

Baseline Distribution of Total Petroleum Hydrocarbons in an Aquatic Organism from Crude Oil Polluted Environment

Nworu J.S.,*^a Ikelle I.I.,^a Berezi O.K.,^b Peter C.C.,^b Arisabor L.^c and Boyitie O.P.^c

^aSchool of Basic Science (Chemistry), Nigeria Maritime University, Okerenkoko, Delta State.

^bMarine Environment and Pollution Control, Nigeria Maritime University, Okerenkoko, Delta State.

^cMeteorology and Climate Change, Nigeria Maritime University, Okerenkoko, Delta State.

*Corresponding author E-mail address: sunday.nworu@ebsu.edu.ng (Nworu J. S.)

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Abstract: In this study, the total concentration of n-alkanes is reported as Σ Aliphatics, total concentration of Polycyclic Aromatic Hydrocarbon as Σ PAH and Σ TPH for the total petroleum hydrocarbon. The values reported followed different trends. For the Σ Aliphatics, the gills had the highest average concentration while the kidney had the lowest average concentration. For Σ PAH, the muscle had the highest average concentration while the gills had the lowest average concentration. In summation Σ TPH, the gill had the highest average concentration while the kidney had the lowest average concentration. The results showed that the organs studied are good bio-accumulators. This study therefore revealed that, there are substantial exposure and bio-accumulation in the commonly consumed tilapia fish species in Kurutie/Okerenkoko from Escravos river, and there could be possible human risk to cancer and other related health challenges.

Keywords: Crude Oil; Total Petroleum Hydrocarbon; Polycyclic Aromatic Hydrocarbon; Escravos River

1. Introduction

The accidental and indiscriminate pollution of marine environment by hydrocarbon discharge caused by man and other natural processes had been the point of increased regulating and thought of the environment due of their chronic effects of such carcinogenic substance to the environment and human health. Pollution that is caused by crude-oil and chemical elements is among the considered issues of crude-oil produced states and industrial locations in Nigeria. Nigeria is one of the main crude-oil producing country and the 6th highest crude oil produced state in the whole world. The economic growth of Nigeria highly depended on the oil unit/sector and the larger numbers of the oil producing industry are situated in the areas of Niger Delta. The fishing community within Niger Delta have chronically been dilapidated by production processes of petroleum for a longer period of time.^[2] Crude oil spillage is a regular occurrence in Niger Delta which occurs mostly as a result of theft, sabotage, pipeline corrosion, crude oil production operation, mishandling and accidental discharge.^[1,3]

Literature has it that about 10,000,000 tonnes of natural crude-oil finds their way into the environments yearly through the unwanted discharge that is related to the normal petroleum operations.^[3] Long-term and little availability of the crude-oil to the aquatic habitat through industrial activities and some man made

processes are adsorbed by aquatic animals due to their long term persistence and low degradability.^[11-13] It has also been reported that about little quantity of natural crude oil spilled on the seawater affected the feeding behaviour of fishes and other aquatic organisms.^[3]

Natural Crude oil also causes acute damages to the organs (tissues, muscles, gills) and other organs of aquatic organisms which also limit their growths. Fishes are very small lipid with very high proteins benefit and it is made up of the sixty percent protein uptake among adults in rural areas.^[8] Despite the plenty advantages of fishes as a human diet, the tendency of human health-risk arose from consistent consumptions of the fishes are of great importance. Humans can be exposed to total petroleum hydrocarbons through different mediums such as atmosphere, waters, foods, or soils. Moreover, the balanced- dietary intakes have been shown to be the main target for exposure to humans to total- petroleum hydrocarbon.^[4-7] So many research works have been stated and expressed the negative impacts of total-petroleum hydrocarbon to human body health.^[1,3] Of recent, researches have showed that major human health cancer including prostate and lung-cancer are to be linked to the human dietary targets.^[18]

Polycyclic-aromatic-hydrocarbon (PAHs) is said to be anthropogenic pollutants that can be found in many places and can be humanly magnified to increased amount of concentration in food-

web. As a result of their lipophilicity (fat soluble), persistency, and increased toxic ability, the residue is always accumulating in the tissue of non-target available organism which they can lead to detrimental defects. Polycyclic Aromatic Hydrocarbons is highly chronic, carcinogenic, and mutagenic to every organism, including human.^[18,21] The metabolite of Polycyclic Aromatic Hydrocarbons can react with the protein and DNA, this can cause bio-chemical disruption and damaging of cells in organisms and cancers in humans.^[3] The major route of the pollutant in the environment includes forest-fire, natural-petroleum seeping, carbonization of fossil fuel, coal combustion, and use of oils to cook and heat.^[13] Other routes should include domestic and industrial wastes water and sewages. As a result, contaminations of environment by Polycyclic Aromatic Hydrocarbons have regularly increased in within this decade. Organic-chemical including hydrocarbon is one of the main content of petroleum and can make their way into the water habitat through either by natural or man-made process. However, very few number of the non-anthropogenic hydrocarbon are available in a given environment that originate from geo-chemicals and bio-synthetics cycle.^[3] Anthropogenic activity which adds to the contamination of water body can be accidentally or intentionally caused and these include; flaring of gas, spillage of oil, discard of consumed lubricants oil, cleaning of tankers, leaking from the water vessel and off-shores production of crude oil, direct ocean dumps, environmental/municipal and waste from industries, run-off through crude oils polluted lands, see-page and wastes/effluents from refinery.^[1-4] Between the hydrocarbon that are parts of crude oil are total petroleum- hydrocarbons. Total-petroleum hydrocarbons (TPH) are mixtures of measured concentration of hydrocarbon-based petroleum that can be seen in crude oils in an environment.^[14] Most of the chemical that are in the Total Petroleum Hydrocarbons includes hexane, methyl-benzene, xylene, naphthalene and some crude oils product and gasolines component. Moreover, it's possible that a sample of Total Petroleum Hydrocarbons can likely have little or much of the chemical.^[1,5] There are many sources of these Total Petroleum Hydrocarbon contaminants in a given environment that could include petroleum extractions, transportations, refining and consumptions.^[12]

