Polybrominated Diphenyl Ethers Pollution in Urban and Rural Settings' Ambient Air in Kenya: An Insight into Concentration Levels, Compositional Profile and Seasonal Variation

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

[1]Department of Chemistry, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya.
*Corresponding author email: osoroenock@yahoo.com

ARTICLE INFO	ABSTRACT
Available online: 30th June 2021 *Keywords:* Air pollution Polybrominated diphenyl ethers Passive air sampling Urban Rural	Air samples were collected from three urban and one rural sites in Kenya with the aim of establishing pollution levels of Polybrominated Diphenyl Ethers. Forty-eight air Samples were collected by passive air sampling, Soxhlet extracted and analysed for brominated diphenyl ethers using gas chromatography coupled with mass spectrometer. The mean concentration of polybrominated diphenyl ethers residue in air ranged from ≤0.9 to 152.72±3.19 pgm−3. The predominant congener was 2,2',4,4'-tetra-bromodiphenyl ether with mean concentration range of 1.94±0.03 to 152.72±3.19 pgm−3 followed by 2,2',4,4',5-penta- bromodiphenyl ether with mean concentration range of 1.32±0.06 to 66.83±1.19 pgm−3. Seasonal variations of the pollutants showed a high level of Polybrominated Diphenyl Ethers in hot dry season in range of 1.94±0.03 to 152.72±3.19 pgm−3. Air samples from Dandora and Industrial area both from urban location recorded high concentrations of the analysed polybrominated diphenyl ethers compared with the air samples from the rural location.

1. Introduction

Flame retardants are a cluster of chemicals added to commercial goods like electronics and electrical goods, textiles, plastics, and furniture to improve their fire resistance [1]. Brominated flame retardants were widely used group of organic flame retardants, particularly, polybrominated diphenyl ethers (PBDEs) [2]. We have three main commercial PBDE formulations namely penta-bromodiphenyl ethers (Penta-BDE), octa-bromodiphenyl ethers (Octa-BDE) and deca-bromodiphenyl ethers (Deca-BDE), the latter accounts for 83% of the overall PBDE manufactured globally [1]. PBDEs exhibit environmental behavior resembling to that of persistent organic pollutants (POPs), characterized by long-range atmospheric transport, persistence, semi volatility, bioaccumulation and lipophilicity [3, 4]. PBDEs are associated with toxic effects that include thyroid hormone disruption [5], neuro-developmental deficits [6], potential carcinogenesis [7] and abnormal pregnancy [8]. Figure 1 shows the general chemical structure of PBDEs.
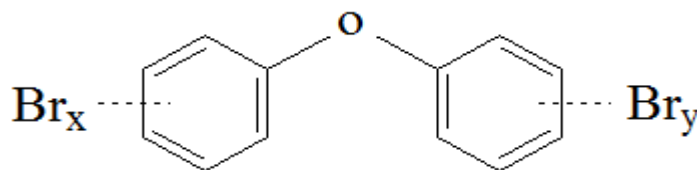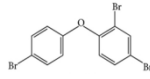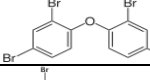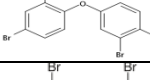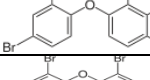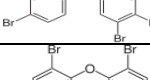
Figure 1: General Chemical Structure of PBDE

In May 2009, the Conference of Parties that are signatory to Stockholm Convention adopted amendments to Annex A and added tetra-, penta-, hexa- and hepta-BDE stopping their manufacture and usage [9]. In the European Union (EU) and the United States of America the manufacture of commercial mixtures of octa- and penta-BDE was forbidden from 2004 due to their wide existence in the atmosphere and associated toxicity [10]. European Union banned the application of Deca-BDE commercial mixture in electronics and electrical applications, and restricted the total acceptable limit of PBDEs to 0.1% w/w in commercial goods [9]. In 2012 companies manufacturing PBDEs in Canada and United States of America phased out importation, sale and manufacture of Deca-BDE [11]. Though in Asia, there are no regulatory restrictions on the production, usage and sale of products with Deca-BDE formulation [11].
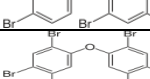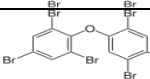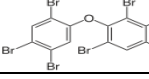
PBDEs contamination in the global environment was first detected in samples of fish caught in Swedish waters in 1981 [12]. Since then, various researchers have reported existence of PBDEs in different ecological and living organism samples across the world. The research conducted on Kenyan soil [13], Indian Ocean sediment [14], Tilapia from four different lakes in Tanzania [15], in Asunle stream water [16] and Lagos lagoon sediments in Nigeria [17], in water, fish and sediments in South Africa [18], in workers and wild marine animals at an electrical waste dismantling location in China [19], in breast milk from central Taiwan [20], dust [21, 22] and in air [23, 24, 25]. Scientific data on the level, distribution and composition of PBDE congeners in environmental media in Kenya is limited to a few studies focussing on soil and sediments [13, 14]. Measuring of these compounds in the city air environments is of particular significance since the air is exposed to all types of contaminants. This study was undertaken in Nairobi, Kenya's capital city which is also an industrial city and Mt. Kenya which is a remote site near Nairobi to provide evidence for long range transport of PBDEs. Due to urbanization, industrialization and rapid population growth, Kenya requires data on the current state of PBDEs.

