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HUMAN HEALTH RISKS ASSESSMENT OF POLYBROMINATED DIPHENYL ETHERS IN FLOODPLAIN SOILS OF THE LOWER REACHES OF RIVER NIGER.

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ABSTRACT

The concentrations of the 39 PCBDs in the floodplain soils of the lower reaches of River Niger, Nigeria, were determined with the aim of providing information on the contamination level, sources, and ecological and human health risks in the soils. Soil samples were collected from thirteen (13) different locations and three depths along the floodplain. Soil samples were soxhlet extracted using dichloromethane (DCM)/n-Hexane and purified with florisil and silica gel column. The PCBDs were quantified using a gas chromatography-mass spectrometry. Similarly, the average concentrations of Σ39 PBDEs in soils of 15-30cm depth were higher than that of 0-15cm and 30-45cm. The 15-30cm and 30-45cm depths of FP12 and 15-30cm depth of FP13 have higher concentrations (1297ng/g^{-1}, 1226ng/g^{-1} and 1169ng/g^{-1} respectively) relative to other samples. On average, the concentration of Σ39 PBDEs in the downstream section (FP9 to FP13) was higher than those in the upstream (FP1 to FP5) and midstream section (FP6 to FP8) of the study area. The total cancer risk values associated with these pollutants in the floodplain soils were higher than the potentially acceptable target risk value of 10^{-6} set by the US EPA signifying a high potential human carcinogenic risk in the floodplain soil of LRRN. Based on the Principal component analysis and diagnostic source ratios, the major sources of metals in these soils include industrial emissions, use of agrochemicals, and traffic emissions as well as the drilling and production activities of the oil and gas industries. The PBDEsD could be from atmospheric deposition and long range transport process as well as component of electrical transformers and those emitted during burning of electronic wastes. The PBDEs could be from both fresh and historical inputs; PBDEs could be from technical mixture used for paints, plastics, hydraulic fluids, dielectric insulating fluids for transformers, and capacitors;

KEYWORDS: Floodplain soils, PBDEs, River Niger, Hazard index, and Total cancer risk

INTRODUCTION.

The two phenyl rings that make up polybrominated diphenyl ethers (PBDEs) are connected by an oxygen atom (Figure 4). Depending on the quantity and position of the bromine atoms in the phenyl rings, 209 different PBDE congeners may result from substituting the phenyl rings (EFSA, 2011). Since their inception in the 1970s, PBDEs have been utilized in a wide variety of polymeric materials, including plastics, foams, resins, and adhesives, as brominated flame retardants (BFRs) (Besis and Samara, 2012; McGrath, Ball and Clarke, 2017). Environmental problems associated with risk to human health have not been resolved despite the use of novel brominated flame retardants (NBFRs), despite widespread environmental contamination (even in polar regions) and toxic effects being well-

soil biota, eating food contaminated with PBDEs, and accidental oral, cutaneous, and inhalation exposure in humans and animals (Assis *et al.,*

documented (McGrath, Ball and Clarke, 2017). Due to soil pollution, novel brominated flame retardants continue to pose a risk to individuals and ecosystems. They have harmful patterns that are similar to PBDEs. Commercial PBDE congener chemical mixes were outlawed internationally and covered by the Stockholm Convention (Besis and Samara, 2012; Stockholm Convention, 2021). PBDEs are classified as persistent organic pollutants based on well-established evidence of their ubiquity, transboundary atmospheric transport, and deposition capabilities, photo-stability, ecological risk, and concerns for human health (Bai *et al.,* 2018; Chakraborty *et al.,* 2018; O'Brien *et al.,* 2019). Environmental PBDEs are linked to cumulative and harmful impacts on the health of

2012; Kolpin *et al.,* 2013; Harmouche-Karaki *et al.,* 2019).

MATERIALS AND METHODS

Description of the Study Area

The River Niger is one of the principal river of West Africa, extending about 4,180 km (2,600 miles). Its drainage basin is 2,117,700 km^2 (817,600 sq/metre) in area. River Niger arises from Fouta Djallon highland in Guinea arriving in Nigeria through Kebbi State and flows through to the Atlantic Ocean (Olatunji, and Osibanjo, 2012). The study area is within the extent of the River Niger stretch traversing Asaba to Aboh area in the lower River Niger regime of Nigeria (Figure 1). The area lies between longitude 6.16^0 to 6.430 E and latitude 6.02^0 to 6.43^0 N. The study area has well defined dry and rainy seasons, and a total rainfall of between 2,700 and 3,000 mm per year spreading over the months of April to October. (Tesi *et al*., 2016; Iwegbue *et al*., 2020). The maximum mean daily temperature ranged from 25^0C to 33^0C throughout the year. The mean relative humidity varies from 65 to 80% (Tesi *et al*., 2016; Iwegbue *et al*., 2020). The soil is hydromorphic and is characterized by rampant flooding and water logging which result from poor drainage, high soil bulk density and crusting, and poor urban settlement and human activities. Flooding is experienced at the peaks of the rainy season (July to September) (Ogbodo,2011) every year and could cover the entire floodplain. A combination of heavy rain and good sunshine along with adequate soil nutrients has generated thick vegetation cover in the study area. The vegetation are made up of mangrove swamp forest, tall evergreen trees including pines with prolific undergrowth of entangled shrubs (Olatunji and Osibanjo, 2012; Oyo-Ita *et al*., 2011). The River Niger system sustains an extensive biological community, hosting diverse ecosystems. The upstream section of the area is characterized by urbanization, industrial development and agricultural development. The mid-stream section (FP1-FP3) is a typical rural setting and the main activity in the area is farming. At the downstream section (FP4-FP6), the major activity in these areas is canoe making, fishing and farming. There are clusters of oil wells, flow stations, pipelines, gas plant, independent power plant and multiple gas flaring points located few kilometers upstream of stations (FP7-FP9). The approximate distance between the uptream sampling points and downstream sampling point is about 102km. The midstream sampling points were approximately 32km from the upstream sampling points.

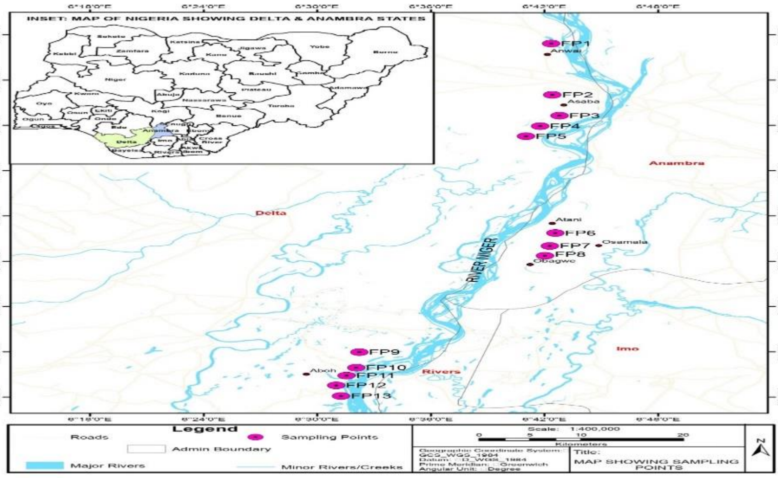


Figure 1: Map of the Study Area

Sample Collection

Soil samples were collected from 13 different locations designated along the floodplain of the River Niger. The soil samples were collected for analysis were stored in polythene bags. Samples were labeled properly and transported to the laboratory. In the laboratory, the soil samples at 0-15 cm, 15-30 cm and 30-45 cm depths respectively, using stainless steel auger. This was done for two years, 2018 and 2019. Soil samples were air dried in the dark, sieved through 2 mm mesh, and stored at - 4 ^{0}C before analysis.

