HUMAN HEALTH RISKS ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SELECTED SEAFOOD FROM NIGER DELTA NIGERIA

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ABSTRACT

The concentration of polycyclic aromatic hydrocarbons (PAHs) in selected seafood samples (prawn, periwinkle, crab and oyster) were determined using Gas chromatography flame ionization detector to evaluate the risk on human health through the consumption of the seafood. Probable human health risks associated with the seafood consumption was evaluated using several models. The Dietary Daily Intake (DDI) value for total PAHs, carcinogenic PAHs, carcinogenic toxic equivalents (TEQ) and PAH4 were highest for Oyster with values of 34.40, 2.64, 32.13 and 8.35 mg/kg. Carcinogenic human health risk assessment using carcinogenic toxic equivalents ranged from 1.85 to 32.13 and cumulative excess cancer risk (ECR) showed a value of 0.00147. This indicates that consumption of oyster has a higher potential to cause carcinogenic risks. Comparison of TEQ values for the seafood and the screening value (SV) showed that the screening value were lower indicating tendencies of potential health effect. The calculated values of PAH4 index for all the assessed seafood exceeded the recommended limit of 0.03 mg/kg by European Union for PAHs in fishery products, signifying probable carcinogenic risk from the seafood consumption. The sum of PAHs (∑ PAHs) and carcinogenic PAHs (∑CPAHs) were computed and was highest in oyster with values of 279.01 and 18.56 mg/kg. Some diagnostic ratios were used to discriminate the source of PAHs and the ratio of Indeno(1,2,3-cd)pyrene/(Indeno(1,2,3-cd)pyrene + Benzo(g,h,i)perylene) IndP/ (IndP + BghiP) was greater than 0.2 but less 0.5 for all seafood samples which is an indication of contribution from petroleum and its products.

Keywords: Carcinogenic risks, Seafood, PAHs, Dietary daily intake, screening value

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are prevalent persistent organic contaminants that is present in nearly all ecological matrices including dust, soil, air and water[1]. Their mode of production is principally from the combustion of biomass and fossil fuels and the pyrosynthesis of organic materials[2]. They are considered one of the highest priority pollutants in the environment due to their widespread

nature, mode of formation and toxicity profiles. More also, a handful of PAHs are known to be carcinogenic, mutagenic, genotoxic, immunotoxic and endocrine-disrupting chemicals[1].

Seafood describes various creatures from the ocean and is categorized into shellfish (e.g. Oysters, squid, missile, lobster, prawns, crab and shrimp) and fish. Seafood is an excellent source of protein and its low – calorific value makes it a healthier alternative to red meats or poultry. They are usually rich in Vitamins A, E, C and D as well as calcium and iron[3]. Anthropogenic influences on aquatic habitats, especially arising from increased industrialization has heightened research on the safe level of seafood. PAHs and heavy metals, among others have continued to pose such environmental hazard[4].

The concentrations of polycyclic aromatic hydrocarbons are particularly of interest because seafood are a class of delicacy for humans. Seafood has become more popular worldwide. However, this growth has attracted the concern of researchers working on the toxic effects of PAHs. Among sea-food, which can be contaminated with PAHs during processing are fish, shrimp, crab, oyster, periwinkle, scallop, and mussels. PAHs can also be spawned in their bodies through metabolic activities (deposits through air and soil) which can be a clue to accumulation of PAHs in the food chain[5].

Researchers such as Zhang et al.[6] have evaluated the level of Polycyclic aromatic hydrocarbons in aquatic species and found fluoranthene, phenanthrene and anthracene present in more than 50% of aquatic seafood such as mandarin fish, Japanese Spanish mackerel, periwinkle, crab, oyster and shrimp. The concentrations of PAHs were remarkably for fish, shrimps, and crabs exceeding the maximum allowable levels of 30 μg/kg established by the French government in 2000[7]. Pollution of the Environment through fossil fuel combustion, oil spillage can be a source of PAH contamination mostly in fish, fishery products and seafood. Benzo(a) pyrene (BaP) is used by many researchers as an indicator for assessing the presence and consequence of carcinogenic PAHs in food. Maximum permissible levels of the carcinogenic PAHs are usually put in place by regulatory organizations to protect public health for some foods where smoking or drying practices might lead to a high level of PAHs contamination. Assessment of the maximum levels of PAHs is also essential in foods wherever pollution of the environment may lead to elevated levels of impact on the fish and fishery products and seafood.

Contamination of seafood by Polycyclic aromatic hydrocarbons can be from the following sources atmospheric deposition, water (deposition and transfer). Anthropogenic sources include stubble

burning and dispersion of contaminated sewage sludge on farmlands, exhausts from automobiles and oil pollution of surface waters[8,9].

This article is aimed at evaluating the human health risks from consumption of selected seafood such as prawn, periwinkle, crab and oyster commonly consumed in the Southern Nigeria.

MATERIALS AND METHODS

Description of Study Area

Ibeno (Latitude 4°33'54.22" N, Logitude 8° 04' 21.29" E) is located in Akwa Ibom state in the south east of Nigeria. Ibeno town lies on the eastern side of the Kwa Ibo river about three kilometers from the river mouth, and is one of the largest fishing settlements on the Nigerian coast. Ibeno lays the mangrove forest belt of the Niger Delta region of Nigeria, it is bounded in the west by eastern Obolo local government area, to the north by Onna, Esit Eket and Eket, to the south by the Atlantic Ocean.

The Ibeno River is constantly receiving organic waste, litter, petroleum hydrocarbons, and toxic chemicals which are source of contamination. The area lies in the Niger Delta wet equatorial climatic which experience extensive-rainy season from March to November, with mean annual rainfall range from 1500 mm around the northern fringe to 4500 mm around the coastal margin[10, 11.]

