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Concentrations, sources, and exposure risk of polychlorinated biphenyls in soil profiles of the floodplain of the lower reaches of the River Niger, Nigeria

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Abstract The concentrations of 28 polychlorinated biphenyls (PCBs) were determined in soils collected at three depths from thirteen different sites along the floodplain of the lower reaches of the River Niger (LRRN) in Nigeria. The aim of the study was to provide data on the levels of contamination, sources of the contaminants, and risks to the ecosystem and humans. Soil samples were Soxhlet extracted with a solvent mixture of dichloromethane (DCM)/n-hexane and cleaned up on a column packed with Florisil and silica gel. The PCBs in the samples were quantified by gas chromatography-mass spectrometry. The Σ28 PCB concentrations in the floodplain soils varied between not detected (nd) and 11,151 ng g^{-1} for different sampling sites and depths. The PCB concentrations and homologue distribution patterns in soil profiles of the floodplain of the LRRN showed remarkable differences with respect to sites and depths. The results obtained were used to evaluate the ecological and human health risks, which indicated that there is a potential risk to organisms and humans from exposure to PCBs in these soil profiles. The source evaluation as determined by principal component analysis suggested that PCBs in these soil profiles came from burnt circuit boards, cable wires, use of paints, discharges from transformers, long-range migration, and deposition.

Keywords Polychlorinated biphenyls · Risk assessment · Floodplain soils · River Niger · Nigeria

Introduction

Floodplains are special ecological zones connecting natural areas along a river with other parts of the hinterland (Thonon, 2006). These ecozones are intensively cultivated worldwide because of their high nutrient and organic matter contents. Most rivers are contaminated, and the associated contaminants are transported to their floodplains through suspended sediment during flooding events. Such overbank deposits can increase the contaminant loads of the floodplain. Flooding events and atmospheric inputs are the main sources of contaminants in the floodplains. On a time scale of years and centuries, most floodplains act as a reservoir for sediments. These

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deposited sediments are rich in nutrients, organic matter, and contaminants such as metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), pesticides, polybrominated diphenyl ethers, and dioxins and furans, among others. Since floodplain soils are intensively cultivated, humans are exposed to the contaminants in them via the human-soil interface, soil–plant-human interface, or soil–plant-animal-human interface (Iwegbue et al., 2020a, b).

PCBs are listed among the 'dirty dozen' persistent organic pollutants under the Stockholm Convention of 2001. They have been produced and distributed with different trade names including Aroclor, Clophen, Fenclor, Kanechlor, Phenoclor, and Sovolin in the USA, Germany, Italy, Japan, France, and the former USSR respectively (Takasuga et al., 2006; Wang et al., 2016). PCBs were never produced in Nigeria but were imported into the country from Asia (India, Japan, and South Korea), Europe (Belgium, England, Poland, Italy, and Sweden), and South Africa, as components of electrical transformers, heat exchangers, and other consumer products. The 2009 Nigerian inventory of PCB-containing equipment and wastes compiled by the Federal Ministry of Environment (FMEnv), although not exhaustive, indicated there are thousands of tons of PCB-containing wastes and PCBs that are still in use in a number of old electrical transformers (Federal Ministry of Environment, 2009; Iwegbue et al., 2020a). Thus, improper disposal and management of these wastes could lead to an upsurge of PCBs in the environment.

PCBs are notable for their high stability, electrical insulating properties, and low flammability. These properties have extended their wide application in various areas, e.g. they are used as coolants, hydraulic oils, dielectric fluids in capacitors and transformers, additives in plastics and paints, flame retardants, wax extenders, lubricants, adhesives, in printing inks, and in many other applications (Iwegbue et al., 2019; Prosser et al., 2016; Tesi & Iniaghe, 2020). PCBs can interfere with functions of the endocrine and immune systems; increase the risk of diabetes and coronary heart disease; decrease verbal learning; increase depression, neurobehavioural disorders, hyporeflexia, and motor immaturity; and lower psychomotor scores, among other effects (Tomasallo et al., 2010; Turyk et al., 2007; Visha et al., 2018). Despite the global prohibition on formulation, trade, and applications of PCBs, these compounds are still found in the environment because of their persistent nature (Wang et al., 2016) and discharges from old equipment and inadvertent sources (Iwegbue et al., 2020a, b).

Soil acts as a sink for contaminants and determines the fate and geochemical cycling of PCBs in and around the biosphere. Thus, it is imperative to quantify the concentrations of PCBs and identify their sources and spatial variability in soils, in addition to determining the possible ecological and human health risks arising from these contaminants. A survey of the literature revealed that there are only few studies concerning the pollution status of the floodplain soils of the lower reaches of the River Niger (LRRN). These studies were limited to speciation of metals (Iwegbue et al., 2017) and polycyclic aromatic hydrocarbons in the floodplain soils (Iwegbue et al., 2020b; Tesi et al., 2016). The floodplains of the LRRN are extensively cultivated like other floodplains in the world. However, the quality and sustainability of the soils of this landscape are seriously threatened by discharges from agriculture, urbanization, and commercial and industrial developments, especially those related to power generation, and oil and gas exploration and production. Given the anthropogenic pressures on the LRRN floodplains and its strategic importance to the economy of the region, there is a clear need to compile data on the extent and patterns of contaminant distribution in the soil profiles. Therefore, the objective of this study was to evaluate the PCB concentrations in soil profiles of the floodplain with a view to discerning potential contamination by flood water, urbanization, agriculture, oil and exploration, and industrial development, and to compare the movement, sources, and ecological and human health risks of PCBs in the floodplain soils. Such information is necessary for source control, designing surveillance schemes, ecosystem restoration, and environmental management programmes.

Materials and methods

The study area

The River Niger is the most significant river in Nigeria as it drains about 60% of the country's landmass (Unyimadu, 2018). The River Niger starts from Fouta Djallon upland in Guinea, flows into Nigeria through

Kebbi State, and enters the Atlantic Ocean (Olatunji & Osibanjo, 2012). The River Niger is approximately 4,180 km (2,600 miles) in length with a drainage basin area of 2,117,700 km^2 (817,600 sq.miles) (Tesi et al., 2016). The study area is located between longitude 6.16° to 6.43° E and latitude 6.02° to 6.43° N and is between Anwai and Aboh areas in the LRRN in Nigeria (Fig. 1). This area is characterized by pronounced wet and dry seasons with an annual total rainfall between 2,700 and 3,000 mm, while the highest average daily temperature ranges from 25 to 33 °C. The average relative humidity falls between 65 and 80%. The annual flooding events occur between July and September (Ogbodo, 2011).

Sample collection

Soil samples were collected during November and December 2018 when the flood water had receded completely into the river channel. Soil samples were obtained at 0–15, 15–30, and 30–45 cm depths by using a stainless steel corer from 13 sites stratified into upstream (FP1–FP5), midstream (FP6–FP8), and downstream sections (FP9–FP13) (Fig. 1). The upstream section of the floodplain is subjected to discharges from agricultural, urbanization, and industrial activities, while the midstream section is a typical rural setting and the main activities are peasant farming and fishing. The downstream section is also a rural setting but hosts different oil fields, multiple gas flaring points, and gas and power generating plants. The mid- and downstream sections of the floodplain were approximately 32 and 102 km respectively from the upstream section. At each site, 10–15 random samples were collected from an area 100 m × 100 m in extent. The random samples from each soil layer were mixed together to form a composite sample. The soil samples were packed in amber glass bottles and conveyed to the laboratory in an ice chest. The samples were dried in a fume cupboard, sieved through a 2 mm mesh sieve, and refrigerated at − 4 °C prior to analysis.

Reagents

All solvents used for extraction (dichloromethane and n-hexane) were of pesticide grade and products of Merck (Darmstadt, Germany). The PCB standard solution containing 28 PCBs (PCB8, PCB18, PCB28, PCB44, PCB52, PCB60, PCB77, PCB81, PCB101, PCB105, PCB114, PCB118, PCB123, PCB126, PCB128, PCB138, PCB153, PCB156, PCB157, PCB167, PCB169, PCB170, PCB180, PCB185, PCB189, PCB195, PCB206, and PCB209) was a product of AccuStandard Inc. (CT, USA). The PCB surrogate standard solution containing six isotopically labelled PCBs ($^{13}C_{12}$ PCB-28, 52, 118, 153, 180, and 209) was a product of Cambridge Isotope Laboratories Inc. (MA, USA). Florisil, copper powder, anhydrous sodium sulphate, and silica gel were of analytical grade obtained from BDH Chemicals (Poole, UK).

