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EVALUATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOME SEADFOODS FROM SELECTED RIVERS IN BAYELSA STATE, NIGERIA

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ABSTRACT

The content of Polycyclic Aromatic Hydrocarbons (PAHs) in sea food (periwinkle, crabs, oysters and shrimps) were determined using Gas chromatography. The results showed that the Polycyclic Aromatic Hydrocarbons content in the various seafood were significantly higher when compared the European Union (EU) permissible level for Polycyclic Aromatic Hydrocarbons 0.03mg/kg in seafood. The PAHS in Oyster (8.58mg/kg) was highest followed by that found in periwinkle (7.73mg/kg), crab (6.59mg/kg) and Shrimp (6.10 mg/kg). Additionally the PAHs in Oyster (8.58mg/kg) and Periwinkle (7.73mg/kg) were significantly ($p<m$) higher as compare to that of Shrimp crab (6.59mg/kg). These implies that the consumption of this seafood may be deleterious to health. Nevertheless, it is recommended that stringent pollution measures should be introduced by the government to prevent increase in anthropogenic activities, resulting in pollution of water bodies with Polycyclic Aromatic Hydrocarbon among other hazardous chemicals.

KEY WORDS: *Polycyclic Aromatic Hydrocarbons, Periwinkle, Crabs, Oysters and Shrimps*

INTRODUCTION

PAHs (polycyclic aromatic hydrocarbons) are a broad category of chemical molecules with two or more fused aromatic rings. They usually consist of molecules with only carbon and hydrogen atoms (unsubstituted parent PAHs and their alkyl-substituted descendants), they also includes functional derivatives (nitro-PAHs) and heterocyclic analogs (aza-arenes) (Blumer *et al*., 1997). PAHs are primarily produced through the exploration and exploitation of crude oil and gas resources. They are also produced by biological processes as well as incomplete combustion from natural (forest and brush fires) and man-made (coal combustion) sources (automobile emissions and cigarette smoke). PAHs can therefore be found in the air, soil, and water. Despite the introduction of better technology in the petroleum sector, accidents still happen, resulting in hydrocarbon contamination of the environment (both land and water) in most oil-producing countries, including Nigeria. Gas flaring, dumping of spent lubricant oils, washings from oil tanks, leakage from maritime vessels, erosion and runoff from crude oil polluted soils, refinery effluents, and ruptures are all ways that oil from the petroleum industry enters the aquatic environment (Djomo., *et al* 2004). PAHs are common in the environment and have negative consequences. There are over 100 PAHs in ambient particulate matter and over 200 in cigarette smoke. PAHs are highly lipophilic and have a low water solubility. They are soluble in many organic solvents and have a low water solubility (Zhang, *et al* 2010).

Invertebrates (shrimps, crayfish, mollusks and crabs) are an important and integral part of the aquatic ecosystem and thus reflect any negative effects caused by pollution in the community structure which can affect trophic relationships. Fish have been reported to be the most sensitive living organism to trace

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concentrations of toxicants in aquatic habitats (Jiang., *et al* 2014). Crabs and fishes are therefore good indicators of pollution in coastal waters and have been used extensively for environmental monitoring.

PAHs have been regarded as the most concerning in terms of possible human exposure and harmful health consequences. Due to the broad distributed dispersion of these chemicals and their toxicological importance, biological monitoring of PAH exposure is of prime interest. Some PAHs are well known as carcinogens, mutagens, and teratogens and therefore pose a serious threat to the health and the well-being of humans. The most significant health effect to be expected from inhalation exposure to PAHs is an excess risk of lung cancer (Kim., *et al* 2013). The impact of PAHs on human health depends mainly on the length and route of exposure, the amount or concentration of PAHs one is exposed to, as well as the relative toxicity of the PAHs. It has been reported that the PAHs induce suppress immune reaction in rodents (Armstrong., *et al* 2004).

