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Concentrations and risks of PCBs in soil contaminated with transformer oil in selected locations in Warri South Local Government Area, Delta State, Nigeria

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Abstract

According to the list of persistent organic pollutants (POP), polychlorinated biphenyls (PCBs) are a class of organic substances whose usage has been outlawed in the majority of nations. In addition to been used in paint, flame retardants, plasticizers, and lubricants, they were principally employed in transformers, capacitors, and other industrial purpose. PCBs have been found everywhere over the world because they are capable of being released into the environment through primary and secondary sources, travel over great distances in the atmosphere and are thus persistent. PCBs were examined in soil from area around transformer installations at several sites in Warri South Local Government Area (LGA), Delta State, Nigeria. Using Agilent 6975 GC-MS at three different locations, the evaluation was conducted for both total PCBs and congeners. The soil samples were cleaned with column chromatography using silica gel and hexane as the eluting solvent and extracted with a 1:1 hexane-acetone solution in an ultrasonic bath. With the following results recorded - Ubeji (0.148 ± 0.019 mg/kg), Ogunu (0.531 ± 0.063 mg/kg) and Edjeba (0.415 ± 0.34 mg/kg), the assessment demonstrate that all locations were polluted with PCBs that were below the maximum limit of 2.0 mg/kg as allowed by the United States Toxic Substance Control Act (USTSCA). The total cancer risk calculated in these chosen locations corresponds to Ubeji (5.41×10^{-7}), Ogunu (1.95×10^{-6}) and Edjeba (1.52×10^{-6}). This result showed that all the locations assessed have very low to low cancer risks compared with the value advised by USTSCA.

Keywords: Warri South: PCBs: Cancer Risk: POP: Congeners: Transformer

1. Introduction

Since 1929, PCBs have been utilized in industrial settings [1]. PCBs can be used in a wide variety of industrial applications thanks to their unique physical and chemical characteristics. They can be used with electrical equipment for cooling and insulating qualities [2]. PCBs are considered to be persistent organic pollutants (POPs) with significant toxicity and adverse impacts on both the environment and people [3]. Due to their great affinity for organic materials, PCBs that have been introduced into the environment may bioaccumulate within the food chain. PCBs are known to adsorb strongly to soil, where they have the tendency to persist due to their characteristic properties [4] and soil acts as a good indicator of pollution and environmental risks. As a result, they have been connected to long-term impacts in people, such as harm to the immune system, impaired lung function, bronchitis, and hormonal interference that can lead to cancer [5,6]. Additionally, research revealed that children exposed to PCBs at relatively high levels (more than 10 pg/kg body weight per day) will exhibit major developmental issues like low birth weight, behavioral difficulties, and hearing loss [7]. The consequences of PCB exposure on animals have also been documented in literature. These effects include liver damage, immune system suppression, aberrant fetal development, enzyme induction, sarcomas, non-Hodgkin lymphomas, and abnormalities in serum lipids [8]. According to Kim et al. [9], the PCBs molecule is made up of two linked benzene rings and chlorine atoms that can attach to any or all of 10 different places, resulting in 209 distinct congeners and 10 distinct homologs. High chlorinated PCB congeners are frequently discovered in organic matter, such as soils and sediments, since they typically have relatively high octanol-water partition coefficients. Low

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water solubility and vapor pressure cause PCBs to partition between the solid and aquatic phases, resulting in their existence in various compartments and broad pollution [10]. According to Van Gerven et al. [11], PCBs can be discharged into the atmosphere by burning PCB-containing garbage, leaking from landfills containing PCB-containing items, and disposing of industrial waste. According to Gomes et al. [12], landfill disposal or incineration are the most popular remediation techniques used in the US for PCB-contaminated soil or sediments. PCB remediation also makes extensive use of additional techniques like biological, chemical, physical, and thermal procedures. The majority of these options, however, are disruptive, unsustainable, and spread PCBs to various parts of the ecosystem rather than eliminating them [13]. In order to identify sustainable, alternative cleanup strategies for persistent organic pollutants, research is now being done. Therefore, the aim of this research is to investigate the occurrence of PCBs in soil contaminated from transformer installation sites in Warri South Local Government Area (LGA) Delta State, Nigeria with the objective of reporting the distribution of PCB congeners in the environmental samples obtained from this transformer Sites