Statement of Problem: Environmental pollution has been increasing exponentially daily within the communities that cut across the Escravos River. Sources of this pollution are mostly crude oil spillage and indiscriminate disposal of hazardous wastes into the river. Crude oil contains different fractions, most of which have been identified as carcinogenic substances. Badger (2011) in his research titled "the carcinogenic hydrocarbon: compound constitutions and carcinogenic activity" revealed that several polycyclic aromatic hydrocarbons are carcinogenic and some direct polycyclic-aromatic-hydrocarbons are having the properties to induce cancerous growth on animals. Different kinds of tumours have over time induced through carcinogenic materials such as ethyl carbonate (urethanes), carbon tetrachloride and methyl benz-anthracenes.

Aim and Objectives of Study: The aim of the study/research is to evaluate the concentration of total petroleum hydrocarbon in different organs of commonly consumed fish species (*Tilapia zilli*) from Escravos River. The study involves sampling, preserve, Dissect

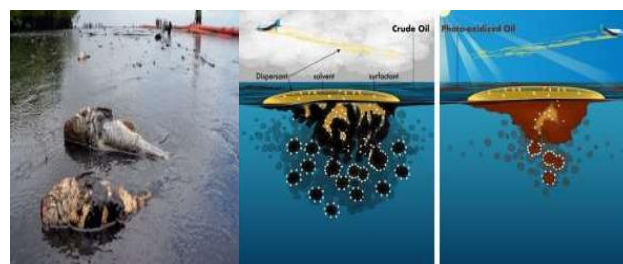


Fig. 1. Typical Crude Oil Pollution and Photo-Oxidation Processes.

and analyse different organs of fish species (*Tilapia zilli*) such as gill, kidney, liver and muscle from petroleum polluted water source (Escravos River) using GC-FID analysis to assay the hydrocarbon level. Statistically analyse the generated data using (ANOVA) to ascertain the level of their significance and compare the results obtained with international and national standards.

2. Methodology: Sampling and Processing

Samples from Escravos River location were collected from local fisher men at the point of fishing, wrapped in a sterile aluminium foil, transported and stored at -20°C until further analysis. The fish samples were removed from refrigerator where it was stored, thawed and cleaned in tap water to remove any dirt. The thawed fishes were dissected using aseptic instrument and dishes and obtained the liver, gills, muscles, and kidney and were placed in a sample bottle and labelled for further analysis.

3. Extraction of Total Petroleum Hydrocarbons and Preparation of Column

Fish samples were crushed with mortar and pestle. A 25 g aliquot of well crushed sample (Gill, Liver, Kidney and Muscle) was weighed into a clean 250 mL beaker. A mixture of solvent containing 50:50 ml of acetone and dichloromethane were prepared in a different beaker. 50ml of the solvent mixture was added into the beakers containing 10g of each sample. To ensure high purity for consistent results, samples were spiked with 1ml of surrogate mixture, placed in a Sonicator (model no-SS 500 US) and agitated for 15 minutes at 70°C . To obtain a clear extract, 10g of anhydrous sodium sulphate were added. Extracts were separated from the mixture into a round bottom flask. These processes were repeated with additional 50ml of solvent mixture, sonicate and allowed the beaker to settle and decanted into the same round bottom flask. Extract were concentrated in rotary evaporator to 3ml (Schwab *et al.*, 1999).^[10] Columns were packed with 10g of 100-200 mesh silica gel and glass fibre wool pre-conditioned (baked) at 105°C overnight. The column was made slurry by adding 10ml of n-hexane.^[2,3]

4. Fractionation, Re-Concentration of Extracts and GC Analysis

Concentrated extracts were ready to be fractionated into aliphatic and aromatic fractions. This process was done in a column packed with a glass fibre wool and silica gel. Fractionation of Polyaromatic

Hydrocarbon was carried out in the prepared column by running dichloromethane (DCM) through the column containing the extract. This solvent DCM was used because it has affinity for PAHs. The fractionated sample of individual component was transferred into a round bottom-flask and concentrated into 2ml. The concentrates were stored in a chromatographic vial ready for Polycyclic Aromatic Hydrocarbon analysis by GC FID 5890 series II. The samples in the vial were stored at 4°C prior to GC analysis. Each extract transferred to a 1.5ml vial was loaded into a gas chromatography system GC FID 5890 series II, with flame ionization detector (FID) and cold on-column injection. 1µL portion of the sample was injected and analysed for TPH (C8-C40). The analytical separation was carried out with a HP-5 column having the dimensions 30m × 0.25mm with a stationary phase thickness of 0.25µm. The carrier gas was purified nitrogen held at a flow rate of 5mL/min. The operating temperature was started at 60°C for 2mins and then increased at the rate of 10°C/min to 300°C for 10min. The injector and detector temperature were maintained at 250°C and 300°C respectively. The minimum detection limit for all the compounds analysed was 0.1µg/kg wet weight.