METHOD OF ANALYING PBDEs.

Extraction solvent (hexane) (10 ml) and acetone (10 ml) of the well mixed sample was transferred into a 250 ml reagent breaker. 50 ml of the solvent was added to the 250 ml reagent bottle or beaker. The mixture was shaken for 5minuties with occasional venting. The mixture was left to settle by gravitation, the organic layer was separated into a round-bottom flask. The process was repeated by adding 50 ml of solvent and was allowed to settle and collected into the round-flask. The sample extract was concentrated using rotary Evaporator, to 2 ml. 5 ml hexane was added to the extract and was evaporated to reduce the volume to 2 ml. The final 2 ml Hexane was obtained. The sample was ready for sulpuric acid/ permanganate cleanup.

Contamination/Pollution Index

Assessment of soil for heavy metal pollution based on absolute metal content values provided inadequate information on the significance of the value obtained with the intrinsic soil feature and how the values are related to the maximum allowable limits for the metals (Iwegbue, 2014; Iwegbue.*et al.,* 2010). The contamination/pollution index was used to highlight the degree of contamination/pollution of the study sites. The contamination/pollution index was computed as the ratio between metal effectively measured by chemical analysis to reference value. The contamination/pollution index was derived by employing the contamination/ pollution index as defined by Lacutusu (2000).

$$\frac{\mathrm{C}}{\mathrm{PI}} = \frac{Concentration\ of\ metal\ in\ soil}{Target\ value} \qquad (6)$$

In the study, the guideline values for metals as specified by the Department of Petroleum Resources of Nigeria was adopted as reference values (DPR, 2002). The conversion formula used for the C/P index varies from one country to another because regulatory control limits vary from one country to another. C/P1> 1 refers to the pollution range while C/PI<1 define the contamination range. Metals in the environment may have synergistic, additive, or antagonistic effect on one another. For this reason, the Multiple Pollution Index (MPI) was derived from the addition of the C/PI values for the individual metals that were greater than 1. The computed C/P index and multiple pollution index (MPI) values was interpreted according to the scheme provided below. The categorization of degree of contamination/pollution based on this index is as follows: <0.1 = Very slight contamination; 0.10-0.25 = Slight contamination; 0.26-0.5=Moderate contamination; 0.51-0.75 = Severe contamination; 0.76-1.00 = Very severe contamination; 1.1-2.0 = Slight pollution. 2.1-4.0 = Moderate pollution; 4.1-8.0 = Severe pollution; 8.1-16.0 = Very severe pollution; >16.0 = Excessive pollution (Lacatusu, 2000).

Quantification of Enrichment Factor (EF)

The enrichment factor (EF), due to its universal formula, is a relatively simple and straightforward tool for measuring the extent of enrichment and for comparing the contamination levels of different environmental media (Agca & Ozdel 2014; Iwegbue, 2014). Heavy metals enrichment factor was used to distinguish between metal originating from human activities and those of natural processes. Enrichment factor of metals in the soil was calculated following the equation of Reimann and De Caritat (2000).

$$\mathrm{EF} = \frac{Cn\ (test\ element)}{Cn\ (Reference)} \div \frac{Bn\ (test\ element)}{Bn\ (Reference)} \qquad (7)$$

Where,

Cn = Concentration of the test metal in the sample

Cn_{ref} = Concentration of the reference metal in the sample

Bn test element = background concentration of the test metal in crustal rock

Bn_{ref} background concentration of the reference metal in crustal rock (Reimann and De Caritat, 2000). The Crustal Abundance Values (CAV) for the respective metals (Turekian and Wedepohl, 1961) were used as background concentrations for the estimation of the enrichment factors. Five contamination categories are recognized on the basis of the enrichment factor (Suntherland, 2000; Loska and Wiechula, 2003). EF<2 =Deficiency to minimal enrichment. EF=2-5 = Moderate enrichment. FE=5-20 = Significant enrichment. EF=20-40 =Very high enrichment. EF>40 =extremely high enrichment.

Pollution Load Index

Pollution load index was estimated using the equation.

$$\mathrm{PLI} = \sqrt[n]{CF1 \times CF2 \times CF3 \times CF4} \times \ldots CFn \qquad (8)$$

Where n = number of metals studied

CF = Contamination factor

$\mathrm{CF} = \frac{Cs}{Cn}$

Where Cs and Cn are metal concentrations for samples and background respectively. Also, the background concentration used are the crustal abundance values of the respective metals (Turiekian & Wedepohl, 1961). PLI provides a simple but a comparative means of assessing site quality where a value of PLI <1 denotes perfection; PLI=1 present a baseline level of pollutant and PLI>1 indicate deteriorating site quality.

Ecological Risk Assessment

The method of determining ecological risks of metals was originally introduced by Hakanson (1980). The index has been applied for ecological risks assessments of metals in soil (Saeedi *et al.,* 2012; Li *et al.,* 2013; Shi *et al.,* 2014). The potential ecological risk index was given by the equation.

$$RI = \Sigma Er \qquad (9)$$

Where $Er = Tr \times CF$

$$CF = \frac{Cs}{Cn}$$

Where; Tr is the biological toxic factor of a single metal. Hekanson (1980) demonstrated Tr value for Cd, Cu, Pb, Cr, Zn, Ni, Co and Mn to be 30, 5, 5, 2, 1, 5, 2 and 1 respectively. CF is contamination factor, Cs and Cn are metal concentrations for samples and background respectively. Also, the background concentrations used are the crustal abundance values of the respective metals (Turiekian &Wedepohl, 1961). Er is the ecological risk of each metal and RI shows the ecological risk of multiple metals. The Er and RI have been classified into five and four categories depending on their values respectively. Er value <40 denotes low potential ecological risk; ≥40<80 moderate potentials ecological risk; ≥80<100 strong potential ecological risk; ≥100<320 very strong potential ecological risk and ≥320 extremely strong potential ecological risk. RI value <150 indicates low ecological risk; ≥150<300 moderate ecological risk; ≥300<600 strong ecological risk and ≥600 very strong ecological risk.

