Atmospheric levels of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDDs) in Gauteng Province, South Africa using passive air samplers.

Katima, Z[1,2], Okonkwo, OJ[1], Olukunle OI[3], Daso AP[1]

[1]Environmental Chemistry Research Group, Department of Environmental, Water and Earth Sciences, Faculty of Science, Tshwane University of Technology, Private Bag X680, Pretoria
[2]University of Dar es Salaam, College of Engineering and Technology, Department of Chemical and Mining Engineering, P.O. Box 35131, Dar es Salaam, Tanzania
[3]School of Public & Environmental Affairs, Indiana University, 1315 East 10th Street, Bloomington, Indiana, United States

Introduction

Brominated flame retardants (BFRs) are a group of brominated organic compounds added to commercial products to reduce the spread of fire in order to minimize fire-related damages and deaths s [8]. PBDEs and HBCDDs have been used as additives in a wide range of consumer and industrial products such as upholstered furniture, electronic devices and curtains. They have been classified as endocrine disruptors because of their interference with the endocrine systems [2]. There is little information on atmospheric (BFR) levels in the African continent, which makes it impossible to understand the regional as well as the global perspective of these pollutants in the atmosphere [5]. It is predicted that the levels are likely to increase due to the rapid development in the African continent. It is well recognized that atmospheric long-range transport (LRT) is commonly considered the swiftest route for semi-volatile organic compounds (SVOCs) to spread into various environmental components, including the remote areas. It becomes imperative characterise and monitor pollutants such as PBDEs, HBCDD and other BFRs that can easily be inhaled through dust and air. South Africa is the only country in Africa that borders two oceans (Atlantic and Indian Oceans). Oceans can act as a sink, a storage compartment, and a source of POPs in the atmosphere due to possible re-volatilization as well as the gravitational settling of pollutants from and to the ocean [7]. Some studies have established the concentrations of BFRs in different environmental compartments of the South African environment: such as in water and sediments, leachates from selected landfills; the indoor air of some selected sites, sewage sludge and wastewater effluent, human breast milk and in bird eggs. These reports indicate that BFRs are indeed present in the environment and humans in South Africa [5]. There are no published studies so far in South Africa on the occurence levels and sources of BFRs in the atmosphere, yet air has been suggested as a useful matrix for regional and global monitoring studies because it responds rapidly to changes in primary emissions of POPs [5]. The objective of this research was, therefore, to measure concentrations of PBDEs and HBCDDs in Gauteng Province, South Africa, and to establish the affected receptor countries at higher pollutant concentrations.

Materials and Methods

Air samples were collected from four different sites, including, a landfill site, an industrial area, a densely populated residential area and a control site. Two polyurethane foam (PUF)-based passive samplers (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2; volume, 207 cm^3; mass, 4.40 g; density, 0.0213 g cm^{-3}) were deployed at each site for a period of 100 days. The entire sampling period ranged from late May 2016 to early January 2017; targeting the winter and summer periods. The PUF samplers were placed at 1.5 – 2 m above ground. Prior to sampling, the PUF disks were pre cleaned with water, then Soxhlet extracted with acetone: hexane mixture (1:1) (Sigma Aldrich, Chemie GmbH,