5. Results

Total Aliphatic Hydrocarbon (TAH) was recorded in the tilapia fish sample with distinct varying concentrations. Thirty-five components of n-alkanes which make up the TAH have been analysed. The Chromatogram for the total aliphatic hydrocarbons of the tilapia specie generated from the Gas Chromatographic Flame Ionization Detector is represented in both Figs. 3 and 4. The Chromatogram for the polycyclic aromatic hydrocarbons of the tilapia specie generated from the Gas Chromatographic Flame Ionization Detector is represented in both Figs. 5 and 6.

6. Discussion

In a given environment (air, water and sediments) polyaromatic hydrocarbons does not exist as individual compound. They exist as a mixture of many other polynuclear aromatic hydrocarbons. Research have revealed that weakly or non-carcinogenic polyaromatic hydrocarbons which exist as a mixture can modify the carcinogenicity effects of a given polyaromatic hydrocarbon such as benzo (a) pyrene.^[1] All fish ingest petroleum hydrocarbons directly or indirectly from contaminated water as food and sediments leading to massive destruction of aquatic biota.^[3] Both aliphatic and polycyclic aromatic hydrocarbon fractions of dissolved petroleum are readily absorbed by most finfish and shellfish because of their high lipid solubility and are bio concentrated in them. Humans are exposed to total petroleum hydrocarbons through air, water, food, or soil. However, dietary intake has been shown to be a major route for human exposure to petroleum hydrocarbons (PAHs).^[6]

Total Aliphatic Hydrocarbon (TAH) was recorded in the tilapia fish sample with distinct varying concentrations. This study analysed both TAH and PAH in the muscles, gills, livers and kidneys of tilapia fish species from Escravos river cut across Kurutie/Okerenkoko in Delta state, Nigeria. Thirty-five components of n-alkanes which make up the TAH have been analysed. From the results, the gills had the highest mean concentrations (10388.16±0.98 mg/kg) of TAH while

the Kidney had the lowest mean concentration (5980.56±1.20 mg/kg) of the TAH. Nworu et al.,^[3] showed that the gills of fish analysed for TAH had the highest mean accumulation while the muscle recorded the lowest mean concentration of TAH. The lower mean concentration of TAH in kidneys suggests that bioaccumulation is lower as against uptake demonstrated by the gills which showed highest bioaccumulation of TAH. The high mean concentration of TAH in the gills could be traced to the constant interaction of the gills during respiration which are highly vascularized with the pollution sources. Respiration keeps this organ constantly exposed to pollutants in water. The oral discussion and interaction with the young and aged people living in Kurutie/Okerenkoko, along Escravos River revealed that the community have recorded over times cancerous diseases, tumours, deafness, excessive skin diseases and many other mutagenic ailments. These diseases are believed to be traceable to the bioaccumulation of millions of carcinogenic polyaromatic hydrocarbons in fishes from the river, since fishing is their major occupation, rate of its consumption is high, and these must have long accumulated causing different ailments.

Table 1 represent the mean ± standard error of the total aliphatic hydrocarbon component from organs of tilapia fish (mg/kg). The results of bioaccumulation of octane (C8) in the four organs of tilapia fish showed that the minimum and maximum concentrations of octane are 55.52 and 149.45 mg/kg respectively. The concentration of C8 hydrocarbon in the gills of the tilapia fish was below detectable limit. The muscle and the liver of the tilapia specie recorded the highest and least concentrations of 144.33±0.46 and 56.25±0.31 mg/kg of octane respectively. The research work of Eneuku et al.,^[17] four organs of commercially available fishes from Oliha market show no record of C8 aliphatic hydrocarbon.

The bioaccumulation result for nonane (C9) aliphatic hydrocarbon showed that the organs of the analysed tilapia fish recorded highest concentration of C9 aliphatic hydrocarbon amongst other aliphatic hydrocarbons. The minimum and maximum concentrations of C9 aliphatic hydrocarbon are 658.25 and 2210.08 mg/kg respectively. Similar research work on the organs of fish samples showed lower concentration of C9 aliphatic hydrocarbon ranging from 3.72-22.32 mg/kg.^[17]

The C10 (decane) aliphatic hydrocarbon concentration were all beyond detectable limit from the four fish organs studied. The C11 (Undecane) aliphatic hydrocarbon concentration from the organs ranges from 185.08-310.37 mg/kg. The muscle and kidney showed highest (310.37±0.05 mg/kg) and lowest (198.58±0.18 mg/kg) bioaccumulation of C11 aliphatic hydrocarbon. The C12 (Dodecane) aliphatic hydrocarbon concentrations ranges from 70.18-90.12 mg/kg. The highest and lowest concentrations were recorded in kidney (88.03±0.12) and gills (71.95±0.01) mg/kg. Several studies have reported the negative effects of petroleum hydrocarbon to human health.^[8,16] Recently, studies have shown that most human cancers such as prostate and lung cancer can be attributed to dietary sources.^[18-21]

The C13 (tridecane) aliphatic hydrocarbon concentration ranges from 64.08-159.36 mg/kg, the liver showed the lowest mean concentration (64.08±0.16 mg/kg) while the gill recorded the highest mean concentration (157.98±0.21 mg/kg). Tetradecane (C14) was not detected from the organs. This shows that their concentration

Table 1. Mean \pm SE of Total aliphatic hydrocarbon component from organs of tilapia fish (mg/kg)