The study area is in the Niger Delta of Nigeria and its geology is thus characteristic of the Niger Delta Basin. The area forms part of a geographical classification of the Quaternary and Tertiary formations of the Niger Delta, which is comprises of three core geologic classifications: The Benin Formation, Agbada Formation, and Akata Formation[12.] It is situated in the Gulf of Guinea and extends throughout the Niger Delta Province, as defined by Klett[13], see Figure 1

Sample Collection

The samples were collected from Ibeno River. A saltwater within the shores of the Atlantic Ocean. The samples were labelled sample A (Prawn), sample B (periwinkle), sample C (Crab) and sample D (Oyster) respectively.

Reagents

The reagents used for the analysis includes Acetone, dichloromethane, anhydrous sodium sulphate (Purity, 99%), -Silica gel (200-400 mesh) (BDH England). All the chemicals and reagents used were of analytical grade and high purity.

Extraction and analysis of PAHs in seafood sample

Ten grams of the sample was mashed with mortar and pestle and then blended with 10g of anhydrous sodium sulphate in an extraction thimble. 150 ml of 1:1 dichloromethane (DCM) /acetone was placed in a round bottom

flask with some clean boiling chips, the extraction thimble was allowed to drain freely for the duration of the extraction period. The round bottom flask was connected to the Soxhlet extractor and the sample extracted for 4-6 hours. The extract was allowed to cool after the extraction process and concentrated in rotary evaporator at 600^{o}C to about 2ml; this was solvent exchanged to hexane phase by addition of excessive hexane and then the volume of the hexane solution was reduced to 2-5ml in rotary evaporator. The final solvent-exchanged extracts were quantitatively transferred to 3g silica gel chromatographic column, which was topped with about 1cm anhydrous granular sodium sulphate which had been pre-conditioned using 20 ml of hexane for sample clean up and fractionation as below.

Fractionation of Sample Extract

A 1ml portion of the sample extract was passed through a packed polypropylene column packed with 10g of activated silica gel. The saturated hydrocarbons were fractionated first by elution with n-hexane and collected in a conical flask, while, the polycyclic aromatic hydrocarbons were fractionated by elution with methylene chloride and collected into a different conical flask. Both sample fractions were concentrated to about 2ml under a gentle stream of air in a fume cupboard. The extracts (aromatic and saturated fractions) were transferred into different 2ml sample vials by the use of a 5 ml pipette.

Gas Chromatography Flame Ionization Detector (GC-FID) Analysis

The polycyclic aromatic hydrocarbons were determined using a Gas Chromatograph (Agilent 6890 N) with HP-5 fused silica column of dimensions 30 m × 250 µm × 250 µm film thickness and 5% phenyl methyl siloxane capillary column. The oven temperature program was maintained at 400 ^{o}C for 2 min and then increased at a rate of 100 ^{o}C/min until a temperature of 3200 ^{o}C was reached. The final temperature was held for 2 min with Nitrogen carrier gas maintained a flow rate of 2.6 ml/min and pressure of 10.4 psi which was ma. PAH analysis of the aromatic hydrocarbon fraction of the samples extract was performed with Agilent 7820 GC with FID to identify Polycyclic Aromatic Hydrocarbons (PAHS). Hydrogen was used as the carrier gas.

Health- Risk Assessment of Seafood Consumption

There are several databases that provide information on the ingestion rate for seafood by humans. The United State Environmental Protection Agency approach based on the estimate of risk-based consumption limits expressed in terms of real meals with special reference to fish was adopted for this research.

