International Journal of Scientific Research in Science, Engineering and Technology
Print ISSN: 2395-1990 | Online ISSN : 2394-4099 (www.ijsrset.com)
doi : https://doi.org/10.32628/IJSRSET218148

Occurrence and Distribution of Polybrominated Diphenyl Ethers in Sediments from Nairobi River Basin, Kenya, East Africa

Enock M. Osoro[1*], Shem O. Wandiga[1], Vincent O. Madadi[1], Deborah A. Abong'o[1]

[1]College of Biological and Physical Sciences, School of Physical Science, Department of Chemistry, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya

*Correspondence Author : osoroenock@yahoo.com

Article Info
Volume 8 Issue 1
Page Number: 274-286

Publication Issue :
January-February-2021

Article History
Accepted : 20 Feb 2021
Published : 28 Feb 2021

ABSTRACT

This study was set to determine the levels and spatial distribution of selected PBDEs in sediments of Nairobi River during the four seasons experienced in Nairobi. Sediment samples were collected from nine sites along the river and analyzed for brominated diphenyl ethers 28, 47, 66, 85, 99, 100, 153, 154, and 183 using gas chromatography coupled with mass spectrometer. The mean concentration of polybrominated diphenyl ethers residue in sediment samples ranged between 134.70±3.07 to 24386.13±207.22 ng/Kg. The high mean concentration of PBDEs in the river sediments indicates that anthropogenic activities along the Nairobi River basin have contributed to polybrominated diphenyl ethers contamination of the river sediment posing a potential risk to aquatic organisms that inhabit the river.

Keywords : Nairobi River Basin; Polybrominated diphenyl ethers; sediments; Residues

I. INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants (FRs) in a range of manufactured goods like electronics and electrical goods, textiles, plastics, and furniture to decrease the risk of fire by interfering with the ignition of the polymeric materials [1,2]. PBDEs have 209 theoretically potential congeners in ten homologue groups (mono to deca) depending on the numbers and positions of the bromine atoms attaching on the two phenyl rings [3].There are three main commercial PBDE formulations namely pentabromodiphenyl ethers (Penta-BDE), octabromodiphenyl ethers (Octa-BDE), and decabromodiphenyl ethers (Deca-BDE) with the latter accounting for 83% of the total PBDE production internationally [3]. PBDEs are associated with adverse health effects that include thyroid hormone disruption [4], neuro-developmental deficit [5], liver problem [6], potential carcinogenesis [7], and abnormal pregnancy [8].

Recently there has been increased research on PBDEs because of the worldwide concern about their non-degradability, bioaccumulation, long-range transport, and toxicity in the atmosphere [9, 10]. PBDEs contamination in the global environment was first detected in samples of fish caught in Swedish waters

in 1981 [11]. Since then, various researchers have reported the existence of PBDEs in different ecological and living organism samples across the world. The research done includes; soil [12], sediments [13, 14] fish [15, 16], water [17, 18] wild aquatic species [19, 20] and mothers' milk [21]. Because of the non-degradability, bioaccumulation, toxicity, increased pollution levels of PBDEs in the environment, and risk to human health; penta, octa, and deca BDEs have been added in the Stockholm Convention on Persistent Organic Pollutants [22, 23].

Nairobi River is a river that flows through Kenya's capital city of Nairobi. It is the key river of the Nairobi river basin, a complex of numerous streams flowing eastwards. Nairobi River courses from Ondiri swamp on the Western part of Nairobi City and traverses settlements, the central business district, heavy and light industries in the mid and downstream and it eventually joins the Athi River at fourteen falls which drains to the Indian Ocean [24]. The river receives a conglomerate of wastes including; industrial waste released directly from factories at Nairobi's industrial area and light industries in Kariobangi [25], the garbage that includes unsorted waste electronics and electrical goods from Dandora dumping site, incorrectly treated sewages from Dandora sewage treatment plant [25], pesticides from urban agricultural activities [26], oil and grease, heavy metals, total petroleum hydrocarbons, polychlorinated biphenyl and other wastes from municipal and industrial activities [27, 28]. Nairobi River is the most contaminated river in Kenya [25].

There are few studies on environmental contamination by PBDEs in Kenya. Only few studies were found in the literature [29, 12]. These studies focused on soil from suburban and rural areas of Kenya leaving the City of Nairobi where the contamination is expected to be high. Hence, research is needed to study the distribution of PBDEs in sediments from Nairobi River. The study will contribute to knowledge on the state of pollution of Nairobi River sediments with PBDEs and the large-scale research findings can serve as a reference for relevant government agencies in policy formulation towards managing river resources.

The aim of this study was to determine the levels and spatial distribution of selected PBDEs in sediments of Nairobi River during the four seasons experienced in Nairobi.

