

# Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) Levels in Two Commercially Important Fish Species from crude oil polluted Waters of Ogoniland and Their Carcinogenic Health Risks

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## Abstract

This work was carried out to assess the levels of Polycyclic Aromatic Hydrocarbon (PAHs) in selected fish species. Concentrations of PAHs were determined in edible tissues of selected important seafood's (*Tilapia queneesis* and *Liza falcipinis*) collected from three coastal water of OgoniLand, namely, Kaa, B-Dere and Bodo City. PAHs levels in the samples were measured by gas chromatography with flame ionization detector (GC/FID). The Average concentrations of these PAHs ranged from below detection limit of 0.0001 to  $120 \pm 1.18$   $\mu\text{g}/\text{kg}$  wet wt. in *Tilapia queneesis* and from 0.0001 to  $78.6 \pm 1.28$   $\mu\text{g}/\text{kg}$  wet wt. in *Liza falcipinis*. The highest average concentration of  $120 \pm 1.18$   $\mu\text{g}/\text{kg}$  wet wt. was recorded for Benzo[b] Fluoranthene from Bodo City. Total PAH concentrations in *Tilapia queneesis* from Kaa were significantly lower ( $P < 0.05$ ) than total PAHs concentrations in fish from B-Dere. Between the two fish species, *Tilapia queneesis* accumulated significantly higher concentrations ( $P < 0.05$ ) of total PAHs. 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 species, indicating anthropogenic, and origin of PAHs in the OgoniLand coastal environment. With the exception of *Tilapia queneesis* from Kaa, Bodo City and *Liza falcipinis* from Kaa, benzo[a]pyrene concentrations in the fish samples analyzed exceeded the EU recommended limit of 2  $\mu\text{g}/\text{kg}$  wet wt. for fish. The estimated carcinogenic potency equivalent concentrations exceeded the screening value for both species from all the study areas, indicating significant carcinogenic health risks associated with the consumption of these fishes.

**Key words:** carcinogenic, *Liza falcipinis*, OgoniLand, PAHs, *Tilapia queneesis*.

## 1.0 Introduction

In recent times, PAHs have received much attention due to their potential adverse human health and ecosystem impacts. Human exposure to these pollutants can result in cancer, mutations and birth defects (Zedec, 1980; White, 1986). Adverse effects of PAHs have also been observed in marine organisms and they include growth reduction (Christiansen and George, 1995), endocrine alteration (Meador *et al.*, 2006), malformations of embryo and larvae (Carls *et al.*, 2008; Camus & Olsen, 2008) and DNA damage (Caliani *et al.*, 2009).

Ingestion of contaminated food (Meador *et al.*, 1995) and diffusion from water across their gills and skin (Gobas *et al.*, 1999) are the major routes of PAHs exposure to fish. Due to the lipophilic nature and high chemical stability of PAHs (Bouloubassi *et al.*, 2001), they accumulate in the fatty tissues of fish following their uptake (Van der Oost *et al.*, 1991). Fishes are, therefore, good indicators of pollution in coastal waters, and they have been used extensively for environmental monitoring (Bouloubassi and Salot 1993; Bouloubassi *et al.*, 2006; and Nyarko, *et al.*, 2011).

PAHs are classified into two broad groups based on their physical and biological properties including high molecular weight (HMW) and low molecular weight (LMW) PAHs. The HMW PAHs consist of 4–6 aromatic rings and are less readily bio-degraded by indigenous microorganisms, hence can persist in the aqueous environment by bio-accumulating in aquatic organisms like fish and mussels and are more carcinogenic (Rocher *et al.*, 2004). The LMW PAHs consists of 2–3 aromatic rings and although less carcinogenic also pose toxic effect to many aquatic organisms (Brown and Peake, 2006). The PAHs composition of water and sediments can give some information about their sources and how they were derived. Larger concentration of LMW PAHs (e.g acenaphthene, fluorene) most often occur in sample matrices contaminated with naturally occurring PAHs (petrogenic and biogenic origins) while the PAHs from combustion processes (pyrolytic origin) often contain elevated concentrations of HMW (e.g. phenanthrene, fluoranthene, pyrene) and fewer LMW PAHs (Yan *et al.*, 2004).

It is important to note that PAHs are one of the first and largest set of compounds known to be strongly mutagenic to laboratory animals and man (Martinez *et al.*, 2004) and many studies have suggested a link between PAHs exposure and incidences of immunotoxicities and cancers (Simko, 2002; Falco *et al.*, 2005; Minique *et al.*, 2009; Effenga and Aramandia, 2009; and Pratt *et al.*, 2009). At present, Nigeria depends largely on oil-exploration as the main source of revenue and crude oil is known to contain PAHs at significant level.

