



DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs) IN SURFACE WATER IN ONDO STATE NIGERIA

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Abstract

Polychlorinated biphenyl compounds (PCBs) were included to the Stockholm Convention's list of typical persistent organic pollutants on May 22, 2001. (POPs). Humans have produced PCBs, which are pervasive in the environment. They are a concern for people all around the world because of their toxic, bioaccumulative, long-lasting, hydrophobic, and transboundary characteristics. The study's goals included describing how PCBs are distributed in surface water and evaluating how certain physicochemical factors affect PCB concentrations. Five separate Okitipupa locations—OAUSTECH, Igodan, Okunmo, Idepe, and Lebi/Ofe River—had their water samples taken. The overall average concentration of PCBs discovered in the samples taken from five (5) distinct places was determined to be as follows: OAUSTECH (5.720±13), Igodan (5.520±00), Okunmo (3.480±03), Idepe (21.830±02), and Lebi/Ofe (0.160±00), with their combined probability being determined to be 0.001. Twenty-five (25) PCB congeners were examined using a gas chromatography-electron capture detector (GC-ECD). The majority of congeners were below the detection threshold at every site. Total PCB values varied from 0.16 g/L to 21.83 g/L. The correlation between the overall level of polychlorinated biphenyls and the total organic carbon was positive (0.214), but it was weak (PCBs) and pH, positive (0.096) but poor correlation between the electrical conductivity, and a positive (0.220). The levels found in this investigation, with the exception of one area, were obviously lower than the 0.5µg/l level advised by the WHO. The water's concentration of polychlorinated biphenyls (PCBs) is not significantly impacted by the physicochemical characteristics, and the water is safe to use for household purposes.

Keywords; Surface water, polychlorinated biphenyls, physicochemical parameters, GC-ECD

Introduction

The rate at which environmental media are polluted as a result of anthropogenic activities cannot be overstretched (Ediagbonya *et al.*, 2013; 2015; 2019; 2020). Higher plants, marine life, and birds may all be poisoned by PCBs. By preventing

cell division, PCBs may hinder some plant species' ability to develop as a whole. They might also interfere with some plants' photosynthesis. In marine biota, PCBs can inhibit ATPases and enhance mixed function oxidase (MFO) enzymes. PCBs are known to influence fish hormones and to have

behavioural and teratogenic effects in birds (Monosson, 2000; Tam *et al.*, 2023; Afolabi *et al.*, 2022). PCBs can be harmed by some microbes, including those in freshwater, the ocean, and soil (WHO 1993). Some algae may have changes in respiration and photosynthesis, whilst some fungus may experience changes in mycelial development and relative RNA content as a result of PCB exposure (WHO, 1993). They are also organic pollutants that are persistent, meaning that their effects linger long after use. They are extensively employed for agriculture reason and as dielectric fluids in transformers, capacitors, coolants, and other devices. Polychlorinated biphenyls (PCBs) were used as coolants and lubricants in transformers, generators, and electrical capacitors because of their electrical insulating properties, chemical inertness and low burning capability (Necibi, 2015). They also contributed to the development of rubber and polyvinyl chloride plasticizers (Erickson, 2011). In the past, PCBs were produced in the US and Europe (Gioia *et al.*, 2013). High PCB concentrations have been discovered in non-producing regions like Africa despite those areas' efforts to drastically reduce PCB emissions from their sources (Gioia *et al.*, 2013). These high levels were attributed by Gioia *et al.*, (2011) to PCB air deposition. The increased amounts of toxins in the regions have also been attributed to the importation of moderately worn and outdated electrical equipment from affluent nations (Gioia *et al.*, 2013). Between the 1930s and the 1980s, PCBs were widely produced all over the world due to their exceptional physical and chemical properties, which included a high dielectric constant, a high solubility in hydrocarbons and almost insolubility in water, a very low volatility, a high chemical stability, and a high heat resistance (Li, *et al.*, 2003;

