Human Health Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHS) In Five Aquatic Biotics from Selected Creeks in Rivers State

[1]Iyaye David (iyayedavid9@gmail.com); **[2]Prof. Ezejiofor Anthonet Ndidamaka** (anthonet.ezejiofor@uniport.edu.ng); **[1]Omineokuma (Iyaye David) Aseminaso Tubonemi** (iyayeaseminaso@gmail.com); **Dagogo-Brown Igirigi Deinabobo** (igidagogo@yahoo.com); & **Gbekumo Gloria** (gbekumoglory@gmail.com)
[1&2]Department of Environmental and Petroleum Toxicology, Africa Centre of Excellence Public Health and Toxicological Research University of Port Harcourt; [3,4&2]Faculty of Nursing Sciences, Federal University Otuoke

DOI: 10.56201/ijhpr.v9.no1.2024.pg13.28

Abstract

Pollution of the creeks in Niger Delta, Rivers State in particular, has become a norm, posing significant environmental and public health problems. This study evaluated the human risk index from consumption of Polycyclic Aromatic Hydrocarbons, (PAHs), in five aquatic biotics in two selected creeks in Rivers State. The creeks are Isaka and Marine Base creeks in Okrika and Port Harcourt local government areas respectively. A specimen of each of the biotics was collected from each creek and analyzed using Gas Chromatography for PAHs. Mean values of total PAHs concentration ranged from 0.051 to 2.79mg/kg in fish, 0 to 1.58mg/kg in periwinkle, 0.004 to 2.038mg/kg in crab, 0 to 2.044mg/kg in oyster, and 0 to 1.932mg/kg in prawn, in Isaka creek; and in Marine Base creek, 0 to 8.64mg/kg in fish, 0 to 1.388mg/kg in periwinkle, 0 to 2.55mg/kg in crab, 0 to 2.17mg/kg in oyster, and 0 to 5.97mg/kg in prawn. The estimated hazard quotients (HQs) of PAHs from consumption of fish, periwinkle, crab, oyster, and prawn from Isaka creek were 0.733732, 0.31875, 0.104186, 0.269268, and 0.035475 respectively, which is below the USEPA measurement limit of one. Thus, the possibility of human contacting any non-carcinogenic ailment is very unlikely. However, the cancer risk (CR) values were above the USEPA acceptable range of 10^{-6}-10^{-4}; and as such there is the likelihood of cancer upon continuous exposure. For Marine Base creek, the total Hazard Quotients in fish was estimated above one indicating the tendency of causing non-carcinogenic health issues upon consumption. The rest biotics have estimated HQs of PAHs values of 0.082268, 0.233357, 0.270179, and 0.432536 respectively in periwinkle, crab, oyster, and prawn. The sum of CR values for fish, periwinkle, oyster, and prawn were 0.008971, 0.010393, 0.009378, and 0.007166 correspondingly, which are beyond the acceptable limit depicting the likelihood of cancer upon continuous consumption.

Keywords: *PAHs, Aquatic Biotics, Creek, Consumption, Human Health Risk.*

1. Introduction

Aquatic biotics like fish, crayfish, and other edible aquatic lives are prone to hazardous chemicals released from industrial, agricultural, and public sources. Most of these chemicals accrue in the tissues of these biotics which pose threat to human health when consumed (Wu *etal* 2012). One of such contaminants is PAHs.

Polycyclic Aromatic Hydrocarbons (PAHs) are organic compounds released into the environment because of the incomplete combustion, theft, and poor handling of oil and gas, crude oil, and industrial wastes (Adeniji *et al*., 2017). This has specifically led to spill and pollution of the waterways and creeks. Isaka and Marine Base creeks are examples of such creeks in the riverine areas of Rivers State that is affected by spills.

According to Iyama *et al.*, (2017), the diverse bases of marine pollution can be home-made (domestic), industrial or natural. Also, report has revealed that organic dirts are responsible for the worsening and pollution of several creeks in Rivers State (Duru *et al.*, 2018). Compounds of hydrocarbons such as, THC, Oil and Grease, PAHs etc. form the typical organic pollutants from many sources that are present in the marine ecology in Rivers State (Adeniji *et al.*, 2017). These compounds are lethal to man, animals, and plants (e.g., PAHs are very recalcitrant and noxious to the biosystem).

The existence of PAHs have been reported in different environmental media including fish and crustaceans in areas like Bonny (Nkpaa *et tal*, Nwachi and Ntorgbo, 2016). PAHs have received notable attention recently due to their highly carcinogenic possibilities (Wu *et tal*); and as such, it is worthy to note that residual levels of PAHs in fish, lobsters, and other seafoods could lead to adverse health challenges in humans (Ilobet *et al*, 2006).

Hence the study to evaluate the level of PAHs in five aquatic biotics, mostly consumed by man within Isaka and Marine base areas and the potential risk to human health from consumption.

2. Materials and Methods

2.1 Description of the Study Area

The study was conducted in Isaka and Marine Base creeks in Okrika and Port Harcourt LGAs, Rivers State. Isaka creek is a salty H_2O body located in Isaka, Okrika L.G.A of Rivers State, Nigeria. It is an armlet of the National Ports Authorities highway-sea that lies between Latitude 4°73 North and Longitude 6°99 East. The river is decked by mangrove vegetation by the sides. However, wastes originating from dumped boats, open bathrooms, municipal trashes, and spills emanating from oil thefts have escalated the unhealthy status of the creek.

Marine base is situated in Port Harcourt at Latitudes 04^0 43^0 and 04^0 57^0 North of the Equator and between Longitudes 06^0 53^0 and 07^0 58^0 East of the Greenwich Meridian and is bounded by the Dockyard creek, Bonny River and Amadi creek, of the Niger Delta, at an elevation of about 12m above sea level. It is roughly 60km from the crest up stream of the Bonny River. Marine base is in

the coastal area of Port Harcourt, were loading and off-loading of crude oil and other petroleum products by ships, cargo oil tankers occur. The marine base surrounding is not free from contaminants from petrol products, effluents from industries and garbage migrating via drains from hinterland. Thus, has a direct impact on the inhabitant H_2O organisms such as mudskippers, periwinkles, oysters, and crabs as well as the consumers.

