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

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ABSTRACT

Polybrominated diphenyl ethers are linked to adverse health effects that include thyroid hormone disruption, neuro-developmental deficit, abnormal pregnancy, and potential carcinogens. This study was aimed at assessing the concentrations of selected Polybrominated diphenyl ether compounds in water of Nairobi River. Water samples were collected by grab method from nine sites along the river and analysed for brominated diphenyl ethers using gas chromatography coupled with mass spectrometer. The mean concentration of polybrominated diphenyl ethers residue in water ranged from <0.0009 to 72.89 ± 6.15 ng/L. The dominant congeners were 2,2',4,4'-tetra- bromodiphenyl ether, 2,2',4,4',5,5'-hexa-bromodiphenyl ether, 2,2',4,4',6-penta-bromodiphenyl ether, 2,2',4,4',5,5'-hexa-bromodiphenyl ether and 2,2',4,4',5,6'-hexa-bromodiphenyl. The highest mean concentration of 2,2',4,4'-tetra- bromodiphenyl ether was 72.89 ± 6.15 ng/L, 2,2',3,4,4'-penta- bromodiphenyl ether was 14.08±0.68 ng/L, 2,2',4,4',6-penta-bromodiphenyl ether was 43.67±1.47 ng/L, 2,2',4,4',5,5'-hexa-bromodiphenyl ether was 24.78±2.49 ng/L, and 2,2',3,4,4',5',6-hepta-bromodiphenyl ether was 11.75±0.97 ng/L. Consequently, as these compounds are known to bio-accumulate in fatty tissues, continued use of the river water poses a health risk to animals and humans due to contamination across the food chain.

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1. Introduction

Flame retardants (FRs) are a group of chemicals that are added to manufactured goods like electronics and electrical goods, textiles, plastics, and furniture to improve their fire resistance [1]. One of the widely used groups of flame retardants is polybrominated diphenyl ethers (PBDEs). Polybrominated diphenyl ethers are organobromine chemicals substances with up to ten bromine atoms usually attached to a biphenyl structure [2]. The number and position of bromine atom attached to the biphenyl ring determines the congener and in total we have 209 congeners of PBDEs [2]. Table 1 shows the names, chemical Structure, abbreviations, and Molecular formula of PBDE congeners investigated in this study. There are three main commercial PBDE formulations namely penta-bromodiphenyl ethers octa-bromodiphenyl ethers and deca-bromodiphenyl ethers with the latter accounting for 83% of the overall PBDE production worldwide [3]. Polybrominated diphenyl ethers 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]. Figure 1 shows the general chemical structure of PBDEs.

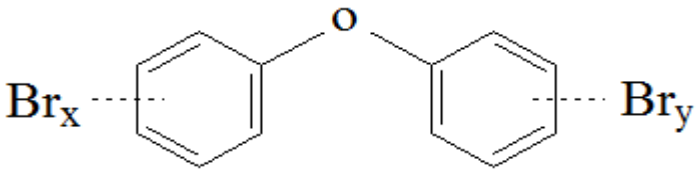


Figure 1: General chemical structure of Polybrominated Diphenyl Ether

Polybrominated diphenyl ethers are of environmental and human wellbeing concern as a result of their non-degradability, bioaccumulation, long-range transport, and toxicity in the atmosphere [9,10]. Environmental contamination by PBDEs 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]. Penta-bromodiphenyl ethers octa-bromodiphenyl ethers and deca-bromodiphenyl ethers have been added in the Stockholm Convention on Persistent Organic Pollutants because of their non-degradability, bioaccumulation, toxicity, increased pollution levels in the environment, and risk to human health [22,23].

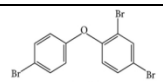
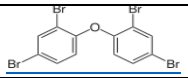
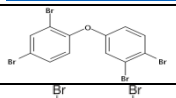
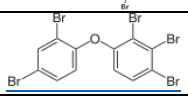
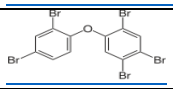
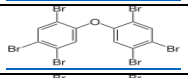
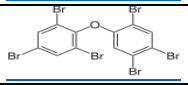
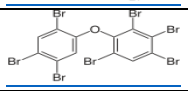
Nairobi River flows through Kenya's capital city, it is the key river of the Nairobi river basin, a complex of numerous streams flowing eastwards [24]. Nairobi River courses from Ondiri swamp on the western part of Nairobi City and traverses settlements, the central business district, heavy and light industries in the mid and downstream and it eventually joins the Athi River at fourteen falls which drains to the Indian Ocean [24]. The Nairobi river is one of the most contaminated rivers in Kenya, [25], it 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].

