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POLYCHLORINATED BIPHENYLS (PCBS) IN SOIL IN ONDO STATE, NIGERIA

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ABSTRACT

Polychlorinated biphenyls (PCBs) adhere to soil particles and persist there for a considerable amount of time. Their near proximity might expose people by ingesting, inhalation, and skin contact, which could have neurotoxic, mutagenic, and cancerous health effects. In Okitipupa, Ondo State, Nigeria, this investigation measured the level of PCBs in soil at five different sites. A GC paired with an ECD detector was used to evaluate the sample. Concentrated H2SO4 was used to clean the extracts. According to the study's findings, the average concentration of PCB congeners at the different sites was 5.364 g/kg, with a range of 0.150 to 13.30 g/kg. Recovery rates for specific PCB congeners ranged from 87% to 100%. The number of polychlorinated biphenyls (PCBs) in the soil was higher than the 0.050 mg/kg WHO acceptable limit. TetraPCB and triPCBs have a strong positive connection. The correlation between the soil's pH and total PCBs was positive and strong (r = 3.95) while the correlation between the soil's EC and total PCBs was negative and strong (r = -0.411). The estimated daily intake (EDI) ranged from 3.0* 10-7 to 6.0* 10-7 incremental lifetime cancer risk (ICLR) ranged from 2.0* 10-6 to 4.0* 10-6. While the quotient hazard (QH) values varied from 9.0* 10-4 to 2.0* 10-3, The EDI, ICLR and QH were within USEPA tolerable risk limit

KEYWORDS: Soil, PCBs, pH electrical conductivity, risk assessment

INTRODUCTION

The soil, water, and air all contain chemicals and persistent organic contaminants that are recyclable [1-6]. Common hazardous and biological reactions they are known to cause include body weight loss, thymicatrophy, cutaneous disease, hepatic damage, teratogenicity, reproductive toxicity, immunotoxicity, and high induction potency of 3-methyl cholanthrene type hepatic microsomal enzymes [7]. The main source of PCBs in developing countries like Nigeria is the importation of products containing PCBs, such

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

as transformers, capacitors, and other agricultural products. PCBs and a variety of other organic and inorganic contaminants are eventually released into the environment, including the soil and other locations. Considering its extensive atmospheric transport (LRAT). PCBs have been found in places far from the plants where they were produced, suggesting that they can travel large distances. [8, 9]. For the past 20 years, the use of microbes and plants in bioremediation tactics like phytoremediation, rhizoremediation, and bioaugmentation to reduce the amounts of organic compounds like Polychlorinated Biphenyls (PCBs) in polluted places has grown in popularity [10, 9, 11-13]. PCBs are pollutants of concern; hence it is necessary to assess their amounts in the environment on a regular basis, just like it is done in industrialised nations. Second, few similar studies have been conducted in Nigeria since earlier research was limited to certain locations. [14] observed. PCBs in Brazilian soil from urban, suburban, rural, and natural locations. PCBs were found in surface soil next to a municipal solid waste (MSW) landfill in Poland by [15]. In 2010, [16] investigated the distribution of PCBs in the world's air and surface soil. Moreover, PCBs were found in Kenya's urban and residential soils by [17-22]. [17] found PCBs in soil in Lagos, Nigeria, from an electrical power context. In five distinct locations in Okitipupa, Ondo State, Nigeria, the amounts of PCBs and physiochemical characteristics in soil are to be determined. Their claimed half-lives in sediment and soil might be anywhere between months and years. The majority of them are trapped in sediments that act as environmental reservoirs because of their extremely poor solubility in water and low volatility. For instance, electrical transformers that contain PCBs have a life expectancy of 30 years or longer.[7].