II. MATERIALS AND METHODS

2.1. Study Area

Nairobi County is among the 47 counties in Kenya and is located between 36° 45'' E to 37° 05'E, and 1° 10''S; to 1°30''S at a mean altitude of 1,700 meters above sea level. Commercial and administrative activities are concentrated in the central business district while most of the industrial activities are located in the South-East. Nairobi experiences four major seasons namely; hot dry season (January to March), heavy rain season (April to June), cool dry season (July to September), and short rain season (October to December). Temperatures generally vary from 11 °C in June/July to about 29 °C from December to March [30].

Nairobi River courses from Ondiri swamp on the Western part of Nairobi City and traverses the central business district, heavy and light industries, and settlements in the mid and downstream and it eventually joins the Athi River at fourteen falls which drains to the Indian Ocean. Figure 1 shows the distribution of the sampling locations along the river profile.

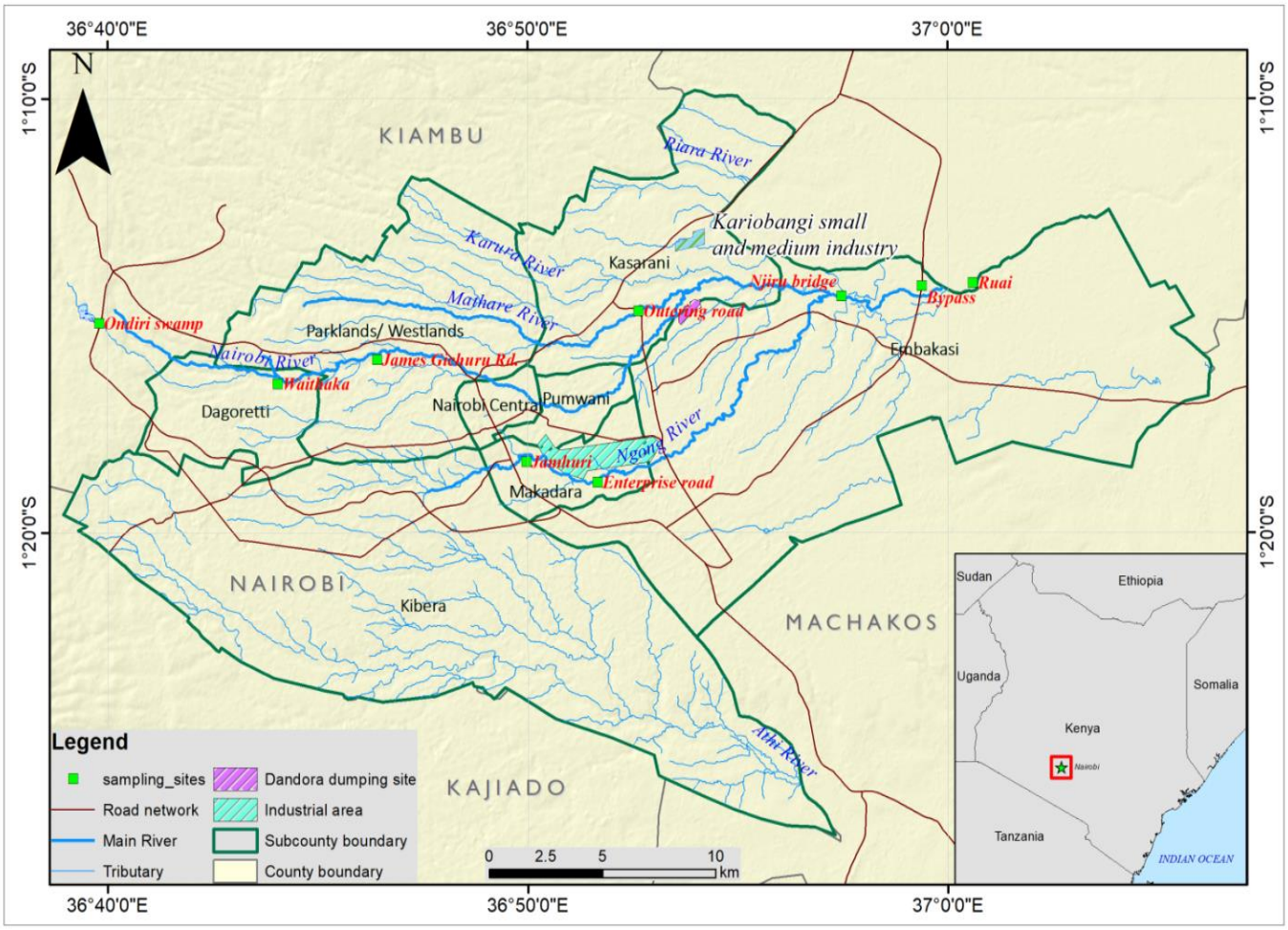

Figure 1 : Map of the study area showing the nine sampling sites along Nairobi River basin, i.e., Ondiri, Waithaka, James Gichuru, Jamhuri, Enterprise road, Outering road, Njiru, By-pass, and Ruai.

