

POLYCHLORINATED BIPHENYL IN SOIL AROUND MUNICIPAL SOLID WASTE DUMPSITES IN SELECTED AREAS OF DELTA STATE, NIGERIA

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ABSTRACT

The concentrations and risks of 28 polychlorinated biphenyls (PCBs) congeners in soil profiles from selected dumpsites in rural, semi-urban and urban areas in Delta State, Nigeria were investigated. A total of 27 soil samples were quantified for $\Sigma 28$ PCBs with gas chromatography-mass spectrometry after soxlet extraction with n-hexane/dichloromethane and purified with florisil and silica gel column. The concentrations of $\Sigma 28$ PCBs in the dumpsites soil ranged from 4.18 to 20.5 ng g⁻¹, 3.02 to 47.0 ng g⁻¹ and 5.29 to 44.5 ng g⁻¹ for the rural, semi-urban and urban areas, respectively. The results shows a distribution pattern of $\Sigma 28$ PCBs in order of urban area > semi-urban > rural area and PCBs congeners in the dumpsites soils originated from industrial and electrical waste. The ecological risk assessment indicated that there were various degrees of ecological risks of PCBs in the soils while the human health risk assessment indicated that there were adverse non-carcinogenic and carcinogenic risks associated with PCBs in the soils.

Keywords: polychlorinated biphenyl (PCBs), physicochemical parameters, soil, dumpsites

INTRODUCTION

Solid waste dump sites are repository for waste management in urban, semi-urban, and rural environment, and have been sources of several pollutants in soils, surface and ground water ecosystem (Abdus-Salam *et al.*, 2011). In Nigeria, where waste segregation is not a common practice most dump site contains all categories of waste (domestic, industrial, commercial, construction and institutional waste). The

leachates from waste containing organic contaminants and other priority pollutants may contaminate the surrounding and adjacent environmental matrices (Lateef *et al.*, 2015)

PCBs are referred to as persistent pollutants which are grouped into 209 congeners. PCBs are persistent chemical listed amongst the twelve most dangerous chemicals known to have ecological and human health effects (UNEP, 2009). PCBs are persistent organic

pollutant in which after use its effect remains in the environment for a long period of time (Igbo *et al.*, 2018). In 1929 PCBs were produced commercially and are used in applied electrical industry (Bentum, 2012; Anh *et al.*, 2019). PCBs are released from several sources which includes sewage sludge, landfill leachate, volatilization from dredged sediments, product or equipment containing PCB such as electronic equipment, waste incineration, coal combustion, steel smelting and various thermal processes (Megson *et al.*, 2019; Dedela *et al.*, 2020). Poor management of damaged electrical equipment and illegal dumping of waste materials containing PCBs are sources of PCBs in the environment (Sohail *et al.*, 2017). Residents that live close to PCBs contaminated dumpsites are at higher exposure risk when compared to non-residents. During the late 1970's PCBs were banned due to their persistence, toxic effects and bioaccumulation (EHHI, 2013; Sauve and Desrosiers, 2014; Fayiga *et al.*, 2017). PCBs are components of capacitors, building insulation, transformers and other electrical-electronic components (Lauby-Secretan *et al.*, 2013; Folarin *et al.*, 2018). PCBs enter humans through ingestion, inhalation and dermal contact from contaminated soil, dust, water and food (USEPA, 2012; Labunska *et al.*, 2015).

Dumpsites are not just a depot for waste material, but also a biochemically active unit where toxic substances are leached or

formed from combination of non-toxic precursors and gradually released into the immediate and adjacent environmental media over a period of time (Papapopoulou *et al.*, 2007). In Nigeria, dumpsites are located within the vicinity of living communities. Local dumpsites are not lined and also do not have basements prepared for selective absorption of toxic substances. Hence, leachate from these dumpsites may contaminate the surrounding soils, surface and ground water with organic contaminants such as PCBs. A number of studies have reported the concentrations of metals, PAHs, TPHs in soil around dumpsites (Daso *et al.*, 2016; Ogoko and Kelle, 2016; Ajah *et al.*, 2015; Adeyi and Oyeleke, 2017; Tesi *et al.*, 2020). However, there are limited studies on the concentrations, sources and associated risks of PCBs in soils around solid waste dumpsites in Delta State, Nigeria. Therefore, this study determined the distribution and risk of 28 PCBs in selected dumpsite soils in Delta State, Nigeria.

MATERIALS AND METHODS

Sample Collection

A total of twenty-seven (27) soil samples were collected from nine dumpsites at three different depths: 0-15 cm, 15-30 cm and 30-45 cm using a soil auger. The soil samples were collected into foil paper, labeled and transported to the laboratory in a cooler of ice. At the laboratory, the samples were air-dried, sieved with a 2 mm sieve and kept in the refrigerator at a temperature of 4°C prior to analysis.



Fig. 1: Map of Delta State Nigeria showing location of study area (Marked in Stars). Inset is a map of Nigeria showing the location of Delta State. Adapted and modified from Efobo et al., (2020)

Sampling locations and site information

Rural area 1 (RA1) is located at Aragba-Orogun junction with longitude N544'1.188" and latitude E68'32.868". Rural area 2 (RA2) is located at Ufuoma Street, Aragba-Orogun with longitude N5'52.854" and latitude E68'18.414". Rural area 3 (RA3) is located at Mission Street close to St. Joseph Catholic Church, Aragba – Orogun with longitude N543'52.704" and latitude E68'11.364". Semi-urban area 4 (SA4) is located at River road along Pleasant School street, Abraka with longitude N548'1.476" and latitude E66'29.364". Semi-urban area 5 (SA5) is located at off Palmer road, Tosac Hostel, Abraka with longitude N547'44.118" and latitude E66'16.002". Semi-urban area 6 (SA6) is located at Business Center road close to Church of God Mission, Abraka, with longitude N547'36.33" and latitude E66'5.628". Urban area 7 (UA7) is located at No. 273 Warri-Patani Road, Ughelli with

longitude N528'59.814" and latitude E61'7.326". Urban area 8 (UA8) is located along Slaughter road, Otovwodo-Ughelli with longitude N529'17.01" and latitude E61'15.198". Urban area 9 (UA9) is located upper Agbarho road, Ughelli with longitude N529'12.816" and latitude E61'18.204".

Determination of soil physicochemical characteristics

The pH of the soil was measured using a pH meter with a glass electrode. The electrical conductivity (EC) in soil was determined using conductivity meter (Abollino et al., 2002). Total organic carbon (TOC) content of the soil was determine using wet dichromate oxidation method (Radojevic & Bashkin 1999).

Sample extraction and clean up

The extraction of PCBs from the soil samples were carried out following the US

EPA method 3540C (USEPA, 1996) as describe by Ierhievwie *et al.* (2020). A mass of 5.0 g of dried soil samples were spiked with a mixed standard solution of isotopically labeled PCB congeners, and soxlet extracted with 150 mL of acetone/dichloromethane/*n*-hexane mixture (1:1:1 v/v) in a 65 °C water bath for 18 h. 1g of activated copper granules and 3 g of anhydrous Na₂SO₄ was added to remove the sulfur and water respectively. The extract was evaporated with rotary kiln to approximately 2 mL and subjected to clean-up in a multilayer alumina-silica gel column packed bottom to top with 4 g of neutral silica gel (5% deactivated), 2 g of neutral alumina (6% deactivated) and 5 g of anhydrous Na₂SO₄. A 40 mL aliquot of *n*-hexane/dichloromethane mixture (3:1 v/v) was used to elute the PCBs from the column and the cleaned eluate was concentrated to approximately 2 mL under a slow stream of nitrogen gas. The separation, detection and quantification of PCBs in the samples was carried out using an Agilent 7890A gas chromatograph coupled with an Agilent 5975c mass selective detector (Palo Alto, CA, USA).

Quality Control/Assurance Measures

All glassware were washed with detergent, rinsed thoroughly with distilled water and acetone, and subsequently baked for 4 hours at 450 °C in an oven. The performances of the analytical procedure were evaluated from the recoveries of the ¹³C-PCBs with matrix spike methods. The quantification of the PCBs was achieved using an external calibration method consisting of 5-point calibration lines obtained as a plot of the congener peak areas versus the standard concentrations.

Statistical analysis

Principal component analysis was used to determine the source of PCBs-congeners

pattern in samples. The analysis of variance (ANOVA) was used to evaluate the differences observed in the Σ28PCBs concentrations from dumpsite soil with respect to depth and location, while the Turkey test was used to compare the mean occurrence of PCBs from different sites. All statistical evaluations were performed using the Statistical Package for the Social Science (SPSS) version 20.

Ecological risk assessment of PCBs in soils

The ecological risks of PCBs in the samples were determined using the potential ecological risk index by Hakanson (1980) as given in equation 1-3.

$$ERI = \sum_{i=1}^n E_r^i$$

(1)

where, $E_r^i = T_f^i \times C_f^i$ and

(2)

$$C_f^i = \frac{C_s^i}{C_b^i}$$

(3)

Where; ERI is the ecological risk index, C_f^i is the contamination factor, C_b^i are the background and sample concentrations of PCBs respectively. E_r^i is the ecological risk factor, T_f^i is the toxic response factor = 40 for PCBs (Hakanson, 1980). The background concentration of 10 ng g⁻¹ PCBs in soil was used based on Hakanson (1980). According to Hakanson (1980), $E_r < 40$ = low risk, $40 \leq E_r < 80$ = moderate risk, $80 \leq E_r < 160$ = considerable risk, $160 \leq E_r < 320$ = high risk and $E_r \geq 320$ = very high risk.

