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Health risk assessment of polychlorinated biphenyls exposure from inland rivers sediments in Warri-South, Warri, Delta State

Shedrack Oritsetimeyin AMURUN,¹ Joel OKPOGHONO^{*},² and Clifford Iheanyichukwu ANUNUSO¹

¹Department of Chemical Sciences, Novena University, Ogume, Delta State, Nigeria ²Department of Biochemistry, Faculty of Science, Delta State University of Science and Technology, Ozoro, Delta State, Nigeria

Abstract. The health risk of polychlorinated biphenyls (PCBs) exposure from Ugbuwangue, Ugbori and Edjeba rivers sediments in Warri-South, Warri, Delta State was investigated. Nine sediment samples were collected; three samples each along the course of the different rivers. The sediment samples were Soxhlet extracted with acetone/dichloromethane/*n*-hexane (1:1:1 v/v). A total of 28 PCBs were quantified using gas chromatography coupled with mass spectrometry detector. The concentration of the 28 PCBs ranges from 178.76-1398.29 ng g⁻¹ for Ugbuwangue river, 224.81-685.19 ng g⁻¹ for Ugbori river and 539.33-7858.3 ng g⁻¹ for Edjeba river. The concentration of 12 PCBs were recorded for dioxin-like PCBs ranged from 0.08-401.52 ng g⁻¹ (Ugbuwangue river 0.13 to 223.11 ng g⁻¹, Ugbori river 0.08 to 153.39 ng g⁻¹ and Edjeba river 0.32 to 401.52 ng g⁻¹), while the concentration of 16 non-dioxin-like PCBs were recorded ranging from 0.13-4245.71 ng g⁻¹ (Ugbuwangue river 0.18 to 386.47 ng g⁻¹, Ugbori river 0.13 to 111.98 ng g⁻¹ and Edjeba river 0.31 to 4245.71 ng g⁻¹). The ecological risks of the nine sediment samples were investigated and it ranges from 25.52 – 1122.616 with Edjeba river sediment having the highest ecological risk while Ugbuwangue river sediment has the least ecological risk.

Keywords: polychlorinated biphenyl; river; sediment; ecological risk.

1. Introduction

Pollution over the century has been a major problem that overwhelms our environment globally. Recently, there have been increasing concerns about toxic organic pollutants in Nigeria and in the rest part of the World. Chemical industries, agricultural and mining industries have heavily contributed to the growing increase of these pollutants [1]. Some of these toxic organic pollutants are transient organic pollutants and others are persistent organic pollutants (POPs). Toxic organic pollutants tend to co-exist in the air, water and soil sediments through urbanization and industrial waste [1].

Polychlorinated Biphenyls (PCBs) are a group of POPs that have been found in the ecosystem and in every part of the world including Nigeria [2]. They tend to persist in the environment due to their low degradation and significant bioaccumulation. PCBs are a group of synthetic oil-like chemicals of the organo-chlorine family [1] and are a class of non-polar toxic chemical compounds consisting of 209 congeners [3, 4]. PCBs are man-made organic compounds and were first manufactured in 1929 in the United States of America by the then Swann Chemical Corporation, which was later absorbed into Monsanto Chemical Company of St. Louis, Missouri. Due to their increasing toxicity into the environment, they were outlawed in 1979 and since then, production of PCBs elapses [5]. Environmental mediums such as air, soil, and water are ways through

which PCBs enters into the environment [1]. PCBs in soil and sediment from river have largely been diagnosed by scholars in recent years. Industrial and anthropogenic activities in urban areas have been a major sources through which PCBs may enter into the aquatic environment via atmospheric deposition, leakage and surface run-off from industrial wastewater discharge and from open dumping municipal waste sites [5-9]. PCBs tend to attach themselves to some of the heavy waste substances and by the reason of their weight, they submerge into the river bed. Due to their low solubility in water, low volatility and the inability to degrade on time, most of them are accumulated in the river sediments that serve as environmental reservoirs from which they may continue to be released over a long period of time [4, 10]. Their reported half-lives in soil and sediment ranges from months to years [4]. Numerous commercial and industrial applications employed PCBs including electrical, heat transfer, and hydraulic equipment; as plasticizers in paints, plastics, and rubber products; in pigments, dyes, carbonless copy paper and many other industrial applications [11] with properties of insulating ability, thermal stability, resistance to acids, oxidation, hydrolysis, and flame resistance [12]. PCBs have been widely employed in numerous items, especially transformers and power capacitors, due to their distinctive physical and chemical qualities [13].