MATERIALS AND METHODS

STUDY AREA

With the coordinates 6.452563N, 4.769374E, Okitipupa is a Local Government Area in Nigeria that is a part of the Ikale-speaking people in Ondo State. The Olusegun Agagu University of Science and Technology (OAUSTECH), which started offering classes in 2010/2011, is housed in the same township as the Okitipupa Local Government offices. Due to widespread fishing activity and several waste sites nearby, the Okitipupa River has a significant economic impact and may cause a high concentration of PCBs in the soil. Because Okitipupa produces palm oil, oil spills exacerbate the area's pollution problems. It is a little rural community with few industrial activities.

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

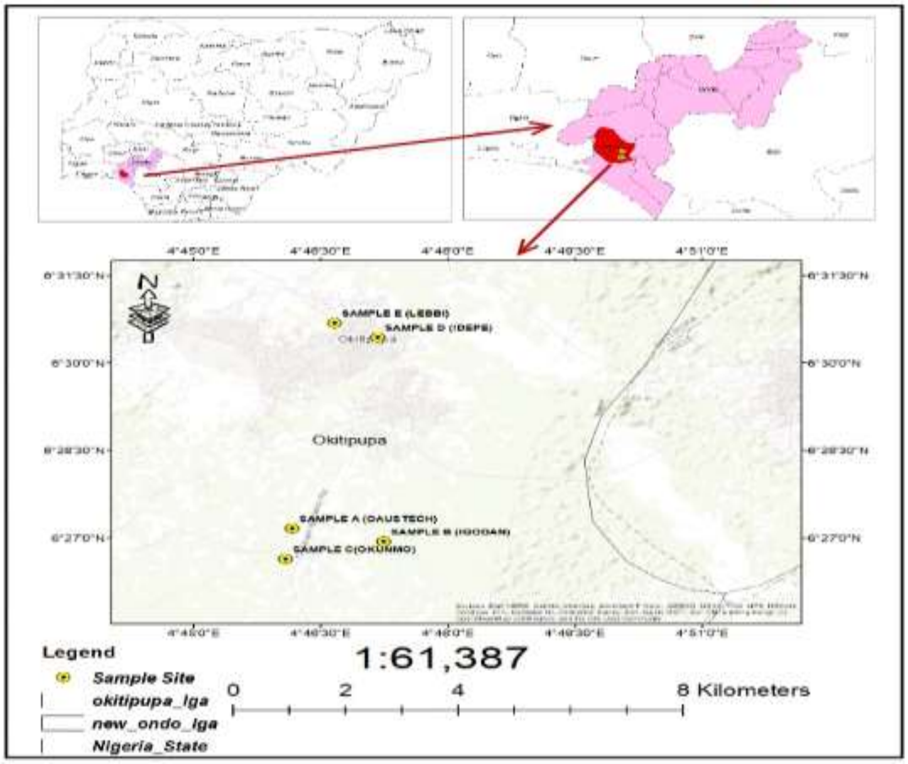

Figure 2: Map of the Study Area

SAMPLING

Five different sites in the Okitipupa local government area had soil samples obtained at a depth of two centimetres using foil paper. The soil samples were labelled sample A, B, C, D, and E, wrapped in aluminium foil, and put into Ziploc bags that had been cleaned before being transported. Figure 1 and Table 1 display the coordinates for the sample location.

Table 1: Sample locations and coordinate

Site code	SITE	LONGITUDE	LATITUDE
OAS	Oaustech Soil	4.769374E	6.452563N
IGS	Igodan Soil	4.787341E	6.4489253N

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

OKS	Okunmo Soil	4.768016E	6.443839N
IDS	Idepe Soil	4.7861504E	6.5072366N
LES	Lebi Soil	4.7777347E	6.5113032N

QUALITY ASSURANCE/CONTROL

Laboratory standard operating procedures, calibration of analytical instruments, and rigorous adherence to specified processes were all included in analytical quality control. The U.S. Environmental Protection Agency's top-notch analytical standards were used to calibrate the GC-ECD (US EPA). The concentrations, physicochemical characteristics, pH, resolution, and detection limit were all checked against standards. Using detergent and distilled water, all laboratory bottles and glassware were cleaned. Before usage, glassware was cleaned using acetone and hexane. Acetone and n-hexane, the extraction solvents, were all Merck pesticide-grade compounds (Darmstadt, Germany).