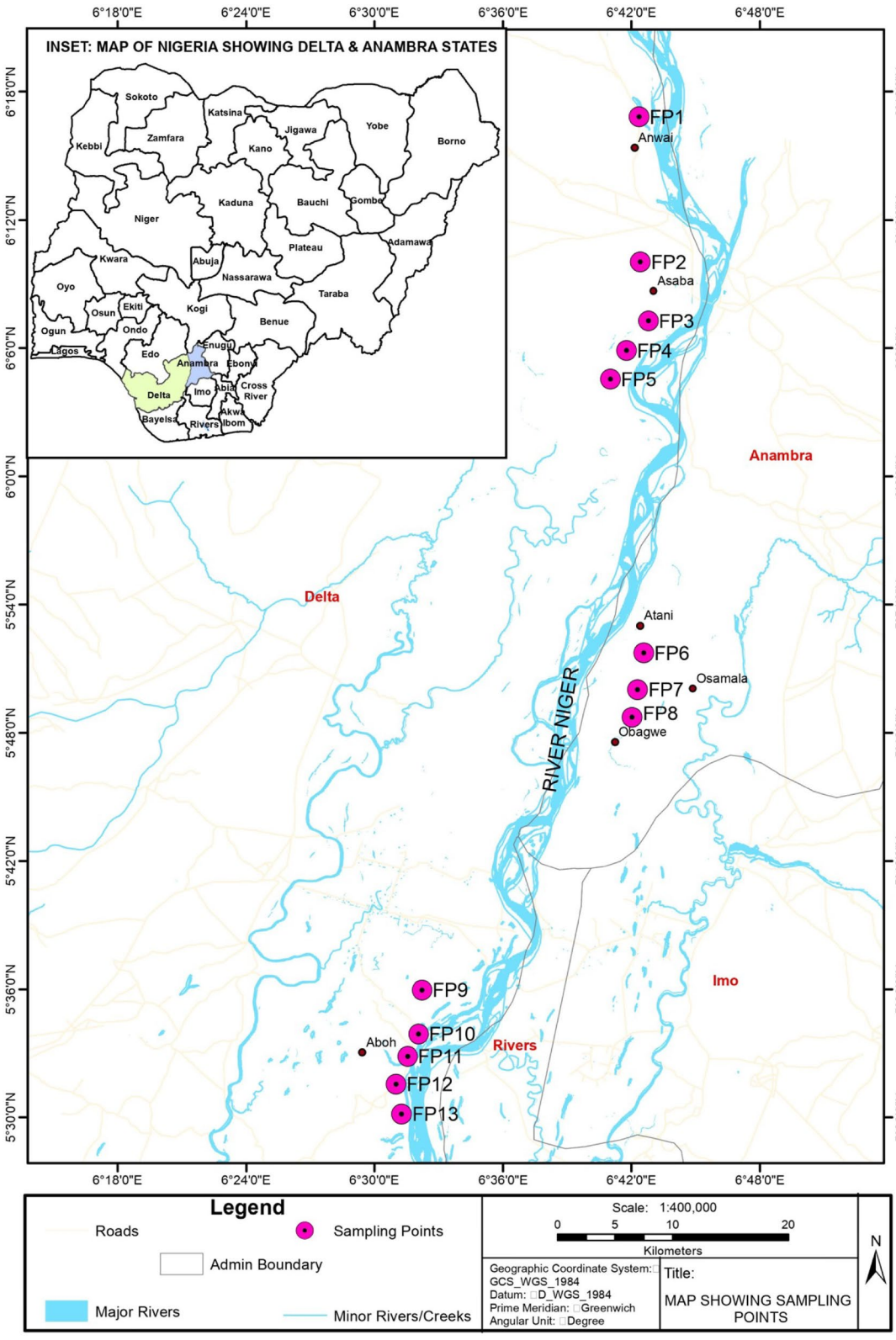
Determination of soil physicochemical characteristics

A pH meter with a glass electrode was used to measure the pH of the soils in a soil/water suspension (1:2 soil to water ratio). A conductivity meter was used to determine the electrical conductivity (EC) of the soils (Abollino et al., 2002). The wet dichromate oxidation method was used to determine the total organic carbon (TOC) content of the soils (Radojevic & Bashkin, 1999), while the particle size distribution was determined by following the method of Bouyoucos (1962).

Sample extraction and chromatographic analysis

A 10 g mass of soil sample was spiked with 200 ng g^{-1} of isotopically labelled PCBs and Soxhlet extracted for 10 h with 100 mL mixture of dichloromethane (DCM)/n-hexane (1:1 v/v). The extract was concentrated to 2 mL by using a rotary evaporator and cleaned up on a column packed from bottom to top with 1.0 g each of anhydrous Na_2SO_4, Florisil, acidified silica gel, and copper powder. The PCBs were eluted from the column with 20 mL of DCM/n-hexane and the eluate was concentrated to approximately 2 mL under a mild stream of pure nitrogen gas and stored in a 2 mL amber vial prior to chromatographic analysis.

The quantification of the PCB concentrations in the samples was carried out with an Agilent 6890N gas chromatograph coupled to an Agilent 5975B mass selective detector (Agilent Technologies, Palo Alto, USA). A HP-5 column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) was used for the


INSET: MAP OF NIGERIA SHOWING DELTA & ANAMBRA STATES
Sokoto
Katsina
Jigawa
Yobe
Borno
Kebbi
Zamfara
Kano
Niger
Kaduna
Bauchi
Gombe
Adamawa
Plateau
Kwara
Abuja
Nassarawa
Oyo
Taraba
Osun
Ekiti
Kogi
Benue
Ogun
Ondo
Enugu
Lagos
Edo
Anambra
Ebonyi
Abia
Cross River
Delta
Imo
Akwa Ibom
Bayelsa
Rivers
6°18'0"E
6°24'0"E
6°30'0"E
6°36'0"E
6°42'0"E
6°48'0"E
6°18'0"N
6°12'0"N
6°6'0"N
6°0'0"N
5°54'0"N
5°48'0"N
5°42'0"N
5°36'0"N
5°30'0"N
FP1
Anwai
FP2
Asaba
FP3
FP4
FP5
Anambra
Delta
Atani
FP6
FP7
Osamala
FP8
Obagwe
RIVER NIGER
Imo
FP9
FP10
Aboh
Rivers
FP11
FP12
FP13
Legend
Roads
Sampling Points
Admin Boundary
Major Rivers
Minor Rivers/Creeks
Scale: 1:400,000
0 5 10 20
Kilometers
Geographic Coordinate System:
GCS_WGS_1984
Datum: D_WGS_1984
Prime Meridian: Greenwich
Angular Unit: Degree
Title:
MAP SHOWING SAMPLING POINTS
N

◂**Fig. 1** Map of the study area showing sampling sites

separation with helium at a pressure of 70.06 kPa and an average velocity of 2 mL/min as the carrier gas. The volume of sample injected into the GC–MS was 2.0 µL via a pulsed splitless mode. The temperature of the injection port and that of the interface was maintained at 280 and 250 °C respectively. The column temperature was initially programmed at 80 °C with a 2 min hold time, then increased to 180 °C at 10 °C/min, and was finally stepped up to 280 °C at 5 °C/min with a 20 min hold time making the run time a total of 52 min. The MS was operated in selective ion monitoring (SIM) mode.

