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Assessment of PAHs levels in some fish and seafood from different coastal waters in the Niger Delta

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ABSTRACT

Levels of sixteen polycyclic aromatic hydrocarbons (PAHs) in 30 edible tissues of selected frequently-consumed fish and seafood collected from three coastal waters of Niger Delta, namely, Sime, Kporghor and Iko were investigated in 2014. Gas chromatographic analysis were employed for PAHs determination. Observed mean PAHs levels in the samples ranged from below detection limit (BD) of analytical instrument to $22.400 \pm 0.050\ \mu g\ kg^{-1}$ wet wt. in *Littorina littorea,* BD to $87.400 \pm 0.030\ \mu g\ kg^{-1}$ wet wt. in *Crassostrea virginica* and from BD to $171.000 \pm 0.430\ \mu g\ kg^{-1}$ wet wt. in *Periophthalmus koeleuteri.* The highest average concentration of $171.000 \pm 0.430\ \mu g\ kg^{-1}$ wet wt. was recorded for Indeno [1,2,3-cd]pyrene from Sime water. High molecular weight PAHs (HMW-PAHs) were generally predominant compared to low molecular weight PAHs (LMW-PAHs). The LMW- PAH/HMW-PAH ratio was <1 for all species, indicating anthropogenic origin of PAHs in the coastal waters of Niger Delta environment. Moreover, the study of the PAHs fingerprints, using specific ratios, suggests the predominance of a pyrolytic origin for observed PAHs.

1. Introduction

Marine and terrestrial environments, in the recent times, have been tagged with abundance of persistent organic pollutants. This sordid situation is worsened by the emergence of densely populated industrial districts as both environmental components are important in most activities leading to economy development, and at the same time cast an ominous pall on the environment directly or indirectly. Oshineye [23] reported Nigeria's oil reserves of about 31.5 billion barrels and crude oil production of about 2.118 million barrels per day in the post- 2000 era, underscoring the enormity or oil and related activities in Nigeria. There are 606 oil fields in the Niger Delta of which 360 are onshore and 246 are offshore [18]. Associated gas flaring, above ground pipeline leakage, oil waste dumping, sabotage and oil spills lead to environmental pollution. Pollution caused by petroleum and its derivatives is the most prevalent problem in the environment. The release of crude oil into the environment by oil spills is receiving worldwide attention [17]. Crude oil spills of January 12, 1998 and July, 1979 at Mobil Unlimited Idoho platform (45,000 barrels) and West of Shell operated forcados terminal storage facility (560,000 barrels) respectively spilled into the Atlantic coastal line in Nigeria, its surrounding land, mangrove swamps and territorial waters. Similarly, other anthropogenic activities in coastal areas contributing to PAHs contamination of coastal environments could include use of creosote—treated wood in aquaculture, bush burning, industrial effluent discharge, dense vehicular emissions, artisanal refining of petroleum products as seen in the Niger Delta among others. These activities Such impact however, is often assessed from changes in the physical, chemical [19] and biological components of the ecosystem.

Human health is largely determined by the diet and recommendable diet should be able to provide sufficient nutrients and low levels of pathogenic microorganisms, as well as chemical contaminants. Fish constitutes an important source of proteins, vitamins and unsaturated essential fatty acids (PUFA), especially omega-3 PUFA's [3]. In contrast to the potential health benefits of dietary fish intake, say in the prevention of coronary heart disease, an issue of concern related to frequent fish consumption is the risk derived from exposure to chemical pollutants. The pollution of the environment by PAHs is a major concern [20]. PAHs are large class of persistent organic pollutants containing two or more fused benzene

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rings. They are known to be ubiquitous in both marine and terrestrial environments [5] and are included in the EU and USEPA priority pollutant list due to their mutagenic and carcinogenic properties [28]. Predominant exposure route is dietary, excluding smokers and occupationally exposed populations. As chemically stable and lipophilic compounds [5], they can easily cross lipid membrane and have the potential to bioaccumulate in aquatic organisms. Based on physical and biological properties, PAHs are classified into high molecular weight (HMW) and low molecular weight (LMW) types. Those consisting of 4–6 aromatic rings are termed HMW and have been shown to be less readily bio-degraded by native microorganisms and can bioaccumulate in the aquatic organisms like fish and mussels. On the other hand, LMW PAHs consists of 2–3 aromatic rings and although less carcinogenic than HMW type [6] a pose toxic to many aquatic organisms. [32] reported the possiblity of using Periwinkles and Oysters as pollution biomonitors due to the fact that they are sedentary or bottom feeders they are good accumulators of heavy. Although for most people, fish and seafood represents only a small part of the total diet, this trend may differ in the Niger Delta communities. European Union established a maximum level of 1 $\mu g\,g^{-1}$ wet weight for benzo (a) pyrene in foodstuff and is used for the carcinogenic risk of PAHs in muscle meat of fish [11] but more recently, it was attributed to dibenzo(a,1) pyrene a carcinogenic potency that is about 100 times that of benzo(a) pyrene [22].

PAHs cause tainting on seafoods, have relatively low solubility and high affinity for particles, and most PAHs can therefore be found attached to particles that have settled or are suspended in the water column [25]. European Union has stressed and recommended that PAHs be measured in as wide as possible in food products in order to obtain data on the occurrence and specific concentrations in a variety of matrices [31].