Estimation of toxic equivalency of the dl-PCBs in soils

The toxic effects of the dl-PCBs were evaluated using toxic equivalency (TEQ). The dl-PCBs TEQ concentrations were obtained by comparing with that of 2,3,7,8-tetrachlorodibenz-p-dioxin (2,3,7,8-TCDD) as a reference using the equation (Van den Berg *et al.*, 2006; Iwegbue *et al.*, 2019; Tesi and Iniaghe, 2020).

$$TEQ = \sum TEF_i \times C_i \quad (4)$$

Where C_i is the concentrations of the dl-PCB congeners in soils and TEF_i is the toxic equivalency factor of the dl-PCB congener. The TEF values of the dl-PCB congeners

For non-cancer risk,

$$Hazard\ Index\ (HI) = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{dermal} \quad (6)$$

$$HQ = \frac{CDI_{nc}}{RfD} \quad (7)$$

$$CDI_{ing-nc} = \frac{C_{soil} \times IngR \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \quad (8)$$

$$CDI_{inh-nc} = \frac{C_{soil} \times InhR \times EF \times ET \times ED}{PEF \times 24 \times AT_{nc}} \quad (9)$$

$$CDI_{dermal-nc} = \frac{C_{soil} \times SA \times AF \times ABS_d \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \quad (10)$$

For cancer risk,

$$Total\ Cancer\ Risk = Risk_{ing} + Risk_{inh} + Risk_{dermal} \quad (11)$$

$$Risk_{ing} = \frac{C_{soil} \times IngR \times EF \times ED \times CCF \times SFO}{BW \times AT} \quad (12)$$

$$Risk_{inh} = \frac{C_{soil} \times EF \times ED \times IUR}{PEF \times 24 \times AT} \quad (13)$$

$$Risk_{dermal} = \frac{C_{soil} \times SA \times AF \times ABS \times EF \times ED \times CCF \times GIABS \times SFO}{BW \times AT} \quad (14)$$

Where CDI_{ing} , CDI_{inh} and CDI_{Derm} are chronic daily intake for ingestion, inhalation and dermal contact respectively; $Risk_{ing}$,

used were 1×10^{-4} for PCB77, 3×10^{-4} for PCB81, 3×10^{-5} for PCB105, 3×10^{-5} for PCB114, 3×10^{-5} for PCB118, 3×10^{-5} for PCB123, 1×10^{-1} for PCB126, 3×10^{-5} for PCB156, 3×10^{-5} for PCB157, 3×10^{-5} for PCB167, 3×10^{-2} for PCB169 and 3×10^{-5} for PCB189 (Van den Berg *et al.*, 2006).

Assessment of human health risk of PCBs in soils

The human health risks of PCBs in the samples were determined using the hazard index (HI) and total cancer risk respectively via the dermal, ingestion, and inhalation contact which are the three exposure pathways for humans. The following equations (6-14) adopted from USEPA (2009) were used.

$Risk_{inh}$ and $Risk_{Derm}$ are risk for ingestion, inhalation and dermal contact respectively. The definitions of terms and values of

variables in the above equations are shown in Tables 1 and 2. The HI value greater than 1 indicates that there is adverse non-carcinogenic risk of PCBs exposure while

total cancer risk values greater than 1.0×10^{-6} depicts a carcinogenic risk from PCBs exposure (USEPA, 2010).

Table 1: Values of variables for estimation of human health risk assessment

| Variables | Unit | Definition | Values | | References |
|-----------|------------------------|---|------------------------|-------|------------------------------|
| | | | Child | Adult | |
| C | ng/g | PCBs concentrations in soil | | | |
| AF | mg/cm ² | Soil to skin adherences factor | 0.2 | 0.07 | USEPA, 2011 |
| BW | Kg | Average body weight | 15 | 60 | Iwegbue <i>et al.</i> (2019) |
| ED | Year | Exposure duration | 6 | 30 | USEPA, 2001 |
| EF | day/yr | Exposure frequency | 350 | 350 | USEPA, 2001 |
| ET | hr/day | Exposure time | 8 | 8 | USEPA, 1987 |
| IngR | mg/day | Ingestion rate for receptor | 200 | 100 | USDOE, 2011 |
| InhR | m ³ /day | Inhalation rate | 12 | 50 | USDOE, 2011 |
| SA | cm ² /event | Skin surface area | 2800 | 5700 | USDOE, 2011 |
| ATnc | D | Averaging time for non-carcinogenic | ED x 365 | | USDOE, 2011 |
| Atca | d | Averaging time for carcinogenic | LT x 365 | | USDOE, 2011 |
| LT | Year | Lifetime | 55 years | | WHO, 2018 |
| PEF | m ³ /kg | Sediment to air particulate emission factor | 1.36 x 10 ⁹ | | USDOE, 2011 |
| RfDo | (mg/kg/d) | Oral reference dose | Contaminant specific | | Table 2 |
| RfDi | | Inhalation reference dose | Contaminant specific | | Table 2 |
| SFO | (mg/kg/d) | Oral slope factor | Contaminant specific | | Table 2 |
| IUR | (µg/m ³) | Inhalation unit risk | Contaminant specific | | Table 2 |

Table 2: Toxicological parameters of the investigated PCBs used for health risk assessment

| PCBs | Oral Ingestion Reference Dose (RfDo) | Inhalation Reference Dose (RfDi) | SFO _{ing} (mg/kg/d) | IUR (µg/m ³) | GIABS | ABS |
|-----------|--------------------------------------|----------------------------------|------------------------------|--------------------------|--------------|--------------|
| PCB 77 | 7.0 x 10 ⁻⁶ | 4.0 x 10 ⁻⁴ | 1.3 x 10 ¹ | 3.8 x 10 ⁻³ | 1 | 0.14 |
| PCB 81 | 2.3 x 10 ⁻⁶ | 1.3 x 10 ⁻⁴ | 3.9 x 10 ¹ | 1.1 x 10 ⁻² | 1 | 0.14 |
| PCB105 | 2.3 x 10 ⁻⁵ | 1.3 x 10 ⁻³ | 3.9 | 1.1 x 10 ⁻³ | 1 | 0.14 |
| PCB 114 | 2.3 x 10 ⁻⁵ | 1.3 x 10 ⁻³ | 3.9 | 1.1 x 10 ⁻³ | 1 | 0.14 |
| PCB 118 | 2.3 x 10 ⁻⁵ | 1.3 x 10 ⁻³ | 3.9 | 1.1 x 10 ⁻³ | 1 | 0.14 |
| PCB 123 | 2.3 x 10 ⁻⁵ | 1.3 x 10 ⁻³ | 3.9 | 1.1 x 10 ⁻³ | 1 | 0.14 |
| PCB 126 | 7.0 x 10 ⁻⁹ | 4.0 x 10 ⁻⁷ | 1.3 x 10 ⁴ | 3.8 | 1 | 0.14 |
| PCB 156 | 2.3 x 10 ⁻⁵ | 1.3 x 10 ⁻³ | 3.9 | 1.1 x 10 ⁻³ | 1 | 0.14 |
| PCB 157 | 2.3 x 10 ⁻⁵ | 1.3 x 10 ⁻³ | 3.9 | 1.1 x 10 ⁻³ | 1 | 0.14 |
| PCB 167 | 2.3 x 10 ⁻⁵ | 1.3 x 10 ⁻³ | 3.9 | 1.1 x 10 ⁻³ | 1 | 0.14 |
| PCB169 | 2.3 x 10 ⁻⁵ | 1.3 x 10 ⁻⁶ | 3.9 x 10 ³ | 1.1 | 1 | 0.14 |
| PCB 189 | 2.3 x 10 ⁻⁵ | 1.3 x 10 ⁻³ | 3.9 | 1.1 x 10 ⁻³ | 1 | 0.14 |
| Reference | USEPA (2012) | USEPA (2012) | USDOE (2011) | USEPA, (2010) | USEPA (2011) | USEPA (2011) |

RESULTS AND DISCUSSION

Physicochemical properties of soils

The results of soil pH, electrical conductivity, and total organic carbon ranged from 5.3-7.8, 52-124 µs/cm and 0.03-1.36 % for rural area, 4.8-7.4, 42-108 µs/cm, 0.06-1.57 % for semi-urban area,

5.2-7.5, 41-118 $\mu\text{s/cm}$, 0.09-1.94 % for urban area (Table 3). The soil pH was acidic to near neutral which depicts typical characteristics of anaerobic soil of the Niger Delta (Puyate et al 2008). Acidity of soils arises from decomposition of organic matter that produced proton (H^+) during respiration (Fatusin *et al.*, 2019). The electrical conductivity obtained in this study were comparable to those reported by Tesi *et al.*

(2020), Akpoveta *et al.* (2010) and Osakwe (2010) from dumpsite soils. The level of organic matter in soil is influence by the chemical and physical properties of soil (Tesi *et al.*, 2020). The values of TOC obtained in this study were similar to those reported by Tesi *et al.*, (2020), Ogbonna (2001) but lower than those reported by Osakwe (2014).

