



## POLYCHLORINATED BIPHENYLS CONTAMINATION IN OXIC SEDIMENT OF SELECTED SITES IN THE LAGOS LAGOON, NIGERIA



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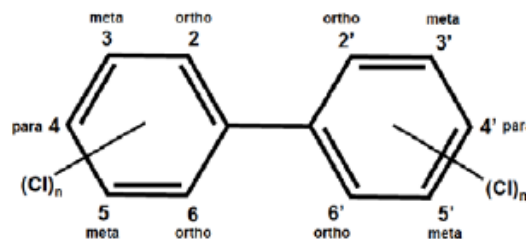
**Abstract:** Polychlorinated Biphenyls (PCBs) are a class of the persistent organic pollutants (POPs) with long-range transport, and the ability to bioaccumulate and biomagnify through the food chain. Seventeen PCBs were analysed in sediment samples collected from six stations in the Lagos lagoon. Using a Van Veen grab sampler and stored in glass bottles following standard procedures. Cleaned extracts were analysed using a Gas Chromatograph interfaced to a Mass Spectrometer (GC-MS) equipped with an Elite-5MS (5% diphenyl/95% dimethyl polysiloxane) fused with a capillary column (30 × 0.25µm ID × 0.25 µm df). The mean concentration of PCBs in sediment samples ranged from 0.093 mg/L in Unilag lagoon front to 2.626 mg/L in Okobaba sampling stations. Analysis of variance showed that there is no significant difference ( $P > 0.05$ ) in the mean PCB concentrations across the stations. The number of low-chlorinated PCB homologues ( $\sum$ di-PCB -  $\sum$ penta-PCB) detected in this study dominated in occurrence with 99.23% while the high-chlorinated ones ( $\sum$ hexa-PCB -  $\sum$ nona-PCB) showed only 0.77% occurrence. These research findings indicate that PCB congeners have been introduced into the Lagos lagoon from anthropogenic sources. Their lipophilic nature, and persistence in the sediment could pose serious ecological and health risks especially as some of the benthic macroinvertebrates, which live at the sediment are sources of food to higher organisms and man. There is need for constant monitoring of the lagoon.

**Keyword:** Polychlorinated Biphenyls; Sediment; Lagos lagoon; Pollution; Anthropogenic.

### Introduction

Developmental and industrial activities associated with urbanization, coupled with inefficient waste management practices have contributed to the generation of increasing amounts of chemical pollutants that degrade environmental quality (Sheriff *et al.*, 2021). Among the many hazardous substances are a group of pollutants classified as persistent organic pollutants (POPs) with long-range transport, as well as the ability to bioaccumulate and biomagnify through the food chain (World Health Organization, 2020). The lipophilic nature of POPs gives them the tendency to accumulate along the food chains and this could pose great risks to the trophic levels of aquatic communities, as well as cause potential human health hazards (Almatari *et al.*, 2017). The most common POPs include polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethane (DDT), industrial chemicals, and unintentional by-products of industrial processes like polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans, commonly known as dioxins (World Health Organization, 2020).

Polychlorinated biphenyls (PCBs) are a class of non-polar toxic chemical compounds consisting of two connected benzene rings and chlorine atoms that can attach to any or all of 10 different positions (Figure 1). The PCBs have 209 different congeners and 10 different homologs (Jing *et al.*, 2018). The chemical formula of PCBs is  $C_{12}H_{10-n}Cl_n$ , where  $n$  (the number of chlorine atoms) ranges from 1 to 10 (Horwat *et al.*, 2015).



**Figure 1:** General chemical structure of polychlorinated biphenyls (Horwat *et al.*, 2015).

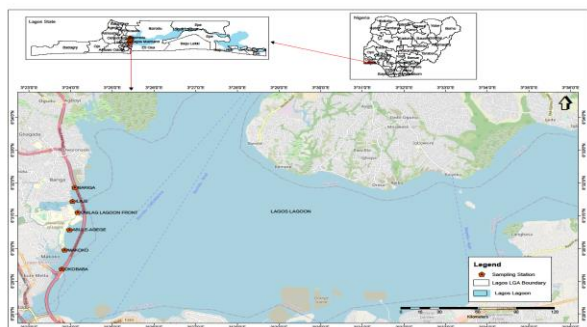
Polychlorinated biphenyls are chemically inert, stable to heat, non-flammable, and have electrical insulating properties and high boiling point (Faroon and Ruiz, 2016). These properties enable their usage in a wide range as coolants, plasticizers in plastics, paints, dyes, pigments, and carbonless copy paper (Faroon and Ruiz, 2016; Jing *et al.*, 2018). Most of these PCB-containing materials are discharged into water bodies (Akinsanya *et al.*, 2020b) due to poor waste disposal methods, majority of them eventually settle and accumulate in sediments (Bamidele *et al.*, 2020). Sediment are deposits of insoluble material, mainly rock and soil particles, remains of aquatic organisms, chemical precipitates from water, and products of volcanic eruption, that makes up the bottom of aquatic ecosystems (Povinec *et al.*, 2021). Sediment are the primary repository for materials that are released into the marine environment, and contaminated sediments are the main indicators of pollution in aquatic ecosystems (Povinec *et al.*, 2021). They have the ability to absorb and act as sinks for PCBs, and also release same to the overlying water through sediment resuspension (Jafarabadi *et al.*, 2019; Cui *et al.*, 2022).