In the present study, we collected air samples from Dandora, which is Nairobi's largest dumping site to provide detailed profiles of PBDEs generated by wastes. Air samples from industrial area of Nairobi City to analyze PBDE concentrations and compositions from local industries and e-waste recycling. Air samples from Kabete area which is a sub-urban to provide detailed profiles of PBDEs generated from other parts and traffic of the city. Air samples from Mount Kenya which is a remote part of the country to provide detailed profiles of PBDEs generated from agricultural activities and long range transport of PBDEs. These was done with the aim of establishing pollution levels of Polybrominated Diphenyl Ethers.

Table 1. Names, Chemical Structure, Abbreviations, and Molecular Formula of PBDE Congeners Investigated in this Study

Name of PBDE	Chemical Structure	Acronym	Molecular formula
2,4,4'-tribromodiphenyl ether		BDE28	$C_{12}H_7Br_3O$
2,2',4,4'-tetra-bromodiphenyl ether		BDE47	$C_{12}H_6Br_4O$
2,3',4,4'-tetrabromodiphenyl ether		BDE66	$C_{12}H_6Br_4O$
2,2',3,4,4'-penta- bromodiphenyl ether		BDE85	$C_{12}H_5Br_5O$
2,2',4,4',5-penta- bromodiphenyl ether		BDE99	$C_{12}H_5Br_5O$
2,2',4,4',6-penta-bromodiphenyl ether		BDE100	$C_{12}H_5Br_5O$
2,2',4,4',5,5'-hexa-bromodiphenyl ether		BDE153	$C_{12}H_4Br_6O$
2,2',4,4',5,6'-hexa-bromodiphenyl ether		BDE154	$C_{12}H_4Br_6O$
2,2',3,4,4',5',6-hepta-bromodiphenyl ether		BDE183	$C_{12}H_3Br_7O$

2. 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 m (meters) above sea level. Commercial and administrative activities are concentrated in the central business district while most of the industrial activities are located to the South-East. Nairobi experiences four major seasons namely the hot dry season (January - March), heavy rain season (April - June), cool dry season (July - September) and the short rain season (October - December). Temperatures generally vary from 11 ^{o}C in June /July to about 29 ^{o}C from December to March [26]. The three urban sampling sites are namely; Dandora (036°053'17" E, 010 15' 05S, and altitude of 1625 m) Industrial area (036°52'30" E, 01018'24" S, and altitude of 1623 m), Kabete (036o 44' 33" E, 01o 14 58" S, and altitude 1841m).

Mt. Kenya was considered a rural area in this study due to absence of human activities on the mountain. In Africa it's the second highest mountain, after Kilimanjaro. The mountain boundaries crosscut parts of Tharaka Nithi, Laikipia, Meru, Nyeri Embu and Kirinyaga counties in Kenya and is located approximately 16.5 kilometers south of the equator, about 93 miles northeast of Nairobi. The site is situated 037^0 17'84''E, 00^0 03' 752''S and altitude 3669m.
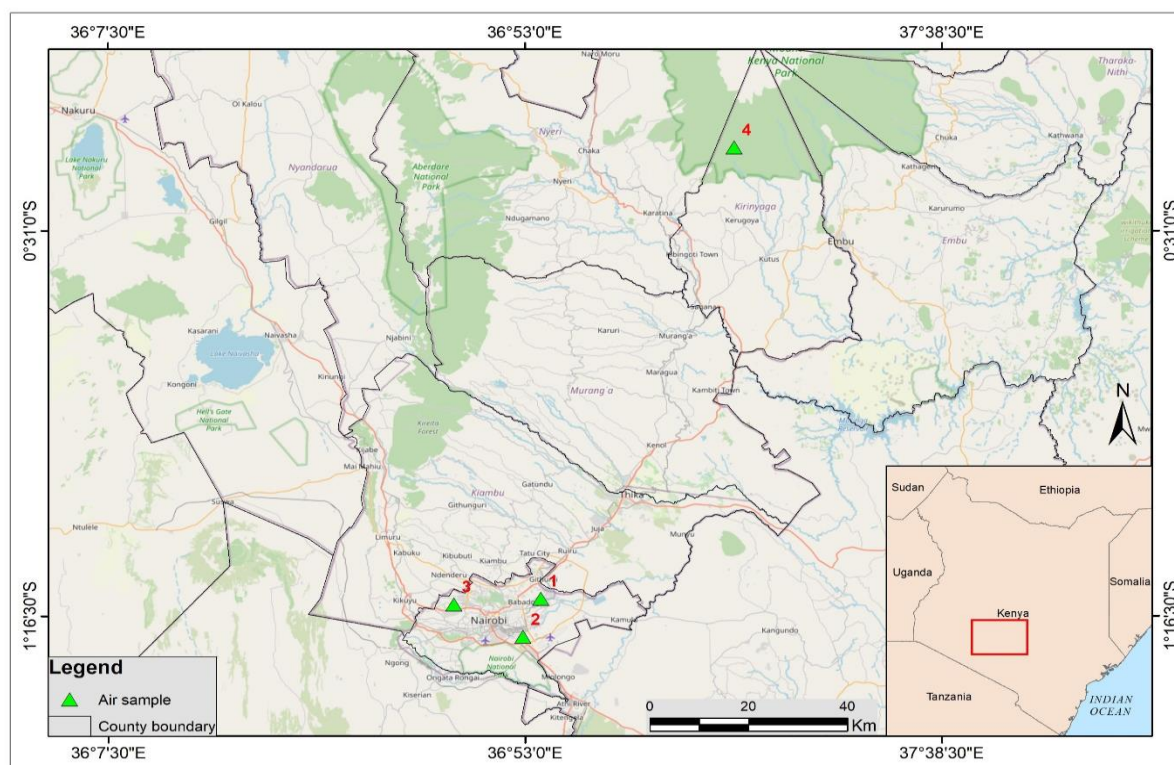
Figure 2: Map of the Study Area Showing the Four Air Sampling Locations i.e., 1-Dandora, 2-Industrial Area, 3-Kabete and 4-Mount Kenya