Components	Muscle	Gill	Liver	Kidney	Min.	Max.
Octane (C8)	144.33 \pm 0.46	BDL	56.25 \pm 0.31	78.17 \pm 0.03	55.52	149.45
Nonane (C9)	1946.70 \pm 0.03	2155.49 \pm 0.44	697.29 \pm 0.21	869.02 \pm 0.41	658.25	2210.8
Decane(C10)	BDL	BDL	BDL	BDL	-	-
Undecane(C11)	310.37 \pm 0.05	303.22 \pm 0.32	215.32 \pm 0.14	198.58 \pm 0.18	185.08	310.37
Dodecane(C12)	80.05 \pm 0.32	71.95 \pm 0.01	86.33 \pm 0.02	88.03 \pm 0.12	70.18	90.12
Tridecane(C13)	86.92 \pm 0.33	157.98 \pm 0.21	64.08 \pm 0.16	65.02 \pm 0.28	64.08	159.36
Tetradecane(C14)	BDL	BDL	BDL	BDL	-	-
Pentadecane(C15)	119.13 \pm 0.22	63.05 \pm 0.30	60.87 \pm 0.04	57.54 \pm 0.11	55.97	120.54
Hexadecane(C16)	300.92 \pm 0.30	413.82 \pm 0.21	287.96 \pm 0.18	301.54 \pm 0.33	287.02	418.69
Heptadecane(C17)	53.53 \pm 0.20	37.68 \pm 0.04	58.21 \pm 0.03	47.01 \pm 0.01	36.85	58.87
Pristane	398.69 \pm 0.15	327.69 \pm 0.35	348.77 \pm 0.14	289.67 \pm 0.13	288.03	399.87
Octadecane(C18)	41.82 \pm 0.17	22.24 \pm 0.01	36.55 \pm 0.05	29.36 \pm 0.11	21.34	38.40
Phytane	51.69 \pm 0.24	77.98 \pm 0.02	59.02 \pm 0.20	68.66 \pm 0.15	51.08	79.58
Nonadecane(C19)	654.82 \pm 0.03	477.07 \pm 0.23	587.98 \pm 0.40	478.09 \pm 0.55	472.05	659.36
Eicosane(C20)	104.54 \pm 0.08	77.25 \pm 0.01	98.14 \pm 0.01	66.57 \pm 0.28	64.88	109.48
UncosaneC21	74.37 \pm 0.05	79.33 \pm 0.34	81.02 \pm 0.01	46.21 \pm 0.42	44.01	81.90
Docosane(C22)	334.72 \pm 0.31	408.41 \pm 0.33	298.46 \pm 0.03	329.07 \pm 0.36	299.47	411.77
Tricosane(C23)	403.07 \pm 0.20	592.23 \pm 0.52	421.02 \pm 0.12	408.55 \pm 0.70	400.98	599.60
Tetracosane(C24)	96.23 \pm 0.15	99.49 \pm 0.15	87.02 \pm 0.19	75.12 \pm 0.07	79.58	101.24
Pentacosane(C25)	357.05 \pm 0.13	274.36 \pm 0.08	125.22 \pm 0.14	149.28 \pm 0.09	125.22	358.09
Hexacosane(C26)	596.29 \pm 0.12	693.02 \pm 0.03	478.98 \pm 0.19	357.48 \pm 0.17	354.55	693.02
Heptacosane(C27)	209.99 \pm 0.25	83.12 \pm 0.20	124.09 \pm 0.22	147.98 \pm 0.05	85.22	212.08
Octacosane(C28)	187.99 \pm 0.41	88.58 \pm 0.40	96.03 \pm 0.08	95.55 \pm 0.02	84.06	189.34
Nonacosane(C29)	146.66 \pm 0.33	327.17 \pm 0.23	108.08 \pm 0.02	147.02 \pm 0.12	108.66	330.58
Triacotane(C30)	215.80 \pm 0.08	102.40 \pm 0.16	145.09 \pm 0.14	125.22 \pm 0.33	101.51	216.01
Untriacontane(C31)	103.99 \pm 0.01	107.37 \pm 0.20	111.87 \pm 0.16	86.69 \pm 0.03	86.01	114.09
Dotriacontane(C32)	236.72 \pm 0.07	95.06 \pm 0.50	158.15 \pm 0.07	251.11 \pm 0.11	94.07	254.10
Trtriacontane(C33)	83.70 \pm 0.22	309.67 \pm 0.06	65.74 \pm 0.31	125.67 \pm 0.17	65.74	310.71
TetratriacontaneC34	797.46 \pm 0.12	1230.76 \pm 0.44	258.39 \pm 0.08	143.54 \pm 0.33	143.07	1230.6
PentatriacontaneC35	52.13 \pm 0.02	125.05 \pm 0.02	88.88 \pm 0.23	77.32 \pm 0.140	52.01	92.44
HexatriacontaneC36	317.87 \pm 0.03	367.54 \pm 0.47	489.18 \pm 0.31	229.36 \pm 0.24	224.58	490.10
HeptatriacontaneC37	470.19 \pm 0.30	222.55 \pm 0.36	189.57 \pm 0.71	217.64 \pm 0.05	189.07	474.05
OctatriacontaneC38	49.87 \pm 0.45	59.16 \pm 0.18	44.02 \pm 0.41	33.21 \pm 0.04	32.51	61.23
NonatriacontaneC39	109.06 \pm 0.03	147.67 \pm 0.04	106.15 \pm 0.05	108.24 \pm 0.33	105.33	149.04
Tetracontane(C40)	165.63 \pm 0.24	789.82 \pm 0.05	136.81 \pm 0.02	188.93 \pm 0.18	134.84	790.17
Total(mg/kg) Aliphatic	9302.33 \pm 1.08	10388.16 \pm 0.98	6270.64 \pm 0.8	5980.56 \pm 1.2	5978	10390

BDL = Below Detectable Limit. The Mean \pm Standard error of Polycyclic Aromatic Hydrocarbon component from organs of tilapia fish (mg/kg) are represented thus. In this research, sixteen components of aromatics which makes up the PAH's has been analyzed.