Table 3: Physicochemical properties of the soil

| Locations | Depth | TOC (%) | EC ($\mu\text{s/cm}$) | pH |
|-----------|-------------|---------|-------------------------|-----|
| RA1 | Top Soil | 0.29 | 73 | 6.8 |
| | Sub Soil | 1.36 | 54 | 7.2 |
| | Bottom Soil | 0.06 | 67 | 5.3 |
| RA2 | Top Soil | 0.64 | 106 | 7.8 |
| | Sub Soil | 0.09 | 74 | 7.3 |
| | Bottom Soil | 0.26 | 52 | 6.2 |
| RA3 | Top Soil | 0.29 | 91 | 5.6 |
| | Sub Soil | 0.12 | 124 | 6.9 |
| | Bottom Soil | 0.03 | 65 | 5.8 |
| SA4 | Top Soil | 0.35 | 62 | 6.7 |
| | Sub Soil | 0.20 | 61 | 6.3 |
| | Bottom Soil | 0.58 | 53 | 4.8 |
| SA5 | Top Soil | 1.22 | 108 | 5.4 |
| | Sub Soil | 0.23 | 83 | 6.2 |
| | Bottom Soil | 0.09 | 105 | 5.8 |
| SA6 | Top Soil | 0.58 | 92 | 7.4 |
| | Sub Soil | 1.57 | 44 | 4.9 |
| | Bottom Soil | 0.06 | 42 | 5.6 |
| UA7 | Top Soil | 0.87 | 63 | 6.9 |
| | Sub Soil | 0.58 | 80 | 6.2 |
| | Bottom Soil | 0.96 | 97 | 6.7 |
| UA8 | Top Soil | 0.70 | 118 | 7.5 |
| | Sub Soil | 0.44 | 77 | 5.8 |
| | Bottom Soil | 0.12 | 41 | 5.2 |
| UA9 | Top Soil | 1.94 | 61 | 6.3 |
| | Sub Soil | 2.29 | 76 | 5.9 |
| | Bottom Soil | 0.09 | 54 | 6.4 |

PCBs concentrations in soils

The summary statistics of PCBs concentrations in these soils studied are shown in Table 4. The concentrations of $\Sigma 28\text{PCBs}$ in the dumpsites soils ranged from 4.18 to 20.5 ng g^{-1} , 3.02 to 47.0 ng g^{-1} and 5.29 to 44.5 ng g^{-1} for the rural, semi-urban and urban areas, respectively with a mean of

9.33 ng g^{-1} , 14.9 ng g^{-1} , 17.7 ng g^{-1} for the rural, semi-urban and urban sites respectively. The results indicate no significant variation ($p > 0.05$) in the concentrations and compositions of PCBs in soil from these three sites (Table 5). The total concentrations and the individual congeners PCBs from the samples showed a

distribution pattern in the order of urban area > semi-urban area > rural area. The high concentration of PCBs in urban area could be related to over population and industrialization (Iwegbue *et al.*, 2020).

