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Carcinogenicity and Distribution of PCBs in Soil from Electrical Transformers Installation Sites in Uvwie Local Government Area, Delta State, Nigeria

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Abstract: **Most nations have outlawed the use of polychlorinated biphenyls (PCBs), a group of chemical substances that are classified as persistent organic pollutants (POP). They were mostly utilised in paint, retardants, plasticizers, lubricants, transformers, and capacitors. PCBs can be released into the atmosphere from primary and secondary sources. They are transported over great distances by the atmosphere, and as a result, have been found all over the world. PCBs were tested in soil near transformer installations at various sites in Uview local government area (LGA) in the metropolis of Warri, Delta state, Nigeria. The evaluation was done using three different Agilent 6975 GC-MS systems for both total PCBs and congeners. The soil samples were cleaned and concentrated by column chromatography utilising silica gel and hexane as the eluting solvent. The soil samples were extracted with 1:1 hexane-acetone in an ultrasonic bath. The Toxic Substance Control Act (TSCA) of the United States permits a maximum PCB concentration of 2.0 mg/kg, but the results show that all areas were polluted with PCBs below this limit, with the following values for Enerhen (1.146 ± 0.023), Ogbomoro (0.340 ± 0.28) and Ekpan (0.225 ± 0.320) in mg/kg. The total cancer risk calculated by adding the cancer risks from ingestion, inhalation, and dermal contact in these particular locations corresponds to Enerhen (4.2×10^{-6}), Ogbomoro (1.25×10^{-6}), and Ekpan (8.26×10^{-7}), and it was found that all of these locations have extremely low to low cancer risks compared to the value advised by the TSCA.**

Keywords: **Transformer, Warri, Carcinogenicity, PCBs, Soil, Uvwie.**

1. INTRODUCTION

In the environment, polychlorinated biphenyls (PCBs) have been widely dispersed and are harmful, persistent pollutants (Subramanian et al. 2017). Due to their high level of toxicity, long-range air transport, and probable carcinogenicity, they are categorised as persistent organic pollutants (POPs) under the Stockholm Convention. According to research evidence, long distance travel is a significant source of this contamination in a remote place (Lao et al. 2018). The majority of polychlorinated biphenyls are synthetic chemicals that have 2–10 atoms of chlorine bonded to the biphenyl molecules. They were first created some years ago and are thought to produce 1.5 million tonnes annually (Andersson et al. 2015). Although most nations outlawed its emission in 1980, it is nevertheless produced today by outdated electrical equipment, poor waste management, leaks from electronic equipment, and incorrect disposal of transformer and capacitor oil (Wang et al. 2016). As PCB congeners, there are 209 different substances. Since the 1930s, their qualities as insulators, flame retardants, plasticizers, and pesticide additives have made them ideal (Everaert et al. 2015). They also have low electrical conductivity and great thermal degradation performance. Out of the 1.5 million tonnes of PCBs produced globally, 48% are utilised in transformer oils, 21% in tiny capacitors, and 10% in other closed systems, such as heat transfer fluids, according to

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Andersson et al. (2015), 21% of open systems use paints and pesticides, 21% use liquid-filled cables and circuit breakers, and the rest use hydronic fluids. Additionally, they have been utilised as organic diluents, plasticizers, adhesives, cutting fluids with dust-reducers, flame retardants, sealants, and in carbonless copy paper. Some of these PCBs usage have directly introduced PCBs into the environment. Polychlorinated biphenyl contamination of the environment is a major worry for environmentalists all over the world. According to reports, they have negative consequences on people, the environment, and the ecosystem (Yuan et al. 2015). They are introduced to the environment as a congener-rich mixture (Sapozhnikova et al. 2004). Despite being phased out in 1970, PCB residues have been found in soil, water, and air across the globe (Whitehand et al. 2015), and it is predicted that their levels will not considerably decline in the coming decades (Gao et al. 2013). The soil can both operate as a source of contamination and as a significant sink for PCBs (Zhang et al. 2014). The loss of agricultural land due to soil contamination is an increasing issue in many nations. Nearly 21,000 tonnes of PCBs have been released into the soil worldwide, according to Meijer et al. (2013) research. This may progressively build up throughout the food chain and negatively impact humans (Sirot et al. 2012). According to Li et al. (2015), the distribution of PCBs in soil can be used to determine the risk to human health, determine the extent of pollution, and determine the source of emissions. Therefore, the purpose of this study is to examine the presence of PCBs in soil from transformer installation sites in Uvwie Local government area (Uvwie LGA) in Warri metropolis, Nigeria, with a view to reporting the distribution of PCB congeners in environmental samples collected from these transformer sites.