The sources of PAHs in the coastal environment are described as either petrogenic (if the source is derived from petroleum, e.g. natural oil seepage and oil spills) or pyrogenic (if the source is derived from the incomplete combustion of organic matter and fossil fuel (Baumard *et al.*, 1998; and Abrajano *et al.*, 2003). The ratio of high molecular weight PAHs (HMW-PAHs) to low molecular weight PAHs (LMW- PAHs) has been used to characterize the origin of PAHs in the environment (Nyarko, *et al.*, 2011). Petrogenic sources of PAHs show characteristically higher proportion of LMW-PAHs such as naphthalene and acenaphthenes while pyrogenic PAHs have characteristically higher proportion of HMW-PAHs such as pyrene and benzo[a]pyrene (Helfrich and Armstrong, 1986; Rocher *et al.*, 2004). Thus, petrogenic sources of PAHs exhibit LMW/HMW ratios  $> 1$  whereas pyrogenic sources of PAHs exhibit LMW/HMW ratios  $< 1$  (Rocher *et al.*, 2004).

In addition to the LMW/HMW ratios, isomeric ratios of PAHs have been widely used as indices for the identification of PAH sources in the environment (e.g. Yunker *et al.*, 2002). For instance, a Benzo[a]anthracene/(Benzo[a]anthracene + Chrysene) (BaA/(BaA + Chry)) ratio  $> 0.35$  indicates pyrogenic or combustion sources while a ratio  $< 0.20$  has been attributed to pyrogenic sources although these sources are indistinguishable for ratios in the range 0.20–0.35 (Yunker *et al.*, 2002; and Nyarko, *et al.* 2011).

A large section of the world's population depends on seafood, especially fish, to meet their nutritional requirements. In Ogoniland and Nigeria at large, fish is recognized as one of the important source of animal protein, and provides over 60% protein intake. Food consumption has been identified as an important pathway of human exposure to many contaminants including PAHs (Cheung *et al.*, 2007) and, therefore, PAHs contamination of fish species that are widely consumed among the population may have serious health implications. The objectives of the study were therefore to (1) determine the levels of polycyclic aromatic hydrocarbon (PAHs) in two commercially important fish species from Ogoniland waters, namely *Tilapia gueneensis* and *Liza falcipinis*, (2) identify the sources of the polycyclic aromatic hydrocarbon (PAHs), and assess the associated carcinogenic health risks.

## 2.0 Materials and method

### 2.1 Study area

Ogoniland has a tragic history of pollution from oil spills and oil well fires; although no systematic scientific information has been available about the ensuing contamination. Ogoniland is a region covering some 1,000 km<sup>2</sup> in the south-east of the Niger Delta basin (**Figure 1**). It has a population of close to 832,000, consisting mainly of the Ogoni people.

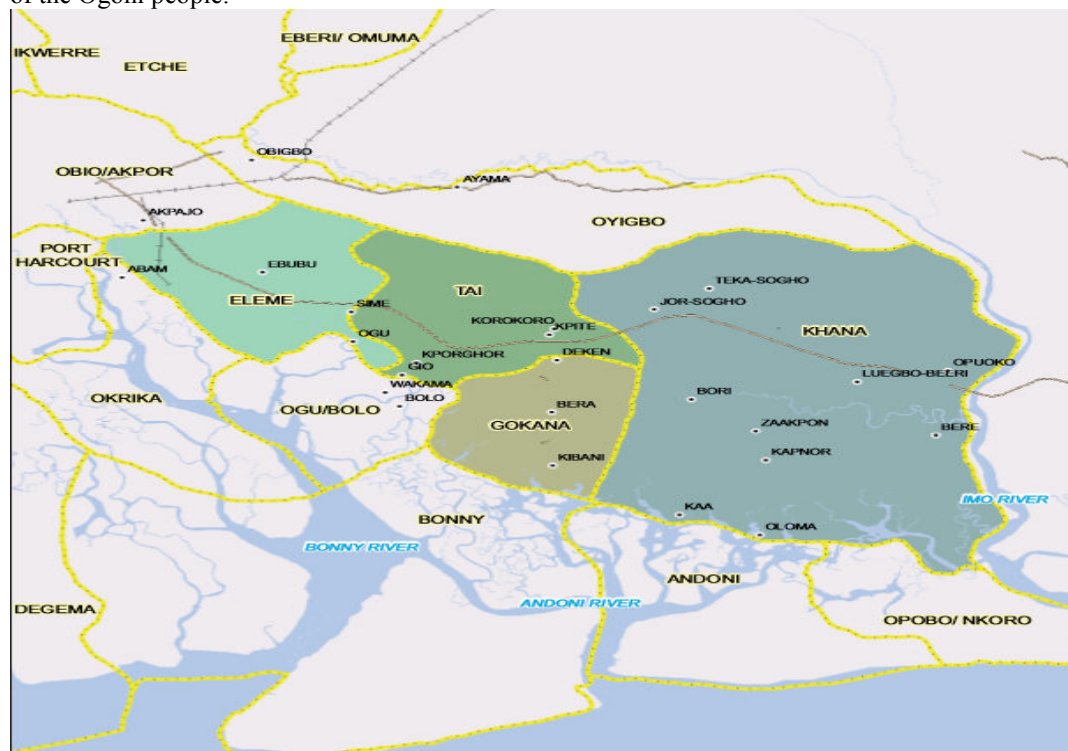


Figure 1.0: Map of Ogoniland showing the two Local Government Areas (LGA) where the study was carried out (Khana and Gokana, LGA).