Mackay, 1997). Dielectric fluids in electrical equipment (capacitors and transformers), plastics, or materials for thermal insulation, adhesives are a few applications for them. According to the literature, half of the cumulative global production in the 1980s—roughly 1.5 million tons—was credited to Monsanto, (De Voogt, 1989) USA. Among industrial compounds with no recognized natural origins in the environment are PCBs (Wang and Zhong, 2011). Accidental spills, transportation leaks, transformer fires containing PCBs, river input, and unauthorised industrial and municipal wastewater discharge are some of the ways they reach the aquatic environment. The main PCB indicators are the seven congeners that ICES (International Council for the Exploration of the Sea) monitors: CB-28, CB-52, CB-101, CB-118, CB-138, CB-153, and CB-180 (Boalt, *et al.*, 2014). This study's objective is to measure the PCB contents and physiochemical characteristics in surface water from five distinct Okitipupa localities. As a result of their widespread use, persistence in the environment, and potential health effects, PCBs have received a lot of attention lately. They pose a serious threat to human due to their behaviour, which is lipophilic and allows them to bioaccumulate in fatty tissues (Brunner *et al.*, 1985). PCBs can get into the body by physical contact, inhaling fumes, or eating food that has PCB residues in it. In either acute or short-term chronic testing, PCBs are not very harmful. For the majority of trophic levels, fatal responses need high doses. PCB buildup and a hazardous reaction can be brought on by high lipid solubility, resistance to metabolism, and protracted sublethal exposure (He *et al.*, 2021). PCBs are known to cause a variety of adverse effects in humans, lab animals, and wildlife. Here are a few instances of the harmful effects that PCBs have on biological systems (Montano *et al.*,

2022; Markowitz & Rosner, 2018; Gaur *et al.*, 2022; Gupta *et al.*, 2018). The Clean Water Act forbids the industrial discharge of polychlorinated biphenyls into water. PCBs' effects reduce the makeup of water's algae to prevent the formation of certain algal species; influence patterns of endocrine, hormone, and enzyme activity as well as accumulation in typical aquatic creatures. Aquatic animals may die or become lethal if the normal body dose is surpassed (Tam *et al.*, 2023; Adeogun *et al.*, 2017, Mitra *et al.*, 2019). Research is currently being conducted to create sustainable, alternative techniques of remediation for persistent organic pollutants as a result (Ren, *et al.*, 2019). This study sought to evaluate the health

hazards connected to specific physiochemical traits and PCB concentrations in Okitipupa water bodies.

Materials and Methods

Study area

The Lebbi, Idepe, Igodan, Okumo, and OAUSTECH surface water were part of five separate settlements in Ondo State's Okitipupa Local Government. The surface water benefits localities in a variety of ways, with fishing serving as a primary source of employment for the majority of the locals. Along the riverbed, people frequently bathe, swim, dump sawdust, slaughter animals, and wash their clothing. Figure 3 displays a map of the research region that shows the locations of the sample points.