2. MATERIALS AND METHODS

Study Area

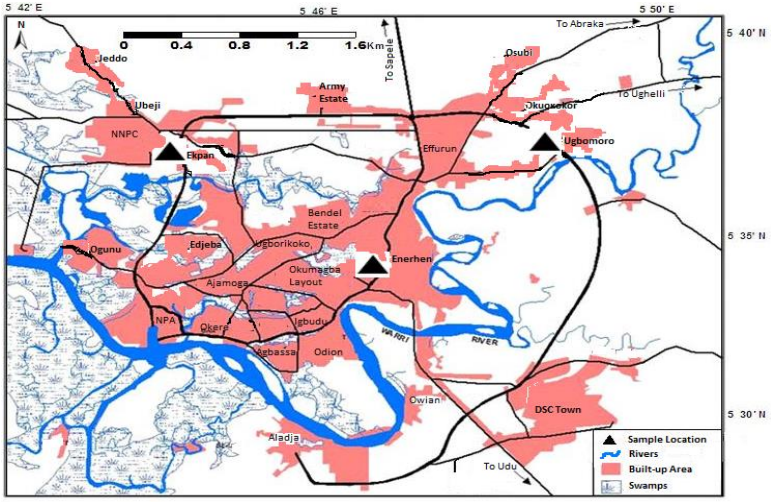

Figure 1. ModifiedMap of Warri Metropolic Showing sampling points. -(Original map by Prof F.O. Odermerho - Urhobo Historical Society, 2008)

Table 1. Samples and Site Information for Uvwie Local Government Area

Location	Landmark	Soil Code	Lat (N)	Long (E)
Enerhen	Close to Humanity Hospital	1m	5^0 32' 27.9812"	5^0 46' 58.7831"
		20m	5^0 32' 27.5881"	5^0 46' 58.8792"
		40m	5^0 32' 27.0701"	5^0 46' 59.3252"
Ugbomoro	Opp Saverid Global Venture(Petrol station)	1m	5^0 34' 3.0079"	5^0 49' 40.5462"
		20m	5^0 34' 3.4223"	5^0 49' 40.2661"
		40m	5^0 34' 4.0144"	5^0 49' 40.0328"
Ekpan	Beside Edo Guest house	1m	5^0 34' 8.1152"	5^0 44' 6.3996"
		20m	5^0 34'7.9381"	5^0 44' 6.5767"
		40m	5^0 34' 7.3369"	5^0 44' 6.4878"

Lat = Latititude, Long = Longitude

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Figure 2. Locations Photos of Transformers (a) Enerhen (b) Ogbomoro and (c) Ekpan in Uvwie Local Government Area, Warri Metropolis

Collection and Preparation of Samples

Soil samples were collected from the vicinity of transformer stations located in Enerhen, Ogbomoro and Ekpan town in Uvwie LGA (Fig. 2). From soils close to the transformer stations in the chosen sites, six (6) soil samples were aseptically collected using a hand auger. Samples were collected, kept in an ice-filled refrigerator until they were transferred to the lab for extraction, and then further examination.

Preparation of Reagents for Polychlorinated Biphenyl (PCBs) Extraction

The internal standard (PCB 209, 200 g/mL), 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 were all a part of the 10 g/mL PCB standard combination. According to the manufacturer's instructions, the different calibration standard solutions were made by combining hexane (97 % purity, HPLC grade, acquired from Sigma Aldrich) with the necessary quantities of primary standards. Both the calibration standards and the samples received an equal amount of 1 g/mL internal standard prior to analysis. Activated anhydrous Sodium sulphate (Merck, Germany) was used before using Florisil cartridges (Suppelco 6ml, 1gbed), purchased from Sigma Aldrich (Folarin et al. 2018), the extract was cleaned.