Quality control and statistical analysis

Method blanks, $^{13}C_{12}$-labelled PCBs and sample matrix spike recoveries were used to validate the analytical procedure. Acceptable percentage recoveries of 85.7 to 96.3% were achieved for the $^{13}C_{12}$-labelled PCBs and sample matrix spikes. The linearity of the calibration curves expressed as R^2 values for the PCBs ranged from 0.9991 to 0.9998, and the relative standard deviations between replicate analyses ranged between 3 and 9%. The limits of quantification (LOQs) for the PCB congeners ranged between 0.1 to 0.6 ng g^{-1}. None of the 28 PCBs was found in the procedural blanks. Analysis of variance (ANOVA) was used to determine if there was a significant variation in the concentrations of PCBs in the floodplain soils with respect to depth and location. Principal component analysis (PCA) was used to establish the sources of PCBs in the soil samples. All statistical analyses were carried out with SPSS version 19 software.

Ecological risk assessment of PCBs in sediments

The ecosystem risk of the presence of PCBs in the soil profiles of the floodplain was evaluated by making use of the method of Håkanson (1980). The potential ecological risk index (ERI) is given as follows:

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

where

$$E_r^i = T_f^i \times C_f^i$$

and $C_f^i = \frac{C_s^i}{C_r^i}$.

E_r^i is the ecological risk factor; T_f^i represents the toxic response factor, which has a value of 40 for PCBs (Håkanson, 1980); C_f^i depicts the contamination factor; C_s^i is the concentration of PCBs in the sample; and C_r^i is the background concentration of PCB. A value of 10 ng g^{-1} was applied as the background concentration of PCBs (Håkanson, 1980). The significance of the ERI is given as follows: $E_r < 40$ signifies a low risk; $40 \le E_r < 80$ depicts a medium risk; $80 \le E_r < 160$ indicates a considerable risk; $160 \le E_r < 320$ shows a high risk; and $E_r \ge 320$ indicates a very high risk (Håkanson, 1980).

Assessment of human health risk associated with exposure to PCBs in floodplain soils

The human health risk as a result of human exposure to PCBs in the floodplain soils was evaluated by using the $UCL_{95\%}$ concentrations of the dioxin-like PCBs (dl-PCBs). The equation for the estimation of the $UCL_{95\%}$ concentration is provided in Supplementary Material S1.

Estimation of toxic equivalency of dioxin-like PCBs in floodplain soils

The toxicity of the dl-PCBs in the soil profiles of the floodplain of the LRRN was evaluated by using the toxic equivalency (TEQ) concentrations. The TEQ concentrations of dl-PCBs were obtained by comparison with that of 2, 3, 7, 8-tetrachlorodibenz-p-dioxin (2,3,7,8-TCDD) as a reference (Van den Berg et al., 2006).

The TEQ is given by the equation:

$$\mathrm{TEQ} = \sum \mathrm{TEF_i} \times C_i$$

where C_i is the concentration of a dl-PCB congener in the soil and TEF_i is the toxic equivalency factor of the dl-PCB congener. The TEF values of the twelve dl-PCB congeners used are 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).

Non-carcinogenic and carcinogenic risks of PCBs in floodplain soils

Human exposure to PCBs could elicit both non-carcinogenic and carcinogenic effects. The hazard index (HI) (non-carcinogenic) and total cancer risk resulting from accidental ingestion, inhalation, and dermal contact with PCBs in soils of the floodplain were computed by making use of the standard equations developed by the United States Environmental Protection Agency (USEPA) (USEPA 1989; USEPA, 2009).

For the non-carcinogenic risk, the relevant equations are:

$$\text{Hazard Index (HI)} = \sum \text{HQ} = \text{HQ}_{\text{ing}} + \text{HQ}_{\text{inh}} + \text{HQ}_{\text{dermal}}$$

$$\text{HQ} = \frac{\text{CDI}_{\text{nc}}}{\text{RfD}}$$

$$\text{CDI}_{\text{ing-nc}} = \frac{\text{C}_{\text{UCL}} \times \text{IngR} \times \text{EF} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}_{\text{nc}}}$$

$$\text{CDI}_{\text{inh-nc}} = \frac{\text{C}_{\text{UCL}} \times \text{InhR} \times \text{EF} \times \text{ET} \times \text{ED}}{\text{PEF} \times 24 \times \text{AT}_{\text{nc}}}$$

$$\text{CDI}_{\text{dermal-nc}} = \frac{\text{C}_{\text{UCL}} \times \text{SA} \times \text{AF} \times \text{ABS}_{\text{d}} \times \text{EF} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}_{\text{nc}}}$$

In the case of the cancer risk, the following equations were applied:

$$\text{Total Cancer Risk} = \text{Risk}_{\text{ing}} + \text{Risk}_{\text{inh}} + \text{Risk}_{\text{dermal}}$$

$$\text{Risk}_{\text{ing}} = \frac{\text{C}_{\text{UCL}} \times \text{IngR} \times \text{EF} \times \text{ED} \times \text{CF} \times \text{SFO}_{\text{ing}}}{\text{BW} \times \text{AT}_{\text{ca}}}$$

$$\text{Risk}_{\text{inh}} = \frac{\text{C}_{\text{UCL}} \times \text{InhR} \times \text{EF} \times \text{ED} \times \text{IUR}}{\text{PEF} \times \text{AT}_{\text{ca}}}$$

$$\text{Risk}_{\text{dermal}} = \frac{\text{C}_{\text{UCL}} \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED} \times \text{CF} \times \text{SFO}_{\text{ing}} \times \text{GIABS}}{\text{BW} \times \text{AT}_{\text{ca}}}$$

where $\text{CDI}_{\text{ing-nc}}$, $\text{CDI}_{\text{inh-nc}}$, and $\text{CDI}_{\text{dermal-nc}}$ were used to designate the chronic daily intake for the ingestion, inhalation, and dermal exposure pathways respectively; and Risk_{ing}, Risk_{inh}, and $\text{Risk}_{\text{dermal}}$ designate the cancer risk arising from the ingestion, inhalation, and skin contact routes respectively. The definitions of terms and values of variables used for evaluating the human health risk are provided in Table 1 and Supplementary Material Table S2. Generally, the significance of the HI value is given as follows: $\text{HI} > 1$ signifies adverse non-carcinogenic effects, while $\text{HI} < 1$ signifies no adverse non-carcinogenic effects. The acceptable total cancer risk value was set as 1.0×10^{-6}, while a value $> 10^{-4}$ is sufficiently large to elicit considerable adverse carcinogenic effects and remedial action is therefore needed (USEPA, 2010).

Results and discussion

Physicochemical characteristics of floodplain soils

The physicochemical properties of the floodplain soils of the LRRN evaluated in this study are shown in Supplementary Material Table S3. The pH values of the soil profiles varied between 4.2 and 7.4 for all sampling locations and depths. The pH values indicated that the soils of the floodplain of the LRRN were generally acidic in nature. The TOC of the soil profiles varied between 0.18 and 3.24%, while the EC of the soil profiles ranged between 28.3 and 138 µS cm^{-1}. The pH, TOC, and EC decreased with depth at all sampling locations. The pH and TOC values obtained in the present study correspond with those previously reported for this study area by Tesi et al. (2016), while the EC values were higher than those reported earlier for the floodplain soils (Tesi et al., 2016). The percent fraction of sand, clay, and silt in these soil profiles of the floodplain ranged from 83.9 to 98.1%, 0.05 to 6.53%, and 0.47 to 12.9% respectively.