## 2.2 Collection of test samples

Fresh samples of two selected important aquatic fauna of *Tilapia queneesis* (tilapia), *Liza falcipinis* (mulletts), were collected from landing beaches of Ogoni communities namely; Bodo City, B-Dere and Kaa water side in Gokana and Khana Local Government Areas (LGA) of Rivers State, Nigeria. The identities of the fish sample were confirmed at the Hydrobiology Unit, Department of Animal and Environmental Biology, University of Port Harcourt, Nigeria. At each site, ten individual fishes of similar size of each species were collected, cleaned and wrapped in aluminum foils, then kept frozen in an ice chest before transported to the laboratory for analysis.

## 2.3 Reagents

All reagents used in this study were of analytical grades with high purity.

## 2.4 Determination of Polycyclic Aromatic Hydrocarbons levels in fish

### 2.4.1 Processing of fish

The fresh fish samples were dried in the oven for 144h. They were then ground with blender (National, MX 795N, Japan) and kept in air tight containers prior to extraction process.

### 2.4.2 Extraction

Two grams (2g) of sample were weighed into a clean extraction container (50ml beaker) and 10ml of extraction solvent (dichloromethane) was added into the sample and mixed thoroughly and allowed to settle. The sample was carefully filtered into clean solvent rinsed extraction bottle, using filter paper fitted into Buchner funnels. The extract was concentrated to 2 ml and then transferred for cleanup/separation.

### 2.4.3 Cleanup/separation

1cm of moderately packed glass wool was placed at the bottom of 10mm ID \* 250mm Loup chromatographic column. Slurry of 2g activated silica in 10ml methylene chloride was prepared and placed into the chromatographic column. To the top of the column was added 0.5cm of sodium sulphate. The column was rinsed with additional 10ml methylene chloride and pre-eluted with 20ml of dichloromethane. This was allowed to flow through the column at a rate of about 2minutes until the liquid in the column was just above the sulphate layer. Immediately 1ml of the extracted samples was transferred into the column. The extraction bottle was rinsed with 1ml of dichloromethane and added to the column as well. The stop clock of the column was opened and the element was collected with a 10ml graduated cylinder.

Just prior to exposure of the sodium sulphate layer to air, dichloromethane was added to the column in 1 – 2 increments. Accurately measured volume of 8 – 10ml of the eluent was collected and labeled.

### 2.4.4 Gas Chromatography Analysis

The concentrated aliphatic fractions were transferred into labeled grass vials with rubber clip cap for gas chromatography analysis. 1 $\mu$ l of the concentrated sample was injected by means of hypodermic syringe through a rubber septum into the column. Separation occurred at the vapor constituent partition between the gas and liquid phase. The sample was automatically detected as it emerges from the column (at constant flow rate) by the FID detector whose response is dependent upon the composition of the vapor.

### 2.4.5 Chromatographic conditions

The gas chromatography was Hewlett Packed 5890 series II, gas chromatography apparatus, coupled with flame ionization detector (FID) (Hewlett Packard, Wilmington, DE, USA), powered with HP chemstation Rev. A 09:01 (10206) software to identify and quantify compounds. . The GC operating conditions were as follow: fused silica column [30m\*0.25 $\mu$ m film of HP-5(thickness)]; the inlet and injection temperature was set at 275 $^{\circ}$ C to 310 $^{\circ}$ C. Split injection was adopted with a split ratio of 8:1. Using rubber septum and volume injected was 1 $\mu$ l. The column temperature was programmed as follow; hold at 65 $^{\circ}$ C for 2min; 65-260 $^{\circ}$ C at 12 $^{\circ}$ C /min; 260-320 $^{\circ}$ C at 15 $^{\circ}$ C /min and maintained at 310 $^{\circ}$ C for 8minutes and oven temperature was set at 65 $^{\circ}$ C. Nitrogen was used as carrier gas. The hydrogen and compressed air pressure was 30psi. The oven programmed was: initial temperature at 65 $^{\circ}$ C. Verification of peaks was carried out based on retention times compared to those of external PAHs. Procedural blank and solvent blanks were analyzed and quantified, but no PAHs were found in these blanks.

