

## CURRENT LEVELS OF POLYBROMINATED DIPHENYL ETHERS IN SELECTED MUNICIPAL SOLID WASTE LANDFILL LEACHATES AND SEDIMENTS FROM GAUTENG

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### INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are high production volume (HPV) chemicals<sup>14</sup> that gained wide popularity and usage in the early 1970s because of their efficiency and low costs. PBDEs like other brominated flame retardants have been synthesised and used at very high volumes in consumer and industrial products to protect lives and properties<sup>3,9</sup>. Three major commercial formulations of PBDEs were produced globally in the last few decades; PentaBDE, OctaBDE and DecaBDE. Because of suspected endocrine disrupting properties of Penta and OctaBDE derivatives they have been recognised as persistent organic pollutants (POPs) and now included on the list of the new POPs under the Stockholm Convention. Consequently, they have been implicated in several adverse effects on human health and are continually being detected in biotic and abiotic samples including human milk, serum and tissues<sup>2, 5, 6, 11, 13, 18</sup>.

PBDEs are added as additives during manufacturing or applied as coating spray on substrates and are not covalently bonded hence they have the tendency to leach out of the product during use or at the end of life. These materials are most often, disposed into landfill sites with household wastes. For example, in Europe, about 96 % of electrical and electronic waste generated in 2002 was dumped into landfills or incinerated<sup>1</sup>. According to a report by e-waste South Africa, between 1,129,000 and 2,108,000 tons of potential e-waste is estimated to be in South African households many of which will find their way into municipal landfills<sup>8</sup>.

Only a handful of studies have so far focused on PBDEs' fate in landfill leachates<sup>12, 18</sup>. Presently, there is paucity of data on the levels of BFRs in landfill sediment which makes it difficult to predict or profile the extent of leakage of BFRs from landfills into surrounding groundwater. So far reports from South Africa, have only concentrated on leachates and not on sediment<sup>10, 17</sup>.

The current paper is, therefore, centred on (1) the determination of current PBDE levels in ) leachates and sediments in some selected landfill sites lined or unlined with geomembrane materials and (2) to compare the current results on leachates with the previous levels by Odusanya et al<sup>10</sup>.

### MATERIALS AND METHODS

Samples were collected from six operational MSWLs within Gauteng province out of which two, namely Chloorkop and Robinson deep are equipped with liners. Raw leachate samples (2L each) were collected (June - August 2013 ) using grab method in pre washed and acetone rinsed 2 L amber bottles from leachates ponds in the selected landfills and stored in cooler boxes for transportation to the laboratory where they were kept at - 4°C in a cold room prior to extraction. The details, description and activation of chemicals such as PBDE standards, SPE cartridges, HPLC grade solvents, copper powder, silica gels and sodium sulphate has been described<sup>15</sup>.

To test the yield and extraction efficiencies of some selected solvents found in the literature, *n*-hexane, toluene, and dichloromethane were used individually and mixed. Dichloromethane gave the best recovery for most of the target analytes than the combination. One hundred micro litre of 3.3 ng  $\mu\text{L}^{-1}$  PBDE surrogate standards was dissolved in 5 mL acetone then spiked into 500 mL Ultra-pure water and left for 24 hrs. for equilibration. The mixture was thereafter extracted by liquid-liquid extraction. Three times extraction by LLE with 50 ml DCM was found adequate for recovery of all analytes. Similarly for solids, sodium sulphate fortified with 1 ng  $\mu\text{L}^{-1}$  x 120  $\mu\text{L}$  (<sup>13</sup>C<sub>12</sub> BDE-139 & -209) was dissolved in acetone before spiking into the sodium sulphate. The impregnated salt was transferred into a glass fibre thimble, 2 g activated copper was added into the mixture and Soxhlet extracted with 180 mL hexane/acetone (2:1, v/v) for 16 h. Solvent containing PBDEs was collected and concentrated to 1 mL by rotary evaporator (Buchi Rotavapor, R-210, supplied by Labotec, South Africa). Clean up followed the procedure earlier reported<sup>15</sup> using *n*-hexane for elution. The eluant was concentrated to near dryness under N<sub>2</sub> to 200  $\mu\text{L}$ . Before injection, BDE-118 (10  $\mu\text{L}$  of 2.5 ng  $\mu\text{L}^{-1}$ ) was added as quantitation internal standard and 1  $\mu\text{L}$  was injected into the GC-MS. The method was validated with the recovery of surrogate

standards  $^{13}\text{C}_{12}$  BDE-139 (90 %) and BDE-209 (81 %). Leachates and sediment samples were subjected to same extraction and clean up procedure.