Shrimp are decapod crustaceans with elongated bodies and a primarily swimming mode of locomotion – most commonly Caridea and Dendrobranchiata. Crabs are decapod crustaceans of
the infraorder Brachyura, which typically have a very short projecting "tail" (abdomen) usually hidden entirely under the thorax. They live in all the world's oceans, in fresh water, and on land, are generally covered with a thick exoskeleton, and have a single pair of pincers (Oluwafumilayo *et al* 2019). Crabs and lobsters have strong walking legs, whereas shrimp have thin, fragile legs which they use primarily for perching. The common periwinkle or winkle (Littorina littorea) is a small edible whelk or sea snail that has gills and an operculum. It belongs to the Littorinidae family of periwinkles. This is a hardy intertidal species with a dark, banded shell. Many oysters are irregular in shape with oval and/ or pear-shaped shells. The shell is usually whitish-grey and inside of the shell is usually whitish, this animal is known to have a very strong adductor muscles that help them in shutting their shell when they hide inside them upon sensing danger (Wang *et al*. 2020).

Polycyclic aromatic hydrocarbon in crabs, shrimps, oysters and periwinkle has been one of the major environmental toxicity problems facing Bayelsa state, Nigeria. This research was done to evaluate the human health risks from consumption of selected seafood such as shrimp, periwinkle, crab and oyster commonly consumed in the Bayelsa.

MATERIALS AND METHODS

Collection of test samples

Samples were collected from Swali River and Oporoma river, the samples were labelled sample A (shrimp) sample B (periwinkle) sample C (crab) sample D (Oyster) respectively.

Reagents

The reagents used for the analysis includes Deionized water, Dichloride methane, Petroleum spirit, Amino acid, Standards Sodium Carbonate, Ethyl chloroformate. All the chemicals and reagents used were of analytical grade and high purity.

Apparatus

Apparatus include Laboratory mortar and pestle, Volumetric flask, Ovum conical flash, Incubator, Borosilicate, Glass container, Gas chromatography, Soxhlet Arrangement Assorted Glassware, Agilent 6890 coupled with FID/PPDD Software, Chem station Data Interpretation system.

Gas Chromatography Analysis

Gas chromatography are used for the separation and detection of non-polar compounds that are volatile and thermally stable. It is also used for the analysis of certain 404 Recent insights in petroleum science and engineering semi-volatile compound including PAHs 4qq.

Chromatographic condition

GC	Hp 6890 powered with HP Chemstation Rev. A09.1
Column:	HP-1
Column length	30m
Column ID	0.25m
Injection Temperature	250C
Detector Temperature	20C
Detector	FID
Initial Temperature	60c for 5mins

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First Rate	15c/mins for 14mins and maintain for 3min
Second Rate	10c/mins for 5mins and maintain for 4mins
Mobile Phase or Carrier	Nitrogen
Nitrogen Column Pressure	30psi
Hydrogen Pressure	28psi
Compressed Air Pressure	32psi

Procedure

The dried and pulverized sample were made to be free of water by ensuring constant weight for a period of time in the laboratory. 0.5g samples A (shrimp) sample B (periwinkle) sample C (crab) sample D (Oyster) respectively were weighed into the 250ml conical flask capacity. The samples were defended by extracting the polycyclic aromatic hydrocarbons content of the sample with 30ml of the petroleum spirit three times with Soxhlet extractor that was equipped with thimble. The sample was hydrolyzed three times for complete hydrolysis to be achieved for the inutility of amino acids recovery. The Pulverized and defamed sample was soaked with 30ml of the IM potassium hydroxide solution and were incubated for 48 hours at 110°C in hermetically closed borosilicate glass container. After the alkaline Ureterolysis, the hydrolysate were neutralized to get pH in the range of 2.5-5.0. The solution was purified by cation-exchange solid-phase extraction. The Polycyclic aromatic hydrocarbons in purified solution were derivatized with ethyl chloroformate by the established mechanism.

Statistical Analysis

Statistical significance was assessed using a one-way analysis of variance (ANOVA). Comparisons of PAHs levels between species within sites were made using student t-test while one way analysis of variance (ANOVA) was performed to compare PAHs levels between species across sites with the statistic package SPSS 14.0.2(SPSS Inc. Chicago, USA).

RESULTS

The concentration of PAHs in Seafood sample

The total of Polycyclic Aromatic Hydrocarbons in Oyster sample was 8.52mg /kg. The highest concentration of individual PAHs compounds was obtained in Indeno(1,23-cd) Pyrene is 8.64mg/kg and the lowest concentration was obtained in Benzo(a) Anthracene is 1.22mg/kg. Based on the research done the total concentration of all the 16 Polycyclic Aromatic Hydrocarbons in Shrimp is 71.06 mg/kg, in this study the result was 6.09mg/kg, the reason for the various values is the lower anthropogenic activities in Oporoma while the total content of PAHs in periwinkle and crabs are 7.73mg/kg and 6.59mg/kg respectively.

