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Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Six Species of Fish Caught Offshore and Landed at the Fishing Port of Boulbinet, Conakry, Republic of Guinea

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) constitute a major family of organic pollutants found in aquatic environments and capable of affecting marine ecosystems as well as human health. They pose a toxic risk due to their carcinogenic and mutagenic effects. The Guinean coastline, which has been subject to significant human pressure in recent years due to port, urban, mining, industrial and fishing activities, represents an environment potentially exposed to these contaminants. This study, the first of its kind in Guinea, aims to assess the levels of contamination by polycyclic aromatic hydrocarbons in six of the most commonly consumed fish species landed at the fishing port of Boulbinet in Conakry. The species studied are: *Dentex congoensis*, *Galeoides decadactylus*, *Sardinella aurita*, *Ethmalosa fimbriata*, *Pseudotolithus senegalensis* and *Decapterus punctatus.* The results of the high-performance liquid chromatography (HPLC) analysis showed that, of the 16 PAHs investigated, only five molecules were identified in the samples studied, namely: fluorene, phenanthrene, anthracene, fluoranthene and pyrene. With the exception of *Decapterus punctatus,* pyrene and fluoranthene were detected at low concentrations (ranging from 0.11 to 0.58 µg/kg) in the five fish species, whilst no fluorene was found in the fish *Ethmalosa fimbriata* and *Pseudotolithus senegalensis.* Low levels of anthracene and phenanthrene were measured in *Sardinella aurita* and *Ethmalosa fimbriata*. This illustrates the ability of fish to metabolise and excrete aromatic hydrocarbons and helps to explain the low concentrations measured in the muscle tissue. However, the average concentrations measured in muscle tissue remain broadly in line with international regulatory thresholds, particularly those established by European regulations, which do not set a specific upper limit for fresh, unsmoked fish. These results therefore suggest that, as things stand, the fish studied do not pose a major health risk to consumers. This study highlights the need to include multiple biological tissues in environmental biomonitoring programmes in order to obtain a more comprehensive assessment of chemical contamination in marine species. Further in-depth investigations are required to better understand the level of PAH contamination in fish species along the Guinean coast.

Keywords

Polycyclic Aromatic Hydrocarbons, Pelagic Fish, Demersal Fish, Guinean Coastline

1. Introduction

There is currently a growing awareness of the role played by the marine environment for humankind and of the urgent need to preserve its balance and conserve its resources. In light of this obligation (Convention on Biological Diversity, 1992), an ecosystem-based approach to managing this environment has become necessary [1]-[3].

Marine coastal zones are home to habitats that are key to the life cycles of many marine species [4]-[9].

However, they are subject to significant human pressure through numerous uses that have changed profoundly in recent decades [10] [11]. And coastal ecosystems are being profoundly affected as a result.

Since the mid-19th century, human activities have produced a vast array of chemical molecules, used in industry, agriculture, metallurgy, transport, consumer goods, medicine, construction and electronics. Globally, nearly 65 million substances are listed in the American Chemical Society's database, and 100,000 of these are or have been produced industrially.

Indeed, runoff from land and landfills into rivers and their tributaries carries pollutants from activities taking place within the catchment area, including urban and industrial development as well as intensive agriculture [12] [13]. In addition to these riverine inputs, there are direct inputs of contaminants resulting from the discharge of urban and industrial wastewater into coastal waters, as well as from offshore activities.

Guinea boasts a wealth of bio-ecological diversity that is unique in West Africa, with a coastline stretching some 300 km, characterised by sandy beaches, vast expanses of plains and lush mangrove forests that serve as spawning grounds, hatcheries and nesting sites for a wide variety of fish, shrimp, molluscs and other species… [14]

Fisheries products make a relatively significant contribution to meeting Guinea's animal protein requirements. According to the Economic Atlas of Guinea, this contribution was estimated at 40% in 2001. Furthermore, the approximate annual average for the decade 2009-2018 is estimated at between 15 and 18 kg per capita per year, with an upward trend throughout the period [15].