1

Steinhiem, Germany) for 24 h.   After sampling, the PUF disks were spiked with a known concentration of ($^{13}C_{12}$-BDE-77 and -139) purchased from Wellington Laboratories (Guelph, Ontario, Canada). The samples were then extracted for 24 h with 400 mL mixture of acetone: hexane (1:1, v/v) then concentrated to 1 mL by rotary evaporation (Buchi Rotavapor, R-210, supplied by Labotec, South Africa). The extract containing the analytes was then cleaned up using Pasteur pipettes (230mm) packed with acidic silica, sodium sulphate and deactivated silica, using hexane for elution. The eluent was later concentrated to incipient dryness under a gentle stream of nitrogen gas and reconstituted with about 300 µL of toluene containing 10 µL of 2.5 ng µL-1 of internal standard (BDE 118) for quantification. The clean extracts were analysed using a Shimadzu GC-MS Model 2010 plus gas chromatograph equipped with a QP 2010 Ultra mass spectrometer (Kyoto, Japan) using electron ionization. The samples were injected automatically by a Shimadzu A0C-20i auto sampler. Operation mode was in the selected ion monitoring (SIM). A 15 m column, DB-5 (0.25 mm, 0.1 µm) was used to chromatographically separate the BFRs and helium (99.999% purity) was used as a carrier gas at a constant flow of 1 mL min^{-1} and a constant linear velocity of 52.4 cm s^{-1}. The oven temperature was initially maintained at 90 °C for 1 min, ramped at 15 °C min^{-1} to 160 °C and at 20 °C min^{-1} to 300 °C and at the rate of 10 °C min^{-1} to 310 °C, was held for 8 min, using the splitless injection mode. The ion source temperature was 250 °C and the interface temperature was set at 315 °C. The samples were analysed for 10 PBDE congeners (17, 28, 47, 77, 99, 100, 153, 154, 183, and 209) and $\sum$ HBCDD. Field and method blanks were both collected and analysed. PBDE levels in both the field and method blanks were similar. The recovery standards were $_{13}C^{12}$-BDE-77 and $_{13}C^{12}$-BDE-139 and the mean recoveries ranged from 77 – 96% and 71 – 130% respectively. The instrument LOD was defined as three times the signal to noise ratio of the lowest calibration standard and were ten times the signal to ratio for the LOQs. Duplicate passive samplers were placed at each site. Forward and backward trajectories were calculated at 72 h intervals for sampling by the Hybrid –Single Particle Langrarian Integrated Trajectories (HYSPLIT) model by the National Oceanic and Atmospheric Administration's (NOAA) Air Resources Laboratory (ARL). Meteorological datasets are supplied from the reanalysis system, which includes archived data of the world. Trajectory heights chosen were at 500 m, 1000 m and 1500 m above ground level. The South African Weather Services (SAWS) provided meteorological data for three stations (OR Tambo International airport for the Kempton Park and Tembisa sites, UNISA for the Lynwood site and Wonderboom Airport for the Ondersterpoort site). The data provided included wind direction, wind speed, and precipitation. Annual wind rose plots for 2015 and 2016 were drawn for the three stations.

Results and Discussion

The concentrations for the target PBDE congeners were developed from the amount accumulated in the PUF disk (ng sampler^{-1}) divided by the effective air volume (V_{air}, m^3). The sampling rate R m^3/d that was used was 4 m^3/d [3]. The levels of PBDEs in the total air samples collected (N = 12) ranged between n.d - 584 pg/m^3, while levels of the HBCDDs ranged from 8- 117 pg/m^3 (Figure 1). As expected, higher levels of PBDEs and HBCDDs were observed at the landfill site, while the control site had the lowest concentrations. BDE 47, 99,100, 183 and 209 were the dominant congeners (Table 1). The landfill site as well as the low residential site had lower levels of PBDEs and HBCDDs in winter than in summer (Figure 1). This can be attributed to the fact that higher temperatures during summer season may have contributed the higher emission rates of BFRs from the products containing these pollutants to the atmosphere [1]. However, this observation was not the case for the high residential area and the industrial site. The high density residential area is renowned for burning several types of fuel to provide heat during winter. Because of the proximity of the industrial site to the densely populated residential site, the same pattern in terms of the concentrations of the targeted compounds was observed.

Table 1: Statistical summary of the measured levels of PBDEs and HBCDD (pg/m^3) in the South African atmosphere

2

Compound	A Mean	G Mean	Median	Minimum	Maximum	DF%
BDE17	202	29.83	23.69	1.93	580.38	37.5
BDE28	169.695	162.28	169.70	120.08	219.31	25
BDE47	160.62	69.85	170.48	3.29	471.92	87.5
BDE77	36.57	36.57	36.57	36.57	36.57	12.5
BDE100	221.16	147.4	161.77	12.17	529.71	100
BDE99	116.12	34.77	20.12	5.13	584.20	87.5
BDE154	40.31	18.59	37.99	1.09	103.31	62.5
BDE153	39.32	17.99	25.89	2.74	97.37	75
HBCDD	18.96	12.70	7.77	5.56	50.29	100
BDE183	115.28	106.35	84.73	79.95	239.68	100
BDE209	59.8	49.59	49.84	11.99	116.96	100