DETERMINATION OF POLYCHLORINATED BIPHENYLS

Anhydrous sodium sulphate was combined with a 5-g sediment sample to create a free-flowing powder. Using a two-hour ultrasonic bath with 50 ml of acetone/hexane (1:1), the resultant material was removed. The samples underwent sonication for thirty minutes. Decanting the extract after extraction, the remaining material was subjected to sonication once more with 50 millilitres of acetone/hexane that has been treated with activated copper to remove Sulphur. A rotary evaporator was used to condense the extract to 5.0 ml. Impurities were eliminated from the extract by adding 10 ml of concentrated sodium sulphate twice or three times after the extract had been separated using a separating funnel. After being washed with 50 ml of a 5% NaCl solution, the organic phase was concentrated to 1-2 ml using a rotary evaporator. The sample was cleaned with 20 g of activated florisil in a glass column. The PCBs were eluted using hexane (100 ml). The eluate was reduced to 0.2 ml when a gentle nitrogen gas stream was present. A gas chromatograph (GC-ECD) system (Agilent 6890 Series 4, Santa Clara, California) was used to analyse the PCB congeners. It featured a Ni-63 electron capture detector, a J&W DB-5 capillary column (30 m 0.25 mm 0.25 m), and helium was used as the carrier gas at a flow rate of 1.8 ml min1.The measurement was done at temperature programmes for the 270 and 300 °C, respectively, injector and detector. First set at 120 °C, the temperature for the GC programme used to separate PCBs was then raised to 200 °C at a rate of 10 °C per minute, 230 °C at a rate of 2 °C per minute and ultimately to 300 °C at a rate of 7 °C per minute, where it was kept for 10 minutes. With the use of an external calibration technique, the PCBs were quantified. Because GC/MS confirmation was not obtained, this investigation simply indicated screening levels [23].

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

PHYSIOCHEMICAL CHARACTERISTICS

Using the pH metre, the pH levels of the soil were determined. The Walkley and Black [24] wet oxidation method was used to determine the samples' total organic carbon content [25]. The conductivity electrode was inserted into the filtrate to measure the electrical conductivities of the sediments.

STATISTICAL ANALYSIS

All statistical analyses were carried out using SPSS software version 26 and Microsoft Excel. The difference in contamination levels between the study sites was evaluated using an analysis of variance, and connections between the PCB congeners and other sediment parameters were established using a Pearson correlation. Analysis of variance and t-tests were employed to see if there were any significant differences in the PCB concentrations between and within the groups, with values less than 0.05 (p 0.05) being considered statistically significant [23].

RESULTS AND DICUSSION

Table 2: The mean concentration of Physiochemical parameters in soil in different locations

	P^H	**Electrical conductivity (EC)**(µS/cm)	**Total organic Compound (TOC)**
Igodan Soil PCB	7.19± 0.01	243.67±2.52	1.64±0.03
Osustech Soil PCB	7.98± 0.03	83.00±2.00	1.46±0.02
Lebi Soil PCB	7.14± 0.06	102.33±1.53	1.57±0.04
Idepe Soil PCB	7.80± 0.10	100.33±2.52	1.51±0.02
Okuma Soil PCB	7.05±	92.33±1.53	1.30±0.02

	0.04

The physicochemical state of the environmental medium determines the fate and transit of PCBs to the biota. These variables include organic carbon, pH, conductivity, and salinity, among others. Increased surface water temperature can result in an increase in physical and chemical processes like difusion, desorption, and solubility are examples of biological activity. Bioturbator activity is another [26, 27]. Table 2 displays the findings of the physicochemical property measurements. Water had a pH in the range of 7.07 to 7.98. The EC values ranged from 83.00 to 243.67. The TOC values ranged between 1.30 and 1.64. Igodan recorded the highest mean for both pH and EC, whereas OAUSTECH had the lowest mean for both. [28, 29] found similar results to those of this study