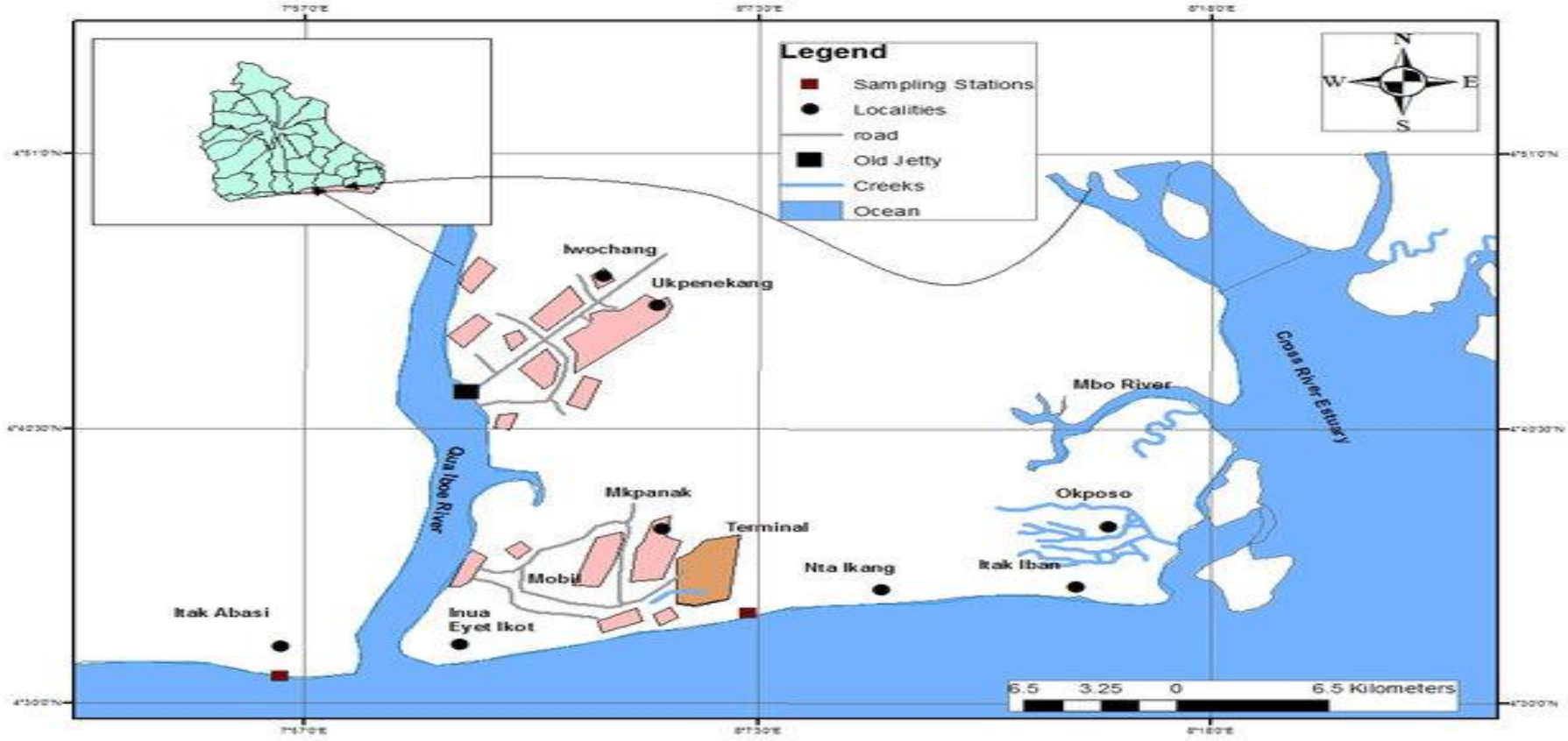

Figure 1. Map showing sample collection site

All consumption limits and risk factors were computed assuming, for adults, a meal size of 227 grams and a body weight (BW) of 70 kg[14]. The predictable daily intake per meal size of seafood (EDI) was calculated according to Eq (1). Where MS is the meal size, C is the PAH concentration (mg kg^{-1} (w/w.)) and BW is the body weight. Based on the USEPA Regulation[15], it was presumed that the ingestion dose is equal to the adsorbed contaminant dose and that cooking has no effect on the contaminants[16].

Carcinogenic and Mutagenic Potency

The carcinogenic and mutagenic potency of PAHs were estimated by comparing the toxicity or carcinogenic/mutagenic potency of the individual PAHs to that of benzo[a]pyrene (BaP). The BaP carcinogenic (BaPTEQ) and BaPMEQ) for the PAH compounds were estimated by means of the following equations

$$\text{BaP TEQ} = \sum Ci \times \text{BaPTEF}, \quad (1)$$

$$\text{BaP MEQ} = \sum Ci \times \text{BaPMEF}, \quad (2)$$

Where BaPTEF is the carcinogenic potency relative to BaP, BaPMEF is the mutagenic potency relative to BaP, and Ci is the concentration of the individual PAH compound. The values of the BaP carcinogenic (BaPTEF) and mutagenic (BaPMEF) equivalency factors for the seven carcinogenic PAHs are given in Table 1.

Potential human health risk from seafood consumption and the regulatory

The assessment of the toxicological risk of the polycyclic aromatic hydrocarbon (PAHs) concentration in seafood was evaluated by comparing the detected level with permissible limits. Concentration of PAHs in seafood for the various individual PAH concentrations, total PAH concentrations and total carcinogenic PAHs (sum of the carcinogenic PAHs, namely Benzo(a)anthracene, Chrysene, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, Indeno(1,2,3) perylene, Dibenzo(a,h)anthracene). The concentrations of Benzo(a)pyrene (B(a)P), was use as indicator for the presence and consequence of carcinogenic PAHs in seafood as specified in the European Commission Regulation (EC) No1881/2006, and were compared with the permissible level of 0.005 mg/kg for benzo [a] pyrene[17].

Several models were employed to assess the human health risks due to exposure to PAHs through consumption of seafood (dietary intake). The Dietary Daily Intake (DDI) concentrations of Polycyclic aromatic hydrocarbons consumption of seafood were evaluated. Carcinogenic risks were also evaluated by computing the carcinogenic potencies of the concentrations of different PAHs (B(A)Pteq), the Carcinogenic toxic equivalents (TEQs) and the Excess Cancer

Risk Index. Table 2 and equations (3) to (8) show values used for the human intake models.

The Dietary Daily Intake (DDI) of Polycyclic Aromatic Hydrocarbons

The model for evaluating the Dietary Daily Intake (DDI) of PAHs in seafood for the mature adult populace is shown in equation (3) according to Halek [18]. The daily intake of PAHs from seafood was estimated by multiplying the respective PAH concentration by the rate of ingestion (IFR) based on the assumption that the average body weight of an adult Nigeria is seventy kilograms (70 kg). Evaluation of Dietary Daily Intake (DDI) was calculated for individual PAHs, the sum of the 16 EPA PAHs and for the carcinogenic PAHs.

The Dietary Daily Intake (DDI) = Ci × IFR (3)

Risk Assessment of Carcinogenic PAHs in Seafood

Evaluation of the risk of cancer by ingestion through dietetic intake or exposure to PAHs in the seafood was achieved by using some indices such as the PAH4 index, the carcinogenic potency of individual PAHs, carcinogenic toxic equivalents (TEQs) and the excess cancer risk (ECR) equations (4) to (8). Organizations such as the European Food Safety Authority in 2008 on the request of European Commission on Polycyclic Aromatic Hydrocarbons in Food in their Technical panel on toxins and contaminants in the food chain proved that PAH4 is a more appropriate indicator of PAHs in Food[19]. This was then computed using as the sum of the values of four dissimilar PAHs such as benzo[a]anthracene, chrysene, benzo[b]fluoranthene, and benzo[a]pyrene. The result of PAH4 index for the seafood species was then compared with the maximum allowable concentrations to determine the effect of carcinogenic PAHs in the samples.

The European Union (EU) Commission Regulation in 2014 proposed a maximum permissible limit of 0.03 mg/kg for the sum of PAH4 for polycyclic aromatic hydrocarbons (PAHs) in traditionally smoked fishery products and this value was applied in the computation.