2.2 Sampling method and procedure.

The sampling method for collection of the biotics in each of the three locations within the creeks is a simple random method, where homogeneous species of each of the biotics (fish, crayfish, crab, periwinkle, and oyster) were selected at three different locations per creek on different days.

The samples were collected in three different basins containing water from each of the creeks. These samples were then taken to the laboratory and a portion of each of the biotics evaluated for PAHs using Gas Chromatography/Flame Ionization Detection Analysis.

2.3 Materials and Reagents

- Weighing balance, 250ml extraction bottle, Glass funnel, Separator funnel, Glass wool, Fume hood, Waterbath, 250ml beakers, 100ml measuring cylinders, Pipette, Volumetric flask, GC/FID
- Hexane, Methanol, Potassium Hydroxide, PAH Standard, Anhydrous Sodium Sulphate, Dichloromethane (DCM)

2.3.1 Standards and Reagent Preparation:

MeOH/ KOH solution: weigh 120g of KOH, add 60ml of water and dilute with 900ml Methanol.

MeOH/H_2O Mixture: Measure 400ml methanol into a 500ml volumetric flask and add 100ml distilledwater to mark.

2.4 Digestion procedure of the collected samples

The processes involve saponification of the Biota, extraction of the hydrocarbon for PAH analysis andwashing of the organic extract.

About 5.00g of the biota sample was taken into an extraction bottle, saponified with MeOH/KOH solution in a H_2O bath for 60 minutes at 60^0C. The sample was cooled and extracted with hexane at leasttwice using separator funnel. The hexane extract was further washed with MeOH/Water to ensure effective saponification. The hexane layer extract was received in beaker and allowed to concentrate to 1ml. The 1ml concentrate was further passed through a column bed packed with oven preheated silicagel; then prior to dryness 10ml of hexane was introduced on the column to elute for Aliphatic components. Immediately the hexane drains down and prior to dryness 10ml of DCM solvent was introduced to elute the PAH components. It was afterward received in a beaker, allowed to concentrate to 1 ml and then packed into 2ml vial ready for GC/FID analysis.

2.5 Data Interpretation

Descriptive statistics was adopted to depict the average, range, mean and standard deviations (SD) of the assayed noxious elements in the aquatic biotics specimens. The test of significance and one-way ANOVA were also employed to depict the causes of PAHs in the studied site, the contamination dynamics and potential linkage among established variables. Statistical analysis was done using IBM SPSS 23 software.

2.6 Health Risk Analysis to Humans

Human wellbeing toxicity was assayed by deducing the probable carcinogenic and non-carcinogenic impact of exposure to PAHs through consumption of contaminated aquatic biotic over a time. The assessment was carried out for adults (70kg) for both non-carcinogenic and carcinogenic health risk.

2.6.1 Chronic daily intake (CDI) indices:

The Chronic daily intake of PAHs through biotics ingestion was deduced from the equation:

$$CDI_{Ingestion} = CS \times IRS / BW \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where:

CDI = chronic day-by-day intake; CS = Concentration of PAHs in the biotics (mg/kg); BW = body weight = 70 kg (USEPA, 1992); IRS = Ingestion Rate = 0.33mg/kg/d for crab and 0.85mg/kg/d for fish and other biotics.

2.6.2 Hazard quotient (HQ) indices: The HQ for **non-carcinogenic** menace was arrived at by the equation:

$$HQ = CDI/ RfD \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where:

The non-cancer hazard quotient (HQ) is the ratio of exposure to perilous substances, and RfD is the chronic reference dose of the toxicant ($mgkg^{-1}d^{-1}$).

According to database (USEPA, 2009b), the oral toxicity indication dose values (RfD) for the PAHs are 0.02mg/kg/day for Naphthalene, 0.04mg/kg/day each for Fluorene, Anthracene, Phenanthrene, Fluoranthene, and Benzo(ghi)perylene.

The exposed population is assumed to be safe when $HQ < 1$ and unsafe when $HQ \geq 1$ (Khan *et al*., 2008).

2.6.3 Chronic hazard index (HI)

$$\text{Chronic Hazard Index (CHI / CHQ)} = \Sigma^{k}_{i}\ CDI_K /RfD_K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where:

CHI is the aggregate of more than one Hazard Quotient for multi-substances or exposure routes, CDIk is the day-by-day intake of a noxious substance (k) and RfDk is the chronic indication dose for the noxious substance k. HI values ≥ 1 shows that there is a chance that non-carcinogenic risk may emanate and when HI < 1, the turnaround is the case.

2.6.4 Cancer risk (CR)

Cancer risk was deduced from:

$$\text{Cancer risk (CR)} = \text{CDI} \times \text{SF} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where: Cancer risk (CR) depicts the prospect of self's lifetime health menace from carcinogens. CDI is the chronic day-by-day carcinogens intake ($mg \cdot kg^{-1} \cdot d^{-1}$); SFk is the slope factor or Toxic Equivalency Factor (TEF) for each congener k ($mg \cdot kg^{-1} \cdot d^{-1}$).

The Carcinogenic potency of individual PAHs was deduced from:

$$B(A)P_{teq} = PAH_i \times TEF_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where: PAH_i is the concentration of individual PAH congeners; TEF_i, the toxicity equivalency factor for each congener.