RESULTS AND DISCUSSION

Summary statistics of PBDEs concentrations (ng/g^{-1}) in floodplain soils for 2018

	0-15 cm Depth					15-30 cm Depth					30-45 cm Depth				
	MEAN	SD	MEDIAN	MIN	MAX	MEAN	SD	MEDIAN	MIN	MAX	MEAN	SD	MEDIAN	MIN	MAX
BDE-1	4.96	8.72	1.09	0.04	32.2	5.93	9.38	0.87	0.24	33.5	3.10	5.82	0.67	0.20	21.2
BDE-2	5.56	8.15	2.64	0.05	28.8	3.73	5.16	0.53	0.26	14.6	3.12	5.87	0.67	0.09	21.2
BDE-3	6.49	11.8	2.37	0.05	43.9	3.35	4.69	1.00	0.33	15.8	2.91	5.82	0.56	0.11	20.0
BDE-7	15.6	33.9	0.90	0.04	119	3.36	5.81	0.75	0.37	21.2	2.74	3.97	0.67	0.09	11.2
BDE-8	4.40	6.08	1.28	0.03	21.5	3.68	4.66	0.82	0.14	14.9	1.32	1.79	0.53	0.09	6.79
BDE-10	4.09	6.64	1.42	0.10	24.2	3.75	4.46	0.76	0.04	11.1	1.17	1.99	0.65	0.07	7.59
BDE-11	4.35	6.78	0.97	0.03	24.7	4.22	5.35	0.63	0.20	16.1	1.13	1.64	1.00	0.07	6.37
BDE-12	3.06	5.14	1.04	0.04	18.3	10.1	22.3	0.53	ND	81.1	1.50	2.24	0.40	0.07	6.59
BDE-13	3.18	5.84	0.81	0.06	20.7	5.35	8.25	0.77	0.03	25.6	1.51	2.79	0.56	0.08	9.71
BDE-15	4.35	6.08	1.26	0.04	22.1	3.79	5.18	0.56	<LDQ	16.2	1.37	2.21	0.52	0.04	7.34
BDE-17	3.99	6.65	0.86	<LDQ	22.6	3.23	3.86	0.59	0.03	10.6	1.18	1.16	0.75	0.05	4.03
BDE-25	2.65	4.72	0.69	0.07	16.6	3.53	4.44	0.58	<LDQ	11.1	1.04	1.51	0.50	0.04	5.66
BDE-28	4.15	7.05	0.36	0.05	24.4	3.55	4.27	1.13	0.02	13.0	1.13	1.54	0.59	0.05	5.73
BDE-30	0.06	0.10	<LDQ	<LDQ	0.31	0.08	0.11	0.00	<LDQ	0.27	0.05	0.11	0.00	<LDQ	0.40
BDE-32	1.24	1.64	0.63	<LDQ	5.66	1.79	2.52	0.24	<LDQ	6.12	0.78	1.44	0.20	<LDQ	5.15
BDE-33	2.96	4.30	0.50	0.04	13.7	2.94	4.28	0.54	0.02	13.2	0.81	1.45	0.51	0.03	5.59
BDE-35	0.76	0.94	0.34	0.02	2.81	1.55	1.84	0.39	<LDQ	4.80	1.31	3.41	0.23	<LDQ	12.5
BDE-37	12.0	24.6	1.73	0.04	89.7	5.62	7.57	0.52	<LDQ	24.4	2.16	4.20	0.40	<LDQ	14.9
BDE-47	1.86	2.14	1.00	0.02	7.03	2.72	3.92	0.61	<LDQ	10.3	2.23	3.98	0.58	0.02	12.7
BDE-49	5.26	9.13	1.69	0.03	33.2	7.44	12.8	0.58	<LDQ	45.6	1.84	3.23	0.53	0.02	9.28
BDE-66	2.08	4.24	0.62	0.03	15.8	1.56	2.09	0.49	<LDQ	7.15	1.80	3.00	0.21	0.06	7.73
BDE-71	3.39	5.92	0.59	<LDQ	17.0	1.84	3.34	0.46	<LDQ	12.5	2.83	6.30	0.19	<LDQ	22.4
BDE-75	11.8	34.5	0.83	<LDQ	126	5.73	10.6	0.71	<LDQ	37.74	1.12	1.43	0.49	0.08	5.16
BDE-77	22.1	31.4	4.69	0.05	94.2	22.8	44.6	1.57	0.03	133	16.4	46.3	0.51	0.09	169
BDE-85	12.4	21.5	1.16	0.04	62.4	19.37	42.4	1.18	<LDQ	145	23.1	49.4	0.61	0.06	172
BDE-99	2.56	6.70	0.55	0.04	24.7	6.10	12.0	0.39	<LDQ	42.4	4.27	13.8	0.16	0.06	50.1

BDE-100	3.74	4.77	1.79	0.07	13.5	20.2	45.7	1.65	<LDQ	153	3.03	5.96	1.02	0.10	21.7
BDE-116	1.31	1.65	0.67	0.02	5.88	3.19	6.43	0.28	<LDQ	23.5	3.31	8.44	0.35	0.04	30.9
BDE-118	24.6	39.7	5.69	0.11	108	18.6	36.1	1.48	0.05	105	15.4	35.2	1.15	0.11	118
BDE-119	5.36	10.9	0.65	0.05	34.1	15.5	45.2	0.37	<LDQ	165	21.2	42.1	1.04	0.04	143
BDE-126	15.4	34.2	1.68	0.14	120	8.15	16.5	1.94	0.06	61.2	6.18	9.55	1.56	0.18	26.6
BDE-137	17.3	27.8	1.49	0.17	78.5	19.4	43.0	2.40	0.08	158	24.5	71.2	1.71	0.23	260
BDE-153	1.79	2.45	0.60	0.04	7.12	8.09	13.4	1.05	0.04	41.9	1.78	2.35	0.68	0.19	7.00
BDE-154	2.80	3.68	1.18	0.06	12.5	10.6	20.6	1.84	0.05	74.7	6.17	17.8	0.55	0.15	65.2
BDE-155	1.66	1.91	0.73	0.06	6.20	19.2	40.6	3.76	0.04	150	5.66	14.0	0.68	0.14	51.6
BDE-166	5.37	9.64	0.74	0.07	34.9	8.75	16.3	1.84	0.04	48.7	6.96	14.2	1.58	0.09	51.6
BDE-181	8.14	13.5	1.91	0.15	47.9	13.3	35.3	1.62	0.13	130	4.55	7.20	1.34	0.35	25.2
BDE-183	4.91	14.5	0.41	0.03	53.1	24.7	53.0	0.72	0.05	189	5.01	9.34	0.49	0.10	30.7
BDE-209	2.36	3.02	1.25	0.09	9.01	11.4	29.6	1.50	0.04	109	13.1	37.2	1.11	0.43	136
TOTAL	**240**	**263**	**197**	**7.30**	**998**	**318**	**436**	**98.7**	**4.37**	**1297**	**199**	**335**	**42.1**	**4.68**	**1226**
Mono-BDEs	17.0	24.2	8.40	0.15	71.0	13.0	15.5	3.13	0.93	44.9	9.14	17.3	2.07	0.40	62.4
Di-BDEs	39.0	54.4	10.3	0.37	157	34.3	45.9	4.27	1.82	128	10.7	13.9	5.23	0.52	52.1
Tri-BDEs	27.8	38.9	5.49	0.25	110	22.3	24.2	4.08	0.07	58.4	8.45	9.75	4.20	0.16	30.5
Tetra-BDEs	46.5	53.9	27.1	0.16	151	42.1	62.9	6.28	0.03	199	26.2	54.1	2.95	0.27	199
Penta-BDEs	65.4	98.6	9.43	0.47	351	91.1	180	6.66	0.11	619	76.5	135	4.83	0.60	493
Hexa-BDEs	28.9	39.3	6.80	0.40	129	65.9	94.1	24.2	0.25	300	45.1	102	5.34	0.83	370
Hepta-BDEs	13.1	21.0	2.61	0.18	65.6	38.0	70.9	2.29	0.18	198	9.55	15.8	1.84	0.46	55.9
Deca-BDEs	2.36	3.02	1.25	0.09	9.01	11.4	29.6	1.50	0.04	109	13.1	37.2	1.11	0.43	136