Sample Extraction and Clean-Up

According to the US Environmental Protection Agency (USEPA) Standard method (USEPA, 1999), a safe operating procedure (SOP) for PCB extraction was adopted. Soil samples were mixed with anhydrous sodium sulphate in an equal ratio to produce free-flowing mixes. In order to disintegrate the cells, macromolecules, and membranes, these mixes were then sonicated for 15 mins throughout the course of three subsequent extractions. Using a water bath with a thermostat set to 40 °C, the mixed extracts were then concentrated to a volume of roughly 5 m.

A florisil cartridge that had been preconditioned with 5 mL of hexane to clean up the extracts received the 5 mL of concentrated extract. Finally, hexane was applied to the florisil cartridge to achieve adsorbed analyte elution. Before the Gas Chromatography (GC) analysis, PCB 209, the internal injection standard, was added to each of the cleaned extracts. Cleansed extracts were maintained at 4 °C in a refrigerator until analysis (Folarin et al. 2018; Tabuanu et al. 2021).

Instrumental Analysis for Polychlorinated Biphenyls

The identification and quantification of polychlorinated biphenyls was carried out 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 a 30 m Agilent Technologies fused silica capillary column, 5 % diphenylpolysiloxane, and 95 % dimethylpolysiloxane. The oven's temperature was originally set at 60°C, held 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 ultimately 270°C at a rate of 7°C/min. The operating temperatures for the injector and detector are 280 °C and 300 °C, respectively. Splitless mode injection was employed. According to Folorin et al. (2018) and Tabuanu et al. (2021), congeners were eluted in the following order: 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.

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Quality Control

How the detector would respond to shifting target analyte concentrations was determined using the calibration factor. For PCB congeners 8, 15, 20, 26 27, 28, 29, 40, 42, 47, 91, 92, 94, 101, 105, 118, 119, 128, 134, 135, 136, 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 % and 12.3 %. This was carried out to ensure that the instrument was operating in line with the manufacturer's requirements. The limits of detection for target analytes were calculated using the calibration parameters at a 3:1 signal-to-noise ratio. Limit of Detection (LOD) values were provided for samples that did not contain the target PCBs. The target analytes were not present during the blank determination of each set of samples. Internal injection standard (PCB 209) was injected to the calibration standard and samples in order to account for changes in the target analytes' retention times (Folarin et al. 2018; Tabuanu et al. 2021).

Data Analysis

The Past 4.11 Windows evaluation version software was used to do an ANOVA and a cluster analysis. The concentrations of PCBs were log-transformed before an analysis of variance (ANOVA) was conducted to normalise the data.

3. RESULTS AND DISCUSSION

Concentration of PCBs in Soil

PCBs were present in every sample taken from the studied sites (Table 2) and fig.3. In Uvwie LGA, Enerhen has the highest total PCB concentration (1.146 ± 0.023 mg/kg). Total PCB concentrations in Ekpan was (0.225 ± 0.32 mg/kg). Ugbomoro had a total PCB concentration of (0.340 ± 0.28 mg/kg). According to Bobovonikova et al. (1993), the overall content of PCBs in the soil samples was below the regulation limit of 60 mg/kg imposed by the now-defunct USSR Ministry of Health in 1991. The total PCB concentrations in the soil samples were also below a number of international regulatory standards, such as the Dutch action intervention values of 1000 g/kg (VROM, 1994), the Canadian soil standard for residential areas (1300 g/kg) (CCME, 2003) and the Basel Convention (2004) guideline with a generally accepted limit of 50mg/kg for waste classification in POP.

Table 2. Mean Concentrations Of PCBs (mg/kg) In Soil Samples From Various Locations In Uvwie Local Government, Warri Metropolis, Nigeria

PCB Congeners No.	Power Station		
	Enerhen	Ugbomoro	Ekpan
	Mean ± SD	Mean ± SD	Mean ± SD
PCB 15	0.019 ± 0.003	0.014 ± 0.012	0.010 ± 0.013
PCB 20	0.022 ± 0.020	0.018 ± 0.014	0.003 ± 0.004
PCB 27	0.012 ± 0.020	0.020 ± 0.014	0.005 ± 0.006
PCB 29	0.003 ± 0.005	0.018 ± 0.009	0.008 ± 0.007
PCB 26	0.011 ± 0.012	0.016 ± 0.013	0.006 ± 0.007
PCB 40	0.005 ± 0.004	0.012 ± 0.004	0.003 ± 0.003
PCB 42	0.005 ± 0.006	0.015 ± 0.006	0.005 ± 0.006
PCB 47	0.006 ± 0.008	0.007 ± 0.002	0.008 ± 0.010
PCB 91	0.002 ± 0.003	0.004 ± 0.004	0.002 ± 0.002
PCB 92	0.002 ± 0.003	0.005 ± 0.002	0.006 ± 0.007
PCB 94	0.003 ± 0.004	0.006 ± 0.004	0.003 ± 0.005
PCB 101	0.001 ± 0.001	0.006 ± 0.004	0.005 ± 0.005