The carcinogenic harmfulness of the high molecular mass PAHs seen in the specimens harnessed from the study sites were assayed relative to benzo[a]pyrene (with enough toxicological data) using toxic equivalent quotient (TEQ). The high molecular high mass PAHs are BaA, Chry, BbF, BkF, BaP, DiahA, Inpy, and BghiP; and their corresponding TEF values used in these calculations were 0.1, 0.01, 0.1, 0.1, 1, 1, 0.1, and 0.01 (Van den Berg *et al*., 2006; CCME 2010; Lerda 2011; Benson *et al*., 2017; Zhao *et al*., 2017).

$$\text{Excess Cancer Risk (ECR)} = \Sigma Q \times B(A)P_{teq} \times \text{IFR} \times \text{ED} / \text{BW} \times AT_n \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where:

3.0. Results and Discussions

3.1 Results of Recovery Analysis

Table 3.1.1 Concentration of PAHs in Aquatic Biotics, Isaka Creek.

Parameters (mg/kg)	**Fish**	**Periwinkle**	**Crab**	**Oyster**	**Prawn**
Naphthalene	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00
Acenaphthylene	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00
Acenaphthene	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00
Fluorene	0.03±0.00	0.01±0.00	0.034±0.002	0.037±0.00	0.028±0.00
Anthracene	0.1±0.00	0.07±0.00	0.12±0.00	0.12±0.00	0.096±0.00
Phenanthrene	0.173±0.02	0.08±0.00	0.18±0.00	0.18±0.00	0.102±0.00
Fluoranthene	**0.3±0.00**	**0.26±0.00**	**0.5±0.00**	**0.5±0.00**	**0.027±0.00**
Pyrene	0.04±0.00	0.11±0.00	0.21±0.00	0.21±0.00	0.031±0.00
Benz(a)anthracene	0.06±0.00	0.04±0.00	0.06±0.00	0.06±0.00	0.045±0.00

Chrysene	0.12±0.00	0.13±0.00	0.1±0.00	0.1±0.00	0.107±0.00
Benzo(b)Fluoranthene	0.01±0.00	0.01±0.00	0.07±0.00	0.07±0.00	0.003±0.00
Benzo(k)Fluoranthene	0.023±0.001	0.04±0.00	0.04±0.00	0.04±0.00	0.019±0.00
Benzo(a) Pyrene	0.06±0.00	0.09±0.00	0.13±0.00	0.13±0.00	0.043±0.00
Benzo(a,h)anthracene	0.03±0.00	0.03±0.00	**0.5±0.00**	**0.5±0.00**	**1.355±0.00**
Indeno(1,2,3-cd) pyrene	0.02±0.01	0.07±0.00	0.034±0.002	0.037±0.00	0.018±0.00
Benzo (ghi) Perylene	**1.782±0.02**	**0.61±0.00**	**0.03±0.00**	**0.03±0.00**	**0.028±0.00**
Total PAHs (ΣPAH)	**2.79±0.051**	**1.58±0.00**	**2.038±0.004**	**2.044±0.00**	**1.932±0.00**
Total Carcinogenic PAHs (ΣcPAH)	**2.105±0.04**	**1.02±0.00**	**0.964±0.002**	**0.967±0.00**	**1.618±0.00**

The result of Table 3.1.1 are the concentrations of PAHs in the various aquatic biotics in Isaka creek. A total of sixteen PAHs were examined; and the result of the experimentation shows that Naphthalene, Acenaphthylene, and Acenaphthene are of the same concentration of 0.01±0.00mg/kg in the five biotics. The concentration of Fluorine was found to be 0.03±0.00mg/kg in fish, 0.034±0.00mg/kg in crab, 0.028±0.00mg/kg in prawn, 0.01 ±0.00mg/kg in periwinkle and 0.037±0.00mg/kg in oyster. For that of Anthracene, mean value of 0.1±0.00mg/kg was observed in both fish and prawn, 0.12±0.00 mg/kg in both crab and oyster, and 0.07±0.00mg/kg in periwinkle. Phenanthrene on the other hand was examined to be of a conc. of 0.18±0.00mgkg^{-1} in crab and oyster, 0.173±0.02 mgkg^{-1} in fish, 0.08±0.00mg/kg in periwinkle and 0.102±0.00mg/kg in prawn. The concentration of Fluoranthene, was found to be 0.5±0.00mg/kg in crab and oyster, 0.3±0.00 mgkg^{-1} in fish, 0.027±0.00mg/kg in prawn, and 0.26±0.00 mg/kg in periwinkle. Pyrene content was found to be, 0.04±0.00mgkg^{-1} in fish and 0.03±0.00mg/kg in prawn, 0.21±0.00mg/kg for crab and oyster and 0.11±0.00mg/kg for periwinkle. The mean concentration of Benz(a)anthracene was found to be 0.06±0.00mg/kg in fish, crab, and oyster, and 0.045±0.00mgkg^{-1} in prawn, and 0.04±0.00 mg/kg in periwinkle. For Chrysene, 0.12±0.00mg/kg concentration was found in fish, 0.107±0.00mg/kg in prawn, 0.10±0.00mg/kg in crab and oyster and 0.13±0.00mg/kg in periwinkle. Benzo(b)Fluoranthene has concentrations of 0.01±0.00mg/kg in fish and periwinkle, 0.003±0.00mg/kg in prawn, and 0.07±0.00mgkg^{-1} in both crab and oyster. The concentration of Benzo(k)Fluoranthene was found to be 0.04 ±0.00mg/kg in periwinkle, crab, and oyster, and 0.019±0.00mg/kg and 0.023±0.01mg/kg in prawn and fish individually. Benzo(a) Pyrene concentration was found to be 0.06±0.00mg/kg in fish, 0.043±0.00mg/kg in prawn, 0.09±0.00mg/kg in periwinkle and 0.13±0.00mg/kg in crab and oyster. For Benzo(a,h)anthracene, concentrations of 0.03±0.00mg/kg was found in fish and periwinkle, 0.5±0.00mg/kg mg/kg in crab and oyster; and concentration of 1.355±0.00mg/kg in prawn. The conc. of Indeno (1,2,3-cd) pyrene was 0.02±0.001mg/kg in fish; 0.07±0.00 mgkg^{-1}, 0.034±0.002mg/kg, 0.037±0.00mg/kg, and 0.018±0.00mg/kg in periwinkle, crab, oyster, and prawn correspondingly. For Benzo(ghi) Perylene, a conc. of 0.03±0.00 mgkg^{-1} was observed in crab and oyster, 1.78±0.002 mg/kg in fish, 0.61±0.00 mgkg^{-1} in periwinkle, and 0.028±0.00 mgkg^{-1} in prawn.

