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THE BIOACCUMULATION AND RISK ASSESSMENT OF TOTAL PETROLEUM HYDROCARBONS IN AQUATIC RESOURCES FROM K- DERE SHORELINE, RIVERS STATE, NIGERIA

Karikpo L. P.[1], Ekweozor I. K. E.[1], Daka E. R.[1], and Boisa N.[2]

[1]Department of Animal and Environmental Biology, Rivers State University.

[2]Department of Chemistry, Rivers State University.

Corresponding Author's Email: letanbari@yahoo.com; Tel.: +2348069492288

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ABSTRACT: *This research was designed to study the levels of Total Petroleum Hydrocarbon (TPH) in aquatic resources (Crab (Goniopsis cruentata), surface water and sediment) from K-Dere shoreline. Samples of sediment were collected intertidally. All samples were collected from six sampling stations, bi-monthly for a period of one year. Collected samples were transported to the laboratory for chemical analysis. Gas Chromatography was used to analyse total petroleum hydrocarbon concentration in samples and data obtained were statistically analysed at p>0.05 using SPSS version 23. The mean concentration results obtained in surface water, sediment and biota across the stations were as follows; (590.75, 623.50, 451.17, 544.42, 674.67, 536.50mg/l) (8152.17, 6146.92, 44200.00, 4860.33, 2069.67and 5089.25mg/kg) and (131.5, 80.17,144.08, 109.08, 82.50, respectively. The mean concentration of TPH in sediment at station 1, 2 and 5 were above the intervention and permissible limit by the former DPR (2022). The ecological risk assessment was expressed in terms Bio-sediment Accumulation Factor (BSAF) and Pollution Index (PI) was calculated for the aquatic resources. PI showed that most chemical compounds of TPH were higher than 1, indicating high pollution from anthropogenic sources. The health risk assessment was expressed in terms of Estimated Daily Intake (EDI) and Health Risk Index (HRI) indicating significant health risk, posing threat to human health of the locals. Further and histopathological studies should be carried out to determine the impact of TPH on biota. Shoreline Clean up should be implemented with post clean-up assessment.*

KEYWORDS: *Total* Petroleum Hydrocarbon (TPH), Ecological Risk Assessment (ERA), Health Risk Assessment (HRA), Gas Chromatography (GC) and Aquatic resources.

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INTRODUCTION

Total Petroleum hydrocarbons (TPH), is a term used to define an enormous family of numerous chemical components that initially come from crude oil. Petroleum products are products of crude oil which can pollute the environment, because there are many chemicals in crude oil other than petroleum components. It is impractical to quantity each component separately. However, it is expedient to quantify the total amount of TPH at any given sample or site.

TPH is a combination of chemicals, but they are all initiated from hydrogen and carbon, called hydrocarbons. Scientists have categorised TPH into sets of petroleum hydrocarbons that have similarities in reactions while in soil or water. These sets are referred to as fractions of petroleum hydrocarbons. Each fraction of petroleum hydrocarbon has many individual chemicals. Many compounds in TPH families are; hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, and fluorene, 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. Some hydrocarbon mixtures may also contain priority pollutants including volatile organic compounds (VOCs), semi-volatile compounds (SVOCs) and metals, each of which have their own specific toxicity information (ATSDR, 1999).

Total petroleum hydrocarbons (TPH) are persistent and priority pollutants that evolve from the increased exploration and exploitation of crude (oil and gas) resources in the coastal zones. These chemical substances rank high among the global environmental disasters and are source from increase in industrial, agricultural and anthropogenic activities in the environment (Copat et al., 2013; Awajiusuk, 2015).

According to USEPA (2012), human health risk assessment can be defined as the classification of present and future adverse human health effects to hazards exposed in the environment. Risk assessment uses methods that are scientific, statistical tools/models, to classify and quantify various hazards, authenticates possible routes, channels of exposure and compute numerical values to represent the impending risks (Lushenko, 2010).

Nigeria is known as an oil producing nation. Oil exploration and exploitation activity has been going on for decades and there are significant impacts on the oil producing and processing communities both in the onshore and offshore installations (Atunbi, 2011). The unpleasant and environmentally undesirable pollution effects of the waste from these activities demand for standard best practices in technology and the processes of obtaining petroleum and petrochemical products from crude oil which generate various types of wastes (Uzoekwe and Oghosanine, 2011).

TPH levels in Nigeria Niger Delta areas have received considerable attention in recent times due to its high carcinogenic and mutagenic potential. Akinola et al. (2019) evaluated the ecological hazards of TPH infected *Nematopalaemon hastatus* and obtained high values attributing it to the pollution status of the environment. The authors called for a study on the potential health risks of eating TPH contaminated aquatic species as food. Since shellfish is highly nutritive and essential in the human diet composition of the Coastal areas of Nigeria (Olawusi-Peters et al., 2017), to sustain a healthy and diverse coastal environment and secure the health benefits of fish consumers thus becomes imperative.

According to OPEC (2022), Nigeria is ranked as the highest oil producer in Africa and the eleventh largest globally with over 37 billions barrels of crude oil reserves and 192 trillion

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cubic of gas reserves (Laden et al, 2022). Niger Delta region is one of the largest wetlands in the world. The region is known for its oil and gas production. The region is also known as the hub of oil pollution (Sam et al, 2017, Bellow 2017). Moreover, the Niger Delta region is the most hydrocarbon impacted ecosystem in the world, this is due to indiscriminate oil exploration and exploitation activities in the region (Sam and Zabbey 2018). This has continued to increase the concentration of pollution problems, dredging water quality and reduced socio-economic development within the area. The sequential industrialisation and increase in the human population have inserted much pressure on the distressed ecosystem, causing the Niger Delta coastal region to be over-exploited and deteriorated (Ibangha et al 2019).

This research is aimed at assessing the levels, ecological risk assessment and health risk impact of TPH in biota, surface water and sediment.

MATERIALS AND METHODS

Study Area

The study area covers six sampling stations across K-Dere shoreline. K-Dere is a famous name in Nigeria, due to oil exploration activities in the community and hosts several oil and gas facilities both on land and shoreline. K Dere is a community in Gokana Local Government Area, Rivers State. Gokana coastal communities had unprecedented records of numerous oil spills in the past decades from poor maintenance of facilities and to vandalism through oil theft. The mangrove vegetation is devastated leaving the mangrove platform with unbroken and dominant algal mat and presence of surface oil.