^{*} Corresponding author. *E-mail address*: okpoghono@gmail.com (Joel Okpoghono)

Exposures to PCBs are mainly through ingestion (food, skin and water) and inhalation by human [4, 14]. Health risk from PCBs, as with all other chemicals, involves both hazard and exposure. While the hazard potential associated with PCBs has not changed over the years, exposure of humans has continued to decline over the past 20 years, a fact that is often unrecognized and underappreciated in today's continuing debate over health risk from exposure [15]. PCBs are carcinogen; alter immune system function; cause adverse alterations of the nervous system, skin, thyroid, and sex steroid hormonal systems; liver, kidney, pancreas, and the cardiovascular system. As a result of these actions on multiple organ systems, humans who are exposed to PCBs are at increased risk of cancer, reduced cognitive function accompanied by adverse behavioral effects, hypothyroidism, infertility, ischemic heart disease, hypertension, diabetes, liver disease, as well as giving birth to infants of lower than normal birth weight [16].

Due to the complexity of marine sediments, numerous methods used to measure organochlorine contaminants (OCs) e.g., PCBs in sediments are timeconsuming, necessitate the use of significant quantities of solvents for extraction and cleanup, and require expensive and specialized detection techniques (e.g., high-resolution gas chromatography [HRGC] with highresolution mass spectrometry [HRMS] detection) [17]. Several techniques are currently being used to quickly extract and analyze for specific OCs in sediments, but these efficient techniques either use pricey detection equipment or don't offer specific information about the contaminants present (like individual PCB congeners) [18]. Therefore, low-cost techniques are required to enable the analysis of several sediment samples quickly. The methods most frequently used for PCBs analysis are GC mass selective detector (MSD) and GC electron capture detector (ECD). Dual columns coated with polar stationary phase are utilized in the GC detector-based approach for PCBs separation and identity verification. For sensitive and targeted detection, the electronegative chlorine in PCB structure creates a high response from the ECD. Retention time (RT) and distinctive ions of each PCB can be utilized to identify congeners for the GC/MSD-based technique. In comparison to the GC-ECD analytical approach, selective monitoring of MSD on targeted ions ensures fewer false positive identifications, particularly when strong matrix interference is present. In this study, the PCBs in the samples were separated, found, and quantified using gas chromatograph connected to a mass selective detector. The purpose of this research is to evaluate the quantity, and ecological danger of PCBs in sediment from the Ugbuwangue, Ugbori, and Edjeba rivers in Warri-South Local Government Area, Delta State, Nigeria.

2. Experimental

2.1. Study area

The study area includes Ugbuwangue River (also known by members of the community as Ugbuwangue Creek), Ugbuwangue community, Ugbori river (also known by members of the community as Milly Creek), Ugbori community and Edjeba river, Edjeba community. The studied areas are all in Warri-South L.G.A, Warri, Delta State, Nigeria. These rivers are tributaries of the Warri river which originally flows from the river Niger and finally ends at the Gulf of Guinea down South of Nigeria. Anthropogenic activities in these rivers have greatly affected the ecological and biota activities in the rivers.



Figure 1. Map of Warri-South showing the inland rivers sediment sites.