2.1. Reagents and Chemicals

Analytical grade silica gel (0.063–0.2 mesh, Merck), acetone, n-hexane, sodium hydroxide, sulphuric acid, copper powder, anhydrous sodium sulphate, and dichloromethane were purchased from Sigma-Aldrich, USA through the local agent Kobian Kenya Ltd. HPLC grade isooctane was procured from Sigma-Aldrich, USA through the local agent Kobian Kenya Ltd. White sport nitrogen (99.999%) gas and helium (99.999%) gas were purchased from BOC Kenya Ltd. High purity (98.80%) PBDEs standard mixture and ^{13}C labeled BDE 77 standard were procured from Sigma-Aldrich, USA. Sodium sulphate and neutral silica were purified by heating at 200 °C for 12 hours.

2.2. Sample Collection

Preliminary fieldwork was carried out before starting the sample collection to determine the exact sampling locations. Sampling locations were selected to cover the whole river profile and to represent the sediments of informal and formal settlement, industrial and commercial locations, dumping sites, and the source of the river. A total of nine sampling sites were selected to represent the upstream, midstream, and downstream of the river profile. Ondiri Swamp (01º15'10S 036 º39'48E), Waithaka (01º 16' 34S, 036º 44'03E) and Jamuhuri (01º 18'22S, 036º49'58E) represented the upstream, James Gichuru Road (01º 18'36S, 036 49'42E), Enterprise road (01º 18'22S, 036º 49'35E) and Outering road (01º 18'22S, 036º 53'21E) represented the midstream while Njiru Bridge (01º 14'44S,036º 59'19E), By-Pass (01º 14' 35S, 036º 56'27E) and Ruai (01º 14' 35S, 036º 56'27E) represented the downstream (Figure 1). Sediments samples were collected quarterly from July 2017 to June 2018 covering the cool dry season (July-September), short

rain season (October -December), hot dry season (January- March) and heavy rain season (April - June) to capture the four seasons experienced in Kenya [30]. Sediments were sampled using a pre-cleaned stainless steel shovel. Three composite samples were mixed on clean piece of aluminium foil and a 500 g representative sample picked, wrapped in another clean piece of aluminium foil, labelled, and then placed into a self-sealing bag. They were then packed in a cooling box and transported to the laboratory where they were stored in a deep freezer at -20 ^{o}C prior to analysis [31]

2.3. Extraction

Sediment samples were removed from freezer and allowed to thaw for 4 hours prior to extraction. Triplicates of 20 g samples were dried with activated anhydrous sodium sulphate (Na_2SO_4) overnight before transferring to the soxhlet thimble and then spiked with ^{13}C labelled BDE 77 extraction standard. This was extracted with 175 ml of dichloromethane in a 200 ml round bottomed flasks for 16 hours in a soxhlet extractor set-up. 2 ml of isooctane added as keeper then concentrated to 3 ml using LABCONCO rotary evaporator. The concentrated extracts were then put in vials and stored in a fridge at -4 ^{o}C a waiting clean-up process.

2.4. Sample Clean up

Sample extracts were cleaned by passing them through a chromatographic glass column packed with 1 cm anhydrous sodium sulphate at the bottom, followed by 1000 mg activated silica, 4 g basic silica (3:1 silica gel: 1M sodium hydroxide, weight/weight), 1000 mg activated silica, 8 g acidic silica (1:1 silica gel: H_2SO_4, weight/weight), 2 g activated silica and on top 1 cm anhydrous Na_2SO_4. The column was preconditioned using 50 mL of n-hexane. The extracts were quantitatively loaded and eluted with 50 mL of n-hexane. 2 mL of isooctane was added to the cleaned samples and reduced to 2 mL then transferred to vial. Activated copper was added to remove the sulphur in the samples. The samples were then transferred into amber 1.5 mL autovials and further reduced under a gentle stream of nitrogen (99.99%) to 0.5 mL for Gas Chromatography-Mass Spectrometry (GC-MS) analysis [31].

