flask and mixed properly.

Each of the fresh fish sample was cut into pieces using a stainless steel knife and crushed in a mortar with pestle. 10g of the crushed sample was weighed into a 100ml beaker and 60ml of TPH extraction mixture was added. The Fish TPH content was extracted by shaking

method based on Schwab *et al.,* (1999). The beaker with the content was placed on magnetic stirrer/heater and shaken for about 10 minutes at 70^{o}C. The extract was decanted into a clean round-bottom flask. 30ml fresh solvent was added and the process repeated. The extracts were combined and 5g of anhydrous sodium sulphate was added to remove water. The extract was concentrated to 3ml with rotary evaporator maintained at 20^{o}C (Webster, 1997a).

1.5ml of the concentrated extract was loaded on a silica gel column. The silica gel column was prepared by loading a 2g glass wool followed by 30g chromatography silica gel, onto a chromatography column (2cm internal diameter and 10cm long).

Each of the bed was conditioned with 40ml HPLC-hexane to remove any organic contaminant. The 1.5ml concentrated extract was loaded and eluted with 30ml HPLC hexane into a labelled 100ml beaker to obtain the aliphatic hydrocarbon components in the sample. While the hexane almost getting dried, it was replaced with 30ml of dichloromethane to elute the aromatic hydrocarbons contents into another labelled 100ml beaker. 2g of anhydrous sodium sulphate was added to remove any traces of water left in the extract. These were re-concentrated using rotary evaporator to about 2ml. 1ml of the extract was transferred into a well labelled chromatography vial ready for gas chromatographic analysis. The samples were stored at 4^{o}C pending GC analysis.

2.4 TPH Extraction from Plant Samples

Having washed the root part of the plants with water, the roots, stem and the leaves were cut into pieces and crushed using mortar and pestle. 10g of the crushed sample was weighed into a 100ml beaker and the above method for fish extraction was repeated for plant samples using acetone/dichloromethane mixture as extraction solvent.

2.6 TPH Extraction from the Water Sample

The extraction was carried out using separatory funnel liquid – liquid extraction method MDEP (2004). This method measures the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons that may be found in a water sample. The method uses a solvent extraction step followed by a silica gel fractionation into two extracts – an aliphatic extract (C_9 - C_{18}, C_{19} – C_{36}) and an aromatic extract (C_{11} – C_{22}). The two extracts were then concentrated and separately analyzed by capillary gas chromatography with flame ionization detector (GC/FID).

The water sample was poured into 1000ml separatory funnel and 30ml dichloromethane was added into the sample bottle to rinse it. The solvent was poured into the separatory funnel. The separatory funnel was shaken vigorously for 2 minutes and periodically vents to release excess pressure. The mixture was allowed to stand for about 10 minutes to allow separation between the organic phase and the aqueous phase. The organic phase was drained from the separatory funnel through anhydrous sodium sulphate into a round bottom flask.

(Whatman No. 40 was placed into filter funnel on which 10gm of anhydrous sodium sulphate was placed and rinsed with small quantity of dichloromethane to remove any organic contaminant).

The procedure was repeated twice with fresh 30ml DCM and the extracts combined. This was concentrated to about 3ml in a rotary evaporator. 1.5ml of the extract was loaded onto a chromatographic column and eluted with 30ml HPLC Hexane and 30ml DCM for recovery aliphatic and aromatic components respectively. These were re-concentrated to about 2ml and 1.5ml of it was transferred into chromatographic vial and stored at 4^{o}C pending the gas chromatography analysis. The method was repeated for each water sample.

2.7 Gas Chromatographic Analysis

Each extract transferred to 1.5ml vial was loaded into a gas chromatography system 6890 series model G1530A, with Flame Ionization Detector (FID), and cold on-column injection. 1μl portion of the sample was injected and analyzed for TPH (C_9 – C_{36}). A HP-5 (cross slinked PH ME siloxane) column having the dimensions 30m x 0.25mm 1.d with a stationary phase thickness of 0.25μ was used for analytical separation. The carrier gas was purified nitrogen held at a flow rate of 50ml/min. The operating temperature program was started at 60^{o}C for 2mins and then increase at a rate of 10^{o}C/min to 300^{o}C for 10min (API, 1968). The injector and detector temperature were maintained at 250^{o}C and 300^{o}C respectively. The oven temperature was 60^{o}C. Aliphatic hydrocarbons are quantitify within C_9 – C_{18}, C_{19} – C_{36}. Aromatic hydrocarbons were quantitify with range C_{11} – C_{22}.

3.0 RESULTS AND DISCUSSION

3.1 Results

Tables 1 present the summary of the levels of TPH in water, fish and plant samples from Ethiope River. Table 2 present the levels of individual aliphatic and polyaromatic hydrocarbon concentrations these samples.

Table 1: Total Petroleum Hydrocarbons in water, fish and plants from Ethiope **River**

Parameter	**River** $\bar{X} \pm$ **SD**	**River Fish** $\bar{X} \pm$ **SD**	**Plant**
Aliphatic Hydrocarbons	0.008 ± 0.008	0.034± 0.001	0.044± 0.001
Aromatic Hydrocarbons	0.004 ± 0.003	0.019± 0.001	0.004± 0.001

