Per- and Polyfluoroalkyl Substances (PFASs) in Seafood from the Gulf of Guinea

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1 Introduction

Seafood is a major source of animal protein for about 3 billion people globally (Landrigan *et al*., 2020). It is a major diet for people in the Gulf of Guinea and also a major export product to Asia, Europe and North America (ECOWAS and FAO, 2020). Among fishery products in the gulf, the genus *Pseudotolithus* (Family Sciaenidae) commonly known as croakers constitute an abundant and commercially important fish in the Gulf of Guinea (Anyanwu, 1983; Isangedighi, 2014). The most dominant species include cassava croaker (*P. senegalensis,* Valenciennes 1833), bobo croaker (*P. elongatus,* Bowdich 1825), and longneck croaker (*P. typus,* Bleeker 1863) (Anyanwu, 1983; Chao and Trewavas, 1990; Isangedighi, 2014). Croakers are demersal species that are distributed throughout the Atlantic coast from Angola to Senegal and sometimes found in Morocco (Chao and Trewavas, 1990). Croakers are mostly coastal and marine species with a depth range of 0-250 metres but bobo and longneck species are also found in brackish and freshwater ecosystems. Croakers feed on fish, shrimps and other crustaceans (Chao and Trewavas, 1990). The growing anthropic activities in the coastal and marine environment across the Gulf of Guinea may potentially increase legacy and emerging contaminant fluxes into the subregion and therefore warrant concern on their occurrence, transport and fate.

Per- and polyfluoroalkyl substances (PFASs) are a large group of complex organofluorine chemical pollutants that are globally detected in all environments (Buck *et al*., 2011). Due to the strength of the carbon-fluorine bond, PFASs have been used extensively for the production of various household and industrial appliances (CDC, 2017). Over the years, PFASs have attracted global attention due to their persistent nature, bioaccumulation potential, and adverse effects on biota and human health (Ahrens and Bundschuh, 2014). Over 95% of PFASs are released directly into the aquatic environment with the largest global reservoirs found in oceans and sediment (Ahrens and Bundschuh, 2014; Dai and Zeng, 2019). Human exposure is from multiple pathways, including drinking water, seafood and aquatic products (Liu *et al*., 2019). Despite their global prevalence and health implications, studies of PFASs in coastal and marine ecosystems and seafood in Africa, particularly in the Gulf of Guinea are very limited (Essumang *et al*., 2017; Vaccher *et al*., 2020). In this study, we reported the first preliminary assessment of PFASs in croakers from the subregion.

2 Materials and Methods

2.1 Study Area

Fishery products for the study were collected from coastal communities in Nigeria and Ghana in January 2022 (Figure 1). Warri (5°17’54”N 5°19’51”E), Ibeno (4°32’56”N 7°59’20”E) and Lagos (6°29’39”N 3°23’11”E) are coastal cities in Akwa Ibom, Delta and Lagos State in southern Nigeria, while Apam (5°17’13”N 0°43’42”W) Cape Coast (5°04’57”N 1°21’01”W) and Sekondi-Takoradi (4°56’17”N 1°42’28”W) are coastal cities in Central and Western region of Ghana. Nigeria and Ghana are located in the Gulf of Guinea with similar climatic and economic activities. Economic activities include petroleum and solid mineral production, agricultural production, maritime traffic, artisanal and trawling. Both countries have an arid region in the north, savannah grassland in the middle belt, and humid and tropical rainforest towards the southern end that terminates in the Atlantic Ocean. The subregion has two major seasons. The dry (November - March) and wet (April - October) season with harmattan in December. Annual rainfall ranges from 1,500 to 2,000 mm. In the Sahel region, rainfall is less than 500 mm per year (Weller and Oberle, 2015). Nigeria with a population of 216 million people ranks as the most populous country in Africa and the 7th most populous nation in the world (NPC, 2022). Delta and Akwa Ibom states have an estimated population of 5 million people each with farming, fishing and petrochemical production from multinational corporations as the main economic activities. Lagos with over 23.5 million people is the most populated metropolis in Africa and the economic hub of Nigeria and West Africa. Lagos is densely populated and poorly treated sewage from residential and industrial effluents reaches the lagoon which divides the mainland from the island before entering the Atlantic Ocean. Ghana with a population of 31 million people is the 13th most populous country in Africa and the 47th in the world (GHS, 2021). Farming and fishing are the major occupation in Apam, tourism for Cape Coast and the production of solid minerals and petroleum in Sekondi-Takoradi.

