[7]. The aquatic environment has been observed to be the

Residual Levels of Polychlorinated biphenyls (PCBs) in the Atlantic Mackerel (Scomber scombrus, Linnaeus, 1758) Marketed within a Niger Delta Community

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Abstract — The residual levels of polychlorinated biphenyls (PCBs) in the Atlantic Mackerel, Scomber scrombrus (mean length 44.87 cm, mean weight 478.35 g) marketed in Asaba, State, Nigeria, were determined Chromatographic (GC) technique in order to ascertain its suitability for human consumption. The summary statistics for the mean concentrations of detectable PCBs in S. scrombrus ranged from 0.04 mg/kg (PCB 153) to 0.65 mg/kg (PCB 126), with a total of 0.93 mg/kg while the mean concentrations of PCBs in S. scrombrus by market ranged from 0.02 mg/kg (PCB 153) at Cable market to 0.82 mg/kg (PCB 126) at Abraka market with no observed significant difference (p>0.05) in the mean concentrations of PCB 153 and PCB 169 in fish between markets. The toxicity quotient (TQ) values for PCBs in S. scrombrus ranged from 0.02 (PCB 153) to 0.33(PCB 126) while the estimated daily intake (EDI) values in mg/person/day for PCBs ranged from 0.00072 (PCB 138) to 0.026 (PCB 126). A toxic equivalency (TEQ) value of 0.0656 was recorded with PCB 126 having the highest Sub-TEQ value of 0.065 while the total PCB content in S. scrombrus according to market ranged from 0.67 mg/kg (Cable market) to 1.20 mg/kg (Abraka market). The observed PCB levels in fish fell below International threshold values indicating suitability for human consumption. However constant monitoring of this aquatic species for hazardous levels of PCBs was highly recommended.

Index Terms — Polychlorinated biphenyls, Scomber scrombrus, Toxic equivalency.

I. INTRODUCTION

Polychlorinated biphenyls (PCBs) are synthetic and persistent organic pollutants (POPs) that were once massively produced for a host of electrical and industrial applications [1]. They are one of the 12 groups of POPs initially listed in the Stockholm Convention on POPs [2]. These substances which go by the trade name Aroclor, are mixtures of 209 individual chlorinated compounds or congeners which still abound in the aquatic environment despite the outright stoppage of their manufacture decades ago. For example, they have been banned in the United States of America since 1979 [3]. Their persistence in the environment has been linked to their low degree of degradability, widespread use, redistribution, high thermal resistance and ability to readily bioaccumulate in the soft and fatty tissues of wildlife including fish [4]-[6]. PCBs principally migrate into the environment as a result of accidental spills and leaks from products containing Aroclor mixtures and then become redistributed amongst environmental compartments by volatilization and runoff

final end point for both persistent organic and inorganic pollutants which has led to the establishment of fish advisories in order to protect the health of man who may consume heavily contaminated fish [8]. According to the United States Environmental Protection Agency [9] fifty (50) states and some U.S. territories currently issue advisories to protect people from potential health risks of consuming tainted fish harvested from local waters. PCBs are vital in ecotoxicological researches around the world owing to their carcinogenic, mutagenic and teratogenic potentials [10]. To this end, the United Environmental Protection Agency (USEPA) has clearly categorized PCBs as probable human carcinogens belonging to Group B2 [11]. PCBs are known to disrupt the growth, reproduction, endocrine systems and enzyme activities of aquatic species including fish. They can also cause mortality amongst Piscean communities [12] and become a serious threat to aquatic ecosytems and human health once bound to sediment particles [13]. Measureable and hazardous concentrations of PCBs have been detected in fish from North America, Europe, the United Kingdom, Atlantic and Pacific Oceans and Gulf of Mexico [14], [15]. Owing to the toxic and deleterious nature of PCBs, several Governments around the world have developed monitoring programmes in order to keep levels below hazardous limits. For example, in Japan, sophisticated analytical measures have been adopted and applied since 2002 to monitor the levels of PCBs in fish, air, water and sediment [16]. In Nigeria, reports regarding the presence of PCBs in natural aquatic media and fish are relatively few [17]. It therefore becomes pertinent to carry out more research on the PCB content in commonly consumed imported fish species in the country against the backdrop that Nigeria has been reported to be the largest fish consuming Nation on the African continent with an annual consumption of about 3.2 million metric tons of which 2.1 million tons are imported annually [18]. The Niger Delta region of Nigeria plays host to a diverse composition of natural aquatic media including Rivers, Creeks, Streams, Tributaries, Swamps and Ponds. The region is particularly known for fishing and crude oil exploration activities. Asaba, the administrative capital of Delta State, Nigeria, was the focal point of this research, as there is paucity of ecotoxicological data on the PCB content in fish marketed in this Niger Delta town. In this light, the potential health risk to humans consuming seafood contaminated with hazardous chemical substances has been emphasized [19]. The fish species of interest (FSI) was the Atlantic Mackerel (Scomber scrombrus, Linnaeus, 1758),

