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Profile, health risk assessment and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in terrestrial snails and some aquatic species consumed in parts of Ogbia LGA, Bayelsa, Nigeria

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Abstract. The determination of Polycyclic Aromatic Hydrocarbons (PAHs) in giant land snails (*Achatina achatina*) and three aquatic species [mudfish (*Clarias anguillaris*), mud crab (*Scylla serrata*), and prawn (*Palaemon maculatus*)] in Ogbia LGA, their origin and their health implications on consumers were the focus of this work. PAHs analysis was done with Gas Chromatography couple to a Mass Spectrometer Detector (GC-MS), after extractions with 1:1 mixture of hexane and dichloromethane and clean-up with silica gel column. Total PAHs ($\sum_{16}$PAHs) in µg/kg in edible tissues averaged: 3342.26±845.70 for snails, 393.14±452.50 for fishes, 382.22±235.72 for crabs, and 344.81±91.93 for prawns respectively. The hazard indices showed some potential for non-carcinogenic harms: very high for snails, moderately high for fishes and crabs, and slightly high for the prawns. The calculated benzo(a)pyrene equivalent concentrations (PEC) for species were higher than the estimated screening value (SV) of 3.95 µg/kg, an indications of possible carcinogenic effects on consumers of these foods. However, the excess cancer risk (ECR) did not indicate threat of additional cancer risk as most of the calculated values (except in some snails' samples with values < 10^{-4}) were less than the acceptable standard of $1.0x10^{-6}$ established by the USEPA. Source diagnostic ratios revealed that source of PAHs were largely pyrolytic. The presence of these PAHs in these edible species, and possible further accumulations and its attendant impacts on human's health calls for periodic monitoring.

***Keywords*:** hazard indices; carcinogenic; source diagnostic ratios; petrogenic; pyrogenic.

1. Introduction

Snails (*Achatina achatina*), mudfish (*Clarias anguillaris*), crabs (*Scylla serrata*), and prawn (*Palaemon maculatus*) have often serve as common delicacy in riverine communities of the Niger-Delta regions of Nigeria. This is because the rivers and wetlands provide convenient habitats for their easy survival, growth and multiplications. They represent a major source of proteins to those living in these coastal communities. They are known to have very low cholesterol, rich in vitamins, and essential polyunsaturated fatty acids (PUFAs), particularly Omega-3-PUFAs which have a major role in risk minimization of neurological problems and heart disease [1]. These foods are patronized by many local populations due to their health benefits in addition to their widespread availability and relatively low price. However, because of their ability to bio-accumulate certain pollutants from the environment, their consumption may also spell dooms for man's health if these pollutants are present beyond safe limits. One of such groups of pollutants of great concern to public health is poly-aromatic hydrocarbons (PAHs). PAHs are group of organic compounds with two or more fused rings. They serve as useful intermediates in the production of most substances such as: pesticides, pigments and dyes, plastics and plasticizers, and are ubiquitous in soil, air, aquatic, and biotic environments. Their genotoxic, carcinogenic, mutagenic and teratogenic properties [2, 3], and ability to cause endocrine disruptions with resultant diseases in animals and human [4-7] have earn some of them a place in the lists of priority pollutants [8]. Their presence in the environment may be natural or anthropogenic. Accountings for most sources of natural inputs are PAHs synthesized by certain plants and bacteria; and those resulting from transformation of natural organic precursors by diagenetic processes [9]. Contributions arising from emissions due to volcanic eruptions, natural forest fire, and moorland fire by lightning flashes constitute less significant sources of natural inputs [3]. In a contaminated environment, the proportions of PAHs from these natural sources are relatively very small in comparison to those of anthropogenic inputs [10, 11]. The anthropogenic sources of PAHs in the environment include: fuel combustion, industrial pyrolysis, vehicular exhausts emissions, oil spills, offshore drilling, and runoff from industrial and urban areas [12]. PAHs are found in coal and coal products, crude oil, and refined petroleum products. Incomplete combustion of fossil fuels, woods, grasses, and other organic substances also produces PAHs [13, 14]. Wastes

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incinerations and industrial processes such as: gasification of coal, production and refining of aluminum, iron, steel, and petroleum also result in the generation of PAHs as by-products [15, 16]. Usually, the anthropogenic sources of PAHs are classified as either petrogenic (inputs from petroleum or related products such as oil spills, road construction materials like coke, carbon black, coal tar, and asphalt) or pyrogenic (due to combustion processes like fossil fuel combustion, electric power generation, incineration of wastes, home heating and industrial emissions [17, 18].