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

This study was aimed at assessing the concentrations of selected Polybrominated diphenyl ethers compounds in the water of

Nairobi River

Table 1. Names, chemical structure, acronym, and molecular formula of Polybrominated Diphenyl Ethers Congeners investigated in this study

Name of PBDE	Chemical Structure	Acronym	Molecular formula
2,4,4'-tribromodiphenyl ether		BDE28	C12H7Br3O
2,2',4,4'-tetra-bromodiphenyl ether		BDE47	C12H6Br4O
2,3',4,4'-tetrabromodiphenyl ether		BDE66	C12H6Br4O
2,2',3,4,4'-penta- bromodiphenyl ether		BDE85	C12H5Br5O
2,2',4,4',5-penta- bromodiphenyl ether		BDE99	C12H5Br5O
2,2',4,4',6-penta-bromodiphenyl ether		BDE100	C12H5Br5O
2,2',4,4',5,5'-hexa-bromodiphenyl ether		BDE153	C12H4Br6O
2,2',4,4',5,6'-hexa-bromodiphenyl ether		BDE154	C12H4Br6O
2,2',3,4,4',5',6-hepta-bromodiphenyl ether		BDE183	C12H3Br7O

2. Materials and Methods

2.1. Study Area

Nairobi County is among the 47 counties in Kenya and is located between 36o45'' E to 37o05'E, and 1o10''S; to 1o30''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 between January and March, heavy rain season between April and June, cool dry season between July and September, and short rain season between October and December. Temperatures generally vary from 11°C from June to July to about 29°C from December to March [30].

Nairobi River courses from Ondiri swamp on the Western part of the City and traversing 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 2 shows the map of Nairobi River basin showing the sampling sites.