2.5. Gas Chromatography-Mass Spectrometry (GC–MS) Analysis

The samples were analyzed for 9 PBDE congeners (BDE 28, 47, 66, 99, 100, 85, 154, 153, and 183) using Agilent 6890N gas chromatography (GC) equipped with a single quadrupole mass spectrometer (Agilent 5973A) and a Thermo scientific traceGOLD column (TG 5SILMS 30m X 0.25mm X 0.25 μm). The mass spectrometer was operated in selected ion monitoring (SIM) mode with electron impact (EI^+) ionization method at a resolution of >5,000. The detector and injection temperature was set at 320 ^{o}C and 280 ^{o}C in that order. High purity (99.999%) helium N6 gas was used as the carrier gas at a flow rate of 1 ml min^{-1}. The oven temperature was set at 90 ^{o}C (1 minute hold time), then ramped from 90 ^{o}C to 180 ^{o}C at 40 ^{o}C min^{-1}, ramped from 180 ^{o}C to 260 ^{o}C at 10 ^{o}C min^{-1} (2 minutes hold time), and finally ramped from 260 ^{o}C to 320 ^{o}C at 25 ^{o}C min^{-1} (8 minutes hold time). 1 microliter of the sample extracts, mixed standard solutions, and calibration standards were injected into the Gas Chromatography-Mass Spectrometry (GC-MS) by splitless injection mode.

Identification of the targeted PBDE analytes was accomplished by relating the retention times and mass spectra of analytes in samples to those of reference standards analyzed at similar GC-MS conditions with the samples. The analytes were also identified using the National Institute of Standards and Technology (NIST) mass spectrometer library, version 2.0 (Standard reference data program of the US National Institute of Standards and Technology). A target PBDE was identified if it had a similar retention time to that of the reference standard (within a deviation of ±0.05 min) and their spectra matched. The peak identification was based on the

base ions and the isotope pattern of each PBDE compound in the mass spectrometer spectra. The base ions were chosen as quantitative ions, while the other ions were selected as confirmatory ions (Table 1). Quantification of all target PBDE congeners was based on peak areas using external multilevel calibration curves prepared by plotting peak areas against the concentrations of the respective PBDE standard using nine calibration points with correlation coefficients (r^2) greater than 0.99 (Table 1).

Table 1 : Analytical figures of merit

PBDEs	BDE 28	BDE 47	BDE 66	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183
Retention Time	9.475	11.581	12.994	13.714	14.548	16.119	17.040	18.313	20.121
Linearity (r^2)	0.998	0.997	0.990	0.996	0.998	0.994	0.992	0.998	0.997
LOD (pg)	1.1	1.1	1.3	1.3	1.4	0.9	1.0	1.4	1.2
LOQ (pg)	3.6	3.3	4.3	4.2	4.3	2.9	3.0	4.6	3.9
Mean Ratio of ion in Sample/ Std	4.1	3.1	2.2	3.5	3.5	5.9	2.3	0.7	1.8
Accuracy (%)	98.14	102.86	105.06	101.51	97.89	89.35	104.31	103.58	102.23
Quantitative ion (m/z)	405	485.70	485.70	405.90	405.90	405.90	483.80	483.80	561.70
Qualifier ion (m/z)	245.90, 407.80, 417.90, 419.90	483.70, 495.70, 497.70, 345.90	483.70, 495.70, 497.70, 345.90	563.60, 565.60, 575.60, 577.60	563.60, 565.60, 575.60, 577.60	563.60, 565.60, 575.60, 577.60	641.50, 643.50, 653.60, 655.50	641.50, 643.50, 653.60, 655.50	721.40, 733.40, 735.40, 723.40

LOD, Limit of Detection
LOQ, Limit of Quantification

2.6. Quality assurance and quality control (QA/QC)

All glassware and apparatus were washed using a detergent and water, and then rinsed with distilled water and solvents (methanol, acetone, and methylene chloride). The glassware were dried in the oven at 110°C for twelve hours before use. All reagents and solvents were of high purity and analytical grade. The PBDEs standard mixture and ^{13}C labelled BDE 77 standard were of high purity of above 98%, kept in amber vials to prevent photo degradation, and stored in a freezer to prevent evaporation.

Many control tests were performed to authenticate the analytical procedures. Field blanks were carried to the field to track any contamination during transportation. The GC-MS machine was regularly injected with solvent blank (isooctane) and procedural blanks. A calibration standard check of 10 ng/L was injected into the GC-MS after analysis of every ten samples to ensure that not more than fifteen per cent difference was established from the

initial calibration standards. A recovery experiment was performed to test for the accuracy of the method. 1ppm ^{13}C labelled BDE 77 standard was spiked to all samples before extraction and the average surrogate recovery in all samples was 89.96± 11.32%. The limit of detection was determined by reviewing the noise in the chromatograms next to the peak of interest. All PBDEs found with concentrations below the detection limit were reported as below detection limit (BDL). The limit of quantification (LOQ) was calculated in the same way using ten times the noise level (Table 1).

Microsoft Excel 2010 was used to process the data. Statistical Package for the Social Science (SPSS) version 20 for window evaluation was employed for the analysis of the data.