Table 4: Summary statistics of PCBs concentrations (ng/g) in soils of dumpsites

| | RURAL AREA | | | | | | SEMI-URBAN AREA | | | | | | URBAN AREA | | | | | |
|-----------------------------|-------------|-------------|-------------|-------------|-------------|-----------|-----------------|-------------|-------------|-------------|-------------|-----------|-------------|-------------|-------------|-------------|-------------|-----------|
| | MEAN | SD | MEDIAN | MIN | MAX | CV% | MEAN | SD | MEDIAN | MIN | MAX | CV% | MEAN | SD | MEDIAN | MIN | MAX | CV% |
| PCB-8 | 1.28 | 0.97 | 0.86 | 0.39 | 2.98 | 76 | 1.02 | 0.80 | 1.05 | 0.07 | 2.16 | 79 | 3.88 | 6.05 | 1.30 | 0.01 | 12.9 | 156 |
| PCB-18 | 2.31 | 2.51 | 1.57 | 0.78 | 7.38 | 109 | 1.70 | 1.53 | 0.68 | 0.14 | 4.20 | 90 | 2.62 | 2.35 | 2.78 | 0.19 | 4.89 | 90 |
| PCB-28 | 0.35 | 0.44 | 0.09 | 0.01 | 1.15 | 129 | 0.06 | 0.06 | 0.04 | 0.01 | 0.20 | 103 | 0.31 | 0.53 | 0.14 | 0.02 | 1.58 | 168 |
| PCB-44 | 0.42 | 0.64 | 0.18 | 0.01 | 1.82 | 153 | 0.03 | 0.05 | 0.01 | 0.00 | 0.11 | 152 | 0.25 | 0.31 | 0.09 | 0.04 | 0.79 | 122 |
| PCB-52 | 0.13 | 0.09 | 0.15 | 0.01 | 0.25 | 67 | 0.15 | 0.29 | 0.03 | 0.01 | 0.90 | 198 | 0.21 | 0.17 | 0.16 | 0.06 | 0.51 | 83 |
| PCB-66 | 0.44 | 0.82 | 0.03 | 0.01 | 1.98 | 188 | 1.00 | 2.81 | 0.02 | 0.01 | 8.49 | 281 | 0.29 | 0.47 | 0.14 | 0.05 | 1.51 | 160 |
| PCB-77 | 2.20 | 4.01 | 0.04 | 0.01 | 9.53 | 182 | 3.30 | 3.77 | 0.87 | 0.01 | 10.1 | 114 | 1.27 | 3.38 | 0.07 | 0.03 | 9.63 | 266 |
| PCB-81 | 0.13 | 0.25 | 0.03 | 0.01 | 0.73 | 192 | 0.31 | 0.63 | 0.04 | 0.01 | 1.83 | 204 | 0.32 | 0.46 | 0.04 | 0.02 | 1.06 | 145 |
| PCB-101 | 0.11 | 0.18 | 0.03 | 0.01 | 0.46 | 164 | 1.65 | 4.86 | 0.03 | 0.01 | 14.6 | 295 | 0.78 | 0.88 | 0.40 | 0.02 | 1.96 | 114 |
| PCB-105 | 0.21 | 0.12 | 0.14 | 0.10 | 0.39 | 55 | 0.39 | 0.46 | 0.13 | 0.12 | 1.19 | 118 | 0.50 | 0.30 | 0.52 | 0.10 | 0.98 | 61 |
| PCB-114 | 0.05 | 0.05 | 0.02 | 0.01 | 0.13 | 107 | 0.09 | 0.14 | 0.02 | 0.01 | 0.38 | 153 | 0.31 | 0.61 | 0.10 | 0.03 | 1.70 | 196 |
| PCB-118 | 0.10 | 0.12 | 0.03 | 0.01 | 0.33 | 122 | 0.12 | 0.13 | 0.10 | 0.02 | 0.39 | 110 | 0.17 | 0.11 | 0.15 | 0.02 | 0.33 | 62 |
| PCB-123 | 0.26 | 0.41 | 0.08 | 0.01 | 1.20 | 158 | 0.18 | 0.35 | 0.03 | 0.01 | 1.09 | 199 | 0.82 | 0.93 | 0.24 | 0.03 | 2.23 | 113 |
| PCB-126 | 0.08 | 0.13 | 0.04 | 0.01 | 0.36 | 159 | 0.15 | 0.34 | 0.02 | 0.02 | 1.06 | 234 | 0.65 | 0.70 | 0.26 | 0.06 | 1.71 | 107 |
| PCB-128 | 0.09 | 0.13 | 0.04 | 0.01 | 0.34 | 146 | 0.49 | 0.81 | 0.03 | 0.01 | 1.90 | 165 | 0.95 | 0.79 | 1.21 | 0.04 | 1.94 | 83 |
| PCB-138 | 0.03 | 0.03 | 0.02 | 0.01 | 0.09 | 110 | 0.38 | 0.55 | 0.04 | 0.01 | 1.23 | 146 | 0.14 | 0.26 | 0.05 | 0.01 | 0.78 | 184 |
| PCB-153 | 0.06 | 0.10 | 0.01 | 0.01 | 0.28 | 179 | 0.06 | 0.06 | 0.04 | 0.01 | 0.17 | 95 | 0.77 | 0.79 | 0.51 | 0.03 | 1.90 | 102 |
| PCB-156 | 0.04 | 0.04 | 0.01 | 0.01 | 0.12 | 116 | 0.92 | 0.90 | 0.81 | 0.01 | 1.95 | 98 | 0.25 | 0.50 | 0.06 | 0.01 | 1.38 | 203 |
| PCB-157 | 0.04 | 0.03 | 0.04 | 0.01 | 0.09 | 81 | 0.02 | 0.01 | 0.02 | 0.01 | 0.03 | 49 | 0.27 | 0.58 | 0.05 | 0.01 | 1.70 | 218 |
| PCB-167 | 0.38 | 0.80 | 0.02 | 0.01 | 1.81 | 213 | 0.25 | 0.45 | 0.04 | 0.01 | 0.92 | 179 | 1.51 | 3.63 | 0.02 | 0.01 | 8.91 | 240 |
| PCB-169 | 0.02 | 0.01 | 0.01 | 0.01 | 0.03 | 56 | 0.07 | 0.14 | 0.02 | 0.01 | 0.42 | 196 | 0.16 | 0.33 | 0.03 | 0.02 | 0.83 | 205 |
| PCB-170 | 0.02 | 0.01 | 0.02 | 0.01 | 0.04 | 59 | 0.08 | 0.13 | 0.02 | 0.01 | 0.40 | 162 | 0.17 | 0.30 | 0.06 | 0.01 | 0.78 | 181 |
| PCB-180 | 0.08 | 0.11 | 0.05 | 0.01 | 0.32 | 142 | 0.03 | 0.01 | 0.03 | 0.01 | 0.05 | 44 | 0.88 | 1.03 | 0.20 | 0.04 | 2.24 | 117 |
| PCB-187 | 0.05 | 0.06 | 0.03 | 0.01 | 0.18 | 121 | 0.06 | 0.06 | 0.02 | 0.01 | 0.17 | 109 | 0.12 | 0.15 | 0.05 | 0.02 | 0.44 | 132 |
| PCB-189 | 0.04 | 0.02 | 0.04 | 0.01 | 0.06 | 51 | 0.02 | 0.01 | 0.02 | 0.01 | 0.05 | 52 | 0.18 | 0.23 | 0.11 | 0.02 | 0.70 | 134 |
| PCB-195 | 0.11 | 0.15 | 0.03 | 0.01 | 0.43 | 133 | 0.04 | 0.02 | 0.04 | 0.01 | 0.07 | 55 | 0.34 | 0.49 | 0.21 | 0.04 | 1.42 | 141 |
| PCB-206 | 0.04 | 0.03 | 0.05 | 0.01 | 0.11 | 78 | 0.05 | 0.03 | 0.06 | 0.01 | 0.11 | 65 | 0.42 | 0.50 | 0.23 | 0.01 | 1.56 | 119 |
| PCB-209 | 2.48 | 2.01 | 1.84 | 0.40 | 6.35 | 81 | 3.14 | 1.86 | 3.13 | 0.69 | 7.24 | 59 | 6.65 | 6.51 | 5.37 | 0.43 | 16.90 | 98 |
| ∑28 PCB | 9.33 | 5.80 | 7.05 | 4.18 | 20.5 | 62 | 14.9 | 13.1 | 9.66 | 3.02 | 47.0 | 88 | 17.7 | 13.6 | 16.6 | 5.29 | 44.5 | 77 |
| Di-PCB | 1.28 | 0.97 | 0.86 | 0.39 | 2.98 | 76 | 1.02 | 0.80 | 1.05 | 0.07 | 2.2 | 79 | 3.88 | 6.05 | 1.30 | 0.01 | 12.90 | 156 |
| Tri-PCBs | 1.89 | 2.18 | 1.62 | 0.02 | 7.42 | 116 | 1.76 | 1.50 | 0.69 | 0.34 | 4.2 | 85 | 1.15 | 1.98 | 0.18 | 0.00 | 4.91 | 172 |
| Tetra-PCBs | 2.94 | 4.28 | 0.86 | 0.20 | 12.44 | 145 | 4.75 | 5.63 | 0.93 | 0.20 | 16.0 | 118 | 2.07 | 3.52 | 0.39 | 0.31 | 10.96 | 170 |
| Penta-PCBs | 0.64 | 0.54 | 0.49 | 0.02 | 1.73 | 85 | 2.35 | 5.46 | 0.37 | 0.10 | 16.9 | 233 | 2.59 | 2.31 | 2.22 | 0.00 | 6.73 | 89 |
| Hexa-PCBs | 0.39 | 0.60 | 0.20 | 0.00 | 1.87 | 152 | 1.60 | 2.05 | 0.35 | 0.05 | 5.6 | 128 | 3.20 | 4.81 | 1.51 | 0.00 | 15.45 | 150 |
| Hepta-PCBs | 0.14 | 0.15 | 0.14 | 0.00 | 0.45 | 103 | 0.18 | 0.19 | 0.08 | 0.03 | 0.6 | 103 | 1.12 | 1.08 | 0.42 | 0.00 | 2.50 | 96 |
| Octa-PCBs | 0.11 | 0.15 | 0.03 | 0.01 | 0.43 | 133 | 0.04 | 0.02 | 0.04 | 0.01 | 0.1 | 55 | 0.34 | 0.49 | 0.21 | 0.04 | 1.42 | 141 |
| Nona-PCBs | 0.04 | 0.03 | 0.05 | 0.01 | 0.11 | 78 | 0.05 | 0.03 | 0.06 | 0.01 | 0.1 | 65 | 0.42 | 0.50 | 0.23 | 0.01 | 1.56 | 119 |
| Deca-PCBs | 2.48 | 2.01 | 1.84 | 0.40 | 6.35 | 81 | 3.14 | 1.86 | 3.13 | 0.69 | 7.2 | 59 | 6.65 | 6.51 | 5.37 | 0.43 | 16.90 | 98 |
| Non-ortho Dioxin-like PCBs | 2.14 | 3.98 | 0.18 | 0.02 | 10.32 | 186 | 3.78 | 4.04 | 0.93 | 0.11 | 10.3 | 107 | 2.06 | 3.26 | 1.43 | 0.18 | 10.61 | 158 |
| Mono-ortho Dioxin-like PCBs | 0.80 | 0.70 | 0.72 | 0.02 | 2.35 | 88 | 1.43 | 1.44 | 0.67 | 0.10 | 4.0 | 101 | 3.06 | 4.46 | 1.51 | 0.00 | 14.58 | 145 |
| ∑Dioxin-like PCBs | 2.94 | 3.91 | 1.38 | 0.04 | 11.16 | 133 | 5.21 | 4.65 | 2.43 | 1.03 | 12.0 | 89 | 5.13 | 5.27 | 4.31 | 0.18 | 16.01 | 103 |
| Indicator PCBs | 0.73 | 0.60 | 0.59 | 0.03 | 1.84 | 83 | 2.28 | 5.42 | 0.30 | 0.10 | 16.7 | 237 | 2.71 | 2.10 | 2.46 | 0.02 | 6.37 | 78 |
| LC-PCBs | 6.46 | 4.51 | 4.22 | 2.00 | 16.02 | 70 | 9.88 | 10.98 | 5.42 | 1.73 | 36.6 | 111 | 7.54 | 8.41 | 4.35 | 0.89 | 29.13 | 112 |
| HC-PCBs | 2.87 | 2.06 | 2.81 | 0.01 | 6.46 | 72 | 5.01 | 3.55 | 3.91 | 1.30 | 11.6 | 71 | 10.19 | 7.93 | 12.27 | 0.01 | 20.82 | 78 |

Table 5: ANOVA results of PCBs in soil from dumpsites

| Source of Variation | SS | Df | MS | Fcal | P-value | F crit |
|---------------------|----------|----|----------|----------|----------|----------|
| Between Groups | 328.4622 | 2 | 164.2311 | 1.259131 | 0.301991 | 3.402826 |
| Within Groups | 3130.37 | 24 | 130.4321 | | | |
| Total | 3458.832 | 26 | | | | |

PCBs compositional pattern in soils

The compositional patterns of PCBs in the soil samples are presented in Figure 2. The compositional pattern of the PCBs is in the order of: tetra-PCBs > deca-PCBs > tri-PCBs > di-PCBs > penta-PCBs > hexa-PCBs > hepta-PCBs > octa-PCBs > nona-PCBs for rural area; tetra-PCBs > deca-PCBs > penta-PCBs > tri-PCBs > hexa-PCBs > di-PCBs > hepta-PCBs > nona-PCBs > octa-PCBs for semi-urban area and deca-PCBs > di-PCBs > hexa-PCBs > penta-PCBs > tetra-PCBs > tri-PCBs > hepta-PCBs > nona-PCBs > octa-PCBs for urban area. The deca- and octa-PCBs were detected in all soil samples in each area which is linked to a noticeable source of PCBs in the soils. The presence of tri-PCBs is due to advertent use of tri-PCBs in capacitors while tetra-PCBs is linked to the burning of solid waste (Aziza et al., 2021). The concentration of the di-PCBs ranged from not detected to 12.9 ng g⁻¹ for all samples from the three areas, and constituted 0.0 to 37.1% of the $\sum 28$ PCBs. The concentration of tri-PCBs ranged from not detected to 7.42 ng g⁻¹ for all samples from the three areas and constituted 0.0 to

77.2% of the $\sum 28$ PCBs. The concentrations of tetra-PCBs ranged from 0.2 to 16.0 ng g⁻¹ for all samples from the three areas and constituted 1.2 to 61.7% of the $\sum 28$ PCBs. The concentrations of penta-PCBs ranged from not detected to 16.9 ng g⁻¹ for all samples from the three areas and constituted 0.1 to 36.0% of the $\sum 28$ PCBs. The concentrations of hexa-PCBs ranged from not detected to 15.5 ng g⁻¹ for all samples from the three areas and constituted 0.1 to 52.6% of the $\sum 28$ PCBs. The concentrations of hepta-PCBs ranged from not detected to 2.5 ng g⁻¹ for all samples from the three areas and constituted 0.0 to 32.3% of the $\sum 28$ PCBs. The concentrations of the octa-PCBs ranged from 0.01 to 1.42 ng g⁻¹ for all samples from the three areas and constituted 0.0 to 22.2% of the $\sum 28$ PCBs. The concentrations of the nona-PCBs ranged from 0.01 to 1.56 ng g⁻¹ for all samples from the three areas and constituted 0.0 to 13.0 % of the $\sum 28$ PCBs. The concentrations of deca-PCBs ranged from 0.4 to 16.9 ng g⁻¹ for the entire sample from the three areas and constituted 0.0 to 61.4% of the $\sum 28$ PCBs.