2. Material and methods

2.1. Study Area

Table 1 Samples and Site Information for Warri South LGA

Location	Landmark	Soil Code	Lat (N)	Long (E)
Ubeji	Behind NNPC Refinery Fence	1m	5^0 34’ 17.8673”	5^0 42’ 21.9946”
		20m	5^0 34’ 17.8140”	5^0 42’ 22.0021”
		40m	5^0 34’ 18.1862”	5^0 42’ 20.2468”
Ogunu	Beside Lake Land School	1m	5^0 31’ 59.9887”	5^0 43’ 5.0855”
		20m	5^0 31’ 59.7684”	5^0 43’ 5.1805”
		40m	5^0 31’ 59.0142”	5^0 43’ 5.2075”
Edjeba	Front of Salvation Baptist Church	1m	5^0 32’ 32.3704”	5^0 44’ 7.9631”
		20m	5^0 32’ 32.3189”	5^0 44’ 8.3080”
		40m	5^0 32’ 32.2700”	5^0 44’ 8.8318”

Lat = Latititude, Long = Longitude

2.2. Collection and Preparation of samples

Soil samples were collected from the vicinity of transformer stations in Ubeji, Ogunu and Edjeba town (Warri South LGA), from soils close to the transformer stations in the chosen location. Six (6) soil samples were aseptically collected at 1m, 20m & 40m away from the Transformer installation using a hand auger. Samples collected were kept in an ice-filled refrigerator until they were transferred to the lab for extraction, and then further examination.

2.3. Preparation of Reagents for Polychlorinated Biphenyl (PCBs) Extraction

A total of 10 µg/mL PCB standard combination containing PCB-15, 20, 27, 29, 26, 40, 42, 47, 91, 92, 94, 101, 105, 118, 119, 128, 134, 136, 135, 151, 170, 171, 204, 205, 207, 208, and 209, internal standard (PCB 209, 200 µg/mL). The different calibration standard solutions were made by combining the requisite amounts of primary standards with hexane (97 % purity, HPLC grade, acquired from Sigma Aldrich). Both the calibration standards and the samples received a constant volume of 1 g/mL internal standard prior to analysis. Anhydrious Sodium Sulphate (Merck, Germany) was activated before use. Florisil cartridges (Supelco 6ml, 1gbed), purchased from Sigma Aldrich were used to clean the extract [14].

2.4. Sample Extraction and Clean-Up

In accordance with the US Environmental Protection Agency's (USEPA) Standard technique, a safe operating procedure (SOP) for the extraction of polychlorinated biphenyls (PCBs) was adopted [15]. Soil samples were mixed with an equivalent volume of anhydrous sodium sulphate to produce free-flowing mixes. Following three separate extractions, these solutions were sonicated for 15 min to disintegrate the cells, macromolecules, and membranes. The mixed extracts were then concentrated using a water bath with a thermostat set at 40 °C to a volume of roughly 5 m. Onto a florisil cartridge that had been preconditioned with 5 mL of hexane, the 5 mL of concentrated extract was transferred. To

achieve the elution of adsorbed analytes, hexane was eventually passed through the florisil cartridge. The internal injection standard PCB 209 was added to each of the cleaned extracts prior to the Gas Chromatography (GC) analysis. Cleansed extracts were stored in a refrigerator at a temperature of 4 °C before examination [14, 16].

