Full Length Research Paper

Polychlorinated biphenyl in fish samples from Lagos Lagoon, Nigeria

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Several fish samples from the Lagos lagoon, Nigeria were analyzed for the presence of polychlorinated biphenyls (PCBs). The fish species analyzed include *Tilapia zilli* (red belly Tilapia), *Ethmalosa fimbriata* (Bonga shad) and *Chrysichthys nigrodigitatus* (catfish). Eight PCB congeners were identified and quantified in muscle of the species analyzed. The concentration of total PCBs in samples ranged from 0.56 to 2.94 ppm. The study shows that concentrations of PCBs were higher in adult than in juvenile of most of the fish, and there was no correlation between fat content and total concentration of PCBs. The concentration of PCBs found in fish samples in this study were above the WHO residual limit of 0.2 ppm. The concentration levels in this study were compared with the levels detected in other parts of the world. The study confirms PCBs persistence in Lagos Lagoon, despite its ban several decades ago.

Key words: PCBs, Lagos Lagoon, fish, gas chromatography (GC), persistent organic pollutants (POPs).

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of non polar toxic chemical compounds consisting of 209 congeners. These persistent organic pollutants (POPs) have spread globally, and are now widely detected in a range of biota including fish (Tanabe et al., 1994; Skare et al., 1985; Risebrough et al., 1976; Focardi et al., 1992). Numerous studies on both human and laboratory mammals provide strong evidence of the toxic potential of exposure to PCBs. The health effect associated with PCBs include liver, thyroid, dermal and ocular changes, immunological alterations, neurodevelopmental changes, reduced birth weight, reproductive toxicity and cancer (Bove et al., 1999; Brown, 1987; Frunkin and Orris, 1999; Kimtiough et al., 1999; Woff et al., 2000). This led to a ban on the manufacture of these compounds in the United States in 1976. However, the continued use of PCBs in the developing countries is of international concern, because of their persistence and ability to undergo long distance atmospheric transport (Risebrough et al., 1976) and eventually getting deposited in areas far from the point of application. Many of the POPs such as PCBs have been used in Africa, including Nigeria for almost half a century without environmental consideration.

PCBs are likely not produced in Nigeria but contamination arises from importation of electrical transformer oils containing PCBs from developed countries such as France, UK and Japan. Between 1970s and 1980s, these transformers were widely used in the energy production sector, resulting in PCBs oil leakage into soil and underground waters. Anthropogenic activities in agriculture, discharge of industrial waste into rivers and incineration are other identifiable sources of PCBs in the country.

Nigeria's vast water resources especially Lagos lagoon are among those most affected by environmental stress imposed by human population growth, urbanization and industrialization. The disposal and management of wastes in Lagos, Nigeria presents serious environmental problems as the usual methods of waste disposal such as land filling, dumping site, and incineration lead to contamination of underground and surface water bodies. Previous studies have confirmed that fish samples from fresh water contain significantly higher concentration of PCBs than sediment and water. In Nigeria, the detection of POPs, including PCBs in 40 fresh water fish samples collected from various locations in Oyo and Ogun States was reported by Osibanjo et al. (1990); the concentration of PCBs in fish ranged from 8.0 - 13.0 ng/g (mean = 8.7

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Table 1. Fish species sampled in this study.

Fish species, common names in bracket	Average size (cm)	Average weight (g)	Lipid per wet weight (g/kg)	Total conc. of PCBs per wet weight (mg/kg)		
T. zilli juvenile (Red Belly Tilapia)	11.70	29.40	4.20	2.94		
T. zilli adult (Red Belly Tilapia	16.60	91.40	12.30	0.63		
E. fimbriata juvenile (Bonga shad)	11.70	13.70	20.40	0.56		
E. fimbriata adult (Bonga shad)	20.70	80.40	6.10	2.53		
C. nigrodigitatus juvenile (Bagrid cat fish)	14.60	19.70	4.60	0.70		
C. nigrodigitatus adult (Bagrid cat fish)	45.00	927.20	13.80	0.88		

ng/g), while similar studies in South Eastern Nigeria revealed 0.7 - 14.0 ng/g (mean 3.8 ng/g) PCBs per fresh weight of fish.