The Lagos Lagoon is located in the low-lying coastal zone of Nigeria (Akinsanya *et al.*, 2020a). The lagoon receives inputs from industrial effluents, domestic sewage, wood wastes, agrochemicals, emissions from automobiles and combustion engines, thermal water from power stations, accidental oil spillage, petroleum by-products, and combustion of organic substances (Doherty and Otitolaju, 2016; Nkwoji *et al.*, 2020; Unyimadu and Benson, 2023) All these inputs are major sources of POPs. Several studies have reported PCBs contamination in sediment samples collected from various marine environments (Oziolor *et al.*, 2018; Jafarabadi *et al.*, 2019; Zhang *et al.*, 2019; Fraser *et al.*, 2020; Cui *et al.*, 2022). However, there is dearth of information on the level of PCBs contamination in the Lagos lagoon, Nigeria. Some of the few studies were conducted (Benson *et al.*, 2020; Osuala *et al.*, 2022; Unyimadu and Benson, 2023) within a short period (between 1 to 3 months), and the sediment samples were more of sediment cores rather than the surface oxic sediment.

**Materials And Methods**

**Description of Study Area and Stations**

The Lagos lagoon (Figure 2) is a great expanse of water which is separated from the Atlantic Ocean by a long sand spit and drains its water through the relatively narrow Commodore Channel into the Atlantic (Fajemila *et al.*, 2020). The lagoon has an average depth of 2 m, and a maximum depth of approximately 5m in its main body, depending on the tidal regime and season (Nkwoji *et al.*, 2020). At high tide, water flows in from the Atlantic Ocean into the Lagos Harbour and the lagoon via the Commodore Channel and the Five Cowries Creek, and the currents are mostly directed towards the east; whereas, the direction of the currents is reversed at low tide (Fajemila *et al.*, 2020). Salinity of the Lagos lagoon varies considerably with the wet and dry seasons and is largely influenced by the introduction of fresh water from rain and rivers, and saline water from the ocean. Moreover, the south-western and western shorelines of the lagoon are densely populated and include clusters of industry spread along the area (Fajemila *et al.*, 2020).



**Figure 2:** Lagos lagoon showing the sampling stations

**Sampling Stations**

Six sampling stations were selected for the study based on accessibility and proximity to expected pollution sources. The exact locations of the stations were determined with the aid of the global positioning system (GPS).

**Table 1: Sampling Stations and their Coordinates**

Station No.	Station Name	Latitude	Longitude
1	Bariga	6° 31' 51.2"N	3° 24' 5.7"E
2	Ilaje	6° 31' 26.4"N	3° 24' 2.6"E
3	Unilag lagoon front	6° 31' 5.9"N	3° 24' 10"E
4	Abule-Agege	6° 30' 34.2"N	3° 23' 58.1"E
5	Makoko	6° 29' 57.2"N	3° 23' 51.2"E
6	Okobaba	6° 29' 22.6"N	3° 23' 47.2"E

**Collection of Sediment Samples**

Sediment samples were collected using a Van-Veen grab monthly at each study station for a period of six months. The grab was lowered gently into the bottom of the water with a rope. Sediment samples were collected and stored in a glass container according to standard procedure for further sediment PCBs analysis in standard laboratory.

**Determination of Polychlorinated Biphenyls Concentration**

The concentration of PCBs in sediment samples was determined according to the methods of Kampire *et al.* (2017) and Iniaghe and Kpomah (2022) as described below.