Organisms in the environment may accumulate polycyclic aromatic hydrocarbons in their tissues through exposure to the contaminants in any of the following pathways: ingestion, respiration, or dermal contacts. The presence of PAHs in these organisms not only pose threats to their wellbeing and reproductive capacities, but also to human consumers of these products due to biomagnifications along the food chain [19]. PAHs are usually classified into low molecular weight PAHs (with 2 – 3 aromatic rings) and high molecular weight PAHs (with 4 or more aromatic rings). The latter are less acutely toxic but more carcinogenic and teratogenic [20].

Ogbia LGA is characterized by rivers, creeks, and mangroves which serve as habitats to various species such as: snails, fishes, crabs, and prawns, etc. However, being located in the heart of the Niger-Delta of Nigeria, notable for oil explorations and oil related activities with its attendant history of oil spills resulting from equipment failure, deliberate negligence, and vandalisms. Exposure of these organisms to oil related and industrial processes' contaminants like PAHs, and subsequent accumulations in body tissues has thus being envisaged. The lipophilic nature of PAHs and their high chemical stability could encourage easier penetration of biological membranes and accumulation in the fatty tissues of organisms following their uptake. Therefore, this study seeks to ascertain the source and levels of the sixteen priority PAHs in snails (*Achatina achatina*), mudfish (*Clarias anguillaris*), crabs (*Scylla serrata*), and prawn (*Palaemon maculatus*) in the study area and to use the human health risk assessment model to evaluate the potential health risk associated with their consumptions.

2. Experimental

2.1. Study area

Ogbia LGA, Balyesa State, Nigeria was the site for collection of samples. It is located in the heart of the Niger Delta (Fig. 1). The Ogbia people primary occupation include: fishing, farming, and trade, with agriculture playing a major role in their local economy. The mangroves, rivers, and creeks prevalence in the region are very crucial for the support of diverse ecosystem and sustenance of the local economy. The area being an oil producing region is also characterized by numerous oil and gas operations which on one hand have contributed to the growth of the economy, and on the other hand to environmental and social challenges.

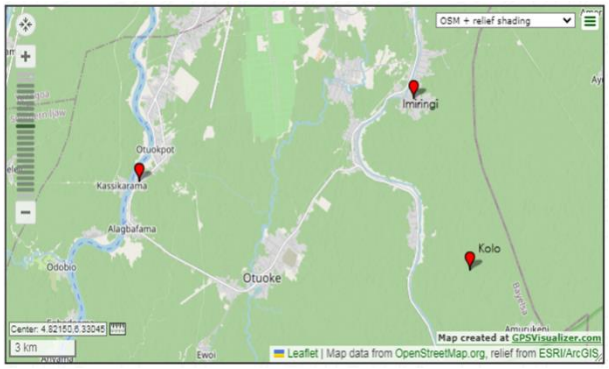

Figure 1. Map showing the communities in Ogbia LGA where the samples were taken.

2.2. Sample collection

Samples of edible giant land Snails (*Achatina achatina*), mudfish (*Clarias anguillaris*), crabs (*Scylla serrata*), and prawn (*Palaemon maculatus*) were collected from the different deports/markets in three communities viz: B1 (Imiringi), B2 (Otuokpoti), and B3 (Kolo), in Ogbia LGA. Samples were taken in batches (August, October, and December). A total of 60 specimens of the 4 species were investigated. Samples of snails were taken whole with their shells, while the others (crabs, fishes, & prawns) were wrapped in aluminium foil, placed in polyethylene bags and housed in a cooler at 4 ^{o}C for onward transportation to the laboratory. In the laboratory, shells of snails were cracked and viscera were removed leaving only the edible portions. Edible portions of snails, crabs, fishes, and prawns were cleaned in tap water to remove any dirt. They were then placed in a well labelled sample bottles and refrigerated at < 4 ^{o}C awaiting extractions.

2.3. Sample processing and extraction

Edible portions of samples of snails, fishes, crabs, and prawns, were each cut into pieces and crushed in a mortal with pestle. 10 g of each species of snails, shrimp crab and fish samples were homogenized with anhydrous sodium sulphate and spiked with surrogate standard (10 µg/mL of *p*-terphenyl and 2-fluorobiphenyl), wrapped in a filter paper, placed in a thimble and then loaded into the main chamber of the Soxhlet extractor. Extraction was performed with 200 mL of 1:1 dichloromethane (DCM)/*n*-hexane mixture for 17 h. Extracts were dried by passing through column of anhydrous sodium sulphate, and reduced by rotary evaporator to 2 mL [19, 21].