2.1. Reagents and Chemicals

Analytical grade silica (0.063–0.2 mesh, Merck), acetone, n-hexane, sodium hydroxide, sulphuric acid, anhydrous sodium sulphate, dichloromethane and HPLC grade isooctane were procured from Sigma-Aldrich, USA. 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 labelled BDE 77 standard were procured from Sigma-Aldrich, USA.

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

Passive air samplers containing polyurethane foam (PUFs) disks housed in stainless steel chambers which help in protecting the PUF from direct deposition of huge particles, sunshine, rainfall and reduce the speed of wind effect on the speed of sampling. The passive samplers were set 2 meters above the ground and deployed for a period of three months each (January – March, 2018; April - June, 2018; July - September, 2018 and October - December, 2018). Before installation of the stainless steel sampling chambers they were prewashed and rinsed with acetone. All PUFs were pre-cleaned using acetone and toluene in soxhlet set up then wrapped in double coatings of aluminum foil, transferred into self-sealing bags and preserved in a deep freezer before deployment at the field. Field deployed filters were covered in double layers of sterile aluminum foil, tagged, transferred into self-sealing polythene bags and kept in polyurethane cooler box comprising dry freeze up. In the research laboratory samples were kept in a deep freezer at ≤ -19 °C for maximum period of 72 hours prior to extraction. Figure 3 shows diagram of polyurethane foam disk air sampling unit.
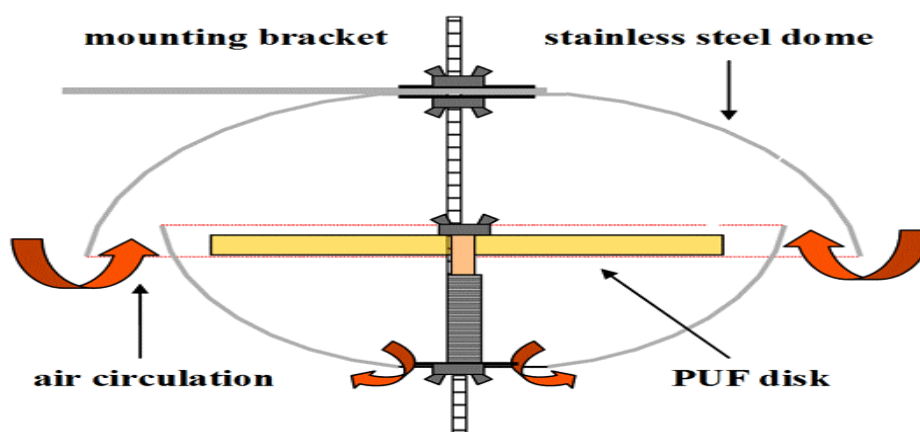
Figure 3: Diagram of Polyurethane Foam Disk Air Sampling Unit

2.4 Sample Extraction and Clean-up

The exposed PUF sorbents initially stored in the freezer at -19 °C were removed and allowed to attain room temperature. The polyurethane foams were placed in the Soxhlet extractor, 100 μl ^{13}C BDE 77 was added as internal standard and extracted for 18 hours using 0.2 liters of dichloromethane. The sample extracts were refrigerated at 4°C preceding to sample cleanup. Extracts were cleaned by eluting through a chromatographic glass column which was wet-loaded with 1 cm anhydrous sodium sulphate, 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 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 nitrogen (99.99%) to 0.5 mL for Gas Chromatography-Mass Spectrometry (GC-MS) analysis [27].

