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AN INVESTIGATION OF POLYCHLORINATED BIPHENYL LEVELS IN TWO MARINE FISH SPECIES *Pseudotolithus senegalensis* and *Pseudotolithus carienensis*

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ABSTRACT

The level of PCBs in the flesh of marine fish species *Pseudotolithus. carienensis* and *Pseudotolithus senegalensis* representing the exotic and local species respectively was investigated in a coastal lagoon, Lagos, Nigeria . Out of 19 congeners of PCBs investigated, a total of 16 were detected in the fish samples comprising of 7 low chlorinated congeners (1, 5, 31, 44, 52, 66, and 87) and 9 high chlorinated congeners (101, 110, 138, 141, 153, 170, 180, 183 and 187). PCBs concentrations in the flesh of *P.senegalensis* (0.438ppm) were slightly higher than that of *P. carienensis* (0.4228ppm). Concentration of PCBs in both species exceeded the WHO maximum limits of 0.2ppm. The study shows the persistence of PCBs in our marine environment despite its ban several decades ago.
KEYWORDS: Polychlorinated biphenyl, *Pseudotolithus senegalensis*, *Pseudotolithus carienensis,* Marine fish.

INTRODUCTION

PCBs are a class of non polar toxic chemical compounds consisting of 209 congeners out of which only about 130 are found in commercial mixtures (Adeyemi et al, 2009).They are water soluble organic compounds with 1 to 10 chlorine atoms attached to biphenyl, which is a molecule composed of two benzene rings with a chemical formula of $C_{12}H_{10-x}Cl_x$, where x = 1-10.

They are also persistent organic pollutants whose effects remain long after their usage. Due to their wild applications and usages in dielectric fluids such as in transformers, capacitors, coolants and other agricultural purposes, they are detected in a range of biota including fish (Tanabe *et al.*, 1994; Skare *et al.,*1985; Risebrough *et al.*, 1976; Focardi *et al*, 1992) They were synthesized for the first time in the last century and produced at an industrial level in the1930's (Fuocoe,1995).

PCBs have been widely used in large quantities in highly developed industrial activities for about 40 years and have been discharged after use without precautions to reduce the environmental impact leading to the diffusion of these pollutants all over the world. Due to their very high chemical stability, the half-life in the environment of these pollutants is very high and is connected to a degree of chlorination. It can be up to 10 to 20 years for higher congeners. This makes PCBs to be one of the most widespread and persistent environmental pollutants. Fuocoe (1995) mentioned that their lipophilic characteristics are responsible for their ability to bioaccumulate, particularly in tissues and organs rich in lipids and this leads to their consequent possible connection with carcinogenesis in living organisms.

Although the production of PCBs was banned in 1979 in the Stockholm Convention on Persistent Organic Pollutants, previous studies (Osibanjo *et al* 1990) have confirmed their presence in fishes in Nigeria within the range of 8.0 – 13.0 mg/g (Adeyemi *et al*., 2009). This has therefore attracted international concern because of their persistence and ability to undergo long distance atmospheric transport (Risebrough *et al.,* 1976). For these reasons, PCBs have been included in the list of priority pollutants that have attracted global attention (Fuocoe, 1995).

In this study the concentration of PCBs congeners in the flesh of two species of fish *Pseudotolithus carienensis* and *Pseudotolithus senegalensis* were analyzed to compare the level of accumulation in the fish species. The PCBs congeners screened for in the samples include 2-chorobiphenyls, 2,3-dichorobiphenly, 2,2$_1$5-trichorobiphenyl, 2,4^1,5-trichorobiphenyl, 2,2^{1}3,5^1-tetrachlorobiphenly, 2,2,5,5^{1-} tetrachorobiphenyl,2,3^{1}4,4-tetrachlorobiphenyl, 2,2^1,3,4,5^1-pentachlorobiphenyl, 2,2,4,5,5^1-pentachlorobiphenyl, 2,3,3^1,4^1,6-pentachorobiphenyl, 2,,2,3,4,4^{1}5,- hexachlorobiphenyl 2,2^1,3,4,5,5^1-hexachlorobiphenyl 2,**2^{1}3,**5,5^1,6-hexachlorobiphenyl. 2,2^1,4,4^1,5,5^1-Hexachorobiphenyl, 2,2^1,3,3^1,4,4^1,5-Heptachorobiphenyl, 2,2^1,3,4,4^1,5,5^1-