## 2.5 Human health risk assessment of polycyclic aromatic hydrocarbons

In determining the carcinogenic risk from exposure to PAHs in fish, the USEPA guideline, as described by Cheung *et. al.* (2007) was followed. By this method, Benzo[a] Pyrene is used as a marker for the occurrence and effect of carcinogenic PAHs in foods and, therefore, the overall carcinogenic health risk from the measured PAHs was estimated based on toxic equivalence factors (TEFs) derived from the cancer potencies of individual PAH compounds relative to the cancer potency of Benzo[a]Pyrene (Nyarko *et. al.* 2011).

The product of the PAH concentration ( $\mu$ g/g) and its TEF gives a Benzo[a]Pyrene equivalent concentration (BaP<sub>eq</sub>) for each PAH. All the individual Benzo[a]Pyrene equivalent were then summed up to give a carcinogenic potency equivalent concentration (PEC) of all the PAHs according to equation (1) (Nisbet & Rasmussen, 1992).

$$PEC = \text{total } \sum (\text{TEF} \times \text{Concentration}) \quad (1)$$

Potency equivalent concentration values were then compared with a screening value for carcinogenic PAHs. The

screening value was calculated from Equation (2) (Russell *et al.* 1997).

$$SV = [(RL/SF) \times BW]/CR \quad (2)$$

Where SV = screening value ( $\mu\text{g/g}$ )

RL = maximum acceptable risk level (dimensionless)

SF = USEPA oral slope factor ( $\mu\text{g/g day}$ )

BW = body weight (g)

CR = consumption rate (g/day).

Screening value (SV) is the threshold concentration of total PAHs in fish tissue that is of potential public health concern; BW is the average body weight (g) and was set to 60000 g (i.e. 60 kg) for the adult population (Jiang *et al.*, 2005); CR is the consumption rate (g/day). Fish consumption rate was set at 68.5 g/day from the annual per capita fish consumption of 25 kg for Nigeria, similar to 68.5 g/day set for the annual per capita fish consumption of 25 kg for Ghana (Nyarko, *et al.*, 2011). RL is the maximum acceptable risk level (dimensionless), which is set to 10 (USEPA, 2000) so that the maximum risk would be one additional cancer death per 100,000 persons, if an adult weighing 60 kg consumed 68.5 g of fish daily with the same measured concentrations of PAHs for 70 years; SF is the USEPA oral slope factor for PAHs, used to estimate an upper-bound probability of an individual developing cancer as a result of a lifetime (70 years) exposure to carcinogenic PAHs and has a value of 7.30  $\mu\text{g/g day}$  (USEPA, 1993). For safety reasons, a consumption rate of 1 g/day was used to estimate the minimum level that a consumer may be protected from the carcinogenic effects of PAHs detected in these fishes (Nyarko, *et al.*, 2011).

### 2.6 Statistical analysis

The results are expressed as mean  $\pm$  standard error of the mean (SEM). One-way analysis of variance (ANOVA) was employed for between and within group comparison while student's t-test was used for paired comparison. 95% level of significance ( $p \leq 0.05$ ) was used for the statistical analysis.

### 3.0 Results

The average concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) (mean  $\pm$  S.E.M,  $\mu\text{g/kg wet wt.}$ ), Total mean PAH concentrations ( $\mu\text{g/kg wet wt.}$ ), PEC values, LMW-PAH/HMW-PAH and BaA/(BaA + Chry) ratios in *Tilapia queneesis* and *Liza falcipinis* are shown in Table 3 and 4. A total of 16 PAHs were analyzed for in *Tilapia queneesis* and *Liza falcipinis* from Kaa, B-Dere and Bodo City in OgoniLand. Average concentrations of these PAHs ranged from below detection limit of 0.0001 to  $120 \pm 1.18 \mu\text{g/kg wet wt.}$  in *Tilapia queneesis* and from 0.0001 to  $78.6 \pm 1.28 \mu\text{g/kg wet wt.}$  in *Liza falcipinis*. The highest average concentration of  $120 \pm 1.18 \mu\text{g/kg wet wt.}$  was recorded for Benzo[b] Fluoranthene from Bodo City. Total PAHs concentrations in this fish sample were  $17.7 \pm 0.65$ ,  $84.7 \pm 3.57$  and  $121 \pm 1.21 \mu\text{g/kg wet wt.}$  at Kaa, B-Dere and Bodo City respectively. Total PAHs concentrations in *Liza falcipinis* were  $20.6 \pm 1.17$ ,  $79.2 \pm 2.33$  and  $96.9 \pm 1.53 \mu\text{g/kg wet wt.}$  at Kaa, B-Dere and Bodo City, respectively. Total PAHs concentrations in *Tilapia queneesis* from Kaa were significantly lower ( $P < 0.05$ ) than total PAHs concentrations in fish from B-Dere. Between the two fish species, *Tilapia queneesis* accumulated significantly higher concentrations ( $P < 0.05$ ) of total PAHs at all the sites except at Bodo.