2.2. Samples collection

The river sediments were collected in situ using a fabricated 30 kg Van Veen grab sampler. A total of nine sediment samples were collected from three different rivers at three locations (60 - 90 m apart). All samples were collected around June, 2022. The geographical coordinates of the nine samples were: Ugbuwangue river - UC1 (Latitude: 5.5244 N 5°31'27.84" and Longitude: 5.72003 E 5°43'12.102"), UC2 (Latitude: 5.52204 N 5°31'19.326" and Longitude: 5.71886 E 5°43'7.896"), UC3 (Latitude: 5.521 N 5°31'15.612" and Longitude: 5.71725 E 5°43'2.082"); Ugbori river – MC1 (Latitude: 5.51523 N 5°30'54.822" and Longitude: 5.73206 E 5°43'55.404"), MC2 (Latitude: 5.51604 N 5°30'57.744" and Longitude: 5.73288 E 5°43'58.374"), MC3 (Latitude: 5.51685 N 5°31'0.654" and Longitude: 5.73284 E 5°43'58.242"); Edjeba river – ER1 (Latitude: 5.54469 N 5°32'40.896" and Longitude: 5.72746 E 5°43'38.868"), ER2 (Latitude 5.544393 N 5°32'38.772 and Longitude 5.729175 E 5°43'44.802"), ER3 (Latitude 5.544209 N 5°32'38.262" and Longitude 5.730833 E 5°43'50.874"). The sediments were subsequently retrieved, scooped into aluminium foil, wrapped and appropriately labelled [19]. The river sediment samples were transported to the laboratory using a cooler containing ice. Replicate samples were taken at each site to minimize potential random variation during sampling, and the final sample was created by thoroughly mixing all of the replicate samples. Sediment samples were air-dried at room temperature, sieved through a 2 mm screen, ground into smaller particles using an agate mortar and pestle, and then placed in the refrigerator until analysis.

2.3. Materials and reagents

Neutral silica gel, neutral alumina, acetone, dichloromethane, and *n*-hexane were all purchased from BDH chemical laboratory England. Anhydrous Na₂SO₄ was purchased from Sigma chemical company, London, England. Every additional reagents that were utilized were of analytical grade.

2.4. Extraction and sample preparation

A mass of 5.0 g of an air dried sediment sample was spiked with a mixed standard solution of isotopically labelled PCB congeners and Soxhlet extracted with 150 mL of an acetone/dichloromethane /n-hexane mixture (1:1:1 v/v) in a 65 °C water bath for 18 h. One gram of activated copper granules and 3 g of anhydrous Na₂SO₄ were added to remove the sulphur and water respectively. The extract was rotary evaporated 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 eluate the PCBs from the column and the cleaned eluate was concentrated to approximately 2 mL under a slow stream of nitrogen gas.

Quantification of PCBs. The PCBs in the samples were separated, found, and quantified using an Agilent 6890A gas chromatograph connected to an Agilent 5975B mass selective detector (Palo Alto, CA, USA). A DB-5 column (30 m in length, 0.25 mm internal diameter, and 0.25 m film thickness) was the type of column that was utilized. High purity helium gas flowing at a rate of 2 mL/min served as the carrier gas. The column's temperature was first set to 85 °C and held there for 1 minute. From there, it was raised to 200 °C at a rate of 35 °C per minute, then 300 °C at a rate of 5 °C per minute over the course of 24.3 minutes. The mass selective detector was configured to operate in electron impact mode with selected ion monitoring (EI/SIM).

2.5. Quality / assurance measure

All glassware were washed with detergent, rinsed thoroughly with double-distilled water and acetone, and then baked for 4 h at 450 °C in a muffle furnace. 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. Procedural blanks were analyzed following all the analysis steps but omitting the samples.

2.6. Ecological risk assessment of PCBs in river sediment

Using the possible ecological risk index developed by Hakanson [20], the ecological risks of PCBs in the samples were calculated as given in Equation 1:

(1)

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

where:

$$E_r^i = T_f^i \times C_f^i$$
(2)
$$C_f^i = \frac{c_s^i}{c_r^i}$$
(3)

where: ERI is the ecological risk index, C_f^i is the contamination factor, C_r^i and C_s^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 [20]. The background concentration of 10 ng g⁻¹ PCBs in soil was used based on the method of Hakanson [20]. According to Hakanson [18], $E_r < 40 =$ low risk, $40 \le E_r < 80 =$ moderate risk, $80 \le E_r < 160 =$ considerable risk, $160 \le E_r < 320 =$ high risk and $E_r \ge 320 =$ very high risk.

2.7. Statistical analysis

The analysis of variance (ANOVA) was used to evaluate if the differences observed in the $\Sigma 28PCBs$ concentrations within sediment profiles were significant (p = 0.05). All statistical evaluations were performed using the Statistical Package for the Social Science (SPSS) version 20.

3. Results and discussion

3.1. PCBs concentrations in river sediment

The quality assurance/quality control measures indicated recoveries of the samples that had been spiked varied between 85.7 and 102.3%, whereas those of the ¹³C₁₂-labeled PCBs ranged between 83.6 and 94.9%. The PCBs' limits of quantification (LOQs) ranged from 1.0 to 3.5 ng g⁻¹, while their limits of detection (LODs) ranged from 0.2 to 1.4 ng g⁻¹. The chromatograms of PCBs levels in sediment from river sites are presented in Figure 2 (a-i).