Figure 1 Locations Photos of Transformers (a) Ubeji (b) Ogunu and (c) Edjeba in Warri South Local Government Area, Warri Metropolis

2.5. Instrumental Analysis for Polychlorinated Biphenyls

Polychlorinated biphenyls were identified and measured using an Agilent 6890 series gas chromatograph equipped with a split/splitless injector and a NiECD (Nickel Electron Chromatograph Detector). The chromatographic separation of the PCB congeners using 5% diphenylpolysiloxane, 95% dimethylpolysiloxane, and a 30m Agilent Technologies fused silica capillary column. The temperature of the oven was first set at 60 °C, maintained for one minute, and then increased to 180 °C at a rate of 30 °C/min, 200 °C at a rate of 2.5 °C/min, and lastly 270 °C at a rate of 7 °C/min. The operating temperatures for the injector and detector are, respectively, 280 °C and 300 °C. Injection in splitless mode was employed. The following PCB order of elution of congener was established: 15, 20, 27, 29, 26, 40, 42, 47, 91, 92, 94, 101, 105, 118, 119, 128, 134, 136, 135, 151, 170, 171, 204, 205, 207, 208, and 209 (internal injection standard) [14, 16].

2.6. Quality Control

The calibration factor, which measures the detector response to shifting target analyte concentrations was evaluated for 27 PCB congeners - 15, 20, 27, 29, 26, 40, 42, 47, 91, 92, 94, 101, 105, 118, 119, 128, 134, 136, 135, 151, 170, 171, 204, 205, 207, 208, and 209 respectively. The Relative Standard Deviation (RSD) of the calibration factors for target analytes from the five-point calibration standards were 4.6 %, 9.2 %, 3.8 %, 5.9 %, 5,4 %,4.4 %, 6.2 %, 7.8 %, 6.6 %, 12.3 %. This was done to ensure that the instrument was functioning in line with the manufacturer's requirements. The calibration parameters were used to determine the limits of detection for target analytes at a signal-to-noise ratio of 3:1. For samples where the target PCBs weren't found, LOD (Limit of Detection) values were provided. The target analytes were not present and each batch of samples was submitted to a blank analysis. Internal injection standard (PCB 209) was injected into the calibration standard and samples [14,16], to account for changes in the target analytes' retention times.

2.7. Data Analysis

Using Origin 8.5 Windows Evaluation Version, ANOVA and cluster analysis were carried out. Prior to running an analysis of variance (ANOVA), PCBs concentrations were log-transformed to normalize the data.

3. Results and discussion

3.1. PCB Concentrations at Different Soils

All the soil samples collected for investigation at Warri South LGA location had PCBs present at the different samplimg point, with the highest total PCB concentrations recorded been in Ogunu site (0.531 ± 0.063 mg/kg). The soil samples from Edjeba and Ubeji location had total PCB concentration of 0.415 ± 0.34 mg/kg and 0.148 ± 0.019 mg/kg respectively (Table 2, Fig.2). The range (0.415 ± 0.34 mg/kg - 0.531 ± 0.063 mg/kg) of the total PCBs in soil samples from this study is lower than those reported in soils from transformer environment in Nigeria ranging (8.4 - 510 mg/kg) [17]. soils around electrical transformer in Ghana ranging 1.32 - 12.94 µg/kg [18]. soils near electronic waste recycling plants with a range of 24.2 - 12045 ng/g [19]. and some international regulatory standards, such as the Dutch guideline and the Australian and New Zealand ecological investigation levels of 1000 µg kg^{-1} [20]. and the Canadian soil standard for residential areas of 1300 µg kg^{-1} [21]. However, comparing the obtained PCBs concentrations with those reported in other investigations is challenging due to differences in the congeners selected and related statistics.