In this study, the three species of fish in Lagos lagoon were analyzed for PCBs both the adult and Juvenile of each species were screened to enable us understand the trend of accumulation in the analyzed fish species. The PCB congeners screened for in the samples include $2,4,4^{1}$ -trichlorobiphenil, $2,2^{1}5,5^{1}$ -tetrachlorobiphenil, $2^{1}3,3^{1}4^{1}5$ -pentachlorobiphenil, $2,3,3^{1}4,4^{1}5$ -hexachlorobiphenil and $2,2^{1}3^{1}4,4^{1}5,5^{1}$ -heptachlorobiphenil. They are known as PCBs 28, 52, 107, 105, 118, 153, 156 and 180, respectively.

METHODOLOGY

Sampling area

Lagos is a densely populated metropolitan city in Nigeria with more than 12 million people. Lagos lagoon is about 50 km long and 3 - 13 km wide, separated from Atlantic ocean by long sand and spit 2 - 5 km wide with swampy margins on the Lagoon side. Lagos Lagoon empties into the Atlantic via the Lagos harbor, a main channel through the heart of the city, 0.25 - 1 km wide and 10 km long. The principal ocean port of Lagos is located at Apapa in a broad western branch off the main channel of the harbor. Lagos Lagoon is fairly shallow and the city spread along more than 30 km of the Lagoons South western and western shoreline. The 11 km long bridge was built off the western shore to bypass congested mainland suburbs. The area west of the lagoon is not well provided with road, and many communities there traditionally relied on water transport. The pollution of the lagoon by urban and industrial waste is major problems as the large population depends on it for potable and recreational water, as well as a source of cheap and affordable protein in form of fish.

Sampling

The fish species were collected in July 2007, during a fishing tour of the lagoon. The fish species were collected alive from their normal environment, martyred and stored in an ice container before transporting to the laboratory where they were stored at temperature of -20^oC until ready for use. The fish species were *Tilapia zilli* (Tilapia), *Ethmalosa fimbriata* (Bonga shad) and *Chrysichthys nigrodigitatus* (Catfish). They were identified by Nigerian institute of Oceanography and Marine Research (Table 1).

Reagents

All chemicals and reagents were of analytical grade and of highest purity possible. LC grade dichloromethane and n-hexane used for the extraction and clean up were obtained from Fisher Scientific. The silica gel used in clean up was supplied by BDH Laboratories. The acetone and anhydrous sodium sulphate used in this study were also obtained from BDH Laboratories. A mixture of 8 PCB congeners (namely PCBs 28, 52, 107, 105, 118, 153, 156 and 180) was obtained from Sigma Aldrich.

Extraction

Prior to extraction, the fish specimens were dissected and the muscle tissue removed. 10 g of muscle tissue was ground with anhydrous sodium sulphate until completely dry homogenate was obtained (Anyakora et al., 2005). Extraction was carried out with dichloromethane in a cold extraction mode (Anyakora et al., 2004). After the extraction, the extracting solvent was evaporated using a rotary evaporator and the mass of the extractable fat determined by gravimetry.

Sample clean up

The isolation of PCBs from the lipid matrix was done by solid phase extraction in a normal phase mode. Activated silica gel was loaded unto a glass chromatographic column (i.d 20 mm, height 400 mm) and conditioned with dichloromethane. The extractable fats from the samples were dissolved in 5 ml n-hexane and loaded on to the column and eluted with about 60 ml n-hexane. The eluents were then concentrated using a rotary evaporator and under a gentle stream of pure nitrogen. The samples were thereafter dissolved in 1 ml acetone and 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 i.d and 0.25 μ m film thickness was used. Nitrogen was used as a carrier gas at a flow rate of flow rate 40 ml/s. Data were processed using an HP 3396 integrator. The operating parameters were as follows: injector temperature set at 250 and 300°C for the detector, the oven temperature was programmed at 150°C initially (5 min hold) and increased to 300 at 4°C/min to give the analysis period of 34 min.