commonly called "Scubia" in the local parlance. This fish

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species is widely consumed in Asaba and has been reported to be imported into the country from European countries, such as Norway [20]. According to the Food and Agriculture Organization of United Nations (FAO), the fish has been described as an epipelagic and mesodemersal species that is most abundant in cold and temperate waters of the world [21]. The fundamental working hypothesis of this research is that it may be possible to find residual levels of PCBs in S. scombrus that are being marketed within the study area. Data generated from the research have been compared to international thresholds for PCB in fish with a view to guiding both actual and potential consumers of the aforementioned experimental fish species.

II. MATERIALS AND METHODS

A. The study area

Asaba (Fig. 1) is a fast developing urban area with a metropolitan population of over half a million people. Geographically, it is gridlocked between Longitude 6° 11' N and Latitude 6° 44' E in Delta State, Nigeria, West Africa and has an average tropical temperature of 32° C during the dry season and an average rainfall of 2,700 millimeters during the rainy season. The town forms a strategic link between the western, eastern and northern regions of Nigeria through the popular River Niger [22]. After a presurvey of markets, four (4) markets namely Ogbogonogo, Cable, Midwifery and Abraka were eventually purposely selected for the collection of fish samples owing to the relative abundance of *S. scrombrus* in these markets.

B. Procurement of samples of fish

Fishes were purchased from the aforementioned markets between June and November 2019. They were placed in new polythene bags, sealed with selotape, labeled and moved to the laboratory in a Thermolineo® ice chest within 24 hours.

C. Laboratory studies and protocol

The identity of fish species (n=48) was confirmed using the electronic version of the Food and Agriculture Organization of the United Nations (FAO) species identification/fact sheet [21]. Total length measurements were taken using a measuring board while weight (g) of fish samples were measured using an electronic scale (Mettler® PM4800 Delta Range). The mean total length was 44.87 cm while the mean weight was 478.35 g (Table 1). All reagents and chemicals used were of analytical grade (BDH, Poole, England and Sigma, USA). All glassware was soaked in detergent and then rinsed alternately with running tap water and distilled water. Ten (10) g of muscle tissue was excised from the flanks with a stainless steel lancet and ground with anhydrous sodium sulphate until a completely dry homogenate was obtained. The extraction of PCB in fish tissue was performed according to standard procedures [23].

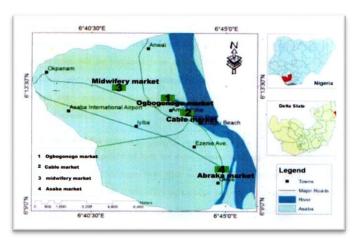


Fig. 1. Map of the study area.

The extract was concentrated to 2 ml with a rotary evaporator (rotovap) at 40 °C. The concentrated extract was thereafter used for clean-up and for gravimetric lipid determination. Clean-up of extracts was done in line with the method by [24] while a Perkin® model 5890 gas chromatograph equipped with Ni 63 electron capture detector was used for quantification of PCBs. The quality control was performed by regular analyses of procedural blanks and blind duplicate samples along with random injection of standards and solvent blanks.