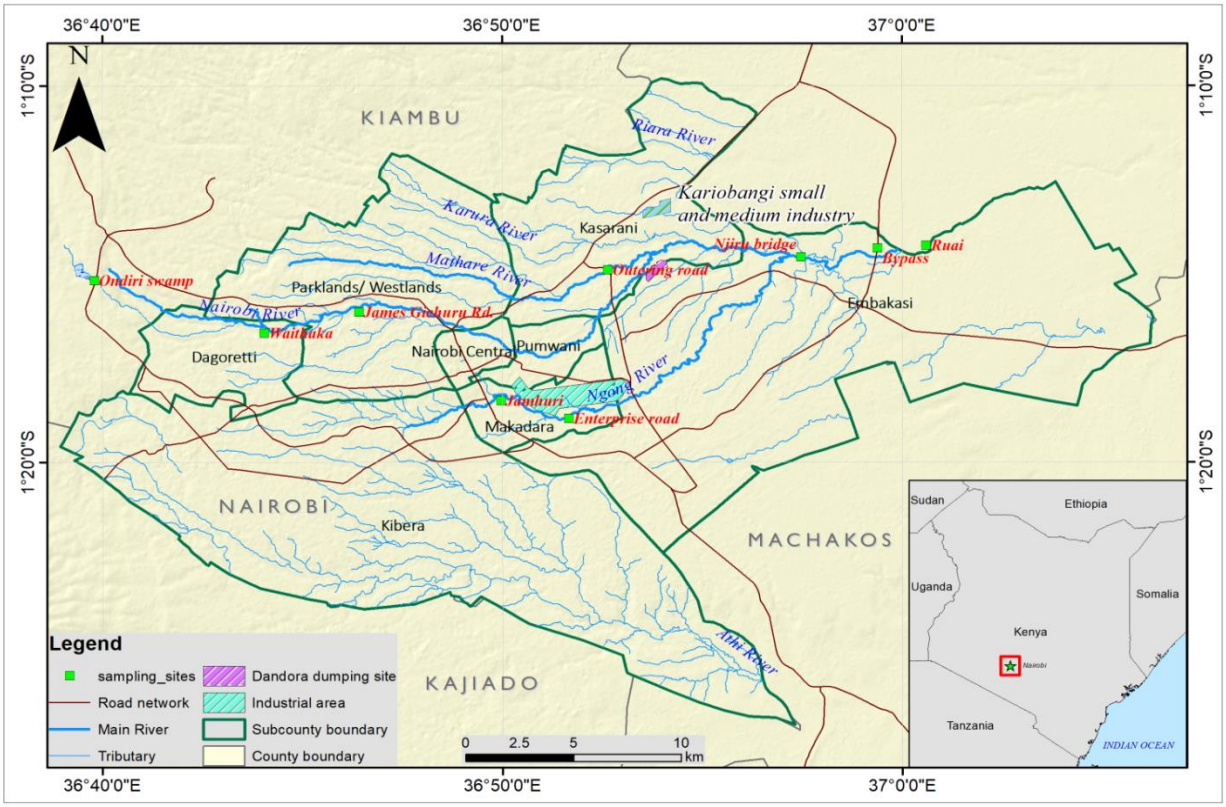


Figure 2: Sampling sites in Nairobi River Basin

2.1. Reagents and Chemicals

Analytical grade silica gel, acetone, n-hexane, sodium hydroxide, sulphuric acid, anhydrous sodium sulphate, isooctane and dichloromethane were purchased from Sigma-Aldrich, USA. White sport nitrogen gas and helium gas were purchased from BOC Kenya limited. High purity PBDEs standard mixture and 13C labelled 3,3',4,4'-Tetrabromodiphenyl Ether 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 water 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, Waithaka and Jamhuri represented the upstream, James Gichuru, Enterprise road and Outering road represented the midstream while Njiru, By-Pass and Ruai represented the downstream. Water was collected quarterly from July 2017 to June 2018 covering the cool dry season, short rain season, hot dry season and heavy rain seasons to capture the four seasons experienced in Kenya [30].

The Sample collection procedure followed the United States environmental protection agency method 1614 [31]. Water was collected by grab method into a clean amber glass bottle then covered by teflon screw cap. The samples were transported to the laboratory in a cooler box

containing ice cubes and kept in a fridge at 4°C for a maximum period of 72 hours before extraction.

2.3. Extraction

Water was extracted by liquid-liquid partitioning using methylene chloride. Two litres of water were transferred into a 2000 mL separatory funnel and spiked with ^{13}C labeled 3,3',4,4'-tetrabromodiphenyl ether extraction standard. Sixty millilitre of dichloromethane was added to the water, shaken vigorously while freeing pressure and allowed to settle to increase separation into two layers. The lower organic phase was collected into a pre-cleaned 250 mL conical flask and the extraction procedure was repeated twice with 60 mL dichloromethane. The collective extracts were dried using anhydrous sodium sulphate, after which 1mL of isooctane was added as a keeper and the extracts reduced to 2 mL using a rotary evaporator [31].

2.4. Sample Clean up

Sample extracts were cleaned by passing them through a chromatographic glass column packed with 1 cm anhydrous sodium sulphate, followed by 1000 mg activated silica, 4 g basic silica, 1000 mg activated silica, 8 g acidic silica, 2 g activated silica and 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, and the eluate reduced to 1 mL then transferred into 1.5 mL autosampler vials. All the samples were further reduced under a gentle stream of white sport nitrogen gas to 0.5 mL for gas chromatography-mass spectrometry analysis [31].