The PAH4 Index (PAH4) = (B[a]A + Chr + B[b]FL + B[a]P) (4)

The Carcinogenic potencies of different PAHs B(A)Pteq were computed by multiplying the PAH concentration in the sample by the individual toxicity equivalency factor (TEF)[20] Carcinogenic potencies of individual PAHs

(B(A)Pteq) = Ci × TEFi (5)

The carcinogenic toxic equivalents (TEQs) was calculated from the above formula by addition of the carcinogenic potencies B(A)Pteq) of individual PAHs

Carcinogenic toxic equivalents
(TEQs) = ∑B(A)Pteq (6)

The screening value (SV) is the maximum absorption level of any toxicant in edible tissue that is of potential public health concern. The equation below was used to calculate the screening value and compared with TEQ value to ascertain the health risks of PAHs to humans through seafood consumption.

Screening Value (SV) = (RL/CSF) × BWSCR (7)
The equation below was used to calculate the excess cancer risk through dietetic exposure to PAHs by seafood consumption. Excess Cancer Risk (ECR)

ECR = ∑Q × B(A)Pteq × SCR × EDBW × ATn (8)

RESULTS AND DISCUSSION

The concentration of PAHs in Seafood samples

The concentration of PAHs determined in seafood are shown in Table 1. A total of eighteen PAHs were analyzed in the seafood. The Σ18 PAHs concentration in the seafood samples from the Ibeno river showed the highest concentration of PAHs in Oyster followed by Crab while prawn is the lowest (Table 1). The reason may be primarily due to the increased ability of these seafood to absorb PAHs from soils and sediments. Significantly higher concentrations of PAHs were found in

The total distributions of polycyclic aromatic hydrocarbons ∑ PAHs in mg/kg in the samples as follows; Prawn with 71.00, Periwinkle 27.49, Crab 168.54 and Oyster 279.01. The total distribution of PAHs in Oyster was found to be higher than other seafood samples as shown in (Table 1). This could be attributed to Oyster which is known to filter a larger volume of water. This is in accordance to various researches which showed that Oyster truly accumulates a lot of PAH pollutants and could also be ascribed to differences in fat and moisture compositions of each seafood species including the nature of the skin cover [21].

The total carcinogenic PAHs concentration (∑CPAHs) were highest in Oyster (18.56 mg/kg), Similar reason stated above may be attributed to the high concentrations observed. The high concentration of total carcinogenic PAHs in the seafood under investigation should be of immense concern as they a major source of delicacy for people in the area. Benzo(a)pyrene concentrations were the highest of the carcinogenic PAHs in Oyster, Crab and Periwinkle. Prawn Dibenzo (a, h) anthracene and Benzo (k) fluoranthene are higher carcinogenic PAHs observed. Significant consideration has been given to B(a)P in seafood because of its carcinogenicity to humans [22].

Table 1. Concentration of PAHs in mg/kg from selected seafood samples

	Samples	Prawn	Periwinkle	Crab	Oyester	BaPTEF	BaPMEF
	PAHs (mg/kg)						
1	1,2,3-Trimethylbenzene	1.02	2.32	0.66	35.87		
2	Naphthalene	6.03	1.57	0.01	1.65		
3	2-Methylnaphthalene	17.67	3.29	0.49	1.58		
4	Acenaphtylene	0.11	0.78	0.08	0.50		
5	Acenaphthene	8.42	2.86	2.67	1.66		
6	Fluorene	10.04	0.00	8.35	6.62		
7	Anthracene	0.31	0.32	7.26	7.35		
8	Phenanthrene	10.49	2.67	2.83	2.31		
9	Fluoranthene	4.57	0.99	7.50	4.02		
10	Pyrene	1.51	0.66	4.44	2.94		
11	Benz(a)anthracene	0.28	0.13	0.40	0.01	0.10	0.08
12	Chrysene	0.05	0.04	0.01	0.01	0.00	0.02
13	Benzo(b)fluoranthene	0.45	0.05	0.02	3.01	0.10	0.25
14	Diben(a,h)anthracene	2.40	0.26	0.83	5.32	1.00	0.29
15	Benzo(a)pyrene	1.50	3.73	2.95	5.32		
16	Benzo(k)fluoranthene	2.06	0.80	1.03	2.19	0.01	0.11
17	Indeno(1,2,3-cd)pyrene	0.58	3.00	2.59	2.71	0.10	0.31
18	Benzo(g,h,i)perylene	3.60	4.00	126.41	195.97		
	∑ PAHs	71.10	27.49	168.54	279.01	USEPA(2012)	DURANT(1996)
	∑ CPAHs	7.33	8.02	7.83	18.56		

Table 2. Estimated Dietary daily intake (DDI), Carcinogenic potencies (B(A)Pteq), and Excess cancer risk (ECR) of PAHs in from selected seafood