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

	Igodan Soil	Oaustech Soil	Lebi Soil	Idepe Soil	Okumo Soil	p
PCB 44	0.63±0.00	13.30±0.01	3.87±0.00	2.44±0.00	0.65±0.00	<0.001
PCB28	BDL	BDL	2.95±0.00	BDL	0.85±1.10	<0.05
PCB170	1.72±0.00	BDL	2.55±0.03	BDL	BDL	<0.001
PCB156	BDL	BDL	1.80±0.00	BDL	BDL	NC
Total PCBs	2.35±0.00	13.30±0.01	11.17±0.03	2.44±0.00	1.50±1.10	<0.001

Although the process is highly chemically dependant, PCBs can degrade or dissolve in the environment. The environment's exposure to PCBs affects how quickly they degrade. PCBs are normally broken down by sunlight or bacteria in the environment. Sunlight is essential for the oxidation of PCBs, whether they are present in shallow water, the atmosphere, or surface soils. Due to their endurance, hydrophobic nature, and poisonous qualities, PCBs are dangerous compounds that microorganisms like bacteria, algae, or fungi biodegrade. [30]. PCBs collect in soils because they are persistent and hydrophobic, which means they will likely be retained there for a long period. A key storage location for these compounds is soil [31].

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

Additionally, these substances harm people's health in several ways, including by causing neurotoxicity, dermatological issues, and lung conditions [32]. Soil samples should continue to be analysed for PCBs using new analytical techniques. The concentration of PCBs in soils is influenced by a variety of variables, including PCB concentration and the trend towards their eradication. The highest concentration values are discovered for those organic waste materials that supply the highest levels of PCBs with a high degree of chlorination and longer persistence value, according to concentration and volume of organic waste contributed. The mean PCBs content, set as a background for soils, was expected to be around 5ng g-1, however the actual results were lower due to the low initial concentration of PCBs in the soils that were the topic of this study and their subsequent loss to the environment. Therefore, using organic waste as fertiliser shouldn't be harmful to human health due to the presence of PCBs [33]. Influence of variables related to irrigated soils, where leaching and particle mobility may facilitate PCB elimination [34, 35]. Based on data from [35, 36] respectively. One of the primary sources of PCBs, elemental composition, and polycyclic aromatic hydrocarbon (PAH) to the soil is the deposition of particulate matter in the air, both through dry deposition and wet deposition [2, 37,1, 5, 38, and 39]. As a result, the reduction in atmospheric PCB levels should lead to a reduction in PCB content in both solid waste and domestic trash [36]. Owing to a drop in environmental PCB concentrations, the behaviour of PCBs is now governed by a kinetic partitioning between air and ground concentrations [35]. The final concentration in the soil has a propensity to decline over time due to the continual decrease in PCB concentration in the environment. The movement of PCBs to lower layers has not been thought to be very significant [40, 41], whereas higher chlorinated PCB congeners are retained by adsorption mechanisms in the soil particles [41], agricultural tillage conditions leave organic waste in the upper soil layers, allowing greater volatilization, particularly in hot and dry periods [42]. Due to their reduced solubility and volatility among the various PCB congeners, or PCBs that had undergone more extensive chlorination, exhibited greater persistence [43]. The literature has already proven that PCBs 28 and 52 had the lowest persistence [44, 45, 42, 41, 39]. According to Table 3 above, PCB44 levels were highest at OAUSTECH soil and lowest at Igodan soil, PCB28 levels were higher in Lebi soil than Okumo, PCB170 levels were higher in Lebi soil than Igodan soil, and PCB156 levels were only reported in Lebi soil. Total PCBs were highest at Oaustech soil and lowest at Okumo soil. For PCB44, PCB28, PCB170, and Total PCBs, statistically significant variations were observed, showing considerable regional variation in these PCBs.