2.5. Gas Chromatography-Mass Spectrometry Analysis

The samples were analysed for 9 PBDE congeners using Agilent 6890N gas chromatography equipped with a single quadrupole Agilent 5973A mass spectrometer and fitted with Thermo scientific traceGOLD TG-5SILMS column of dimensions 0.25 um thickness; 0.25 mm internal diameter and 30 m length. The mass spectrometer was operated in selected ion monitoring mode with electron impact ionization method at a resolution of >5,000. The detector and injection temperature was set at 320 - 280°C in that order. High purity helium gas was used as the carrier gas at a flow rate of 1 ml min^{-1}. The oven temperature was set at 90°C held for 1 minute then ramped from 90 to 180°C at 40°C min^{-1}, ramped from 180 to 260°C at 10°C min^{-1} held for 2 minutes, and finally ramped from 260 to 320°C at 25°C min^{-1} held for 8 minutes. Injection volume of 1µL was used for both the sample extracts, mixed standard solutions, and calibration standards following 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 analysed at similar gas chromatography mass spectrometer conditions with the samples. The analytes were also identified using the National institute of standards and technology mass spectrometer library, version 2.0 Standard reference data program of the United States 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 minutes 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. 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 greater than 0.99. Table 2 shows the retention time, linearity, limit of detection, limit of quantification, accuracy, and monitoring ions of PBDE congeners investigated in this study.

Table 2: Retention time, linearity, Limit of Detection (LOD), Limit of Quantification (LOQ), accuracy, and monitoring Ions of PBDE Congeners investigated in this study

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/ Standard	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

PBDEs, polybrominated diphenyl ethers; LOD, Limit of detection; LOQ, Limit of quantification; BDE28, 2,4,4'-Tribromodiphenyl ether; BDE47, 2,2',4,4'-tetra- bromodiphenyl ether; BDE, 2,3',4,4'-Tetrabromodiphenyl ether; BDE85, 2,2',3,4,4'-penta- bromodiphenyl ether; BDE99, 2,2',4,4',5-penta- bromodiphenyl ether; BDE100, 2,2',4,4',6-penta-bromodiphenyl ether; BDE153, 2,2',4,4',5,5'-hexa-bromodiphenyl ether; BDE154, 2,2',4,4',5,6'-hexa-bromodiphenyl ether; BDE183, 2,2',3,4,4',5',6-hepta-bromodiphenyl ether

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, methanol, acetone, and methylene chloride. The glassware was 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 13C labeled 3,3',4,4'-tetrabromodiphenyl ether standard were of high purity of above 98%, kept in amber vials to prevent photo degradation, and stored in a freezer to prevent evaporation. Amber glass bottles were used for sampling and storage of water samples mainly to prevent photo degradation of PBDEs.

Control tests were performed to authenticate the analytical procedures. Field blanks were carried to the field to track any contamination during transportation. The gas chromatography mass spectroscopy machine was regularly injected with solvent blank and procedural blanks. A calibration standard check of 10 ng/L was injected into the gas chromatography mass spectroscopy machine after analysis of every ten samples to ensure that not more than fifteen percent difference was established from the initial calibration standards. A recovery experiment was performed to test for the accuracy of the method. Before extraction 1ppm ^{13}C labelled 3,3',4,4'-tetrabromodiphenyl ether standard was spiked to all samples and the average surrogate recovery in all samples was 78.34±9.2%. 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. The limit of quantification was calculated in the same way using ten times the noise level.

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.

3. Results and Discussion

The nine PBDE congeners selected for analysis have been classified as "PBDEs of primary interest" by the United States environmental protection agency method 1614 and are frequently found in lake and river water [31, 32]. The mean concentration of $\sum_9$PBDEs in the water ranged between below detection limit to 72.89±6.15 ng/L. The most frequently detected PBDEs are BDEs 47 99, 100, 153, and 154 with a detection frequency of 100%. The result in this study was comparable to a similar study by Olutona and Co-workers in Asunle Stream, Ile-Ife, Nigeria which had a mean concentration of 0.03 to 0.45 ng/mL [17] but the concentration was lower than the levels reported in Diep River, Cape Town, South Africa which had a concentration of 0.84 to 12,000 ng/ml [18]. Median, detection frequency, range and mean concentration of PBDEs in Nairobi River Water is presented in Table 3.