2.4. Sample clean-up and separation

Sample clean-up and separation were done in accordance to USEPA method 3630C [55]. The concentrated extracts were loaded onto the prepared silica-gel column (10 mm id x 30 cm) parked with 10 g activated silica gel slurry about 2 cm anhydrous Na_2SO_4 layer on top. The aromatic fractions were eluted using 30 mL of a dichloromethane solution, collected after aliphatic fractions elution (30 mL *n*-hexane). The eluates were concentrated to approximately 2 mL with rotary evaporator at 30 °C; solvent exchanged to cyclohexane and re-concentrated to 2 mL. 1.5 mL of each were transferred into chromatographic vials and stored at 4 °C prior to gas chromatographic analysis.

Procedural blank were performed for the purpose of quality assurance [14, 18, 21].

2.5. Gas chromatography analyses

Polycyclic aromatic hydrocarbons (16PAHs) were determined by gas chromatography (Agilent 6890N) coupled to a mass spectrometer as detector (Agilent 5975B Technologies, Santa Clara, USA). Separation was effected by a DB-5 capillary column with dimension of 30m × 0.32mm × 0.25µm. Pure helium gas at a flow velocity of 1 mL/min was used as the carrier gas. Samples were injected into GC via a pulsed split-less mode with an injection volume of 1 µL. The chromatographic column had an initial temperature of 70 °C, which was held for 20 min, and was then increased at 25 °C min^{-1} to 150 °C. The temperature was further ramped to 200 °C at 3 °C min^{-1}, and finally to 300 °C at 2 °C min^{-1}. The temperature of the injection port, ion source, quadrupole and transfer line were 250, 230, 150 and 280 °C respectively.

2.6. Identification and quantification

Identifications of PAHs were done by comparing their retentions time with those of corresponding standards. The response factors associated with the respective internal standards based on five-point calibration curve for the individual PAH were employed in quantifications. Deuterated PAH internal standard solutions (naphthalene-d8, acenaphthene-10, phenanthrene-d10, chrysene-d12, and perylene-d12) and surrogate standard solutions (2-fluorobiphenyl and 4-terphenyl-d14) were also utilized in sample quantification and quantifying procedural recovery.

2.7. Assessment of health risks

Risks to human health from exposure to PAHs through consumption of edible portions of these species were characterized by non-carcinogenic and carcinogenic risk. Non-carcinogenic risk was considered by hazard quotient (HQ) as follows [2, 22]:

$$DDI = C \times CR/Bw \quad (1)$$

$$HQ = DDI/ RfD \quad (2)$$

$$HI = \sum_{i=1}^{n} DDI/RfD \quad (3)$$

where: DDI is dietary daily intake; C is the concentrations (µg/kg) of single or compound PAHs; CR is the consumption rate; Bw is the average body weight (60 kg) of an adult; HQ and HI connote the hazard quotient and hazard index respectively. While, RfD represent the reference dose for the PAH. In calculating the DDI, the consumption rate of the species was taken to be 7.6 kg per capita the consumption rate of fish in Nigeria which is equivalent to 20.8 g/day. The reference values were taken from US EPA [23]. HQ and HI values below one indicate negligible health effects, while values above one represent possible adverse effects [22, 24].

The health implications associated with carcinogenic PAHs were assessed by calculations of benzo(a)pyrene equivalent concentrations (PEC) given by Eq. (4)

$$PEC = \sum C_i \times TEF_i \quad (4)$$

where C_i (µg/kg) is the concentration of a single PAH ($_i$) in the edible tissue, and TEF represent the toxicity equivalence factor of the PAH ($_i$). Values of TEF were taken from [25].

The PEC values were then compared to the screening value (SV) given by:

$$SV = [(RL/SF) * Bw]/CR \quad (5)$$

where Bw and CR have already been defined. RL represent the maximum acceptable risk level (dimensionless); SF is the slope factor which is the upper-bound probability of an individual developing cancer due to lifetime (70 yrs) exposure to a particular level of a potential carcinogen [23]. The risk level (RL) was chosen at 10^{-5}. This RL means that if a person weighing 60 kg consumed 20.8 g of these edible tissues per day with the same concentration of contaminant, for 70 years, the increased risk would be at most one additional cancer death per 100,000 persons. The risk of cancer is implied when the calculated PEC is larger than the screening value. The screening value (SV) is defined as the concentration in edible tissue that is of potential public health concern, and serves as a threshold against which tissue residue level of contaminations in similar tissue in the environment are measured [26].