Table 1 Definitions and values of variables for human health risk assessment of PCBs in floodplain soils

Variables	Unit	Definition	Values		References
			Child	**Adult**	
C	ng g^{-1}	PCB concentration in soil			
AF	mg cm^{-2}	Soil to skin adherence factor	0.2	0.07	USEPA, 2011
BW	kg	Average body weight	15	60	Iwegbue et al., (2020a, b)
ED	year	Exposure duration	6	30	USEPA, 2001
EF	day yr^{-1}	Exposure frequency	350	350	USEPA, 2001
ET	h day^{-1}	Exposure time	8	8	USEPA, 1989
IngR	mg day^{-1}	Ingestion rate	200	100	USDOE, 2011
InhR	m^3 day^{-1}	Inhalation rate	12	50	USDOE, 2011
SA	cm^2 $event^{-1}$	Skin surface area	2800	5700	USDOE, 2011
AT_{nc}	days	Averaging time for non-carcinogens	ED × 365		USDOE, 2011
AT_{ca}	days	Averaging time for carcinogens	LT × 365		USDOE, 2011
LT	years	Lifetime	55 years		WHO, 2018
PEF	m^3 kg^{-1}	Soil to air particulate emission factor	1.36×10^9		USDOE, 2011
RfD_o	mg kg^{-1} d^{-1}	Oral reference dose	Contaminant specific		SM Table S2
RfD_i		Inhalation reference dose	Contaminant specific		SM Table S2
SFO	mg kg^{-1} d^{-1}	Oral slope factor	Contaminant specific		SM Table S2
IUR	μg m^{-3}	Inhalation unit risk	Contaminant specific		SM Table S2

PCB concentrations and occurrence patterns in floodplain soils

A summary of the concentrations of PCBs measured in soil profiles of the floodplain of the LRRN is given in Table 2, while the results for the individual samples are shown in Supplementary Material Table S4. The Σ28 PCB concentrations in these soil profiles ranged from not detected (nd) to 11,151 ng g^{-1} for all sampling locations. The concentrations of PCBs in the floodplain soils showed significant discrepancies ($p < 0.05$) with sampling locations and depth. The PCB concentrations in soils of the floodplain of the LRRN might have arisen from the remobilization and redistribution of PCB-containing sediments from the River Niger and/or pollution via flood water. The PCBs in flood water may have been mobilized from flooded, polluted terrestrial areas, such as dumpsites, roads, farmlands, sewage treatment plants, warehouses, industries, landfills, oil installations, and septic tanks, among others (Hilscherova et al., 2007). The concentrations of the Σ28 PCBs did not show any regular pattern with depth, which may be related to bioturbation and mechanical disturbances during farming. A similar trend was observed for metal and PAH distributions in soil profiles of the floodplain (Tesi et al., 2016; Iwegbue et al., 2017; 2020a). Similarly, the average concentration of Σ28 PCBs in soils at a depth of 30–45 cm was higher than those at depths of 15–30 and 0–15 cm. The highest concentrations of Σ28 PCBs (11,200 ng g^{-1}) were observed at a depth of 30–45 cm for site FP4, and none of the 28 congeners analysed was detected at a depth of 15–30 cm for sites FP7, FP9, and FP10; at a depth of 30–45 cm for site FP12; and at a depth of 0–15 cm for site FP13. The average concentration of PCBs in the soil profile of site FP4 was higher than those of other sites. This may be related to the level of anthropogenic activities in this area especially burning of tyres, plastic components of cars, electrical cables, and electronics, as well as discharges from the Asaba and Onitsha townships. On average, the concentration of Σ28 PCBs in the upstream section (FP1 to FP5) was higher than those in the midstream (FP6 to FP8) and downstream sections (FP9 to FP13) of the study area. The elevated levels of Σ28 PCBs in the upstream section might be due to discharges from anthropogenic activities in that section of the floodplain.

Table 2 Summary statistics of PCB concentrations (ng g^{-1}) in floodplain soils of the lower reaches of the River Niger

	0–15 cm depth							15–30 cm depth							30–45 cm depth							$C_{UCL95\%}$
	Mean	SD	Median	Min	Max	Skew	Kurt	Mean	SD	Median	Min	Max	Skew	Kurt	Mean	SD	Median	Min	Max	Skew	Kurt	
PCB8	24.9	24.0	29.3	0.0	71.9	0.5	−0.4	55.4	106.3	30.3	0.0	391	3.0	9.8	67.9	155	0.0	0.0	558	3.1	9.9	62.2
PCB18	34.2	30.0	47.3	0.0	70.3	−0.2	−1.9	99.5	178.6	51.8	0.0	676	3.3	11.1	136.0	236	39.6	0.0	749	2.2	3.9	107
PCB28	51.9	55.3	44.1	0.0	227	3.0	10.1	150.8	370	45.5	0.0	1361	3.4	11.9	157.1	269	40.6	0.0	856	2.0	3.3	148
PCB44	55.7	55.2	51.7	0.0	204	1.6	3.8	53.3	52.5	60.0	0.0	154	0.8	0.1	91.4	112	59.4	0.0	342	1.9	2.5	73.3
PCB52	28.9	45.2	0.0	0.0	161	2.3	6.3	89.1	203.3	37.8	0.0	756	3.4	12.1	80.3	156	0.0	0.0	528	2.4	5.9	82.7
PCB60	24.4	28.4	0.0	0.0	68.0	0.4	−1.8	21.8	40.1	0.0	0.0	134	2.1	4.8	29.1	36.6	0.0	0.0	105	0.9	−0.4	27.9
PCB77	27.6	23.6	39.1	0.0	61.2	−0.2	−1.7	30.0	41.7	34.7	0.0	152	2.2	6.4	260.8	865	0.0	0.0	3139	3.6	13.0	193
PCB81	31.1	27.6	41.3	0.0	77.6	0.0	−1.4	23.7	34.5	0.0	0.0	99.6	1.2	0.3	329.1	1120	0.0	0.0	4055	3.6	13.0	240
PCB101	36.5	50.2	10.9	0.0	176	2.0	4.6	30.0	44.6	0.0	0.0	156	2.1	5.0	32.8	49.3	0.0	0.0	172	2.1	5.0	37.1
PCB105	9.2	17.5	0.0	0.0	41.0	1.5	0.1	6.6	16.2	0.0	0.0	47.0	2.2	3.6	6.3	15.5	0.0	0.0	43.0	2.2	3.3	9.79
PCB114	3.1	11.1	0.0	0.0	40.0	3.6	13.0	3.3	12.0	0.0	0.0	43.2	3.6	13.0	14.3	22.5	0.0	0.0	55.0	1.0	−1.1	9.65
PCB118	15.1	23.7	0.0	0.0	52.4	1.0	−1.2	7.2	17.8	0.0	0.0	52.0	2.2	3.7	81.7	241.7	0.0	0.0	881	3.5	12.6	59.5
PCB123	32.2	32.1	48.0	0.0	79.4	0.1	−2.0	20.5	28.5	0.0	0.0	81.0	1.0	−0.4	18.8	24.9	0.0	0.0	52.2	0.6	−2.0	25.9
PCB126	29.1	29.1	40.8	0.0	72.0	0.1	−2.0	13.0	20.3	0.0	0.0	45.0	1.0	−1.3	18.9	25.2	0.0	0.0	58.3	0.6	−1.8	22.3
PCB128	14.6	22.8	0.0	0.0	51.0	1.0	−1.2	6.2	15.2	0.0	0.0	41.0	2.2	3.2	25.0	47.1	0.0	0.0	156	2.2	4.7	19.3
PCB138	6.5	15.9	0.0	0.0	43.5	2.2	3.3	6.8	16.6	0.0	0.0	44.7	2.2	3.2	16.2	27.3	0.0	0.0	83.0	1.5	1.6	12.6
PCB153	8.8	21.5	0.0	0.0	59.3	2.2	3.3	44.5	93.0	0.0	0.0	339	3.0	10.0	55.2	69.1	40.3	0.0	203	1.1	0.1	43.3
PCB156	29.9	29.9	44.4	0.0	78.0	0.1	−1.8	53.6	152.3	0.0	0.0	556	3.5	12.4	14.9	23.4	0.0	0.0	53.3	1.0	−1.2	47.9
PCB157	3.5	12.5	0.0	0.0	45.2	3.6	13.0	3.0	10.9	0.0	0.0	39.2	3.6	13.0	14.2	40.8	0.0	0.0	145	3.2	10.6	11.8
PCB167	3.5	12.5	0.0	0.0	45.2	3.6	13.0	6.3	15.5	0.0	0.0	41.2	2.2	3.2	17.5	30.1	0.0	0.0	94.0	1.7	2.3	12.2
PCB169	23.0	26.4	0.0	0.0	59.7	0.3	−2.1	10.1	19.3	0.0	0.0	47.6	1.5	0.2	21.5	32.6	0.0	0.0	106	1.6	2.6	20.8
PCB170	17.0	28.1	0.0	0.0	82.0	1.4	0.7	3.0	10.9	0.0	0.0	39.3	3.6	13.0	3.1	11.1	0.0	0.0	40.0	3.6	13.0	10.7
PCB180	12.0	23.0	0.0	0.0	56.8	1.5	0.3	3.3	11.8	0.0	0.0	42.6	3.6	13.0	12.9	35.9	0.0	0.0	126	3.1	9.8	13.3
PCB185	11.0	21.0	0.0	0.0	50.6	1.5	0.2	6.5	15.8	0.0	0.0	43.8	2.2	3.3	36.4	93.9	0.0	0.0	335	3.1	10.2	27.3
PCB189	3.4	12.2	0.0	0.0	44.0	3.6	13.0	3.3	12.0	0.0	0.0	43.2	3.6	13.0	37.4	134.8	0.0	0.0	486	3.6	13.0	29.4
PCB195	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PCB206	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.9	10.3	0.0	0.0	37.1	3.6	13.0	7.9	28.6	0.0	0.0	103	3.6	13.0	7.8
PCB209	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TOTAL	**537**	**453**	**446**	**0**	**1219**	**0.3**	**−1.6**	**716**	**1123**	**423**	**0.0**	**4251**	**3.0**	**9.7**	**1587**	**3055**	**283**	**0.0**	**11,151**	**3.0**	**9.4**	**1180**
Di-PCB	24.9	24.1	29.3	0.0	72.0	0.5	−0.4	55.4	106	30.0	0.0	391	3.0	9.8	67.9	155.2	0.0	0.0	558	3.1	9.9	
Tri-PCBs	86.1	55.5	91.0	0.0	227	1.1	2.8	250.3	548	97.0	0.0	2037	3.4	11.7	293	501.5	77.6	0.0	1605	2.1	3.7	
Tetra-PCBs	168	146	130	0.0	504	0.9	0.8	217.9	310	198.0	0.0	1191	2.9	9.6	791	2116.8	108.0	0.0	7769	3.5	12.4	
Penta-PCBs	125	122	163	0.0	328	0.2	−1.6	80.7	104	0.0	0.0	270	0.8	−1.1	173	333.9	0.0	0.0	1215	2.9	9.2	