III. RESULTS AND DISCUSSION

Sediments were selected as matrices of interest for assessment since they acts as sinks for most hydrophobic organic contaminants, which strongly bind to the particulate matter owing to their high octanol-water partition coefficient (Kow) [32,33]. The analysis of sediment samples from nine sites along Nairobi River showed presence of PBDEs residues at varying concentrations. The mean concentration of the $\sum_9$PBDEs in sediment ranged between 134.70±3.07 to 24386.13±207.22 ng/Kg (Table 2). PBDE levels measured in this study were higher compared to those reported by Olutona and Co-workers for Asunle Stream, Ile-Ife, Nigeria, where the mean concentration of the $\sum_6$PBDEs in the sediments ranged between 0.83 to 10.45 ng/g [34] and surface sediment samples from a recharge point of Guarani Aquifer in Ribeirão Preto, Brazil whose concentration ranged from nd –5.4 ng/g [35]. However, the levels in the current study were lower than those reported in surface sediment samples from from Lake Chaohu, central eastern China whose concentration ranged from 8.93–45 ng/g [36], sediment from the artificial Lake Shihwa, Korea whose concentration ranged from 1.13–18700 ng/g [37], those in the river and coastal areas of Portugal whose concentration ranged from 185.50 to 277.20 mg/kg [37], Osaka Bay of Japan whose concentration ranged from 8.80 to 13.52 mg/kg [38] and those in San Francisco Estuary of US whose concentration ranged from ND to 2.12 mg/kg [39]. The mean concentrations of PBDEs in this study were below Environment Canada's (EC's) safe limit (6124 ng/g) [40].

Table 2 : Range and Mean Concentration of PBDEs Residue Level in Sediments (ng/Kg)

Site/ PBDE		BDE 28	BDE 47	BDE 66	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183
Ondiri	Range	216.27-1321.44	1051.23-6521.00	191.55-718.43	478.48-1232.15	1021.53-3059.17	134.70-538.22	352.63-2813	233.48-1645.22	653.87-864.27
	Mean± SD	860.79 ±463.60	3871.46± 2968.49	515.70± 235.11	824.56± 363.28	12505.76 ±1349.87	296.96± 192.84	1078.65 ±1161.9	701.65±654.02	727.04± 93.52
Jamhuri	Range	791.75-1688.62	1116.73-8733.92	464.78-1785.67	758.45-1687.27	876.89-5742.18	582.51-1758.99	987.72-3699.28	681.06-3913.25	478.38-1536.18
	Mean± SD	1232.09 ±366.32	5035.78 ±3894.92	1097.08 ±625.05	1236.87 ±395.87	3437.43± 2260.99	911.04± 566.26	2182.61 ±1294.7	1775.11± 1491.99	940.22± 498.83
Waithaka	Range	524.36-1532.4	1517.75-6980.11	141.67-1294.00	330.64-711.51	1087.44-5196.00	364.68-924.20	738.19-1247.23	371.64-1725.64	761.89-2315.00
	Mean± SD	1018.78 ±433.26	4041.02 ±2932.24	662.49± 475.63	445.54± 206.65	13050.73 ±2239.57	661.61± 299.55	1161.93 ±379.12	893.67±583.06	1187.58 ±753.52
James Gichuru Road	Range	515.67-1165.42	1792.16-8912.09	281.76-1826.03	1526.29 -1843.1	1839.76-10785.00	361.00-1224.11	816.91-2526.00	586.70-2226.21	271.54-1981.99
	Mean± SD	1214.30 ±830.65	5684.26 ±3272.53	879.58± 666.10	1771.86 ±300.41	4960.32± 3973.66	805.44± 428.50	1269.08 ±838.28	1135.62± 747.96	939.26± 828.45