Table 3: Median, detection frequency, range and mean concentration of Polybrominated Diphenyl Ethers in Nairobi River water (ng/L)

Congener/ Seasons	**Cooler Dry (N=27)**			**Short Rain (N=27)**			**Hot Dry (N=27)**			**Heavy Rain (N=27)**		
	Median (min-max)	Mean	DF (%)	Median (min-max)	Mean	DF (%)	Median (min-max)	Mean	DF (%)	Median (min-max)	Mean	DF (%)
BDE 28	3.76 (<0.001-7.71)	3.79± 2.20	89	5.17 (2.13-8.06)	5.31± 1.72	100	12.18 (4.14-20.79)	12.01± 5.04	100	5.91 (1.37-12.74)	6.17± 3.72	100
BDE 47	10.79 (1.23-72.89)	17.61± 17.58	100	4.14 (1.43-15.05)	5.63± 3.99	100	8.26 (3.61-22.10)	10.04± 6.41	100	8.00 (3.66-27.44)	6.09± 3.99	100
BDE 66	0.78 (<0.0013-7.32)	2.37± 2.76	89	1.72 (<0.0013-7.30)	2.69± 2.47	78	0.33 (0.02-0.71)	0.31± 0.21	100	0.42 (<0.0013-1.45)	3.22± 7.21	89
BDE 85	0.01 (<0.0009-7.59)	1.92± 2.98	33	3.55 (0.30-6.38)	3.49± 1.77	100	4.73 (1.04-14.08)	8.28± 4.22	100	6.41 (1.64-10.57)	8.39± 7.75	100
BDE 99	10.79 (0.65-53.24)	26.61± 25.78	100	1.83 (0.11-13.44)	4.66± 5.61	100	4.08 (1.92-28.41)	10.27± 9.78	100	7.85 (3.01-12.71)	14.17± 10.18	100

Congener/ Seasons	Cooler Dry (N=27)			Short Rain (N=27)			Hot Dry (N=27)			Heavy Rain (N=27)		
BDE 100	3.06 (0.88-20.86)	6.16± 6.58	100	2.22 (0.22-10.59)	3.66± 3.62	100	8.73 (4.09-24.78)	10.32± 7.14	100	3.64 (1.65-18.74)	5.55± 5.43	100
BDE 153	2.93 (0.93-10.26)	3.21± 2.83	100	1.48 (0.69-5.49)	1.93± 1.47	100	1.96 (1.21-6.87)	3.13± 1.90	100	2.68 (0.91-4.89)	3.08± 2.27	100
BDE 154	0.07 (0.05-0.14)	0.09± 0.03	100	0.85 (0.49-1.80)	1.01± 0.41	100	0.36 (0.12-1.24)	0.61± 0.55	100	2.39 (0.41-5.76)	2.14± 1.70	100
BDE 185	4.09 (1.83-11.75)	6.08± 4.19	100	2.31 (0.95-10.74)	3.39± 3.12	100	0.55 (<0.0012 -2.41)	0.78± 0.81	89	3.17 (<0.0012-5.50)	3.62± 2.63	78

DF, Detection Frequency; N, Number of Samples

The main contributor to the PBDE levels detected is BDE 47 and 99. The high levels of BDE 47 may be as a result of leachate or deposits from the inappropriate dumping of penta-BDE formulations like the polyurethane foams used in furniture pillows, vehicle seats, cushions, freezers wrapping, electronic wrapping, mat, and shoes [33] which are washed into the river. Lower brominated PBDE congeners are more toxic and more bioaccumulative than higher brominated PBDE congeners resulting in increased risk to the environment [34].

3.1 Spatial and Seasonal Variation of Polybrominated Diphenyl Ethers

Nairobi River was divided into three sections, namely, the upstream, midstream, and downstream locations. The mean concentration of the $\sum_9$PBDEs for the upstream, midstream, and downstream locations in Nairobi River ranged from below detection limit to 43.67±1.47, below detection limit to 40.46±1.08, and below detection limit to 72.89±6.15 ng/L, respectively. The observed trend of contamination of PBDEs downstream of the river profile can be attributed to human activities around the river since the river is located in residential areas at the upstream and industrial areas in the midstream and downstream of the river. The results show that the use of consumer goods containing PBDEs formulations in Kenya is higher despite the effort made by the international organization to stop the manufacture and use of PBDEs by 2013 [35]. This shows that the Kenyan government has not eradicated the use of PBDEs products despite the increasing fear of the health effect posed by PBDEs.