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

The samples were analysed 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 ^oC and 280 ^oC respectively. 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 ^oC (1 minute hold time), then ramped from 90 ^oC to 180 ^oC at 40 ^oC min⁻¹, ramped from 180 ^oC to 260 ^oC at 10 ^oC min⁻¹ (2 minutes hold time), and finally ramped from 260 ^oC to 320 ^oC at 25 ^oC min⁻¹ (8 minutes hold time). 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 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 2). 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 (r2) greater than 0.99 (Table 2). 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, Limit of Quantification, 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

PBDEs	BDE 28	BDE 47	BDE 66	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	BDE 183
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 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 13C labeled 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. Amber glass bottles were used for sampling and storage of water samples mainly to prevent photo degradation of PBDEs.

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 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 13C labelled BDE 77 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 (BDL). The limit of quantification (LOQ) was calculated in the same way using ten times the noise level (Table 2).

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

3.1 Level of PBDEs in Air

Analysis of field, solvent and laboratory blank samples displayed no peaks for the PBDE congeners of interest, thus excluding possibilities of cross contamination from glassware, solvents and the field. The sampling sites covered industrial area of Nairobi City to track contamination from industries, Dandora which is Nairobi's largest dumping site to track PBDEs that can leak from the wastes, Kabete is sub-urban was chosen to track contamination from other parts and traffic of the city and Mount Kenya was considered has the rural part of the country to track contamination due to agricultural activities and long range transport of PBDEs.

The rate of sampling for passive PUF disk has been reported to be averagely 4 m^3/day [28] hence deployment of the sampler for three months provided an equal air capacity of about 360 m^3, which is adequate for analysis of majority of persistent organic pollutants [9].

Nine target PBDE congeners, BDE 28, 47 66, 85, 99, 100, 153, 154 and 183 were analysed in all 48 samples collected from four sampling sites. The concentration of nine PBDEs measured in air samples ranged between ≤0.9 to 152.72±3.19 pgm^{-3} with those of BDE 47 and 99 being 1.94±0.03 to 152.72±3.19 pgm^{-3} and 1.32±0.06 to 66.83±1.19 pgm^{-3} respectively (Table 2). In the environment of Nairobi and Mount Kenya the abundant PBDEs were BDEs 47 and 99 with 100% detection frequency. The high proportion of BDE 47 and 99 in air has been reported in a number of other research, for instance, in the Northern Lake Victoria region, Entebbe, East Africa [23], Guiyu (an electrical waste reprocessing location), three municipal locations [31].

The mean concentration of the PBDE congeners for the urban locations (Dandora, Industrial area and Kabete) ranged from 1.22± 0.01 to 152.72±3.19 pgm^{-3}, 1.33± 0.03 to 69.34± 0.72 and ≤0.9 to 22.84±0.04 pgm^{-3} respectively. Rural location (Mount Kenya) the concentration level ranged from ≤0.9 to 4.56±0.39 pgm^{-3} respectively. The result in this study was comparable to similar studies by Hu and co-workers in Beijing, China which recorded average concentration of 210 pgm^{-3} using an active high-volume air sampler [32] but the concentration was higher than the levels reported by Arinaitwe and Co-workers in Northern Lake Victoria region, East Africa which had a mean concentration of 9.84 pgm^{-3} [23]. Table 3 summarizes the mean concentration of PBDEs in air.

Table 3: Mean Concentration (pgm^{-3}) of PBDE Residue in Air (n=48)

Site/ PBDE	Season	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Kabete	Cool Dry	2.27± 0.76	13.57± 0.67	≤1.3	≤0.9	7.29± 2.89	≤1.3	1.65± 0.01	≤1.0	2.18± 0.01
	Short Rain	3.54± 0.16	14.96± 0.41	≤1.3	2.07± 0.08	7.28± 0.53	1.07± 0.02	1.84± 0.03	≤1.0	2.14± 0.02
	Hot Dry	6.76± 0.29	15.48± 0.49	2.66± 0.01	1.36± 0.00	22.84± 0.04	4.86± 0.06	2.26± 0.04	3.56± 0.16	3.45± 0.52
	Heavy Rain	2.35± 0.30	3.88± 0.09	≤1.3	≤0.9	9.21± 0.11	≤1.3	2.24± 0.02	1.39± 0.01	≤1.2
Dandora	Cool Dry	4.58± 0.43	79.24± 8.59	6.79± 2.02	1.22± 0.01	26.07± 1.73	15.48± 1.05	8.59± 0.40	7.06± 0.08	4.88± 0.23