Table 2. Mean \pm SE of Polynuclear Aromatic Hydrocarbon component from organs of tilapia fish (mg/kg)

Components	Muscle	Gill	Liver	Kidney	Min	Max
Naphthalene	4.32 \pm 0.12	3.06 \pm 0.11	3.54 \pm 0.01	7.36 \pm 0.05	2.85	8.33
Acenaphthylene	11.08 \pm 0.33	3.86 \pm 0.25	4.54 \pm 0.02	4.26 \pm 0.14	3.20	12.09
Acenaphthene	7.70 \pm 0.14	26.32 \pm 0.03	15.34 \pm 0.12	8.26 \pm 0.11	7.52	26.77
Fluorene	7.37 \pm 0.18	2.96 \pm 0.15	3.69 \pm 0.30	4.65 \pm 0.25	2.47	8.30
Phenanthrene	3.98 \pm 0.02	9.99 \pm 0.13	8.14 \pm 0.12	7.77 \pm 0.24	3.42	10.23
Anthracene	135.57 \pm 0.33	85.12 \pm 0.01	122.36 \pm 0.33	129.39 \pm 0.18	85.02	136.88
Fluoroanthene	35.68 \pm 0.21	7.58 \pm 0.11	26.36 \pm 0.31	13.26 \pm 0.22	6.55	36.09
Pyrene	16.51 \pm 0.33	8.25 \pm 0.02	8.87 \pm 0.05	12.22 \pm 0.04	8.25	17.87
Chrysene	3.32 \pm 0.25	6.15 \pm 0.14	3.95 \pm 0.12	8.69 \pm 0.13	3.08	8.94
Benzo(a)anthracene	6.78 \pm 0.17	2.69 \pm 0.54	5.37 \pm 0.19	4.23 \pm 0.08	2.33	7.45
Benzo(b)fluoranthene	3.76 \pm 0.24	4.90 \pm 0.20.16	4.09 \pm 0.27	5.64 \pm 0.17	3.24	6.80
Benzo(k)fluoranthrene	3.95 \pm 0.18	3.76 \pm 0.18	14.02 \pm 0.24	12.08 \pm 0.31	3.47	12.66
Benzo(a)pyrene	20.95 \pm 0.32	3.12 \pm 0.11	7.14 \pm 0.08	16.65 \pm 0.11	2.85	21.12
Indeno(1,2,3-cd)pyrene	36.33 \pm 0.44	14.17 \pm 0.30	24.56 \pm 0.15	18.21 \pm 0.36	13.18	38.02
Dibenz(a,h)anthracene	8.94 \pm 0.14	6.08 \pm 0.22	6.23 \pm 0.11	7.09 \pm 0.09	5.54	9.30
Benzo(g,h,i)perylene	7.10 \pm 0.17	4.90 \pm 0.05	7.89 \pm 0.01	6.88 \pm 0.05	4.80	7.95
Total PAH (mg/kg)	313.43 \pm 0.67	192.96 \pm 0.45	266.17 \pm 0.81	266.72 \pm 0.36	192.96	318.02

Total petroleum hydrocarbon is the summation of total aliphatic hydrocarbon and polycyclic aromatic hydrocarbon in a given sample. Table 3 represents the Mean \pm SE of Total Petroleum Hydrocarbon (TPH).

Table 3. Mean \pm SE of Total Petroleum Hydrocarbon (TPH)

Components	Muscle	Gill	Liver	Kidney
Σ Aliphatics	9302.33 \pm 1.85	10388.16 \pm 1.52	6270.64 \pm 1.87	5980.56 \pm 1.08
Σ PAHs	313.43 \pm 1.64	192.96 \pm 1.09	266.17 \pm 1.35	266.72 \pm 1.07
Σ TPH (mg/kg)	9615.76 \pm 1.06	10581.13 \pm 1.09	6536.81 \pm 1.54	6247.29 \pm 1.87

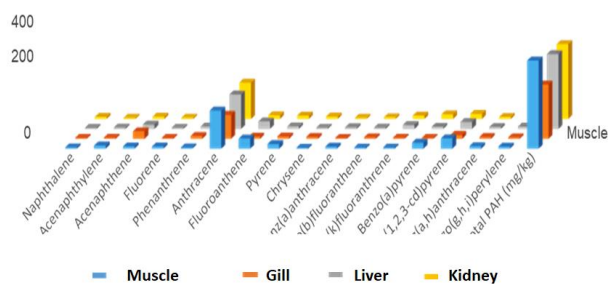


Fig. 2. Polynuclear Aromatic Hydrocarbon Content (mg/kg) from the Tilapia Fish Sample

and bioaccumulation in the organs were below the detectable limit of the GC-FID.