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Heptachorobiphenyl, 2,2^1,3,4,4^1,5^1,6,- Heptachorobiphenyl, 2,2^1,3,4^1,5,5^1,6- Heptachorobiphenyl and 2,2,3,3,4,4,5,5,6.- Nonachorobiphenyl. They are known as congeners (1, 5, 18, 28, 31, 44, 52, 66, 87, 101, 105, 110, 138, 141, 153, 170, 180, 183 187) respectively.

MATERIALS AND METHODS

SAMPLING STATIONS

The sampling stations were the Makoko Better Life market and the Ijora sea food market both in Lagos state Nigeria.

DESCRIPTION OF STUDY SITES

Makoko Better Life Market

Makoko market is a low density market located at the shores of Makoko creek very close to the sawmill at Okobaba on the western shores of Lagos lagoon. Makoko creek experiences similar environmental conditions like the rest of the lagoon, notably freshwater discharge from adjacent wetlands through creeks and rivers in the wet season and tidal incursion predominantly in the dry season. The shores of Makoko are always littered with dirt. The water is consistently black/dark in colour due to persistent industrial wastes (Sawmill dust, dyes, paints) being regularly transported from the Okobaba to the Makoko waters. Due to the nearness to the shores, the pollutants find their way to the coastal shore which on decomposition release fouls odours.

Makoko market is mainly used by fishermen as a landing site for their fisheries resources sourced from the Lagos lagoon and offshore Lagos. It is patronized by both retailers and wholesalers.

Ijora Sea Food Market

Ijora market is a high density market located in Ijora Olopa in Apapa Local Government Area of Lagos State. It is used as a landing site for imported sea food. It is also patronized by both retailers and consumers.

FIELD SAMPLING

The samples of *P.senegalensis and P.carienensis* were collected monthly between the months of August and October, 2010 at two stations (Makoko market and Ijora sea food market) between the hours of 0600 and 0800. The mean standard length of the fish samples were 39.5 and 38cm respectively for both the local and exotic samples while the mean standard weight were 600 and750g respectively for both species also. A total of ten samples were collected from the two different markets each month and transported to the laboratory of the Physical and Chemical Oceanography Department of the Nigerian Institute for Oceanography and Marine Research at a temperature of –4^{0}C for analysis of PCBs in the fishes.

LABORATORY ANALYSIS OF PCBs

Reagents for PCBs Analysis

PCBs analysis was carried out according to the method used by (Adeyemi et al 2009).

The chemicals and reagents used were of analytical grade and of highest purity possible. LC grade dichloromethane and n-hexane used for the extraction and clean up was obtained from Fisher Scientific .The silica gel used in clean up was supplied by BDH Laboratories The acetone and anhydrous sodium sulphate that was used in this study was obtained from BDH Laboratories. A mixture of 19 PCB congeners namely (PCBs 1, 5, 18, 31, 44, 52, 66, 87, 101, 110, 138, 141, 151, 153, 170, 180, 183, 187, and 206) was obtained from Sigma Aldrich.

Extraction

Before extraction, the fish specimens were dissected and their flesh removed. Five grams of each flesh was ground with anhydrous sodium sulphate until completely dry homogenate is obtained (Anyakora *et al*., 2005). Extraction was carried out with dichloromethane in a cold extraction mode. After the extraction, the extracting solvent was left to evaporate using a rotary evaporator and the mass of the extractable fat determined by gravimetric method.

Sample clean up

The isolation of PCBs from the lipid matrix was done by solid phase extraction in a normal phase mode. Activated silica was then loaded into a glass chromatographic column (width 20 mm, height 400 mm) and

conditioned with dichloromethane. The extractable fats from the samples were dissolved in 5ml n-hexane and loaded on to the column and eluted with about 60ml n-hexane. The eluents were then concentrated using a rotary evaporator and under a gentle stream of pure nitrogen. The samples were dissolved in 1ml acetone ready for GC analysis.