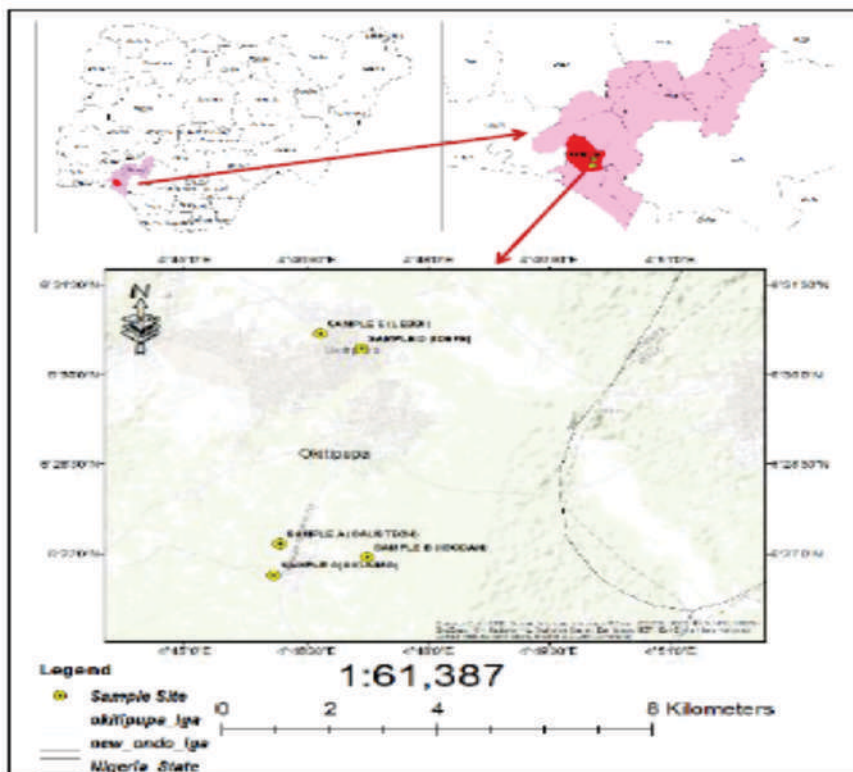


Figure 1. Showing the map of the study area.

Sampling and Sample preparation

Water samples were taken from the five (5) rivers (Lebbi, Idepe, Igodan, Okumo, and OAUSTECH) that are close to populated areas. Water samples were taken in a glass container. Using pre-cleaned amber bottles, water samples were taken from surface water (up to 1 metre deep). After being cleaned with detergent, distilled water, acetone, hexane, and water from the sampling locations, the samples were then placed in glass bottles (Skrbic, 2018). These were carried to the laboratory in ice chests. Duplicate samples were taken at each location in order to minimise any random variation during sampling, and the final sample was created by thoroughly mixing all of the replicate samples. Water samples were kept in the lab at a temperature of 4°C. In order to maintain their original condition as the same in the environment and avoid post-contamination, the samples were refrigerated.

Quality control

Analytical quality control included the strict adherence to documented procedures, laboratory standard operating procedures and calibration of analytical instrument. The GC-ECD was calibrated using high quality analytical standards from the U.S. Environmental Protection Agency (US EPA). Standards were run to check for the concentrations, physicochemical parameters, pH, resolution, and detection limit. All glassware and bottles used in laboratory were cleaned with detergent, rinsed with distilled water. Glassware was rinsed with acetone and hexane before use. All solvents used for extraction (acetone and n-hexane) were of pesticide grade and products of Merck (Darmstadt, Germany). The analysis was done in Nigeria Institute for Oceanography and Marine Research.

Determination of Polychlorinated biphenyls

Igbo *et al.*'s (2018) previously developed approach was used to analyse PCBs. PCBs were removed from the samples using ultrasonic extraction and 50 mL of hexane/acetone (1:1 v/v) and an internal standard. By using a rotary evaporator, the extract was concentrated to a volume of around 3 mL. For cleanup, concentrated H₂SO₄ was added to the sample solution and agitated in a test tube. The acid layer was then centrifuged and discarded. Until the hexane layer was dried with anhydrous sodium sulphate and then concentrated to about 1 mL for column chromatographic clean-up, this procedure was done numerous times. Using a GC-ECD Agilent 7820A, the concentrations of 28 PCB congeners were determined. Individual PCB congener recovery rates varied from 87% to 100%. The detection limit (0.0004-0.014 ng/ul)

Physicochemical parameters

Standard techniques were used to measure physicochemical characteristics such pH, electrical conductivity total organic carbon (Rajendran, 2005).

Statistical Analysis

SPSS version 26 was used to conduct data analyses. Data were submitted to a two-way analysis of variance (ANOVA), and the Duncan Multiple Range test was used to distinguish between significant means (p 0.05). The mean and standard error were used to express the results.