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PCB 105	0.001 ± 0.001	0.0003 ± 0.001	0.003 ± 0.004
PCB 118	0.001 ± 0.001	0.004 ± 0.006	0.003 ± 0.002
PCB 119	0.0003 ± 0.001	0.003 ± 0.004	0.002 ± 0.002
PCB 128	0.0003 ± 0.001	0.007 ± 0.010	0.002 ± 0.003
PCB 134	0.001 ± 0.000	0.015 ± 0.026	0.003 ± 0.002
PCB 136	0.003 ± 0.003	0.002 ± 0.002	0.003 ± 0.003
PCB 135	0.003 ± 0.002	0.002 ± 0.001	0.003 ± 0.002
PCB 151	0.006 ± 0.001	0.003 ± 0.003	0.004 ± 0.004
PCB 170	0.004 ± 0.001	0.009 ± 0.010	0.003 ± 0.004
PCB 171	0.006 ± 0.002	0.002 ± 0.010	0.004 ± 0.004
PCB 204	0.003 ± 0.003	0.004 ± 0.002	0.003 ± 0.003
PCB 205	0.271 ± 0.026	0.037 ± 0.060	0.009 ± 0.013
PCB 207	0.165 ± 0.078	0.022 ± 0.030	0.017 ± 0.028
PCB 208	0.240 ± 0.204	0.032 ± 0.040	0.094 ± 0.160
PCB 209	0.352 ± 0.195	0.056 ± 0.070	0.010 ± 0.014
Total PCB (mg/kg)	1.146 ± 0.023	0.340 ± 0.280	0.225 ± 0.320

SD = Standard deviation

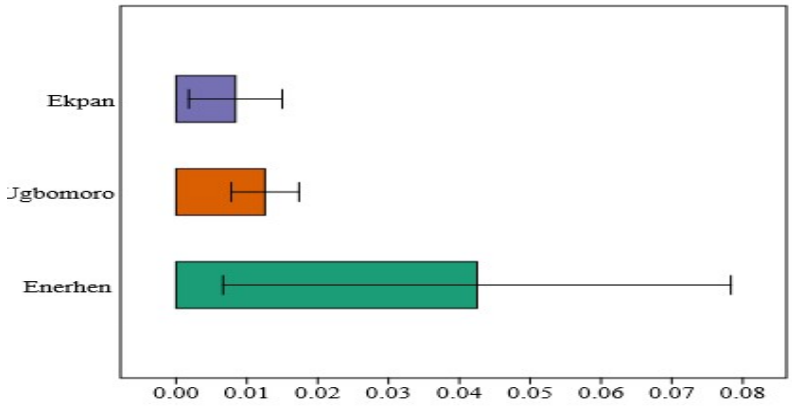

Figure 3. Box diagram of PCBs (mg/kg) in soil samples from various locations in Uvwie Local Government Area, Warri Metropolis

Pearson's Correlation Matrix for PCBS

At $p < 0.05$, significant positive correlations between PCB-204, 94, 91, with 42 ($r^2 = 1.00$) and PCB-94, 47 with 91 ($r^2 = 1.00$) were found (Figure 4). The relationships between PCB-204 and 170, 135 and 136, as well as between 135 and 136 and 94, 91, and 42, are negative ($r^2 = -1.00$; $p < 0.05$). These PCBs that are closely related to one another show positive correlations. (Apau et al., 2022 and Boateng et al., 2019). Muir et al. (1996) employed correlation analysis to look at the relationships between certain PCB homologues in their study of PCB-contaminated sediments. The Muir investigation found no statistically significant associations between tetra-, penta-, hexa-, or heptachlorobiphenyls. Select pairs of PCB homologues found in soil samples from Warri Metropolis, in contrast to PCB homologues found in sediment samples, revealed statistically significant and positive relationships (Table 3).