Concentration of Polycyclic aromatic hydrocarbons (mg/kg) in periwinkle, crabs, oyster and shrimp.

NAME OF PAHs	AMOUNT in PERIWINKLE [mg/kg]	AMOUNT in CRABS [mg/kg]	AMOUNT in OYSTER [mg/kg]	AMOUNT in SHRIMP [mg/kg]
Naphthalene	2.52	2.19	3.44	1.80
Acenaphthylene	2.59	1.76	1.77	1.39
Acenaphthene	1.45	1.32	1.29	1.15
Fluorene	6.10	5.43	6.16	5.15
Phenanthrene	1.39	9.64	1.22	9.77
Anthracene	8.42	6.35	8.40	5.62
Fluoranthene	7.41	5.88	8.30	8.43
Pyrene	4.96	4.47	6.26	4.28

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Benzo (A) Anthracene	1.43	1.21	1.22	1.20
Chrysene	2.59	2.28	2.25	2.38
Benzo (b) Fluoranthene	3.94	5.88	6.52	5.88
Benzo (k) Fluoranthene	3.90	3.50	3.46	3.42
Benzo (a) Pyrene	2.47	2.09	2.22	1.81
Indeno {1,2,3-cd} Pyrene	9.51	6.78	8.64	6.17
Dibenzo (a, h) Anthracene	1.43	1.09	1.33	1.03
Benzo (g, h, i) Perylene	1.58	1.57	1.64	1.47
TOTALS	**7.73**	**6.59**	**8.58**	**6.09**

From the table above, the sixteen PAHs recommended as priority pollutants by the U.S Environmental protection Agency (USEPA) were determined in crabs and periwinkle which are; Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene Benzo (a) Anthracene, Chrysene, Benzo (b) Fluoranthene, Benzo (k) Fluoranthene, Benzo (a) Pyrene, Indeno {1,2,3-cd} Pyrene, Dibenzo (a, h) Anthracene and Benzo (g, h, i) Perylene.

DISCUSSION

Sixteen PAHs were detected which are; Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene Benzo (a) Anthracene, Chrysene, Benzo (b) Fluoranthene, Benzo (k) Fluoranthene, Benzo (a) Pyrene, Indeno {1,2,3-cd} Pyrene, Dibenzo (a, h) Anthracene and Benzo (g, h, i) Perylene. Ratio of fluoranthene to pyrene greater than one (Fla/Pyr>1) is attributed to pyrolytic sources while (Fla/Pyr<1) is attributed to petroleum hydrocarbon sources (Kong *et al.*, 2005***).*** Data from the analysis of our samples revealed that PAHs were found in all samples gotten from both rivers. The concentration range of PAHs found in crabs, periwinkle, shrimp and oyster ranged from 1.09 - 9.64mg/kg, 1.39 - 9.81mg/kg, 1.03 - 9.77mg/kg and 1.22 - 8.64mg/kg respectively. The total PAHs content in oyster, shrimp, periwinkle, and crabs was 8.58mg/kg, 6.09mg/kg, 7.73mg/kg and 6.59mg/kg respectively, which is slightly lower than that of (Onojake, *et al 2020*) of which they got 8.02mg/kg and 7.83mg/kg for periwinkle and crabs respectively, this indicate there is higher level of PAHs accumulation in their samples as a result of the high oil exploration activities in Ibeno River, Akwa Ibom state.

This result suggest that the PAHs detected from the samples from Swali and Oporoma originate from pyrolytic sources (combustion of fossil fuel, electric power generator, refuse incineration, home heating, industrial emission etc.) which is as a result of commercial activities around Swali and Oporoma rivers.

CONCLUSION

PAHs are among the major organic pollutants found in the aquatic systems. They are mostly generated from both natural and anthropogenic sources. Many of them are highly carcinogenic in nature and are also linked with endocrine system disruption at levels higher than the maximum concentration limit within a short period of time. Data obtained from this study, the concentration of PAHs in analysed in Crabs, oyster, shrimp and periwinkle were higher than the maximum permissible limit of the European union of 0.03mg/kg which poses a high risk of carcinogenic potencies.

Declarations
This research was funded personally. The authors declare that there is no conflict of interest

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