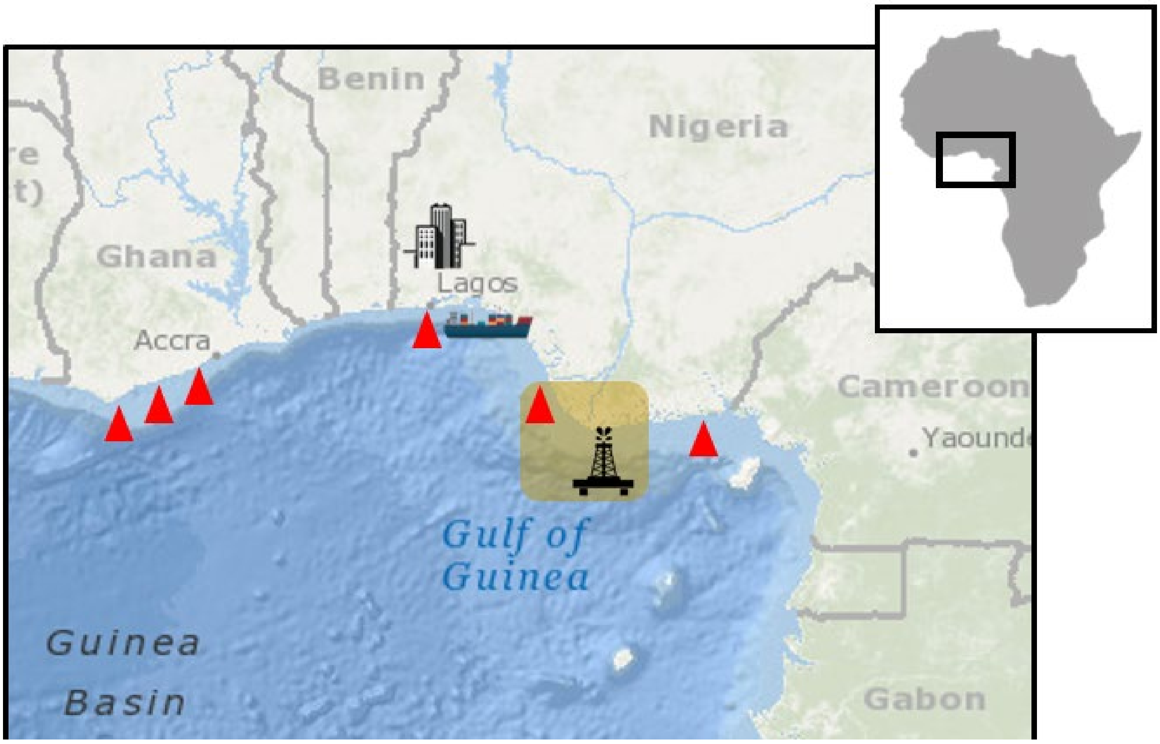

Figure 1: Map of the study area showing Africa and the Gulf of Guinea

2.2 Sample Collection

Freshly caught (<24 h) croakers were purchased from boat landings of artisanal fishers at the various coastal communities in Nigeria and Ghana between 10 and 23 of January 2022. Collected fish products were wrapped in aluminium foil, stored in dry ice and shipped to the laboratory at IFREMER, France, and kept in cold (-20°C) storage until further treatment.

2.3 Laboratory Analysis

At the lab, samples were defrosted, measured (total and standard lengths), weighed, and dissected for sex determination before the collection of the target tissues. The muscles were freeze-dried, homogenized and liquid-solid extraction was done with methanol/KOH, followed by a two-step clean-up on anion-exchange (Oasis WAX, Waters) and graphitic (ENVI-Carb, Merck) sorbents (Munschy *et al.*, 2019). Samples were transferred into vials and analysed with liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) in the electrospray negative ionization mode (Xevo TQS, Waters Corporation). All chemicals used were of analytical grade. Strict QA/QC procedures were followed, including extraction and injection blanks and the use of internal reference material. The target analytes (PFBS, PFPS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS, PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFECHS, 6:2Cl-PFAES, FOSA, 5:3FTCA, 7:3FTCA, 6:2FTS, 8:2FTS and 10:2FTS) were quantified against ^{13}C-labelled internal standards and recoveries were calculated on each sample using a different set of ^{13}C-labelled injection standards.

2.4 Data Analyses

Data were analysed using Microsoft Excel 2019 and XLSTAT 2022 for descriptive statistics (means, standard deviation and percentages of PFASs concentration in croakers). A non-parametric test (Kruskal-Wallis test) was applied at a $p < 0.05$ significance level to check for the differences between the means.