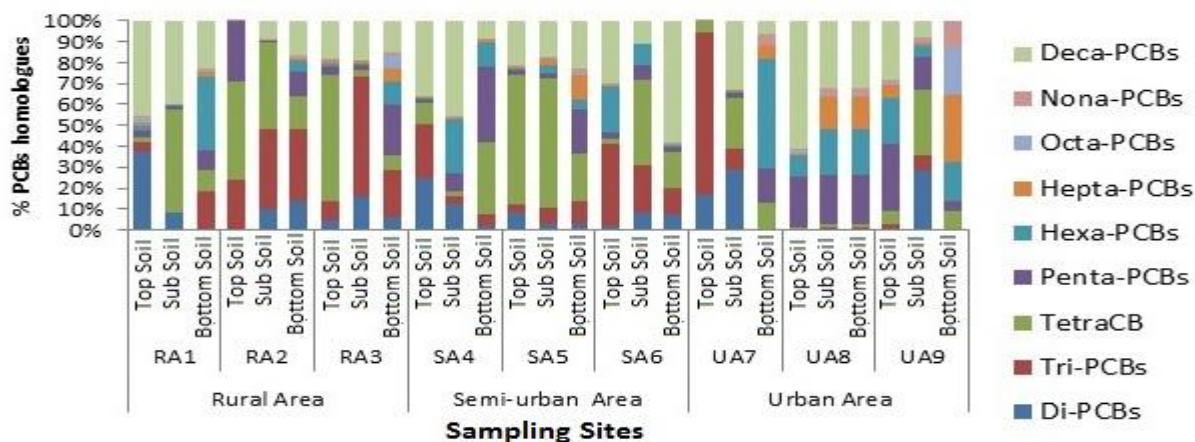


Figure 2: Compositional pattern of PCBs in soils of the dumpsites

Among the 28 congeners that were analyzed, lower chlorinated (Di-Cl to Penta-Cl) PCBs dominated higher chlorinated (Hexa-Cl to Deca-Cl) PCBs in the three areas. The lower chlorinated PCBs are product of dechlorination which cannot further be chlorinated (Iwegbue *et al.*, 2020). In a country like China, lower chlorinated PCBs are used in industrial and electrical products (Yadav *et al.*, 2017). This study shows numbers of sites where the concentration of higher chlorinated PCBs is abundant than those of lower chlorinated PCBs which is linked to the high k_{ow} value that support the relationship with suspended particulate matter and consequent deposition while the low detection of higher chlorinated of PCBs in soils is associated to low water solubility (Liu *et al.*, 2017). Di to tetra PCBs are vulnerable to microbial degradation (Baqur *et al.*, 2017). The indicator PCBs (i-PCBs) concentration of rural and urban area are below the upper limit of ecological assessment criteria (EAC), while semi-urban area is above the upper limit of ecological assessment criteria (EAC) set at 1.0 to 10 ng g^{-1} (OSPAR Commission, 2000) which suggest an unsafe effect to the ecology (Iwegbue, 2020).

The non-ortho dioxin-like PCBs (dl-PCBs) concentration in this soil was higher than

mono-ortho dl-PCBs in the rural and semi-urban areas except in urban area. The high concentration of non-ortho (coplanar) dl-PCBs in soil in the rural and semi-urban areas is of concern because of indistinguishable characteristics of carcinogenic properties with tetra chlorodibenzo-p-dioxin (Baqur *et al.*, 2017).

Ecological Risk of PCBs in the soils

The potential ecological risk (E'_r) of PCBs in dumpsites soils from the rural, semi-urban and urban areas varied from 16.72 to 82, 12.08 to 188, 21.16 to 178 respectively in Figure 3. The soil samples at top soil of sites RA3 and RA2 accounted for the highest and lowest E'_r for rural area. The soil samples at bottom soil of sites SA4 and SA5 accounted for the highest and lowest E'_r for semi-urban area while the soil samples at sub soil of sites UA7 and UA9 accounted for the highest and lowest E'_r for urban area. Sub soil at Sites RA1, RA3, SA4, SA6, and UA8, site SA5 at top soil, site UA8 at bottom soil have E'_r less than 80 indicating moderate ecological risk. Top soil at Site RA3 and UA8, Site UA7 at bottom soil, have E'_r greater than 80 but less than 160 indicating considerable ecological risk. Site SA4 at bottom soil, Site UA7 at sub soil

have E'_r greater than 160 but less than 320 indicating high ecological risk. Top soil at sites RA1, RA2, SA4, SA6, UA7 and UA9, subsoil at sites RA2, SA5 and UA9, bottom soil at sites RA1, RA2, RA3, SA5, SA6 and

UA9 soil have an ecological risk index less than 40 indicating low potential ecological risk for soil biota. The average potential ecological risk (E'_r) of PCBs in these dumpsites was moderate ecological risk.

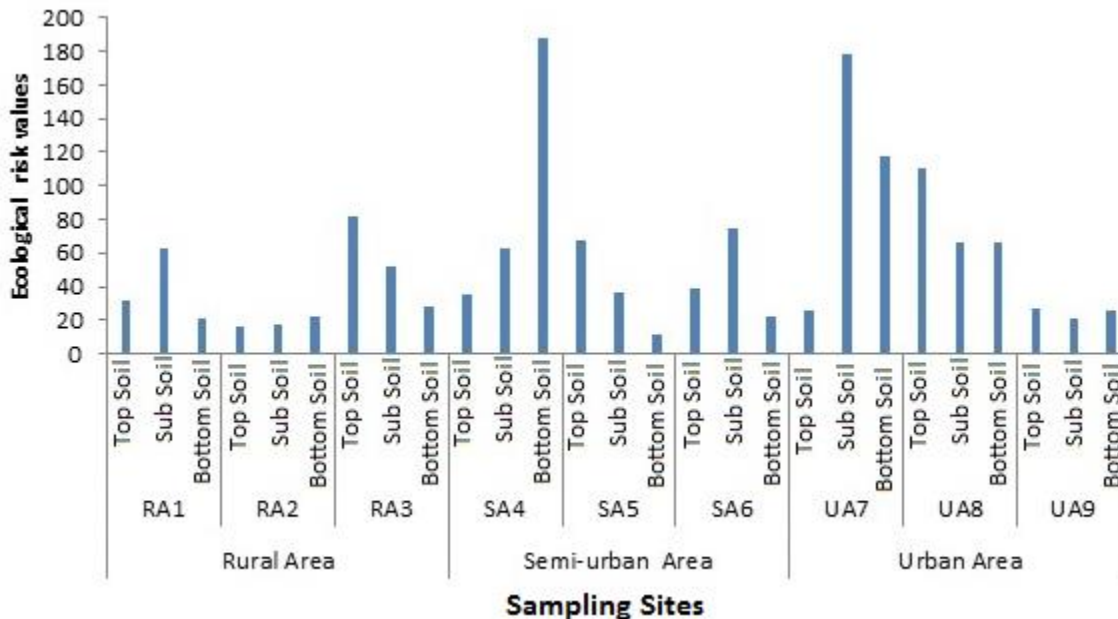


Figure 3: Ecological Risk of PCBs in the soils

Human health risk of PCBs in soils

Toxic Equivalency (TEQs) of PCBs in the soils

The TEQs of PCBs in the soil samples are presented in Table 6. The total toxic equivalence (TTEQ) values in the rural, semi-urban and urban areas ranged from 4.60E-06 to 3.63E-02 ng TEQ g⁻¹, 2.16E-03 to 1.20E-01 ng TEQ g⁻¹ and 1.80E-05 to 1.72E-01 ng TEQ g⁻¹ respectively. Site RA3 at bottom soil has a higher proportion of the TTEQ value as against other samples for

rural area; Site SA4 at bottom soil has a higher proportion of the TTEQ value as against other samples for semi-urban area, while site UA8 at top soil has a higher proportion of the TTEQ value as against others for urban area. The TEQs of dl-PCBs in these soils were below the Canadian sediment quality value of 21.5 pg TEQ and WHO guideline value 20 ng TEQ (CCME 2007; Andersson et al 2011) which signifies no potential health risk with an organism expose to PCBs in soil from these dumpsites.