Many marine organisms accumulate contaminants in very high concentrations within their tissues. Their use for monitoring aquatic pollution originated 35 years ago in studies on the abundance of radionuclides in marine ecosystems [16]. As the concentrations measured are usually high, they are not particularly susceptible to accidental contamination. Furthermore, they represent the bioavailable fraction for marine organisms.

Throughout the world, fish are used as indicators of environmental and ecological changes in estuarine habitats [17]-[19]. As the concentrations measured are usually high, they are not particularly susceptible to accidental contamination. Furthermore, they represent the bioavailable fraction for marine organisms.

The aim of this study is to assess the levels of environmental contamination in the area by polycyclic aromatic hydrocarbons using sentinel fish, many of which are consumed by the local population. We will discuss the results from the fish targeted to assess the quality of our coastline. We also aim to identify future needs in this area of research.

2. Selection of Sentinel Species

A sentinel species is a species that triggers an alert when a situation poses a risk to the environment or to human health. It can be defined as 'an organism whose known characteristics can be measured to assess the extent of environmental contamination and its implications for human health, thereby enabling early prevention of its consequences [20].

The selection of species to be studied as a priority was based on:

- their accessibility and popularity among Guinean households
- their wide geographical distribution and abundance off the Guinean coast
- their lifestyle and biological characteristics (whether they are benthic or pelagic, their relative sedentary nature, whether they belong to the "fatty fish" or "lean fish" groups, etc.), which make it possible to identify the environmental and biological factors influencing bioaccumulation. The particular importance attached to the first criterion has led to the selection of six species likely to be present in all areas. These are: *Dentex congoensis*, *Galeoides decadactylus*, *Sardinella aurita*, *Ethmalosa fimbriata*, *Pseudotolithus senegalensis* and *Decapte rus punctatus.*

Dentex congoensis PoIl, 1954

This is the smallest species of dentex: it rarely exceeds 20 cm in length. Its jaws are typical of the genus Dentex and the spines of its dorsal fin are 'normal'. Its body is red, almost vermilion, with no distinctive markings. The species is coastal and common in the tropical African Atlantic, where it is caught by trawl on sandy-muddy bottoms at depths of 50 to 200 m.

Available information on its diet indicates that juveniles are detritivores and adults are omnivores with a more or less pronounced carnivorous tendency depending on the size the species can reach [21]-[25]. Consequently, it likely has a varied diet with a distinct carnivorous tendency.

Galeoides decadactylus (*Bloch*, 1795)

The "little captain" or "plexiglass captain" is found from the coast down to depths of 20 m, with a preference for depths between 10 and 18 m. It is usually caught on bottoms covered with silty sand. In 1982, CAVERIVIERE even noted that this species avoids seabeds of putrid mud [26]. This is undoubtedly a behaviour designed to avoid oxygen depletion caused by redox phenomena associated with the presence of pure mud. In 1974 in the Congo, SAMBA also noted that *Galeoides decadactylus* avoids oxygen-deficient areas. Juveniles are mainly concentrated in the deepest part of the distribution range, whereas larger individuals are found closer to the coast [27]. This was also observed by CAVERIVIERE in Côte d'Ivoire in 1982 [26].

Sardinelles

Sardinellas grow to a length of 25 to 30 cm. They are pelagic species of the continental shelf found in coastal waters and on the edge of the shelf, at depths of around 150 m. The species *Sardinella aurita* is widely distributed in the tropical and subtropical waters of the North and South Atlantic, and is also thought to occur in the western Pacific. The juveniles of S. *aurita* remain in nursery grounds until they reach maturity, then join the adult stock which migrates offshore following the movements of cold water. *Sardinella aurita* is indeed most abundant during the cold hydrological season, from December to May, that is to say, during the trade wind period, which causes cold, salty water to rise towards the coast. Sardinella are caught using purse seines and beach seines. A study of the diet of sardinellas has shown that these species have a very broad food range. Like most Clupeidae, their diet consists mainly of plankton [28]-[31].

Size-related variations are significant in *Sardinella aurita*. Analysis of stomach contents has shown that crustaceans and molluscs are consumed more by adults, whilst juveniles tend to target inorganic detritus and various terrestrial debris. This variability in the diet of *Sardinella aurita* supports the hypothesis of size segregation, with juveniles living near the coast and frequenting estuaries, and adults living further offshore [32].