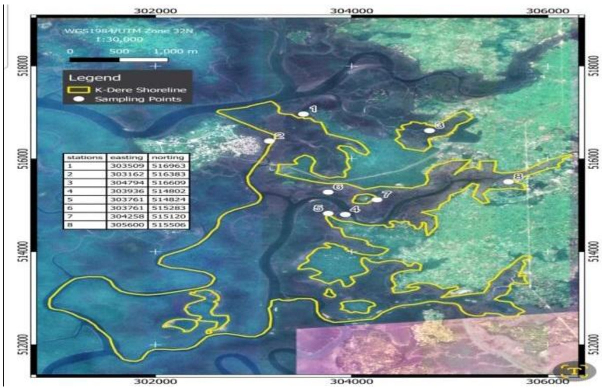

Plate 1. Map of sampling stations

Laboratory Analysis for Determination of TPH in samples

2gm of sediment samples were weighed into a clean extraction container. 10ml of extracted solvent (pentane) was added into the samples and mixed thoroughly and allowed to settle. The mixtures were carefully filtered into clean solvent-rinsed extraction bottles, using filter papers fitted into Buchner funnels. The extracts were concentrated to 2ml and then transferred for cleanup/separation.

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Cleanup/ Separation

The concentrated aliphatic fractions were transferred into labelled glass vials with rubber crimp caps for GC analysis. 1ml of the concentrated sample was injected by means of hypodermic syringe through a rubber septum into the column. Separation occurs as the vapour constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column (at a constant flow rate) by the FID detector whose response is dependent upon the composition of the vapour.

Bio-Sediment accumulation Factor

The bio-sediment accumulation factor (BSAF) was calculated for TPH in order to estimate the absorption rate of TPH between sediments and tissue, using the equation below by Shen et al (2011)

BSAF = Ci/Cw

Where BSAF, Ci, Cw is the given as

BSAF = Biota Sediment accumulation factor of total hydrocarbon

Ci= TPH concentration in aquatic organism

Cw= TPH concentration in sediment.

Single Pollution Index (PI)

The single pollution index is a tool used to determine the pollution state of coastal environments and aquatic products. When assessing the pollution state of hydrocarbon, the Single Pollution tool is usually used (Kowalska et al. 2018 and Cao et al, 2020), and the formula is given as:

$$\mathbf{PI = C_i / C_{io}}$$

Where PI, $\mathbf{C_i}$, $\mathbf{C_{io}}$ is given as;

PI = Evaluated result

$\mathbf{C_i}$ = the actual measured data

$\mathbf{C_{io}}$ = evaluated standard of hydrocarbon

The evaluation standard of hydrocarbons in surface water, sediment and biota are given as 0.05mg/l, 500 mg/kg and 15 mg/kg respectively.

Health Implications Total Petroleum Hydrocarbons (Carcinogens)

A risk assessment is used to evaluate common, potential environmental contaminants released into the environment and determine the need for additional and remedial actions. The risks assessed were the estimated dietary intake (EDI) and health risk index (HRI). Calculations were done using standard methods. A risk assessment index greater than 1 indicates a threat to human health (USEPA, 1986).

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Potential dietary intake estimation (EDI).

The estimated dietary intake of the aliphatic hydrocarbons in biota was determined by the following equation:

EDI = ¼ Cm DFI BW

Where: EDI is Estimated Dietary Intake.

Cm: Concentration of chemical substances.

DFI: Daily fish intake is 0.048 mg/kg (FAO, 2007). BW: Average body weight is 70 kg (FAO, 2014).

Health risk index (HRI).

Health risk index of the aliphatic hydrocarbons through consumption of the contaminated seafood was calculated using the equation below (US EPA, 2000). Values greater than 1 is an indicator of the potential cancer risk.

HRI = ¼EDI SF

Where: HRI is Health Risk Index.

EDI: Estimated Dietary Intake.

SF: Slope Factor, which is 2.0 (mg/kg/day).

Data Analysis

Descriptive statistics and one-way anova were used for measurement of central tendencies. Duncan was used for means' separations. Pearson correlation was used to determine the correlation coefficient between variables. All at 95% confidence interval with SPSS version 23

RESULTS AND DISCUSSION

TPH levels in Surface Water

The mean concentration of TPH in surface water obtained in this study showed that station 5 had the highest concentration in surface water, followed by station 2, <station1, <station 4, <station 6 and < station 3. There was no significant difference in the levels of TPH in surface water across the stations. However, station 2 and station5 were higher than the recommended limits as illustrated in table 1 and 2. Table 2 showed that 32 TPH fractions were identified and some chemical compounds were below detectable limits.

However, higher levels of Total Petroleum Hydrocarbon in water than the result obtained in this present study were recorded in Obeni, Warrri, Delta State Nigeria by Adewuyi *et al.* (2011). They reported 73,500 µg/l mean concentration of Total Petroleum Hydrocarbon in water, which was more than the EU standard for surface water of 300 µg/l.

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However, low concentrations of Total Petroleum Hydrocarbons in water have been reported by many researchers too. Joshua et al 2019 reported a low concentration of 4.07mg/l in brackish water from Ayetoro within the coastal area of Ondo State (Ilaje Local Government Area). The high concentration of TPH in surface water in our studied area can be linked to the recurrence of oil spillage and artisanal refinery activities within Gokana shoreline and because it is a tidal environment, it is evenly distributed along the shoreline.

Fig 4.1 showed that TPH was higher in the rainy season (May, June and September) than in the dry season (November, January and March) across the stations.