Mean concentrations for total carcinogenic PAHs (sum of BaA, Chr, BkFL, Bap, BbFL, Ind, DBA, BP) accounted for **84%, 75%, 65%, 47%, and 47%** respectively in prawn, fish, periwinkle, crab, and oyster of the total PAHs. Total mean carcinogenic PAHs**(**ΣcPAH) and Total mean PAH **(**ΣPAH) concentrations were higher in fish than other biotics, with values of 2.105mg/kg and 2.79mg/kg respectively.

For individual concentration of PAHs, Benzo(ghi)Perylene was the most dominant congener in fish and periwinkle samples, and the concentrations are significantly higher than the other congeners, with mean concentrations of 1.782±0.02mg/kg and 0.61±0.00mg/kg, accounting for 64% and 39% of the total PAHs in fish and periwinkle respectively. Fluoranthene and Benzo(a,h)anthracene were the most dominant congeners in crab and oyster with the same mean concentration of 0.05±0.0mg/kg and percentage contribution of 24.5%. For prawn, Benzo(a,h)anthracene happen to be the most predominant congener with a mean concentration of 1.355±0.00mg/kg amounting to 70% of the total level of PAHs in prawn. Benzo(a,h)anthracene concentration in prawn was significantly higher than the other congeners.

The PAH composition shape by ring type showed a considerable predominance of the three-ring, four-ring type, and five-ring type PAHs. The mean percentage concentration of the higher molecular weight PAHs (HMWPAHs) (four to six rings) was higher than the lower molecular weight PAHs (LMWPAHs) (two to three rings) in all the aquatic biotics with fish and periwinkle accounting for 88% each, prawn 87%, and crab and oyster 82% each in Isaka creek.

Table 3.1.2 Concentration of PAHs in Aquatic Biotics, Marine Base Creek

Parameters	Fish	Periwinkle	Crab	Oyster	Prawn
Naphthalene	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00
Acenaphthylene	0.03±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00
Acenaphthene	0.06±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00
Fluorene	0.08±0.00	0.01±0.00	0.01±0.00	0.04±0.00	0.01±0.00
Anthracene	0.13±0.00	0.012±0.00	0.01±0.00	0.12±0.00	0.05±0.00
Phenanthrene	0.11±0.00	0.013±0.00	0.02±0.00	0.18±0.00	0.06±0.00
Fluoranthene	0.38±0.00	0.119±0.00	0.01±0.00	0.5±0.00	0.17±0.00
Pyrene	0.47±0.00	0.064±0.00	0.13±0.00	0.21±0.00	0.35±0.00
Benz(a)anthracene	0.41±0.00	0.017±0.00	0.1±0.00	0.06±0.00	0.16±0.00
Chrysene	0.35±0.00	0.07±0.00	0.08±0.00	0.1±0.00	0.14±0.00
Benzo(b)Fluoranthene	0.33±0.00	0.017±0.00	0.05±0.00	0.07±0.00	0.07±0.00
Benzo(k)Fluoranthene	0.02±0.00	0.044±0.00	0.04±0.00	0.04±0.00	0.04±0.00
Benzo(a) Pyrene	0.59±0.00	0.089±0.00	0.07±0.00	0.15±0.00	0.98±0.00
Benzo(a,h)anthracene	0.01±0.00	0.752±0.00	0.05±0.00	0.6±0.00	0.47±0.00
Indeno(1,2,3-cd) pyrene	0.03±0.00	0.054±0.00	0.04±0.00	0.04±0.00	0.08±0.00

Benzo (ghi) Perylene	**5.63±0.00**	**0.097±0.00**	**1.91±0.00**	**0.03±0.00**	**3.36±0.00**
Total PAHs (ΣPAH)	**8.64±0.00**	**1.388±0.00**	**2.55±0.00**	**2.17±0.00**	**5.97±0.00**
Total Carcinogenic PAHs (ΣcPAH)	**7.37±0.00**	**1.14±0.00**	**2.34±0.00**	**1.09±0.00**	**5.30±0.00**