The mean concentrations of PBDEs at the nine sampling sites along Nairobi river basin were assessed to measure their variation designs. The result shows that the PBDE congeners 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 2.91 and 8.11 ng/L. The mean level of the spatial allocation of PBDEs in the Nairobi River water samples for the nine sampling sites is shown in Table 4.

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

The mean concentration of these contaminants increased downstream from the source of the river. The sampling sites; Ruai, By-pass, Njiru, Outering road, and Enterprise road had a relatively higher concentration of PBDEs that are associated with their close proximity to Dandora municipal dumpsite where unsorted wastes are dumped including plastics, domestic and industrial wastes from factories at industrial area hence leaching of the contaminants into the receiving river is highly probable.

Dismantling and burning of electronic wastes are considered key sources of PBDEs in Kenya [36]. It is projected that 7350 tons of electronic wastes were produced yearly generating 143.19 tons of PBDEs into the environment per year [36]. The upstream section of Nairobi River had a relatively low concentration of PBDEs that could be attributed to atmospheric deposition from the open burning of solid wastes. This suggests that atmospheric deposition is a route of transport of particulate contaminants to Nairobi River's ecosystem [33].

Table 4. Mean Levels (ng/L) of the spatial allocation of Polybrominated Diphenyl Ethers in the Nairobi River watersamples.

Sites/PBDEs	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	$\sum_9$ PBDEs
Ondiri	2.61± 1.02	6.54± 3.21	0.37± 0.29	1.24± 1.15	4.34± 4.46	7.58± 4.14	1.87± 1.78	0.32± 0.16	1.31± 1.93	2.91
Waithaka	6.41± 4.17	6.32± 2.04	0.19± 0.15	2.06± 1.38	2.57± 1.46	6.62± 6.29	2.01± 1.55	0.44± 0.32	2.11± 1.29	3.2
James Gichuru	6.41± 4.36	11.9± 14.67	1.98± 2.05	4.81± 3.49	4.39± 4.12	3.32± 2.87	1.44± 0.40	0.56± 0.33	4.28± 5.33	4.35
Jamhuri	8.45± 4.67	6.88± 2.56	2.23± 1.89	4.54± 2.88	16.03± 16.64	5.34± 3.72	3.74± 2.16	1.19± 1.11	5.06± 4.17	5.94
Outering Road	9.66± 4.32	18.78± 12.96	8.58± 8.23	2.84± 4.16	5.06± 4.89	3.16± 1.76	2.34± 1.81	1.34± 0.83	1.66± 1.06	5.94
Enterprise Road	7.59± 1.92	12.26± 7.97	0.17± 0.30	4.78± 3.77	8.49± 6.63	3.57± 4.45	3.65± 3.02	1.87± 2.26	3.85± 3.80	5.14
Bypass	4.97± 1.61	8.68± 6.09	3.35± 2.59	5.15± 0.51	14.51± 11.93	5.17± 3.24	3.22± 1.60	0.89± 0.91	5.76± 3.99	5.74
Njiru	5.56± 2.39	22.61± 29.06	0.31± 0.11	6.47± 2.09	18.57± 15.08	13.36± 9.64	3.25± 0.91	0.69± 0.59	2.21± 1.35	8.11
Ruai	9.70± 7.02	14.37± 7.73	1.49± 1.31	5.53± 2.17	15.44± 7.49	9.68± 5.46	4.03± 4.28	1.32± 1.13	4.96± 4.6	7.39

Figure 3 shows the seasonal variation in the concentration of PBDE congeners in water samples from Nairobi River. The concentrations of BDE 47 and 99 congeners showed significant differences in the cool dry season in the river water but the value obtained for BDE 47 during the cool dry season was more distinct. The predominance of BDE 47 and 99 during the cool dry season is attributed to the high technical formulation of BDE 47 and 99 compounds available in the waste at Dandora dumping site. Additionally, the less flora cover of the Nairobi River allows the penetration of sunshine thereby enhancing the debromination of the PBDE congeners to different levels [33]. Polybrominated diphenyl ether congeners leak from the dumpsite due to heavy precipitation and

consequent release of runoff into the river leading to the high concentration of PBDE congeners observed in the cool dry season after the heavy rain season.