Table 4.1 Mean Concentration of TPH in Surface water by stations

Stations	Mean (mg/l)	Standard Deviation	Standard (600 mg/l) (DPR 2002) and EGAPSIN intervention
Station 1	590.75	± 225.91	(600 mg/l)
Station 2	623.50	± 546.77	(600 mg/l)
Station 3	451.17	± 216.39	(600 mg/l)
Station 4	544.42	± 320.49	(600 mg/l)
Station 5	674.67	± 677.60	(600 mg/l)
Station 6	536.50	± 349.48	(600 mg/l)

Table 4.2 Matrix of TPH fractions in surface water

TPH ID	**Station1 mg/kg**	**Station2 mg/kg**	**Station3 mg/kg**	**Station 4 mg/kg**	**Station 5 mg/kg**	**Station 6 mg/kg**
n-C8	0.00	0.00	0.00	0.00	4.001	0.00
n-C9	0.00	0.00	0.00	0.00	3.0E-03	1.01
n-C10	0.00	0.6	4.3E-03	1.12	1.06	0.00
n-C11	1.28	1.86	1.67	0.11	4.1E-01	0.00
n-C12	0.00	5.67	4.85	0.02	12.01	0.00
n-C13	44.06	0.05	6.03	0.04	34.61	1.23
n-C14	15.17	10.00	1.5	0.2	0.85	15.07
n-C15	4.38	0.48	30.03	2.01	32.11	3.12
n-C16	10.11	17.60	15.60	54.10	17.88	1.33
n-C17	16.01	28.10	12.11	10.00	61.43	0.00
Pristane	13.39	14.07	14.60	5.88	13.18	2.55
n-C18	12.70	4.82	3.2E-02	40.12	14.40	43.11
Phytane	9.18	11.10	66.43	21.02	17.83	17.10
n-C19	10.10	15.60	31.25	21.09.	42.77	1.01
n-C20	10.07	10.03	30.97	1..00	80.68	18.08
n-C21	42.31	5.10	27.23	30.12	57.90	8.33
n-C22	25.60	5.80	150.91	17.33	73.11	1.09
n-C23	10.31	45.40	7.1E-02	44.06	11.0	6.00
n-C24	20.20	85.41	15.40	108.11	2.01	50.10
n-C25	0.06	22.18	10.32	4..70	1.27	10.60
n-C26	84.13	50.03	14.02	10.18	44.00	1.43

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n-C27	62.11	0.43	11.05	20.09	12.01	41.00
n-C28	41.80	0.74	21.00	23.41	70.00	13.48
n-C29	8.10	40.00	36.12	9.60	7.01	1.87
n-C30	20.02	11.70	21.00	9.1E-02	11.12	71.20
n-C31	10.42	13.31	3.61	71.00	32.12	8.10
n-C32	13.14	11.10	31.10	13.06	9.21	40.44
n-C33	0.66	0.07	12.20	12.91	7.08	32.78
n-C34	14.86	45.08	45.83	14.04	12.07	67.23
n-C35	17.05	16.00	10.13	20.08	10.00	1.45
n-C36	8.84	18.01	16.23	12.10	34.22	5.23
n-C37	16.42	30.30	53.28	10.60	40.14	6.1
n-C38	20.00	0.91	5.30	1.90	12.40	1.08
n-C39	14.11	0.05	97.40	31.01	19.16	20.20
n-C40	10.99	14.16	85.10	15.20	14.05	5.61
TPH	590.75	623.50	451.17	544.41	674.67	536.50
Intervention level	600ml/kg	600ml/kg	600ml/kg	600ml/kg	600ml/kg	600ml/kg

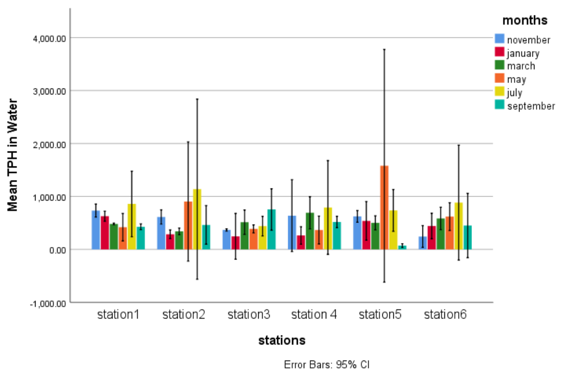

Fig 4.1 Mean Concentration of TPH in surface water by stations across months

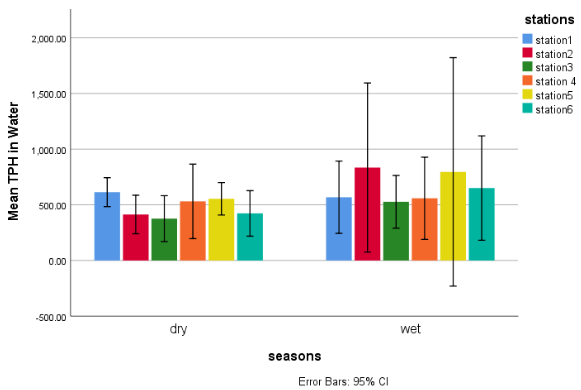

Fig 4.2 Mean Concentration of TPH in surface water by seasons across stations

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TPH levels in Sediment

In table 3, station 2, 3, 4 and 6 were significantly different from station 1 and 5. However, station 1 was significantly different from station 5, all at p>0.05. Station 1 had the highest concentration in sediment followed by station 2, station 6, station 4, station 3 and station 5. Stations 1, 2 and 3 were higher than the permissible limit of TPH in sediment of 5000 mg/kg by (FMEvn., 2018) and table 4 showed the matrix of TPH fractions in table 3. In this present study the mean concentration of TPH in sediment was 5123.39mg/kg above the Nigerian Tier 1 intervention level of 5000mg.kg (DPR 2018). This high level of TPH in sediment can be attributed to anthropogenic activities within the studied areas.

Higher concentrations of TPH in sediment have been reported by Ediae *et al.* (2020). They recorded a mean concentration of 30,979mg/kg from Bodo Creek, Rivers State. This result was a pre-spill result in Bodo before Bodo Mediated Initiative (BMI) embarked on remediation.

However, Owhonda *et al.* (20221) stated a lower concentration of TPH in sediment across all sampling stations in Woji creek, River State, Nigeria. They reported mean concentration of 8.758mg/kg, 7.675mg/kg, 5.515mg/kg, 5.075mg/kg, 3.162mg/kg for station1, station 3, station 5, station 4 and station 2 respectively.

Similar to this present work, Alinnor *et al.* (2014) reported mean concentration of Total Petroleum Hydrocarbon values of (1242-5200) mg/kg in sediment within Niger Delta communities. However, the result in this present study was lower than values obtained from Arabian Gulf Kuwait by Masssod et al. (1999). He stated 1,100mg/kg concentration of Total Petroleum Hydrocarbon in sediment.

However, Moslen and Ekweozor (2017) recorded a lower concentration of Total Petroleum Hydrocarbon in sediments from Ekerekana Creek than the result obtained in this study. They reported a mean value of 7.6mg.kg- 264mg/kg in sediment samples. Also, Ediae *et al.* (2020), recorded mean concentration of 30,979mg/kg from Bodo Creek, Rivers State. The high concentration of TPH in sediment in this study, could be attributed to the reoccurring oil spillages in Gokana intertidal ecosystem and artisanal refinery activities within the study area.