Ethmalosa fimbriata (Bowdich, 1825)

The ethmalosa is an estuarine and coastal clupeid found in abundance from Mauritania to Angola. It is planktonivorous, although it was previously considered "limnivorous" [33]. As "all stomach contents reveal sand or silt" or "a microphagous silt-grazer" [34]. These characterisations of its diet are explained by the fact that sand and unidentified organic matter may constitute a significant proportion of the stomach contents [35] [36]. However, this phenomenon appears to be linked to flood seasons when the water's suspended particle content is high.

Furthermore, BAINBRIDGE did not find a significantly high proportion of benthic organisms in the stomach contents; it is therefore accepted that the Ethmalose's

Pseudotolithus senegalensis (Valenciennes, 1833)

This species is relatively widespread along the coast. It is less dependent on muddy substrates and is found on silty-sand bottoms and even near rocky outcrops. It is caught by trawl and by small-scale fisheries (gillnets and lines). As with most sciaenids, juveniles are found near the coast and larger individuals further offshore. In 1979, FONTANA hypothesised that spawners migrate to shallow waters solely to release their gametes [37].

Pseudotolithus senegalensis are active predators that hunt the swimming fraction of the mobile fauna in the coastal zone, primarily the small shrimp, *Palaemon hastatus aurivillius*.

Decapterus punctatus. (E. Geoffroy Saint-Hilaire, 1817)

The term "chinchards" encompasses several species of the Carangidae family that share a similar overall body shape, reminiscent of that of mackerel. It is a relatively small coastal pelagic species (25 to 35 cm long), which can grow to lengths of 60 and 70 cm respectively.

3. Materials and Methods

3.1. Selection of Study Areas

The fishing port of Boulbinet is located in the municipality of Kaloum in Conakry, the capital of the Republic of Guinea as shown in **Figure 1**. This port is one of the capital's main centres of fishing activity. It is heavily influenced by port operations, maritime traffic, urban discharges and commercial activities.

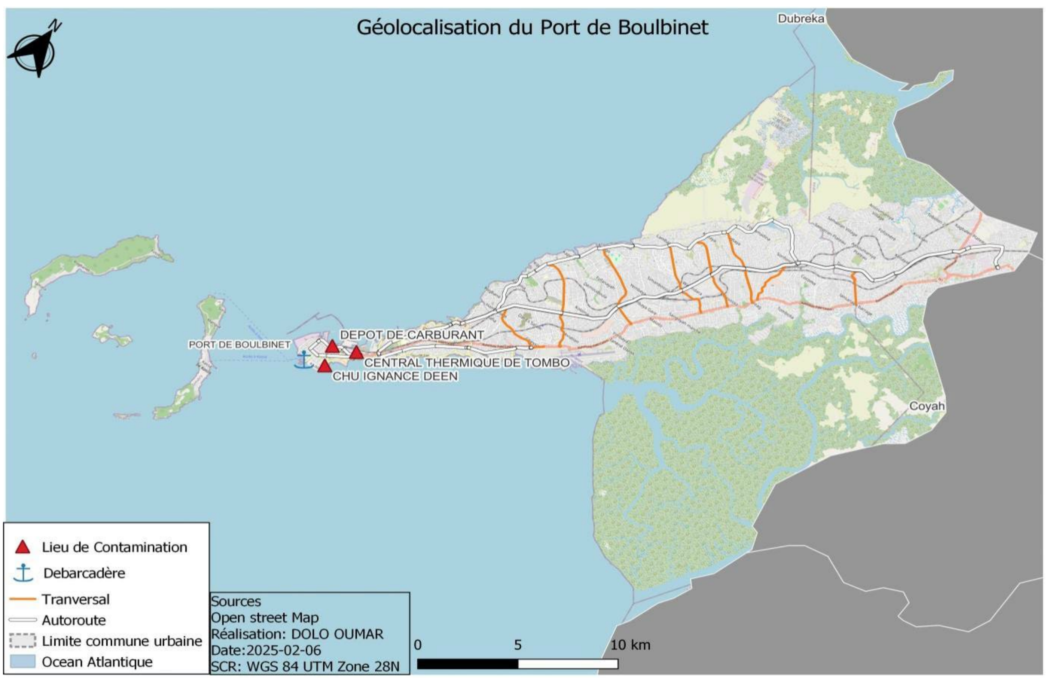

Figure 1. The coastline of the city of Conakry of the Republic of Guinea [38].