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

Table 4: The range of mean concentration of (PCBs) (µg/kg) in this study and other studies

Congeners (µS/cm)	**Range**	**Mean**	**Range** **Aganbi et al 2019**	**Mean**	**Range** **Adeyinka et al 2018**	**Mean**
PCB 44	0.63-13.30	4.178	____________	______	__________	________
PCB28	0.851-2.95	0.78	0.00001-0.00009	0.00002	86.33-165.54	140.24
PCB170	1.72-2.55	0.854	0.00001-0.0008	0.0205	___________	________
PCB156	0.00-1.80	0.0165	_____________	______	____________	________
Total PCBs	0.150-13.30	5.364	_____________	______	____________	_________

According to Table 4, The range of the total mean PCB content in soil was 0.150 to 13.30 µg/kg.This number is consistent with what [46, 47, and 48]. According to various physiochemical characteristics that might cause rise in PCB content throughout specific seasons has been attributed to excessive pollutant buildup on particulate matter in the environment. [2, 49-53]. The high number of PCBs discovered in this research may be due to the high pollution load coming from the area, including open dumping, which is a common practise in Ondo South, Nigeria, heavy vehicle activity, and uncontrollable oil spills that may seep into the soil. Previous research has demonstrated that these actions cause the environment to become contaminated with PCBs [54, 55 and 48]. Open burning, especially during the dry season, which is a frequent practice in preplanting by the people in the villages and the addition of garbage, containing tiny quantities of PCBs, which they apply to their farm land, may be the root of the elevated PCB levels in the region [56]. The high total levels of PCB may be attributed to fluids used in transformers, other electrical appliances, and the paint industry [57]. Table 4 demonstrates that the findings of this investigation are consistent with those of another comparable study that used samples of sediment and soil from the centre of South Africa [58].

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

Table 5: Pearson correlation coefficients for the relationship between the PCB homologs.

	triPCB	tetraPCB	HexaPCB
triPCB	1	.856*	0.982
tetraPCB	.856*	1	0.756
HexaPCB	0.982	0.756	1

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

TetraPCB and triPCBs have a strong positive connection, as seen in Table 5. This suggests that a higher tetraPCB level will follow a higher triPCB level, and vice versa. TetraPCB and triPCB did not, however, exhibit any statistically significant association with hexaPCB. Light PCB congeners, particularly tri-, tetra-, and hexa-CBs, dominated the PCB composition in the soils of the five study sites. Tri- and tetra-CBs may penetrate deeper into the sediment or soil as a result of downhill migration, which also causes a significant amount of light PCB homologues to do the same. Their leaching and deposition of light PCB congeners may provide an explanation for this [59]. Moreover, anaerobic biodegradation of PCBs may result in the transformation of heavy PCBs into light PCBs because anaerobic bacteria have the ability to dechlorinate PCBs from heavier congeners in an oxygen-free environment [60]. Tri-CB concentrations were much higher in top soils than in deeper soils, and these differences were highly correlated with aerobic biodegradation and photolysis [60]. Tri-CBs, however, made up a lesser fraction compared to other congeners, which may be because less than three chlorines in PCB congeners facilitate easier degradation [61]. The quantity of low-chlorinated PCBs (tri-CBs and tetra-CBs), however, increased with depth, according to Zhang et al. (2011a). 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) as seen in Table 5

International Journal of Applied Science and Engineering Review

IJASER

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

Table 6: Correlation of the Physiochemical parameters between the PCB homologs

	pH	EC	TOC	Total PCBs
pH	1	-0.363	0.037	0.395
EC	-0.363	1	.641*	-0.411
TOC	0.037	.641*	1	0.165
Total PCBs	0.395	-0.411	0.165	1