Also, fig 4.2 illustrated the mean concentration of TPH in sediment by stations across the months of sampling. The levels were higher in the dry season than in the wet season.

Stations	Mean	Std (mg/kg)	Standard(5000 mg/kg) (former DPR 2002) and EGAPSIN intervention
Station 1	8152.17	±3361.88[c]	(5000 mg/kg)
Station 2	6146.92	±1574.31[b]	(5000 mg/kg)
Station 3	4422.00	±1322.31[b]	(5000 mg/kg)
Station 4	4860.33	±2598.95[b]	(5000 mg/kg)
Station 5	2069.67	±1573.59 [a]	(5000 mg/kg)
Station 6	5089.25	±2761.71[b]	(5000 mg/kg)
P value	0.00		

Table 4.3 Mean Concentration of TPH in sediment by station

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Table 4.4 Matrix of TPH fractions by in Sediment across stations

TPH ID	Station1 mg/kg	Station2 mg/kg	Station3 mg/kg	Station 4 mg/kg	Station 5 mg/kg	Station 6 mg/kg
n-C8	56.81	87.83	0.00	5.0E-03	4.001	8.0E-03
n-C9	67.21	0.000	0.00	9.0E-03	3.0E-03	7.0E-02
n-C10	120.11	7.6E-03	7.6E-03	120.68	1.006	3.0E-02
n-C11	0.002	0.002	8.5E-02	4.66	4.1E-01	4.08
n-C12	5.7E-02	3.0E-03	4.85	10.55	12.01	7.0E-01
n-C13	44.60	5.0E-02	11.63	16.84	34.61	120.5
n-C14	145.71	1.14	6.15	4.31	0.85	48.09
n-C15	84.38	12.56	4.43	44.09	32.11	86.03
n-C16	180.11	40.47	15.60	24.11	17.88	28.41
n-C17	167.21	60.67	12.11	13.07	61.43	120.11
Pristane	433.30	188.11	14.60	18.23	13.18	210.55
n-C18	120.71	85.41	28.03	80.38	14.40	130.71
Phytane	99.18	44.82	66.43	74.13	17.83	107.41
n-C19	600.14	117.14	31.25	93.09	42.77	167.01
n-C20	110.17	151.10	30.97	1.0E-02	80.68	183.44
n-C21	42.31	12.75	27.23	320.16	57.90	172.63
n-C22	215.68	315.10	150.91	47.98	73.11	248.01
n-C23	740.30	75.81	7.1E-02	69.04	120.11	141.60
n-C24	200.23	450.3	135.47	140.85	68.40	95.01
n-C25	461.76	60.05	120.88	466.02	24.17	310.60
n-C26	684.15	225.18	161.71	210.10	53.83	208.1
n-C27	620.11	150.71	171.31	620.09	202.02	471.30
n-C28	410.85	438.43	101.08	84.13	141.91	134.08
n-C29	348.16	210.44	536.14	143.77	101.63	48.61
n-C30	120.72	160.87	221.09	167.09	75.14	190.09
n-C31	100.42	181.71	66.01	413.22	66.58	108.32
n-C32	113.14	101.23	421.10	352.74	81.40	235.17
n-C33	210.66	121.18	183.40	312.18	33.05	307.34
n-C34	141.86	244.01	45.83	148.36	48.23	88.26
n-C35	127.85	128.64	109.98	520.08	17.91	127.55
n-C36	85.84	110.96	44.01	132.14	94.01	56.23
n-C37	106.42	120.51	650.28	140.63	200.66	201.82
n-C38	200.00	1480.38	105.80	85.77	112.34	102.48
n-C39	854.11	460.05	398.40	431.54	59.86	220.20
n-C40	138.50	140.86	384.10	156.08	104.25	205.61
Total	8152.17	6146.92	4422.00	4860.33	2069.67	5089.25
Intervention level	5000 mg/kg	5000 mg/kg	5000 mg/kg	5000 mg/kg	5000 mg/kg	5000 mg/kg

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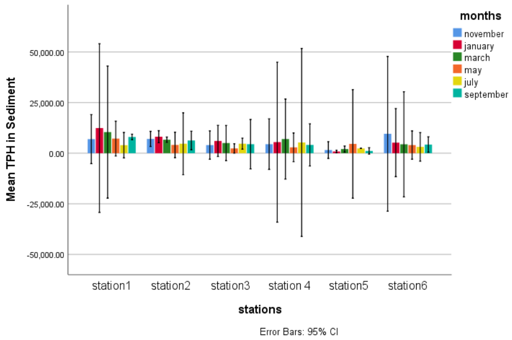

Fig 4.3 Mean Concentration of TPH in sediment by stations across months

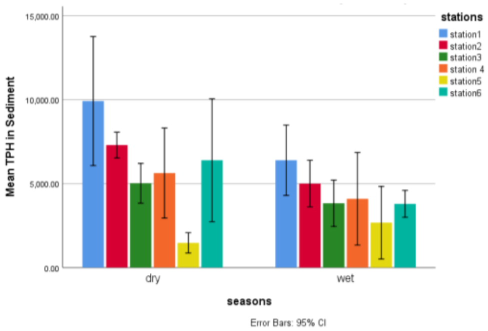

Fig 4.4 Mean Concentration of TPH in Sediment by stations and by months.

TPH levels in Biota

Table 5 TPH had the highest mean and standard deviation concentration in station 6 followed by station 3, station1, station 4, station 5 and station 2. There was no significant difference in the mean concentration of TPH across the stations. Station 2 and station 5 were higher than the permissible limits of TPH in biota and table 6 showed the matrix of TPH fractions in table 5. Many aquatic organisms have been identified to accumulate persistent organic compounds including hydrocarbon compounds. This study has evaluated the levels of total petroleum hydrocarbon in crab across the six stations along K-Dere shoreline for a duration of one year. However, it was assessed bi-monthly for the mentioned period. In this present work, total petroleum hydrocarbon was evaluated in the tissue of crab and the result obtained was 118.68mg/kg. This was greater than the permissible limit by DPR (2011).