Table 7: TEQs concentrations (ng/g) of PCBs in soils from the dumpsites

| Locations | Codes | Depth | PCB-77 | PCB-81 | PCB-105 | PCB-114 | PCB-118 | PCB-123 | PCB-126 | PCB-156 | PCB-157 | PCB-167 | PCB-169 | PCB-189 | TTEQ | |
|-----------------|-------|-------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------------|-----------------|
| Rural Area | RA1 | Top Soil | 0.00E+00 | 2.40E-05 | 3.90E-06 | 0.00E+00 | 0.00E+00 | 1.50E-06 | 4.00E-03 | 3.00E-07 | 2.70E-06 | 6.00E-07 | 9.00E-04 | 9.00E-07 | 4.93E-03 | |
| | | Sub Soil | 7.75E-04 | 9.00E-06 | 4.20E-06 | 3.00E-07 | 9.00E-07 | 3.00E-07 | 2.00E-03 | 3.00E-07 | 0.00E+00 | 0.00E+00 | 3.00E-04 | 3.00E-07 | 3.09E-03 | |
| | | Bottom Soil | 2.00E-06 | 3.00E-06 | 1.02E-05 | 6.00E-07 | 2.40E-06 | 6.00E-07 | 1.00E-03 | 3.00E-07 | 3.00E-07 | 5.43E-05 | 3.00E-04 | 1.80E-06 | 1.38E-03 | |
| | RA2 | Top Soil | 1.80E-05 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 3.60E-05 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 5.40E-05 |
| | | Sub Soil | 1.00E-06 | 3.00E-06 | 0.00E+00 | 3.00E-07 | 3.00E-07 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 4.60E-06 |
| | | Bottom Soil | 1.00E-06 | 3.90E-05 | 3.90E-06 | 3.90E-06 | 5.40E-06 | 3.30E-06 | 2.00E-03 | 3.60E-06 | 6.00E-07 | 3.00E-07 | 6.00E-04 | 6.00E-07 | 2.66E-03 | |
| | RA3 | Top Soil | 9.53E-04 | 2.19E-04 | 3.00E-06 | 3.30E-06 | 9.90E-06 | 5.70E-06 | 6.00E-03 | 1.80E-06 | 3.00E-07 | 0.00E+00 | 0.00E+00 | 1.20E-06 | 7.20E-03 | |
| | | Sub Soil | 6.00E-06 | 3.00E-06 | 6.90E-06 | 6.00E-07 | 9.00E-07 | 6.00E-07 | 4.00E-03 | 9.00E-07 | 1.50E-06 | 6.00E-07 | 3.00E-04 | 1.20E-06 | 4.32E-03 | |
| | | Bottom Soil | 2.00E-06 | 9.00E-06 | 1.17E-05 | 9.00E-07 | 6.00E-07 | 1.41E-05 | 3.60E-02 | 3.00E-07 | 2.10E-06 | 6.00E-07 | 3.00E-04 | 1.80E-06 | 3.63E-02 | |
| Semi-urban Area | SA4 | Top Soil | 8.70E-05 | 9.00E-06 | 0.00E+00 | 3.00E-07 | 6.00E-07 | 6.00E-07 | 2.00E-03 | 0.00E+00 | 9.00E-07 | 0.00E+00 | 3.00E-04 | 6.00E-07 | 2.40E-03 | |
| | | Sub Soil | 1.00E-06 | 3.00E-06 | 1.17E-05 | 1.14E-05 | 5.10E-06 | 6.00E-06 | 7.00E-03 | 2.43E-05 | 6.00E-07 | 6.00E-07 | 6.00E-04 | 6.00E-07 | 7.66E-03 | |
| | | Bottom Soil | 4.69E-04 | 5.49E-04 | 3.60E-06 | 0.00E+00 | 0.00E+00 | 3.27E-05 | 1.06E-01 | 5.37E-05 | 9.00E-07 | 2.76E-05 | 1.26E-02 | 6.00E-07 | 1.20E-01 | |
| | SA5 | Top Soil | 1.01E-03 | 2.40E-05 | 3.90E-06 | 3.90E-06 | 0.00E+00 | 6.00E-07 | 5.00E-03 | 3.00E-07 | 3.00E-07 | 3.00E-07 | 6.00E-04 | 9.00E-07 | 6.64E-03 | |
| | | Sub Soil | 5.36E-04 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 3.00E-06 | 1.80E-06 | 4.00E-03 | 2.70E-06 | 6.00E-07 | 1.50E-06 | 2.40E-03 | 1.50E-06 | 6.95E-03 | |
| | | Bottom Soil | 6.00E-06 | 1.35E-04 | 3.60E-06 | 1.80E-06 | 1.17E-05 | 9.00E-07 | 2.00E-03 | 9.00E-07 | 3.00E-07 | 0.00E+00 | 0.00E+00 | 9.00E-07 | 2.16E-03 | |
| | SA6 | Top Soil | 1.60E-05 | 3.00E-06 | 0.00E+00 | 6.00E-07 | 3.30E-06 | 3.90E-06 | 2.00E-03 | 5.85E-05 | 3.00E-07 | 0.00E+00 | 3.00E-04 | 3.00E-07 | 2.39E-03 | |
| | | Sub Soil | 7.56E-04 | 1.20E-05 | 3.57E-05 | 3.00E-07 | 9.00E-07 | 3.00E-07 | 2.00E-03 | 5.37E-05 | 3.00E-07 | 0.00E+00 | 3.00E-04 | 3.00E-07 | 3.16E-03 | |
| | | Bottom Soil | 8.70E-05 | 9.00E-06 | 0.00E+00 | 3.00E-07 | 6.00E-07 | 6.00E-07 | 2.00E-03 | 0.00E+00 | 9.00E-07 | 0.00E+00 | 3.00E-04 | 6.00E-07 | 2.40E-03 | |
| Urban Area | UA7 | Top Soil | 1.80E-05 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 1.80E-05 | |
| | | Sub Soil | 9.63E-04 | 2.76E-04 | 3.00E-06 | 3.30E-06 | 9.90E-06 | 5.70E-06 | 6.00E-03 | 1.80E-06 | 3.00E-07 | 0.00E+00 | 0.00E+00 | 1.80E-06 | 7.26E-03 | |
| | | Bottom Soil | 7.00E-06 | 3.18E-04 | 1.92E-05 | 5.10E-05 | 6.60E-06 | 9.00E-07 | 3.00E-02 | 4.14E-05 | 5.10E-05 | 2.67E-04 | 0.00E+00 | 0.00E+00 | 3.08E-02 | |
| | UA8 | Top Soil | 3.00E-06 | 6.00E-06 | 1.74E-05 | 3.00E-06 | 4.50E-06 | 6.69E-05 | 1.71E-01 | 1.80E-06 | 1.50E-06 | 0.00E+00 | 9.00E-04 | 2.40E-06 | 1.72E-01 | |
| | | Sub Soil | 7.00E-06 | 1.20E-05 | 1.56E-05 | 1.80E-06 | 3.30E-06 | 5.34E-05 | 1.37E-01 | 1.50E-06 | 3.90E-06 | 6.00E-07 | 9.00E-04 | 3.90E-06 | 1.38E-01 | |
| | | Bottom Soil | 7.00E-06 | 1.20E-05 | 1.56E-05 | 1.80E-06 | 3.30E-06 | 5.34E-05 | 1.37E-01 | 1.50E-06 | 3.90E-06 | 6.00E-07 | 9.00E-04 | 3.90E-06 | 1.38E-01 | |
| | UA9 | Top Soil | 3.00E-06 | 6.00E-06 | 2.94E-05 | 9.00E-07 | 6.00E-07 | 8.70E-06 | 2.20E-02 | 3.00E-07 | 1.50E-06 | 6.00E-07 | 6.00E-04 | 3.30E-06 | 2.27E-02 | |
| | | Sub Soil | 7.00E-06 | 3.90E-05 | 3.90E-06 | 3.90E-06 | 8.10E-06 | 3.30E-06 | 8.00E-03 | 3.60E-06 | 9.00E-07 | 3.00E-07 | 6.00E-04 | 6.00E-07 | 8.67E-03 | |
| | | Bottom Soil | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 4.80E-06 | 1.20E-02 | 0.00E+00 | 9.00E-07 | 2.10E-06 | 2.49E-02 | 2.10E-05 | 3.69E-02 | |

Non-carcinogenic and carcinogenic risk

The hazard index (HI) and the total cancer risks (TCR) of PCBs in the soil samples are shown in Tables 7 and 8 respectively. The HI values for children ranged from 1.18×10^{-1} to 9.16×10^2 , 5.31×10^1 to 2.72×10^3 and 4.58×10^{-1} to 4.35×10^3 for rural, semi-urban and urban areas respectively while the HI for adults ranged from 1.66×10^{-2} to 1.28×10^2 , 7.43 to 3.81×10^2 and 6.41×10^{-2} to 6.09×10^2 for rural, semi-urban and urban area respectively. The HQ values were in the order of $HQ_{ing} > HQ_{dermal} > HQ_{inh}$, it was notice that HQ_{ing} and HQ_{dermal} for child exposure were greater than those of adult. This is attributed to the smaller body weight of the child and their hand to mouth characteristics during play time, However the HQ_{inh} for adult was greater than in child this is as a result of longer exposure duration

for adult (Emoyan *et al.*, 2021; Iwegbue *et al.*, 2016). In this study, the HI levels for human exposures to PCBs for rural, semi-urban and urban areas were greater than 1, suggesting the presence of adverse non-carcinogenic risk for human exposure to PCBs in soils from the dumpsites. The total cancer risk values of PCBs for children ranged from 7.94×10^{-6} to 6.27×10^{-2} for rural, 3.73×10^{-3} to 2.07×10^{-2} for semi-urban and 3.11×10^{-5} to 2.97×10^{-1} for urban area. For adults, the total cancer risk values ranged from 8.12×10^{-7} to 6.42×10^{-3} for rural area, 3.82×10^{-4} to 2.11×10^{-2} for semi-urban area and 3.18×10^{-6} to 3.04×10^{-2} for urban area. The total cancer risk values were greater than the risk level of 1×10^{-6} (USEPA, 2010). This suggests a severe carcinogenic risk in relation to human exposure to PCBs in the soils from the dumpsites.