Identification and quantitation

PCB congeners in the fish were identified by retention time match

Species of fish										Total conc.
(common names in bracket)	28	52	101	105	118	138	153	156	180	of PCBs
T. zilli juvenile (Red Belly Tilapia)	0.38	0.40	0.19	0.39	0.78	0.10	0.02	0.20	0.09	2.94
<i>T. zilli</i> adult (Red Belly Tilapia	0.07	0.06	0.10	0.25	0.02	0.00	0.02	0.06	0.05	0.63
<i>E. fmbriata</i> juvenile (Bonga shad)	0.07	0.08	0.18	0.11	0.01	0.03	0.07	0.05	0.02	0.56
E. fimbriata adult (Bonga shad)	0.33	0.10	0.54	0.34	0.66	0.11	0.11	0.15	0.19	2.53
C. nigrodigitatus Juvenile (Bagrid cat fish)	0.01	0.05	0.17	0.13	0.06	0.21	0.03	0.01	0.04	0.70
C. nigrodigitatus adult (Bagrid cat fish)	0.02	0.11	0.22	0.10	0.26	0.04	0.01	0.08	0.04	0.88

Table 2. Mean concentration of PCB congener in fish species (mg/kg wet weight).

 Table 3. Mean concentration of PCB congeners fish species mg/kg lipid weight.

Species of fish (common names in bracket)	28	52	101	105	118	138	153	156	180
<i>T. zilli</i> juvenile (Red Belly Tilapia)	89.40	95.40	139.60	91.70	185.70	24.70	5.20	48.10	21.20
T. zilli adult (Red Belly Tilapia	3.62	4.56	0.77	20.10	1.94	0.18	1.80	5.10	3.80
<i>E. fmbriata</i> juvenile (Bonga shad)	3.61	3.85	8.76	5.40	0.42	1.38	0.58	2.47	1.17
E. fimbriata adult (Bonga shad)	53.30	16.70	87.90	55.14	10.57	17.89	18.53	19.86	30.99
C. nigrodigitatus juvenile (Bagrid cat fish)	2.57	10.26	36.60	24.40	13.62	44.40	6.79	1.25	8.85
C. nigrodigitatus adult (Bagrid cat fish)	1.75	8.05	15.87	7.10	18.53	2.67	0.92	6.01	2.70

Mean concentration of PCBs = 1.37.

with those of the standards. The standard mixture contains PCBs 28, 52, 107, 105,118, 153, 156 and 180. Hence only these congeners were identified and determined in the fish samples during this study, quantitation was done based on area count match with those of known concentration of the standards.

RESULT AND DISCUSSION

Prior to the analysis the recovery studies were carried out using decaflourobiphenyls and found to range between 78 and 80%. The linearity of response was ascertained using standard mixture of PCBs and it ranged from 0.945 to 0.994. The relative standard deviation was less than 7%. Table 1 shows the lipid content in the different species. In tilapia and catfish, the adult fish samples contain on the average more lipids per body weight than the juvenile samples, but the reverse was observed for Bonga Shad. Analysis of the samples revealed presence of PCBs in all the fish species. Both adult and juvenile show some level of contamination in the Lagos Lagoon. The mean concentration of PCBs per wet weight and lipid weight is summarized in Table 2 and 3, respectively. The concentration of PCBs ranged from 0.56 to 2.94 mg/kg wet weight, highest concentration was observed in tilapia juvenile, (2.94 mg/kg wet weight) while the lowest concentration of PCBs was observed in Bonga shad Juvenile.