3 Results

3.1 Length-Weight of Croakers

Forty samples consisting of cassava (n = 20), longneck (n = 13) and bobo (n = 7) croakers across the six study sites were analysed. The total length for cassava, longneck and bobo croaker were 31±6, 29±3 and 28±3 cm while the weight was 308±144, 197±64 and 208±65 g wet weight (ww) respectively.

3.2 PFASs Concentration and Profile in Croakers

The summary result for the PFASs concentration in the muscles of croakers is shown in Figure 2. Only 8 PFASs were detected above the limits of quantification (LOQ) in the croaker muscles. The detection frequency for individual

PFASs in the three species ranges from 45 to 95 %. PFOS and PFUnDA had detection frequencies of 95%. PFTrDA had 90%, PFDA and PFNA had 85 and 83 %, while PFDoDA, PFTeDA and FOSA had 70, 58 and 45 % respectively. For the three species of croakers, $\sum_8$PFASs concentration ranges from 449-2475, 2211-4753 and 2487-7089 pg g^{-1} dry weight (dw) with a mean of 1051±539, 3255±793 and 3483±1606 pg g^{-1} dw for cassava, longneck and bobo croakers respectively. Taken together, the mean concentration of PFOS (1096±744 pg g^{-1} dw) was significantly higher than PFUnDA (354±357 pg g^{-1} dw), PFTrDA (321±203 pg g^{-1} dw), PFDA (228±129 pg g^{-1} dw), PFDoDA (201±161 pg g^{-1} dw), PFTeDA (148±68 pg g^{-1} dw) and PFNA (103±40 pg g^{-1} dw) in the three species.
In cassava croakers, the mean of PFOS (534±223 pg g^{-1} dw) was 3-4 times higher than PFTrDA, PFUnDA, PFTeDA, and PFDA. There was a variation in the distribution of PFASs in the three species across the study location. In cassava croakers, the mean PFOS concentration in Lagos was 2 times higher than Apam and Cape Coast and 3 times higher than Sekondi. In longneck croakers, PFOS concentration in Warri was 1.5-2 times higher than Ibeno and Lagos. The same trend was also found for bobo croakers between Warri and Ibeno.

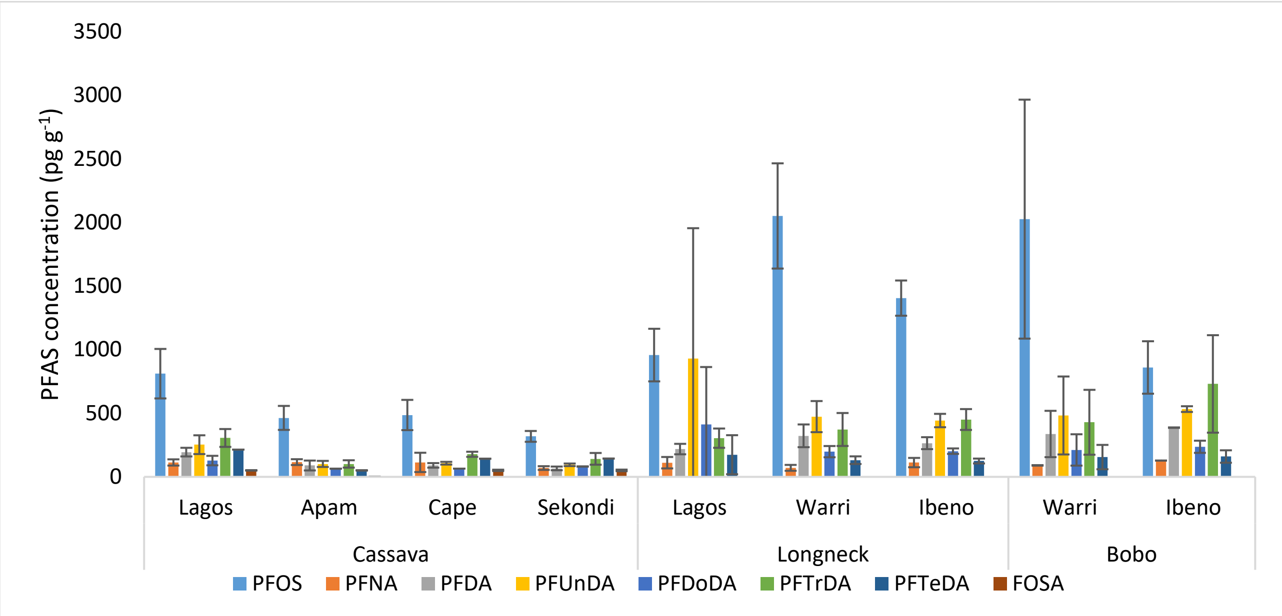

Figure 2: PFASs concentration (pg g^{-1} dw) in the three species of croakers across the study locations

PFAS profiles in the three species are shown in Figure 3. Overall, PFOS (49±10 %) was significantly higher than the other compounds while PFTrDA (15±6 %), PFUnDA (14±6 %) and PFDA (10±3 %) were relatively higher than PFNA (7±6 %), PFDoDA (7±3 %), PFTeDA (6±6 %) and FOSA (6±2 %).