Summary statistics of PBDEs concentrations (ng/g^{-1}) in floodplain soils for 2019

	0-15cm Depth					15-30cm Depth					30-45cm Depth				
	MEAN	SD	MEDIAN	MIN	MAX	MEAN	SD	MEDIAN	MIN	MAX	MEAN	SD	MEDIAN	MIN	MAX
BDE-1	4.29	8.65	0.55	0.02	32.2	5.50	9.44	0.78	0.24	33.5	2.88	5.88	0.50	0.17	21.2
BDE-2	4.60	7.89	1.39	0.03	28.8	3.35	5.07	0.42	0.13	14.6	2.88	5.94	0.54	0.08	21.2
BDE-3	4.43	6.2	1.19	0.03	22.0	2.88	4.48	0.79	0.22	15.8	2.71	5.86	0.35	0.10	20.0
BDE-7	13.5	32.6	0.60	0.02	119	2.95	5.75	0.72	0.20	21.2	2.21	3.27	0.35	0.08	9.3
BDE-8	3.86	6.07	1.04	0.03	21.5	3.35	4.65	0.74	0.07	14.9	1.15	1.83	0.39	0.08	6.79
BDE-10	3.43	6.53	0.97	0.05	24.2	3.41	4.44	0.42	0.02	11.1	1.03	2.02	0.33	0.06	7.59
BDE-11	3.63	6.65	0.97	0.02	24.7	3.93	5.42	0.42	0.10	16.1	0.96	1.66	0.50	0.06	6.37
BDE-12	2.75	5.14	0.52	0.02	18.3	9.8	22.4	0.31	<LDQ	81.1	1.36	2.17	0.30	0.06	6.14
BDE-13	2.98	5.92	0.41	0.03	20.7	5.09	8.33	0.39	0.02	25.6	1.38	2.83	0.28	0.07	9.71
BDE-15	3.97	6.14	0.63	0.02	22.1	3.33	4.87	0.28	<LDQ	16.2	1.23	2.26	0.34	0.04	7.34
BDE-17	3.67	6.59	0.43	<LDQ	22.6	2.83	3.60	0.41	0.02	10.6	1.02	1.19	0.40	0.05	4.03
BDE-25	2.46	4.76	0.36	0.02	16.6	3.08	4.05	0.31	<LDQ	11.1	0.91	1.55	0.35	0.04	5.66
BDE-28	3.88	7.05	0.25	0.04	24.4	3.17	4.24	0.93	0.01	13.0	0.91	1.50	0.30	0.05	5.73
BDE-30	0.05	0.10	<LDQ	<LDQ	0.31	0.08	0.11	0.00	<LDQ	0.27	0.05	0.11	<LDQ	<LDQ	0.40
BDE-32	1.04	1.59	0.32	<LDQ	5.66	1.52	2.22	0.16	<LDQ	5.68	0.70	1.46	0.17	<LDQ	5.15
BDE-33	2.46	4.01	0.31	0.02	13.7	2.36	3.28	0.49	0.01	9.5	0.69	1.48	0.30	0.03	5.59
BDE-35	0.67	0.94	0.17	0.01	2.81	1.38	1.81	0.21	<LDQ	4.80	1.31	3.41	0.13	<LDQ	12.5
BDE-37	8.3	13.4	1.39	0.02	44.9	4.29	5.40	0.33	<LDQ	14.6	1.51	2.48	0.32	<LDQ	7.5
BDE-47	1.60	2.10	0.50	0.01	7.03	2.26	3.35	0.31	<LDQ	10.3	2.03	4.04	0.50	0.02	12.7
BDE-49	4.94	9.21	1.07	0.02	33.2	6.95	12.8	0.50	<LDQ	45.6	27.5	95.1	0.37	0.02	344
BDE-66	1.93	4.28	0.61	0.02	15.8	1.37	2.03	0.25	<LDQ	7.15	1.46	2.54	0.17	0.05	6.78
BDE-71	2.58	4.65	0.35	<LDQ	15.9	1.64	3.35	0.25	<LDQ	12.5	2.50	5.75	0.14	<LDQ	20.2
BDE-75	6.8	17.3	0.42	<LDQ	63.0	4.07	6.3	0.71	<LDQ	18.9	0.95	1.44	0.34	0.07	5.16
BDE-77	19.2	29.7	4.69	0.03	84.8	21.7	44.8	0.88	0.02	133	15.4	46.3	0.37	0.08	169
BDE-85	11.2	21.4	1.13	0.02	62.4	18.44	42.5	1.06	<LDQ	145	20.5	48.3	0.40	0.05	172
BDE-99	2.41	6.72	0.29	0.02	24.7	5.82	12.0	0.35	<LDQ	42.4	4.19	13.8	0.10	0.05	50.1
BDE-100	3.41	4.83	1.47	0.04	13.5	19.8	45.8	0.92	<LDQ	153	2.03	3.35	0.92	0.09	10.9
BDE-116	1.18	1.68	0.49	0.01	5.88	2.93	6.40	0.19	<LDQ	23.5	3.18	8.47	0.26	0.04	30.9
BDE-118	17.7	29.8	5.12	0.06	101	17.5	36.1	0.92	0.03	105	12.8	32.8	0.82	0.10	118
BDE-119	5.08	11.0	0.41	0.03	34.1	15.3	45.3	0.33	<LDQ	165	19.8	41.4	0.82	0.04	143
BDE-126	15.0	34.4	0.94	0.07	120	5.50	8.7	1.75	0.03	30.6	4.72	7.24	0.78	0.16	23.9