There was no correlation between the total concentration of PCBs (per wet weight) and parameters such as length, weight or lipid content of the species, but the variation may be due to the different metabolic charac-

teristics and feeding habit of the species. Tilapia is primarily a herbivorous cichlidae, its diet is dominated by (chlorophyllcea, phytoplankton cyanophycea, and euglenophycea) or benthic algae, and often becomes omnivorous under aquaculture condition. The African catfish represents the most common species in aquatic ecosystem and feeds on insects (mainly chironomidae), and detritus. The bonga fish also feeds on detritus, phytoplankton and sand grains depending on the size. The small sized ones had higher index of food preponderance in detritus while large size ones had higher index of food preponderance in phytoplankton. In this study, higher concentration of PCBs (2.53 mg/kg wet weight) was detected in a large sized adult Bonga shad while 0.56 mg/kg wet wt was detected in the juvenile ones. The same trend is observed for catfish but the reverse is the case for Tilapia (Table 1).

The accumulation pattern of PCBs in the fish species does not seem to implicate fish diet as the only pathway for bioaccumulation, which could either be as a result of either presence of PCBs in the water column or food chain (Kasozi et al., 2005), a conclusion we will attempt to draw in further studies by investigating the concentration of PCBs in the entire food web. The mean concentrations of high chlorinated biphenyl congeners (138, 153, 156, and 180) are relatively lower than the low chlorinated ones (Table 2). Figures 1 and 2 show the distribution of PCBs in the studied samples per wet weight and per lipid weight respectively. Reports indicated that the Lagos lagoon is fairly contaminated with PCBs and DDTs, higher than what is obtained in

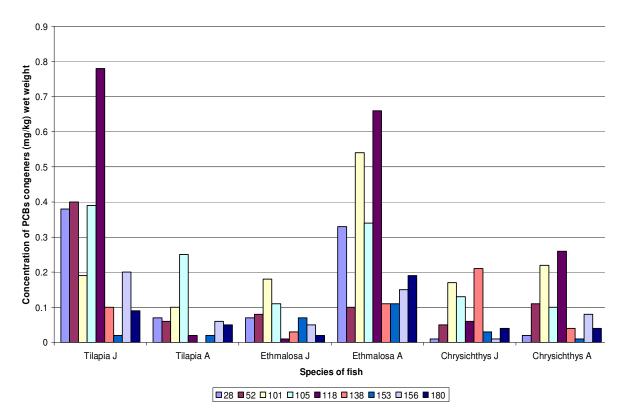


Figure 1. Mean concentration of PCB_S congeners (mg/kg wet weight).

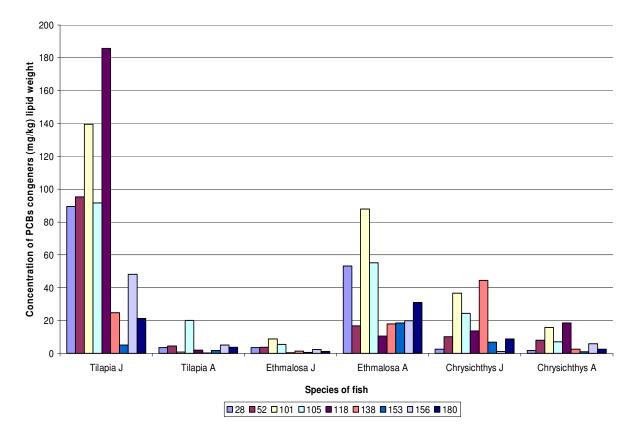


Figure 2. Mean concentration of PCBs congeners (mg/kg lipid weight).

most places in developed countries (Osibanjo et al., 1994) and suggesting agricultural and industrial activities as sources of contamination in the Lagoon.

A previous report on fish analysis of samples from Ogun river, inflow location of the Lagos Lagoon revealed mean concentration of PCBs 0.11 to 0.29 (ug per Kg wet weight) compared to fish samples from River Saar, Federal Republic of Germany, 0.004 to 0.01 mg per kg wet weight PCBs. (Unyimandu et al., 2002). The concentrations of PCBs detected in fish samples analyzed in this work were higher.