Kporghor and Iko rivers are located in Eastern Obolo Local Government Area (LGA) of AkwaIbom state (lying by Rivers state), and have been exposed to oil spill from the Shell Petroleum Development Company (Nigeria) Ltd pipeline, artisanal refining and pipeline vandalization. Sime (Tai) water is located in Tai LGA Rivers State (a known oil polluted zone), all in the Niger Delta region of Nigeria. Map of study area is as shown in Fig. 1 as reported in a study report by UNEP (2011). Average consumption of seafood in these communities is about 370 g per week going by measured dry weight of possible number at random per meal consumed. This study seeks to assess the levels of PAHs in commonly consumed and commercially viable fish and seafood species, *Periophthalmus koeleuteri* (Mudskipper), *Littorina littorea* (Periwinkle) and *Crassostrea virginica* (Oyster) from Nigerian coastal waters and identify the probable sources.

2. Material and methods

2.1. Sample collection and preparation

Fresh samples of *L. littorea*, *P. koeleuteri* and *C. virginica* were collected from landing beaches of Kpoghor, Iko and Sime towns using harvesting buckets provided by local fishermen. At each site, ten individual Mudskippers, Periwinkles and Oysters of similar size and species were collected, cleaned and wrapped in aluminum foils, and kept frozen in an ice chest cooler for onward transportion to the laboratory for analysis.

2.2. Determination of polycyclic aromatic hydrocarbons levels

Fresh samples were well cleaned in distilled water to remove any external dirt. Dissection was performed on fresh samples, using instruments and glass dishes rinsed with solvent. Tissues were dissected and minced into smaller pieces, and a subsample was taken from the homogenate. The samples were then blended and kept in air tight containers prior to extraction process. Two grams of samples were weighed into a clean extraction container (50 ml beaker). A 10 ml analar grade extraction solvent (dichloromethane) was added into the sample and mixed thoroughly and allowed to settle. The mixtures were carefully filtered into clean solvent rinsed extraction bottle, using filter paper fitted into Buchner funnels. Transfered extracts were concentrated to 2 μl for cleanup/separation in gas chromatographic analysis (HP 5890 series II, GC apparatus, coupled with flame ionization detector (FID) HP Wilmington, DE, USA equiped with HP chemstation Rev. A 09:01 (10206) software). Elution protocol as given in instruction manual was strictly followed as in high pressure solvent extraction. Separation occured as the vapor constituent partition between the gas and liquid phase and the sample was automatically detected as it eluted from the column (at constant flow rate) by the FID detector which response is dependent upon the composition of the vapor. To determine whether analyte detection was affected by the difference between diluent used for PAHs extraction and the experimental sample matrix, prepared standard curves were used to extrapolate the amount of added analyte in each case which denoted the spike recovered. There were no discrepancies observed. This was done by an addition of evenly spaced four (4) aliquots of spike to samples and these spiked aliquots were used to generate a calibration line and amount in the sample was calculated.

Table 1
PAHs levels ($\mu g\,kg^{-1}$ wet wt.) for *Littorina littorea* from the study areas (Sime, Kporghor and Iko coastal waters).

PAHs	Sime Tai	Kpoghor	Iko
Naphthalene	BD	BD	BD
Acenaphthylene	BD	BD	BD
Acenaphthene	BD	BD	BD
Fluorene	BD	0.040 ± 0.004	BD
Phenanthrene	0.030 ± 0.004	0.010* ± 0.002	0.020 ± 0.003
Anthracene	0.020 ± 0.002	0.010* ± 0.000	0.020 ± 0.003
Fluoranthene	0.010 ± 0.000	0.030 ± 0.004	0.030 ± 0.004
Pyrene	0.030 ± 0.004	0.040 ± 0.004	0.040 ± 0.003
Benzo[a]anthracene	0.050 ± 0.004	0.002* ± 0.004	0.080 ± 0.004
Chrysene	0.080* ± 0.004	BD	0.010* ± 0.002
Benzo[b]fluoranthene	4.240* ± 0.010	13.300 ± 0.030	16.800 ± 0.040
Benzo[k]fluoranthene	0.004.001	BD	0.040* ± 0.004
Benzo[a]pyrene	0.010* ± 0.000	0.010* ± 0.000	0.020* ± 0.003
Indeno[1,2,3-cd]pyrene	2.650* ± 0.010	22.400* ± 0.050	13.100* ± 0.020
Dibenzo[a,h]anthracene	0.010* ± 0.002	0.002 ± 0.000	0.002 ± 0.000
Benzo[g,h,i]perylene	0.020* ± 0.002	0.010 ± 0.002	0.010 ± 0.002
Total	7.150* ± 0.040	35.800* ± 0.100	30.100*h ± 0.090
LMW-PAH/HMW-PAH	0.010* ± 0.001	0.002* ± 0.000	0.001* ± 0.000
BaA/(BaA + Chry)	0.380 ± 0.001	1.000* ± 0.003	0.890 ± 0.001

Means with superindices (*) across rows are significantly different ($P < 0.05$), values are mean ± S.E.M ($n = 10$). BD = below detection limit of 0.0001.

2.3. Statistical analysis

Means of ten replicates were subjected to ANOVA using Excel windows 10 and Duncan Multiple Range Test was employed for comparisons.

3. Results

From the results obtained, mean levels ($\mu g\,kg^{-1}$ wet wt.) of the sixteen PAHs distribution in *L. littorea, C. virginica* and *P. koeleuteri* collected from Sime, Kporghor and Iko coastal waters are as shown in Tables 1, 2 and 3 respectively. Also, low molecular weight: high molecular weight PAHs, LMW-PAH/HMW-PAH and Benzo(a) anthracene divided by the sum of Benzo(a) anthracene and Chrysene, BaA/(BaA + Chry) ratios