**Extraction procedure for polychlorinated Biphenyls**

About 5g of the dried milled sediment was weighed into 100ml conical flask. 25 ml of the mixture of Acetone / N-hexane / Dichloromethane (1:2:1) was added, sonicated for about 30 minutes at room temperature. The clear portion was decanted into a separate 100ml beaker. Another 25 ml of the above solvent was added to the residue in the conical flask and the extraction was repeated. The clear portion was decanted into the 100ml beaker. The extract was centrifuged at 1000RPM for 5 minutes. The clear supernatant was decanted into another clean 100ml beaker. The extract was allowed to concentrate to about 5ml under cool air in the absence of light. Then, the extract was cleaned up in a column containing anhydrous sodium sulphate and silica gel.

**Clean up procedure**

A column was packed with cotton wool containing 1g each of anhydrous sodium sulphate and silica gel. 2ml of N-hexane was used to condition the column. The extract was allowed to run through the column and was later eluted with a 2ml mixture of n- hexane & Dichloromethane (1:1). Then, the eluted sample was ready for gas chromatography-mass spectrometry analysis.

**Gas Chromatography-Mass Spectrometry (GC-MS) Analysis**

GC-MS analysis of the extract was performed using an Agilent 5977B GC/MSD system coupled with Agilent 8860 auto-sampler, a Gas Chromatograph interfaced to a Mass Spectrometer (GC-MS) equipped with an Elite-5MS (5% diphenyl/95% dimethyl polysiloxane) fused with a capillary column (30 × 0.25µm ID × 0.25 µm df). For GC-MS detection, an electron ionization system was operated in electron impact mode with ionization energy of 70 eV. Helium gas (99.999%) was used as a carrier gas at a constant

flow rate of 1 ml/min, and an injection volume of 1µl was employed (a split ratio of 10:1).

The injector temperature was maintained at 300°C, and the ion-source temperature was 250°C, and the oven temperature was programmed from 100°C (isothermal for 0.5 min), with an increase of 20°C/min to 280°C (2.5 min), Mass spectra were taken at 70 eV; a scanning interval of 0.5s and fragments from 45 to 450 Da. The solvent delay was 0 to 3 mins, and the total GC/MS running time was 21.33mins.

**Identification of photo components**

Interpretation of mass spectrum GC-MS was conducted using the database of the National Institute Standard and Technology (NIST) having more than 62,000 patterns and

the National Centre for Biotechnology Information. the unknown components were compared with the spectrum of known components stored in the NIST library. The names of the compounds were identified.

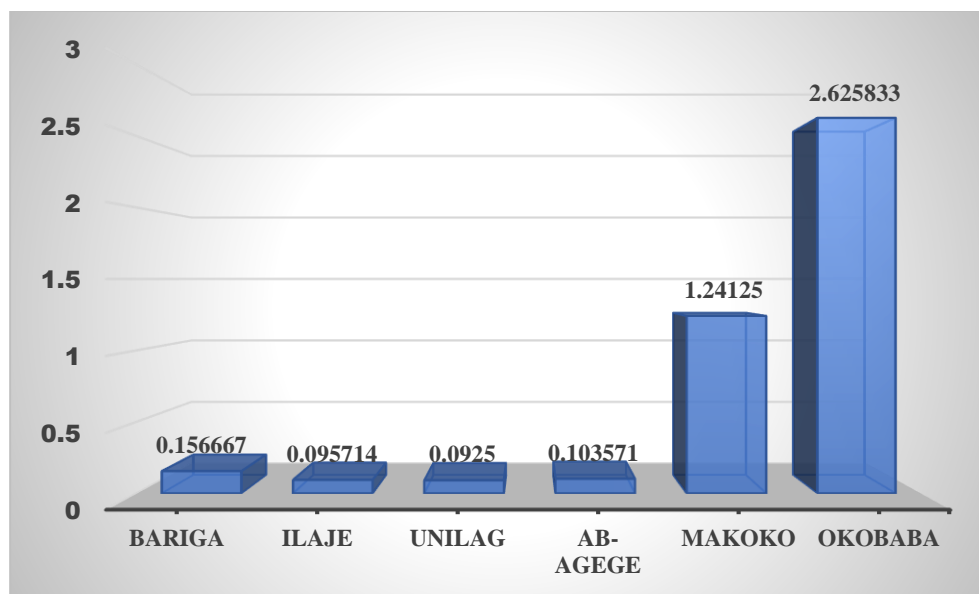
**Results and Discussion**

The mean concentration of PCBs in the six sampled stations of the study area are presented in Table 9. Okobaba sampling station recorded the highest concentration (2.625833) of PCBs in the study, while the lowest (0.092500) was recorded in Unilag lagoon front. However, there was no significant difference (P>0.05) in the mean PCB concentrations across the six sampled stations.