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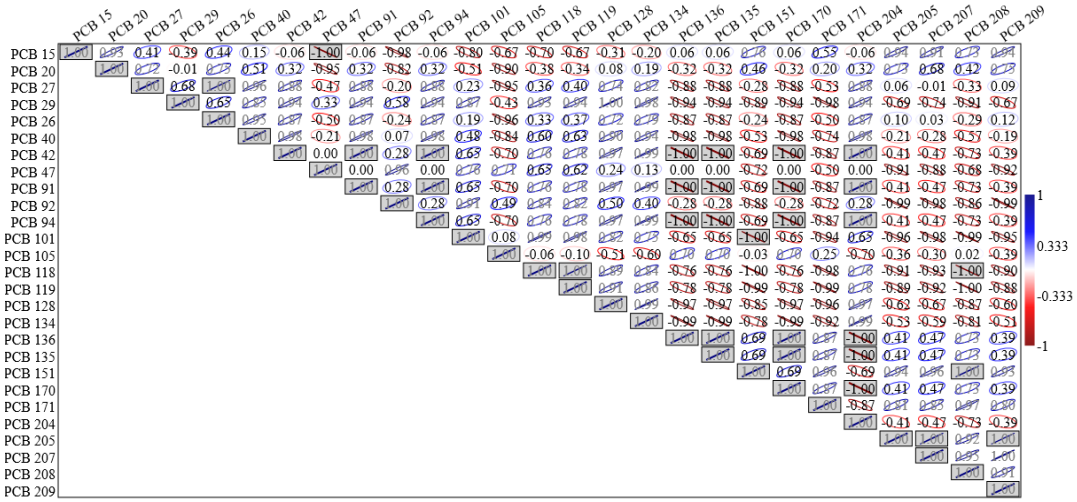
Table 3. Pearson's Correlation Matrix for PCBs (mg/kg) in soil samples from various locations in Uvwie Local Government Area, Warri Metropolis, Nigeria



Principal Component Profile of PCBs

Principal component analysis (PCA), a widely known statistical technique, was used to find probable sources of contaminants and their interactions by combining varimax rotation with Kaiser normalisation (Hadlich et al. 2018; Christophoridis et al. 2020). A huge number of variables are condensed by PCA into a manageable number of significant scores (components). Figures 4 shows the principal parameters impacting PCB quality as well as the percentage of variation after the eigenvalues and eigenvectors were removed from the correlation matrix. In order to determine the distribution of the PCBs evaluated from the soil collected, two significant components were found that accounted 99.66 % of the overall variation in the Uvwie, LGA (Figures 4). The first principal component (PC1) for PCB-205, 207, 208, and 209 had values of 0.0092, 0.002, and 0.0014, respectively; these were severely weighted by loadings of 0.23, 0.12, 0.20, and 0.31 in Uview LGA, In a previous study (Hadzi et al. 2019 and Liu et al. 2022) factor loadings of 0.6, 0.4–0.6, and 0.3–0.4 were categorised as substantially, moderately, and weakly linked with PCB in the same class, respectively. These standards showed that the studied Local Government PCB-205, 207, 208, and 209 had a tenuous grip on PC1. Additionally, PC2 (0.0074 and 0.0062 in Uview LGA) had a sizable amount of PCB 170 and 209 placed onto it. These findings show that PCB-170 and 209 in the tested soil originated from sources that were more intricate.

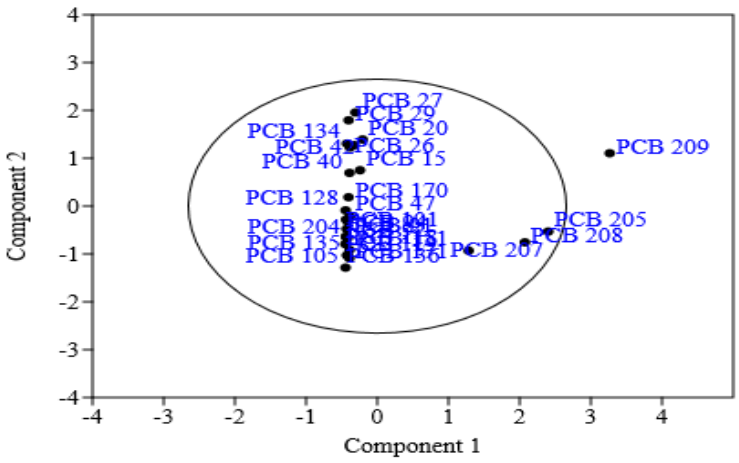


Figure 4. Principal component profile of PCBs (mg/kg) in soil samples from various locations in Uvwie Local Government, Warri Metropolis.