Benzo[b]fluoranthene concentrations in *Tilapia queneesis* from B-Dere and Bodo City respectively, showed marked elevation when compared with the control fish (Kaa). There was no significant difference ( $P \leq 0.05$ ) in naphthalene, anthracene, phenanthrene, fluoranthene, chrysene, Benzo[k]fluoranthene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene concentrations of *Tilapia queneesis* from all the sites. Similarly, Benzo[b]fluoranthene levels in *Liza falcipinis* from B-Dere and Bodo City were much higher than those from Kaa.

The calculated Potency Equivalent Concentration (PEC) values were 0.003, 0.006 and 0.012 in *Tilapia queneesis* at Kaa, B-Dere, and Bodo City, respectively and were 0.002, 0.010 and 0.011 in *Liza falcipinis* at Kaa, B-Dere and Bodo City respectively. The calculated Screening Value (SV) for Polycyclic Aromatic Hydrocarbons PAHs in fish was 0.001. LMW-PAH/HMW-PAH ratios in *Tilapia queneesis* were 0.028, 0.480 and 0.010 at Kaa, B-Dere and Bodo City, respectively and were 0.202, 0.114 and 0.116 in *Liza falcipinis* at Kaa, B-Dere and Bodo City respectively. The LMW-PAH/HMW-PAH ratios in *Tilapia queneesis* and *Liza falcipinis* from all the sites were  $< 1$ . BaA/(BaA + Chry) ratios in *Tilapia queneesis* were 0.148, 0.873 and 0.482 in *Tilapia queneesis* at Kaa, B-Dere, and Bodo City respectively and were 0.750, 0.941 and 0.942 in *Liza falcipinis* at Kaa, B-Dere and Bodo City, respectively.

The BaA/(BaA + Chry) ratios in *Tilapia queneesis* from B-Dere is, however, markedly higher relative to the ratios found in *Tilapia queneesis* at Kaa and Bodo City. The BaA/(BaA + Chry) ratios in *Tilapia queneesis* and *Liza falcipinis* from B-Dere and Bodo City were  $> 0.35$  while that of Kaa in *Tilapia queneesis* was below. Benzo[a] Pyrene concentrations in *Tilapia queneesis* from B-Dere and Benzo[a]Pyrene concentrations in *Liza falcipinis* at B-Dere and Bodo City analyzed exceeded the European Union (EU) limit of  $2 \mu\text{g/kg wet wt.}$  while Benzo[a]Pyrene concentrations in *Tilapia queneesis* from Kaa and Bodo City were below European Union (EU)

limit.

#### 4.0 Discussion

Exposure pathways of Polycyclic Aromatic Hydrocarbons (PAHs) to fish include bioconcentration from water across their gills and skin (Gobas *et al.*, 1999) and ingestion of PAH-contaminated particulate matter along with food (Meador *et al.*, 1995), as PAHs readily adsorb onto particulate organic matter (Fowler & Knauer, 1986; Raoux *et al.*, 1999) especially soil sediments. PAH are lipophilic and so they accumulate in the fatty tissues of fish following their uptake (Bouloubassi *et al.*, 2001).

*Tilapia queneesis* showed high amount of PAHs as compared to *Liza falcipinis* from all the sites. *Liza falcipinis* feed on detritus and most species have unusually muscular stomach and pharynx that help in digestion (Sikoki and Francis, 2007; Schneider, 1990). These may be the reasons why some of this fish species have a significant higher ( $P < 0.05$ ) concentration of PAHs. Total PAHs concentrations in *Tilapia queneesis* from Kaa were significantly lower ( $P < 0.05$ ) than total PAHs concentrations in fish from B-Dere. High molecular weight PAHs (HMW-PAHs) were generally predominant compared to low molecular weight PAHs (LMW-PAHs).

The United Nation Environmental Protection agency report on Environmental Assessment of OgoniLand (UNEP\_OEA, 2011) showed the presence of 16 PAHs in fish; oysters and mussels from the four Ogoni Local Government Areas which include two of the LGAs (Khana and Gokana) were this research was carried out. As contained in the report, PAHs were low in all samples. It also reported that fresh fish and seafood, concentrations were below the detection limit for most of the different PAHs and in a few cases, measurable but low levels were found. Their report on PAHs concentration in marine life concluded by saying; “WHO recommends a maximum intake of 20  $\mu\text{g}/\text{kg}$  (human) body weights. Hypothetically, assuming a human body weight of 75 kg and the concentrations of PAH's in smoked fish found in the present investigation, a person could eat up to half-a-kilo of smoked fish per day and still be below the WHO recommended maximum daily intake. Thus, fish consumption in Ogoniland, either of those caught locally or purchased from markets, including smoked fish, was shown not to pose a health risk to the community. The possible presence of hydrocarbons in fish was a matter of serious concern for the Ogoni community. This investigation showed that the accumulation of hydrocarbons in fish tissue is not a serious health risk in Ogoniland. However, the fisheries sector itself is suffering due to the destruction of fish habitat in the mangrove zone and highly persistent contamination of many creeks, making them unsuitable for fishing” (UNEP\_OEA, 2011).