The Excess Cancer Risk (ECR) resulting from dietary exposure to PAHs was further calculated using equation (5):

$$ECR = \frac{\sum Q \times B(a)Pteq \times CR \times ED}{(Bw \times ATn)} \quad (5)$$

where: Q (µg kg^{-1} day^{-1}) is the carcinogenic potency of B(a)P; ED (70 yrs) is the exposure duration; Bw and CR have their usual meaning as above; ATn is the averaging time (365 day/year x number of years). The value of Q is 7.3 x 10^3 µg kg^{-1} day^{-1} [24, 27]. The calculated ECR values were compared to the accepted standard of 1.0 x10^{-6} set by the USEPA [28]. The USEPA considered one in a million (ECR = 10^{-6}) lifetime cancer risk (70 years life time period) acceptable; while an instance of lifetime cancer risk of one in ten thousand or greater (ECR = 10^{-4}) is regarded as serious [28].

3. Results and discussion

3.1. Concentrations and composition patterns of PAHs in the tissues

Table 1 and Fig. 1 show the range of concentrations, average concentrations, and distribution patterns of PAHs in the various tissues. Individual concentrations of PAHs in µg/kg range from not detected (nd) – 2684.08 in snails, nd – 199.37 in fishes, nd – 194.21 in crabs, and nd – 97.72 in prawns. Pyr, BaA, Chr, BbF and BkF were particular below detection limit in snails' samples. The non-detection or very low values of certain PAHs in some species may be attributed to their fast depuration or bio-transformations in body tissues.

The distribution patterns (Fig. 1) show that two and three rings PAHs were more predominant in snail samples contributing on the average 92.10% of the total PAHs. Four rings and five-to-six rings PAHs only contributed to 0.72 and 7.19% respectively. In the fish samples, except at Kolo (B3) (where we had a large

proportion of five and six ring PAHs, the other fish samples B1 and B3 also reflected high proportions of two and three rings PAHs. In all other samples (crabs and prawns), the two and three rings PAHs, were in abundance. The average proportions of two and three rings, four rings, and five-to-six rings PAHs were: 73.31, 3.20, and 23.49% in fish, 61.13, 4.39, and 34.49% in crabs, and 61.67, 4.38, and 33.94% in prawns respectively. The predominance of this low molecular weight (LMW) PAHs (2 & 3 rings) relative to high molecular weight (HMW) PAHs (4, 5 & 6 rings) tend to suggest that the source of PAHs is petrogenic [18, 29, 30]. However, it may also be as a result of higher solubility of the LMW PAHs, which promote their absorption into body tissues on dermal contact.