Human Health Risk

Using the BaP toxicity equivalency approach (US EPA 1993; Durant *et al.* 1996; Nisbet and LaGoy 1992; Larsen and Larsen 1998) and the model equations developed by the US EPA for evaluating noncarcinogenic and carcinogenic risks due to exposure to PCBs in water (US EPA 1989; 2001; 2009), the potential health risk imposed on the population relating to the exposure of PCBs in Ondo State was assessed. Using the exposure-point upper confidence limit CUCL95% of PCBs, the BaP toxicity,

carcinogenic risks, and non-carcinogenic risks were computed. In particular for skewed data, the CUCL95% is the best suitable concentration measure (Zheng *et al.*

2010a, b). The formula used to calculate CUCL95% has previously been published. (Iwegbue *et al.* 2021; Iwegbue *et al.* 2017).

Results and Discussion

Table 1: Physicochemical parameters for PCB at different locations

	pH	Electrical conductivity (EC) ($\mu\text{S}/\text{cm}$)	Total organic Compound (TOC)
Lebi/ofe	5.80 \pm 0.10	35.15 \pm 0.58	1.56 \pm 0.02
Idepe	6.50 \pm 0.26	71.17 \pm 0.15	1.57 \pm 0.03
Okumo	6.47 \pm 0.35	53.17 \pm 0.15	1.39 \pm 0.02
OAUSTECH	7.30 \pm 0.10	172.00 \pm 1.00	1.15 \pm 0.05
Igodan	6.33 \pm 0.25	66.67 \pm 1.15	0.40 \pm 0.05

The physicochemical state of the surface water medium determines how PCBs are transported and their eventual destiny in the biota. pH, dissolved oxygen, conductivity, and organic carbon are a few of these characteristics. Increased surface water temperature can result in an increase in Physical/chemical processes include desorption, diffusion, and solubility, as well as biological processes like microbial and

bioturbator activity (Nair and Abraham, 2019; Aziza, *et al.*, 2021). Table 1 displays the findings of the physicochemical property measurements. Water had a pH in the range of 5.80 to 7.30. The EC values ranged from 35.15 to 172 μcm^2 . While the TOC levels ranged from 0.40 to 1.57 The lowest mean pH and EC were found in Lebi, whereas the greatest mean pH and EC were found in OAUSTECH

Table 2: The mean concentration of Polychlorinated biphenyls (PCBs)($\mu\text{g}/\text{l}$) in different locations

	Lebi/ofe	Idepe	Okumo	Oaustech	Igodan	p
PCB 44	0.16 \pm 0.00	3.58 \pm 0.00	0.72 \pm 0.01	0.60 \pm 0.00	0.01 \pm 0.00	<0.001
PCB 18	BDL	14.70 \pm 0.00	0.19 \pm 0.00	BDL	BDL	<0.001
PCB28	BDL	1.01 \pm 0.00	0.95 \pm 0.01	1.17 \pm 0.12	5.51 \pm 0.00	<0.001
PCB170	BDL	2.54 \pm 0.03	1.62 \pm 0.00	2.30 \pm 0.00	0.00 \pm 0.00	<0.001
PCB156	BDL	BDL	BDL	1.66 \pm 0.00	BDL	NC
Total PCBs	0.16 \pm 0.00	21.83 \pm 0.02	3.48 \pm 0.03	5.72 \pm 0.13	5.52 \pm 0.00	<0.001

BDL - Below Detection Limit, NC - Not Computed

PCBs can degrade or dissolve in the environment, although the process depends heavily on chemicals. The environment's exposure to PCBs affects how quickly they degrade. Microbes or sunlight are typically

responsible for PCB degradation in the environment. Sunlight is essential for destroying PCBs when they are present in the air, shallow water, or surface soils. Microorganisms including bacteria, algae,