BDE-137	14.8	25.4	0.75	0.09	78.5	17.2	42.8	2.16	0.04	158	3.6	5.5	0.91	0.21	18
BDE-153	1.46	2.15	0.30	0.02	7.12	7.38	13.3	0.68	0.02	41.9	1.63	2.42	0.38	0.16	7.00
BDE-154	2.39	3.44	1.05	0.03	12.5	10.0	20.7	0.92	0.03	74.7	7.13	17.9	0.55	0.15	65.2
BDE-155	1.34	1.48	0.44	0.03	4.35	17.4	36.9	1.88	0.02	135	5.49	14.1	0.48	0.13	51.6
BDE-166	4.99	9.72	0.67	0.04	34.9	8.40	16.5	1.66	0.02	48.7	6.60	14.3	0.81	0.08	51.6
BDE-181	7.45	13.6	1.46	0.08	47.9	13.0	35.5	0.83	0.07	130	4.23	7.34	0.84	0.31	25.2
BDE-183	2.80	7.2	0.28	0.02	26.6	22.4	48.3	0.65	0.03	170	4.18	8.53	0.25	0.10	30.7
BDE-209	1.94	2.52	0.91	0.06	9.01	11.1	29.8	0.75	0.02	109	12.7	37.3	1.00	0.30	136
TOTAL	**200**	**262**	**165**	**4.07**	**907**	**292**	**440**	**49.4**	**2.19**	**1286**	**187**	**285**	**33.6**	**4.22**	**968**
Mono-BDEs	13.3	20.0	5.15	0.08	71.0	11.7	15.4	2.82	0.78	45.0	8.47	17.5	1.58	0.36	62.4
Di-BDEs	34.1	54.2	9.2	0.19	157	31.9	46.3	3.84	0.93	128	9.3	14.2	2.62	0.46	52.1
Tri-BDEs	22.5	32.5	2.85	0.11	110	18.7	22.2	2.66	0.04	58.4	7.10	9.44	3.29	0.15	30.5
Tetra-BDEs	37.1	44.4	26.6	0.08	136	38.0	63.4	3.71	0.02	199	49.8	109	1.75	0.24	363
Penta-BDEs	56.0	96.3	8.48	0.24	351	85.2	180	5.99	0.06	618	67.2	134	3.49	0.55	493
Hexa-BDEs	25.0	36.8	3.40	0.20	129	60.4	93.7	12.1	0.13	300	24.4	40	3.74	0.76	112
Hepta-BDEs	10.2	15.5	1.68	0.09	48.3	35.4	67.9	1.48	0.09	198	8.41	15.5	1.03	0.45	55.9
Deca-BDEs	1.94	2.52	0.91	0.06	9.01	11.1	29.8	0.75	0.02	109	12.7	37.3	1.00	0.30	136

A similar trend was observed for metals and PAHs distribution in soil profiles of the floodplain (Tesi *et al.*, 2015; Iwegbue *et al.*, 2018; 2020). Similarly, the average concentrations of Σ39 PBDEs in soils of 15-30cm depth were higher than that of 0-15cm and 30-45cm. The 15-30cm and 30-45cm depths of FP12 and 15-30cm depth of FP13 have higher concentrations (1297ng/g^{-1}, 1226ng/g^{-1} and 1169ng/g^{-1} respectively) relative to other samples. On average, the concentration of ∑39 PBDEs in the downstream section (FP9 to FP13) was higher than those in the upstream (FP1 to FP5) and midstream section (FP6 to FP8) of the study area. In this study, there was no significantpositive correlation between ∑39 PBDEs concentration andTOC of the soil (R^2 = 0.0004) (Figures 4.8). The absence of significant positive correlation between ∑39 PBDEs concentration andTOC suggests organic matter alone does not determine the fate of PBDEs in the floodplain soils. Thus, the PBDEs may have come from different sources as well as constantinput of fresh PBDEs contamination (Yang *et al.*, 2012; Tesi *et al.*, 2016). The PBDEs homologues profiles in the soil of the LRRN floodplain showed remarkable differences with respect to sampling locations and depths (Figures 4.9). On average, the profile of PBDEs homologues in the floodplain soils was in the order of Penta-BDEs > Hexa-BDEs > Tetra-BDEs > Hepta-BDEs > Di-BDEs > Deca-BDEs > Tri-BDEs > Mono-BDEs for all sampling locations and depths. Comparison of PBDEs in the floodplain soils of the LRRN with those reported in literatures .