Samples	RfD	TEF	Prawn	DDI	B(A)Pteq	ECR	Periwinkle	DDI	B(A)Pteq	ECR	Crab	DDI	B(A)Pteq	ECR	Oyester	DDI	B(A)Pteq	ECR	BaPTEF	BaPMEF
PAHs (mg/kg)		0.001		(mg/day)	(mg/kg)	(mg/kg)		(mg/day)	(mg/kg)	(mg/kg)		(mg/day)	(mg/kg)	(mg/kg)		(mg/day)	(mg/kg)	(mg/kg)		
1,2,3-Trimethylbenzene			1.0178	0.14493	0	0	2.32	0.33099	0	0	0.66	0.09398	0	0	35.87	5.10769	0	0		
Naphthalene	0.02	0.001	6.0276	0.85833	0.00603	2.8E-07	1.57	0.22306	0.00157	7.2E-08	0.01	0.00075	5.3E-06	2.4E-10	1.65	0.23559	0.00165	7.6E-08		
2-Methylnaphthalene			17.6686	2.51601	0	0	3.29	0.46845	0	0	0.49	0.07003	0	0	1.58	0.22428	0	0		
Acenaphtylene	NA	0.001	0.1132	0.01612	0.00011	5.2E-09	0.78	0.11133	0.00078	3.6E-08	0.08	0.01198	8.4E-05	3.8E-09	0.50	0.0705	0.0005	2.3E-08		
Acenaphthene	0.06	0.001	8.4199	1.19899	0.00842	3.8E-07	2.86	0.40761	0.00286	1.3E-07	2.67	0.38045	0.00267	1.2E-07	1.66	0.23603	0.00166	7.6E-08		
Fluorene	0.04	0.001	10.0436	1.43021	0.01004	4.6E-07	0.00	0.00013	9E-07	4.1E-11	8.35	1.18864	0.00835	3.8E-07	6.62	0.94314	0.00662	3E-07		
Anthracene	0.3	0.001	0.3097	0.0441	0.00031	1.4E-08	0.32	0.04614	0.00032	1.5E-08	7.26	1.03392	0.00726	3.3E-07	7.35	1.04627	0.00735	3.4E-07		
Phenanthrene	0.03	0.001	10.4875	1.49342	0.01049	4.8E-07	2.67	0.38039	0.00267	1.2E-07	2.83	0.40336	0.00283	1.3E-07	2.31	0.32845	0.00231	1.1E-07		
Fluoranthene	0.04	0.001	4.5706	0.65085	0.00457	2.1E-07	0.99	0.14132	0.00099	4.5E-08	7.50	1.06803	0.0075	3.4E-07	4.02	0.57179	0.00402	1.8E-07		
Pyrene	0.03	0.001	1.5056	0.2144	0.00151	6.9E-08	0.66	0.09377	0.00066	3E-08	4.44	0.63191	0.00444	2E-07	2.94	0.41863	0.00294	1.3E-07		
Benz(a)anthracene	NA	0.1	0.2812	0.04004	0.02812	1.3E-06	0.13	0.01857	0.01304	6E-07	0.40	0.05709	0.04009	1.8E-06	0.01	0.00142	0.001	4.6E-08	0.10	0.08
Chrysene	NA	0.01	0.0549	0.00782	0.00055	2.5E-08	0.04	0.0059	0.00041	1.9E-08	0.01	0.00128	0.00009	4.1E-09	0.01	0.00199	0.00014	6.4E-09	0.00	0.02
Benzo(b)fluoranthene	NA	1	0.447	0.06365	0.447	2E-05	0.05	0.00713	0.0501	2.3E-06	0.02	0.00271	0.019	8.7E-07	3.01	0.42858	3.0097	0.00014	0.10	0.25
Diben(a,h)anthracene	NA	5	2.4022	0.34207	12.011	0.00055	0.26	0.03762	1.321	6E-05	0.83	0.11889	4.1745	0.00019	5.32	0.75721	26.5875	0.00121	1.00	0.29
Benzo(a)pyrene	NA	0.01	1.504	0.21417	0.01504	6.9E-07	3.73	0.53149	0.03732	1.7E-06	2.95	0.41997	0.02949	1.3E-06	5.32	0.75694	0.05316	2.4E-06		
Benzo(k)fluoranthene	NA	0.1	2.0623	0.29367	0.20623	9.4E-06	0.80	0.11446	0.08038	3.7E-06	1.03	0.14723	0.10339	4.7E-06	2.19	0.31126	0.21858	1E-05	0.01	0.11
Indeno(1,2,3-cd)pyrene	NA	0.1	0.5828	0.08299	0.05828	2.7E-06	3.00	0.42683	0.29974	1.4E-05	2.59	0.36833	0.25866	1.2E-05	2.71	0.38536	0.27062	1.2E-05	0.10	0.31
Benzo(g,h,i)perylene	NA	0.01	3.6025	0.513	0.03603	1.6E-06	4.00	0.56923	0.03997	1.8E-06	126.41	18.0011	1.26413	5.8E-05	195.97	27.9062	1.95971	8.9E-05		

Table 3. Estimated Carcinogenic Risk Indices of PAHs in mg/kg from selected seafood

Carcinogenic Risk Index	Prawn	Periwinkle	Crab	Oyster
∑ DDI	10.12	3.91	24.00	39.73
∑ DDI for carcinogenic PAHs	1.04	1.14	1.12	2.64
TEQ	12.84	1.85	5.92	32.13
PAH4	2.29	3.95	3.38	8.35
SV	0.0006734	0.000673	0.000673	0.000673

Table 4. Calculated diagnostic ratios of PAHs from selected seafood

Diagnostic Ratios of PAHs	Prawn	Periwinkle	Crab	Oyster
Ant/(Ant +Phen)	0.029	0.108	0.719	0.761
BaA/(BaA + Chry)	0.837	0.759	0.978	0.417
Flt/(Flt +Pyr)	0.752	0.601	0.628	0.577
IndP/(IndP + BghiP)	0.139	0.429	0.020	0.014

Human health risk assessment of PAHs in Seafood

Dietary daily intake (DDI) of PAHs from consumption of Seafood

The high rate of consumption of seafood in the southern part of Nigeria necessitates the employment of the concept of DDI to assess the health risk of toxicants (PAHs). Table 2 shows the dietary daily intake (DDI) of PAHs in the analyzed Seafood samples for an adult (70 kg) and the daily seafood consumption rate (0.1424 kg/d) for the population in southern Nigeria. The values of DDI (kg/day) estimated from individual PAHs concentrations in Seafood are shown in table 2. The value for Benzo(a)pyrene, one of the greatest potent animal carcinogens were 0.21 for Prawn, 0.114 for Periwinkle, 1.04 for Crab and 0.311 for Oyster.

The sum of the DDI for the various seafood are 10.12, 3.91, 24.00 and 39.73 for Prawn, Periwinkle, Crab and Oyster. The sum of the carcinogenic DDI are 1.04, 1.14, 1.11 and 2.64 mg/kg (Table 3). Oyster has the highest DDI and the carcinogenic DDI of 39.73 and 2.64 mg/kg. The implication of the result is the consumption of oyster will expose them to high risk of carcinogenic CPAHs which may have an adverse effect on their health. The high values of DDI may be attributed to many factors. It may be connected with activities of petroleum industries which introduces

hydrocarbons into the water body and over time accumulate in the seafood[2]. Other possible sources of PAHs include discharges from the activities of diesel and petrol engine boats, the effluent from discharge point close to the oil terminal and refinery effluent which from the petroleum tank farm to the Ibeno River[5, 20].