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Normality Tests

According to Delorme (2011), the foundation of any statistical method is probability theory. He cautioned against using inferential processes based on probability distribution if the underlying probability distribution is misinterpreted or violated, as this could lead to erroneous and illogical results. Vickers (2005) pointed out that, of the two types of statistical test techniques, 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. In contrast to parametric test methods, non-parametric test methods are distribution free. In other words, non-parametric statistical procedures are not reliant on any certain underlying distribution. Before adopting 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 Uvwie LGA). The first test to evaluate if the total PCB contents found in soil samples from Warri Metropolis are spread uniformly is the Anderson-Darling test for normality. The Anderson-Darling normality test's guidelines and reasoning are provided by Thode (2002). According to Snedecor and Cochran (1989), equation (1) represents the Anderson-Darling statistics for the upper.05 percentile for a sample of size n roughly as follows:

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

The sample size, or overall number of samples, is n, and A^2 is the Anderson-Darling statistics. If the calculated A^2 from equation 1 is greater than the A^2 from a cumulative normal distribution table (critical value), the population is not normally distributed. The Past 4.11 software version automatically performed the Anderson-Darling test by calculating A^2 (Fig. 5) and generating a p-value (Table 4). It may be deduced that the total PCB concentrations found in soil samples from the Local Government are not representative of the population as a whole because A^2 for each set of data is higher than the p-value.

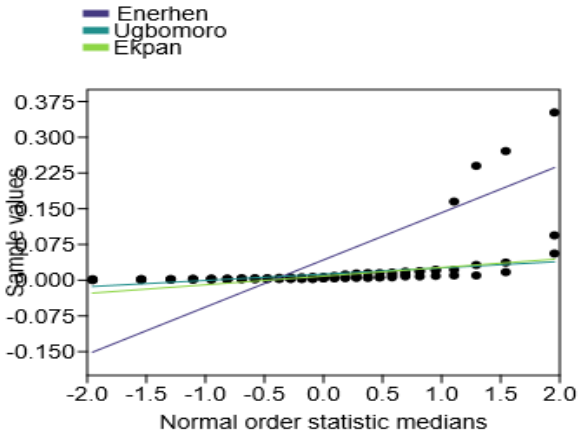

Figure 5. Normal probability plot for the concentrations of total PCBs measured in soil samples from various locations in Uvwie Local Government, Warri Metropolis.

Table 4. Anderson-Darling for the concentrations of total PCBs measured in soil samples from various locations in the studied Local Government Area, Warri Metropolis

Site	Anderson-Darling (A^2)	p(normal)
Enerhen	6.517	1.857×10^{-16}
Ugbomoro	1.636	0.0003
Ekpan	6.689	7.074×10^{-17}

Ecological Risk Assessment

The carcinogenicity associated with PCB exposure was determined using the deterministic method from USEPA's assessment guidance (USEPA, 2013). The potential exposure to PCBs in topsoil in residential areas was evaluated by exposure routes through ingestion, inhalation of particulate, and skin absorption, according to the USEPA screening

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threshold calculation for initial cleanup targets. In this instance, residential land use was considered when deciding whether a PCB was carcinogenic; its concentration was indicated in mg/kg as shown in Table 5 displays the lifetime cancer risk of the four dioxin-like PCBs collectively.

$$ILCR_{dem} = \frac{C_{soil} \times SA \times AF_{soil} \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times AT} \quad (2)$$

$$ILCR_{inh} = \frac{C_{soil} \times InhR \times EF \times ED \times ET \times IUR}{PEF \times AT} \quad (3)$$

$$ILCR_{ing} = \frac{C_{soil} \times IngR \times EF \times ED \times CF \times SFO}{BW \times AT} \quad (4)$$