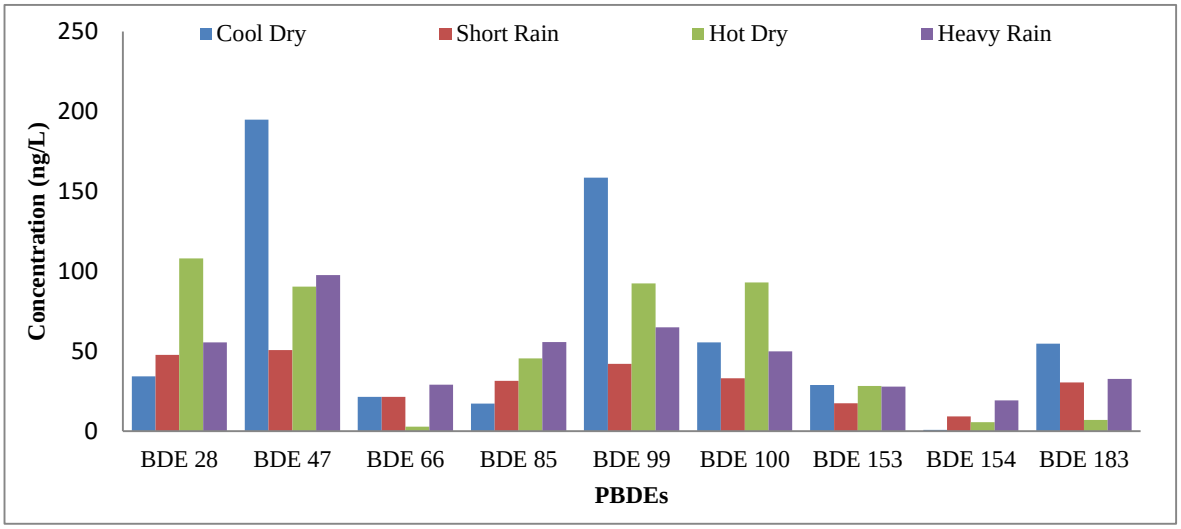


Figure 3: Seasonal variation in the levels of Polybrominated Diphenyl Ether Congeners in Nairobi River water samples

Detection frequencies of PBDE congeners during the four seasons in water were as follows; BDE 28 97%, BDE 47 100%, BDE 66 86%, BDE 85 83%, BDE 99 100%, BDE 100 100%, BDE 153 100%, BDE 154 100% and BDE 183 94%. The high frequency of all the PBDEs analysed in this study suggests the widespread distribution of PBDEs in the water of Nairobi River basin. Penta-BDE congeners were higher in water. This was attributed to deposits from the dumping of polyurethane foams into the river. The octa-PBDE formulation is mostly used in plastics. They are deposited into the soil when plastic materials are burned and are eventually washed by runoffs. Kenya does not manufacture PBDEs, it imports products containing PBDEs but comprehensive information about its composition is not known [36]. Moreover, Liu and co-workers reported that BDE 47 and BDE 99 were the predominant PBDEs in Chaohu Lake in China [37].

The PBDEs levels in the present study were compared to Environment Canada set limit for surface water, which are 46 ng/L for BDE 28, 24 ng/L for BDE 47, 24 ng/L for BDE 66, 0.2 ng/L for BDE 85, 4 ng/L for BDE 99, 0.2 ng/L for BDE 100, 120 ng/L for BDE 153, 120 ng/L for BDE 154 and 17 ng/L for BDE 183 [38]. The mean concentration recorded for BDE 47, 85, 99, and 100 far exceeded the guideline levels provided by Environment Canada signifying the shocking nature of Nairobi River's water pollution situation.

Lower molecular weight PBDE congeners are more toxic and hence more bioaccumulative, when consumed they accumulate in human fatty tissues [34]. Hence, their presence especially the high level of BDE 47, 85, 99, and 100 could have had a substantial contribution to the increased cases of cancer and other forms of diseases in Kenya [39], since this BDE are suspected cancer agents [40].