Figure 2a. Chromatogram of PCBs levels in UC1 of Ugbuwangue river sediment.



Figure 2b. Chromatogram of PCBs in levels UC2 of Ugbuwangue river sediment.



Figure 2c. Chromatogram of PCBs levels in UC3 of Ugbuwangue river sediment.



Figure 2d. Chromatogram of PCBs levels in MC1 of Ugbori river sediment.



Figure 2e. Chromatogram of polychlorinated biphenyl levels in MC2 of Ugbori river sediment.



Figure 2f. Chromatogram of PCBs levels in MC3 of Ugbori river sediment.



Figure 2g. Chromatogram of PCBs levels in ER1 of Edjeba river sediment.



Figure 2h. Chromatogram of PCBs levels in ER2 of Edjeba river sediment.



Figure 2i. Chromatogram of PCBs levels in ER3 of Edjeba river sediment.

| | UGBUWANGUE RIVER | | | U | GBORI RIVE | ER | EJEBA RIVER | | | |
|-------------------|------------------|--------|--------|--------|------------|--------|-------------|--------|--------|--|
| | UC1 | UC2 | UC3 | MC1 | MC2 | MC3 | ER1 | ER2 | ER3 | |
| PCB 8 | 386.47 | 61.03 | 111.15 | 39.2 | 101.54 | 20.75 | 1224 | 214.25 | 95.39 | |
| PCB 18 | 157.69 | 4.62 | 28.62 | 1.46 | 51.04 | 4.67 | 33.3 | 92.39 | 166.39 | |
| PCB 28 | 0 | 0 | 0 | 0 | 0 | 0 | 2.05 | 0 | 0 | |
| PCB 44 | 174.66 | 5.56 | 121.78 | 3.75 | 34.39 | 15.79 | 1144.53 | 63.23 | 84.25 | |
| PCB 52 | 113.24 | 25.73 | 11.05 | 102.72 | 39.26 | 2.86 | 211.56 | 87.49 | 15.89 | |
| PCB 66 | 36.4 | 4.07 | 96.55 | 29.69 | 6.93 | 111.98 | 4245.71 | 16.99 | 71.04 | |
| PCB 77 | 17.88 | 4.69 | 28.2 | 7.17 | 4.7 | 22.43 | 106.55 | 8.27 | 17.67 | |
| PCB 81 | 223.11 | 14.61 | 8.97 | 153.39 | 73.53 | 5.66 | 401.52 | 139.44 | 10.62 | |
| PCB 101 | 76.68 | 14.89 | 21.99 | 3.98 | 28.72 | 4.25 | 165.09 | 58.79 | 18.82 | |
| PCB 105 | 8.28 | 12.27 | 7.23 | 1.01 | 2.84 | 5.98 | 188.87 | 11.58 | 9.02 | |
| PCB 114 | 65 | 2.18 | 3.8 | 18.95 | 22.77 | 2.87 | 26.81 | 45.23 | 4.31 | |
| PCB 118 | 61.73 | 4.22 | 16.55 | 132.48 | 22.45 | 4.01 | 34.2 | 43.27 | 12.5 | |
| PCB 123 | 9.74 | 9.08 | 3.79 | 80.81 | 21.48 | 14.88 | 29.68 | 45.53 | 12.35 | |
| PCB 126 | 34.46 | 4.48 | 7.61 | 26.33 | 14.11 | 0.63 | 20.81 | 30.45 | 2.4 | |
| PCB 128 | 6.32 | 0.27 | 1.27 | 15.95 | 2.46 | 0.23 | 4 | 5.17 | 1.54 | |
| PCB 138 | 1.88 | 3.1 | 2.3 | 12.19 | 1.45 | 1.53 | 2.04 | 4.11 | 2.45 | |
| PCB 153 | 10.22 | 0.66 | 1.54 | 11.11 | 3.85 | 0.48 | 6.18 | 9.23 | 1.12 | |
| PCB 156 | 1.33 | 0.27 | 0.35 | 0.83 | 0.49 | 0.11 | 0.77 | 1.24 | 0.32 | |
| PCB 157 | 0.72 | 0 | 0.21 | 0.26 | 0.28 | 0.08 | 0.32 | 0.82 | 0 | |
| PCB 167 | 0 | 0 | 0 | 1.32 | 0 | 0 | 0.93 | 0 | 0 | |
| PCB 169 | 1.31 | 0.13 | 2.18 | 10.46 | 0.89 | 1.26 | 0.62 | 1.85 | 0.78 | |
| PCB 170 | 2.11 | 0 | 1.85 | 8.69 | 0.49 | 0.81 | 1.06 | 1.82 | 2.68 | |
| PCB 180 | 1.7 | 0.18 | 0.27 | 2.7 | 0 | 0.65 | 0.44 | 0.31 | 2.21 | |
| PCB 187 | 1.59 | 0.39 | 1.58 | 6.6 | 0 | 0.21 | 0.68 | 1.42 | 0.51 | |
| PCB 189 | 5.77 | 1.48 | 5.21 | 3.97 | 0.35 | 2.19 | 4.37 | 0 | 4.99 | |
| PCB 195 | 0 | 1.65 | 0.53 | 1.47 | 0 | 0.37 | 0.69 | 0 | 0.49 | |
| PCB 206 | 0 | 2.88 | 3.01 | 0 | 1.47 | 0 | 1.52 | 0.62 | 1.59 | |
| PCB 209 | 0 | 0.32 | 0 | 8.7 | 0.13 | 0.13 | 0 | 0.66 | 0 | |
| $\Sigma_{28}PCBs$ | 1398.29 | 178.76 | 487.59 | 685.19 | 435.62 | 224.81 | 7858.3 | 884.16 | 539.33 | |