Site/ PBDE	Season	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
	Short Rain	4.64± 0.74	110.08± 3.63	8.64± 0.14	3.58± 0.09	44.95± 4.95	6.57± 0.58	6.75± 0.45	1.89± 0.62	4.64± 0.20
	Hot Dry	2.04± 0.08	152.72± 3.19	40.19± 3.62	1.48± 0.64	66.83± 1.19	15.41± 1.94	10.29± 0.55	6.29± 0.43	8.57± 0.24
	Heavy Rain	5.04± 0.46	84.50± 3.01	6.57± 0.05	1.39± 0.21	42.88± 3.34	3.00± 0.13	5.02± 0.07	2.36± 0.26	7.46± 0.87
Industrial Area	Cool Dry	6.04± 0.10	19.71± 0.64	3.39± 0.43	1.87± 0.12	14.38± 0.43	3.29± 0.15	5.69± 0.33	5.67± 0.88	4.91± 0.58
	Short Rain	3.67± 0.51	46.57± 0.58	8.16± 0.15	2.80± 0.22	44.96± 0.14	6.80± 0.21	5.31± 0.18	2.57± 0.29	7.13± 0.61
	Hot Dry	7.85± 0.92	69.34± 0.72	41.96± 3.51	3.24± 0.25	51.93± 4.68	24.71± 0.53	12.94± 1.35	7.94± 0.06	9.56± 1.44
	Heavy Rain	3.11± 0.06	26.98± 3.86	4.63± 0.19	1.33± 0.03	36.76± 2.19	5.79± 0.06	3.78± 0.16	1.67± 0.01	6.06± 0.42
Mt. Kenya	Cool Dry	BDL	1.52± 0.01	≤1.3	≤0.9	1.32± 0.06	≤1.3	1.24± 0.09	≤1.0	1.07± 0.02
	Short Rain	1.44± 0.04	3.36± 0.01	≤1.3	1.3± 0.03	2.05± 0.08	1.65± 0.05	≤1.4	≤1.0	1.17± 0.12
	Hot Dry	2.48± 0.05	4.56± 0.39	1.99± 0.00	1.34± 0.01	2.33± 0.11	2.55± 0.01	1.87± 0.05	1.21± 0.07	1.22± 0.013
	Heavy Rain	1.23± 0.16	1.94± 0.03	≤1.3	≤0.9	1.45± 0.07	≤1.3	1.51± 0.05	≤1.0	≤1.2
Detection Frequency	%	94	100	63	75	100	75	94	69	88

The percentage composition of total PBDEs in air are as follows; BDE 28 (4%), BDE 47 (43%), BDE 66 (8%), BDE 85 (2%), BDE 99 (25%), BDE 100 (6%), BDE 153 (4%), BDE 154 (2%) and BDE 183 (4%). Among the commercial mixture of penta-PBDEs is 2,2',4,4',5 penta-bromodiphenyl ether is the main congener (approx. 44–58%) followed by 2,2',4,4' tetra-bromo diphenyl ether (approx. 24–42%). High concentration of BDE 47 and 99 are detected in air samples, their fraction is inverted (BDE 47: BDE 99 approx. 2:1) related to the novel mixtures [33]. This is because of the chemical stabilities and differences, based on the vapour pressure of BDE 47 and 99 [33]. Furthermore, Leonetti and co-workers have reported BDE 47 as the abundant congener in human tissue [34].

Among the three urban locations studied, Dandora was the most polluted due to leaching from industrial and domestic waste which include electrical and electronic and other articles (carpets, firefighting foams, aviation hydraulic fluids, shoes, textiles, etc.) and due to ignorance and lack of appropriate technical infrastructures in Nairobi city's largest dumping site. Open incineration of electronic waste has shown to contribute to PBDEs pollution [35]. Secondly, it may be from the activities of nearby light industries such as construction material production and metal degreasing that are situated in Kariobangi. Industrial area was also contaminated and the pollution can be attributed to leaching from end-of-life vehicles (cars, buses, minibuses, trucks) from the vehicle body parts recycling plants and other industrial activities in the area. The low concentration of PBDEs at Mount Kenya site recorded in this study is as a result of long range transport.