Where the terms $ILCR_{ing}$" and $ILCR_{dem}$refer to the incremental lifetime cancer risk from unconscious ingestion and dermal contact, respectively. $ILCR_{inh}$stands for incremental lifetime cancer risk when breathing in soil particles, C_{soil} is the observed PCB concentration in soil (mg kg^{-1}), , *IngR* is the rate at which soil is consumed (100 mg per day for an adult). *CF* = conversion factor (1×10^{-6}), EF stands for exposure frequency (350 days per year, excluding 15 days for holidays), ED for exposure duration (52 years, based on the average life expectancy of a Nigerian), SFO = oral slope factor (2.0 mg kg^{-1} d^{-1}), BW for average body weight (65 kg), and AT for averaging time for carcinogens (days), which is calculated as 52×365 = 25,550 days. SA stands for the skin's surface area in contact with the ground (3300 cm^2), which includes exposed hands and arms. ABS = dermal absorption factor (0.1), *InhR* is the inhalation rate which is 15.8 m^3 d^{-1} for humans, and AF_{soil}*is* skin adherence factor for soil (0.2 mg cm^{-2}). PEF stands for soil to air particle emission factor (1.36×10^9 m^3 kg^{-1}). GIABS stands for gastrointestinal absorption factor (1), ET stands for exposure time (8 h d^{-1}), and IUR stands for inhalation unit risk (5.7×10^{-1} µgm^{-3}) (Van den Berg et al. 2006; Van den Berg et al. 1998). However, the answers to equations (2) - (4) were used to calculate the total cancer risk from eating, cutaneous absorption, and inhalation. This is because exposure to multiple exposure directions might increase cancer risk for the same individual, according to the human health evaluation manual (USEPA, 1989). Using the qualitative grading of cancer risk calculations, the risk was classified as extremely low (value 10^{-6}) and low (10^{-6} value 10^{-4}), as indicated in Table 4. (ATSDR, 2000). According to Tables 5, none of the Uview sites require cleaning because their overall PCB concentrations are below the remediation level of 2.00 mg/kg set by the Toxic Substance Control Act (TSCA) of the United States (USEPA, 2012). PCBs are known to bioaccumulate; however, this issue still has to be addressed. The results of additional investigations (Idowu et al. 2020; Ibrahim et al. 2021) indicated that soil samples taken from transformer installation locations in University of Port Harcourt and Jos had more than 2.00 mg/kg of total PCBs. These data demonstrate that the studied soil samples are far less contaminated than more developed countries like China and the US when compared to other global studies (Jun et al. 2015; Guanghu et al. 2017).

Table 5. Incremental lifetime cancer risk assessment (ILCR) for PCBs in soil samples from various locations in Uvwie Local Government, Warri Metropolis

Location	$ILCR_{ing}$	$ILCR_{dem}$	$ILCR_{inh}$	Total Cancer risk
Enerhen	2.50×10^{-6}	1.66×10^{-6}	4.32×10^{-8}	4.2×10^{-6}
Ugbomoro	7.45×10^{-7}	4.92×10^{-7}	1.28×10^{-8}	1.25×10^{-6}
Ekpan	4.93×10^{-7}	3.25×10^{-7}	8.49×10^{-9}	8.26×10^{-7}

Analysis Of Variance (ANOVA)

The one-way ANOVA findings for the total mean concentration in the soil samples from Uvwie Local Governments are shown in Table 6 ($p < 0.05$ level of significance). The results show that F_{cal} values in soil samples are lower than F_{crit} values (Table 6). As a result, the effects of soil heterogeneity on PCB concentration levels are not greatly different. These findings suggest that there were no appreciable differences in PCB levels between the soil samples ($P < 0.05$).

Table 6. ANOVA for PCBs in soil samples from various locations in Uvwie Local Government, Warri Metropolis

Source of Variation	SS	df	MS	F_{Cal}	P-value	F_{Crit}
Between Group	0.0187	2	0.0093	2.952	0.058	3.114
Within Group	0.2468	78	0.0032			
Total	0.2655	80				

4. CONCLUSION

In Uview local government area of Delta State, Nigeria, soil samples from transformer installation sites were tested for polychlorinated biphenyl distributions and carcinogenicity. It was found that the soil was polluted in all of the sites, but 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. Adult residents of this residential neighbourhood have extremely low to low cancer risk, according to the assessment of human health risks related to carcinogenicity. The Basel Convention recommendation value of 50 mg/kg is typically regarded as the limit for waste classification under the POPs regulation, and individual congener concentrations are well below this amount.

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