TABLE I: MORPHOMETRIC MEASUREMENTS FOR EXPERIMENTAL SCOMBER SCROMBRUS

	Total	Mean Total		Mean
Month	Length	Length	Length Weight (g)	
	(cm)	(MTL, cm)		(MW, g)
June	41.35-42.28	41.67	300.25-305.15	302.46
July	54.65-56.82	55.49	645.18-650.24	648.48
August	47.76-50.11	48.96	560.25-600.67	580.32
September	43.68-44.84	44.17	301.17-302.45	301.21
October	39.36-41.42	40.26	345.24-350.03	347.75
November	38.24-39.51	38.68	387.62-390.34	388.65
		MTL=44.87		MW=478.35

D. Estimation of Daily Intake (EDI) of PCBs by man

The EDI was calculated based on the method by [25], [26].

Where:

40g/person/day = Estimated average fish consumption in the Niger Delta belt, Nigeria.

(CPCB) = PCB concentration in fish.

E. Toxicity/hazard quotient (TQ) for PCBs

The Toxicity/hazard quotient (TQ) for chemical elements is a comparison of the measured concentration of siterelated chemical elements in ecological matrices with specific health-based criteria [27], [28].

$$TQ = \frac{Concentration \ of \ PCB \ in \ fish \ sample}{Health \ based \ criteria}$$

F. Toxic equivalency (TEQ) for PCBs

According to [29, 30], the toxic equivalency (TEQ) for PCBs is expressed as follows:

$TEQ = \sum PCBi * TEF$

Where TEQ = Toxic equivalency,

PCBi = PCB concentration in fish,

TEF = Toxic equivalency factor for specific congener.

G. Statistical methods

GENSTAT® computer software (Version 12.1 for Windows) was used for statistical analysis. Data were subjected to Analysis of variance (ANOVA) to determine significant differences between mean values of PCBs while significance means (P<0.05) were separated with Duncan multiple range test (DMRT). Microsoft® Excel (for windows 2010) was used for all graphical presentations.

III. RESULTS

The summary statistics for the mean concentrations of detectable PCBs in Scomber scrombrus ranged from 0.04 mg/kg for PCB 153 to 0.65 mg/kg for PCB 126 as shown in Table II while the mean concentrations of detectable PCBs in S. scrombrus by market ranged from 0.02 mg/kg (PCB 153) at Cable market to 0.82 mg/kg (PCB 126) at Abraka market with no observed significant difference (p>0.05) in the mean concentrations of PCB 153 and PCB 169 in fish between markets (Table III). The mean concentrations of detectable PCBs in S. scrombrus by month ranged from 0.02 mg/kg (PCB 153) in August to 0.68 mg/kg (PCB 126) in July with no observed significant difference (p>0.05) in the mean concentrations of the PCB congeners in fish between months (Table IV). The toxicity quotient (TQ) values for PCBs in S. scrombrus ranged from 0.02 for PCB 153 to 0.33 for PCB 126 as presented in Fig. 2 while the estimated daily intake (EDI) values in mg/person/day for PCBs ranged from 0.00072 (PCB 138) to 0.026 (PCB 126) as shown in Fig. 3. As presented in Fig. 4, a TEQ value of 0.0656 was recorded with PCB 126 having the highest Sub-TEO value of 0.065 while the total PCB content in S. scrombrus according to market ranged from 0.67 mg/kg at Cable market to 1.20 mg/kg at Abraka market (Fig. 5). The overall quota for PCB congeners in S. scrombrus ranged from 4.30 % for PCB 153 to 69.89 % for PCB 126 as shown in Figure 6 while the specific PCB quota in S. scrombrus according to market ranged from 2.98 % (PCB 153) at Cable market to 76.11 % (PCB 126) also at Cable market (Fig. 7).

TABLE II: SUMMARY STATISTICS FOR CONCENTRATIONS OF DETECTABLE

PCBs (MG/KG) IN SCOMBER SCROMBRUS					
Congener	Mean	Minimum	Maximum	Threshold	
PCB 126	0.65	0.42	0.88	2.0	
PCB 138	0.18	0.09	0.33	2.0	
PCB 153	0.04	0.00	0.08	2.0	
PCB 169	0.06 Σ=0.93	0.02	0.09	2.0	

TABLE III: MEAN CONCENTRATIONS OF DETECTABLE PCBs (MG/KG) IN

SCOMBER SCROMBRUS BY MARKET					
Market	PCB 126	PCB 138	PCB 153	PCB 169	
Ogbogonogo	0.77^{a}	0.22^{b}	0.04^{a}	0.06^{a}	
Cable	0.51^{b}	0.09^{b}	0.02^{a}	0.05^{a}	
Midwifery	0.48^{b}	0.18^{a}	0.05^{a}	0.06^{a}	
Abraka	0.82^{a}	0.24^{a}	0.06^{a}	0.08^{a}	
3.6 2.4 .4		• .		.1 11.00	

Means with the same superscripts are not significantly different (p>0.05). Vertical comparisons only.