**Table 9: The Mean Concentration of Polychlorinated Biphenyls in Sediments of the Lagos Lagoon**

		Sampling Stations					
		Bariga	Ilaje	Unilag	Ab-Agege	Makoko	Okobaba
PCB Compounds	Congener No.	PCB Concentrations (Mean ± SD)					
4-Chloro-1,1'-biphenyl	PCB 3	0.06 ± 0.01	0.06 ± 0	0.06 ± 0	0.07 ± 0.01	N.D.	0.055± 0.005
2,3-Dichloro-1,1'-biphenyl	PCB 5	0.135 ± 0.05	0.115 ± 0.005	0.11 ± 0	0.145 ± 0.035	0.13 ± 0	0.11 ± 0
2,3,4'-Trichloro-1,1'-biphenyl	PCB 22	0.1 ± 0	0.11 ± 0	N.D.	0.11 ± 0	4.61 ± 0	0.1 ± 0
2,2',4,4'-Tetrachloro-1,1'-biphenyl	PCB 47	0.25 ± 0.06	0.23 ± 0	0.14 ± 0.05	0.3 ± 0	4.89 ± 0	5.17 ± 0
2,3',4,5-Tetrachloro-1,1'-biphenyl	PCB 67	0.06 ± 0	0.06 ± 0	N.D.	0.06 ± 0	0.12 ± 0.07	0.06 ± 0
2,2',4,4',5-Pentachloro-1,1'-biphenyl	PCB 99	N.D.	N.D.	N.D.	N.D.	0.06 ± 0	N.D.
2,3,3',5,5'-Pentachloro-1,1'-biphenyl	PCB 111	0.335 ± 0.295	0.095 ± 0.085	0.06 ± 0.01	0.02 ± 0	N.D.	10.26 ± 8.98
2,3',4,4',5',6-Hexachloro-1,1'-biphenyl	PCB 168	N.D.	N.D.	N.D.	0.02 ± 0	N.D.	N.D.
2,2',3,4',5,5',6-Heptachloro-1,1'-biphenyl	PCB 187	N.D.	N.D.	N.D.	N.D.	0.12 ± 0	N.D.
<b>Total Mean</b>		<b>0.156667</b>	<b>0.095714</b>	<b>0.092500</b>	<b>0.103571</b>	<b>1.241250</b>	<b>2.625833</b>
<b>ANOVA</b>							
Source of Variation	SS	df	MS	F	P-value	F crit	
Between Groups	32.80601	5	6.561201554	1.69734272	0.16369563	2.51225495	
Within Groups	123.6983	32	3.865572619				
Total	156.5043	37					

\*N.D. means not detected



**Figure 3:** Mean spatial variation in PCB concentration during the period of study

The number of low-chlorinated PCB homologues (mono- to penta-chlorinated PCBs) detected in this study were more than that of the high-chlorinated ones (hexa-chlorinated PCBs). This is in agreement with Unyimadu and Benson (2023). Out of the six stations sampled in this study, only Makoko and Okobaba had mean sediment PCB concentrations (0.18) that are above the effect range median (ERM) limit for total PCBs. The ERM estimates the likely adverse effects on organisms with respect to individual PCBs and also the cumulative toxic effects with respect to the sum of all the PCBs. Thus, a concentration above ERM limit infers that adverse biological effects will frequently occur (Benson *et al.*, 2020). The mean sediment PCBs concentrations in Makoko and Okobaba were 1.24 and 2.63 respectively. This could be as a result of the high level of anthropogenic activities in these areas. These include activities like boat construction, fishing, and trading in Makoko, as well as sawmilling activities and log transportation in Okobaba. Benson *et al.* (2020) also reported significant levels of PCBs in sediment samples from the Lagos lagoon which were above the ERM limit. Similarly, Benson *et al.* (2023) reported the presence of considerable amounts of PCBs in Makoko and Okobaba.

**Conclusion**

Potentially toxic levels of PCBs were observed in some of the study stations with corresponding high level of anthropogenic activities. This level PCBs contamination in the oxic sediment may pose considerable ecotoxicological risk to the community structure of benthic macroinvertebrates. Some of these benthic macroinvertebrates like the shellfishes are consumed by the local communities and this might pose great health risk. There is need to improve our waste management systems to prevent the entry of PCBs and other persistent organic pollutants into the Lagos lagoon and ultimately conserve the health of this very important marine ecosystem. There should be more researches conducted to assess the presence of emerging contaminants and their impacts on sediment

of the lagoon. These findings would help guide decision-making for sustainable environmental management policies.

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