Carcinogenic potencies (B(A)Pteq) and risk assessment of PAHs in Seafood

The results of the carcinogenic potencies (B(A)Pteq) of the PAHs are shown in Table 2 . The carcinogenic potencies of the PAHs varied among the seafood under investigation. Dibenzo(a,h)anthracene has the highest value for Prawn (12.01 mg/kg), periwinkle (1.32 mg/kg), crab (4.17 mg/kg) and Oyster (26.48 mg/kg). The values were higher than the results obtained from smoked fish species by some researchers such as Yusuf et al. [23] and Tongo et al. [24]. The values are higher than the recommended allowable limit of the maximum acceptable level of 0.005 mg/kg for benzo[a]pyrene in seafood by European Commission [25].

The result of PAH4 showed that oyster has the highest value (8.35 mg/kg), periwinkle (3.95 mg/kg), crab (3.38 mg/kg) and prawn (2.29 mg/kg) as shown in Table 3. The computed values are higher than the maximum allowable limits of (0.03 mg/kg) recommended by the European Union for PAHs in smoked fish and smoked fishery products [19]. The implication is that continuous consumption of these seafood could constitute possible health effects to humans.

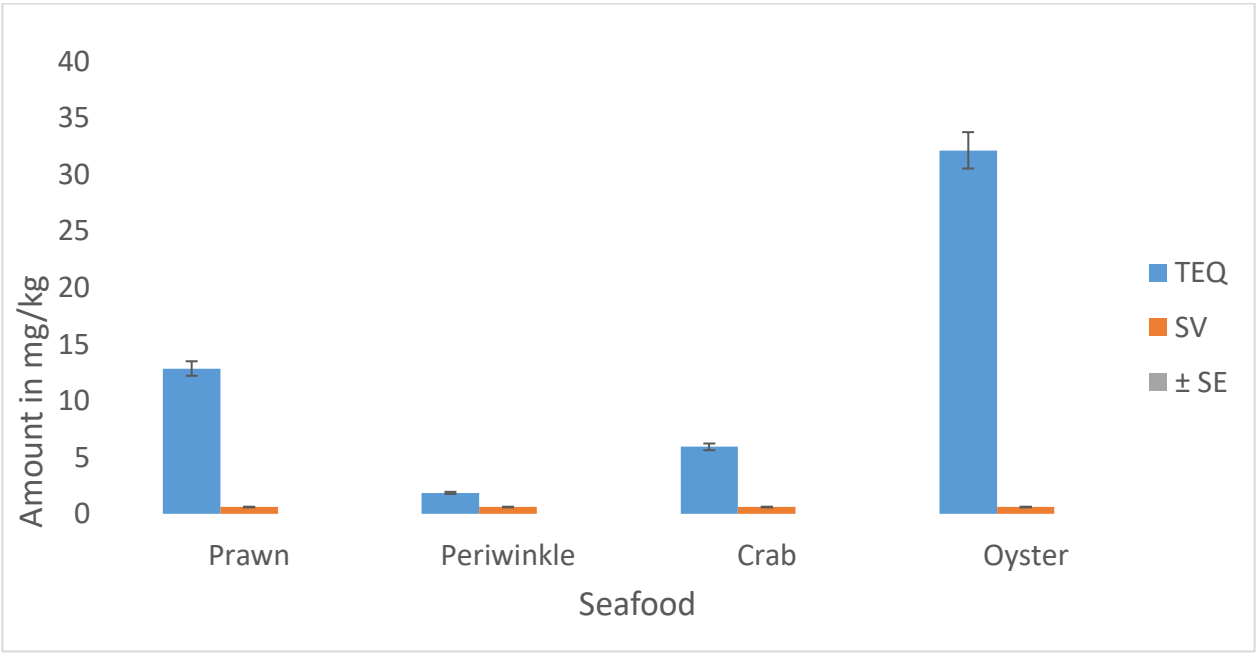

Figure 2. Plot of the carcinogenic toxic equivalents (TEQ) and the screening values (SV)