TABLE IV: MEAN CONCENTRATIONS OF DETECTABLE PCBs (MG/KG) IN

SCOMBER SCROMBRUS BY MONTH					
Month	PCB 126	PCB 138	PCB 153	PCB 169	
June	0.62a	0.12 ^a	0.04^{a}	0.04^{a}	
July	0.68^{a}	0.17^{a}	0.03^{a}	0.06^{a}	
August	0.67^{a}	0.17^{a}	0.02^{a}	0.07^{a}	
September	0.66^{a}	0.17^{a}	0.05^{a}	0.07^{a}	
October	0.61a	0.23^{a}	0.05^{a}	0.07^{a}	
November	0.65^{a}	0.23^{a}	0.06^{a}	0.07^{a}	

Means with the same superscripts are not significantly different (p>0.05). Vertical comparisons only.

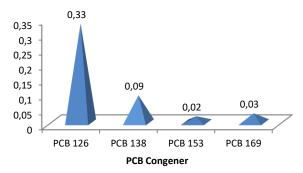


Fig. 2: Toxicity quotient (TQ) values for PCBs in Scomber scrombrus.

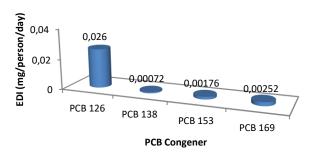


Fig.3: Estimated daily intake (EDI) values for PCBs.

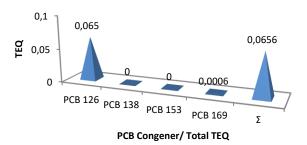


Fig 4: Toxic equivalency (TEQ) for PCBs in Scomber scrombrus.

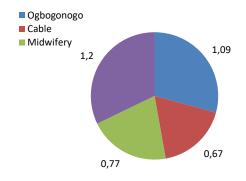


Fig. 5. Total PCB content (mg/kg) in Scomber scrombrus according to market.

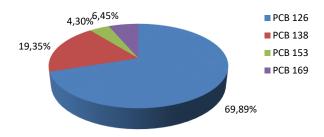


Fig. 6. The overall quota for PCB congeners in Scomber scrombrus.

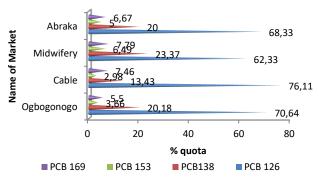


Fig. 7. Specific PCB quota in Scomber scrombrus according to market.

IV. DISCUSSION

Four (4) out of the recognized and existing 209 PCB congeners were detected in S. scrombrus in this research. They were PCBs 126, 138, 153 and 169. The IUPAC names for these congeners are

3,3',4,4',5-Pentachlorobiphenyl, 2,2',3,4,4',5'-Hexachlorobiphenyl, 2,2',4,4',5,5'-Hexachlorobiphenyl and 3,3',4,4',5,5'-Hexachlorobiphenyl respectively. PCBs 126 and 169 are also known as non-ortho PCBs or coplanar PCBs (cPCBs) and are regarded as "dioxin-like" congeners while PCB 138 and PCB 153 are "non-dioxin like" congeners [31-32]. The mean concentrations of PCB congeners in S. scrombrus took the rank profile PCB 126>PCB 138>PCB 169 >PCB 153, with PCB 126 accounting for well over half (69.89%) of the amount of detectable PCBs. A similar trend was observed with the quota of PCB 126 in fish according to individual markets. These congeners were probably detected in S. scrombrus as a result of bioaccumulation in which case these substances were not metabolized quickly enough by the fish species which resulted in this scenario. It has been observed that wildlife including fish can easily bioaccumulate xenobiotics such as PCBs especially when such substances are available in much higher levels in the environment than what is obtainable within the host organism [33]. Dietary bioaccumulation of POPs in the common sole Solea solea from French waters has been reported [34]. From a biochemical point of view, PCBs would be expected to bioaccumulate to varied levels in fish owing to their unique composition and location of chlorine atoms which would invariably exhibit different potential for bioavailability and consequent uptake by fish. This opinion lends credence to the observation by [35] who noted that different PCB congeners show different distribution patterns environmental media. The species of fish, feeding habitat/trophic position and specific conditions of the habitat, may influence the distribution of PCBs in the body