The results of PAHs analysis in the various aquatic biotics in Marine Base Creek are shown in Table 3.1.2. The result of the experimentation has it that Naphthalene is of the same concentration of 0.01±0.00mg/kg in the five aquatic biotics.
Similarly, it was found out that Acenaphthylene and Acenaphthene are of the same concentration of 0.01±0.00mg/kg in four of the other biotics except the fish with 0.03±0.00mg/kg and 0.06±0.00mg/kg correspondingly.
For Fluorine, concentrations of 0.08mg/kg was found in fish, 0.01±0.00mg/kg in crab, periwinkle, and prawn and 0.04±0.00mg/kg in oyster. The concentration of Anthracene was found to be 0.13±0.00mg/kg in fish, 0.012±0.00mg/kg in periwinkle, 0.12±0.00mgkg^{-1} in crab and 0.05±0.00mg/kg in prawn, while that of Phenanthrene was found to be 0.11±0.00mg/kg in fish, 0.013±0.00mgkg^{-1} in periwinkle, 0.02±0.00mg/kg in crab, 0.18±0.00mg/kg in oyster, and 0.06±0.00mg/kg in prawn. For Fluoranthene, concs. of 0.38±0.00mg/kg were found in fish, 0.119±0.00mgkg^{-1} in periwinkle, 0.01±0.00mgkg^{-1} in crab, 0.5±0.00mgkg^{-1} in oyster, and 0.17 ±0.00mgkg^{-1} in prawn, while Pyrene was found to be of a concentration of 0.47±0.00mg/kg in fish, 0.064±0.00mg/kg in periwinkle, 0.13±0.00 mg/kg in crab, 0.21±0.00mg/kg in oyster and 0.35±0.00 mg/kg in prawn. on the other hand, Benz(a)anthracene was found to be of concentrations of 0.41 ±0.00mg/kg in fish, 0.017±0.00mg/kg in periwinkle, 0.1±0.00 mg/kg in crab, 0.06±0.00 mgkg^{-1} in oyster, and 0.16±0.00mgkg^{-1} in prawn.
In the same vein, varying concentrations of Chrysene were observed in the biotics. Concentrations of 0.3±0.00mg/kg was found in fish, 0.07±0.00 mgkg^{-1} in periwinkle, 0.08±0.00mg/kg in crab, 0.1±0.00 mgkg^{-1} in oyster and 0.14±0.00 mgkg^{-1} in prawn. For Benzo(b)Fluoranthene, conc. of 0.33±0.00mg/kg was found in fish, 0.017 ±0.00mg/kg in periwinkle, 0.05±0.00mg/kg in crab and 0.07±0.00mg/kg in oyster and prawn. Benzo(k)Fluoranthene was found to be of the same concentration of 0.04 mg/kg in crab, oyster, and prawn, and varying concentration of 0.02±0.00 mgkg^{-1} in fish and 0.044±0.00 mgkg^{-1} in periwinkle, while Benzo(a) Pyrene was 0.59±0.00mg/kg in fish, 0.089±0.00mg/kg in periwinkle, 0.07±0.00mg/kg in crab, 0.15±0.00 mgkg^{-1} in oyster and 0.98±0.00 mgkg^{-1} in prawn. The concentration of Benzo(a,h)anthracene was observed to be 0.01mg/kg in fish, 0.752±0.00mg/kg in periwinkle, 0.05±0.00mg/kg in crab, 0.6±0.00mg/kg in oyster and 0.47±0.00mg/kg in prawn. And for Indeno(1,2,3-cd) pyrene, mean value concentration of 0.04 ±0.00mg/kg was found in crab and oyster, 0.03±0.00 mgkg^{-1} in fish, 0.054±0.00 mgkg^{-1} in periwinkle, and 0.08±0.00 mgkg^{-1} in prawn; whereas conc. of Benzo (ghi) Perylene was 5.63±0.00mg/kg in fish, 0.097±0.00 mgkg^{-1} in periwinkle, 1.91±0.00mg/kg in crab, 0.03mg/kg in oyster, and 3.36±0.00 mg/kg in prawn.

Mean concentrations for total carcinogenic PAHs (sum of BaA, Chr, BkFL, Bap, BbFL, Ind, DBA, BP) accounted for **92%, 89%, 85%, 82%, and 50%,** respectively in crab, prawn, fish, periwinkle, and oyster of the total PAHs. Total mean carcinogenic PAHs concentrations were higher in fish (7.37mg/kg) than other biotics and differences in concentrations between the species is quite

significant. Total mean PAH concentrations were also higher in fish (8.64mg/kg) than the other biotics.

For individual concentration of PAHs, Benzo(ghi)Perylene was the most dominant congener in crab, fish, and prawn samples, and the concentrations are significantly higher than the other congeners, with mean concentrations of 1.91±0.00mg/kg, 5.63±0.00mg/kg, and 3.36±0.00mg/kg, accounting for 75%, 65%, and 56% of the total PAHs in crab, fish, and prawn respectively. Benzo(a,h)anthracene was the most dominant congener in periwinkle and oyster with mean concentrations of 0.752±0.0mg/kg and 0.60±0.0mg/kg respectively, accounting for 54% and 28% of the cumulative PAHs in both species.

The PAH composition pattern by ring type from marine base creek also showed a considerable predominance of the three-ring, four-ring, and five-ring type PAHs. The mean percentage concentration of the higher molecular weight PAHs (HMWPAHs) (four to six rings) was higher than the lower molecular weight PAHs (LMWPAHs) (two to three rings) in all the aquatic biotics with crab, prawn, fish/periwinkle, and oyster accounting for 100%, 98%, 95%, and 83% respectively. Differences in concentrations between the HMWPAHs and LMWPAHs among the species were also statistically significant.

3.2 Human Health Risk Index from consumption PAHs via the biotics

Table 3.2.1. Human HRI from consumption of PAHs in Fish, Isaka Creek

PAHs	Mean Conc. (mg/kg)	CDI	RfD	HQ	SF	CR
Naphthalene	0.01	0.000121	0.02	0.00607143		
Acenaphthylene	0.01	0.000121	NR			
Acenaphthene	0.01	0.000121	NR			
Fluorene	0.03	0.000364	0.04	0.00910714		
Anthracene	0.1	0.001214	0.04	0.03035714		
Phenanthrene	0.173	0.002101	0.04	0.05251786		
Fluoranthene	0.3	0.003643	0.04	0.09107143		
Pyrene	0.04	0.000486	NR			
Benz(a)anthracene	0.06	0.000729	NR		0.1	7.28571E-05
Chrysene	0.12	0.001457	NR		0.01	1.45714E-05
Benzo(b)Fluoranthene	0.01	0.000121	NR		0.1	1.21429E-05
Benzo(k)Fluoranthene	0.023	0.000279	NR		0.1	2.79286E-05
Benzo(a) Pyrene	0.06	0.000729	NR		1	0.000728571
Benzo(a,h)anthracene	0.03	0.000364	NR		1	0.000364286
Indeno(1,2,3-cd) pyrene	0.02	0.000243	NR		0.1	2.42857E-05
Benzo (ghi) Perylene	1.794	0.021784	0.04	0.54460714	0.01	0.000217843