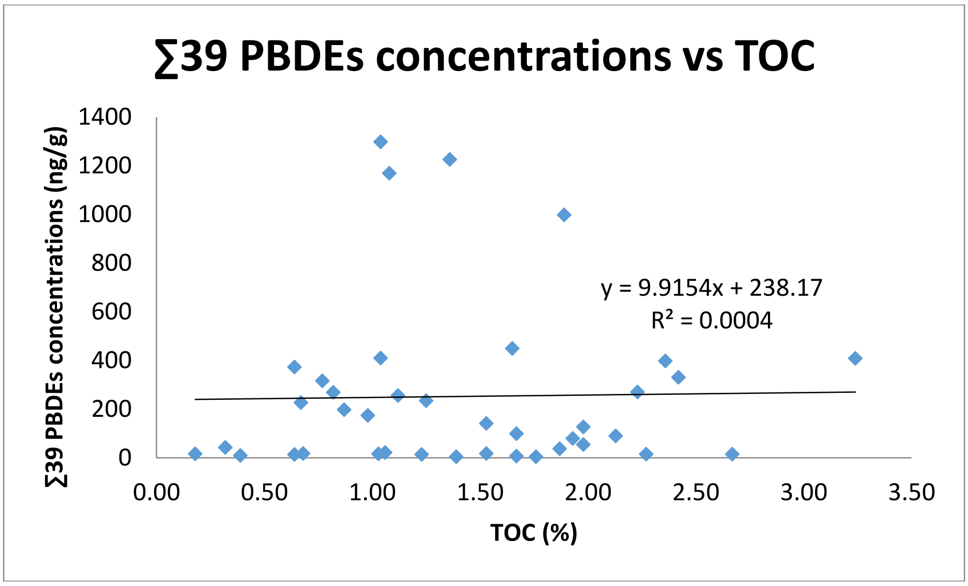


Figure 4.8: Plot of TOC versus the concentrations of the ∑39 PBDEs

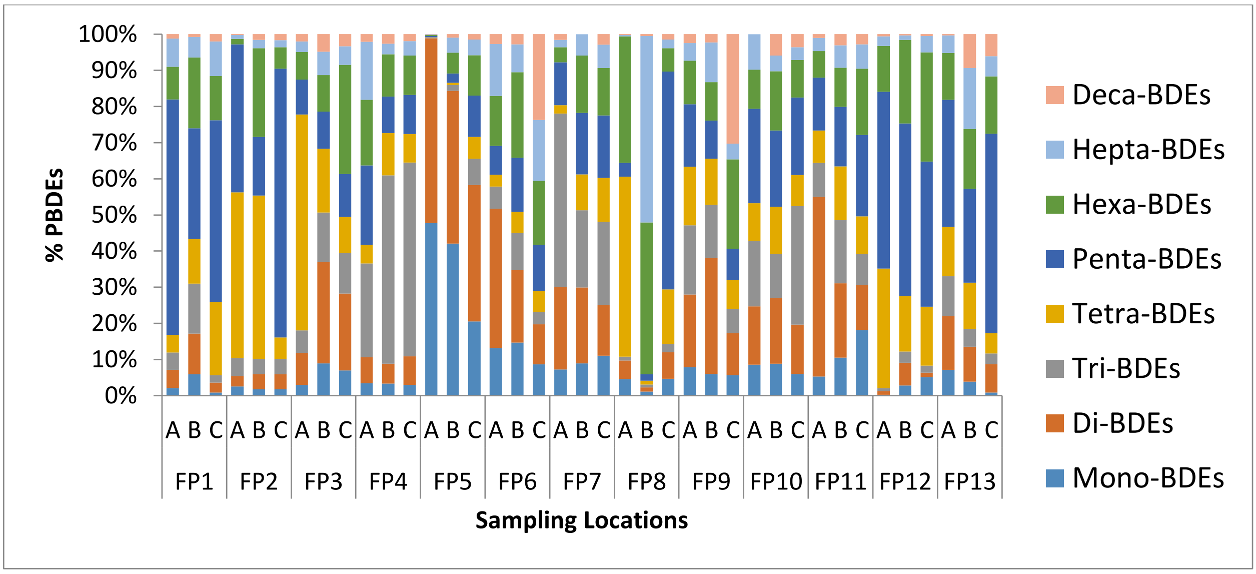


Figure 4.9: Profiles of PBDEs homologues in the floodplain soils

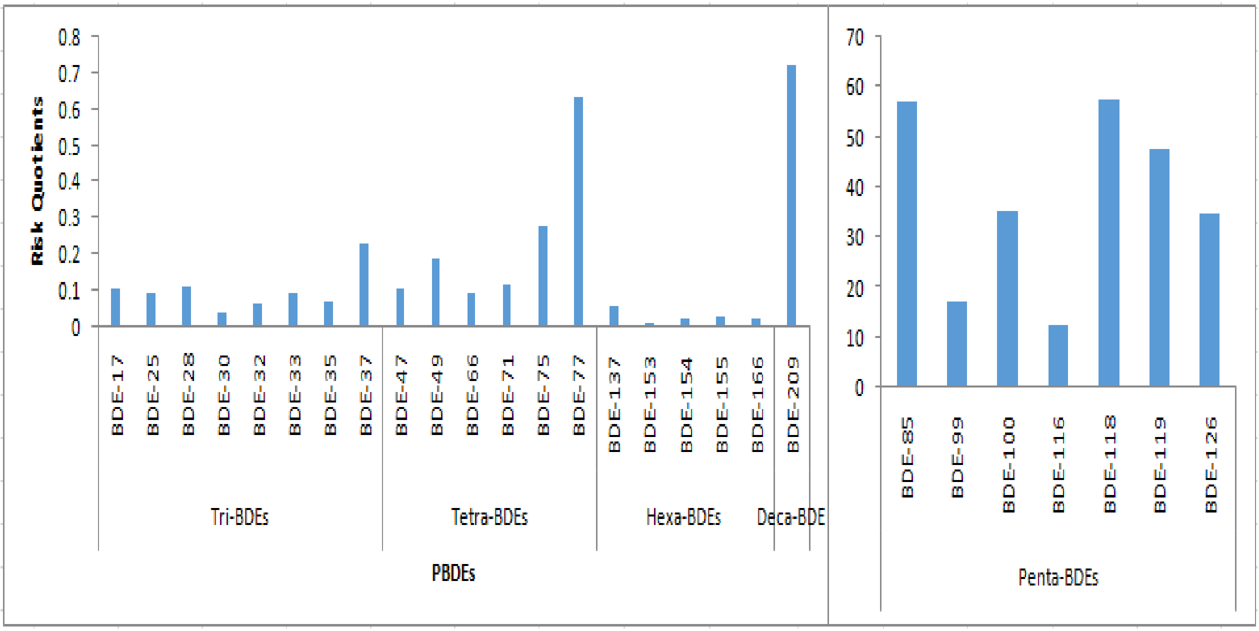
Table4.43: Comparison of PBDEs in floodplain soils of LRRN with others in literatures

Location	Soil type	No. of Samples	No. of PBDEs congeners	BDE-47	BDE-99	BDE-153	BDE-209	Total BDEs	Reference
River Niger, Nigeria 2019	Floodplain	39	38	<LDQ-12.7	<LDQ-50.1	0.02-41.9	0.02-136	2.19-1286	This study
River Niger, Nigeria 2018	Floodplain	39	38	<LDQ-12.7	<LDQ-50.1	0.04-41.9	0.04-136	4.37-1297	This study
Shiawassee, USA	Floodplain	-	-	0.09-6.290	0.10-5.78	<0.01-0.490	0.60-41.17	0.21-14.67	Yum *et al.* (2008)
Saginaw, USA	Floodplain	-	-	0.01-0.68	0.01-0.52	<0.01-0.07	<0.04-19.22	0.03-1.40	Yum *et al.* (2008)
Saginaw, USA	Floodplain	-	-	0.01-0.42	<0.01-0.27	<0.01-0.02	<0.04-21.6	0.02-0.83	Yum *et al.* (2008)
Guiyu, Shantou, China,	Agricultural	30	10	0.68-900	0.52-1425	0.51-126	3.0-3072	10-4454	Zhang *et al.*(2013)
Guiyu, Shantou, China,	Residential	16	10	0.84-177	0.72-200	1.74-47.6	101-3793	168-6535	Zhang *et al.* (2013)