Table 7: Hazard index of PCBs in soils from the dumpsites

| Locations | Sites | Depth (cm) | CHILD | | | | ADULT | | | |
|-----------------|-------|-------------|----------|----------|----------|-----------------|----------|----------|----------|-----------------|
| | | | HQING | HQINH | HQDERM | HI | HQING | HQINH | HQDERM | HI |
| Rural Area | RA1 | Top Soil | 7.37E+01 | 3.50E-04 | 2.89E+01 | 1.03E+02 | 9.21E+00 | 1.46E-03 | 5.15E+00 | 1.44E+01 |
| | | Sub Soil | 5.10E+01 | 2.18E-04 | 2.00E+01 | 7.10E+01 | 6.37E+00 | 9.10E-04 | 3.56E+00 | 9.93E+00 |
| | | Bottom Soil | 1.97E+01 | 9.77E-05 | 7.71E+00 | 2.74E+01 | 2.46E+00 | 4.07E-04 | 1.37E+00 | 3.83E+00 |
| | RA2 | Top Soil | 9.96E-01 | 3.87E-06 | 3.90E-01 | 1.39E+00 | 1.24E-01 | 1.61E-05 | 6.95E-02 | 1.94E-01 |
| | | Sub Soil | 8.50E-02 | 3.31E-07 | 3.33E-02 | 1.18E-01 | 1.06E-02 | 1.38E-06 | 5.93E-03 | 1.66E-02 |
| | | Bottom Soil | 3.77E+01 | 1.89E-04 | 1.48E+01 | 5.25E+01 | 4.71E+00 | 7.87E-04 | 2.63E+00 | 7.34E+00 |
| | RA3 | Top Soil | 1.32E+02 | 5.08E-04 | 5.16E+01 | 1.83E+02 | 1.64E+01 | 2.12E-03 | 9.18E+00 | 2.56E+01 |
| | | Sub Soil | 7.35E+01 | 3.05E-04 | 2.88E+01 | 1.02E+02 | 9.18E+00 | 1.27E-03 | 5.13E+00 | 1.43E+01 |
| | | Bottom Soil | 6.58E+02 | 2.56E-03 | 2.58E+02 | 9.16E+02 | 8.23E+01 | 1.07E-02 | 4.60E+01 | 1.28E+02 |
| Semi-urban Area | SA4 | Top Soil | 3.84E+01 | 1.70E-04 | 1.50E+01 | 5.34E+01 | 4.79E+00 | 7.07E-04 | 2.68E+00 | 7.47E+00 |
| | | Sub Soil | 1.29E+02 | 5.42E-04 | 5.06E+01 | 1.80E+02 | 1.61E+01 | 2.26E-03 | 9.01E+00 | 2.51E+01 |
| | | Bottom Soil | 1.96E+03 | 8.47E-03 | 7.67E+02 | 2.72E+03 | 2.45E+02 | 3.53E-02 | 1.37E+02 | 3.81E+02 |
| | SA5 | Top Soil | 1.10E+02 | 4.70E-04 | 4.33E+01 | 1.54E+02 | 1.38E+01 | 1.96E-03 | 7.71E+00 | 2.15E+01 |
| | | Sub Soil | 8.31E+01 | 4.94E-04 | 3.26E+01 | 1.16E+02 | 1.04E+01 | 2.06E-03 | 5.80E+00 | 1.62E+01 |
| | | Bottom Soil | 3.95E+01 | 1.53E-04 | 1.55E+01 | 5.50E+01 | 4.94E+00 | 6.36E-04 | 2.76E+00 | 7.70E+00 |
| | SA6 | Top Soil | 3.81E+01 | 1.69E-04 | 1.49E+01 | 5.31E+01 | 4.77E+00 | 7.04E-04 | 2.66E+00 | 7.43E+00 |
| | | Sub Soil | 5.23E+01 | 2.23E-04 | 2.05E+01 | 7.28E+01 | 6.53E+00 | 9.31E-04 | 3.65E+00 | 1.02E+01 |
| | | Bottom Soil | 3.84E+01 | 1.70E-04 | 1.50E+01 | 5.34E+01 | 4.79E+00 | 7.07E-04 | 2.68E+00 | 7.47E+00 |
| Urban Area | UA7 | Top Soil | 3.29E-01 | 1.27E-06 | 1.29E-01 | 4.58E-01 | 4.11E-02 | 5.29E-06 | 2.30E-02 | 6.41E-02 |
| | | Sub Soil | 1.33E+02 | 5.13E-04 | 5.20E+01 | 1.85E+02 | 1.66E+01 | 2.14E-03 | 9.27E+00 | 2.59E+01 |
| | | Bottom Soil | 5.62E+02 | 2.17E-03 | 2.20E+02 | 7.82E+02 | 7.03E+01 | 9.04E-03 | 3.92E+01 | 1.10E+02 |
| | UA8 | Top Soil | 3.13E+03 | 1.21E-02 | 1.23E+03 | 4.35E+03 | 3.91E+02 | 5.05E-02 | 2.18E+02 | 6.09E+02 |
| | | Sub Soil | 2.50E+03 | 9.73E-03 | 9.82E+02 | 3.49E+03 | 3.13E+02 | 4.06E-02 | 1.75E+02 | 4.88E+02 |
| | | Bottom Soil | 2.50E+03 | 9.73E-03 | 9.82E+02 | 3.49E+03 | 3.13E+02 | 4.06E-02 | 1.75E+02 | 4.88E+02 |
| | UA9 | Top Soil | 4.03E+02 | 1.60E-03 | 1.58E+02 | 5.61E+02 | 5.04E+01 | 6.66E-03 | 2.81E+01 | 7.85E+01 |
| | | Sub Soil | 1.47E+02 | 6.13E-04 | 5.78E+01 | 2.05E+02 | 1.84E+01 | 2.55E-03 | 1.03E+01 | 2.87E+01 |
| | | Bottom Soil | 2.20E+02 | 2.65E-03 | 8.63E+01 | 3.07E+02 | 2.75E+01 | 1.10E-02 | 1.54E+01 | 4.29E+01 |