The numerous recent studies on fish indicate the maximum concentration of PCBs in fish is a few parts per million with higher levels found in bottom feeders such as carp (Ceccarini and Ginnarelli, 2007), and concentration of PCBs is relatively higher in samples from ocean and seas with higher industrial activities (Vourimen et al., 1985; Larsson et al., 1991). This study corroborates these findings in a more specific way by bringing out data on PCBs on fish samples from the Lagos lagoon.

REFERENCES

- Anyakora CA, Ogbeche KA, Palmer P, Coker H (2005). Determination of Polynuclear aromatic hydrocarbos in the marine samples of Siokolo fishing settlement. J. Chromatogr. A, 1073(1-2): 323 -330.
- Anyakora CA, Ögbeche KA, Unyimadu J, Olayinka K, Alani R, Alo B (2004). Determination of Polynuclear Aromatic Hydrocarbons in the water sample of the Lagos lagoon. Niger. J. Pharm. 35: 35-39.
- Bove FJ, Slade BA, Canady RA (1999). Evidence of excess cancer mortality in a cohort of workers exposed to polychlorinated biphenyls. J. Occup. Environ. Med. 41(9): 739-740.
- Brown DP (1987). Mortality of workers exposed to polychlorinated biphenyls an update. Arch. Environ. Health 42(6): 333-339.
- Ceccarini A, Giannarelli S (2007). Polychlorobiphenyls. In: Handbook of Water Analysis (Leo Nollet ed.)CRC Press, Boca Raton, pp. 529-562.
- Frunkin H, Orris P (1999). Evidence of excess cancer mortality in a cohort of workers exposed to polychlorinated biphenyls. J. Occup. Environ. Med. 41(9): 739-745.

- Kasozi GN, kiremire BT, Bugenyi FWB, kirsch NH, Nkedi Kizza P (2005). Organochlorine residue in fish and water samples from Lake Victoria Uganda.
- Kimbrough RD, Doemland ML, LaVois ME (1999). Mortality in male and female capacitor workers exposed to polychlorinated biphenyls. J. Occup. Environ. Med. 41(3): 161-171.
- Larsson P, Hamrin S, Okla L (1991). Factors determining the uptake of persistentpollutants in Eel population. Environ. Pollut. 69: 39-50.
- Osibanjo O, Bamigbose (1990). Review of chlorinated substance in marine fish and shellfish of Nigeria. Marine pollution bull. 21: 581-586.
- Osibanjo O (1994). Review of chlorinated hydrocarbon substances in African aquatic environment. FAO. fish Rep., 502: 37-45.
- Risebrough RW, Reiche P, Peakahi DB, Herman SG, Kirven MN (1976). Polychlorinated biphenyls in the global ecosystem. Nat. 220: 1098-1102.
- Skare JO, Stenersen J, Kvseth N, Polder A (1985). Time trends of organochlorine chemical residues in seven sedimentary marine fish species from a Norweigian jordduring the period 1972-1982. Arch. Environ. Contam. Toxicol. 14: 33-41.
- Tanabe S, Iwata H, Tatsukwa R (1994). Global contamination by persistent Organochlorine and their ecotoxicological impact on marine mammals. Sci. Total Environ. 154: 163-177.
- Vourimen PJ, Paasivirta J, Pillola T, Surma- Aho K, Tarhanen J (1985). Organochlorine compounds in Baltic salmon and trout. I. chlorinated hydrocarbons and chlorophenols. Chemosphere, 14: 1729-1740.
- Wang G, Lee AS, Lewis M, Kamath B, Archer RK (1999). Accelerated solvent extraction and gas chromatography/mass spectrometry for determination of polycyclic aromatic hydrocarbons in smoked food samples. J. Agric. Food Chem. 47(3): 1062-1066.
- Woff MS, Zeluniuch-Jacquotte A, Dubin N (2000). Risk of Breast Cancer and Organochlorine Exposure. Cancer Epidemiol. Biomarker Prev., 9: 271-276.
- Unyimandu JP, Udochu (2002). Comparative studies of organochlorine and PCBs in fish from the Lagos Lagoon, River Elber Saar. J. Agric. Biotech. Environ. 4(1-2): 14-17.