Table 4: Mean Levels (pgm^{-3}) of the Spatial Allocation of PBDEs in the Air Samples

	BDE 28	BDE 47	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	∑$_9$PBDEs
Kabete	3.53± 2.16	11.97± 5.45	1.30± 1.30	0.85± 0.89	9.91± 8.94	1.48± 1.99	2.00± 0.30	1.24± 1.46	1.94± 1.43	3.77
Dandora	5.86± 2.21	106.64 ±33.66	15.51± 14.25	2.66± 1.48	35.72± 26.38	10.12± 5.48	7.72± 2.25	4.40± 2.29	6.38± 1.94	22.00
Industrial Area	5.17± 2.19	40.65± 22.23	14.04± 15.06	2.31± 0.75	28.76± 23.31	10.15± 8.50	6.93± 4.09	4.46± 2.50	6.92± 1.98	13.54
Mt. Kenya	1.29± 1.02	2.85± 1.39	1.00± 0.99	0.58± 0.59	1.80± 0.47	1.05± 1.09	0.91± 0.66	0.30± 0.52	0.87± 0.58	1.255

The sampling period covered the hot dry, heavy rain, cool dry and short rain seasons that are witnessed in four sampling locations. The highest PBDEs concentration in air was recorded during the hot dry season. This is owed to the high ambient temperature (27 °C) throughout the sampling time (January-March), resulting in increased rates of PBDEs volatilization. Research has shown that high temperatures increase the amount of POPs in ambient air due to increased rate of volatilization from polluted sites (Ashraf, 2017). Fig. 4 shows the seasonal variation of the PBDEs in air.
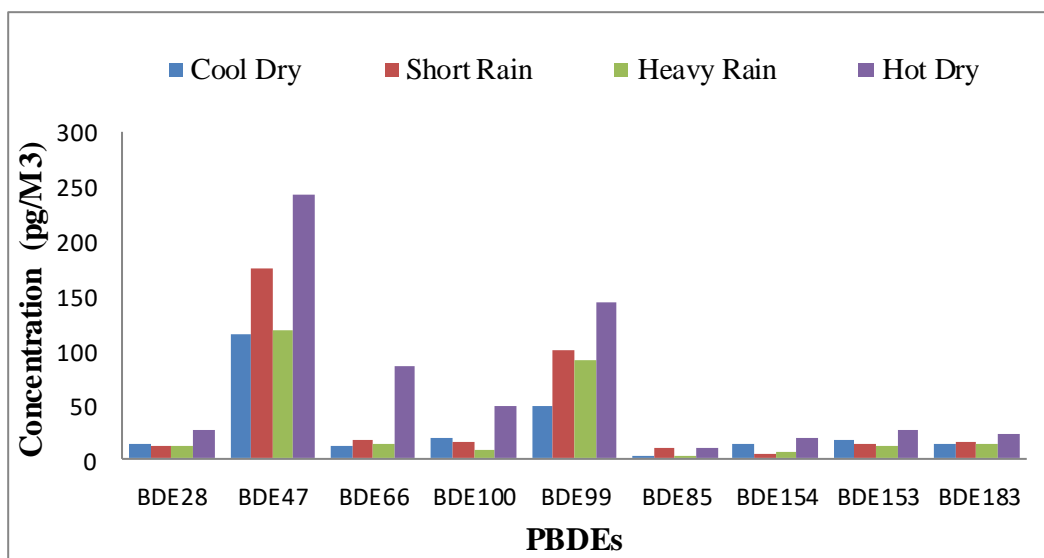

Figure 4: Seasonal Variation in the Levels of PBDE Compounds in Air

4. Conclusion

The air from three urban sites and one rural site in Kenya was found to be polluted by PBDEs with mean concentration range of ≤0.9 to 152.72±3.19 pgm^{-3}. Seasonal variations of the contaminants showed a high level of polybrominated diphenyl ethers in hot dry season in range of 1.94±0.03 to 152.72±3.19 pgm^{-3}. The predominant congener were BDEs 47 and 99 with mean concentration range of 1.94±0.03 to 152.72±3.19 pgm^{-3} and 1.32±0.06 to 66.83±1.19 pgm^{-3} respectively. The abundance of BDEs 47 and 99 in the air samples shows the predominance of legacy penta-BDE residues in the environment. The concentration of PBDEs in air samples from the urban location

ranged between ≤0.9 to 152.72±3.19 pgm^{-3} which was high compared with the air samples from the rural location which had concentration range between ≤0.9 to 22.84±0.04 pgm^{-3}. The high levels of polybrominated diphenyl ethers pose a health risk to urban residents of Nairobi City.

Disclosure statement

The authors declare no conflict of interest.

References

[1] Adewuyi, G., O., & Adeleye, A., O. (2013). Evaluation of polybrominated diphenyl ethers in sediment of Lagos Lagoon, Nigeria. *African Journal of Environmental Science and Technology*, 7(7), 686-693.

[2] Aliyeva, G., Sinnott-Clark, C. A., Audy, O., Škrdlíková, L., Kukučka, P., Klánová, J., Halsall, C. A. (2018). Contemporary assessment of polybrominated diphenyl ethers (PBDE) in the ambient air and soil of Azerbaijan. *Environmental Science Pollution Research,* 25(32), 31863-31873.

[3] Andersson, O.B., Blomqvist, G. (1981). Polybrominated aromatic pollutants found in fish in Sweden. *Chemosphere,* 10, 1051–1060.