Akinlola *et al* (2019) have reported higher concentration of Total Petroleum Hydrocarbon in brackish water shrimps *Nematopalaemon hastatus* (AURIVILLIUS 1898). They recorded a mean concentration of 2585mg/kg in biota. This was greater than the recommended or permissible limit of TPH in bitota by DRP (2011). They attributed the higher concentration of TPH in biota to long term accumulation.

Ololade *et al* (2009) reported high concentration of total petroleum hydrocarbons in tissues of crab and attributed them to high lipid contents of crab that enhanced the absorption of more molecules of hydrocarbons in crab. Similarly, Ibigoni *et al* (2019) reported high concentration of Total Petroleum Hydrocarbon in biota beyond the recommended limit. They recorded an average level of 449.30µg/l and 278.57µg/l in *Tympanotonous fuscastus* and *Periophthalmus papillio* respectively.

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Contrarily, Asuquo et al 2004 observed a lower concentration of TPH in O. nitoculus from Cross River System compared to the result obtained in this study. Mean concentration of 55.1µg/l was recorded by them. Ugwu and Achadu (2020) reported lower concentrations of TPH biota when compared with the present study. However, TPH levels were slightly higher than the European Union recommended standard for TPH concentrations in biota.

In this present study, there was no significant difference in the mean concentration of Total Petroleum Hydrocarbon at $p<0.05$ across the six stations and months of sampling.

Table 4.5 Mean Concentration of TPH in biota across stations

Stations	Mean and standard Deviation	Regulatory Standard (DPR 2002) and EGAPSIN intervention
Station 1	131.25±93.25	(50 mg/kg)
Station 2	80.17±58.85	(50 mg/kg)
Station 3	144.08±93.77	(50 mg/kg)
Station 4	109.08±86.36	(50 mg/kg
Station 5	82.50±60.23	(50 mg/kg)
Station 6	165.00±142.35	(50 mg/kg)

Table 4.6 Matrix of TPH fractions in biota across stations.

TPH ID	Station1 mg/kg	Station2 mg/kg	Station3 mg/kg	Station 4 mg/kg	Station 5 mg/kg	Station 6 mg/kg
n-C8	0.00	0.00	0.00	0.00	0.01	0.00
n-C9	0.00	0.00	0.01	0.00	0.00	0.00
n-C10	0.00	0.00	0.00	0.00	0.00	0.00
n-C11	0.00	0.00	0.00	0.00	0.01	0.05
n-C12	0.00	0.00	1.5	0.05	1.01	0.01
n-C13	2.06	0.03	0.05	0.02	0.20	1.43
n-C14	10.07	0.05	4.85	0.10	0.00	0.07
n-C15	1.11	0.48	4.67	0.03	4.09	5.05
n-C16	1.09	5.60	1.01	14.77	0.23	10.44
n-C17	12.00	2.10	1.07	0.00	1.07	0.06
Pristane	0.10	5.01	0.11	7.05	8.11	15.02
n-C18	3.33	2.2	0.12	3.04	0.22	1.40
Phytane	2.01	1.10	3.13	1.02	3.44	12.01
n-C19	5.90	1.02	0.5	0.01	0.33	0.30
n-C20	3.00	0.23	9.07	0.12	12.03	4.03
n-C21	7.31	0.10	7.23	0.00	1.04	0.51
n-C22	5.60	2.80	0.91	0.31	2.01	5.26
n-C23	10.31	0.40	2.00	4.90	0.10	0.99
n-C24	2.20	10.00	5.40	23.02	0.21	15.00
n-C25	0.06	2.18	2.32	0.20	2.02	12.07
n-C26	4.13	1.00	1.02	1.01	1.06	7.32

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n-C27	2.11	0.43	6.03	2.90	1.02	8.03
n-C28	1.80	0.74	0.67	5.41	13.07	17.09
n-C29	8.10	4.60	25.00	12.08	3.08	3.02
n-C30	2.02	1.70	11.0	5.07	0.20	10.04
n-C31	10.42	3.31	4.61	0.00	0.00	4.23
n-C32	1.14	1.10	20.13	2.06	0.12	0.40
n-C33	3.13	0.07	14.3	13.10	3.01	1.12
n-C34	1.86	0.08	2.05	0.05	0.40	21.06
n-C35	13.01	0.00	0.99	10.08	10.00	0.60
n-C36	10.00	1.01	3.34	4.21	6.85	3.48
n-C37	4.2	2.01	3.00	0.12	0.04	0.90
n-C38	2.00	2.67	4.91	0.68	2.01	3.01
n-C39	1.11	0.05	0.13	0.88	0.11	4.11
n-C40	1.99	0.63	2.95	1.20	5.04	0.72
Total	131.5	80.17	144.08	109.08	82.50	165.00
Intervention level	50 mg/kg	50 mg/kg	50 mg/kg	50 mg/kg	50 mg/kg	50 mg/kg

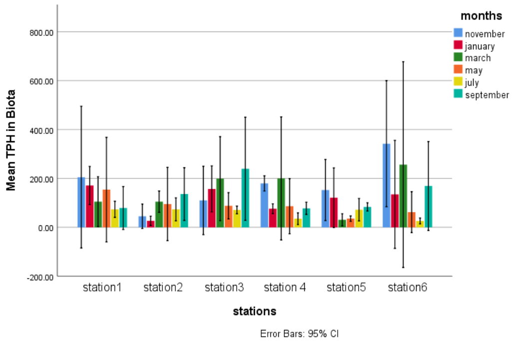

Fig 4.5 Mean Concentration of TPH in biota by stations across months

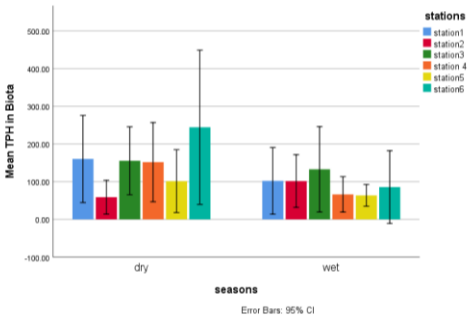

Fig 4.6 Mean Concentration of TPH in biota by seasons and by stations

Ecological Risk Assessment

The ecological risk associated with Total Petroleum Hydrocarbon in this present study, expressed in terms of Bio-Sediment Accumulation Factor (BSAF) and Pollution Index are shown in table 7 and 8 respectively.