As is evidenced in this study, the people of Ogoniland that depend on marine foods from water of B-Dere and Bodo City are at great risk of having cancer and other serious ailments. At B-Dere, *Liza falcipinis* accumulated significantly lower ( $P < 0.05$ ) concentrations of total PAHs than *Tilapia queneesis*. This is possibly due to local physical mixing, which can result in re-suspension of bottom sediments and redistribution of PAHs into the water column (Jurado *et al.*, 2007), thereby, exposing both fishes to PAHs irrespective of where these fishes may be found. The observed differences in PAH bioaccumulation in both species may also be attributed to differences in feeding preferences and general behavior (Fisher, 1995), as well as the mode of feeding in these species (Kong *et al.*, 2005). The LMW- PAH/HMW-PAH ratios indicate that the HMW-PAHs were generally predominant compared to the LMW-PAHs. The predominance of HMW-PAHs may be due to the fact that LMW-PAHs are preferentially degraded during PAH transport and burial into sediments (Berto *et al.*, 2009).

The levels of concentrations of contaminants such as Polycyclic Aromatic Hydrocarbons in fish reflect the state of contamination of the environment (Lanfranchi *et al.*, 2006) and, therefore, the observed levels of total PAHs in fish in this study indicate high levels of PAH contamination at B-Dere and Bodo City relative to Kaa (control). The LMW-PAH/HMW-PAH ratios observed in both species from all the three sites were  $< 1$ , indicating that the sources of these PAHs in the fish analyzed are mainly pyrogenic (Rocher *et al.*, 2004), and is a clear indication of anthropogenic pollution of PAHs in the coastal marine environment.

The observed BaA/(BaA + Chry) ratios in both species from all the sites were  $> 0.35$  except *Tilapia queneesis* from Kaa, this also indicated pyrogenic sources of PAHs contamination. This finding also confirms the finding of Gilbert *et al.* (2006). Possible anthropogenic sources include combustion of petroleum, automobile tire, and wood and vehicle emission. PAHs may then be transported from their points of release to the coastal environment via surface runoff and atmospheric deposition (Lipiatou & Saliot, 1991).

It would be observed that *Tilapia queneesis* from B-Dere, *Liza falcipinis* from B-Dere and Bodo City average value of Benzo[a] Pyrene concentrations exceeded the European Union (EU) limit of 2  $\mu\text{g}/\text{kg}$  wet wt. for fish, the safe level for human consumption. The PEC values also exceeded the SV in all the fish analyzed, indicating that consumption of *Tilapia queneesis*, and *Liza falcipinis* at a rate of 68 g/day can have adverse health effects. Although the estimated fish consumption rate of 68 g/day for people of OgoniLand and Nigeria at large is less than the USEPA fish consumption rate of 142.2 g/day for subsistence consumers (USEPA, 2000), the PEC values for the two fish species from all sites (0.001–0.011) were above the calculated SV (0.001), about 1–11 times higher. This indicates high levels of PAHs in *Tilapia queneesis*, and *Liza falcipinis*. Thus, these fish

species could be an important source of PAHs exposure among the Ogoni population. As fish constitutes a major source of animal protein in the diet (FAO, 2004).

The coastal people who tend to consume larger quantities of fish (Wei *et al.*, 2006) could be at a greater risk. A consumption rate of 1 g/day, however, appears to be protective from the carcinogenic effects of the current PAH levels (Nyarko, *et al.*, 2011). This is because the PEC values associated with a consumption rate of 1 g/day are found to be less than the screening value (Russell *et al.*, 1997). It is also important to note that the Benzo[a]Pyrene equivalent-based approach used for carcinogenic risk assessment is limited to a few PAHs that have been monitored in ambient air, and does not account for the toxicity of all PAHs to which the general population is exposed (Chen and Liao, 2006). Because PAHs are also known to cause growth reduction (Christiansen and George, 1995), endocrine alteration (Meador *et al.*, 2006), malformations of embryo and larvae (Carls *et al.*, 2008; Camus & Olsen, 2008) and DNA damage (Caliani *et al.*, 2009) in fish, as well as human health effects such as cancer, mutations and birth defects (Zedec, 1980; White, 1986), they may also have adverse impacts on marine life (Nyarko, *et al.*, 2011). From the present study, it would be deduced that the population living around the study areas may be exposed to substantial levels of PAH.