Table 8: Total Cancer Risk of PCBs in soils from the dumpsites

| Locations | | CHILD | | | | | Adult | | | |
|-----------------|-----|-------------|------------|----------------------|---------------------|-----------------------|-------------------|----------------------|---------------------|-----------------------|
| | | Codes | Depth (cm) | RISK _{ling} | RISK _{inh} | RISK _{iderm} | Total Cancer risk | RISK _{ling} | RISK _{inh} | RISK _{iderm} |
| Rural Area | RA1 | Top Soil | 8.20E-03 | 4.38E-11 | 3.12E-04 | 8.51E-03 | 5.59E-04 | 2.39E-11 | 3.12E-04 | 8.71E-04 |
| | | Sub Soil | 5.14E-03 | 2.75E-11 | 1.96E-04 | 5.33E-03 | 3.50E-04 | 1.50E-11 | 1.96E-04 | 5.46E-04 |
| | | Bottom Soil | 2.29E-03 | 1.22E-11 | 8.71E-05 | 2.37E-03 | 1.56E-04 | 6.64E-12 | 8.71E-05 | 2.43E-04 |
| | RA2 | Top Soil | 8.98E-05 | 4.71E-13 | 3.42E-06 | 9.32E-05 | 6.12E-06 | 2.57E-13 | 3.42E-06 | 9.54E-06 |
| | | Sub Soil | 7.65E-06 | 4.00E-14 | 2.91E-07 | 7.94E-06 | 5.21E-07 | 2.18E-14 | 2.91E-07 | 8.12E-07 |
| | | Bottom Soil | 4.42E-03 | 2.36E-11 | 1.68E-04 | 4.59E-03 | 3.02E-04 | 1.29E-11 | 1.68E-04 | 4.70E-04 |
| | RA3 | Top Soil | 1.20E-02 | 6.42E-11 | 4.56E-04 | 1.24E-02 | 8.16E-04 | 3.50E-11 | 4.56E-04 | 1.27E-03 |
| | | Sub Soil | 7.18E-03 | 3.85E-11 | 2.74E-04 | 7.46E-03 | 4.90E-04 | 2.10E-11 | 2.74E-04 | 7.63E-04 |
| | | Bottom Soil | 6.04E-02 | 3.24E-10 | 2.30E-03 | 6.27E-02 | 4.12E-03 | 1.77E-10 | 2.30E-03 | 6.42E-03 |
| Semi-urban Area | SA4 | Top Soil | 3.99E-03 | 2.13E-11 | 1.52E-04 | 4.14E-03 | 2.72E-04 | 1.16E-11 | 1.52E-04 | 4.24E-04 |
| | | Sub Soil | 1.27E-02 | 6.82E-11 | 4.85E-04 | 1.32E-02 | 8.69E-04 | 3.72E-11 | 4.85E-04 | 1.35E-03 |
| | | Bottom Soil | 1.99E-01 | 1.07E-09 | 7.58E-03 | 2.07E-01 | 1.36E-02 | 5.81E-10 | 7.58E-03 | 2.11E-02 |
| | SA5 | Top Soil | 1.10E-02 | 5.91E-11 | 4.21E-04 | 1.15E-02 | 7.53E-04 | 3.23E-11 | 4.21E-04 | 1.17E-03 |
| | | Sub Soil | 1.15E-02 | 6.13E-11 | 4.40E-04 | 1.20E-02 | 7.87E-04 | 3.34E-11 | 4.40E-04 | 1.23E-03 |
| | | Bottom Soil | 3.59E-03 | 1.93E-11 | 1.37E-04 | 3.73E-03 | 2.45E-04 | 1.05E-11 | 1.37E-04 | 3.82E-04 |
| | SA6 | Top Soil | 3.97E-03 | 2.12E-11 | 1.51E-04 | 4.12E-03 | 2.70E-04 | 1.16E-11 | 1.51E-04 | 4.21E-04 |
| | | Sub Soil | 5.25E-03 | 2.81E-11 | 2.00E-04 | 5.45E-03 | 3.58E-04 | 1.53E-11 | 2.00E-04 | 5.58E-04 |
| | | Bottom Soil | 3.99E-03 | 2.13E-11 | 1.52E-04 | 4.14E-03 | 2.72E-04 | 1.16E-11 | 1.52E-04 | 4.24E-04 |
| Urban Area | UA7 | Top Soil | 2.99E-05 | 1.61E-13 | 1.14E-06 | 3.11E-05 | 2.04E-06 | 8.77E-14 | 1.14E-06 | 3.18E-06 |
| | | Sub Soil | 1.21E-02 | 6.48E-11 | 4.60E-04 | 1.25E-02 | 8.23E-04 | 3.53E-11 | 4.60E-04 | 1.28E-03 |
| | | Bottom Soil | 5.11E-02 | 2.75E-10 | 1.95E-03 | 5.31E-02 | 3.49E-03 | 1.50E-10 | 1.95E-03 | 5.43E-03 |
| | UA8 | Top Soil | 2.86E-01 | 1.54E-09 | 1.09E-02 | 2.97E-01 | 1.95E-02 | 8.38E-10 | 1.09E-02 | 3.04E-02 |
| | | Sub Soil | 2.29E-01 | 1.23E-09 | 8.74E-03 | 2.38E-01 | 1.56E-02 | 6.72E-10 | 8.74E-03 | 2.44E-02 |
| | | Bottom Soil | 2.29E-01 | 1.23E-09 | 8.74E-03 | 2.38E-01 | 1.56E-02 | 6.72E-10 | 8.74E-03 | 2.44E-02 |
| | UA9 | Top Soil | 3.77E-02 | 2.02E-10 | 1.43E-03 | 3.91E-02 | 2.57E-03 | 1.10E-10 | 1.43E-03 | 4.00E-03 |
| | | Sub Soil | 1.44E-02 | 7.72E-11 | 5.49E-04 | 1.50E-02 | 9.83E-04 | 4.21E-11 | 5.49E-04 | 1.53E-03 |
| | | Bottom Soil | 6.14E-02 | 3.22E-10 | 2.34E-03 | 6.37E-02 | 4.18E-03 | 1.76E-10 | 2.34E-03 | 6.52E-03 |

Principal component analysis (PCA) of PCBs in the samples

The PCA for PCBs in soils of the rural and semi-urban were resolved into three components while that of urban area was resolved into four components (Table 9). The total variance was 76.512%, 86.711% and 92.475% for the soils from the rural, semi-urban and urban areas respectively. In rural dumpsite soil, component 1 explained 36.391% of the variance with a high positive loading values for tetra-, penta-, hepta-, octa- and nona-PCB homologues and component 2 accounted for 21.984% of variance with a high positive values for di- and deca-PCBs and component 3 accounted 18.138% of variance with a high positive

values for tetra- and deca-PCBs. In semi-urban dumpsite soil, component 1 explained 47.350% of the variance with a positive loading values for tetra-, penta-, hexa-, hepta-, octa- and nona-PCB homologues while component 2 accounted for 23.799% of the variance with a positive loading values for di-, hexa-, deca-PCBs, and component 3 accounted for 15.563% of variance with a positive tri-PCBs. However, in the case of the urban dumpsite, component 1 explained 29.778% of the variance and was dominated by the hexa-, hepta-, and nona-PCB homologues, while component 2 represented 29.531% of the variance and had positive loading values for di-, tri-, tetra-PCBs. Component 3 accounted for 17.918% of variance and was dominated penta- and deca-PCBs while component 4

accounted for 15.248% dominated with octa-PCBs. High chlorinated PCBs (HC-PCBs) are found in commercial mixtures of Aroclor 1254, and originated by several processes such as soil burial, degradation,

plant uptake and solubilization. Whereas, lower chlorinated PCBs (LC-PCBs) are linked to long-range transport processes and atmospheric deposition, paint pigment and electrical product (Iwegbue *et al.*, 2022)

Table 9: PCA of PCBs in the soils of the dumpsites

| | RURAL AREA | | | SEMI-URBAN AREA | | | URBAN AREA | | | |
|--------------------|---------------|---------------|---------------|-----------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | Component | | | Component | | | Component | | | |
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 4 |
| Di-PCB | .024 | .931 | -.044 | -.170 | .845 | .191 | -.230 | .959 | .082 | -.026 |
| Tri-PCBs | .006 | .474 | -.625 | .040 | .026 | .973 | -.404 | .662 | -.314 | -.303 |
| Tetra-PCBs | -.028 | .125 | .859 | .750 | .075 | .296 | .087 | .972 | .097 | -.083 |
| Penta-PCBs | .709 | -.452 | -.055 | .917 | .178 | .237 | .387 | -.334 | .837 | -.173 |
| Hexa-PCBs | .327 | -.497 | -.135 | .684 | .556 | .238 | .945 | -.069 | .124 | -.259 |
| Hepta-PCBs | .962 | .043 | .008 | .917 | -.259 | -.144 | .670 | -.216 | .042 | .485 |
| Octa-PCBs | .955 | .014 | .014 | .844 | -.345 | -.096 | .017 | -.097 | -.099 | .953 |
| Nona-PCBs | .909 | -.130 | -.044 | .893 | .174 | -.386 | .959 | -.086 | -.042 | .178 |
| Deca-PCBs | -.014 | .632 | .692 | .096 | .929 | -.195 | -.209 | .417 | .877 | .007 |
| Variance % | 36.391 | 21.984 | 18.138 | 47.350 | 23.799 | 15.563 | 29.778 | 29.531 | 17.918 | 15.248 |
| Cumm Var. % | 36.391 | 58.375 | 76.512 | 47.350 | 71.149 | 86.711 | 29.778 | 59.309 | 77.227 | 92.475 |

Conclusion

The concentrations and risks of PCBs in soils from selected rural, semi-urban and urban solid waste dumpsites in Delta State were investigated in this study. The results show that the soils pH was acidic to near neutral which depicts typical characteristics of anaerobic soil of the Niger Delta and were contaminated with PCBs which was originated from industrial and electrical wastes. The total concentrations and the individual PCBs congeners from the soil samples showed a distribution pattern in order of urban > semi-urban > rural area. The high concentration of PCBs in urban area could be related to over population and industrialization. The compositional pattern of the PCBs is in the order of: tetra-PCBs

>deca-PCBs > tri-PCBs > di-PCBs >penta-PCBs >hexa-PCBs >hepta-PCBs >octa-PCBs >nona-PCBs for rural area; tetra-PCBs >deca-PCBs >penta-PCBs > tri-PCBs >hexa-PCBs > di-PCBs >hepta-PCBs >nona-PCBs >octa-PCBs for semi-urban area and deca-PCBs > di-PCBs >hexa-PCBs >penta-PCBs > tetra-PCBs > tri-PCBs >hepta-PCBs >nona-PCBs >octa-PCBs for urban area. The ecological risk assessment indicated variable degree of ecological risks of PCBs in the soils while the human health risk assessment indicated that there that there were adverse non-carcinogenic and carcinogenic risks associated with PCBs in the samples, it also signifies no potential health risk to soil dwelling organism from this dumpsites.

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