ΣHQ = **0.733732143**; ΣCR = **0.001462486**

Table 3.2.2. Human HRI from consumption of PAHs in Periwinkle, Isaka Creek

PAHs	Mean Conc. (mg/kg)	CDI	RfD	HQ	SF	CR
Naphthalene	0.01	0.000121	0.02	0.006071		
Acenaphthylene	0.01	0.000121	NR			
Acenaphthene	0.01	0.000121	NR			
Fluorene	0.01	0.000121	0.04	0.003036		
Anthracene	0.07	0.00085	0.04	0.02125		
Phenanthrene	0.08	0.000971	0.04	0.024286		
Fluoranthene	0.26	0.003157	0.04	0.078929		
Pyrene	0.11	0.001336	NR			
Benz(a)anthracene	0.04	0.000486	NR		0.1	4.86E-05
Chrysene	0.13	0.001579	NR		0.01	1.58E-05
Benzo(b)Fluoranthene	0.01	0.000121	NR		0.1	1.21E-05
Benzo(k)Fluoranthene	0.04	0.000486	NR		0.1	4.86E-05
Benzo(a) Pyrene	0.09	0.001093	NR		1	0.001093
Benzo(a,h)anthracene	0.03	0.000364	NR		1	0.000364
Indeno(1,2,3-cd) pyrene	0.07	0.00085	NR		0.1	0.000085
Benzo (ghi) Perylene	0.61	0.007407	0.04	0.185179	0.01	7.41E-05

ΣHQ = **0.31875**; ΣCR = **0.001741**

Table 3.2.3. Human HRI from consumption of PAHs in Crab, Isaka Creek

PAHs	Mean Conc. (mg/kg)	CDI	RfD	HQ	SF	CR
Naphthalene	0.01	4.71429E-05	0.02	0.002357		
Acenaphthylene	0.01	4.71429E-05	NR			
Acenaphthene	0.01	4.71429E-05	NR			
Fluorene	0.034	0.00016029	0.04	0.004007		
Anthracene	0.12	0.00056571	0.04	0.014143		
Phenanthrene	0.18	0.00084857	0.04	0.021214		
Fluoranthene	0.5	0.00235714	0.04	0.058929		
Pyrene	0.21	0.00099	NR			
Benz(a)anthracene	0.06	0.00028286	NR		0.1	2.82857E-05
Chrysene	0.1	0.00047143	NR		0.01	4.71429E-06
Benzo(b)Fluoranthene	0.07	0.00033	NR		0.1	0.000033
Benzo(k)Fluoranthene	0.04	0.00018857	NR		0.1	1.88571E-05
Benzo(a) Pyrene	0.13	0.00061286	NR		1	0.000612857
Benzo(a,h)anthracene	0.5	0.00235714	NR		1	0.002357143
Indeno(1,2,3-cd) pyrene	0.034	0.00016029	NR		0.1	1.60286E-05

Benzo (ghi) Perylene	0.03	0.00014143	0.04	0.003536	0.01	1.41429E-06

ΣHQ = **0.104186**; ΣCR = **0.0030723**

Table 3.2.4. Human HRI from consumption of PAHs in Oyster, Isaka Creek

PAHs	Mean Conc. (mg/kg)	CDI	RfD	HQ	SF	CR
Naphthalene	0.01	0.000121	0.02	0.006071		
Acenaphthylene	0.01	0.000121	NR			
Acenaphthene	0.01	0.000121	NR			
Fluorene	0.037	0.000449	0.04	0.011232		
Anthracene	0.12	0.001457	0.04	0.036429		
Phenanthrene	0.18	0.002186	0.04	0.054643		
Fluoranthene	0.5	0.006071	0.04	0.151786		
Pyrene	0.21	0.00255	NR			
Benz(a)anthracene	0.06	0.000729	NR		0.1	7.29E-05
Chrysene	0.1	0.001214	NR		0.01	1.21E-05
Benzo(b)Fluoranthene	0.07	0.00085	NR		0.1	0.000085
Benzo(k)Fluoranthene	0.04	0.000486	NR		0.1	4.86E-05
Benzo(a) Pyrene	0.13	0.001579	NR		1	0.001579
Benzo(a,h)anthracene	0.5	0.006071	NR		1	0.006071
Indeno(1,2,3-cd) pyrene	0.037	0.000449	NR		0.1	4.49E-05
Benzo (ghi) Perylene	0.03	0.000364	0.04	0.009107	0.01	3.64E-06

ΣHQ = **0.269268**; ΣCR = **0.007917.**

Table 3.2.5. Human HRI from consumption of PAHs in Prawn, Isaka Creek

PAHs	Mean Conc. (mg/kg)	CDI	RfD	HQ	SF	CR
Naphthalene	0.01	4.71429E-05	0.02	0.002357		
Acenaphthylene	0.01	4.71429E-05	NR			
Acenaphthene	0.01	4.71429E-05	NR			
Fluorene	0.028	0.000132	0.04	0.0033		
Anthracene	0.096	0.000452571	0.04	0.011314		
Phenanthrene	0.102	0.000480857	0.04	0.012021		
Fluoranthene	0.027	0.000127286	0.04	0.003182		
Pyrene	0.031	0.000146143	NR			

Benz(a)anthracene	0.045	0.000212143	NR		0.1	2.12E-05
Chrysene	0.107	0.000504429	NR		0.01	5.04E-06
Benzo(b)Fluoranthene	0.003	1.41429E-05	NR		0.1	1.41E-06
Benzo(k)Fluoranthene	0.019	8.95714E-05	NR		0.1	8.96E-06
Benzo(a) Pyrene	0.043	0.000202714	NR		1	0.000203
Benzo(a,h)anthracene	1.355	0.006387857	NR		1	0.006388
Indeno(1,2,3-cd) pyrene	0.018	8.48571E-05	NR		0.1	8.49E-06
Benzo (ghi) Perylene	0.028	0.000132	0.04	0.0033	0.01	1.32E-06

ΣHQ = **0.035475**; ΣCR = **0.006637**

The estimated **hazard quotients** (HQs) of PAHs from consumption of fish, periwinkle, crab, oyster, and prawn from the surface water from Isaka creek were 0.733732143, 0.31875, 0.104186, 0.269268, and 0.035475 respectively as shown in **tables 3.2.1 to 3.2.5**. The result indicates that HQs for all the aquatic biotics in the water is below the USEPA measurement limit of one. Thus, the possibility of human contacting any **non-carcinogenic** ailment is very unlikely. However, the **cancer risk(CR)** values were above the acceptable range; and as such there is the likelihood of cancer upon continuous exposure. The calculated CR values were 0.00146248, 0.001741, 0.0030723, 0.007917, and 0.006637 in fish, periwinkle, crab, oyster, and prawn respectively**.**

