Polycyclic Aromatic Hydrocarbons (PAHs)

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Polycyclic aromatic hydrocarbons (PAH), persistent organic pollutants, metals, and microplastics in freshwater and marine fish in Nigeria with reference to international maximum levels for contaminants in food and the potential risk to human health.

Keywords: Nigeria ; PAHs ; POPs ; metals ; microplastics ; marine fish

1. Polycyclic Aromatic Hydrocarbons (PAHs)

The major sources of environmental PAH contamination have been largely attributed to anthropogenic activities, particularly in the oil-producing states in Nigeria [1][2].

PAHs and their derivatives can be characterized by their genotoxic and carcinogenic potential. The 16 PAHs that are usually analyzed for environmental pollution are naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Ph), anthracene (An), fluoranthene (Fla), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno [1,2,3-cd]pyrene (InD), dibenz[a,h]anthracene (DahA), and benzo[ghi]perylene (BghiP) [3]. These are all exogenous PAHs from polluted agricultural land and air (atmospheric). However for food (and human health), the European Food Safety Authority (EFSA) included the following PAHs based on concerns for human health: benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, chrysene, cyclopenta(c,d)pyrene, dibenz[a,h]anthracene, dibenzo(a,e)pyrene and dibenzo(a,h)pyrene, dibenzo(a,i)pyrene, dibenzo(a,l)pyrene, indeno(1,2,3,-cd)pyrene, 5-methylchrysene, and benzo(c)fluorene [4].

2. PAHs in Fish from Fresh and Brackish Water

The degree of contamination is strongly associated with the level of pollutants in the water; hence, many studies have focused on monitoring the levels of PAHs in different aquatic environments. There are three rivers (Sime, Kporghor and Iko) in Akwa-Ibom state in the Niger Delta region of Nigeria that are well known for petroleum pollution from refinery and pipeline vandalization [5]. From these locations, 16 PAHs (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) were analyzed in the edible tissues of 30 species of fish and other seafood (periwinkles (*Littorina littorea*) and oysters (*Crassostrea virginica*)) commonly consumed in these communities [5]. The mean PAH concentration in *P. koelreuteri* from the Iko coastal waters was 49 µg/kg (wet weight). This value exceeded the EU maximum level for sum PAH4 (sum of (BaP, BaA, BbF, and chrysene) in smoked fish of 12 µg/kg wet wt. [6]. From the Sime River, the detected PAHs ranged from below the level of detection (LOD) to 22 µg/kg wet wt. in *Littorina littorea*, from the LOD to 87 µg/kg wet wt. in *Crassostrea virginica*, and from LOD to 171 µg kg^{-1} wet wt. in *Periophthalmus koelreuteri*. The highest average concentration of 171 g kg^{-1} wet wt. was recorded for Indeno from Sime waters. These rivers are generally heavily polluted by anthropogenic activities in the surrounding communities, which has resulted in the different levels of PAHs in the fish samples. In the Sime River, *C. virginica* accumulated significantly lower ($p < 0.05$) concentrations of total PAHs than *L. littorea* and *P. koeleuteri* [7].

There were twelve fish samples from the brackish water of Lagos Lagoon (a highly polluted site) that had high levels of PAHs (di, tri and tetra-aromatic isomers of naphthalene, acenaphthylene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)-anthracene, and chrysene) [8]. The fish species investigated were *Caranx hippos*, *Mugil cephalus*, *Sphyraena barracuda*, *Sarotherodon melanotheron*, *Tilapia guineensis*, *Ethmalosa fimbriata*, *Tarpon atlanticus*, *Scomberomorus trito*, *Lutjanus agennes*, *Pomadasys jubelini*, *Chrysichthys nigrodigitatus*, *and Lutjanus dentatus.* The highest mean concentration of PAHs (275 µg/kg dry wt.) was found in *Mugil cephalus* while 48 and 30 ng/g dry wt. were reported for *Chrysichthys nigrodigitatus* and *Tilapia guineensis*, respectively.

Studies on PAHs in marine fish are scarce in Nigeria, as the main focus is on environmental PAH pollution rather than on their presence in food. The detrimental effects of these contaminants on fish populations have been reported [9][8]. However, the effects of different remediation actions on PAH levels in fish have not been fully documented.

3. PAHs in Smoked Fish

PAHs can also be produced during food processing such as grilling, roasting, smoking, and barbecuing [10][11][12]. Fish smoking is highly practised as a means of prolonging shelf-life, enhancing flavour, and increasing utilization [13]. Nigeria produces 194,000 metric tons of dried fish annually, 61% of which is smoked fish [10]. Since smoking is a major source of PAH contamination in fish, the health risks associated with the consumption of smoked fish in Nigeria may be high [14][15]. The impact of the smoking techniques on the amount and type of PAHs that are generated, however, varies [5]. Silva et al. [10], reported the effect of using sawdust, charcoal, and firewood for smoking on the PAH levels in three species of fish (*Arius heude loti*, *Cynoglossus senegalensis* and hake). While charcoal with minimal production of smoke, gave the lowest concentration of sum PAHs, the sawdust on the other hand gave the highest level of PAHs. This was attributed to the pyrolysis of cellulose, hemicellulose and lignin and the limited availability of oxygen at the high processing temperature (>7000 C) [12][16]. The sum PAHs obtained is also related to the oil content of the fish species [13][17]. During fish smoking, the fish oil drips into the fire, and pyrolytic compounds are released. However, this can be controlled if the oil is prevented from dripping into the fire during the smoking process.

A similar study using traditional smoking methods, was carried out by Ubwa et al., (2015) [18]. Five fish species *Arius heudeloti*, *Cynoglussuss enegalensis*, *Clarias gariepinus*, *Blunt hwake* and *Mud minnow* were obtained from a fish farm in Benue state and analysed for the presence of 16 priority PAHs [18]. The results showed the highest sum PAH concentration in fish smoked with sawdust. The PAH levels in fish smoked with sawdust ranged from 815–1550 µg/kg, followed by fish smoked with firewood (738–994 µg/kg) and charcoal producing fish with the lowest PAH concentrations (135–614 µg/kg). The benzo(a)pyrene (BaP) concentration in *Arius heude loti* was 5.7 µg/kg and the BaP concentration in mud minnow was 5.4 µg/kg, a direct effect of using sawdust [18]. These values exceed the EU maximum level for BaP in smoked fish of 2 µg/kg [6]. In line with these findings, Tongo et al., (2017) [19] reported the presence of PAHs in the tissue of four smoked fish species (*Clarias gariepinus*, *Ethmalosa fimbriata*, *Tilapia zilli*, and *Scomber scombrus*) obtained from three major markets (Oreogbe, New Benin and Santana markets) in Edo State. *S. scombrus* had the highest sum PAHs concentration while the sum PAHs concentrations were 0.7, 1.0, 0.7, and 3.6 µg/kg in *C. gariepinus*, *T. zilli*, *E. fimbriata*, and *S. scombrus*, respectively. The estimated cumulative excess cancer risk index for *E. fimbrata* and *C. gariepinus* were higher than that of the other smoked fish species and the values exceeded the USEPA's acceptable cancer risk level of 10^{-6} [19][20]. The findings suggest that consumption of smoked *E. fimbriata* poses a higher potential carcinogenic risk than the other fish species investigated. Most of the studies on PAHs in smoked fish are focused on the smoking method and little information is available on the initial level of PAHs prior to the smoking. In some other cases, the source of the smoked fish and the method of smoking are not indicated [19].

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