Enterprise Road	Range	1683.65-2382.6	10772.95-12332.5	681.91-2556.37	681.91-2556.37	4843.61-10082.93	1168.27-2867.6	1564.46-5736.1	1257.73-3687.57	1156.76-2167.1
	Mean± SD	1978.01 ±302.93	11608.75 ±751.06	1622.63 ±911.44	1622.63 ±911.44	8260.61± 2364.73	1738.36 ±776.90	2314.03 ±2357.6	2332.64± 1006.51	1715.84 ±417.19
Outering Road	Range	1262.81-1886.7	6692.03-10483.16	682.69-2476.83	967.00-1362.15	7716.94-11914.72	1119.56-1716.2	1700.31-3916.3	1172.34-3916.30	1054.80-3279.9
	Mean± SD	1982.75 ±936.45	9593.26 ±2163.92	1709.68 ±757.85	12737.07±4174	10051.19 ±1795.85	1400.51 ±245.58	2533.43 ±1005.4	1991.31± 1300.43	1828.03 ±1022.7
By-Pass	Range	1954.36-3816.8	8968.24-14117.73	1669.87-3226.2	1262.23-3491.3	5731.03-12856.34	952.41-2554.23	1328.61-3851.7	1841.91-4213.69	1384.45-2616.3
	Mean± SD	2515.14 ±877.88	10656.23 ±2366.47	2260.27 ±691.45	1900.57 ±1068.3	9468.08± 2975.65	1687.33 ±658.98	2420.17 ±1094.6	3324.55± 1043.42	2016.93 ±648.41
Njiru	Range	1345.30-3362.4	8955.9-24386.1	1768.59-3971.4	1731.89-2832.0	6961.86-11245.21	1296.74-2719.5	2816.99-4752.2	1861.51-5497.66	1520.14-3116.9
	Mean± SD	2475.48 ±853.71	13686.91 ±7189.32	2635.09 ±1018.5	2107.50 ±556.08	9380.82± 1777.98	1884.55 ±607.69	3665.49 ±810.87	3224.94± 1620.95	12029.70±743.2
Ruai	Range	1731.88-3095.2	6874.90-10556.99	1119.79-3331.6	1334.52-2786.1	8445.89-10668.32	1015.74-2554.3	2154.19-3914.2	1519.88-3648.79	1199.74-3007.7
	Mean± SD	2309.06 ±571.07	9248.14 ±1676.06	2372.47 ±1072.1	12089.14±620.9	9651.81± 1066.34	1726.40 ±642.92	2780.32 ±810.20	2635.29± 909.44	2509.26 ±874.55
Detection Frequency	%	100	100	100	100	100	100	100	100	100

SD, standard deviation; BDL, below detection limit, n=3

3.1 Spatial and Seasonal Variation of PBDEs Residue Level in Sediment

The mean concentrations of PBDEs in sediment at the nine sampling sites along Nairobi river basin were assessed to measure their variation designs. The data gotten for the nine sampling sites are shown in Table 3. The result showed that the PBDE congeners were portable and can be moved over a long distance over period. Additionally, the nine PBDEs investigated were present in all of the nine sampling sites in the river at different concentrations. Spatially, the average concentration of the total PBDEs ranged between 1191.57 and 4400.49 ng/Kg.

Njiru site situated downstream of the river recorded the highest level of PBDEs among the nine locations which was attributed to leaking of the PBDEs from open burning of wastes including plastics at Dandora dumpsite and discharge of industrial wastewater from light industries at Kariobangi.

Generally, from the source of the river (Ondiri), the mean concentration of these contaminants increased downstream. The sampling sites; Ruai, By-pass, Njiru, Outering road and Enterprise road had relatively higher concentration of PBDEs that is associated with their close proximity to Dandora municipal dumpsite where unsorted wastes are dumped including plastics, domestic and industrial wastes hence leaching of the contaminants into the receiving river is highly probable. The upstream section of Nairobi River had relatively low concentration of PBDEs that is attributed to atmospheric deposition from open burning of solid wastes. This suggests that atmospheric deposition is a route of movement of particulate pollutants to Nairobi River's ecosystem [41]. Also these could be attributed to the varying distances of the sampling locations to the source of contaminants.

Table 3 : Mean Levels (ng/Kg) of the Spatial Allocation of PBDEs in the Nairobi River Sediment Samples

	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	∑9 PBDEs
Ondiri	860.78 ±463.60	3871.46 ±2968.49	515.69 ±235.12	296.93 ±192.84	2505.75 ±1349.87	824.56 ±363.28	701.65 ±654.02	1078.65 ±1161.93	68.62 ±93.52	1191.57
Waithaka	1018.78 ±433.26	4041.02 ±2932.24	662.48 ±475.63	661.60 ±299.54	3050.73 ±2239.56	445.54 ±206.65	893.67 ±583.06	1161.93 ±379.12	563.71 ±753.52	1388.83
James Gichuru	1214.29 ±830.64	5684.26 ±3272.52	879.58 ±666.11	805.44 ±428.50	4960.31 ±3973.66	1771.87 ±300.41	1135.62 ±747.96	1269.08 ±838.28	666.24 ±828.45	2042.97
Jamhuri	1232.09 ±366.32	5035.77 ±3894.92	1097.08 ±625.05	911.04 ±566.26	3437.42 ±2260.99	1236.86 ±395.56	1775.11 ±1491.99	2182.80 ±1294.78	409.81 ±468.83	1924.22
Outering	1982.74 ±936.74	9593.26 ±2163.92	1709.68 ±757.85	2900.51 ±3017.9	10051.18 ±1795.85	1187.07 ±215.69	1991.31 ±1300.43	2533.43 ±1005.43	725.95 ±1022.78	3630.57
Enterprise Rd	1948.01 ±302.93	11608.75 ±751.05	1801.85 ±802.24	1738.35 ±776.90	8260.60 ±2364.73	1622.63 ±911.44	2332.65 ±1006.51	2314.03 ±2357.68	279.54 ±417.19	3545.16
Bypass	2515.13 ±877.87	10656.23 ±2366.47	4760.27 ±5057.4	1687.32 ±658.97	9468.07 ±2975.65	1900.57 ±1068.3	3324.55 ±1043.42	2420.17 ±1094.67	449.71 ±648.41	4131.34
Njiru	2475.47 ±853.71	13686.91 ±7189.32	2635.08 ±1018.5	1884.55 ±607.69	9380.81 ±1777.97	2107.49 ±556.08	3224.94 ±1620.95	3665.49 ±810.87	543.63 ±743.27	4400.49
Ruai	2309.05 ±571.07	9248.14 ±1676.06	2534.60 ±844.41	1726.40 ±642.91	9651.81 ±1066.34	2089.14 ±620.94	2635.29 ±909.43	2780.32 ±810.20	654.76 ±874.54	3736.61