Table 3.2.6. Human HRI from consumption of PAHs in Fish, Marine Base Creek

PAHs	Mean Conc. (mg/kg)	CDI	RfD	HQ	SF	CR
Naphthalene	0.01	0.000121	0.02	0.006071		
Acenaphthylene	0.03	0.000364	NR			
Acenaphthene	0.06	0.000729	NR			
Fluorene	0.08	0.000971	0.04	0.024286		
Anthracene	0.13	0.001579	0.04	0.039464		
Phenanthrene	0.11	0.001336	0.04	0.033393		
Fluoranthene	0.38	0.004614	0.04	0.115357		
Pyrene	0.47	0.005707	NR			
Benz(a)anthracene	0.41	0.004979	NR		0.1	0.000498
Chrysene	0.35	0.00425	NR		0.01	4.25E-05
Benzo(b)Fluoranthene	0.33	0.004007	NR		0.1	0.000401
Benzo(k)Fluoranthene	0.02	0.000243	NR		0.1	2.43E-05
Benzo(a) Pyrene	0.59	0.007164	NR		1	0.007164
Benzo(a,h)anthracene	0.01	0.000121	NR		1	0.000121
Indeno(1,2,3-cd) pyrene	0.03	0.000364	NR		0.1	3.64E-05
Benzo (ghi) Perylene	5.63	0.068364	0.04	1.709107	0.01	0.000684

ΣHQ = **1.927679**; ΣCR = **0.008971**

Table 3.2.7. Human HRI from consumption of PAHs in Periwinkle, Marine Base Creek

PAHs	Mean Conc. (mg/kg)	CDI	RfD	HQ	SF	CR
Naphthalene	0.01	0.000121	0.02	0.006071		
Acenaphthylene	0.01	0.000121	NR			
Acenaphthene	0.01	0.000121	NR			
Fluorene	0.01	0.000121	0.04	0.003036		
Anthracene	0.012	0.000146	0.04	0.003643		
Phenanthrene	0.013	0.000158	0.04	0.003946		
Fluoranthene	0.119	0.001445	0.04	0.036125		
Pyrene	0.064	0.000777	NR			
Benz(a)anthracene	0.017	0.000206	NR		0.1	2.06E-05
Chrysene	0.07	0.00085	NR		0.01	8.5E-06
Benzo(b)Fluoranthene	0.017	0.000206	NR		0.1	2.06E-05
Benzo(k)Fluoranthene	0.044	0.000534	NR		0.1	5.34E-05
Benzo(a) Pyrene	0.089	0.001081	NR		1	0.001081
Benzo(a,h)anthracene	0.752	0.009131	NR		1	0.009131
Indeno(1,2,3-cd) pyrene	0.054	0.000656	NR		0.1	6.56E-05
Benzo (ghi) Perylene	0.097	0.001178	0.04	0.029446	0.01	1.18E-05

ΣHQ = **0.082268**; ΣCR = **0.010393**

Table 3.2.8. Human HRI from consumption of PAHs in Crab., Marine Base Creek

PAHs	Mean Conc. (mg/kg)	CDI	RfD	HQ	SF	CR
Naphthalene	0.01	4.71E-05	0.02	0.002357		
Acenaphthylene	0.01	4.71E-05	NR			
Acenaphthene	0.01	4.71E-05	NR			
Fluorene	0.01	4.71E-05	0.04	0.001179		
Anthracene	0.01	4.71E-05	0.04	0.001179		
Phenanthrene	0.02	9.43E-05	0.04	0.002357		
Fluoranthene	0.01	4.71E-05	0.04	0.001179		
Pyrene	0.13	0.000613	NR			
Benz(a)anthracene	0.1	0.000471	NR		0.1	4.71E-05
Chrysene	0.08	0.000377	NR		0.01	3.77E-06
Benzo(b)Fluoranthene	0.05	0.000236	NR		0.1	2.36E-05
Benzo(k)Fluoranthene	0.04	0.000189	NR		0.1	1.89E-05
Benzo(a) Pyrene	0.07	0.00033	NR		1	0.00033
Benzo(a,h)anthracene	0.05	0.000236	NR		1	0.000236
Indeno(1,2,3-cd) pyrene	0.04	0.000189	NR		0.1	1.89E-05

Benzo (ghi) Perylene	1.91	0.009004	0.04	0.02143	0.01	9E-05

ΣHQ = **0.233357**; ΣCR = **0.000768**

Table 3. 2.9. Human HRI from consumption of PAHs in Oyster, Marine Base Creek

PAHs	Mean Conc. (mg/kg)	CDI	RfD	HQ	SF	CR
Naphthalene	0.01	0.000121	0.02	0.006071		
Acenaphthylene	0.01	0.000121	NR			
Acenaphthene	0.01	0.000121	NR			
Fluorene	0.04	0.000486	0.04	0.012143		
Anthracene	0.12	0.001457	0.04	0.036429		
Phenanthrene	0.18	0.002186	0.04	0.054643		
Fluoranthene	0.5	0.006071	0.04	0.151786		
Pyrene	0.21	0.00255	NR			
Benz(a)anthracene	0.06	0.000729	NR		0.1	7.29E-05
Chrysene	0.1	0.001214	NR		0.01	1.21E-05
Benzo(b)Fluoranthene	0.07	0.00085	NR		0.1	0.000085
Benzo(k)Fluoranthene	0.04	0.000486	NR		0.1	4.86E-05
Benzo(a) Pyrene	0.15	0.001821	NR		1	0.001821
Benzo(a,h)anthracene	0.5	0.007286	NR		1	0.007286
Indeno(1,2,3-cd) pyrene	0.037	0.000486	NR		0.1	4.86E-05
Benzo (ghi) Perylene	0.03	0.000364	0.04	0.009107	0.01	3.64E-06