Table 2 (continued)

	0–15 cm depth							15–30 cm depth							30–45 cm depth							$C_{UCL95\%}$
	Mean	SD	Median	Min	Max	Skew	Kurt	Mean	SD	Median	Min	Max	Skew	Kurt	Mean	SD	Median	Min	Max	Skew	Kurt	
Hexa-PCBs	89.8	107	78.0	0.0	333	1.1	0.5	130.6	255	0.0	0.0	895	2.6	7.3	165	215.8	69.0	0.0	712	1.5	2.3	
Hepta-PCBs	43.5	66.2	0.0	0.0	186	1.3	0.4	16.1	36.5	0.0	0.0	126	2.7	7.5	89.8	261.2	0.0	0.0	948	3.5	12.2	
Octa-PCBs	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Nona-PCBs	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.9	10.3	0.0	0.0	37.1	3.6	13.0	7.9	28.6	0.0	0.0	103	3.6	13.0	
Deca-PCBs	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Non-ortho dl-PCBs	110.9	91.8	147.0	0.0	229	−0.1	−2.0	76.9	73.4	78.7	0.0	187	0.2	−1.7	630.2	2022	42.6	0.0	7354	3.6	13.0	
Mono-ortho dl-PCBs	99.9	110	97.3	0.0	332	0.7	−0.3	103.9	192	0.0	0.0	637	2.2	4.6	205.2	457	0.0	0.0	1673	3.2	10.8	
∑Dioxin-like PCBs	211	194	244.0	0.0	506	0.1	−1.9	180.9	245	100	0.0	789	1.6	1.9	835.4	2468	42.6	0.0	9027	3.6	12.8	
Indicator PCBs	160	164	116.0	0.0	565	1.4	1.9	331.9	697	140	0.0	2612	3.4	11.9	436.2	644	175.0	0.0	1892	1.6	1.4	
LC-PCBs	404	348	413.3	0.0	1131	2.7	1.5	604.3	1068	325	0.0	3889	10.1	30.1	1324.6	3107	185.6	0.0	11,147	11.6	35.2	
HC-PCBs	259	296	241.0	0.0	847	2.6	−0.7	230.2	406	0.0	0.0	1328	9.7	26.8	435.2	839	69.0	0.0	2978	11.5	36.7	

In Nigeria, there are no stipulated guideline values or permissible limits for PCBs in soils. Thus, the PCB concentrations in the floodplain soils were compared with those stipulated by some international regulatory bodies. The Canadian Soil Quality Guideline (CSQG) value for PCBs in agricultural soils is 500 ng g^{-1} (CCME, 1999), and the Australian and New Zealand Ecological Investigation Level (ANZEIL) and Dutch action value for PCBs is 1000 ng g^{-1} (ANZECC, 1992; VROM, 1994), while a value of 220 ng g^{-1} total PCBs was stipulated by the US EPA as the health-based screening level designed to avert adverse health effects relating to long-term exposure (Rudel et al., 2008). The PCB concentrations in 46% of the soil samples were above the CSQG value for PCBs in agricultural soils, while 21% of samples had Σ28 PCB concentrations above the Dutch action value and that of ANZEIL, and 64% of the soil samples had Σ28 PCB concentrations above the health-based screening level of the US EPA.

Table 3 presents a comparison of the PCB concentrations obtained in this study with those found in other floodplain soils in the world. Such a comparison has its shortcomings given the discrepancies in soil lithology and physicochemical properties, the number of samples and congeners analysed, and the different extraction procedures and instrumental analytical methods applied. However, these shortcomings do not outweigh the importance of providing a global picture of PCB concentrations and occurrence patterns in soils of floodplains. The concentrations of PCBs obtained in soils of the floodplain of the LRRN were higher than others previously reported (Table 3) except for those reported by Brosnan et al. (2001) for soils of the Hudson River floodplain in the USA. In our study, there was no significant positive correlation between the Σ28 PCB concentrations and TOC of the soil ($R^2 = 0.003$) (Supplementary Material Figure S5). The absence of a significant positive correlation between the Σ28 PCB concentrations and TOC suggests organic matter alone does not determine the fate of PCBs in the floodplain soils. Therefore, PCBs in these soil profiles are associated with different sources as well as constant input of fresh PCB contamination (Tesi et al., 2016; Yang et al., 2012).

PCB homologue composition of floodplain soil profiles

The PCB homologue distribution patterns in soil profiles of the floodplain of the LRRN showed remarkable differences with respect to sites and depths (Fig. 2). On average, the occurrence pattern of PCB homologues at a depth of 0–15 cm followed the order: tetra-PCBs > penta-PCBs > hexa-PCBs > tri-

Table 3 Comparison of PCB concentrations in floodplain soils of the lower reaches of the River Niger with those of other floodplain soils in other regions of the world

Location	Soil type	Concentrations (ng g^{-1})	Reference
Nigeria (River Niger)	Floodplain	ND-11151	This study
USA (Hudson River)	Floodplain	< 11.0–360,000	Brosnan et al. (2001)
USA (Shiawassee River)	Floodplain	1.95–2890	Kannan et al. (2008)
USA (Saginaw River)	Floodplain	0.07–1070	Kannan et al. (2008)
USA (Saginaw Bay)	Floodplain	1.03–42.3	Kannan et al. (2008)
Netherlands (Rhine River)	Floodplain	23.4–59.6	Hendriks et al. (1996)
Germany	Floodplain	8.0–23.0	Schulze et al. (2014)
Russia (River Oka)	Floodplain	0.7–28.8	Zimmer et al. (2010)
Russia (Yachroma River)	Floodplain	10.4–1404	Galiulin and Bashkin (1996)
Morava River	Floodplain	0.65–24.84	Babek et al. (2008)
Poland	Flooded alluvial	0.41–4.77	Maliszewkwa-Kordybach et al. (2013)
Czech Republic	Flooded alluvial	3.3–40.8*	Hilscherova et al. (2007)
Czech Republic (Elbe River)	Flooded soil	4.0–7.2	Pulkrabovia et al. (2008)
China (Pearl River Estuary)	Wetland	17.68–169.26	Zhao et al. (2016)