of such fish [36]. Furthermore, PCBs are lipophilic substances which can easily build up in the fatty tissues of recipient organisms. An investigation on the PCB levels in the Lagos Lagoon, Nigeria revealed PCB values (mg/kg) of 0.00 and 0.02 for PCB 138 and PCB 153 in Tilapia zillii. PCB 126 and PCB169 were not detected in that study but the authors attributed the PCB content in the Lagoon to anthropogenic impact [17]. Much higher concentrations of total PCBs in the Rock Sole (Lepidopsetta bilineata) and Rock Greenling (Hexagrammos lagocephalus) of 285 mg/kg and 104 mg/kg respectively from the Aleutia Islands of Alaska was reported by [37] clearly suggesting a much higher level of anthropogenic impact. As observed by the Alabama Fish Consumption Advisories [38] PCBs abound in the fatty areas of fish and by removing such fatty pieces the amount of contaminants eaten by man can be reduced drastically. Regarding the levels of PCBs in fish by market, there was no observed significant difference (p>0.05) in the mean concentrations of PCB 153 and PCB 169 in fish between markets, suggesting that such fish may have been sourced from the same distributor. It was further observed that Cable and Abraka markets had the lowest and highest total PCB levels compared to the other markets suggesting that prospective buyers of S. scrombrus could visit the former for the purchase of this fish species owing to the obvious lower PCB burden. Regarding the levels of PCBs in fish by month, there was no observed significant difference (p>0.05) in the mean concentrations of PCBs in fish between months, suggesting a relatively steady profile of PCBs in the sampled fish species during the period of research. The TQ values for non-carcinogenic risk revealed that none of such values exceeded unity even though PCB 126 had the highest value of 0.33. This observation is a clear indication that all the detected PCBs do not presently portray a risk to potential consumers of the product. The EDI values for PCBs were lowest and highest for PCB 138(0.00072 mg/person/day) and PCB 126 (0.026 mg/person/day) respectively. This trend is clearly linked with the lowest and highest mean concentrations of PCBs in fish. According to [39] the direction in which the EDI follows is directly related to the concentrations of contaminants in fish, thus the highest EDI value will be obtained for the contaminant with the highest concentration in fish and vice-versa. The overall TEQ value in this research was 0.0656 with PCB 126 accounting for a hefty 99% of this figure, suggesting a greater potency over the other detected PCBs. In order to be able to sum up the toxicity of different PCB congeners, toxic equivalency factors (TEFs) are applied to facilitate risk assessment and regulatory control [30]. In addition, in order to compare the toxicity of different samples, TEFs are generally used [40]. TEFs have so far been established for several congeners including PCB 126 and PCB 169. However, these factors are not available for PCBs 138 and 153 hence their exclusion from the overall TEQ computation. Regarding the direct human health risk via the consumption of S. scrombrus marketed in Asaba, both the total PCB level (0.93 mg/kg) and individual mean concentrations of the respective congeners did not exceed the 2.0 mg/kg threshold as established by [4]-[42]. This observation indicates that the consumption of S. scrombrus is relatively safe for

human consumption, an assertion that has been buttressed by the TQ values earlier mentioned.

V. CONCLUSION

The levels of detectable PCB congeners in S. scrombrus marketed in Asaba, Delta State, Nigeria, has been successfully presented. It is commendable to observe that the concentrations of these persistent organic pollutants in the experimental fish species fell below established International thresholds thus indicating the suitability of such fish for human consumption. However, the ideal situation is not to have any trace or residue of PCBs in fish as their presence in fish is actually not a welcome development against the myriad of potential health problems that they are known to cause. In this light, constant monitoring of this aquatic species for hazardous levels of PCBs is highly recommended as a non-hazardous outcome today may not be the case in future. This research is thus considered to be an integral part of such monitoring efforts

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