Table 5 shows a two-tailed correlation of PBDE congeners in Nairobi River water samples. Bromodiphenyl ether 28 had a positive correlation with BDEs 85, 100, and 153. Bromodiphenyl

ether 47 showed a positive correlation with BDEs 99, 153, and 183. Bromodiphenyl ether 66 had a positive correlation with BDEs 154 and 183. Bromodiphenyl ether 85 had a positive correlation with BDEs 100, 153, and 154. Bromodiphenyl ether 99 was positively correlated with BDEs 47, 100, 153, and 183. Bromodiphenyl ether 100 was positively correlated with BDE 153. The observed positive correlations demonstrated by the majority of PBDE congeners investigated suggests that the PBDEs originated from the same source mostly from end-user products containing PBDEs discarded into the dumpsite from which the PBDE congeners leak into the river.

Table 5: Correlation coefficient of Polybrominated Diphenyl Ether congeners in Nairobi River water samples

	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
BDE 28	1	-.394	-.842	.555	-.194	.851	.246	-.002	-.934
BDE 47		1	.118	-.567	.963*	.148	.685	-.529	.697
BDE66			1	-.019	-.148	-.844	-.180	.533	.702
BDE 85				1	-.606	.265	.157	.822	-.656
BDE 99					1	.344	.691	-.702	.527
BDE 100						1	.652	-.313	-.606
BDE 153							1	-.113	.074
BDE 154								1	-.207
BDE 183									1

*** Correlation is significant at the 0.01 level (2-tailed); * Correlation is significant at the 0.05 level (2-tailed)*

3.2 Comparison of Polybrominated Diphenyl Ether Levels in Nairobi River Water Samples with Levels in Various Countries of the World

A comparison of different research done around the globe is challenging because of variations in the PBDE contaminants analysed. The mean concentration of nine PBDEs analysed in this study ranged between below detection limit to 72.89±6.15 ng/L was lower than those observed in Mendoza River Argentina States [41], Diep/Kuils Rivers in South Africa [18], Chaohu Lake in China [37] and wastewater treatment plant in California [32] but they were comparable to levels measured in water from Asunle Stream, Ile-Ife in Nigeria [17] The concentration of PBDEs in Nairobi River were higher than those reported in water from Lake Shihwa in Korea [42]. A comparison of the concentration of PBDEs in the current study with similar studies around the world is summarized in Table 6.

Table 6: Comparison of Polybrominated Diphenyl Ethers levels in Nairobi River water samples with other studies around the world

Location	ΣPBDEs (ng/L)	Reference
Chaohu Lake, China	110–4,480 [a]	[37]
Asunle Stream, Ile-Ife, Nigeria	30 to 450[b]	[17]
Mendoza River, Argentine	<0.0004 - 1.9 [c]	[41]
Pearl River, China	0.344–68[d]	[43]
Diep/Kuils Rivers, South Africa	2.6 – 4.830[e]	[18]
Lake Shihwa, Korea	0.16–11.0[f]	[42]
Nairobi River	<0.0009 -72.89	Data for current study

[a]Total concentrations BDE 28, 47, 99, 100, 153, 154, 183, and 209; [b]Mean concentration of BDE 28,47,99,100,153 and 154; [c]PBDE analyzed are BDE 47, 99, 100 and 153; [d]sum of BDE 28, 47, 66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 203, 206, 207, 208, and 209; [e]mean concentrations of the sum of BDE 28, 47, 100, 99, 154, 153, 183, and 209; [f]total concentration of BDE 17, 28, 47,49, 66, 71, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191,196, 197, 206, 207 and 209

4. Conclusion

The water from Nairobi River was found to be contaminated with PBDEs especially at Njiru site. The concentration of PBDE congeners increased from <0.0009 to 72.89 ng/L down the river profile, giving the impression that cumulative human activities contributed to 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 dominant PBDEs were BDE 47, 85, 99, 100 and 183 and their highest concentrations were 72.89 ± 6.15, 14.08±0.68, 43.67±1.47, 24.78±2.49 and 11.75±0.97 ng/L, respectively, meaning that continued pollution of the river may completely interfere with the river ecology. The river water poses a health risk to animals and humans due to contamination across the food chain. The current research forms a baseline data on the pollution of Nairobi River with PBDEs.

Disclosure statement

The authors declare no conflict of interest.

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