Table 2 Mean Concentrations of PCBs (mg/kg) in Soil Samples from various locations in Warri South LGA, Delta State, Nigeria

PCB Congeners No.	**Power Station**		
	Ubeji	Ogunu	Edjeba
	Mean ± SD	Mean ± SD	Mean ± SD
PCB 15	0.008 ± 0.014	0.019 ± 0.015	0.023 ± 0.035
PCB 20	0.013 ± 0.010	0.015 ± 0.012	0.029 ± 0.042
PCB 27	0.009 ± 0.005	0.014 ± 0.013	0.013 ± 0.010
PCB 29	0.005 ± 0.008	0.012 ± 0.012	0.008 ± 0.010
PCB 26	0.004 ± 0.005	0.011 ± 0.010	ND
PCB 40	0.004 ± 0.005	0.005 ± 0.003	0.017 ± 0.017
PCB 42	0.008 ± 0.009	0.009 ± 0.007	0.024 ± 0.026
PCB 47	0.004 ± 0.005	0.006 ± 0.008	0.008 ± 0.006
PCB 91	0.001 ± 0.000	0.004 ± 0.004	0.012 ± 0.010
PCB 92	0.006 ± 0.003	0.003 ± 0.003	0.005 ± 0.005
PCB 94	0.002 ± 0.001	0.001 ± 0.001	0.003 ± 0.003
PCB 101	0.003 ± 0.002	0.002 ± 0.002	0.011 ± 0.012
PCB 105	0.004 ± 0.005	0.001 ± 0.001	0.004 ± 0.002
PCB 118	0.0003 ± 0.001	0.001 ± 0.000	0.007 ± 0.005
PCB 119	0.001 ± 0.002	0.001 ± 0.001	0.003 ± 0.002
PCB 128	0.0003 ± 0.001	0.001 ± 0.001	0.003 ± 0.002
PCB 134	0.001 ± 0.002	0.001 ± 0.001	0.004 ± 0.002
PCB 136	0.001 ± 0.001	0.006 ± 0.001	0.002 ± 0.000
PCB 135	0.001 ± 0.001	0.003 ± 0.002	0.001 ± 0.000
PCB 151	0.001 ± 0.000	0.005 ± 0.002	0.003 ± 0.003

PCB 170	0.001 ± 0.002	0.008 ± 0.004	0.004 ± 0.001
PCB 171	0.002 ± 0.002	0.016 ± 0.002	0.002 ± 0.001
PCB 204	0.001 ± 0.001	0.011 ± 0.003	0.004 ± 0.000
PCB 205	0.006 ± 0.007	0.098 ± 0.070	0.011 ± 0.001
PCB 207	0.015 ± 0.009	0.088 ± 0.040	0.036 ± 0.031
PCB 208	0.024 ± 0.022	0.064 ± 0.035	0.091 ± 0.120
PCB 209	0.020 ± 0.014	0.124 ± 0.103	0.087 ± 0.060
Total PCB (mg/kg)	0.148 ± 0.019	0.531 ± 0.063	0.415 ± 0.340

SD = Standard deviation ND = Not dictated

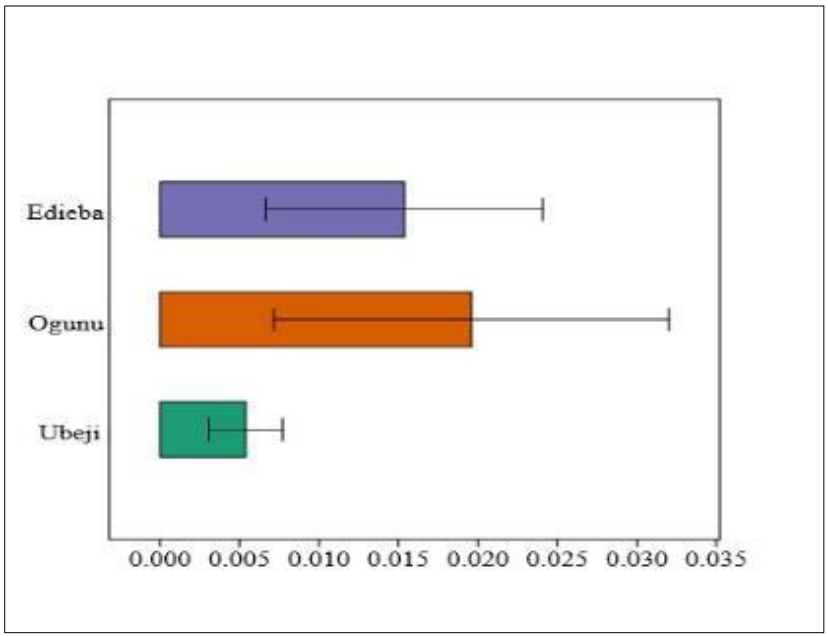

Figure 2 Box diagram of PCBs (mg/kg) in soil samples from various locations in Warri South LGA, Delta State, Nigeria