[4] Arinaitwe, K., Muir, D. C. G., Kiremire, B. T., Fellin, P., Li, H., & Teixeira, C. (2014). Polybrominated Diphenyl Ethers and Alternative Flame Retardants in Air and Precipitation Samples from the Northern Lake Victoria Region, East Africa. *Environmental Science Technology,* 48, 1458–1466.

[5] Barón, B., Giménez, J., Verborgh, P., Gauffier, P., de Stephanis, R., Eljarrat, E., Barceló, D. (2015). Bioaccumulation and biomagnification of classical flame retardants related halogenated natural compounds and alternative flame retardants in three delphinids from Southern European waters. *Environmental Pollution,* 203, 107-115.

[6] Besis, A., & Samara, C. (2012). Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments—a review on occurrence and human exposure. *Environmental Pollution,* 169, 217–229.

[7] BSEF (Bromine Science and Environmental Forum) (2012). Legislation on Decabromodiphenyl Ether (Deca-BDE) in North America (USA and Canada). http://www.bsef.com/regulation/north-america/deca-bde-3 (accessed Dec 02 2020).

[8] Chen, S. J., Ma, Y. J., Wang, J., Chen, D., Luo, X. J., & Mai, B. X. (2010). Brominated Flame Retardants in Children's Toys: Concentration, Composition, and Children's Exposure and Risk Assessment. *Environmental Science & Technology,* 43(11), 4200-4206.

[9] Choi, S.D., Baek, Y.S. & Chang. Y.S. (2008). Atmospheric levels and distribution of dioxin-like polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in the vicinity of an iron and steel making plant, *Atmospheric Environment*, 42 (10), 2479-2488.

[10] Chokwe, T. B., Makhosazane, N. M., Abafa, A. O., Okonkwe, J. O., & Sibiya, V. I. (2019). Levels, distributions, and ecological risk assessments of polybrominateddiphenyl ethers and alternative flame retardants in river sediments from Vaal River, South Africa. *Environmental Science and Pollution Research*, 26, 7156-7163.

[11] Deng, W. J., Zheng, J. S., Bi, X. H., Fu J. M., & Wong, M. H. (2007). Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China. *Environment International,* 33(8), 1063-1069.

[12] Dunnick, J. K., Pandiri, A. R., Merrick, B. A., Kissling, G. E., Cunny, H., Mutlu, E., Waidyanatha, S., Sills, R., Hong, H. L., Ton, T. V., Maynor, T., Recio, L., Phillips, S. L., Devito, M. J., & Brix, A. (2018). Carcinogenic activity of pentabrominated diphenyl ether mixture (DE-71) in rats and mice. *Toxicology Reports*, 5, 615–624.

[13] Ghimire, A., Dela, C. A.L.N., Wong, R., Navasumrit, P., Cormier, S. & Lomnicki, S.M. (2019). Polybrominated Diphenylethers (PBDEs) in ambient air samples at the electronic waste (e-waste) reclamation site. *Waste Disposal & Sustainable Energy,* 1(1), 79-89.

[14] Gorini, F., Iervasi, G., Coi, A., Pitto, L., & Bianchi, F. (2018). The Role of Polybrominated Diphenyl Ethers in Thyroid Carcinogenesis: Is It a Weak Hypothesis or a Hidden Reality? From Facts to New Perspectives. *International Journal of Environment Resources Public Health,* 15 (9), 1834-1841.

[15] Hongwei, S., Yueling, Q, Di, Z., Qing, X., Li, D., Jun, W. (2016) Concentrations, distribution, sources and risk assessment of organohalogenated contaminants in soils from Kenya, Eastern Africa. *Environmental Pollution*, 209, 177-185.

[16] How-Ran, C., Shu-Li, W., Wen-jhy, L., Ya-fen, W., Olaf, P. (2007). Levels of polybrominated diphenyl ether (PBDEs) in breast milk from central Taiwan and their relation to infant birth outcome and maternal menstruation effects. *Environment international,* 33, 239-245.

[17] Hu, J., Jin, J., Wang, Y., Ma, Z., Zheng, W. (2011). Levels of polybrominated diphenyl ethers and hexabromocyclododecane in the atmosphere and tree bark from Beijing, China. *Chemosphere,* 84(3), 355-360.

[18] Jonathan, C., Kim, G.H., Asa, B., Myriam, G., Andreas, S., Brenda, E. (2010) Polybrominated Diphenyl Ether (PBDE) Flame Retardants and Thyroid Hormone during Pregnancy. *Environmental Health Perspectives,* 118(10), 1444–1449.

[19] Kenya Meteorological Department. (2018). The outlook for the October-November-December 2018 season and review of rainfall during the "long rains" (March to May) and June-July-August 2018 seasons. Government press. Nairobi.

[20] LaGuardia, M. J., Hale, R. C., & Harvey, E. (2006). Detailed polybrominated diphenyl ethers (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environmental Science & Technology,* 40(20), 6247-6254.