The C15, C16, C17, Pristane, C18, Phytane, C19 and C20 minimum concentration from the organs are 55.97, 287.02, 36.85, 288.03, 21.34, 51.08, 472.05 and 64.88 mg/kg respectively while the maximum concentration across the four organs are 120.54, 418.69, 58.87, 399.87, 38.40, 79.58, 659.36 and 109.48 mg/kg respectively. The minimum concentrations of TAH in C21, C22, C23, C24, C25, C26, C27, C28, C29 and C30 are 44.01, 299.47, 400.98, 79.58, 125.22, 354.55, 85.22, 84.06, 108.66 and 101.51 mg/kg respectively while their maximum concentrations are 81.90, 411.77, 599.60, 101.24, 358.09, 693.02, 212.08, 189.34, 330.58 and 216.01 mg/kg respectively. The minimum concentrations of C31, C32, C33, C34, C35, C36, C37, C38, C39 and C40 are 86.01, 94.07, 65.74, 143.07, 52.01, 224.58, 189.07, 32.51, 105.33 and 134.84 mg/kg respectively, while their maximum concentrations are 114.09, 254.10, 310.71, 1230.76, 92.44, 490.10, 474.05, 61.23, 149.04 and 790.17 mg/kg respectively. The high concentrations of the TAH in the organs of the tilapia fishes analysed, clearly indicates that the Escravos river has been highly exposed to contaminants and pollutants, these pollutions could be the major causes of the ailments in the riverine areas across the Escravos river. Fig. 2 and 3 represent the Chromatogram for the Aliphatic Hydrocarbons from the muscles and gills of the tilapia specie respectively while Fig. 4 and 5 represent the Chromatogram for the Polyaromatic Hydrocarbons from the muscles and gills of the tilapia specie.

Table 2 represent the Mean \pm Standard error of Polycyclic Aromatic Hydrocarbon component from organs of tilapia fish (mg/kg). In this research, sixteen components of aromatics which makes up the PAH's has been analysed. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous anthropogenic pollutants that can be biologically amplified to high concentrations in food webs. Due to their lipophilicity, persistence, and high toxicity, these residues are readily accumulated in the tissues of non-target living organisms where they may cause detrimental effects. PAHs are toxic, carcinogenic, and mutagenic to all organisms, including humans.^[9] The metabolites of PAHs may bind to proteins and DNA, which causes biochemical disruption and cell damage in animals and cancer in human.^[2,3,14]

Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Anthracene, Fluoranthene and Pyrene are less carcinogenic, while benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, indeno(1,2,3)perylene,

dibenzo(a,h)anthracene and benzo(g,h,i)perylene are highly carcinogenic.^[19]

For the PAH, the maximum and minimum concentrations of naphthalene are 8.33 and 2.85 mg/kg respectively. Highest average bioaccumulation was recorded in the kidney of the tilapia fish as 7.36 ± 0.05 mg/kg while the gills recorded the least value of 3.06 ± 0.11 mg/kg. Acenaphthylene and acenaphthene minimum bioaccumulation across the organs are 3.20 and 7.52 mg/kg respectively while their maximum concentrations are 12.09 and 26.77 mg/kg respectively. The highest average concentration of acenaphthylene and acenaphthene were observed in the muscles (11.08 ± 0.33 mg/kg) and gills (26.32 ± 0.03 mg/kg) of the tilapia fish respectively, while their lowest mean concentrations were recorded in the gills (3.86 ± 0.25 mg/kg) and the muscles (7.70 ± 0.14 mg/kg) of the tilapia fish respectively. The PAH stated here are far higher than the values reported by Olaji *et al.*,^[2] in the investigation from four species of fish at Degele Community, Nigeria. The high mean concentrations recorded in the gills and muscles are similar to the fact that they have direct interaction with the contaminated medium, thereby ingesting higher concentrations.

The minimum concentrations of Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene and Chrysene are 2.47, 3.42, 85.02, 6.55, 8.25 and 3.08 mg/kg while their maximum concentrations are 8.30, 10.23, 136.88, 36.09, 17.87 and 8.94 mg/kg respectively. Anthracene showed a very high mean concentration across the organs. The muscle concentration is as high as 135.57 ± 0.33 mg/kg while the gill recorded 85.12 ± 0.01 mg/kg. Anthracene when consumed targets the human skin, blood, intestines, blood and the lymph system. Exposure to high doses of anthracene for a short time can cause skin damage. It can also cause itching, burning and edema, a build-up of fluid in tissues. Humans exposed to anthracene experiences headache, loss of appetite, nausea, swelling or inflammation of the stomach and intestines. Anthracene has also been recorded to have caused tumours in laboratory animals that were exposed to anthracene, through their foods, breathing from contaminated air and direct skin application.^[1-5]

The minimum concentrations of benzo (a) anthracene, benzo (b) fluoranthene, benzo (k) fluoranthene and benzo (a) pyrene are 2.33, 3.24, 3.47 and 2.85 mg/kg respectively while their maximum concentrations are 7.45, 6.80, 12.66 and 21.12 mg/kg respectively. In a report of Faust, (1991), when a pregnant mice were fed with high doses of PAH (benzo (a) pyrene) they experienced reproductive problems. The offspring of the pregnant mice showed birth defects and a decrease in their body weight. The animal study reported that exposure of mice to 308 ppm of PAH (benzo(a)pyrene) in food for 10 days (short term exposure) caused birth defects of the offspring, while mice exposed to 923 ppm of benzo(a)pyrene in food for months caused liver and blood problems.