Table 1. The ranges and average concentrations of PAHs in the various tissues

	Snails		**Fishes**		**Crabs**		**Prawns**	
	Range	Ave.±SD	Range	Ave.±SD	Range	Ave.±SD	Range	Ave.±SD
Nap	nd – 153.61	90.46 ±65.6	2.10 – 18.59	11.19 ±8.5	2.10 – 18.24	10.87 ±8.2	2.10 – 21.82	12.24 ±9.9
Ace	nd – 1222.73	607.95 ±499.2	2.10 – 207.76	85.34 ±108.3	2.10 – 202.29	83.02 ±105.6	2.10 – 97.72	51.05 ±47.9
Acp	nd – 678.96	226.32 ±30.06	4.20 – 199.37	69.95 ±112.1	4.20 – 194.21	68.16 ±109.2	7.27 – 80.23	30.57 ±43.0
Flr	nd – 1120.33	373.44 ±528.1	2.10 – 163.69	74.15 ±82.2	6.30 – 159.46	73.49 ±78.3	51.35 – 86.50	51.35 ±43.9
Ant	88.07 – 948.28	389.14 ±395.8	4.20 – 18.89	11.19 ±7.4	2.10 – 10.13	5.44 ±4.18	6.40 – 30.66	30.66 ±37.2
Phe	700.46-2684.08	1392.73 ±913.9	4.20 – 77.65	36.38 ±37.6	4.20 – 74.97	35.25 ±36.2	41.49 – 89.70	45.13 ±42.9
Flt	nd – 72.71	24.24 ±34.3	nd – 4.20	2.10 ±2.1	nd – 4.09	2.06 ±2.0	nd – 2.43	1.51 ±1.3
Pyr	nd	0.00 ±0.0	2.10 – 4.20	3.50 ±1.2	2.10 – 4.09	3.41 ±1.1	2.10 – 4.85	3.65 ±1.4
BaA	nd	0.00 ±0.0	2.10 – 4.20	2.80 ±1.2	2.03 – 6.30	3.46 ±2.5	2.42 – 6.30	4.26 ±1.9
Chr	nd	0.00 ±0.0	2.10 – 8.39	4.20 ±3.6	2.03 – 8.39	4.16 ±3.7	2.42 – 6.30	4.54 ±1.9
BbF	nd	0.00 ±0.0	2.10 – 18.89	8.39 ±9.2	2.03 – 25.18	10.43 ±12.8	2.42 – 18.89	11.20 ±8.3
BkF	nd	0.00 ±0.0	nd – 31.48	11.89 ±17.1	nd – 25.18	9.76 ±13.51	nd – 27.28	12.92 ±13.7
BaP	nd – 124.94	66.91 ±51.4	4.20 – 18.89	11.89 ±7.4	4.09 – 18.89	11.04 ±7.4	12.12 – 18.89	14.67 ±3.7
DhA	69.64 – 141.32	106.84 ±29.3	16.79 – 62.96	32.88 ±26.1	16.35 – 44.07	26.22 ±15.5	21.82 – 56.66	36.45 ±18.1
IcP	nd – 65.54	21.85 ±30.90	4.20 – 29.38	13.99 ±13.5	4.05 – 20.99	11.07 ±8.8	4.85 – 39.87	19.25 ±18.3
BgP	nd – 73.73	44.38 ±31.9	4.20 – 31.48	13.99 ±15.2	4.05 – 62.96	24.38 ±33.4	4.85 – 28.70	15.38 ±12.2
∑16PAHs	2150.54–4005.12	3344.26 ±845.7	264.43 – 671.56	393.14 ±452.5	237.15 – 668.09	382.22 ±235.7	279.12– 444.16	344.81 ±91.9

*nd: not detectable; Nap: naphthalene; Acy: acenaphthylene; Acp: acenaphthene; Flr: fluorine; Ant: anthracene; Phe: phenantrene; Flt: fluoranthene; Pyr: pyrene; BaA: benzo[a]anthracene; Chr: chrysene; BbF: benzo[b]fluoranthene; BkF: benzo[k]fluoranthene; BaP: benzo[a]pyrene; DhA: dibenzo[a,h]anthracene; IcP: indeno[1,2,3-cd]pyrene; and BgP: benzo[g,h,i]perylene.

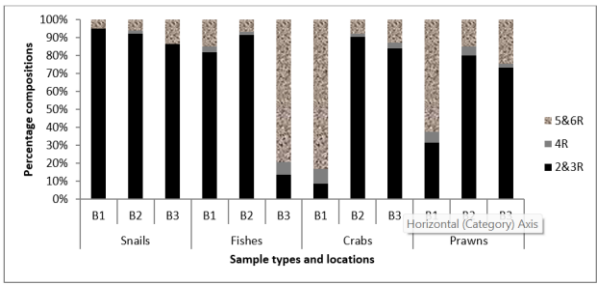

Figure 1. Distribution patterns of rings PAHs in the various sampled tissues (*2&3R = two-and-three rings, 4R = four rings, 5&6R = five-and-six rings).

Total PAHs ($\sum_{16}$PAHs) in µg/kg in edible tissues (Table 1) averaged: 3342.26±845.70 (range: 2150.54 – 4005.12) for snails, 393.14±452.50 (range: 264.43 – 671.56) for fishes, 382.22±235.72 (range: 237.15 – 668.09) for crabs, and 344.81±91.93 (range: 279.12 – 444.16) for prawns respectively. The mean and range of values obtained in this study were higher than those reported by Bandowe et al. [24] from the coast of Ghana, Benin, Europe, Asia and Latin America (Table 2). They were however comparable to those reported for most edible species in the Niger Delta and coastal regions of Nigeria; as well as those from the Red Sea Coast of Yemen and the Iraqi waters (Table 2). The concentrations of PAHs recorded in these edible species were largely above background concentrations of 0.01 – 1.0 µg/kg in uncooked foods [31] an evidence of contaminations. The values for benzo(a)pyrene – a typical PAHs marker – was also significantly higher than the European Union (EU) limit of 2 µg/kg in the various tissues [32].