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

Total Organic Content (TOC), Electrical Conductivity (EC), and pH are physical and chemical traits that have a big impact on how PCBs behave in soil. This has a big impact on how mobile and dispersed PCBs are in the polluted environment. Table 6 displays the findings of the physicochemical property measurements. Table 6's total PCB concentrations and TOC were investigated using statistical correlation analysis, which revealed a weak but positive connection (r = 0.165) between the two variables. Kanem et al. reported this positive association in 2019; during the wet season, he saw a positive but negligible correlation, and during the dry season, he saw a positive but significant correlation. hence influencing the dispersion of PCBs in the water. The correlation between the soil's pH and total PCBs was positive and strong (r = 3.95) while the correlation between the soil's EC and total PCBs was negative and strong (r = -0.411), but other research found that the correlation between individual PCBs was positive and good [62].

Table 7: Health risk of PCBs congener in soil

Congener	EDI	ICLR	HQ
PCB 44	6E-07	4E-06	2E-03
PCB28	3E-07	2E-06	9E-04
PCB170	3E-07	2E-06	1E-03
PCB156	3E-07	2E-06	9E-04

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

Total PCBs	9E-07	6E-06	3E-03

Many negative effects on health caused by PCBs have been demonstrated [63, 64]. They have been shown to have significant negative health effects on animals other than cancer, including negative effects on the immunological system, reproductive system, neurological system, endocrine system, and other negative effects. Animals can develop cancer as a result, according to research. PCBs may have both cancer-causing and non-cancerous effects, according to studies on humans. It's possible that the many health effects of PCBs are related. The way that the body's other systems work may be significantly impacted by changes in one system. More information on the potential negative consequences of PCB exposure is provided below. The estimated daily intake (EDI) ranged from 3.0* 10-7 to 6.0* 10-7 incremental lifetime cancer risk (ICLR) ranged from 2.0* 10-6 to 4.0* 10-6 . While the quotient hazard values varied from 9.0* 10-4 to 2.0* 10-3, as shown in Table 7 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). The risk evaluation revealed that the exposed population is susceptible to both long-term cancer and unfavorable non-cancer health impacts. Therefore, steps should be taken to limit future human exposure to PCBs by eating these chosen fish species, as well as ongoing monitoring of these edible fish species. The USEPA's acceptable risk limit (1*10-6) was exceeded by all values [65]. [66]. Previous studies conducted in Taizhou found that PCBs had substantially contaminated the air, soil, trees, and sediment around the e-waste dumping places [67-71].