3.2. Pearson's Correlation Matrix for PCBs

PCB-40 strongly correlated with 42, 118, 119, and 134, PCB-135 significantly connected with 171, 205, and 209, and PCB-135 significantly correlated with 27 and 171. However, there are negative connections between PCB-105 and 135, 176, 205, and 209 (Figure 3). These PCBs that are closely linked to a single source show positive connection with one another. [22-24] employed correlation analysis to look at the relationships between certain PCB homologues in their research of PCB-contaminated sediments. According to the Muir investigation, no statistically significant associations were found between tetra-, penta-, hexa-, or heptachlorobiphenyls. Selected pairs of PCB homologues found in soil samples from Warri South LGA revealed statistically significant and positive relationships, in contrast to PCB homologues found in the soil samples (Figure 3).

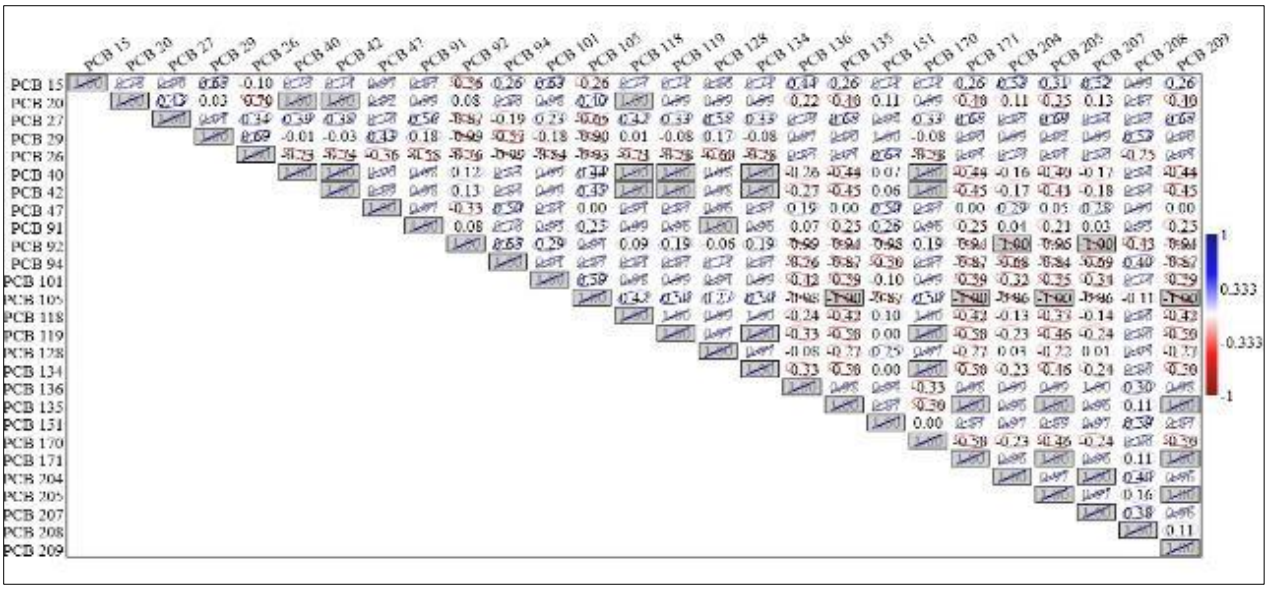

Figure 3 Pearson's Correlation Matrix for PCBs (mg/kg) in Soil Samples from various Locations in Warri South LGA, Delta State, Nigeria