The minimum concentrations of indeno (1,2,3-cd) pyrene, Dibenz (a,h) anthracene and benzo (g,h,i) perylene are 13.18, 5.54 and 4.80 mg/kg respectively while their maximum concentrations are 38.02, 9.30 and 7.95 mg/kg respectively. Biological monitoring of exposure to PAHs is of primary interest, due to the widespread diffusion of these compounds and to their toxicological relevance. However, the health effects of individual PAHs are not exactly alike. In fact, the

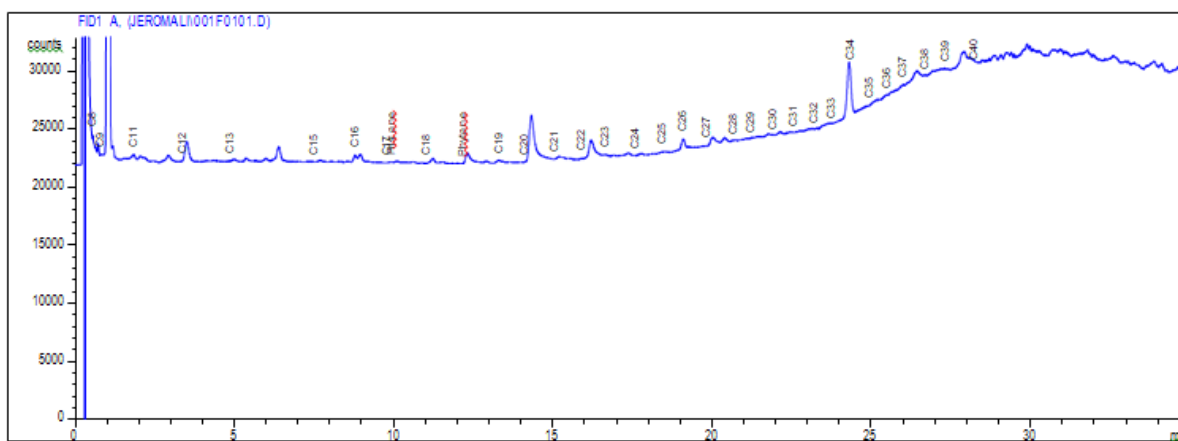


Fig. 3. Chromatogram for the Aliphatic Hydrocarbons from the muscles of the tilapia specie

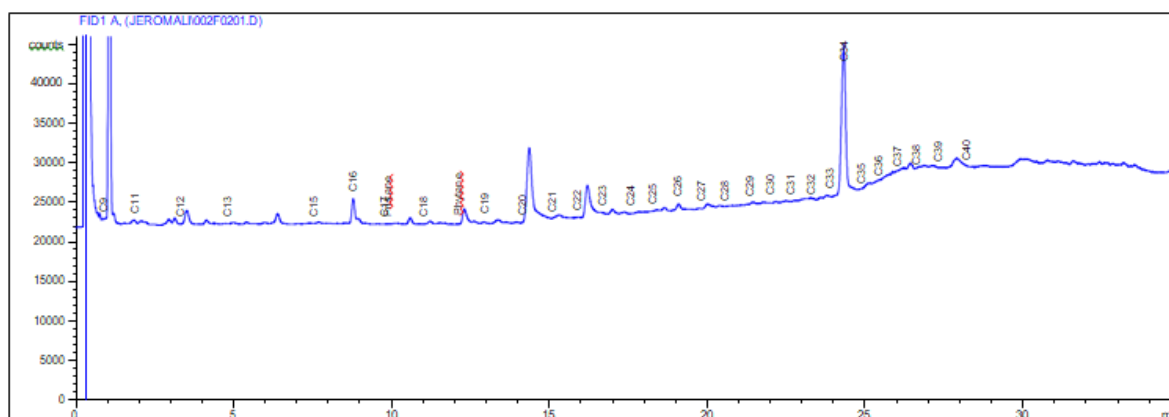


Fig. 4. Chromatogram for the Aliphatic Hydrocarbons from the

International Agency for Research on Cancer classifies some PAHs as known, possibly, or probably carcinogenic to humans (Group 1, 2A or 2B). Among these are benzo[*a*]pyrene (Group 1), naphthalene, chrysene, benzo[*a*]anthracene, benzo[*k*]fluoranthene and benzo[*b*]fluoranthene (Group 2B).^[6-9] Some PAHs are well known as carcinogens, mutagens, and teratogens and therefore pose a serious threat to the health and the well-being of humans. The most significant health effect to be expected from inhalation exposure to PAHs is an excess risk of lung cancer.^[8,11]

In this study, the total concentration of *n*-alkanes is reported as Σ Aliphatics, total concentration of Polycyclic Aromatic Hydrocarbon as Σ PAH and Σ TPH for the total petroleum hydrocarbon. The values reported followed different trends. For the Σ Aliphatics, the gills had the highest average concentration while the kidney had the lowest average concentration. For Σ PAH, the muscle had the highest average concentration while the gills had the lowest average concentration. In summation (Σ TPH), the gill had the highest average concentration while the kidney had the lowest average concentration. In other studies, the Σ Aliphatics and Σ PAH followed similar trend. The gills recorded the highest average concentration while the muscles recorded the lowest concentrations. The reported mean concentrations of TAH and PAH in the organs of tilapia fish were far higher than the European Union recommended limit of 2 μ g/kg; wet weight for fish. This claim, arrayed the extent of human impacts on the Escravos River.