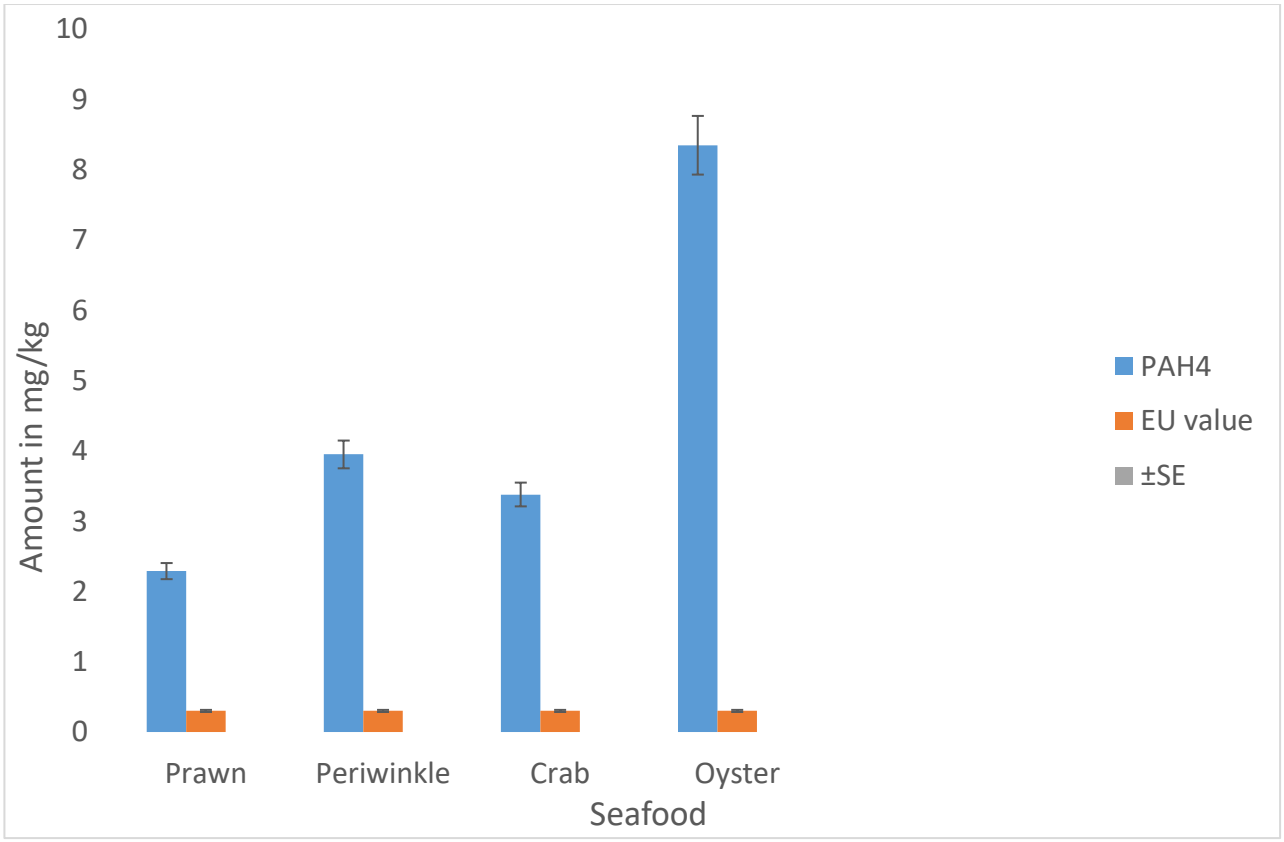

Figure 3. Comparison of PAH4 index and the recommended value by European Union

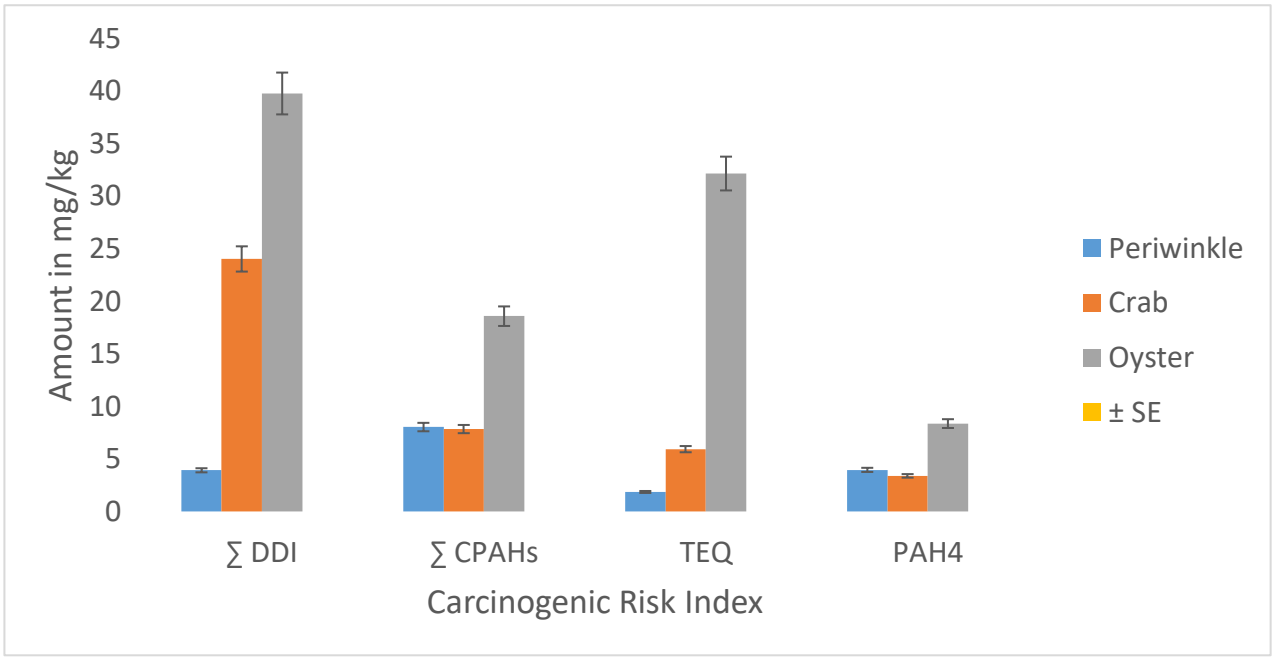

Figure 4. Comparison of the carcinogenic risk indexes for the seafood

Carcinogenic toxic equivalents (TEQ) and Screening value (SV) of PAHs in seafood

The Carcinogenic toxic equivalents (TEQ) is used to determine the level of carcinogenicity of PAHs in seafood. The calculated results for TEQ for the seafood samples as shown in Table 3 are Prawn (12.84 mg/kg), Periwinkle (1.85 mg/kg), Crab (5.92 mg/kg) and Oyster (32.13 mg/kg) respectively. The result indicates that Oyster and Prawn have the highest TEQ and have the potential to cause carcinogenic risk. The value of TEQ reported by authors like Iwegbue et al. [26], Yusuf et al. [23], and Tongo et al. [24] for some fish species in the Niger Delta showed some appreciable value of TEQ.