## 5.0 Conclusion

This study established the fact that Polycyclic Aromatic Hydrocarbons levels detected in *Tilapia queneesis* and *Liza falcipinis* are high and, thus, consumption of these fishes may pose significant health risk to the populace who consume this fish species. A consumption rate of 1 g/day may, however, be protective from carcinogenic health risk but the possibility that people living in these regions will consume only 1 g/day of fish is very slim. High molecular weight PAHs were predominant over low molecular weight PAHs, indicating that PAH contamination in coastal waters of the study area are mainly from pyrogenic. The results also suggest that fishes from Kaa area are safer for consumption compared to species found in B-Dere and Bodo City. The community should take a proactive and public stand against individuals or groups who engage in illegal activities such as bunkering and artisanal refining. These activities result in a huge environmental footprint, seriously impacting public health and livelihood activities, particularly fishing and agriculture.

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**Table 1:** Shows the Polycyclic Aromatic Hydrocarbons and their Toxic Equivalent Factors (Nisbet & LaGoy, 1992).

PAH Compound	TEF
Benzo[a]pyrene	1
Naphthalene	0.001
Acenaphthylene	0.001
Acenaphthene	0.001
Fluorene	0.001
Phenanthrene	0.001
Anthracene	0.01
Fluoranthene	0.001
Pyrene	0.001
Benzo[a]anthracene	0.1
Chrysene	0.01
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Indeno[1,2,3-cd]pyrene	0.1
Dibenz[a,h]anthracene	5

**Table 2:** PAH concentrations ( $\mu\text{g}/\text{kg}$  wet wt.) in *Tilapia queneesis* from the study areas (Kaa, B-Dere and Bodo City). Value are mean  $\pm$ S.E.M for three replicates, (n=3).

PAH COMPOUND	KAA (CONTROL)	B-DERE	BODO CITY
Naphthalene	0.11 $\pm$ 0.00 <sup>a</sup>	BDL <sup>a</sup>	BDL <sup>a</sup>
Acenaphthylene	0.32 $\pm$ 0.01 <sup>a</sup>	14.1 $\pm$ 0.56 <sup>b</sup>	BDL <sup>a</sup>
Acenaphthene	0.03 $\pm$ 0.00 <sup>a</sup>	6.54 $\pm$ 0.26 <sup>b</sup>	BDL <sup>a</sup>
Fluorene	0.02 $\pm$ 0.00 <sup>a</sup>	6.29 $\pm$ 0.25 <sup>b</sup>	0.30 $\pm$ 0.00 <sup>a</sup>
Anthracene	0.01 $\pm$ 0.00 <sup>a</sup>	0.13 $\pm$ 0.01 <sup>a</sup>	0.73 $\pm$ 0.01 <sup>a</sup>
Phenanthrene	0.01 $\pm$ 0.00 <sup>a</sup>	0.43 $\pm$ 0.02 <sup>a</sup>	0.03 $\pm$ 0.00 <sup>a</sup>
Fluoranthene	0.04 $\pm$ 0.00 <sup>a</sup>	0.63 $\pm$ 0.03 <sup>a</sup>	0.13 $\pm$ 0.00 <sup>a</sup>
Pyrene	0.10 $\pm$ 0.02 <sup>a</sup>	2.71 $\pm$ 0.11 <sup>b</sup>	0.05 $\pm$ 0.00 <sup>a</sup>
Benz[a]anthracene	BDL <sup>a</sup>	7.58 $\pm$ 0.30 <sup>b</sup>	0.05 $\pm$ 0.00 <sup>a</sup>
Chrysene	0.04 $\pm$ 0.17 <sup>a</sup>	0.51 $\pm$ 0.02 <sup>a</sup>	0.03 $\pm$ 0.00 <sup>a</sup>
Benzo[b]Fluoranthene	15.9 $\pm$ 0.31 <sup>a</sup>	40.6 $\pm$ 1.61 <sup>b</sup>	120 $\pm$ 1.18 <sup>c</sup>
Benzo[k]Fluoranthene	0.01 $\pm$ 0.00 <sup>a</sup>	0.15 $\pm$ 0.07 <sup>a</sup>	0.04 $\pm$ 0.00 <sup>a</sup>
Benzo[a]Pyrene	0.01 $\pm$ 0.00 <sup>a</sup>	3.51 $\pm$ 0.10 <sup>b</sup>	0.03 $\pm$ 0.00 <sup>a</sup>
Indeno[1,2,3-cd] Pyrene	0.84 $\pm$ 0.16 <sup>a</sup>	BDL <sup>a</sup>	0.66 $\pm$ 0.01 <sup>a</sup>
Dibenz[a, h]anthracene	0.28 $\pm$ 0.00 <sup>a</sup>	0.20 $\pm$ 0.12 <sup>a</sup>	0.001 $\pm$ 0.00 <sup>a</sup>
Benzo[g, h, l]perylene	0.001 $\pm$ 0.00 <sup>a</sup>	1.34 $\pm$ 0.13 <sup>b</sup>	0.03 $\pm$ 0.01 <sup>a</sup>
Total PAHs	17.7 $\pm$ 0.65 <sup>a</sup>	84.7 $\pm$ 3.57 <sup>b</sup>	121 $\pm$ 1.21 <sup>c</sup>
PEC	0.003	0.006	0.012
LMW-PAH/HMW-PAH ratio	0.03	0.48	0.01
BaA/(BaA + Chry) ratio	0.15	0.87	0.48

Values with different superscript letters (a,b,c) in the same column are significantly different at the 0.05 level ( $P \leq 0.05$ ). BDL implies below detection limits of 0.0001  $\mu\text{g}/\text{kg}$  wet wt.).