and fungi biodegrade PCBs. The Clean Water Act forbids the industrial discharge of polychlorinated biphenyls into water. Although there should be no pollution in drinking water at all, the legal maximum is 0.5 µg/l (WHO, 1993). When the concentration of these contaminants in the water bodies is high, the sediments may build up excessively and affect the ecosystem either directly or indirectly, leading to considerable pollution and the extinction of desirable species (Burton, 2002). Except for Lebi, where the overall concentration was lower as shown in According to Table 2, greater levels were found in all of the locations above the USEPA's maximum PCB limit for water (0.0005 mg/L). (USEPA, 2009). Organic pollutants are dispersed in the surrounding by air and water, but because they are hydrophobic, it is anticipated that they will travel to the sediments (Bayer and Biziuk, 2009). Concentrations in related investigations conducted in Nigeria (Obanya, *et al.*, 2019; Ezemonye, 2005a; Ezemonye, 2005b; Archibong, *et al.*, 2017) reported above the USEPA PCBs limit for water. The greater amount of the found PCB congener compared to the USEPA safe limit in the previously examined area may have been due to a point source of industrial effluents, although this current study is not as industrialised as other regions in Nigeria, where the majority of the companies are inactive. Heavy rains during the rainy season have a tendency to flood additional

wastes discharged from a variety of sources into water bodies, which increases the concentrations of several poisons in the water (Gao, *et al.*, 2013). Numerous findings have demonstrated that substantial concentrations of PCBs in aquatic settings are harmful to living things. According to a research, aquatic animals exposed to PCBs at doses of 1 to 25 µg/g saw a dose-dependent decline (Nakayama, *et al.*, 2005). According to Lerner, (2007), the preference for saltwater in fingerlings exposed to 1 and 10 g/L of PCBs during the smolting process decreased in a dose-dependent manner (Gonzalez, 2016). Table 2 revealed that Idepe River had the highest detected PCB44 concentration and Igodan River had the lowest, while Idepe and Okumo Rivers were the only ones to have PCB18, with Idepe River having the greatest concentration. PCB170 was highest in Idepe River and lowest at Igodan River, whereas PCB28 was highest at Igodan River and lowest in Okumo River. The only place where a value for PCB156 was reported was at OAUSTECH. Idepe River has the most total PCBs, and Lebi/Ofe River had the least. With the exception of PCB156, for which no calculations were made since there is only one location with a measured value, there were substantial spatial differences in the PCBs throughout the research locations. Water had a total of 0.16 to 21.83 g/L PCBs. The outcomes are consistent with (Zhang, *et al.*, 2011), who discovered that tetra-CBs were the main pollutants.

Table 3: The mean concentration of Polychlorinated biphenyls (PCBs)(µg/l) in different locations

Congeners	Present study		Lagos/Osun study (Okunola 2011)		China (Zhang, 2002)	
	range	Mean	Range	mean	range	mean
PCB 44	0.01-3.58	1.015	0.03-1.41	1.82	0.0334-0.01064	2.47
PCB 18	0.19-14.70	2.978	0.06-1.08	1.65	0.00247-0.00675	2.50
PCB28	0.93-5.51	1.728	0.03-1.57	0.59		
PCB170	0.01-2.54	1.292	0.01-2.52	0.53		
PCB156	0.00-1.66	0.332	0.01-1.79	2.02		
Total PCBs	0.16-21.83	7.342	0.14-11.99	6.61	-----	-----

Table 3, the entire range of PCB values in water samples taken from Lagos/Osun was 0.14–11.99 µg/L by Okunola (2011), while the total mean was 6.61 µg/L (Adeyemi, et al.,2009). Zhang, (2002); Nie, et al. (2003), revealed that the PCB values of water from the Pearl River Estuary were 0.0334-0.01064 µg/L and 0.00247-0.00675 µg/L, respectively. However, a comparison of these research might shed light on how PCB levels are shifting globally (Table 3). In comparison to earlier studies conducted in Nigeria and overseas, the PCB concentrations observed in the current research were greater (Ye, et al.,2009).

According to the USEPA guidelines, the concentration of PCBs should be less than 14 ng/lor surface water to be considered no hazard to aquatic or human health (USEPA, 2002). Table 3 shows those locations with low-levels of PCBs in water. At Ase and Forcados Rivers, for instance, where there are industrial emissions, the concentration level ranged from 13.5 to 277 ng g. Although the contamination level was extremely low in this area, the trace amounts present suggest that atmospheric transfer may be a working pathway for PCBs to enter the area (Ossai et al.,2023).