 Table 1. Polychlorinated biphenyl concentrations (ng g⁻¹) in sediment from river sites

Ugbuwangue River =UC, Ugbori River = MC Edjeba River = ER

| UGBUWANGUE RIVER | | | | | UGBORI RIVER | | | | EJEBA RIVER | | | | | | |
|------------------|-------|-------|-------------|-------|--------------|-------|-------|-------------|-------------|-------|--------|--------|-------------|-------|--------|
| | MEAN | SD | MEDI- AN | MIN | MAX | MEAN | SD | MEDI- AN | MIN | MAX | MEAN | SD | MEDI- AN | MIN | MAX |
| PCB 8 | 186.2 | 175.2 | 86.1 | 61.0 | 386.5 | 53.8 | 42.3 | 39.2 | 20.8 | 101.5 | 511.2 | 620.1 | 214.3 | 95.4 | 1224.0 |
| PCB 18 | 63.6 | 82.3 | 16.6 | 4.6 | 157.7 | 19.1 | 27.7 | 4.7 | 1.5 | 51.0 | 97.4 | 66.7 | 92.4 | 33.3 | 166.4 |
| PCB 28 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 | 1.2 | 0.0 | 0.0 | 2.1 |
| PCB 44 | 100.7 | 86.5 | 63.7 | 5.6 | 174.7 | 18.0 | 15.4 | 15.8 | 3.8 | 34.4 | 430.7 | 618.3 | 84.3 | 63.2 | 1144.5 |
| PCB 52 | 50.0 | 55.3 | 64.2 | 11.1 | 113.2 | 48.3 | 50.5 | 39.3 | 2.9 | 102.7 | 105.0 | 99.0 | 87.5 | 15.9 | 211.6 |
| PCB 66 | 45.7 | 46.9 | 33.0 | 4.1 | 96.6 | 49.5 | 55.3 | 29.7 | 6.9 | 112.0 | 1444.6 | 2426.0 | 71.0 | 17.0 | 4245.7 |
| PCB 77 | 16.9 | 11.8 | 12.5 | 4.7 | 28.2 | 11.4 | 9.6 | 7.2 | 4.7 | 22.4 | 44.2 | 54.2 | 17.7 | 8.3 | 106.6 |
| PCB 81 | 82.2 | 122.0 | 84.0 | 9.0 | 223.1 | 77.5 | 73.9 | 73.5 | 5.7 | 153.4 | 183.9 | 199.2 | 139.4 | 10.6 | 401.5 |
| PCB 101 | 37.9 | 33.8 | 18.4 | 14.9 | 76.7 | 12.3 | 14.2 | 4.3 | 4.0 | 28.7 | 80.9 | 75.6 | 58.8 | 18.8 | 165.1 |
| PCB 105 | 9.3 | 2.7 | 7.8 | 7.2 | 12.3 | 3.3 | 2.5 | 2.8 | 1.0 | 6.0 | 69.8 | 103.1 | 11.6 | 9.0 | 188.9 |
| PCB 114 | 23.7 | 35.8 | 11.4 | 2.2 | 65.0 | 14.9 | 10.6 | 19.0 | 2.9 | 22.8 | 25.5 | 20.5 | 26.8 | 4.3 | 45.2 |
| PCB 118 | 27.5 | 30.3 | 39.1 | 4.2 | 61.7 | 53.0 | 69.5 | 22.5 | 4.0 | 132.5 | 30.0 | 15.8 | 34.2 | 12.5 | 43.3 |