A Mean= Arithmetic mean, G Mean = Geometric mean, DF = Detection frequency
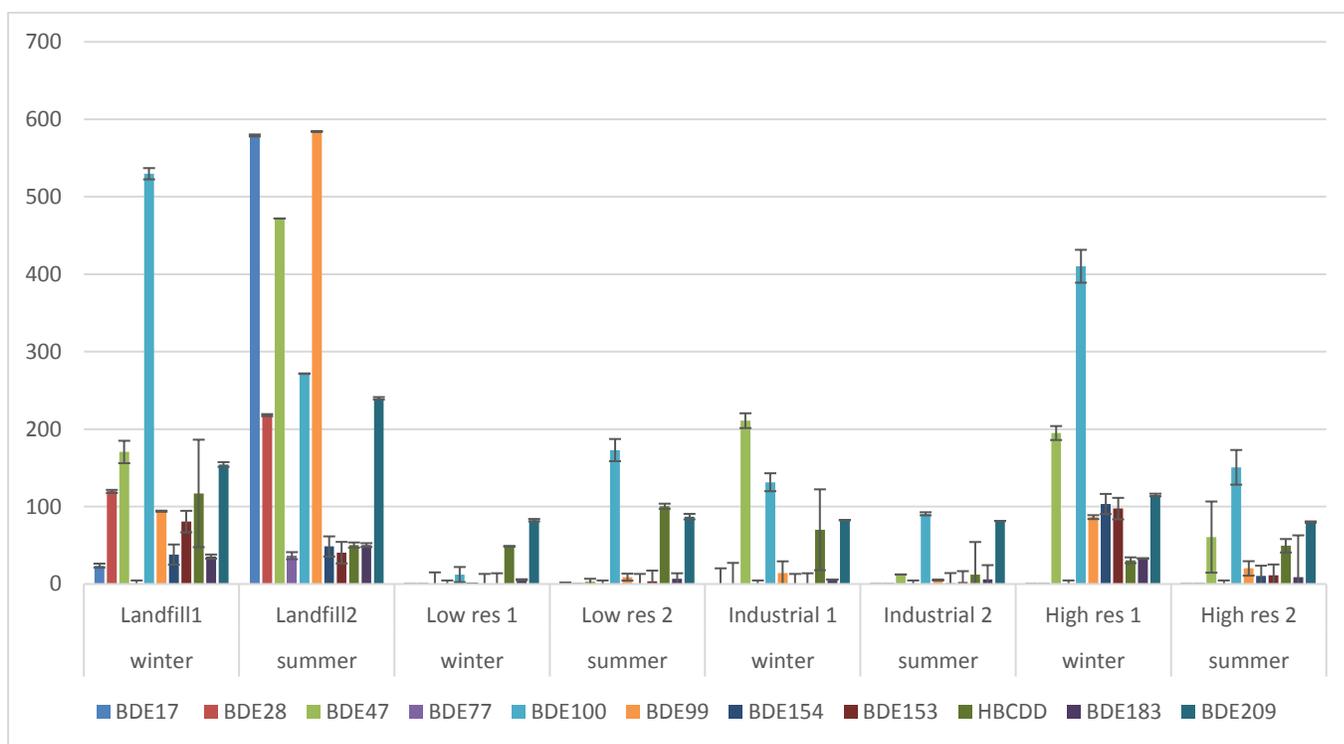
Figure 1: Comparison of PBDE congeners and HBCDD concentrations (pg/m^3) across sampling sites.