ΣHQ = **0.270179**; ΣCR = **0.009378**

Table 3.2.10. Human HRI from consumption of PAHs in Prawn., Marine Base Creek

PAHs	Mean Conc. (mg/kg)	CDI	RfD	HQ	SF	CR
Naphthalene	0.01	4.71E-05	0.02	0.002357		
Acenaphthylene	0.01	4.71E-05	NR			
Acenaphthene	0.01	4.71E-05	NR			
Fluorene	0.01	4.71E-05	0.04	0.001179		
Anthracene	0.05	0.000236	0.04	0.005893		
Phenanthrene	0.06	0.000283	0.04	0.007071		
Fluoranthene	0.17	0.000801	0.04	0.020036		
Pyrene	0.35	0.00165	NR			
Benz(a)anthracene	0.16	0.000754	NR		0.1	7.54E-05
Chrysene	0.14	0.00066	NR		0.01	6.6E-06

Benzo(b)Fluoranthene	0.07	0.00033	NR		0.1	0.000033
Benzo(k)Fluoranthene	0.04	0.000189	NR		0.1	1.89E-05
Benzo(a) Pyrene	0.98	0.00462	NR		1	0.00462
Benzo(a,h)anthracene	0.47	0.002216	NR		1	0.002216
Indeno(1,2,3-cd) pyrene	0.08	0.000377	NR		0.1	3.77E-05
Benzo (ghi) Perylene	3.36	0.01584	0.04	0.396	0.01	0.000158

ΣHQ = **0.432536**; ΣCR = **0.007166**

From tables 3. 2.6, the total non-CR or HQ for consumption of PAHs in fish was estimated as above one. This implies that continuous consumption of fish from this creek directly or indirectly may cause non-carcinogenic health issues. The sum CR for PAHs in the fish of marine Base Creek was 0.008971which is beyond the tolerable limit of 10^{-6} - 10^{-4} showing the possibility of cancer risk.

Meanwhile, as shown from table 3.2.7 to 3.2.10, the estimated hazard quotients of PAHs from Marine Base creek surface H_2O by consumption of periwinkle, crab, oyster, and prawn were **0.082268, 0.233357, 0.270179, and 0.432536 respectively**, which is lesser than one, implying that there is no possibility of non-carcinogenic health issues. However, the cancer risk values of periwinkle, oyster and prawn were above the permissible range depicting the tendency of cancer upon continuous consumption. The estimated values were **0.010393, 0.009378, and 0.007166 respectively. Cancer Risk for PAHs in crab is within the acceptable limit, t**here is thus no likelihood of cancer upon continuous consumption of prawn.

4.0 Conclusions

The concentrations PAHs in most of the aquatic biotics of both creeks were found to be of a risk upon consumption by man, which implies that the major sources of these pollutants within the creeks must be checked to forestall serious public health issues.

REFERENCES

Adeniji, A. O., Okoh, O. O., & Okoh, A. I. (2019). Levels of polycyclic aromatic hydrocarbons in the water and sediment of Buffalo River Estuary, South Africa, and their health risk assessment. *Archives of Environmental Contamination and Toxicology*, *76*(4), 657-669.

Aderinola, O. J., Mekuleye, G. O. &Whenu, O. O. (2018). Total and Polyaromatic Hydrocarbons in Water, Sediment, Fin and Shellfishes from Badagry Creek and Ologe Lagoon, Lagos, Nigeria. *Journal of Applied Science and Environmental Management*, 22 (5), 675-680.

Aigberua, A. O., Ekubo, A. T., Inengite, A. K., & Izah, S. C. (2016). Evaluation of total hydrocarbon content and polycyclic aromatic hydrocarbon in an oil spill contaminated soil in Rumuolukwu community in Niger Delta. *Journal of Environmental Treatment Techniques*, *4*(4), 130-142.

Duru, C. C., Daniel, U. I. & Ogbulie, J. N. (2018). Impacts of Organic Wastes on Water Quality of Woji Creek, Port Harcourt, Nigeria. *Journal of Applied Sciences and Environmental Management*, 22(5), 625-630.

Elenwo, E .I. & Akankali, J. A. (2015). The Effects of Marine Pollution on Nigerian Coastal Resources. *Journal of Sustainable Development Studies*, 8, 209-224.

Gu, J. D., & Wang, Y. S. (2015). Coastal and marine pollution and ecotoxicology. *Ecotoxicology*, *24*(7), 1407-1410.

Inyang, S. E., Aliyu, A. B., & Oyewale, A. O. (2018). Total petroleum hydrocarbon content in surface water and sediment of Qua-Iboe River, Ibeno, Akwa-Ibom State, Nigeria. *Journal of Applied Sciences and Environmental Management*, *22*(12), 1953-1959.

Jerry Neff, (2002) Bioaccumulation in Marine Organisms (pp.57-78),

Moja, S. J., Mtunzi, F. & Madlanga, X. (2013). Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in River Water Samples from the Vaal Triangle Area in South Africa. *Journal of Environmental Science, Health, Toxic and Hazardous Substances and Environmental Engineering*, 48(8), 847-54.

Moslen, M. & Miebaka, C. A. (2017). Hydrocarbon Contamination of Sediment in the Niger Delta Region: a case study of the Azubie Creek, Upper reaches of the Bonny Estuary, Nigeria. *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 11(9), 26-32.

Wokoma, O. A. F. (2014). The level of total hydrocarbon concentration in the Kua/Kinabere Creek in Ogoni land an estuary of the bonny River. *International Journal of Scientific and Technology Research*, *3*(12), 9-16.

Wokoma, O. A. F. (2015). Levels of Total Hydrocarbons in Water and Sediment of a Polluted Tidal Creek, Bonny River, Niger Delta, Nigeria. *International Journal of Scientific and Technology Research*, 3(12), 351-354.