The coastal waters of this region also receive inputs from land-based runoff and urban effluents, which are likely to introduce various organic contaminants into the marine environment.

3.2. Sampling

Samples were taken upon the arrival of three fishing boats at the small-scale fishing port of Boulbinet. Sampling was carried out on the same day on three different boats. Each boat was considered a sampling campaign.

For each campaign, six samples of different species were taken to reflect the various varieties of the most commonly consumed marine species. This was done with the consent of the fishermen, who agreed to sell part of their catch. In total, nine (9) individuals of each fish species were sampled, at a rate of three (3) fish per species per sampling campaign. The fish were collected and bagged by species and individual in sterile plastic bags and labelled. The fish were then placed in a cool box containing ice packs and transported to the laboratory. The lengths measured were broadly identical, ranging from 21.9 to 23.3 cm with an average of 22.25 ± 1.59 cm, and weights ranging from 145 to 165 g, also with an average of 150 g ± 2 g.

3.3. Research Framework

Analyses of polycyclic aromatic hydrocarbons were carried out at the Regional Centre for Research in Ecotoxicology and Environmental Safety (CERES-Locustox), which is accredited to ISO/IEC 17025:2017 by the West African Accreditation System (SOAC) under Agreement No. SOAC-ES190007.

3.4. Equipment

High-performance liquid chromatography (HPLC) system with binary gradient elution, featuring a 1-litre solvent reservoir, a membrane filter for the mobile phase, pump, sample injector, column temperature control set at 25˚C, time-programmable fluorometric detector for different excitation and emission wavelengths, and a computer-assisted data acquisition and processing system. The concentration of PAHs is determined by comparing the chromatographic areas obtained at a given retention time between the sample and those of each of the PAH standards, whilst taking into account the areas obtained for the volumetric standards (internal standards).

3.5. Principle

2 g of fish flesh per sample and per sampling campaign were collected, immersed in an acetonitrile/acetone mixture, then purified on C18 reverse-phase cartridges and subsequently on Florisil cartridges. The determination of the content of individual polycyclic aromatic hydrocarbons after separation is carried out using high-performance liquid chromatography (HPLC) by measuring fluorescence at different excitation and emission wavelengths.

The limit of quantification is 0.2 µg·kg^{-1} for most of the compounds analysed, with the exception of fluoranthene and benzo(g,h,i)perylene, for which the limit of quantification is 0.3 µg·kg^{-1}, and indeno(1,2,3-c,d)pyrene, for which the limit of quantification is 1.0 µg·kg^{-1}.

A standard solution containing 16 PAHs designated as priority substances by the EPA (Environmental Protection Agency) in toluene, with a concentration of 100 µg/ml (100 mg/l): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene.

Stock standard solution at 200 ng/ml (200 µg/l)

Working standard solution at 50 ng/ml (50 µg/l).

3.6. Validation of the Acid Digestion Protocol

To validate the protocol's effectiveness, blanks and a certified reference material for the analysis of polycyclic aromatic hydrocarbons were analysed under the same conditions as the fish samples from the small-scale fishing port of Boulbinet.

The analysis reveals that all blanks used during the sample analyses are free from contamination. The recovery rate obtained between the measured and certified values of the certified reference material is acceptable, as these values range from 90% to 109%. This allows us to validate the protocol and the results obtained during this study.

4. Results and Interpretations

The average concentrations for each individual polycyclic aromatic hydrocarbon and the average concentrations of total PAHs are shown in Table 1.