*Median values

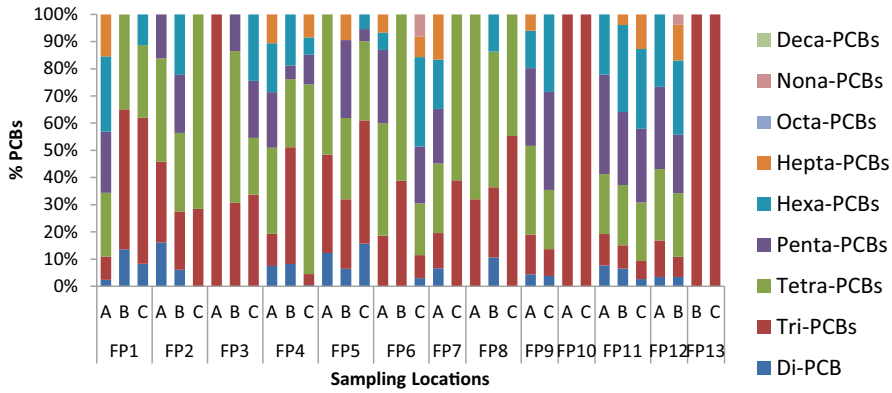


Fig. 2 Occurrence pattern of PCB homologues in the floodplain soils of the lower reaches of the River Niger: **A** 0–15 cm depth, **B** 15–30 cm depth, and **C** 30–45 cm depth

PCBs > hepta-PCBs > di-PCBs, while the PCB homologue distribution pattern in soils at a depth of 15–30 cm was in the order: tri-PCBs > tetra-PCBs > hexa-PCBs > penta-PCBs > di-PCBs > nona-PCBs. In the case of the 30–45 cm depth, the homologue distribution pattern followed the order: tri-PCBs > tetra-PCBs > hexa-PCBs > penta-PCBs > di-PCBs > nona-PCBs. The octa- and deca-PCBs were not detected in any of the soil samples, which rules out inadvertent sources of PCBs in soils of the floodplain. Similarly, the octa- and deca-PCBs were not prominent in sediments from the LRRN and Ase River (Irerhievwie et al., 2020). In addition, the homologue distribution especially for the 0–15 cm depth followed a similar pattern to that found in sediments from the LRRN (Irerhievwie et al., 2020). The di-PCB (PCB8) was found in 54% of the soil samples from the LRRN. The concentrations of the di-PCB ranged from 37.1 to 103 ng g^{-1} for all sampling locations and depths and constituted 3.9 to 8.2% of the Σ28 PCBs. The tri-PCBs were more prevalent in the soil profiles of the floodplain with a detection frequency of 87% in the soil samples. The concentrations of tri-PCBs varied from 35.8 to 2037 ng g^{-1} and represented 4.1 to 100% of the Σ28 PCBs. Of the tri-PCBs investigated in this study, PCB28 was dominant at all depths, while PCB44, PCB52, and PCB77 were the dominant tetra-PCBs at depths of 0–15, 15–30 and 30–45 cm respectively. The tetra-PCBs had higher concentrations than other PCB homologues in the floodplain soils but were second to tri-PCBs in terms of occurrence frequency (74%). The tetra-PCB concentrations in floodplain soils varied from 56.0 to 7769 ng g^{-1} and accounted for 19.1 to 72% of the Σ28 PCBs. The dominance of tri-PCBs in the floodplain soils is believed to be related to the widespread use of tri-PCBs in power capacitors (Ren et al., 2007; Zhang et al., 2014), while the presence of tetra-PCBs is related to burning of municipal solid waste (Zhang et al., 2014). The detection frequency of penta-PCBs in the floodplain soils was 51% with concentrations in the range of 37.0 to 1215 ng g^{-1}, and they accounted for 4.5 to 36.5% of the Σ28 PCBs. Of the six penta-PCBs analysed, PCB101 was the dominant species at depths of 0–15 and 15–30 cm, while PCB118 was more prominent at the 30–45 cm depth. In the case of hexa-PCBs, PCB156 was prominent in the 0–15 and 15–30 cm depths, while PCB153 was the dominant species in the 30–45 cm depth. The hexa-PCBs and hepta-PCBs were detected in 49% and 28% of the soil samples respectively. The concentrations of hexa-PCBs varied from 57.8 to 895 ng g^{-1} and constituted 5.4 to 32.9% of the Σ28 PCBs. The hepta-PCB concentrations in the floodplain soils ranged from 39.3 to 948 ng g^{-1}. The hepta-PCB homologues constituted 3.9 to 16.7% of the Σ28 PCBs. PCB170, PCB185, and PCB189 were the prominent hexa-PCB homologues at depths of 0–15, 15–30, and 30–45 cm respectively. The nona-PCBs were detected only in the 30–45 cm depth of site FP6, and at a depth of 15–30 cm for site FP12, at concentrations of 26.0 ng g^{-1} and 558 ng g^{-1} respectively for the two sites. The nona-PCBs represented 0.5% of the Σ28 PCBs at a depth of 30–45 cm for site FP6, and 16.2% of the Σ28 PCBs at a depth of 15–30 cm for site FP12. The lower chlorinated PCBs (LC-PCBs) (di- to penta-PCBs) were the dominant PCBs in the floodplain soils in terms of concentrations and frequency of occurrence. The concentrations of the LC-PCBs ranged from not detected to 11,147 ng g^{-1}, while the concentrations of higher

chlorinated PCBs (HC-PCBs) (hexa- to deca-PCBs) ranged from not detected to 2978 ng g^{-1}. The LC-PCBs and HC-PCBs constituted 0.0 to 100% and 0.0 to 48.7% respectively of the total PCBs. The HC-PCBs can be dechlorinated to some LC-PCBs under anoxic conditions with time (Mattura et al., 2016; Combi et al., 2016). Nevertheless, the prevalence of LC-PCBs as compared with HC-PCBs in the soil profiles of the floodplain is related to their migration capacity, high water solubility, and ability to accumulate in the atmosphere and be scavenged from the atmosphere by precipitation (Gao et al., 2013). Given the high concentrations of LC-PCBs in the soil profiles of the floodplain, it is unlikely that PCBs in these soils arise from long-distance migration. Thus, PCBs in the floodplain soils of the LRRN are related to local contamination sources.

The dl-PCBs were detected in 64% of the floodplain soil samples with concentrations between not detected and 9027 ng g^{-1} and represented 7.0 to 81% of the Σ28 PCBs. The non-ortho PCBs, which are also called the coplanar PCBs (PCB77, PCB81, PCB126, and PCB169), are the dominant dl-PCBs in the soil samples. The concentrations of the non-ortho PCBs ranged from not detected to 7354 ng g^{-1} and represented 3.6 to 65.9% of the Σ28 PCBs, while the concentrations of the mono-ortho dl-PCBs (PCB105, PCB114, PCB118, PCB123, PCB156, PCB157, PCB167, and PCB189) ranged from not detected to 1673 ng g^{-1} and constituted 2.3 to 31.9% of the Σ28 PCBs. Of these coplanar PCBs, PCB126, PCB77, and PCB81 had the highest mean levels at depths of 0–15, 15–30, and 30–45 cm respectively. The indicator PCBs [i-PCBs] (PCB28, PCB52, PCB101, PCB118 (dl), PCB138, PCB153, and PCB180) are the most frequently analysed PCB congeners in monitoring programmes. The i-PCBs were detected in 74% of the soils with concentrations between not detected to 1892 ng g^{-1}. The i-PCBs represented 16.3 to 100% of the Σ28 PCBs.