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

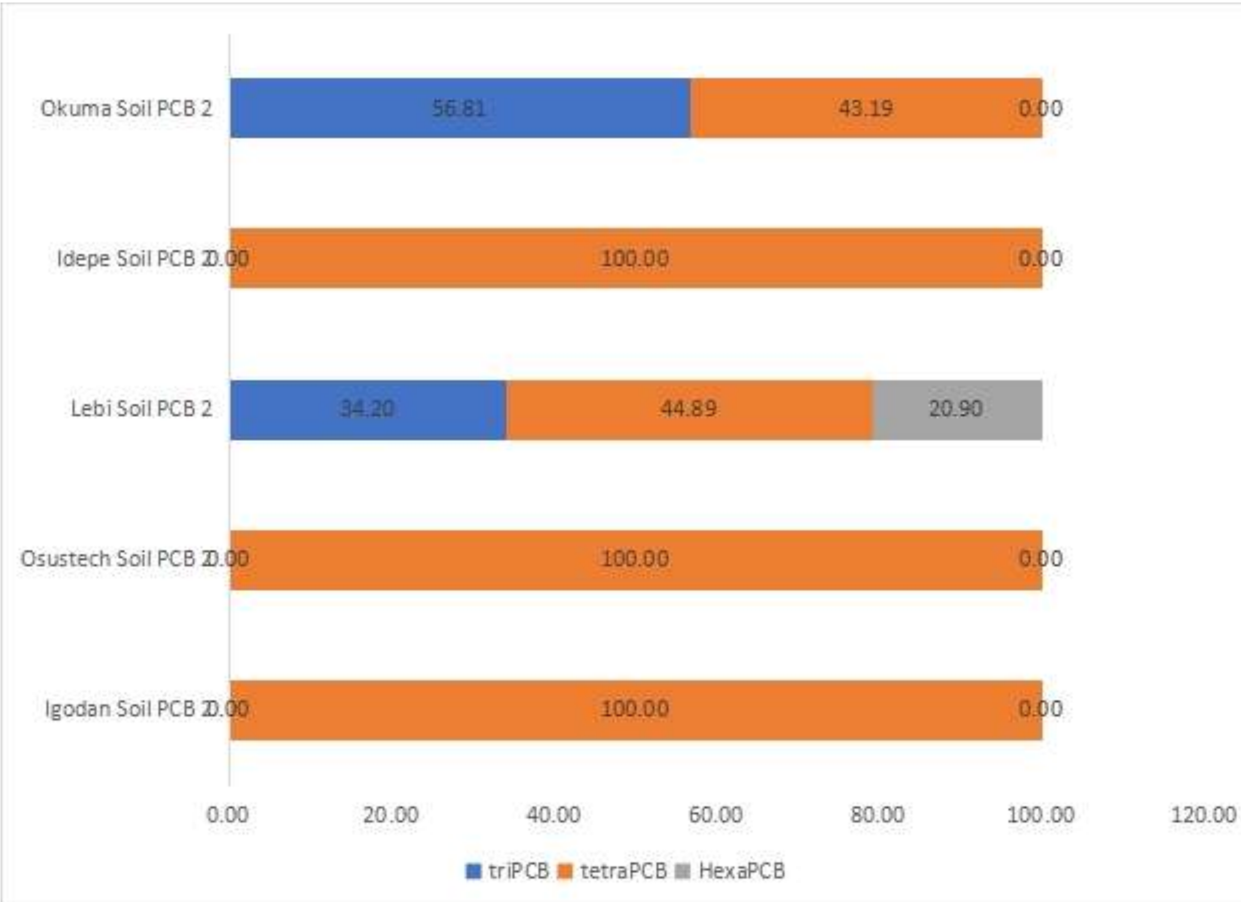

Figure 1: Distribution of the PCB homologs in Soil

PCB homologue distribution patterns in soils have already been described by various authors using the distribution patterns of PCBs [63, 72, 23, 73, and 74]. In the Okuma soil, triPCBs supplied a greater proportion than tetraPCBs and HexaPCBs, whereas at Lebi soil, tetraPCBs contributed more than triPCBs and HexaPCBs. At OSUSTECH, Idepe and Igodan soil reported 100% tetraPCB contribution. Tri-PCBs are thought to predominate in food plain soils because to their widespread usage in electrical appliances [75, 76], whereas tetra-PCBs are thought to be present due to the burning of municipal solid trash [75]. PCB fingerprints in soil were found to be similar. [76, 77]. Out of the five soil samples analysed, one to four contained tri-, tetra-, penta-, and hexa-PCBs. According to Aganbi et al., soil samples had minute concentrations of the tri-, tetra-, and hexa-PCBs (2019)

ISSN: 2582-6271

Vol. 4, Issue.4, July-Aug 2023, page no. 41-59

CONCLUSION

In Ondo South, Nigeria, soil samples from five separate locations contained high quantities of five PCB congeners. PCB concentrations were greater in the soil. The greatest PCB contamination levels were detected at OAUSTECH and the lowest at Idepe in all of the sample locations used for this investigation. The findings from this study's analysis of a total of five PCB concentrations were contrasted with those from earlier investigations using soil samples from Okitipupa in Ondo State, Nigeria. It's likely that, as compared to other places, the study area is more contaminated with the chosen PCB congeners.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Funding information

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Consent to publish

We give our consent to publish the manuscript

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