Table 1. Average results from the sampling campaigns and average concentrations of total PAHs.

fish	PAH congeners µg·kg^{-1}					ΣHAP
	Pyrene	Fluorene	Fluoranthene	phenanthrene	Anthracene	
Dentex congoensis	0.11	2.39	0.11	Undetermined	Undetermined	2.61
Galeoides decadactylus	0.19	0.79	0.19	Undetermined	Undetermined	1.17
Pseudotolithus senegalensis	0.32	Undetermined	0.32	Undetermined	Undetermined	0.64
Ethmalosa fimbriata	0.11	Undetermined	0.11	0.17	0.17	0.56
Sardinella aurita	0.58	0.13	0.58	0.1	0.1	1.49
Decapterus punctatus	Undetermined	1.3	Undetermined	Undetermined	Undetermined	1.3

The histograms for polycyclic aromatic hydrocarbons (PAHs) are shown in Figures 2-5.

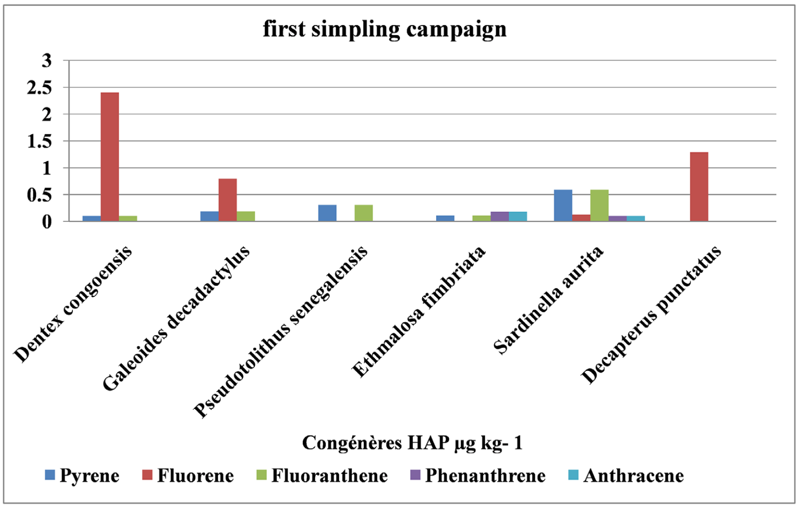

Figure 2. First sampling campaign.

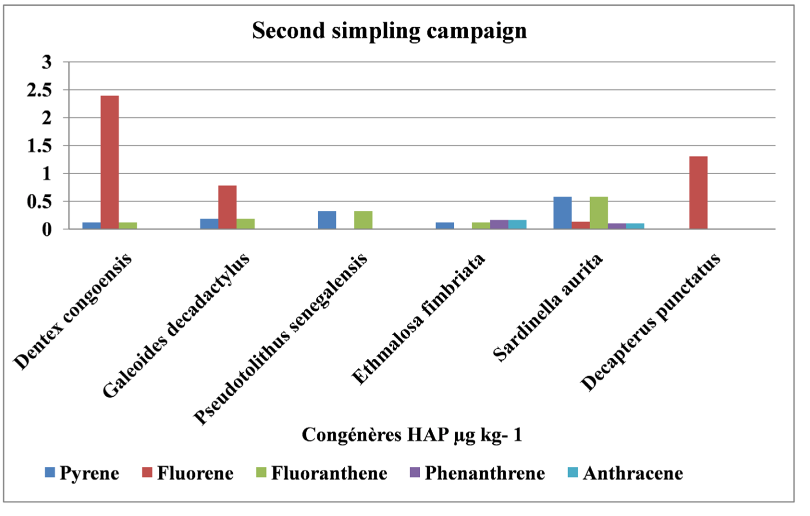

Figure 3. Second sampling campaign.