Ecological risk assessment of PCBs in floodplain soils

A comparison of the total PCB concentrations in the floodplain soils with those of sediment/soil quality guidelines is presented in Table 4. The concentrations of PCBs in 64% of the floodplain soil samples in our study were higher than the

Table 4 PCBs concentrations in floodplain soils in comparison with soil quality guidelines

	Conc. range	ERL[a]	ERM[a]	ISQGs/TEL[b]	PEL[b]	TEC[c]	PEC[c]	< ERL (%)	ERL-ERM (%)	> ERM (%)	< TEL (%)	TEL-PEL (%)	> PEL (%)	< TEC (%)	TEC-PEC (%)	> PEC (%)
∑28PCBs	ND-11151	22.7	180	21.5	187	60	676	5 (13)	9 (23)	25 (64)	5 (13)	9 (23)	25 (64)	9 (23)	13 (33)	17 (44)

[a]Long and Morgan (1990); [b]MacDonald et al. (1996); [c]MacDonald et al. (2000). ERL, effect range low; ERM, effect range medium; ISQGs, interim sediment quality guidelines; PEL, probable effect level; TEC, threshold effect concentration; PEC, probable effect concentration

respective stipulated effect range medium (ERM) and probable effect level (PEL) values, while the levels of PCBs in 44% of the soil samples exceeded the probable effect concentration (PEC) value. This signifies a high ecological risk to organisms arising from exposure to PCBs in the floodplain soils of the LRRN. The computed ecological risk values for PCBs in the floodplain soils are displayed in Fig. 3. The potential ecological risk (ERI) of PCBs in the soil profiles varied from 0.0 to 44,604, with site FP4 having the highest index value. With the exception of sites FP10 and FP13, the ecological risk index values for the other sites in the LRRN were greater than 320. This suggests that there is a very high ecotoxicological risk for exposure of organisms to PCBs in the floodplain soils.

Human health risk assessment of PCBs in the floodplain soils

Toxic equivalence of PCBs in floodplain soils

The TEQ values for dl-PCBs in the floodplain soils are given in Table 5. The total toxic equivalence (ΣTEQ) value for the dl-PCBs in the soils was 2.96 ng TEQ g^{-1}, with PCB126 contributing 75% of the TEQ value in comparison to the other dl-PCB congeners. The TEQ value obtained in this study was above the maximum limit of 21.5 pg TEQ g^{-1} set by the Canadian Council of Ministers of Environment (CCME, 2007) and the 20 ng WHO-TEQ kg^{-1} set by the World Health Organization (WHO) (Andersson et al., 2011). The TEQ value obtained in this study was also above the screening level of 50 pg TEQ g^{-1} set by the Agency for Toxic Substances and Disease Registry (ATSDR, 1998). According to the ATSDR (1998), a TEQ value of soil above 50 pg TEQ g^{-1} requires evaluation of site-specific factors including pathway and soil cover analyses. The TEQ value for the floodplain soils of the LRRN indicates that there is a significant health risk for organisms exposed to PCBs in the floodplain soil. The TEQ values obtained in our study were far above the range of 1.3 to 20.9, 1.4 to 82.6, and 1.0 to 55 pg g^{-1} TEQ reported for floodplain soils of the Shiawassee River, Saginaw River, and Saginaw Bay respectively (Kannan et al., 2008), and 0.04 to 853 pg g^{-1} TEQ reported for wetland soils (Zhao et al., 2016).

Non-carcinogenic and carcinogenic risk

The hazard indices and total cancer risks associated with exposure to PCBs in the floodplain soils by children and adults are shown in Table 5.

The hazard quotients (HQ) for human exposure to PCBs in the floodplain soils followed the order: $HQ_{ing} > HQ_{dermal} > HQ_{inh}$. The HQ values for the ingestion and dermal contact routes were higher for children than for adults, but the HQ_{inh} values were higher for adults than for children. The higher HQ_{ing} and HQ_{dermal} values for children are attributed to their characteristic hand-to-mouth habits and also to the exposure of their skin to soil when playing, while the higher HQ_{inh} values for adults are attributed to their longer exposure times. The HI values for the exposure of children and adults were 5.93×10^4 and 8.31×10^3 respectively. In this study, the HI values for

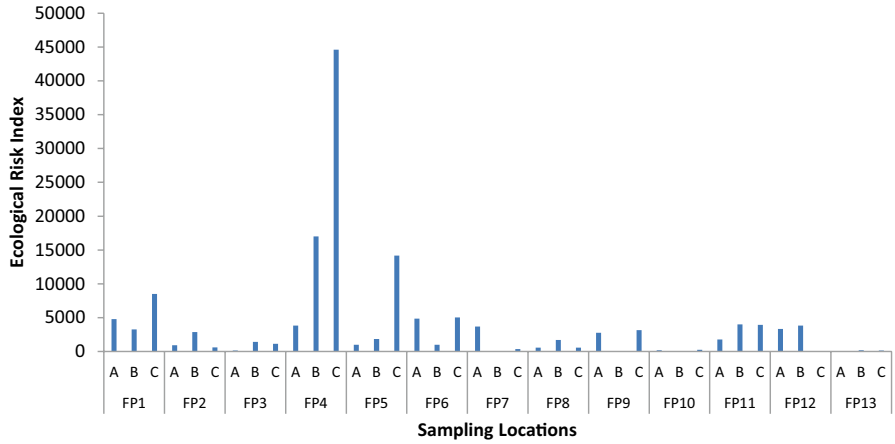


Fig. 3 Ecological risk index of PCBs in the floodplain soils of the lower reaches of the River Niger: **A** 0–15 cm depth, **B** 15–30 cm depth, and **C** 30–45 cm depth

Table 5 Total toxic equivalence (ΣTEQ), hazard indices, and total cancer risks of PCBs in floodplain soils

PCB congeners	ΣTEQ	Hazard index								Total cancer risk							
		Child				Adult				Child				Adult			
		HQ_{ing}	HQ_{inh}	HQ_{dermal}	HI	HQ_{ing}	HQ_{inh}	HQ_{dermal}	HI	$Risk_{ing}$	$Risk_{inh}$	$Risk_{dermal}$	Total cancer risk	$Risk_{ing}$	$Risk_{inh}$	$Risk_{dermal}$	Total cancer risk
PCB77	1.93×10^{-2}	352	4.08×10^{-3}	138	**490**	44.0	1.70×10^{-2}	24.6	**68.7**	3.21×10^{-2}	6.20×10^{-9}	1.26×10^{-2}	4.46×10^{-2}	2.21×10^{-3}	1.42×10^{-8}	1.23×10^{-3}	3.44×10^{-3}
PCB81	7.20×10^{-2}	1330	1.56×10^{-2}	523	**1860**	167	6.51×10^{-2}	93.2	**260**	1.20×10^{-1}	2.23×10^{-8}	4.69×10^{-2}	1.67×10^{-1}	8.24×10^{-3}	5.12×10^{-8}	4.60×10^{-3}	1.28×10^{-2}
PCB105	2.94×10^{-4}	5.44	6.37×10^{-5}	2.13	**7.58**	0.68	2.66×10^{-4}	0.38	**1.06**	4.88×10^{-4}	9.12×10^{-11}	1.91×10^{-4}	6.80×10^{-4}	3.36×10^{-5}	2.09×10^{-10}	1.88×10^{-5}	5.24×10^{-5}
PCB114	2.90×10^{-4}	5.37	6.28×10^{-5}	2.10	**7.47**	0.67	2.62×10^{-4}	0.38	**1.05**	4.81×10^{-4}	8.98×10^{-11}	1.89×10^{-4}	6.70×10^{-4}	3.31×10^{-5}	2.06×10^{-10}	1.85×10^{-5}	5.16×10^{-5}
PCB118	1.79×10^{-3}	33.1	3.87×10^{-4}	13.0	**46.1**	4.14	1.61×10^{-3}	2.31	**6.45**	2.97×10^{-3}	5.54×10^{-10}	1.16×10^{-3}	4.13×10^{-3}	2.04×10^{-4}	1.27×10^{-9}	1.14×10^{-4}	3.18×10^{-4}
PCB123	7.78×10^{-4}	14.4	1.69×10^{-4}	5.65	**20.1**	1.80	7.03×10^{-4}	1.01	**2.81**	1.29×10^{-3}	2.41×10^{-10}	5.07×10^{-4}	1.80×10^{-3}	8.89×10^{-5}	5.53×10^{-10}	4.97×10^{-5}	1.39×10^{-4}
PCB126	2.23	40,800	4.73×10^{-1}	16,000	**56,800**	5100	1.97	2850	**7950**	3.71	7.18×10^{-7}	1.46	5.17	2.56×10^{-1}	1.65×10^{-6}	1.43×10^{-1}	3.98×10^{-1}
PCB156	1.44×10^{-3}	32	3.12×10^{-4}	10.4	**42.4**	3.33	1.30×10^{-3}	1.86	**5.19**	2.87×10^{-3}	4.46×10^{-10}	9.37×10^{-4}	3.81×10^{-3}	1.64×10^{-4}	1.02×10^{-9}	9.19×10^{-5}	2.56×10^{-4}
PCB157	3.55×10^{-4}	5.48	7.69×10^{-5}	2.58	**8.05**	0.82	3.21×10^{-4}	0.46	**1.28**	4.91×10^{-4}	1.10×10^{-10}	2.31×10^{-4}	7.22×10^{-4}	4.06×10^{-5}	2.52×10^{-10}	2.27×10^{-5}	6.32×10^{-5}
PCB167	3.65×10^{-4}	6.77	7.93×10^{-5}	2.65	**9.42**	0.85	3.30×10^{-4}	0.47	**1.32**	6.07×10^{-4}	1.13×10^{-10}	2.38×10^{-4}	8.45×10^{-4}	4.18×10^{-5}	2.60×10^{-10}	2.33×10^{-5}	6.51×10^{-5}
PCB169	6.23×10^{-1}	11.6	1.35×10^{-1}	4.53	**16.2**	1.44	5.64×10^{-1}	0.81	**2.81**	1.04	1.93×10^{-7}	4.06×10^−1	1.44	7.13×10^{-2}	4.44×10^{-7}	3.98×10^{-2}	1.11×10^{-1}
PCB189	8.83×10^{-4}	16.4	1.91×10^{-4}	6.41	**22.8**	2.04	7.98×10^{-4}	1.14	**3.19**	1.47×10^{-3}	2.41×10^{-10}	5.75×10^{-4}	2.04×10^{-3}	1.01×10^{-4}	6.28×10^{-10}	5.64×10^{-5}	1.57×10^{-4}
Total	**2.96**	**42,600**	**6.29E-01**	**16,700**	**59,300**	**5330**	**2.62**	**2980**	**8310**	**4.91**	$\mathbf{9.42\times10^{-7}}$	**1.93**	**6.84**	$\mathbf{3.38\times10^{-1}}$	$\mathbf{2.16\times10^{-6}}$	$\mathbf{1.89\times10^{-1}}$	$\mathbf{5.27\times10^{-1}}$