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Bio-Sediment Accumulation Factor (BSAF)

BSAF is defined as the occurrence of TPH between aquatic organisms and the environment (Liu *et al.* 2012). Biological accumulation is agreed to have happened when BSAF is very close to or greater than 1 (Yang et al 2019). In this present study, the BSAF were less than 1 for TPH fractions across the six sampling stations except for n-C15 at station 3. The low values of BSAF obtained may be attributed to high concentration of Total Petroleum Hydrocarbon in the sediment from artisanal refining activities in the studied area.

Table 4.7 BSAF of TPH

TPH ID	Station1	Station2	Station3	Station 4	Station 5	Station 6
n-C8	0.00	0.00	0.00	0.00	0.00	0.00
n-C9	0.00	0.00	0.00	0.00	0.00	0.00
n-C10	0.00	0.00	0.00	0.00	0.00	0.00
n-C11	0.00	0.00	0.00	0.00	0.02	0.01
n-C12	0.00	0.00	0.03	4.7E-03	0.08	0.14
n-C13	0.05	0.60	0.70	1.3E-03	0.01	0.01
n-C14	0.07	0.04	0.79	0.02	0.00	1.5E-03
n-C15	0.01	0.04	1.05	6.8E-04	0.13	0.06
n-C16	6.1E-03	0.14	0.06	0.61	0.01	0.37
n-C17	0.07	0.03	0.09	0.00	0.02	5.0E-04
Pristane	2.3E-04	0.03	0.01	0.39	0.62	0.07
n-C18	0.03	0.03	4.3E-03	0.04	0.02	0.01
Phytane	0.02	0.02	0.05	0.01	0.19	0.11
n-C19	9.8E-03	8.7E-03	0.02	1.1E-04	7.7E-03	1.8E-03
n-C20	0.03	1.5E-03	0.29	9.9E-04	0.15	0.02
n-C21	0.17	0.01	0.27	0.00	0.02	3.0E-03
n-C22	0.03	0.01	0.01	0.01	0.03	0.02
n-C23	0.01	0.01	0.17	0.07	8.3E-04	0.01
n-C24	0.01	0.22	0.04	0.16	3.1E-03	0.16
n-C25	1.3E-03	0.04	0.02	4.3E-04	0.08	0.04
n-C26	0.01	0.04	0.01	4.8E-03	0.02	0.02
n-C27	3.4E-03	2.8E-03	0.04	4.6E-03	5.05E-03	0.02
n-C28	4.3E-03	1.69E-03	6.63E-03	0.06	0.09	0.13
n-C29	0.02	0.02	0.05	0.08	0.03	0.01
n-C30	0.01	0.01	0.04	0.03	2.66E-03	0.05
n-C31	0.10	0.01	0.06	0.00	0.00	0.03
n-C32	0.01	0.01	0.04	5.83E-03	1.47E-03	1.70E-03
n-C33	0.01	5.77E-04	0.07	0.04	0.09	3.64E-03
n-C34	0.01	3.57E-03	0.04	3.37E-04	8.29E-04	0.23
n-C35	0.10	0.00	8.18E-03	0.01	0.58	4.7E-03
n-C36	0.11	9.10E-03	0.07	0.03	0.07	0.06
n-C37	0.03	0.01	4.61E-03	8.53E-04	1.99E-04	4.45E-04

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n-C38	0.01	1.80E-03	0.04	7.92E-03	20.01	0.02
n-C39	1.29E-03	1.08E-04	3.26E-04	2.03E-03	1.83E-03	0.01
n-C40	0.01	4.47E-03	7.76E-03	7.69E-03	0.04	3.50E-03
Standard	1	1	1	1	1	1

Pollution Index for TPH in Water, Sediment and Biota

Pollution Index is an environmental tool used to determine the health status of the aquatic environment (Yuan *et al*. 2014 and Khudur et al 2018). The PI obtained for many TPH fractions for water, sediment and biota were greater than 1 across the six sampling stations. This is an indication that the studied area was polluted with hydrocarbons. Similar results obtained in this study were recorded by (Yuan *et al* 2021). The result is shown in table 8,9 and 10.

Table 4.8 PI for surface water

TPH ID	SS1 mg/l	SS2 mg/l	SS3 mg/l	SS4 mg/l	SS5 mg/l	SS6 mg/l
n-C8	0	0	0	0	80.02	0
n-C9	0	0	0	0	0.06	20.2
n-C10	0	12	0.086	22.4	21.2	0
n-C11	25.6	37.2	33.4	2.2	8.2	0
n-C12	0	113.4	97	0.4	240.2	0
n-C13	881.2	1	120.6	0.8	692.2	24.6
n-C14	303.4	200	30	4	17	301.4
n-C15	87.6	9.6	600.6	40.2	642.2	62.4
n-C16	202.2	352	312	1082	357.6	26.6
n-C17	320.2	562	242.2	200	1228.6	0
Pristane	267.8	281.4	292	117.6	263.6	51
n-C18	254	96.4	0.64	802.4	288	862.2
Phytane	183.6	222	1328.6	420.4	356.6	342
n-C19	202	312	625	21.09.	855.4	20.2
n-C20	201.4	200.6	619.4	1..00	1613.6	361.6
n-C21	846.2	102	544.6	602.4	1158	166.6
n-C22	512	116	3018.2	346.6	1462.2	21.8
n-C23	206.2	908	1.42	881.2	220	120
n-C24	404	1708.2	308	2162.2	40.2	1002
n-C25	1.2	443.6	206.4	4..70	25.4	212
n-C26	1682.6	1000.6	280.4	203.6	880	28.6

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n-C27	1242.2	8.6	221	401.8	240.2	820
n-C28	836	14.8	420	468.2	1400	269.6
n-C29	162	800	722.4	192	140.2	37.4
n-C30	400.4	234	420	1.82	222.4	1424
n-C31	208.4	266.2	72.2	1420	642.4	162
n-C32	262.8	222	622	261.2	184.2	808.8
n-C33	13.2	1.4	244	258.2	141.6	655.6
n-C34	297.2	901.6	916.6	280.8	241.4	1344.6
n-C35	341	320	202.6	401.6	200	29
n-C36	176.8	360.2	324.6	242	684.4	104.6
n-C37	328.4	606	1065.6	212	802.8	122
n-C38	400	18.2	106	38	248	21.6
n-C39	282.2	1	1948	620.2	383.2	404
n-C40	219.8	283.2	1702	304	281	112.2
Standard	1	1	1	1	1	1