Table 4: Pearson correlation coefficients for the relationship between the PCBs homologs.

	triPCB	tetraPCB	HexaPCB
TriPCB	1	.878**	0.896
TetraPCB	.878**	1	0.554
HexaPCB	0.896	0.554	1

* Correlation is significant at the 0.05 level (2-tailed). * Correlation is significant at the 0.01 level (2-tailed).

According to Table 4, triPCB and tetraPCBs have a substantial positive connection. Accordingly, greater or lower triPCB readings will imply correspondingly higher or lower tetraPCB values. The homologs of PCBs have not been correlated in any studies. Table 4's comparison of the triPCB

with other PCB homologs reveals a strong positive correlation between the triPCB and the hexaPCB. TriPCB and HexaPCB had a correlation of (0.896), TetraPCB and HexaPCB had a correlation of (0.876), and TriPCB and TetraPCB had a correlation of (0.896). (0.554).

Table 5: Correlation coefficient of physicochemical properties (pH, Electrical Conductivity (EC) and Total Organic Content (TOC) with Total PCBs

	pH	EC	TOC	Total PCBs
pH	1	.872**	-0.145	0.214
EC	.872**	1	-0.174	0.096
TOC	-0.145	-0.174	1	0.220
Total PCBs	0.214	0.096	0.220	1

* Correlation is significant at the 0.05 level (2-tailed). * Correlation is significant at the 0.01 level (2-tailed).

The fate of PCBs in water is greatly influenced by physical and chemical properties for instance Total Organic

Content (TOC), Electrical Conductivity (EC), and pH. The mobility and dispersion of PCBs in the local water bodies close to the affected

area are significantly impacted by this. As shown in Table 5, a statistical study of correlation conducted to determine the link between total PCB concentrations and TOC revealed a negligible but positive correlation ($r=0.220$). Consequently, TOC was not a significant influence. Ekanem *et al.* reported this favourable association in 2019; they showed a positive but negligible association during the wet season, but a

positive and substantial correlation during the dry season. While a slight but favourable correlation between pH and total PCBs was found. ($r = 0.214$), there was a substantial link between EC and total PCBs ($r = 0.096$). While the pH and EC did not correlate well with TOC, they did so favourably with EC. This outcome can also be compared to the research done by Irerhievwie, *et al.* (2020).

Table 6: The Health risk of various PCBs congener

	EDI	ICLR	HQ
PCB 44	1E-07	1E-06	5E-04
PCB 18	1E-06	8E-06	4E-03
PCB28	3E-07	2E-06	1E-03
PCB170	2E-07	2E-06	8E-04
PCB156	2E-07	2E-06	8E-04
Total PCBs	1E-06	8E-06	3E-03