Screening value (SV) of PAHs in the seafood

The screening value (SV) is very useful when it comes to health risk management. The USEPA has established a screening value by estimating a bodyweight of 70 kg for adult and consumption rate of 0.1424 kg/day respectively[14]. The calculated screening value (SV) are shown in table 3. The essence of screening value is to assess the health risk of the Polycyclic hydrocarbon to human beings through the consumption of seafood. The screening value is the threshold concentration of a chemical in edible tissues that is of potential public health concern [27, 28]. The computed screening value for the seafood was 0.00067 mg/kg. The result showed the SV was lower than the TEQ values for all the seafood samples. This is in agreement with the result of Nozar et al.[29] who reported higher TEQ values to SV for some seafood. When the calculated TEQ value is above the SV, there are tendencies of potential health effect.

Excess cancer risk and PAH4 index of PAHs in the seafood

The excess cancer risk (ECR) was calculated based on the assumption that the average weight of an adult population whose diet/meal is exposed to PAHs is 70 kg. The projected ECR due to lifetime exposure to PAHs through seafood consumption were compared to the permissible limit of 10^{-6} set by USEPA[30]. The United states environmental agency specifies a certain level of risk that may be acceptable especially where there is a lifetime cancer risk of one in a million (ECR = 10^{-6}) for a 70 year lifetime period, but when there is a further lifetime cancer risk of one in ten thousand or more (ECR = 10^{-4}), it is considered serious[31].

. The results in Table 2 showed that the calculated ECR for seafood were lower than the USEPA permissible limit (10^{-6}) for a few PAHs. In Prawn all ECR Benzo(b)fluoranthene (2.0×10^{-5}) and Diben(a,h)anthracene (5.5×10^{-4}), Periwinkle Diben(a,h)anthracene (6×10^{-5}) and Indeno(1,2,3-cd)pyrene (1.4×10^{-5}); crab Diben(a,h)anthracene (1.9×10^{-4}),

Indeno(1,2,3-cd)pyrene (1.2×10^{-5}) and Benzo(g,h,i)perylene (5.8×10^{-5}); Oyster Benzo(b)fluoranthene (1.4×10^{-4}), Diben(a,h)anthracene (1.21×10^{-3}), Benzo(k)fluoranthene (1.0×10^{-5}), Indeno(1,2,3-cd)pyrene (1.2×10^{-5}), Benzo(g,h,i)perylene ($8.9 \times^{-5}10$).

Nevertheless, cumulative excess cancer risk for Prawn (0.00058653 mg/kg), Periwinkle ($8.46E^{-05}$ mg/kg), Crab (0.00027046 mg/kg), and oyster (0.001467153 mg/kg) all exceeded the USEPA's permissible cancer risk level of 10^{-6} This shows that consumption of these seafood could result in potential cancer risk. Some researchers such as (Dhananjayan, and Muralidharan [32] and Bandowe, et al.[33] reported predictable excess cancer risk (ECR) from consumption of fish greater than the permissible limit of the USEPA. Other researchers such as Ossai et al.[34] in their separate research reported ECR higher than the USEPA permissible limit for of polycyclic aromatic hydrocarbons (PAHS) in roasted plantain and plantain chips sold in Warri, Delta State.

Besides, similar studies on excess cancer risk from the consumption of other foods have also been reported above the guideline values[35].

The 6-ring PAHs are the dominant PAH homologues in the seafood samples with Benzo(g,h,i)perylene having the highest concentration. Considering the total concentrations of 18 PAHs, 6-ring PAHs constituted up to 92.4%. 2-Methylnaphthalene was dominant in Prawn.

Research has shown that toxicity and persistent of PAHs increases with an increase in the number of rings. The four rings fused PAHs such as benzo (a)anthracene and chrysene, are not so much carcinogenic and persistent. The five or six-fused ring PAHs, such as benzo(b)fluoranthene, benzo(a-)pyrene, and indo(1,2,3-cd)pyrene, Benzo(g,h,i)perylene are very potent carcinogens and also persist[1].

Source Apportionment of PAHs

Source identification and distribution of PAHs provides useful information on the fate and transference of PAHs in the environments. It is useful in for source control and to minimize risk. Some diagnostic ratios, such as Ant/(Ant + Phen), BaA/(BaA + Chry), Flt/(Flt + Pyr) and IndP/(IndP + BghiP), have been used to discriminate between petrogenic and pyrogenic sources[26, 36, 37]. The ratios of BaA/ (BaA + Chry) and IndP/(IndP + Chry) with values less than 0.2 designate petroleum and petrogenic sources. Computed ratios of BaA/(BaA + Chry) greater than 0.2 and less than 0.35; IndP/ (IndP + BghiP) greater than 0.2 and less 0.5 propose contributions from petroleum combustion. BaA/(BaA + Chry) and IndP/ (IndP + Chry) ratios greater than 0.5 indicate contributions from combustion of

coal, grass and wood[1]. The table of the computed diagnostic ratios show that the IndP/ (IndP + BghiP) greater than 0.2 and less 0.5 for all seafood samples which indicate contributions from petroleum combustion such as liquid fossil fuels, vehicles and crude oil. The possible sources of the contamination based sources such as two-stroke vessel discharge.

CONCLUSION

Assessment of polycyclic aromatic hydrocarbons in commonly seafood samples such as prawn, periwinkle, crab and oyster showed the sum of PAHs (∑ PAHs) and carcinogenic PAHs (∑ CPAHs) to be high in was highest in Oyster. Some diagnostic ratios were used to discriminate the source of PAHs as all seafood samples indicate contributions from petroleum. The human health risks associated with seafood consumption was evaluated using certain the Dietary Daily Intake (DDI), carcinogenic toxic equivalents (TEQ) and PAH4 and cumulative excess cancer risk (ECR) were highest for Oyester. This presupposes that consumption of oyster frequently has a higher potential to cause carcinogenic risks. This was confirmed with the result of the screening value (SV) lower than the TEQ values for seafood indicating tendencies of potential health effect. The result from research showed the calculated values of PAH4 index for all the assessed seafood exceeded the recommended permissible limit by European Union for PAHs in fishery products, indicating potential carcinogenic risk from seafood consumption.

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Declarations

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The authors declare that there is no conflict of interest

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