Table 2. Comparison of PAHs levels in samples tissues in this study with those of others

Region	∑PAHs (µg/kg)	No. of PAHs	References
Coast of Ghana (fish muscle)	71 - 481	28	Bandowe et al. [24]
Gulf of Benin (fish Muscle)	12 - 102	12	Soclo et al. [33]
Multiple locations, Sweden (fish muscle)	5.4 - 130	15	Brorstóm-Lundén et al. [34]
Huelva, Spain (fish muscle)	8.2 – 71.4	16	Bordajandi et al. [35]
Hongkong (fish muscle)	1.57 – 67.2	16	Cheung et al. [36]
Northern China, China (fish muscle)	4.8 - 144	16	Xu et al. [37]
Busan, South Korea (fish muscle)	12.3 - 243	16	Moon et al. [38]
Guanabara bay, Brazil (fish edible parts)	4.0 - 53	16	De Silva et al. [39]
Niger Delta, Nigeria coastal waters (Sea food)	45.9 – 171.9		Nwaichi and Ntorgbo [40]
Coastal area of Ondo, Nigeria (crab: *Callinectes sapidus*)	101100 - 151490	16	Ololade et al. [41]
Red Sea Coast, Yemen	(23900 - 57900		Al- Saad et al. [42]
Iraqi National waters (fish muscles)	197.54 – 381.42	21	Al-Imarah et al. [43]
Ogbia LGA (snails: edible portion)	2150 – 4005		
Ogbia LGA (fishes: edible portion)	264 – 671	16	This study
Ogbia LGA (crabs: edible portion)	237 – 668		
Ogbia LGA (prawns: edible portion)	279 - 444		

3.2. Estimation of daily dietary intake (DDI) and risk assessment

Evaluation of health risk of PAHs using the concept of DDI is important because of the difference in consumption rates. DDI values (µg kg^{-1}bw day^{-1}) estimated from individual PAH concentrations ranged from 0 – 0.930 in snails; 0 – 0.072 in fishes; 0 – 0.067 in crabs; and 0 – 0.034 in prawns. The average DDI value for benzo(a)pyrene – one of the main indicators of PAHs – was: 0.023 in snails; 0.004 in fishes and crabs, and 0.005 in prawns. The calculated DDI values in µg/day for total PAHs (∑16PAHs) in the biota were: 1.16±0.35 (range: 0.75 – 1.39) for snails; 0.14±0.08 (range: 0.08 – 0.23) for fishes; 0.13±0.09 (range: 0.08 – 0.23); for crabs, and 0.12±0.03 (range: 0.10 – 0.15) for prawns (Table 3, Table S1 for additional information). This implies that among the species sampled, snails pose the highest risk to consumers as it has significantly higher values of DDI compared to the others. The values of DDI obtained in this study are comparable to the range of 0.626 – 0.712 µg/day reported in Spain [44] and the 0.00177 – 0.0107 µg/day in India [45] but were much lower than the 7.548 µg/day reported for fishes in Ghana [24]. The ranges were also much lower than the range of 38 – 195 µg/day reported for total PAHs in smoked fish species in Southern Nigerian market by [2]. Food processing techniques such as: drying, smoking, roasting, grilling, barbecuing, curing, and refining have been implicated for increased levels of PAHs in foods [31].

The hazard quotients (HQ) calculated from the ratio of DDI to reference dose for each particular PAH were used for the assessment of the effects of non-carcinogenic PAHs. The sum of the hazard quotients (∑HQ) gives the hazard index (HI) for the total PAHs (Table 3).

Table 3. Calculated HQ, HI, DDI, PEC, SV, and ECR for the PAHs in various tissues