3.3. Principal Component Profile of PCBs

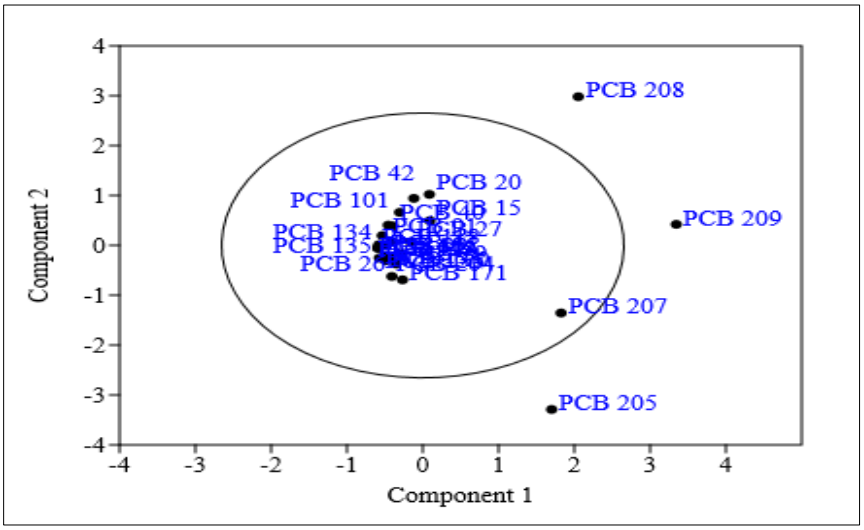

Figure 4 Principal Component Profile of PCBs (mg/kg) in Soil Samples from various locations in Warri South LGA, Delta State, Nigeria

Principal component analysis (PCA), a widely used statistical technique, was used to find potential sources of contaminants and their correlations [25, 26]. This was accomplished by combining varimax rotation with Kaiser normalisation. PCA condenses a vast set of variables into a select group of important scores (components). The correlation matrix's eigenvalues and eigenvectors were eliminated, and the principal variables influencing PCB quality were identified, along with the variance's percentage, in Figure 4. In order to determine the distribution of the PCBs determined from the soi sampled, two significant components that accounted for 88.34 % of the variation in Warri South LGA were found (Figure 4). First principal component (PC1) values for PCB-205, 207, 208, and 209 were 0.0092, 0.002, and 0.0014, respectively. Warri South LGA severely weighted these values with loadings of 0.064, 0.069, 0.078, and 0.13. Prior research [27, 28] categorised factor loadings of 0.6, 0.4–0.6, and 0.3–0.4 as substantially, moderately, and weakly linked with components in the same class, respectively. These standards indicated that PCB-205, 207, 208, and 209 in the studied Local Government had a tenuous grip on PC1. PC2 in Warri South LGA also had a sizable amount of PCB 15 and 209 loaded onto it (0.0068 and 0.0058, respectively). These findings imply that the origins of PCB-15 and 209 in the soil under investigation were more intricate.

3.4. Normality Tests

According to [29], probability theory serves as the foundation for all statistical techniques. He cautioned that the application of inferential techniques based on probability distribution may produce erroneous and illogical results if the underlying probability distribution is misinterpreted or violated. Among the two categories of statistical test techniques, [30] observed that parametric test methods are based on or assume that the samples are drawn from a population that is normally distributed or is from a particular probability distribution. Unlike parametric test methods, non-parametric test methods do not consider distribution. . In other words, the foundation for non-parametric statistical procedures is not a certain underlying distribution. Before deciding on and employing inferential statistical methods of analysis, this study decided to determine the normality of each data set (i.e. the total PCBs found in soil samples from Warri South LGA). The first test to establish the normality of the total PCB contents detected in soil samples from Warri South LGA is the Anderson-Darling test for normality. The Anderson-Darling normality test is explained and supported by [31]. The following equation (1), according to [32] closely represents the Anderson-Darling statistics for the upper.05 percentile for a sample of size n:

$$A^2{}_{n,}\ .05 = .7514(1 - .795n^{-1} - .89n^{-2} \quad (1)$$

n denotes the sample size or overall number of samples, and A^2 denotes the Anderson-Darling statistics. The population is not normally distributed if the calculated A^2 from equation 1 is greater than the A^2 from a cumulative normal distribution table (critical value). By calculating A^2 and producing a p-value, Past 4.11 software automatically performed the Anderson-Darling test (Table 5 and Figure 5). The overall PCB concentrations discovered in soil samples from the chosen location in Warri South Area are therefore judged to not be typical of the population as a whole because A^2 for each set of data is higher than the p-value.

Table 3 Anderson-Darling for the Concentrations of total PCBs measured in Soil samples from various locations in the studied LGA, Delta State, Nigeria

Local Government Area	Site	Anderson-Darling (A2)	p(normal)
Warri South	Ubeji	2.193	9.951×10^{-6}
	Ogunu	4.797	3.16×10^{-12}
	Edjeba	3.837	7.588×10^{-10}

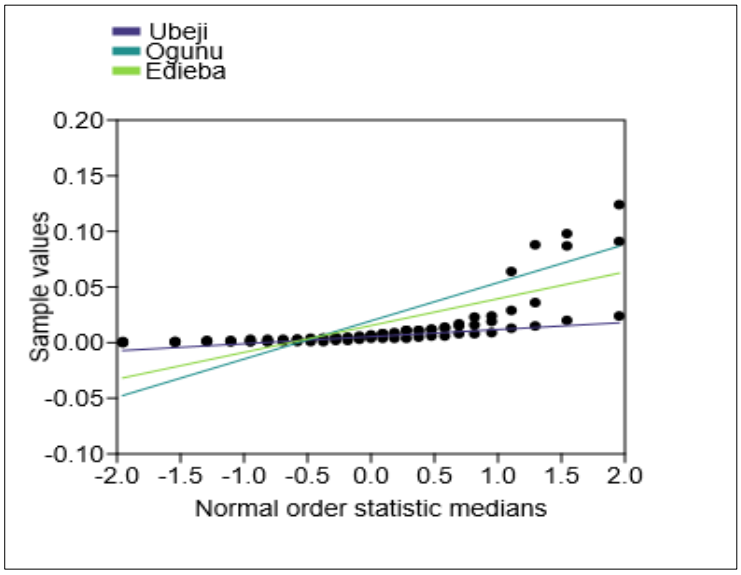

Figure 5 Normal Probability Plot for the Concentrations of Total PCBs measured in Soil samples from various locations in Warri South LGA, Delta State, Nigeria

3.5. Health Risk Assessment

To calculate the carcinogenicity associated with PCB exposure, the deterministic method from USEPA's assessment guidance was employed [33]. The USEPA screening threshold equation for first cleanup targets calculated the likelihood

of exposure to PCBs in topsoil in residential areas based on the pathways of ingestion, particle inhalation, and skin absorption. In this case, residential land use was considered when establishing whether a PCB was carcinogenic; its concentration was expressed in mg/kg as shown in Table 1, and Table 4 provides the lifetime cancer risk of the four dioxin-like PCBs collectively.

To calculate the carcinogenic risk for ingestion, inhalation, and cutaneous absorption, equations (2) - (4) were utilised. Tables 6 present the findings.

$$ILCR_{ing} = \frac{C_{soil} \times IngR \times EF \times ED \times CF \times SFO}{BW \times AT} \quad (2)$$

$$ILCR_{dem} = \frac{C_{soil} \times SA \times AF_{soil} \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times AT} \quad (3)$$

$$ILCR_{inh} = \frac{C_{soil} \times InhR \times EF \times ED \times ET \times IUR}{PEF \times AT} \quad (4)$$