| PCB 123 | 7.5 | 3.3 | 9.4 | 3.8 | 9.7 | 39.1 | 36.3 | 21.5 | 14.9 | 80.8 | 29.2 | 16.6 | 29.7 | 12.4 | 45.5 |
| PCB 126 | 15.5 | 16.5 | 17.0 | 4.5 | 34.5 | 13.7 | 12.9 | 14.1 | 0.6 | 26.3 | 17.9 | 14.3 | 20.8 | 2.4 | 30.5 |
| PCB 128 | 2.6 | 3.2 | 3.8 | 0.3 | 6.3 | 6.2 | 8.5 | 2.5 | 0.2 | 16.0 | 3.6 | 1.9 | 4.0 | 1.5 | 5.2 |
| PCB 138 | 2.4 | 0.6 | 2.7 | 1.9 | 3.1 | 5.1 | 6.2 | 1.5 | 1.5 | 12.2 | 2.9 | 1.1 | 2.5 | 2.0 | 4.1 |
| PCB 153 | 4.1 | 5.3 | 5.9 | 0.7 | 10.2 | 5.1 | 5.4 | 3.9 | 0.5 | 11.1 | 5.5 | 4.1 | 6.2 | 1.1 | 9.2 |
| PCB 156 | 0.7 | 0.6 | 0.6 | 0.3 | 1.3 | 0.5 | 0.4 | 0.5 | 0.1 | 0.8 | 0.8 | 0.5 | 0.8 | 0.3 | 1.2 |
| PCB 157 | 0.3 | 0.4 | 0.2 | 0.0 | 0.7 | 0.2 | 0.1 | 0.3 | 0.1 | 0.3 | 0.4 | 0.4 | 0.3 | 0.0 | 0.8 |
| PCB 167 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 | 0.8 | 0.0 | 0.0 | 1.3 | 0.3 | 0.5 | 0.0 | 0.0 | 0.9 |
| PCB 169 | 1.2 | 1.0 | 1.7 | 0.1 | 2.2 | 4.2 | 5.4 | 1.3 | 0.9 | 10.5 | 1.1 | 0.7 | 0.8 | 0.6 | 1.9 |
| PCB 170 | 1.3 | 1.2 | 2.0 | 0.0 | 2.1 | 3.3 | 4.6 | 0.8 | 0.5 | 8.7 | 1.9 | 0.8 | 1.8 | 1.1 | 2.7 |
| PCB 180 | 0.7 | 0.9 | 1.0 | 0.2 | 1.7 | 1.1 | 1.4 | 0.7 | 0.0 | 2.7 | 1.0 | 1.1 | 0.4 | 0.3 | 2.2 |
| PCB 187 | 1.2 | 0.7 | 1.6 | 0.4 | 1.6 | 2.3 | 3.8 | 0.2 | 0.0 | 6.6 | 0.9 | 0.5 | 0.7 | 0.5 | 1.4 |
| PCB 189 | 4.2 | 2.3 | 4.6 | 1.5 | 5.8 | 2.2 | 1.8 | 2.2 | 0.4 | 4.0 | 3.1 | 2.7 | 4.4 | 0.0 | 5.0 |
| PCB 195 | 0.7 | 0.8 | 1.0 | 0.0 | 1.7 | 0.6 | 0.8 | 0.4 | 0.0 | 1.5 | 0.4 | 0.4 | 0.5 | 0.0 | 0.7 |
| PCB 206 | 2.0 | 1.7 | 1.4 | 0.0 | 3.0 | 0.5 | 0.8 | 0.0 | 0.0 | 1.5 | 1.2 | 0.5 | 1.5 | 0.6 | 1.6 |
| PCB 209 | 0.1 | 0.2 | 0.2 | 0.0 | 0.3 | 3.0 | 4.9 | 0.1 | 0.1 | 8.7 | 0.2 | 0.4 | 0.0 | 0.0 | 0.7 |
| Σ28PCBs | 688.2 | 721.3 | 490.0 | 142.0 | 1479.8 | 448.5 | 465.7 | 307.6 | 77.7 | 960.3 | 3093.9 | 4346.1 | 912.2 | 311.2 | 8058.3 |