7. Summary

From this research, it is very evident that Escravos River across Kurutie/Okerenkoko in Delta State Nigeria is highly polluted with substances containing large amount of aliphatic and polycyclic aromatic hydrocarbons. Fishes in the river accumulates large quantity of them over time. The polycyclic aromatic hydrocarbons are carcinogenic and could be of health challenge over time. Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Anthracene, Fluoranthene and Pyrene are less carcinogenic, while benzo (a) anthracene, chrysene, benzo (k) fluoranthene, benzo (a) pyrene, benzo (b) fluoranthene, indeno (1,2,3) perylene, dibenzo (a,h) anthracene and enzo (g,h,i) perylene are highly carcinogenic. The tilapia fish analysed accumulated high concentration of aromatic hydrocarbon. Most aromatic hydrocarbon has no trace of carcinogenicity, but their presence in environment elevates the effects of polycyclic aromatic hydrocarbon which have proven to be carcinogenic. In this study, the total concentration of *n*-alkanes is reported as Σ Aliphatics, total concentration of Polycyclic Aromatic Hydrocarbon as Σ PAH and Σ TPH for the total petroleum hydrocarbon. The values reported followed different trends. For the Σ Aliphatics, the gills had the highest average concentration while the kidney had the lowest average concentration. For Σ PAH, the muscle had the highest average concentration while the gills had the lowest average concentration. In summation Σ TPH, the gill had the highest average

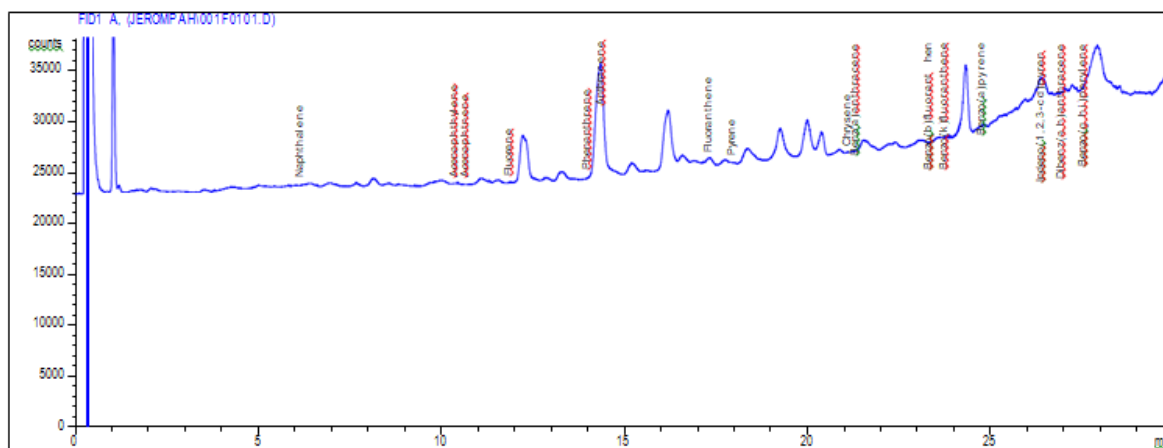


Fig. 5. Chromatogram for the Polyaromatic Hydrocarbons from the muscles of the tilapia specie

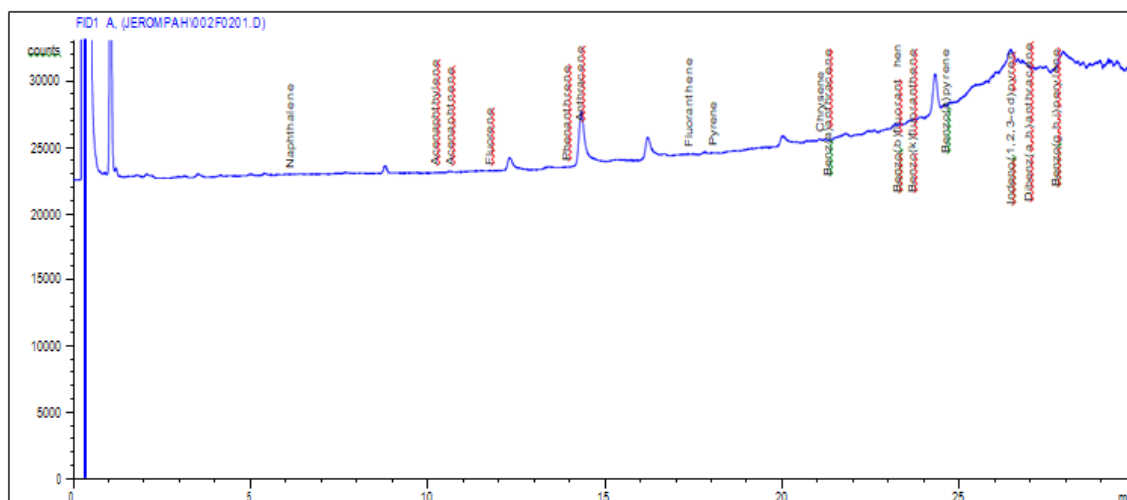


Fig. 6. Chromatogram for the Polyaromatic Hydrocarbons from the Gills of the tilapia specie

concentration while the kidney had the lowest average concentration. The results showed that the organs studied are good bio-accumulators. This study therefore revealed that, there are substantial exposure and bioaccumulation in the commonly consumed tilapia fish species in Kurutie/Okerenkoko from Escravos River, and there could be possible human risk to cancer and other related health challenges.

8. Conclusions

The sampling of tilapia fish was carried out from the polluted Escravos River. The organs (liver, kidney, muscle and gills) of the tilapia fish showed high accumulation of total petroleum hydrocarbon which is an indication that Escravos River is highly polluted with organic matters containing hydrocarbons. Results obtained from GC-FID were subjected to ANOVA using SPSS version 16. The level of confidence interval was above 95%. In comparing the results obtained with EU benchmark, the concentrations of the fish species were much above the recommended EU permissible limit of each of the polycyclic aromatic hydrocarbon in consumables.

Conflicts of Interest

The authors declare no conflict of interest.

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