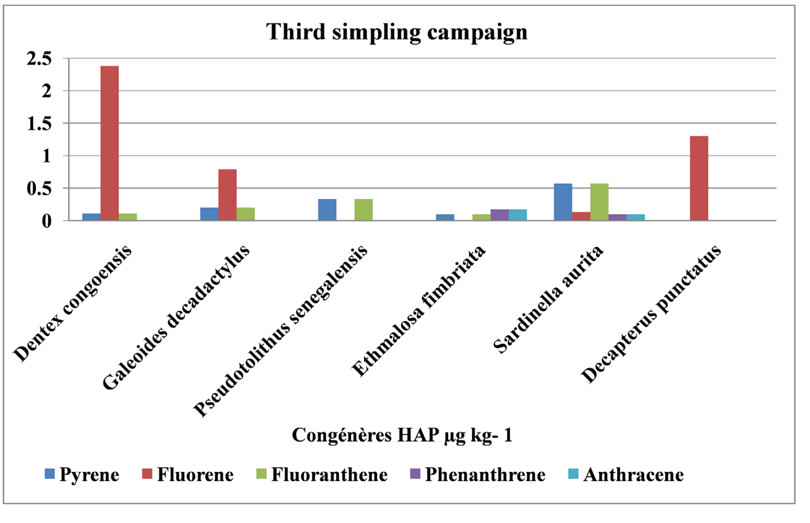

Figure 4. Third sampling campaign.

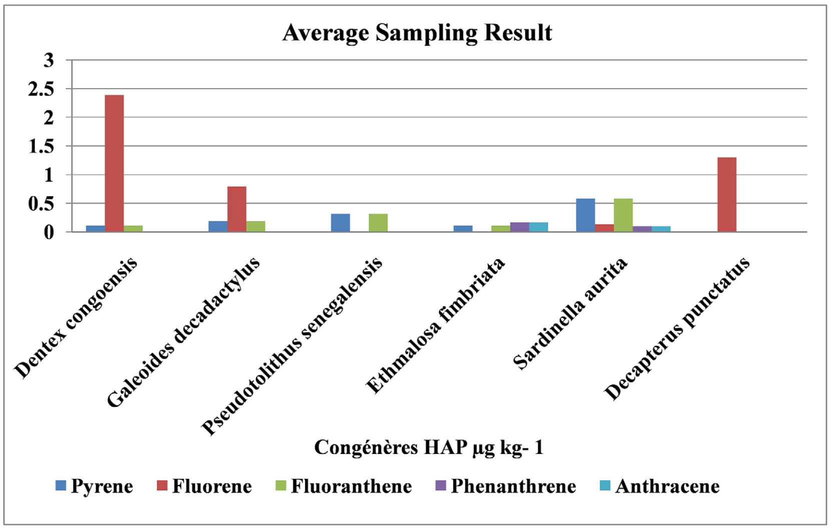

Figure 5. Average sampling result.

In our study, sixteen (16) different molecules were analysed in our samples, Of these, only pyrenes, fluorene, fluoranthene, phenanthrene and anthracene could be quantified in the muscle tissue of a few samples, with average concentrations per polycyclic aromatic hydrocarbon ranging from 0.11 to 2.39 µg·kg^{-1} wet weight. The results obtained reveal the presence of low-molecular-weight polycyclic aromatic hydrocarbons (PAHs), indicating contamination that is predominantly of petrogenic origin. Due to their physicochemical properties, these compounds are found mainly in the water column. Conversely, high-molecular-weight PAHs, generally associated with pyrolytic sources, have a strong affinity for particulate matter and are more readily adsorbed onto suspended particles [39].

With the exception of *Decapterus punctatus*, pyrene and fluoranthene were detected in low concentrations in all five fish species, whilst no trace levels of fluorene were found in *Ethmalosa fimbriata* and *Pseudotolithus senegalensis*. Low levels of anthracene and phenanthrene were measured in *Sardinella aurita* and *Ethmalosa fimbriata*. This further illustrates the ability of fish to metabolise and excrete aromatic hydrocarbons and helps to explain the low concentrations measured in the muscle tissue.