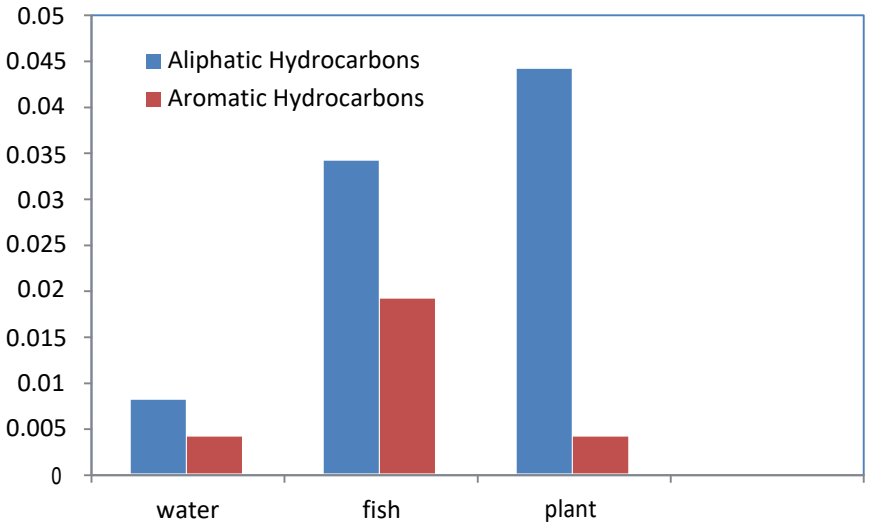

Fig 1: level of Total Petroleum Hydrocarbons in water, fish and plants from Ethiope **River**

Table 2: Individual Aliphatic and Aromatic Hydrocarbons Content (mg/L)

In Water, Fish and Plant from Ethiope River

Component	**River**	**Fish**	**PL_R** **Plant**
(a) Aliphatic	$\bar{X}$ ± **SD**	**X ± SD**	-
Nonane	0.0007±0.0006	0.0055±0.0007	0.008

Decane	0.0003±0.0006	0.0290±0.0014	0.000
Dodecane	0.0020±0.0000	ND	0.032
Tetradecane	0.0020±0.0017	ND	0.004
Hexadecane	0.0017±0.012	ND	0.000
Octadecane	0.0007±0.0006	ND	0.000
Nonadecane	0.0010±0.0000	ND	0.000
Eicosane	0.0010±0.0000	ND	0.000
Docosane	0.0017±0.0021	ND	0.000
Tetracosane	0.0020±0.0017	ND	0.000
Hexacosane	ND	ND	0.000
Octacosane	ND	ND	0.000
Traicontane	ND	ND	0.000
Hexacosane	ND	ND	0.000
(b) Polyaromatic		-	
Naphthalene	0.0007±0.0006	0.0020±0.0000	0.000
2-methylenaphthealene	0.0003± 0.0006	ND	0.000
Acenaphthalene	ND	ND	0.000
Acenaphthene	0.0003± 0.0006	ND	0.000
Florene	0.0017± 0.0012	0.0045±0.0007	0.000
Phenathrene	0.0020± 0.0017	0.0085±0.0007	0.000
Anthracene	0.0017± 0.0012	0.0040±0.0000	0.000
Fluoranthene	ND	ND	0.000
Pyrene	ND	ND	0.000
Benzo(a)anthracene	ND	ND	0.000
Crysene	ND	ND	0.000
Benzo(b)fluoranthrene	ND	ND	0.000
Benzo(a)pyrene	ND	ND	0.000
Benzo (k) fluoranthrene	ND	ND	0.000
Indeno 1,2,3(	ND	ND	0.000

perylene)			
Benzo(g,h,i)perylene	ND	ND	0.000
Benzo (a,h) anthracene	ND	ND	0.000

ND – Not Detected

DISCUSSION

The levels of Total Petroleum Hydrocarbons (TPH) in water, fish and plant samples are presented in Table 1 and illustrated in Fig 1. While that of the individual aliphatic and aromatic hydrocarbons examined are presented in Table 2 and 3 respectively. As presented in Table 1, the level of total aliphatic hydrocarbon was higher in the plant sample while that of the total aromatic hydrocarbon was higher in the fish sample. This may be due to their level of absorption and bioaccumulation of this contaminant Gao and Zhu, (2004). Also, the variation in the concentration of individual aromatic and aliphatic hydrocarbon in water, fish and plant may be due to anthropogenic activities around the river and from atmospheric emission from numerous automobile exhausts.

The level of total Petroleum Hydrocarbons (TPH) and individual aliphatic and aromatic hydrocarbons in water, fish and plant are below World Health Organization (WHO, 2003), and standard Organization of Nigeria (Son, 2007) Standards of 0.007 mg/l. However the trace amounts of aromatic hydrocarbon can bio accumulate in the body tissue as occupants of the area continue to drink and from this river on the long run (Benson *et al*., 2008). Aromatic hydrocarbons are known to be carcinogenic in nature. Also there was no evidence of oil spillage before or within the sampling period. The presence of the aromatic hydrocarbon may be attributed to waste from the community market, inputs from atmospheric emissions from numerous automobile exhausts. Burning of organic matter (wood) might have contributed to the level of TPH in the river. Some of these hydrocarbons might have found their way into the river through erosion thus increase the TPH level content as indicated in Table 2.

P- Value calculated from the one way analysis of variance (ANOVA) was greater than 0.5 for water, fish, and plants sample at 95% confidence level. Statistically this indicates that

there was a significant different in TPH concentration even low level of Petroleum Hydrocarbons in aquatic environment can have deleterious effect on zooplanktons and phytoplankton's.

CONCLUSION

The level of total petroleum hydrocarbons in the study area when compared to another ecosystem with many industrial and domestic activities showed a low to moderate hydrocarbons contents. The samples collected from this River are not polluted with TPH since the level of TPH in these samples are below the level stipulated by SON and WHO. However, this study will contribute to knowledge base by providing distribution level of total hydrocarbon in water, fish and plant from the study area. However, intermittent monitoring and test on sediment, water and plant of the study area should be carried-out, because of the toxic and bio accumulative nature of total petroleum Hydrocarbon (TPH).

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