**Table 9:** PAH concentrations ( $\mu\text{g}/\text{kg}$  wet wt.) in *Liza falcipinis* from the study areas (Kaa, B-Dere and Bodo City). Value are mean  $\pm$ S.E.M for three replicates, (n=3).

PAHs COMPONENTS	KAA (CONTROL)	B.DERE	BODO CITY
Naphthalene	BDL <sup>a</sup>	BDL <sup>a</sup>	BDL <sup>a</sup>
Acenaphthylene	BDL <sup>a</sup>	0.20 $\pm$ 0.01 <sup>a</sup>	0.25 $\pm$ 0.00 <sup>a</sup>
Acenaphthene	0.54 $\pm$ 0.02 <sup>a</sup>	1.19 $\pm$ 0.04 <sup>b</sup>	1.48 $\pm$ 0.02 <sup>b</sup>
Fluorene	1.65 $\pm$ 0.55 <sup>a</sup>	5.77 $\pm$ 0.18 <sup>b</sup>	7.14 $\pm$ 0.12 <sup>c</sup>
Anthracene	0.84 $\pm$ 0.03 <sup>a</sup>	0.45 $\pm$ 0.02 <sup>a</sup>	0.53 $\pm$ 0.01 <sup>a</sup>
Phenanthrene	0.43 $\pm$ 0.02 <sup>a</sup>	0.50 $\pm$ 0.03 <sup>a</sup>	0.64 $\pm$ 0.01 <sup>a</sup>
Fluoranthene	0.04 $\pm$ 0.00 <sup>a</sup>	0.20 $\pm$ 0.01 <sup>a</sup>	0.25 $\pm$ 0.00 <sup>a</sup>
Pyrene	0.05 $\pm$ 0.00 <sup>a</sup>	0.24 $\pm$ 0.01 <sup>a</sup>	0.30 $\pm$ 0.01 <sup>a</sup>
Benz[a]anthracene	0.003 $\pm$ 0.00 <sup>a</sup>	0.64 $\pm$ 0.02 <sup>a</sup>	0.79 $\pm$ 0.01 <sup>a</sup>
Chrysene	0.001 $\pm$ 0.00 <sup>a</sup>	0.04 $\pm$ 0.00 <sup>a</sup>	0.05 $\pm$ 0.00 <sup>a</sup>
Benzo[b]Fluoranthene	17.1 $\pm$ 0.55 <sup>a</sup>	63.5 $\pm$ 1.93 <sup>b</sup>	78.6 $\pm$ 1.28 <sup>c</sup>
Benzo[k]Fluoranthene	BDL <sup>a</sup>	0.03 $\pm$ 0.00 <sup>a</sup>	0.03 $\pm$ 0.00 <sup>a</sup>
Benzo[a]Pyrene	BDL <sup>a</sup>	3.18 $\pm$ 0.00 <sup>b</sup>	2.81 $\pm$ 0.00 <sup>b</sup>
Indenol[1,2,3-cd]Pyrene	BDL <sup>a</sup>	3.13 $\pm$ 0.10 <sup>b</sup>	3.87 $\pm$ 0.06 <sup>b</sup>
Dibenz[a, h]anthracene	0.002 $\pm$ 0.00 <sup>a</sup>	0.004 $\pm$ 0.00 <sup>a</sup>	0.01 $\pm$ 0.00 <sup>a</sup>
Benzo[g, h, l]perylene	0.001 $\pm$ 0.00 <sup>a</sup>	0.18 $\pm$ 0.01 <sup>a</sup>	0.22 $\pm$ 0.00 <sup>a</sup>
Total PAHs	20.6 $\pm$ 1.17 <sup>a</sup>	79.2 $\pm$ 2.33 <sup>b</sup>	96.9 $\pm$ 1.53 <sup>c</sup>
PEC	0.002	0.010	0.011
LMW-PAH/HMW-PAH ratio	0.20	0.11	0.12
BaA/(BaA + Chry) ratio	0.75	0.94	0.94

Values with different superscript letters (a,b,c) in the same column are significantly different at the 0.05 level ( $P \leq 0.05$ ). BDL implies below detection limits of 0.0001  $\mu\text{g}/\text{kg}$  wet wt.).

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