Table 4.9 PI for Sediment

TPH ID	SS2 mg/kg	SS2 mg/kg	SS3 mg/kg	SS4 mg/kg	SS5 mg/kg	SS6 mg/kg
n-C8	0.11362	0.17566	0	0.00001	0.008002	0.000016
n-C9	0.13442	0	0	0.000018	0.000006	0.00014
n-C10	0.24022	1.52E-05	1.52E-05	0.24136	0.002012	0.00006
n-C11	0.000004	0.000004	0.00017	0.00932	0.00082	0.00816
n-C12	0.000114	0.000006	0.0097	0.0211	0.02402	0.0014
n-C13	0.0892	0.0001	0.02326	0.03368	0.06922	0.241
n-C14	0.29142	0.00228	0.0123	0.00862	0.0017	0.09618
n-C15	0.16876	0.02512	0.00886	0.08818	0.06422	0.17206
n-C16	0.36022	0.08094	0.0312	0.04822	0.03576	0.05682
n-C17	0.33442	0.12134	0.02422	0.02614	0.12286	0.24022
Pristane	0.8666	0.37622	0.0292	0.03646	0.02636	0.4211
n-C18	0.24142	0.17082	0.05606	0.16076	0.0288	0.26142
Phytane	0.19836	0.08964	0.13286	0.14826	0.03566	0.21482
n-C19	1.20028	0.23428	0.0625	0.18618	0.08554	0.33402
n-C20	0.22034	0.3022	0.06194	0.00002	0.16136	0.36688
n-C21	0.08462	0.0255	0.05446	0.64032	0.1158	0.34526
n-C22	0.43136	0.6302	0.30182	0.09596	0.14622	0.49602
n-C23	1.4806	0.15162	0.000142	0.13808	0.24022	0.2832
n-C24	0.40046	0.9006	0.27094	0.2817	0.1368	0.19002
n-C25	0.92352	0.1201	0.24176	0.93204	0.04834	0.6212
n-C26	1.3683	0.45036	0.32342	0.4202	0.10766	0.4162
n-C27	1.24022	0.30142	0.34262	1.24018	0.40404	0.9426
n-C28	0.8217	0.87686	0.20216	0.16826	0.28382	0.26816

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n-C29	0.69632	0.42088	1.07228	0.28754	0.20326	0.09722
n-C30	0.24144	0.32174	0.44218	0.33418	0.15028	0.38018
n-C31	0.20084	0.36342	0.13202	0.82644	0.13316	0.21664
n-C32	0.22628	0.20246	0.8422	0.70548	0.1628	0.47034
n-C33	0.42132	0.24236	0.3668	0.62436	0.0661	0.61468
n-C34	0.28372	0.48802	0.09166	0.29672	0.09646	0.17652
n-C35	0.2557	0.25728	0.21996	1.04016	0.03582	0.2551
n-C36	0.17168	0.22192	0.08802	0.26428	**0.18802**	0.11246
n-C37	0.21284	0.24102	1.30056	0.28126	0.40132	0.40364
n-C38	0.4	2.96076	0.2116	0.17154	0.22468	0.20496
n-C39	1.70822	0.9201	0.7968	0.86308	0.11972	0.4404
n-C40	0.277	0.28172	0.7682	0.31216	0.2085	0.41122
Standard	1	1	1	1	1	1

Table 4.10 PI for biota

TPH ID	SS1 mg/kg	SS2 mg/kg	SS3 mg/kg	SS4 mg/kg	SS5 mg/kg	SS6 mg/kg
n-C8	0	0	0	0	0.000667	0
n-C9	0	0	0.000667	0	0	0
n-C10	0	0	0	0	0	0
n-C11	0	0	0	0	0.000667	0.003333
n-C12	0	0	0.1	0.003333	0.067333	0.000667
n-C13	0.137333	0.002	0.003333	0.001333	0.013333	0.095333
n-C14	0.671333	0.003333	0.323333	0.006667	0	0.004667
n-C15	0.074	0.032	0.311333	0.002	0.272667	0.336667
n-C16	0.072667	0.373333	0.067333	0.984667	0.015333	0.696
n-C17	0.8	0.14	0.071333	0	0.071333	0.004
Pristane	0.006667	0.334	0.007333	0.47	0.540667	1.001333
n-C18	0.222	0.146667	0.008	0.202667	0.014667	0.093333
Phytane	0.134	0.073333	0.208667	0.068	0.229333	0.800667
n-C19	0.393333	0.068	0.033333	0.000667	0.022	0.02
n-C20	0.2	0.015333	0.604667	0.008	0.802	0.268667
n-C21	0.487333	0.006667	0.482	0	0.069333	0.034
n-C22	0.373333	0.186667	0.060667	0.020667	0.134	0.350667

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n-C23	0.687333	0.026667	0.133333	0.326667	0.006667	0.066
n-C24	0.146667	0.666667	0.36	1.534667	0.014	1
n-C25	0.004	0.145333	0.154667	0.013333	0.134667	0.804667
n-C26	0.275333	0.066667	0.068	0.067333	0.070667	0.488
n-C27	0.140667	0.028667	0.402	0.193333	0.068	0.535333
n-C28	0.12	0.049333	0.044667	0.360667	0.871333	1.139333
n-C29	0.54	0.306667	1.666667	0.805333	0.205333	0.201333
n-C30	0.134667	0.113333	0.733333	0.338	0.013333	0.669333
n-C31	0.694667	0.220667	0.307333	0	0	0.282
n-C32	0.076	0.073333	1.342	0.137333	0.008	0.026667
n-C33	0.208667	0.004667	0.953333	0.873333	0.200667	0.074667
n-C34	0.124	0.005333	0.136667	0.003333	0.026667	1.404
n-C35	0.867333	0	0.066	0.672	0.666667	0.04
n-C36	0.666667	0.067333	0.222667	0.280667	0.456667	0.232
n-C37	0.28	0.134	0.2	0.008	0.002667	0.06
n-C38	0.133333	0.178	0.327333	0.045333	0.134	0.200667
n-C39	0.074	0.003333	0.008667	0.058667	0.007333	0.274
n-C40	0.132667	0.042	0.196667	0.08	0.336	0.048
Standard	1	1	1	1	1	1

Health Impact Assessment

The health impact of TPH was expressed in terms of Estimated Daily Intake (EDI) and Health Risk Index (HRI). The result obtained in this study from EDI and HRI in table 10 and 11 below showed that *Goniopsis cruentata*, which is a common source of protein and means of livelihood to the local community posed health risk to humans. Some of the chemical compounds were capable of causing diseases of varying levels if consumed by the locals. Also, similar results of EDI and HRI were reported by Akinola et al 2020 in *Nematopalaemon hastatus* also known as brackish water prawn.