Gas chromatography

Analyses were performed with Perkin model 5890 gas chromatograph equipped with Ni 63 electron capture detector. A low polar HP–5 column of 30 m length, 0.32 mm width and 0.25 mm film thickness were used. Nitrogen was used as a carrier gas at a flow rate of 40 ml/s. Data was processed using an HP 3396 integrator.
The operating parameters are as follows:

Injector temperature set at 250 and 300°C for the detector, the oven temperature programmed at 0°C initially (5 min hold) and increased to 300 at 4°C/min to give the analysis period of 34 min. PCB congeners in the fish were identified by retention time.

RESULT AND DISCUSSION

PCBs LEVELS IN THE FLESH OF *PSEUDOTOLITHUS* SPECIESTable 1: Summary of the PCB Concentrations in *P. senegalensis* and *P.carienenis* in the sampling periods

Fish Species	PCBs Congeners	Mean (Range)	WHO max. (mg/kg)
P. senegalensis	1	0.060 (ND-0.060)	N/A
	5	0.1075 (0.23-0.192)	N/A
	31	0.096 0.001-0.026)	N/A
	52	0.0265 (0.002-0.051)	N/A
	66	0.0085 0.004-0.013	N/A
	101	0.024 (ND- 0.024)	0.01
	110	0.012 (0.003-0.031)	N/A
	138	0.02 (0.001-0.051)	0.01
	153	0.026 (0.002-0.062)	0.01
	170	0.041 (0.001-0.106)	N/A
	180	0.043 (0.014-0.071	0.008
	183	0.027 (ND-0.027)	N/A
	187	0.001 ND-0.001)	N/A
		∑PCB 0.438	

Total congeners identified 13
Summation of the mean PCBs 0.438
Maximum permitted level of total PCB 0.2

Table 2: Summary of the PCB Concentrations in *P.carienenis* in the sampling periods

Fish Species	PCBs Congeners	Mean (Range)	WHO max. (mg/kg)
P. cariensis	5	0.1075	0.1075 (0.23-0.192
	31	0.096	0.096 (0.001-0.026)
	44	0.002	0.002 (0.001-0.003)
	66	0.0085	0.0085 (0.004-0.013)
	87	0.056	0.017 (0.015-0.094)

110	0.012	0.012 (0.003-0.031)
138	0.020	0.02 (0.001-0.051)
141	0.0115	0.0115 (0.006-0.0017)
153	0.026	0.026 (0.002-0.062)
170	0.0408	0.041 (0.001-0.106)
180	0.0425	0.0425 (0.014-0.071)
	∑PCB 0.4228	

Total congeners identified 11
Summation of the mean PCBs 0.4228
Maximum permitted level of total PCB 0.2

The table above indicates slightly higher PCBs concentration in the flesh of *P. senegalensis* than that of *P. carienensis*. The PCBs values in the flesh of both fish species were generally higher than the WHO maximum limit.

The analysis of variance (ANOVA) in the summation concentration of PCB for both the exotic and local samples recorded no significant difference at 0.05 levels.

The study reveals the presence of 16 congeners of PCBs out of the 19 investigated comprising the presence of 7 low chlorinated biphenyls and 9 high chlorinated biphenyls. Congeners 5, 31, 66, 110, 138, 153, 170, and 180 were found in both samples while congeners 1, 44, 52, 87, 101, 141, 183,and 187 appeared only in either of the samples and not in both . This result confirms the presence of both low and high chlorinated biphenyls in our waters (Osibanjo *et al*.,1990) and their ability to undergo long distance atmospheric transport (Risebrough *et al.,* 1976). However there is the absence of congeners 18, 151 and 206.

The presence of more congeners of PCBs in *P.senegalensis* than in *P.carienensis* indicates that our coastal waters are more polluted with industrial effluents and agricultural run-offs than those of the developed world and this is contrary to Osibanjo (1994).

The value of total PCB concentration recorded in this study is slightly higher than the values obtained by Unyimadu and Udochu (2002). The total PCBs concentration in the flesh of both species were higher than WHO maximum limits.

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