Table 2. Summary statistics of PCBs concentrations (ng g⁻¹) in sediment from sample sites

Table 3. ANOVA results of PCBs in the three rivers sites

| Source of variation | SS | df | MS | F | P-value | F crit |
|---------------------|----------|-----|----------|----------|----------|---------|
| Between groups | 1709340 | 8 | 213667.5 | 2.683755 | 0.007626 | 1.97663 |
| Within groups | 19346477 | 243 | 79615.13 | | | |
| Total | 21055817 | 251 | | | | |

Summary information and an ANOVA for the PCB concentrations found in sediment are shown in Tables 1-3.

The PCBs concentration in these river sediment samples ranged from 178.76 - 1398.29 ng g⁻¹ for Ugbuwangue river sediment, 224.81 - 435.62 ng g⁻¹ for Ugbori river sediment and 539.33 - 7858.3 ng g⁻¹ for Edjeba river sediment with a mean of 688.2 ng g⁻¹, 448.5 ng g⁻¹, 3093.9 ng g⁻¹ for Ugbuwangue, Ugbori and Edjeba river sediments location respectively. The total concentrations of PCBs from the river sediment locations shows a distribution pattern as follows, Edjeba river sediment. The concentration of 12 PCBs were discovered as dioxin-like PCBs which are PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189 and are ranged between 0.13 - 223.11 ng g⁻¹ for Ugbuwangue river sediment, 0.08 - 153.39 ng g⁻¹ for

Ugbori River sediment and 0.32 - 401.52 ng g⁻¹ for Edjeba River sediment respectively. The concentration of 16 PCBs were also discovered as non-dioxin-like PCBs which are PCB8, 18, 28, 44, 52, 66, 101, 128, 138, 153, 170, 180, 187, 195, 206 and 209 and they ranged between 0.18 - 386.47 ng g⁻¹ for Ugbuwangue river sediment, 0.13 – 111.98 ng g⁻¹ for Ugbori river sediment and 0.31 - 4245.71 ng g⁻¹ for Edjeba river sediment. Polychlorinated biphenyls are extremely carcinogenic compounds that may be present in industrial and consumer foodstuffs [21]. A comparison of $\sum 28$ PCBs concentrations in river sediments studied with others reported for river sediment in literature are shown in Table 4. The 28 PCB readings in the river sediments under investigation are compared to comparable quantities for river sediment reported in the literature. However, the PCB concentrations were higher than those seen in previous studies for river sediment.

Table 4. Comparison of $\sum 28$ polychlorinated biphenyls concentrations in river sediment studied with others reported for riversediment in literature

| Location | No. of PCBs studied | Concentration range (ng g ⁻¹) | References | | |
|---------------------------|------------------------|--|-------------------------|--|--|
| Ugbuwangue, Warri Nigeria | 28 | 178.76-1398.29 | This study | | |
| Ugbori, Warri Nigeria | 28 | 224.81-685.19 | This study | | |
| Edjeba, Warri Nigeria | 28 | 539.33-7858.3 | This study | | |
| Udu, Nigeria | 29 | 5.34-16.1 | Iniaghe and Kpomah [21] | | |
| Ethiope, Nigeria | 8 | 0.73-6.7 | Ezemonye et al. [22] | | |
| Benin,Nigeria | 8 | 0.35-15.15 | Ezemonye et al. [22] | | |
| Calabar, Nigeria | 8 | 0.21-2.16 | Ilechukwu et al. [23] | | |

3.2. Cumulative of PCBs in the nine sediment sites

The concentration of the 28 PCBs in the sediment samples were looked upon in percentage as show in Figure 3. From the chart, each sediment sites are represented by colors as seen below. The chart illustrates the rate of the 28 PCB in the nine sediment site which gives proper understanding as to the concentration in percentage of PCB present in each sample site (Figure 3).