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Table 4.11 EDI for Adult population across the stations

TPH ID	Station1 mg/kg	Station2 mg/kg	Station3 mg/kg	Station 4 mg/kg	Station 5 mg/kg	Station 6 mg/kg
n-C8	0.00	0.00	0.00	0.00	0.03	0.00
n-C9	0.00	0.00	0.03	0.00	0.00	0.00
n-C10	0.00	0.00	0.00	0.00	0.00	0.00
n-C11	0.00	0.00	0.00	0.00	0.03	0.17
n-C12	0.00	0.00	5.04	0.17	3.39	0.03
n-C13	6.92	0.10	0.17	0.07	0.67	4.80
n-C14	33.84	0.05	4.85	0.10	0.00	0.07
n-C15	3.37	1.61	15.69	0.10	13.74	16.97
n-C16	3.66	18.82	3.39	49.63	0.77	35.08
n-C17	40.32	7.06	3.60	0.00	3.60	0.21
Pristane	0.34	16.83	0.37	23.69	27.24	50.47
n-C18	11.19	7.39	0.40	10.21	0.74	4.70
Phytane	6.75	3.70	10.52	3.43	11.56	40.35
n-C19	19.82	3.43	1.68	0.03	1.11	1.01
n-C20	10.08	0.77	30.48	0.40	40.42	13.54
n-C21	24.56	0.34	24.29	0.00	3.49	1.71
n-C22	18.81	9.40	3.06	1.04	6.75	17.67
n-C23	34.64	1.34	6.72	16.46	0.34	3.33
n-C24	7.39	33.6	18.14	77.35	0.71	50.4
n-C25	0.71	24.60	26.21	0.67	22.81	40.56
n-C26	2.38	3.36	3.43	3.39	3.56	24.60
n-C27	7.10	1.44	20.26	9.74	3.43	26.98
n-C28	6.05	2.49	2.25	18.18	43.91	57.42
n-C29	27.22	15.46	84.00	40.59	10.35	10.15
n-C30	6.79	5.71	36.96	17.03	0.67	33.73
n-C31	35.01	11.12	15.49	0.00	0.00	14.21
n-C32	3.83	3.70	67.63	6.92	0.40	1.34
n-C33	10.52	0.24	48.48	44.02	10.11	3.76
n-C34	6.25	0.27	6.69	0.17	1.34	70.76
n-C35	43.71	0.00	3.33	33.87	33.6	2.02
n-C36	33.6	3.39	11.22	14.15	23.02	11.69
n-C37	47.41	22.68	33.86	0.40	0.04	0.90
n-C38	6.72	8.97	16.50	2.28	6.75	10.11
n-C39	3.72	0.17	0.44	2.95	0.37	13.81
n-C40	6.69	2.12	9.91	4.03	16.93	2.42
Standard	1	1	1	1	1	1

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Table 4.12 Health Risk Assessment

TPH ID	Station1	Station2	Station3	Station4	Station5	Station6
n-C8	0	0	0	0	0.06	0
n-C9	0	0	0.06	0	0	0
n-C10	0	0	0	0	0	0
n-C11	0	0	0	0	0.06	0.34
n-C12	0	0	10.08	0.34	6.78	0.06
n-C13	13.84	0.2	0.34	0.14	1.34	9.6
n-C14	67.68	0.1	9.7	0.2	0	0.14
n-C15	6.74	3.22	31.38	0.2	27.48	33.94
n-C16	7.32	37.64	6.78	99.26	1.54	70.16
n-C17	80.64	14.12	7.2	0	7.2	0.42
Pristane	0.68	33.66	0.74	47.38	54.48	100.94
n-C18	22.38	14.78	0.8	20.42	1.48	9.4
Phytane	13.5	7.4	21.04	6.86	23.12	80.7
n-C19	39.64	6.86	3.36	0.06	2.22	2.02
n-C20	20.16	1.54	60.96	0.8	80.84	27.08
n-C21	49.12	0.68	48.58	0	6.98	3.42
n-C22	37.62	18.8	6.12	2.08	13.5	35.34
n-C23	69.28	2.68	13.44	32.92	0.68	6.66
n-C24	14.78	67.2	36.28	154.7	1.42	100.8
n-C25	1.42	49.2	52.42	1.34	45.62	81.12
n-C26	4.76	6.72	6.86	6.78	7.12	49.2
n-C27	14.2	2.88	40.52	19.48	6.86	53.96
n-C28	12.1	4.98	4.5	36.36	87.82	114.84
n-C29	54.44	30.92	168	81.18	20.7	20.3
n-C30	13.58	11.42	73.92	34.06	1.34	67.46
n-C31	70.02	22.24	30.98	0	0	28.42
n-C32	7.66	7.4	135.26	13.84	0.8	2.68
n-C33	21.04	0.48	96.96	88.04	20.22	7.52
n-C34	12.5	0.54	13.38	0.34	2.68	141.52
n-C35	87.42	0	6.66	67.74	67.2	4.04
n-C36	67.2	6.78	22.44	28.3	46.04	23.38
n-C37	94.82	45.36	67.72	0.8	0.08	1.8
n-C38	13.44	17.94	33	4.56	13.5	20.22
n-C39	7.44	0.34	0.88	5.9	0.74	27.62
n-C40	13.38	4.24	19.82	8.06	33.86	4.84
Standard	1	1	1	1	1	1

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CONCLUSION

The high TPH concentration in sediment across the six stations was higher than intervention threshold (NUPRC, former DPR 2012) and immediate and proactive active actions should be taken. The accumulation of TPH in crab is a sign that crab can be used as an environmental indicator and monitoring of pollutants, especially persistent organic pollutants.

The ecological risk associated with TPH showed high risk of TPH concentrations in surface water, sediment and biota obtained from the six sampled stations. The Pollution index of TPH was greater than 1 for most chemical compounds of TPH in aquatic resources examined. The estimated daily intake and health risk index obtained showed that consumption of biota within the studied location may pose health risk to locals that consumed the studied species within the studied area. This is an indication that the TPH in the studied area are from anthropogenic sources.

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