Hong Kong, China	Agricultural	5	22	1.77	0.71	0.90	2.24	27.5	Man *et al.* (2011)
Hong Kong, China	Organic farm	5	22	1.62	0	0	0	23.5	Man *et al.* (2011)
UK	Grassland	7	-	0.007-0.52	0.078-3.20	0.019-0.60	-	0.015-5.0*	Hassanin *et al.* (2004)
UK	Woodland	7	-	0.05-1.40	0.19-3.20	0.038-1.20	-	0.075-5.60*	Hassanin *et al.* (2004)
Norway	Woodland	7	-	0.012-0.86	0.063-1.40	0.011-0.27	-	0.09-2.60*	Hassanin *et al.* (2004)
Spain	Agricultural	-	-	-	-	-	14.6-332	21.0-690	Eljarrat *et al.* (2008)
Indonesia	Agricultural	-	8	-	-	-	-	0.08-0.35	Ilyas *et al.* (2011)
Bratislavia, Slovakia	Urban	-	8	0.065	0.034	0.016	<LDQ	0.161	Thorenz *et al.* (2010)
Abuja, Nigeria	Municipal dumps	96	7					112-366	Oloruntoba *et al.* (2021)
Manaus, Brazil	Urban	-	8	<LDQ	0.071	0.33	0.50	0.434	Thorenz *et al.* (2010)
Mainz, Germany	Urban	-	8	0.49	0.091	0.29	0.76	1.043	Thorenz *et al.* (2010)
Kuwait	Urban	11	8	68.7-2100	107-2957	11.8-295	3121-66,597	213-6031	Gevao *et al.* (2011)
Kuwait	Rural	11	8	8.0-81.4	7.4-149	1.2-23.1	289-15,594	-	Gevao *et al.* (2011)
Birmingham, UK	Urban	-	6	0.10-0.91	0.12-1.71	0.04-0.41	-	0.40-3.89	Harrad and Hunter (2006)
Birmingham, UK	Rural	-	6	0.03-0.07	0.09-0.131	0.01-0.03	-	0.07-0.29	Harrad and Hunter (2006)
Shanghai, China	Urban	-	28	3.2-230	0.17-137	<LDQ-28.4	1.29-2910	23.6-3799	Jiang *et al.* (2010)
Japan	Urban	3	23	0.06-1.0	0.25-1.6	0.036-0.34	29-730	32-740	Li *et al.* (2016)
Japan	Rural	8	23	0.02-0.41	0.12-3.6	0.007-0.096	<LDQ-1000	1.0-1000	Li *et al.* (2016)
China	Urban	58	23	<LDQ-0.53	0.016-3.4	<LDQ-0.96	0.47-790	0.6-800	Li *et al.* (2016)
China	Rural	39	23	<LDQ-0.46	0.005-1.5	<LDQ-0.64	0.25-270	0.46-280	Li *et al.* (2016)
South Korea	Urban	5	23	0.017-0.22	0.044-0.91	0.012-0.90	3.10-88	3.7-94	Li *et al.* (2016)
South Korea	Rural	13	23	0.005-0.38	0.011-1.50	0.003-0.29	0.042-38.0	0.46-41.0	Li *et al.* (2016)
Vietnam	Urban	4	23	0.004-0.94	0.042-0.92	<LDQ-0.034	0.10-0.37	0.20-2.40	Li *et al.* (2016)
Vietnam	Rural	8	23	0.004-0.013	0.013-0.26	0.001-0.12	0.08-1.50	0.24-1.80	Li *et al.* (2016)
India	Urban	12	23	<LDQ-0.029	0.003-0.13	<LDQ-0.035	<LDQ-12.3	0.13-13.0	Li *et al.* (2016)
India	Rural	12	23	<LDQ-0.006	<LDQ-0.081	<LDQ-0.006	<LDQ-3.7	0.06-3.8	Li *et al.* (2016)

Ecological Risk Assessment of PBDEs in the floodplain soils

The computed risk quotient values for the PBDEs using their $C_{UCL95\%}$ in the floodplain soils are presented in Figure 4.10. The RQ values of the tri-BDEs and hexa-BDEs except BDE-37 were between 0.01 and 0.1 indicating that they pose low ecological risk in the floodplain soil. The RQ values of the tetra-BDEs and deca-BDEs were between 0.1 and 1.0 indicating that they pose medium risk. But the RQ values of the penta-BDEs were > 1 indicating that there is high risk associated with them in these floodplain soils.



Risk quotients of PBDEs in the floodplain soils

Non-carcinogenic and carcinogenic risk

The computed hazard index and total cancer risks associated with the PBDEs exposure in the floodplain soils for children and adults . The hazard quotient (HQ) for human exposure to PBDEs in the floodplain soils was in the order of HQIng> HQDerm> HQInh. The HQ for ingestion and dermal contact were higher in child than adults but HQ inhalation was higher in adult than child. The higher HQIng and HQDerm in child is attributed to the characteristic hand-to-mouth habits of children and also opening of their bodies when playing while the higher HQInh for adult is attributed to longer exposure time for adult. The HI values from child and adult exposure to PBDEs the floodplain soils for child exposure was 1.53×10^{-7} and 2.84×10^{-6} for BDE-209 and ∑38 PBDEs respectively. However, for adult exposure the total cancer risk of PBDEs in the floodplain soils were 1.19×10^{-8} and 2.24×10^{-7} for BDE-209 and ∑38 PBDEs respectively for 2018 sampling and 1.16 × in the floodplain soils for 2018 and 2019 sampling periods were all < 1 indicating that there is no adverse non-carcinogenic risk for human exposure to PBDEs in the floodplain soils.

The Risk values for human exposure to PBDEs in the floodplain soils were also in the order of RiskIng> RiskDerm> RiskInh. Like the HI, the Risk via ingestion and dermal contact were higher in child than adults but Risk via inhalation was higher in adult than child. For 2018 sampling, the total cancer risk of PBDEs in the floodplain soils for child exposure was 1.57×10^{-7} and 3.13×10^{-6} for BDE-209 and ∑38 PBDEs respectively while for 2019 sampling, the total cancer risk of PBDEs in 10^{-8} and 2.15×10^{-7} for BDE-209 and ∑38 PBDEs respectively for 2019 sampling. The total cancer risk values were lower than level of 1×10^{-6}. This indicates that there is no carcinogenic risk associated with human exposure to the floodplain soil.