			Snails			Fish			Crabs			Prawns		
	RfD		B1	B2	B3	B1	B2	B3	B1	B2	B3	B1	B2	B3
Nap	0.02		0.00	2.66	2.04	0.33	0.22	0.04	0.04	0.32	0.21	0.04	0.38	0.22
Acy	0.02		21.19	10.42	0.00	0.80	3.60	0.04	0.04	3.51	0.77	0.04	0.92	1.69
Acp	0.06		3.92	0.00	0.00	0.40	1.15	0.02	0.02	1.12	0.04	0.02	0.04	0.46
Flr	0.04		9.71	0.00	0.00	0.49	1.42	0.02	0.05	1.38	0.47	0.02	0.57	0.75
Ant	0.30	HQ	0.10	0.15	1.10	0.01	0.00	0.02	0.00	0.00	0.01	0.08	0.01	0.01
Phe	NA		-	-	-	-	-	-	-	-	-	-	-	-
Fit	0.04		0.00	0.63	0.00	0.00	0.04	0.02	0.02	0.04	0.00	0.02	0.02	0.00
Pyr	0.03		0.00	0.00	0.00	0.05	0.05	0.02	0.02	0.05	0.05	0.02	0.05	0.06
HI			34.93	13.86	3.14	1.72	6.48	0.18	0.20	6.42	1.55	0.24	1.99	3.19
$\sum_{16}$DDI(µg/d)			1.39	1.34	0.75	0.09	0.23	0.084	0.082	0.23	0.08	0.097	0.11	0.15
$\sum_{8}$PEC(µg/Kg)			194.6	116.7	217.8	27.4	23.0	90.7	71.4	30.3	21.3	85.0	35.2	48.1
$\sum_{16}$PEC(µg/Kg)			199.2	121.6	228.2	28.3	23.6	90.9	71.5	30.9	21.6	85.7	35.5	48.5
SV(µg/Kg			3.95	3.95		3.95	3.95	3.95	3.95	3.95	3.95	3.95	3.95	3.95
ECR			1.34 E-6	8.09 E-7	1.51 E-6	1.90 E-7	1.59 E-7	6.28 E-7	4.95 E-7	2.10 E-7	1.48 E-7	5.89 E-7	2.44 E-7	3.33 E-7

HQ value equal to or less than one (≤1) connotes no considerable health hazard. Hazard index (HI) (∑HQ) value of less than or equal to one (≤1) indicates no health hazard either from any individual PAH or in combination with others. Due to lack of reference dose data, HQ for phenanthrene (Phe) could not be calculated. Acenaphthylene (Acy) appears to have the highest HQ in most samples averaging 10.54 in snails, 1.48 in fish, 1.44 in crabs, and 0.88 in prawns. This was next followed by fluorene (Flr) with an average HQ value of 3.24 in snails, 0.64 in fish and in crabs, and 0.45 in shrimps. The other non-carcinogenic PAHs reflected average HQs which were typically less than one except for naphthalene (Nap) in the snails' samples. This indicates that health hazard due to these individual PAH are negligible. The average HI however, was 17.31 in

snails, 2.77 in fish, 2.72 in crabs, and 1.81 in shrimps. The result implied that health hazard due combinations of the eight non-carcinogenic PAHs were very high for snails, moderately high for fish and crabs, and slightly high for the prawns.

The calculated benzo(a)pyrene equivalent concentrations (PEC) values in µg/kg for the eight carcinogenic PAHs in the edible species ranged from 116.7 – 217.8 in snails, 23.0 – 90.7 in fish, 21.3 – 71.4 in crabs, and 35.2 – 85.0 in prawns (Table 3). These values were all significantly higher than the screening value of 3.95 µg kg^{-1}bw d^{-1}. This indicates a potential of having cancer as a results of consumptions of these edible food species.

The carcinogenic potencies of these edible species were further evaluated by calculating the excess cancer risk (ECR) and comparing the results with the standard (10^{-6}) recommended by USEPA. The result shows that except for the snails' species at B3 (Kolo), the calculated ECR values were all less than the recommended USEPA standard (Table 3). This indicates that there is no additional cancer risk arising from consumption of these species (fish, crabs, & prawns) other than the one in a million (10^{-6}) set by the USEPA. The ECR for the snails ranged from $8.09x10^{-7}$ – $1.51x10^{-6}$. The upper bound boundary (obtained at B3) which was greater than $1.0x10^{-6}$ indicate an additional risk of developing cancer due consumption of snails from the area. It was however much less than $1.0x10^{-4}$ (one in ten thousand) which is considered serious by USEPA.