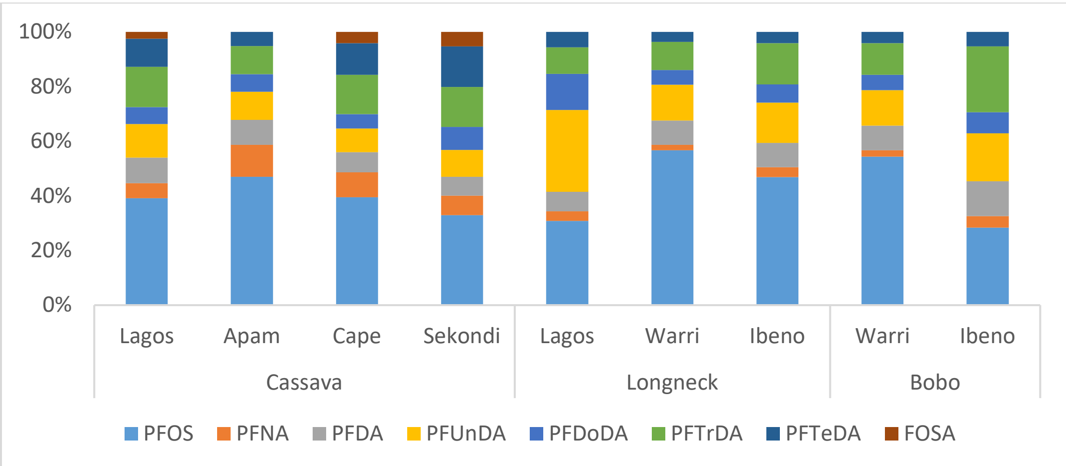

Figure 3: PFAS profiles in muscles of croakers across the sample location

4 Discussion

In this study, we collected and assessed the concentration and profiles of PFASs in the three most abundant species of croakers in the Gulf of Guinea. From our sampling, cassava croaker was more prevalent in Ghana, while longneck and bobo croakers are more predominant in Nigeria for the sample period. This may partly be attributed to fishing efforts and the season of sampling. As indicated by previous workers (Zafeiraki *et al*., 2019; Fair *et al*., 2019) for herring, hake, cod, mackerel, dab, haddock, plaice, sole, whiting, sea bass and croaker in the Netherlands and the United States, PFOS was significantly higher than other PFASs in the three species of croakers across the study location.

Cassava croakers sampled from Nigeria had higher PFAS levels compared to those from any of the three sites (Apam, Cape Coast and Sekondi) in Ghana. This is expected as Lagos has increased anthropic pressure compared to Ghana. Longneck and bobo croakers also appear to have higher PFAS levels compared to cassava croakers. The ecology and feeding habits of the croakers could also influence the distribution of PFASs in the three species. Bobo croakers (*P. elongatus*) are found in shallow coastal areas, while cassava (*P. senegalensis*) and longneck (*P. typus*) croakers are open sea species, but longnecks roam into shallow waters and estuaries, while cassava rarely does so. The concentration of PFASs reported in this study is lower than that reported for Atlantic croakers from Charleston Harbor, South Carolina, United States (Fair *et al*., 2019). PFOS concentrations in our study are also one order of magnitude lower than those of sea bass in the North Sea, a fish of similar trophic level (Zafeiraki *et al*., 2019). In our study, we observed that the length and weight of croakers do not correlate with the distribution of PFAS. This is similar to the observation of Fair *et al*. (2019) that species length and weight do not play any significant role in the profile of PFASs found in fishes.

5 Conclusions

The fishery sector is a major component of the economic development of countries within the Gulf of Guinea and provides seafood to the rest of the world. Further laboratory study is ongoing to improve our understanding of PFAS and other organic pollutants in the various tissues of croakers from the subregion. There is also a need to expand studies on other persistent and emerging contaminants in various fishery resources across the Gulf of Guinea to evaluate the risk to seafood along the seafood supply chain and the blue economy of the subregion.

6 Acknowledgements

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