Table 4.44: Hazard index and total cancer risk of PBDEs in the floodplain soils

			HQIng	HQInh	HQDerm	HI	RISKIng	RISKInh	RISKDerm	TCR
2018	CHILD	PBDE47	$5.22\text{x}10^{-5}$	$1.15\text{ x}10^{-8}$	$1.46\text{ x}10^{-7}$	**$5.24\text{ x}10^{-5}$**				
		PBDE99	$8.89\text{x}10^{-5}$	$1.96\text{ x}10^{-8}$	$2.49\text{ x}10^{-7}$	**$8.92\text{ x}10^{-5}$**				
		PBDE153	$8.11\text{x}10^{-5}$	$1.79\text{ x}10^{-8}$	$2.27\text{ x}10^{-7}$	**$8.13\text{ x}10^{-5}$**				
		PBDE209	$1.23\text{x}10^{-7}$	$2.71\text{ x}10^{-11}$	$3.44\text{ x}10^{-10}$	**$1.23\text{ x}10^{-7}$**	$1.23\text{x}10^{-7}$	$8.12\text{ x}10^{-11}$	$3.44\text{ x}10^{-8}$	**$1.57\text{x}10^{-7}$**
		∑4PBDEs	$2.78\text{x}10^{-7}$	$6.14\text{ x}10^{-11}$	$7.79\text{ x}10^{-10}$	**$2.79\text{ x}10^{-7}$**				
		∑38PBDEs	$2.45\text{x}10^{-6}$	$5.39\text{ x}10^{-10}$	$6.85\text{ x}10^{-9}$	**$2.45\text{ x}10^{-6}$**	$2.45\text{ x}10^{-6}$	$1.62\text{ x}10^{-9}$	$6.85\text{ x}10^{-7}$	**$3.13\text{ x}10^{-6}$**
	ADULT	PBDE47	$6.53\text{x}10^{-6}$	$4.80\text{ x}10^{-8}$	$2.60\text{ x}10^{-8}$	**$6.60\text{ x}10^{-6}$**				
		PBDE99	$1.11\text{x}10^{-5}$	$8.17\text{ x}10^{-8}$	$4.44\text{ x}10^{-8}$	**$1.12\text{ x}10^{-5}$**				
		PBDE153	$1.01\text{x}10^{-5}$	$7.45\text{ x}10^{-8}$	$4.04\text{ x}10^{-8}$	**$1.02\text{ x}10^{-5}$**				
		PBDE209	$1.53\text{x}10^{-8}$	$1.13\text{ x}10^{-10}$	$6.12\text{ x}10^{-11}$	**$1.55\text{ x}10^{-8}$**	$8.37\text{ x}10^{-9}$	$1.85\text{ x}10^{-10}$	$3.34\text{ x}10^{-9}$	**$1.19\text{ x}10^{-8}$**
		∑4PBDEs	$3.48\text{x}10^{-8}$	$2.56\text{ x}10^{-10}$	$1.39\text{ x}10^{-10}$	**$3.52\text{ x}10^{-8}$**				
		∑38PBDEs	$3.06\text{x}10^{-7}$	$2.25\text{ x}10^{-9}$	$1.22\text{ x}10^{-9}$	**$3.09\text{ x}10^{-7}$**	$1.54\text{ x}10^{-7}$	$3.68\text{ x}10^{-9}$	$6.65\text{ x}10^{-8}$	**$2.24\text{ x}10^{-7}$**
2019	CHILD	PBDE47	$4.84\text{ x}10^{-1}$	$1.07\text{ x}10^{-8}$	$1.35\text{ x}10^{-7}$	**$4.84\text{ x}10^{-1}$**				

	PBDE99	8.69 x10^{-1}	1.92 x10^{-8}	2.43 x10^{-7}	**8.69 x10^{-1}**				
	PBDE153	3.83 x10^{-1}	1.69 x10^{-8}	2.15 x10^{-7}	**3.83 x10^{-1}**				
	PBDE209	1.20 x10^{-6}	2.64 x10^{-10}	3.35 x10^{-9}	**1.20 x10^{-6}**	1.20 x10^{-7}	7.91 x10^{-11}	3.35 x10^{-8}	**1.53 x10^{-7}**
	∑4PBDEs	2.68 x10^{-7}	5.91 x10^{-11}	7.50 x10^{-8}	**2.69 x10^{-7}**				
	∑38PBDEs	2.21 x10^{-5}	4.88 x10^{-9}	6.20 x10^{-8}	**2.22 x10^{-5}**	2.21 x10^{-6}	1.47 x10^{-9}	6.20 x10^{-7}	**2.84 x10^{-6}**
ADULT	PBDE47	6.05 x10^{-2}	4.45 x10^{-8}	2.41 x10^{-8}	**6.05 x10^{-2}**				
	PBDE99	1.09 x10^{-1}	7.98 x10^{-8}	4.33 x10^{-8}	**1.09 x10^{-1}**				
	PBDE153	4.79 x10^{-2}	7.04 x10^{-8}	3.82 x10^{-8}	**4.79 x10^{-2}**				
	PBDE209	1.49 x10^{-7}	1.10 x10^{-9}	5.96 x10^{-10}	**1.51 x10^{-7}**	8.15 x10^{-9}	1.80 x10^{-10}	3.25 x10^{-9}	**1.16 x10^{-8}**
	∑4PBDEs	3.35 x10^{-8}	2.46 x10^{-10}	1.34 x10^{-10}	**3.39 x10^{-8}**				
	∑38PBDEs	2.77 x10^{-6}	2.04 x10^{-8}	1.10 x10^{-8}	**2.80 x10^{-6}**	1.51 x10^{-7}	3.33 x10^{-9}	6.02 x10^{-8}	**2.15 x10^{-7}**

Principal component analysis of PBDEs in the floodplain soils

The result of the PCA for PBDEs in the floodplain soils is shown in Table 4.45. Two componentfactors were identified in the two sampling periods and accounted for 69.705% and 70.177% of the total variance for 2018 and 2019 respectively. Factor 1 was responsible for 39.654% and 38.429% of the variance for 2018 and 2019 samplings respectively and has high loading of tetra-BDEs, penta-BDEs and hexa-BDEs with moderate loading of mono-BDEs. Factor 2 was responsible for 30.052% and 31.748% for 2018 and 2019 sampling periods respectively and has high loading of di-BDEs and deca-BDEs with moderate loading of mono, tri and hepta-BDEs.

Table 4.45: PCA of PBDEs in the floodplain soils

	2018		**2019**	
	Component		**Component**	
	1	**2**	**1**	**2**
MonoPBDE	**.642**	**.536**	**.732**	**.510**
DiPBDEs	.321	**.740**	.471	**.640**
TriPBDEs	.343	**.688**	.532	**.612**
TetraPBDEs	**.910**	.180	**.810**	-.005
PentaPBDEs	**.950**	.175	**.914**	.204
HexaPBDEs	**.865**	.297	**.700**	.520
HeptaPBDEs	.247	**.647**	.224	**.724**
DecaPBDEs	-.006	**.726**	-.033	**.812**
Variance (%)	**39.654**	**30.052**	**38.429**	**31.748**
Cumm (%)	**39.654**	**69.705**	**38.429**	**70.177**

CONCLUSION

The results of this study revealed that POPs (PBDEs) contamination in floodplain soils of the LRRN. There is high ecological risk and human health risk associated POPs(PBDEs) in the floodplain soils. The absence of significant positive correlation between ∑39 PBDEs concentration andTOC suggests organic matter alone does not determine the fate of PBDEs in the floodplain soils The Risk values for human exposure to PBDEs in the floodplain soils were also in the order of RiskIng> RiskDerm> RiskInh. Like the HI, the Risk via ingestion and dermal contact were higher in child than adults but Risk via inhalation was higher in adult than child. PBDEs were from both fresh and historical inputs; PBDEs were from technical mixture used for paints, plastics, hydraulic fluids, dielectric insulating fluids for transformers, and capacitors;

RECOMMENDATION

Based on the findings of this study, the remediation and clean-up of the floodplain soils of the lower reaches of River Niger, Nigeria is therefore recommended. Also further study on other organic pollutants such as organophosphate pesticides should be carried out.

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