Table 4. Diagnostic ratios and source apportionment of PAHs in various tissues

Sites		∑LMW/∑HMW	Ant/(Ant+Phe)	Flt/(Flt+Pyr)	BaA/(BaA+Chr)	IcP/(IcP+BgP)
SN	B1	19.58^{p}	0.11^{r}	∞	∞	∞
	B2	11.62^{p}	0.05^{r}	1.0^{c}	∞	0.52^{r}
	B3	6.39^{p}	0.54^{r}	∞	∞	0.0
FH	B1	4.48^{p}	0.12r	0.0	0.50^{r}	0.06^{p}
	B2	10.85^{p}	0.13^{r}	0.50^{r}	0.50^{r}	0.11^{p}
	B3	0.16^{r}	0.82^{r}	0.50^{r}	0.33^{c}	0.30^{c}
CB	B1	0.10^{r}	0.33^{r}	0.50^{r}	0.43^{r}	0.25^{c}
	B2	9.58^{p}	0.13^{r}	0.50^{r}	0.50^{r}	0.57^{r}
	B3	5.24^{p}	0.12^{r}	0.0	0.50^{r}	0.50^{r}
PR	B1	0.46^{r}	0.95^{r}	0.50^{r}	0.50^{r}	0.76^{r}
	B2	4.06^{p}	0.12^{r}	0.38^{p}	0.45^{r}	0.50^{c}
	B3	2.73^{p}	0.13^{r}	0.0	0.50^{r}	0.31^{c}

Indications: p = petrogenic; r = pyrogenic; c = petroleum combustion. SN, FH, CB, PR represent snails, fishes, crabs, and prawns in the various sites B1, B2, and B3 respectively.

3.3. Sources of PAHs in the tissues

The Ant/(Ant+Phe) ratio (Table 4) shows that all samples have values that were greater than 0.1; this is an indication of pyrolytic source. Ant/(Ant+Phe) ratio less than 0.1 implied petrogenic source while that above 0.1 connotes pyrolytic inputs [19, 46, 47]. The other diagnostic indices viz: Flt/(Flt+Pyr), BaA/(BaA+Chr), and IcP/(IcP+BgP) also showed that source of PAHs was mainly pyrolytic from combustion of biomass (r) and combustion of liquid fuel (c). These ratios have been largely used for source identifications of PAHs in the environment. Flt/(Flt +Pyr) ratio less than 0.4 is associated with petroleum origin, ratio greater than 0.5 indicate PAHs from combustion of wood, grass, and coal. Ratio in the range of 0.4 – 0.5 however, implicates a mixture of combusted and non-combusted petrol fuels in conjunction with biomass combustion and degradation [18, 47, 48]. Ratio less than 0.2 for BaA/(BaA+Chr) index typifies petrogenic source [48, 49]. Whereas ratio greater than 0.35 is implicative of pyrogenic source [50]. Ratio within 0.2 – 0.35 suggests combustion processes [30, 48]. PAHs input of grass, wood and coal combustion is indicated by IcP/(IcP + BgP) ratio above 0.5, whereas values below 0.2 represents PAHs input from petroleum. IcP/(IcP + BgP) ratio within 0.2 – 0.5 connotes petroleum combustion [18, 48, 51-53]. The ratio of sum of low molecular weight to high molecular weight PAHs (∑LMW/∑HMW) tend to suggest that the source of PAHs were petrogenic. Petrogenic contaminations are usually characterized by the dominance of low-molecular weight PAHs (two and three rings PAHs), while high-molecular weight PAHs (four to six rings PAHs) are predominant with pyrolytic inputs [29, 30, 54]. The contrary evidences from other diagnostic indices however suggest that higher solubility of the LMW PAHs, which promote their absorption into body tissues on dermal contact, may be responsible for their large presence and not much as a result of petroleum inputs, though the inputs from petroleum cannot be ruled out.

4. Conclusions

Priority poly-aromatic hydrocarbons (PAHs) presences were indicated in edible tissues of terrestrial land snails and aquatic species from Ogbia LGA, Bayelsa, Nigeria. Diagnostic source evaluation reveals sources of PAHs to be largely pyrolytic. The amount found in these species and the ability to induce non-carcinogenic diseases as shown by the calculated hazard indices were largely due to acenaphthylene (Acy) and fluorene (Flr) concentrations. The ability to induced carcinogenic diseases to consumers of these foods was evidenced by the calculated benzo(a)pyrene equivalent concentrations (PEC). However, the excess cancer risk (ECR) revealed that there was no additional cancer risk as a result of consumptions of these foods at of 20.8 g kg^{-1}bw day^{-1} for an adult of 60 kg body weight over a life-time of 70 years, except slight increased risk that was noted for the snails' samples. The order of accumulations of total PAHs in the species tissues was:

snail > fish > crab > prawn, tending to suggest that the snail is a better bio-indicator of PAHs in this area than the other species.

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