the exposure of children and adults were > 1, indicating the presence of adverse non-carcinogenic risks for human exposure to PCBs in the floodplain soils.

The cancer risk values for human exposure to PCBs in the floodplain soils were also in the order of $Risk_{ing} > Risk_{dermal} > Risk_{inh}$. Like the HQ values, the risk via ingestion and dermal contact was higher in children than in adults but the risk via inhalation was higher in adults than in children. The total cancer risk values of PCBs in the floodplain soils were 6.84 for children and 5.27×10^{-1} for adults. The total cancer risk values were higher than the US EPA (2010) risk level of 1×10^{-6}. This indicates that there is an elevated carcinogenic risk associated with human exposure to the floodplain soil.

Principal component analysis of PCBs in the floodplain soils

The result of the PCA of 28 PCBs in the floodplain soils is shown in Supplementary Material Table S6. Two component factors were identified for each of the depths and the factor loadings for the various soil layers were entirely different which may be related to the interplay between flooding events, the contaminant loads, deposition rate, dechlorination, and changes in source inputs over the years. At a depth of 0–15 cm, the two components accounted for 84.7% of the variance in the data. Factor 1 explained 49.3% of the variance and was dominated by high positive loading factors for tri-PCBs, tetra-PCBs, and penta-PCBs. The penta-PCBs are used as additives in paints, while tri-PCBs are used as transformer oils. The tetra-PCBs were among the prominent PCBs in air around open burning sites for circuit boards and cable wires (Xing et al., 2009), and soil around municipal solid waste incinerators (Zhang et al., 2014). Therefore, factor 1 relates to PCBs associated with the use of paints, discharges from electrical transformers, and burning of electronic and municipal solid wastes (Ren et al., 2007; Xing et al., 2009; Yadav et al., 2018). Factor 2 represented 35.4% of the variance and consists of high positive loadings for di-PCBs, hexa-PCBs, and hepta-PCBs. Di-PCBs are associated with dechlorination of higher PCB homologues (Wu et al., 2012), long-range atmospheric migration processes, and inadvertent sources, whereas hexa- and hepta-PCBs were prominent in air around e-waste recycling sites (Chakraborty et al., 2013, 2016). Therefore, factor 2 contained PCBs related to dechlorination processes

and those arising from open burning of electronic wastes especially plastic casings. The two component factors of PCBs in soils from the 15–30 cm depth represented 94.7% of the total variance. Factor 1 explained 67.7% of the variance and has high positive loading values for di-PCBs, tri-PCBs, tetra-PCBs, and hexa-PCBs, while factor 2 was dominated by penta- and hepta-PCBs and represented 27% of the variance. The PCBs in factor 1 are linked to atmospheric deposition and long-range transport processes, paint pigments, and components of electrical transformers and those emitted during burning of electronic wastes. For instance, di- and tetra-PCBs are by-products associated with the synthesis of azo and phthalocyanine pigments. These pigments are components of residential and industrial paints (Butcha et al., 1985; Knobeloch et al., 2012). Factor 2 contained PCB homologues associated with components of paints. In the case of the 30–45 cm depth, the two components accounted for 94.7% of the variance in the data. Factor 1 explained 61.8% of the variance in the data and was dominated by tetra-, penta-, hexa-, and hepta-PCBs. The PCB homologues in factor 1 are related to the use of paints, burning of electronic wastes, and discharges from secondary aluminium and copper metallurgy (Zhang et al., 2014). The penta- and hexa-PCBs are formed as inadvertent by-products in chemical factories and power plants (Zhang et al., 2014). Factor 2 explained 32.9% of the variance and was characterized by high positive loading values for di- and tri-PCBs. Tri-PCBs are used as dielectrics in transformers and could also be discharged from production and recycling of carbon-free papers (Wang et al., 2016), while di-PCBs are related to dechlorination processes and long-range atmospheric migration. The PCB homologues in factor 2 are related to discharges from electrical capacitors, and atmospheric deposition and long-range transportation.

Conclusion

This study has shown that floodplain soils of the LRRN are severely contaminated with PCBs. The concentrations of Σ28 PCBs in the majority (64%) of the floodplain soils exceeded the health-based screening level for total PCBs specified by the US EPA and were above those reported for other floodplain soils in other regions of the world. The PCB concentrations and homologue distribution patterns in soil profiles of the floodplain of the LRRN showed remarkable differences with respect to sites and depths. The ecological risk index indicates that there is an ecological risk for biotas in the floodplain soils. The results of the health risk evaluation suggest potential cancer and non-cancer risks to humans from exposure to PCBs in these soil profiles. The PCA indicated that PCBs in the floodplain soils originated from burning of circuit boards and cable wires, the use of paints, discharges from electrical transformers, atmospheric deposition, and long-range transportation.

Author contribution Andrew E. Aziza: Methodology, Resources, Investigation, Writing—original draft; Chukwujindu M. A. Iwegbue: Conceptualization, Methodology, Formal analysis, Writing—original draft, Supervision; Godswill O. Tesi: Resources, Visualization, Formal analysis; Godwin E. Nwajei: Methodology, Resources, Investigation, Supervision; Bice S. Martincigh: Writing—review and editing, Supervision.

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Data availability All data associated with this article are available in the text and supplementary material.

Declarations

Ethics approval Ethical approval is not required since this study does not involve the use of animals or humans in the experiments.

Consent to participate The study does not involve the use of animals or humans in the experiments and therefore requires no consent to participate.

Consent for publication All the authors gave their consent to publish this article in EMAS.

Conflict of interest The authors declare no competing interests.

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