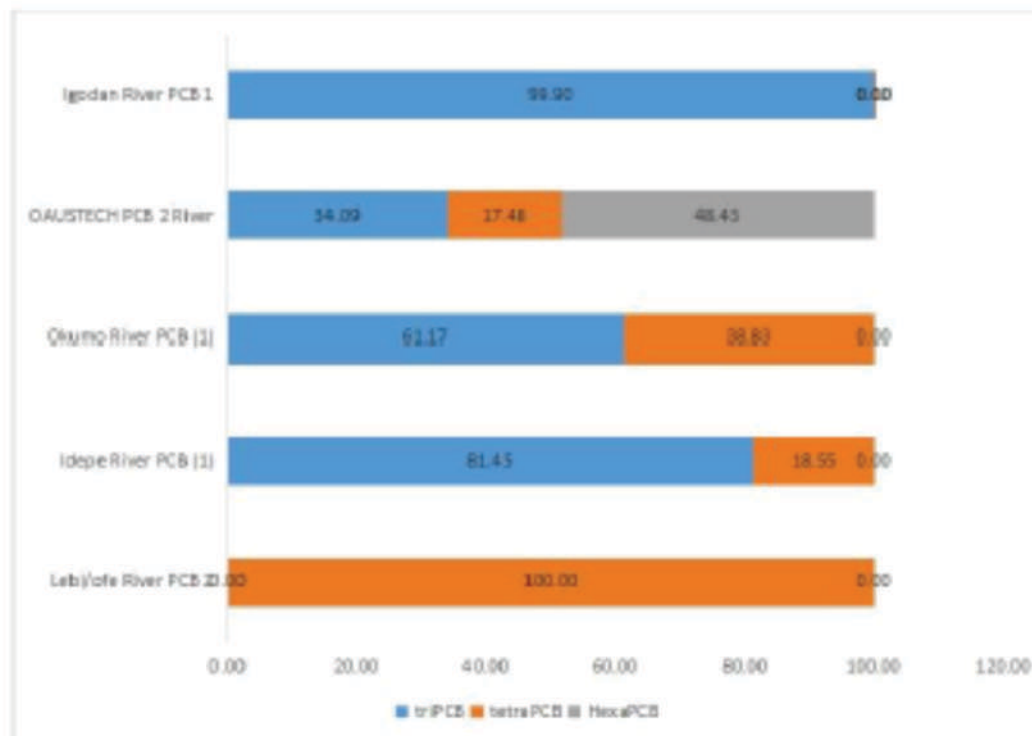


Figure 2. Distribution of the PCB homologs in River samples

Common hazardous and biological effects of PCBs include strong induction potency of 3-methyl cholanthrene type hepatic microsomal enzymes, hepatic damage, skin disease, immunotoxicity, teratogenicity, thymic atrophy, reproductive toxicity, and body weight loss (Wang, *et al.*, 2011). A higher level of genotoxic activity may result from PCB exposure of related substances, leading to more harmful toxic consequences (Boalt, *et al.*, 2014; Burreau, *et al.*, 2006). While there is now no proof that acute PCB exposure causes human deaths, long-term occupational exposure can raise the risk of heart disease and cancer mortality (Pavuk, *et al.*, 2004). Chemicals known as PCBs have a high chlorination level that ranges from 4.69 to 8.05 (Zhou, *et al.*, 2005). The estimated daily intake (EDI) ranged from 1.0×10^{-7} to 1.0×10^{-6} incremental lifetime cancer risk (ICLR) ranged from 1.0×10^{-6} to 2.0×10^{-6} . While the quotient hazard values varied from 5.0×10^{-4} to 1.0×10^{-3} , as shown in Table 6 which were within USEPA tolerable risk limit, the non-carcinogenic hazard quotient (HQ) of dioxin like congeners above the threshold for children and adults (1×10^{-6}).

Figure 2 demonstrates that tetraPCBs were the only PCBs recorded at the Lebi River, whereas hexaPCBs and triPCBs both reported the highest measured amounts in the Igodan, Okumo, and Idepe Rivers. Additionally, the water sample PCB homolog patterns from the Ondo South River were displayed (see Fig. 1). The most frequent compounds were tri- and tetra-PCBs, and the bulk of the patterns matched those of Aroclor 1242. Similar conclusions were reached by Zhang, *et al.*, (2011).

Conclusion

PCB levels were assessed in water samples taken from several locations in Ondo South, Nigeria. The surface water included the majority of the tri-, tetra-, and penta-PCBs

and other PCB congeners that were found. Surface water tests from the OAUSTECH contained more PCBs than those from other places. However, there was a big difference in the samples from the different locations. The PCB concentrations in the study's surface waters were equivalent to those seen in many other parts of Nigeria and the rest of the world. Additionally, all of the water samples have total PCB contents that are greater than the WHO-recommended limit values. The study's PCB exposures do provide a risk to aquatic or human health. Future PCB monitoring programmes can utilise the study's conclusions as a reference for acceptable limits since they provided information on the Patterns of homolog distribution and PCB concentration in one of Ondo South's fastest-growing neighbourhoods.

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