Figure 2 presents the seasonal variation in the levels o f PBDE congeners in sediment samples from Nairobi River. The concentrations (ng/kg) of these congeners f or the cooler dry, short rain, hot dry, heavy rain seaso ns are as follows: BDE 28 (16775.18, 21561.29, 10601. 35 and 13287.66); BDE 47 (91149.51, 79440.51, 67841. 373 and 55271.90); BDE 66 (19954.93, 9516.69, 10220. 91 and 16044.32); BDE 85 (7924.16, 11323.09, 11066. 72 and 14134.71); BDE 99 (77271.25, 62410.76, 61811. 29 and 41573.61); BDE 100 (10645.37, 16509.36, 1191 1.14 and 13677.12); BDE 153 (30474.33, 15067.16, 11 475.13 and 15042.5); BDE 154 (31787.23, 14453.72, 13 478.16 and 17904.42); BDE 183 (15038.36, 9963.61, 13 818.61 and 16754.80). The sums of nine PBDE congen ers in sediment were higher during the cooler dry se ason just after the heavy rain this can be attributed to seasonal differential influx of industrial wastes into th e river due to the surfance runoff during the heavy rai n season.

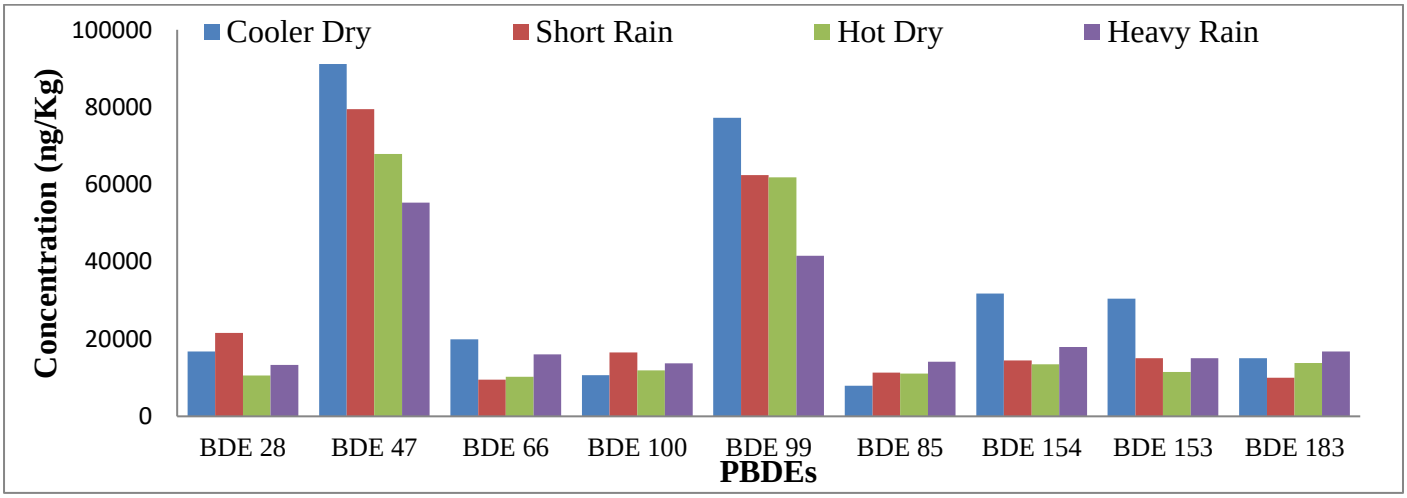

Figure 2 : Seasonal Variation of PBDEs Residue Levels

PBDEs in sediment samples from Nairobi River basin are likely to come from a combination of point and non-point sources and atmospheric deposition. Larger amounts of industrial activities (like dismantling electronic products, cables and wires, oils depot and chemical plants) were probable accountable for the high levels of PBDEs in sediment samples of Nairobi River. Higher detection frequencies of 100% for all the PBDE congeners in sediment in this study suggest a widespread distribution of the contaminants in Nairobi River basin. The high levels of penta-BDE formulation in the river sediment can be attributed to inappropriate dumping of polyurethane foam products. The octa-PBDE formulation is mostly used in plastics which when burned release PBDEs into the environment.