[21] Law, R. J., Covaci, A., Harrad, S., Herzke, D., Abdallah, M. A., Fernie, K., Toms, L. M., & Takigami, H. (2014). Levels and trends of PBDEs and HBCDs in the global environment: status at the end of 2012. *Environment International,* 65(2), 147–158.

[22] Lee, E., Kim, T.H., Choi, J.S., Nabanata, P., Kim, N.Y., Ahn, M.Y., Jung K.K., Kang, I.H., Kim, T.S., Kwack, S.J., Park, K.L., Kim, S.H., Kang, T.S., Lee, J., Lee, B.M. & Kim, H.S. (2010). Evaluation of liver and thyroid toxicity in Sprague-Dawley rats after exposure to polybrominated diphenyl ether BDE-209. *Journal of Toxicology Science*, 35 (4), 535-545.

[23] Lei, Y., Chengzhong, Z., Deming, H., & Zheng, J. (2019). Characterization and Source Identification of Polybrominated Diphenyl Ethers (PBDEs) in Air in Xi'an: Based on a Five-Year Study. *International Journal of Environmental Resources & Public Health,* 16(3), 520-529.

[24] Leonetti, C., Butt, C. M., Hoffman, K., Miranda, M. L., & Stapleton, H. M. (2016). Concentrations of polybrominated diphenyl ethers (PBDEs) and 2,4,6-tribromophenol in human placental tissues. *Environment International*, 88, 23-29.

[25] Makokha, V. A., Ndung'u, A. W., Mungai, T. M., Yan, X., & Wang, J. (2018) Concentrations, Sources, and Risk Assessment of Organohalogen Compounds in Soils from Kiambu to Mombasa, Kenya. *Bulletin of Environmental Contamination and Toxicology,* 101(6), 766–772.

[26] Ohajinwa, C. M., Van, M. P., Xie, Q., Chen, J., Vijver, M. G., Osibanjo, O. O., & Peijnenburg, W. J. G. M. (2019). Hydrophobic Organic Pollutants in Soils and Dusts at Electronic Waste Recycling Sites: Occurrence and Possible Impacts of Polybrominated Diphenyl Ethers. *International Journal of Environmental Research and Public Health*, 16(3), 360-369

[27] Olutona, O.G., Oyekunle, O.A.J., Ogunfowokan, O.A., Fatokin, S.O. (2017). Concentrations of polybrominated diphenyl ethers in Water from Asunle Stream, Ile-Ife, Nigeria. *Toxics,* 5, 13.

[28] Pernilla, B. N., Lisa, M., Kevin, B. W., Jiří, K., Madadi, V. O., Kumi, S. A., Prokeš, R., Přibylová, P., Klánová, J. (2020). Field- and model-based calibration of polyurethane foam passive air samplers in different climate regions highlights differences in sampler uptake performance. *Atmospheric Environment*, 73(1), 114-121.

[29] Polder, A, Müller, M.B., Lyche, J.L., Mdegela, R. H., Nonga, H.E., Mabiki, F.P., Mbise, T.J., Skaare, J.U., Sandvik, M., Skjerve, E., Lie, E. (2014) Levels and patterns of persistent organic pollutants (POPs) in tilapia (Oreochromis sp.) from four different lakes in Tanzania: geographical differences and implications for human health. *Science of the Total Environment,* 488, 252-260.

[30] U.S. EPA. (2010). Method 1614A Brominated Diphenyl Ethers in Water, Soil, Sediment, and Tissue by HRGC/HRMS. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology Engineering and Analysis Division (4303T). 1200 Pennsylvania Avenue, NW Washington, DC 20460.

[31] UNEP (2015). Guidance on the global monitoring plan for persistent organic pollutants. Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants, Seventh meeting. Geneva. 4–15 May 2015.

[32] Venier, M., Hites, R. A. (2008). Flame retardants in the atmosphere near the great lakes. *Environmental. Science Technology,* 42 (13), 4745–4751.

[33] Wenrui, Z., Yingzhuan, L., Shutao, G., Xuwei, J., Zhiqiang, Y., Xiangying, Z., Guoying, S., & Jiamo, F. (2015). Determination of polybrominated diphenyl ethers in soils and sediment of Hanfeng Lake, Three Gorges*. Journal of Environmental Science and Health,* 50, 1316–1323.

[34] Wu, J. P., Luo, X. J., Zhang, Y., Yu, M., Chen, S. J., Mai, B. X., & Yang, Z. Y. (2009). Biomagnification of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls in a highly contaminated freshwater food web from South China. *Environmental Pollution,* 157(3), 904-909.

[35] Yao-wen, Q., Dong-Xiao, W., Gan, Z. (2020) Assessment of persistent organic pollutants (POPs) in sediments of the Eastern Indian Ocean. *Science of the Total Environment*, 710, 136-139.