The pelagic species *Sardinella aurita* has the highest average concentration of fluoranthene and pyrene, at 0.58 µg·kg^{-1}, whilst the demersal species *Dentex congoensis* has the highest concentration of fluorene, at 2.39 µg·kg^{-1}. The highest concentration of phenanthrene and anthracene was found in the fish *Ethmalosa fimbriata*, whereas the lowest levels were recorded in the fish *Sardinella aurita*. Indeed, these results do not correspond to those obtained as part of the monitoring carried out under the Water Framework Directive (WFD) along the Atlantic coast between the Charente and the Bidasoa rivers during the period 2009-2012. Indeed, this research has shown that wild oysters collected from two sites at the bottom of the Arcachon Basin (Jacquets and Comprian) generally exhibited higher levels of contamination with polycyclic aromatic hydrocarbons (PAHs), including the seven PAHs classified as carcinogenic, than those observed in other coastal areas monitored along this stretch of coastline. Furthermore, analysis of the profile of the PAHs predominantly present in the Arcachon Basin suggests a predominantly pyrolytic origin. The compounds exhibiting the highest concentrations found in oysters are pyrene, fluoranthene, benzo(b)fluoranthene, chrysene, benzo(a)anthracene and benzo(a)pyrene.

Furthermore, the results also highlight the presence of a variety of polycyclic aromatic hydrocarbons (PAHs) in the species studied. The highest average concentrations of total PAHs were observed in *Dentex congoensis* and *Sardinella aurita*, at 2.61 µg/kg and 1.49 µg/kg respectively as shown in **Table 1**. Conversely, the lowest average levels of total PAHs were recorded in *Ethmalosa fimbriata* (0.56 µg/kg), followed by *Pseudotolithus senegalensis* (0.64 µg/kg). In this context, a study conducted by Ndadani *et al.* [40] on cephalopods from the Moroccan Atlantic coast revealed the presence of several polycyclic aromatic hydrocarbons (PAHs), including benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene and chrysene. Total PAH levels varied between species, with concentrations of (2.68 µg/kg) in octopus, (0.96 µg/kg) in squid and (0.41 µg/kg) in cuttlefish, reflecting differences in contamination depending on the species considered.

In general, the observed PAH profiles are characterised by a predominance of low-molecular-weight compounds. PAHs such as anthracene and phenanthrene are indeed more volatile and more susceptible to degradation processes than high-molecular-weight PAHs [41] [42]. Consequently, the presence of these compounds can thus be interpreted as a marker of anthropogenic contamination. However, the PAH concentrations measured in the muscle tissue of the fish studied are generally in line with current international standards and recommendations, in particular the requirements of European regulations on chemical contaminants in foodstuffs. Although there are no specific thresholds for fresh, unsmoked fish, the levels recorded remain low. Consequently, the results obtained indicate that the consumption of these fish is not currently likely to pose a major health risk to exposed populations.

5. Conclusions

This study assessed the levels of contamination by polycyclic aromatic hydrocarbons in six species of fish landed at the fishing port of Boulbinet in Conakry.

The results show variable bioaccumulation of PAHs depending on the species studied. The highest average concentrations of total PAHs were observed in *Dentex congoensis* and *Sardinella aurita*, at 2.61 and 1.49 µg/kg, respectively.

Although the levels recorded remain within food safety standards and do not pose any apparent health risk to consumers, the detection of these contaminants demonstrates the impact of human activities on Guinea's coastal ecosystems. Determining the concentrations of chemical contaminants in aquatic organisms is a useful tool for assessing their bioavailability in the environment, as it allows for both their identification and quantification. Their presence in biological tissues thus confirms that organisms are indeed exposed to environmental contaminants. However, these measurements do not necessarily accurately reflect actual exposure levels, due to physiological mechanisms of biotransformation, detoxification and excretion that may alter the concentrations accumulated in organisms. Furthermore, the quantification of contaminants alone does not provide an understanding of the biological effects they may induce. A more comprehensive assessment of their impact, therefore, requires the use of complementary biological indicators capable of providing information on the physiological and toxicological responses of exposed organisms.

Ultimately, this study highlights the need to strengthen monitoring programmes along Guinea's coastline and to conduct further research into organic contaminants in fishery resources. This is a fundamental step towards equipping policymakers with the tools and effective, sustainable solutions required to tackle environmental pollution.

6. Outlook

In future, it will be necessary to supplement this study with experimental contamination approaches, whilst also taking into account markers of oxidative stress and measuring PAH metabolites, in order to better explore the functional links between: bioaccumulation, biotransformation, immune responses and various forms of cellular damage (genotoxicity, lipid peroxidation, etc.) in aquatic organisms.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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