All the nine PBDEs congeners studied were commonly identified because they are the major compounds in the penta-BDE commercial mixture [42]. The congener BDE 47 is most frequently employed in the furniture and fabrics [43]. The penta-BDE mixture, which includes BDE 47, 99, 100, 153 and 154, is typically applied in furniture, whereas the octa and deca-BDEs mixtures are used in the manufacture of many types of polymers, especially those used in televisions, computers, and cables [43]. BDE-47 accounted for more than 50% of the total concentration of PBDEs, which showed that it was the most prevalent congener in the sediment samples, followed by BDE 99. According to literature, BDE 47 and 99 are the PBDE congeners that are most frequently detected in environmental samples and biological fluids [44]

3.2 Comparison of PBDE Residue Levels in the Study Area with Levels in Other Countries

In order to better analyse the results obtained in the current study, the PBDEs levels obtained was compared with the concentrations reported worldwide, as portrayed in Table 4. Compared to some regions in the Fuhe River, the Baiyangdian Lake, and the Chaohu Lake, all of them in China, and on the Olkhon Island, in Russia, the mean concentrations of PBDEs detected in this study were higher. Cheng-Yu, an economic region in China, presented much lower mean values of PBDEs as compared to the Nairobi River investigated herein. Compared to some regions in Korea (four major rivers) or even in China (Jiaojian River), our values were much lower, which means that the Nairobi River sediments were moderately contaminated with PBDEs. A comparison of the concentration of PBDEs in the current study with similar studies around the world is summarized in Table 4.

Table 4 : PBDE Residue Level in Sediment Samples in Other Studies around the World

Country	**Aquatic System**	**ΣPBDEs (ng/g)**	**Reference**
Brazil	Saibro Lagoon	nd –5.4	[35]
Brazil	Paranoá Lake	2.5–8.1	[45]
Chile	Copncepción Bay	0.02–21	[46]
China	Fuhe River	0.13–6.39	[47]
China	Shanghai rivers	0.44–12.0	[48]
China	Jiaojiang River	8.93–45	[36]
South Korea	Shihwa Lake	1.13–18700	[37]
Canada	Nigara River	1.10–148	[49]
USA	White Lake	0.39–2,4	[50]
USA	Muskegon Lake	0.98–3.9	[50]
Italy	Maggiore Lake	0.02–27.1	[51]
Russia	Olkhon Island	0.164–0.670	[52]
Kenya	Nairobi River	0.134 – 24.386	This study

Nd, Not Detected

IV. CONCLUSION

A lot of works on persistent organic pollutants have been done internationally but there is a scarcity of data about PBDEs in the Kenyan environment. The current research forms a baseline data on the pollution of Nairobi River sediments with PBDEs. The concentration of PBDE congeners increased down the river profile, giving the impression that cumulative human activities play a major role in the contamination of the river. The detection frequency of PBDEs was high during the cool dry season than in the hot dry, heavy rain and short rain seasons respectively. The PBDE levels recorded in this study are of urgent concern because of the potential health impact on the riparian community using the water and river biodiversity.

Disclosure statement

The authors declare no conflict of interest.

Acknowledgments

This study was funded by the International Foundation for Science (IFS) grant Number I-2-W-6107-1. The authors thank the Research Centre for Toxic Compounds in the Environment (RECETOX), Czech Republic for the donation of the PBDEs standard mix. We also thank the International Science Programme (ISP) whose collaboration lead to the donation of the GC/MS that was used for the analysis of our samples at the University of Nairobi.

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Cite this article as : Enock M. Osoro, Shem O. Wandiga, Vincent O. Madadi, Deborah A. Abong'o, "Occurrence and Distribution of Polybrominated Diphenyl Ethers in Sediments from Nairobi River Basin, Kenya, East Africa", International Journal of Scientific Research in Science, Engineering and Technology (IJSRSET), Online ISSN : 2394-4099, Print ISSN : 2395-1990, Volume 8 Issue 1, pp. 274-286, January-February 2021. Available at doi : https://doi.org/10.32628/IJSRSET218148
Journal URL : https://ijsrset.com/IJSRSET218148