The wind rose plots for South Africa indicated that the winds blew in the south-eastern and south-western directions. The prevalent wind directions may have significantly influenced the measured levels of the PBDEs and HBCDDs at the industrial site. This is because the samplers were placed against the direction of the wind, while majority of the industries are located in the South.The forward trajectories indicated that most pollutants from South Africa are

3

transported into the Indian Ocean, Swaziland and Lesotho, whereas the back trajectories indicated that the possible emission sources could be from the Indian Ocean, Atlantic Ocean, Mozambique and Zimbabwe.
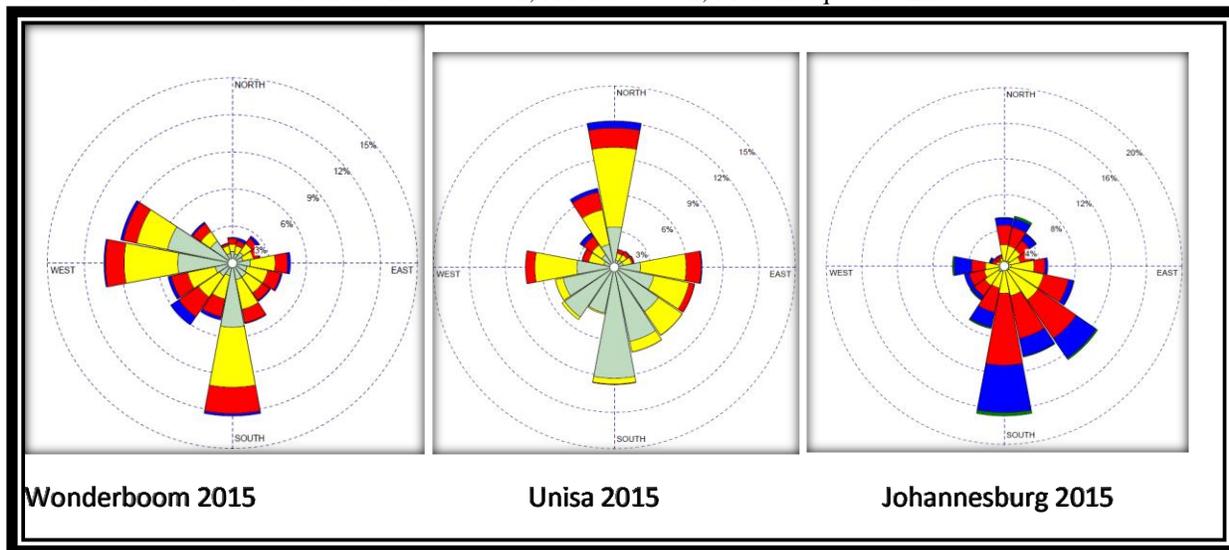
Figure 3: Windrose Plots for the three different Meteorological stations.

The concentrations of 10 PBDE congeners and ∑HBCDD in the atmosphere of Gauteng Province, South Africa were reported. The most abundant PBDE congeners were BDE 47, 99,100, 183 and 209, with detection frequency ranging from 88 to 100%. The ∑HBCDD was also detected in all the analysed samples. The obtained values are higher than those reported in similar studies in Uganda, Italy, and Canada but lower than those obtained in China. This is the first detailed study to obtain PBDEs and HBCDDs in the South African atmosphere.

References
1. Akortia, E., Olukunle, O.I., Daso, A.P. & Okonkwo, J.O. (2017). Ecotox. & Environ. Safety, **137**:247-255.
2. Besis, A. & Samara, C. (2012). Environ. Pollut. **169**:217-229.
3. Harner, T., Mitrovic, M., Ahrens, L. & Schuster, J. (2014). . Organohalogen Compd, **76**, 442-445 (2014) 76(1).
4. Harrad, S., Goosey, E., Desborough, J., Abdallah, M.A.-E., Roosens, L. & Covaci, A. (2010). Environ. Sci. & Tech., **44**(11):4198-4202.
5. Katima, Z., Okonkwo, O.J. & Daso, A.P. (2017). Atmosph. Pollut. Res. Article in Press.
6. La Guardia, M.J., Hale, R.C. & Newman, B. (2013). Environ. Sci. & Tech. **47**(17):9643-9650.
7. Li, J., Li, Q., Gioia, R., Zhang, Y., Zhang, G., Li, X., Spiro, B., Bhatia, R.S. & Jones, K.C. (2011). Atmosph Environ, **45**(37):6622-6628.
8. Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A. & Webster, T.F. (2009). Environ. Sci. & Tech., **43**(19):7490.

4