Figure 3. A cumulative chart showing the concentration (%) of PCBs in the nine sediment sites.

According to Figure 4, UC1 had higher concentration of PCBs than UC2 and UC3, with PCB8 predominating at UC1 and UC2 and PCB 44 have the highest concentration at UC3.



Figure 4. PCBs concentrations in Ugbuwangue river sediment sites. Ugbuwangue River = UC

The results in Figure 5 and 6 show the concentration of the three sediments sites at Ugbori and Edjeba river. The concentration of PCBs was higher at site MC1 than it was at sites MC2 and MC3, with PCB81 dominating site MC1, PCB8 dominating site MC2, and PCB66 had the highest concentration at site MC3. Additionally, the graphic showed that ER1 had a higher concentration of PCBs than ER2 and ER3, with PCB66 predominating ER1 (Figure 6).



Figure 5. Concentrations of PCBs in Ugbori River sediment sites. Ugbori River = MC



Figure 6. Concentration of PCBs in Edjeba river sediment site. Edjeba River = ER.

Accidental leaks and spills, releases from contaminated soil in landfills and hazardous waste sites, deposition of vehicle emissions near roadway soil, and land application of PCB-containing sewage sludge are all possible sources of PCB release to soil [4, 24]. Uncontrolled hazardous waste sites, the burning of wastes containing PCBs, the usage of obsolete electrical equipment and can all cause high PCBs to be released into the atmosphere [24, 25].

3.3. Ecological risk analysis

Ecological risks of the nine sediment sites are illustrated Figure 7. The potential ecological risk (E'_r) of PCBs in the river sediment for Ugbuwangue river, Ugbori river and Edjeba river ranged from 25.52 to 199.76, 32.116 to 97.88 and 77.048 to 1122.616 respectively. The river sediment samples at ER1 accounted for the highest and UC2 account for the lowest E'_r . Ecological risk assessment entails evaluating the dangers that, in theory, exist for all living things in the various ecosystems that make up the environment due to the presence of substances introduced into the environment by humans [4]. It has been shown that crude oil can have a number of harmful impacts on health [26-28] and PCBs are found in crude oil production areas [22]. They have been proven to have substantial non-cancer health impacts on animals, including effects on the immune system, reproductive system, neurological system, endocrine system, and other health consequences [15]. They have also been proved to induce cancer in animals. Some international agencies establish effect range low (ERL) and effect range medium (ERM) values of 0.000023 ng g⁻¹ and 0.00018 ng g⁻¹respectively [29] the threshold effect level (TEL) and probable effect level (PEL) values of 0.000022 ng g^{-1} and 0.000187 ng g^{-1} [30] and threshold effect concentrations (TEC) and probable effect concentrations (PEC) values of 60 and 676 ng g⁻¹ [30]. The concentration of Σ 28PCBs in the studied areas were above TEL, ERL, ERM, PEL and also above TEC and PEC stipulated values. The ecological risk of PCBs based on Hakanson [20] method the sample sites were classified as follow: site UC3 is classified as lowest risk, site MC3 is classified as moderate risk, site MC2, UC3, ER3 and MC1 are classified as high risk, site ER2 and UC1 are classified as very high risk and site ER1 is classified as destructive risk.



Figure 7. Ecological risks of the nine sediment site. Ugbuwangue River = UC; Ugbori River = MC; Edjeba River = ER.

4. Conclusions

The status of PCBs in the inland river in Delta State was investigated in this study. The result of this study has shown that the river sediments are contaminated with PCBs and these PCBs in the river sediment originated from domestic, industrial, commercial, construction and electrical wastes. The ecological risk assessment indicated that there were various degrees of ecological risks of PCBs. It is hereby recommended that continuous monitoring of these rivers for PCBs concentrations should be carried out to avoid potential ecological and residential exposure risks. Further studies should be carried out to investigate the spatial and temporal variations of other legacy pollutants in sediments of rivers in Delta State, Nigeria.

Conflict of interests

There is no conflict of interest to declare by the authors.

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