Where

$ILCR_{inh}$ is for incremental lifetime cancer risk via inhalation of soil particles, $ILCR_{ing}$is for incremental lifetime cancer risk from unconscious ingestion, while $ILCR_{dem}$ stands for dermal contact. Inhaling soil particles increases a person's lifetime cancer risk. IngR is the rate at which soil is consumed (100 mg per day for an adult), and C_{soil} is the determined PCB concentration in soil (mg kg^{-1}). EF = exposure frequency (350 days per year, excluding 15 days for holidays), ED = exposure duration (52 years was used based on the average life expectancy of a Nigerian), CF = conversion factor (1×10^{-6}), SFO = oral slope factor (2.0 mg kg^{-1} d^{-1}), BW = average body weight (65 kg), AT = averaging time for carcinogens (days), which was calculated as 52365 = 25,550 days, SA stands for the skin's exposed surface area (3300 cm^2), which includes the arms and hands. ABS is the dermal absorption factor (0.1), *InhR* is the inhalation rate which is 15.8 m^3 d^{-1}, and AF_{soil} is skin adherence factor for soil (0.2 mg cm^{-2}), GIABS stands for gastrointestinal absorption factor (1), ET for exposure time (8 h d^{-1}), PEF for soil to air particle emission factor (1.36×10^9 m^3 kg^{-1}), and IUR for inhalation unit risk, all of which are equal to one [34, 35].

However, using the answers to equations (2) - (4), the overall cancer risk due to ingestion, cutaneous absorption, and inhalation was calculated. Even though PCBs are known to bioaccumulate, this problem needs to be resolved. [36, 37] found that the overall PCBs content in soil from transformer installation sites in University of Port Harcourt and Jos metropolis was greater than 2.00 mg/kg. These statistics (Table 6) demonstrate that we are far less polluted than more developed countries like China and the US [38,39] when compared to other studies from around the world.

Table 4 Incremental Lifetime Cancer Risk Assessment (ILCR) for PCBs in Soil Samples from various locations in Warri South LGA, Delta State, Nigeria

Location	$ILCR_{ing}$	$ILCR_{dem}$	$ILCR_{inh}$	Total Cancer risk
Ubeji	3.24×10^{-7}	2.11×10^{-7}	5.58×10^{-9}	5.41×10^{-7}
Ogunu	1.16×10^{-6}	7.68×10^{-7}	2.00×10^{-8}	1.95×10^{-6}
Edjeba	9.10×10^{-7}	6.00×10^{-7}	1.57×10^{-8}	1.52×10^{-6}

3.6. Analysis of Variance (ANOVA)

The overall mean concentration in the soil samples from Warri South Local Governments Area is shown in Table 7 as the one-way ANOVA findings (0.05 level of significance). According to the results (Table 7), F_{cal} values in soil samples are lower than F_{crit} values. There aren't many notable variations in how soil variability impacts PCB concentration levels as a result. These findings show that there was no statistically significant difference in PCB levels between the soil samples ($P < 0.05$).

Table 5 ANOVA for PCBs in Soil Samples from various locations in Warri South LGA, Delta State, Nigeria

Source of Variation	SS	df	MS	F_{Cal}	P-value	F_{Crit}
Between Group	0.0029	2	0.0014	2.602	0.081	3.114
Within Group	0.043	78	0.0006			
Total	0.046	80				

4. Conclusion

Investigations into the distribution and carcinogenicity of polychlorinated biphenyls in soil samples from transformer installation sites in Warri South Local Government Area, Delta State, Nigeria revealed that all of the sites under investigation had soil contamination below the 2.00 mg/kg threshold set by the United States Toxic Substance Control Act (TSCA), suggesting that these may not need to be cleaned up. In this residential region, adults have a very low to low risk of developing cancer, according to the assessment of human health risks related to carcinogenicity. The Basel Convention's recommended value of 50 mg/kg generally regarded as the threshold for waste classification under the POPs regulation—is much below the level of individual congeners.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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