The clean extracts was analysed by Shimadzu model 2010 plus gas chromatograph coupled with a model QP 2010 Ultra mass spectrometer (Shimadzu, Japan) using electron ionisation and injected by a Shimadzu A0C-20i auto sampler. Operation mode was in the selected ion-monitoring (SIM). A 15m column of ZB 5 (0.25 mm ID, 0.25  $\mu\text{m}$   $d_f$ ) was used for separation. The initial oven temperature was set at 90  $^{\circ}\text{C}$  (1 min) and at 30  $^{\circ}\text{C}$  /min to 300  $^{\circ}\text{C}$  (5 min) and at 10  $^{\circ}\text{C}$  /min to 310 (10 min). Carrier gas used was Helium (purity 99.999 %) and set at a constant flow of 1.5 mL  $\text{min}^{-1}$ . The injector, transfer line and ion source temperatures were set at 290  $^{\circ}\text{C}$ , 300  $^{\circ}\text{C}$  and 250  $^{\circ}\text{C}$  respectively. Prior to sample analysis and after, an initial solvent blank, a laboratory performance standard check (linearity of the calibration curve) was performed using individual and mixtures of the most common brominated flame retardants. This was to ensure proper performance of the GC-MS. Check standard was run after every five samples to monitor retention time deviation. The use of surrogate standards during extraction and after clean-up was done to ensure accuracy. Soxhlet apparatus was covered with foil during extraction and plastics were avoided. Retention times matched those of the standards and quantification was done by monitoring the molecular and reference ions using both internal and external methods. External calibration of the GCMS was done using seven level calibration standards. The limit of detection was taken as greater than 3 times the signal-to-noise ratio. For all the congeners good linear regression of 0.999 was obtained. LOD values ranged from 0.02  $\text{ng } \mu\text{L}^{-1}$  to 0.3  $\text{ng } \mu\text{L}^{-1}$  and 0.9  $\text{ng } \mu\text{L}^{-1}$  for BDE-209 respectively. Statistical analysis was performed using Microsoft windows statistical package.

## RESULTS AND DISCUSSION

Table 1 shows the geographical coordinates and summary of PBDE concentrations in Leachates and sediment samples respectively. The following PBDEs; BDE-47, -100, -99, 154, -153, -189 and -209 were detected in all the leachate samples except BDE-209 in Soshanguve leachates. The observed total concentrations of sum PBDEs in landfill leachates from the six sampled landfill sites ranged from 127  $\text{pg L}^{-1}$  to 3703  $\text{pg L}^{-1}$  for Soshanguve and Chloorkop respectively. Soshanguve landfill is unlined and absorbs untreated waste while Chloorkop on the other hand, is a MSWL lined with geomembrane material in order to protect groundwater from pollution from landfill leachates and waste treated by incineration respectively. Elevated levels of BDE-209 (1930  $\text{pg L}^{-1}$ ) was found in a sample from Chloorkop MSWL. Robinson deep MSWLs came second with  $\sum$ PBDEs of 2678  $\text{pg L}^{-1}$ . Both Chloorkop and Robinson deep MSWLs are lined, contributing 86.2 % of the total PBDEs (7264  $\text{pg L}^{-1}$ ) from the six MSWLs in the present study. Similarly, for sediment all target congeners were quantified except BDE-209 in Soshanguve, BDE-47 and BDE-100 in Garstkloof samples which were observed below limits of detection. Concentration ranged from 0.8  $\text{ng g}^{-1}$  to 8.4  $\text{ng g}^{-1}$  dry weights. Total PBDE was 30  $\text{ng g}^{-1}$  and BDE-209 was observed to be the predominant congener with a concentration of 9.5  $\text{ng g}^{-1}$  followed by BDE-153, BDE-99 and BDE-47 with concentrations of 3.9, 3.8 and 2.4  $\text{ng g}^{-1}$  respectively.

**Table 1:** Geographical coordinates and summary of PBDE concentrations in landfill leachates and sediment from the six sites.

	Onderstepoort	Garstkloof	Hatherly	Soshanguve	Chloorkop	Robinson deep
<b>Geographical coordinates</b>	<b>-25.6506, 28.18417</b>	<b>-25.8317, 28.2688</b>	<b>-26.008, 27.8646</b>	<b>-25.5269, 28.10889</b>	<b>-26.0418, 28.16794</b>	<b>-26.2331, 28.03744</b>
BDE 47	11.6(0.08)	2.7(0.00)	9.5(0.10)	15.4(0.54)	127.2(1.36)	89.8(0.34)
BDE 100	10.8(0.13)	2.9(0.00)	12.0(0.09)	16.3(0.48)	112.2(0.67)	1294.0(0.27)
BDE 99	254.5(0.07)	3.9(0.81)	14.5(0.08)	18.2(0.67)	149.6(1.70)	231.9(0.52)
BDE 154	7.7(0.20)	4.6(0.89)	22.1(0.06)	21.8(0.57)	149.6(0.40)	172.0(0.30)
BDE 153	19.3(0.08)	3.9(1.05)	19.5(0.10)	20.0(0.53)	964.9(0.83)	157.1(3.85)
BDE 183	31.6 (0.44)	5.2(1.51)	35.9(0.14)	35.4(0.80)	269.3(0.41)	202.0(0.62)
BDE 209	134.2(1.98)	113.7(4.17)	35.9(0.24)	0.0(0.00)	1929.8(0.59)	531.1(2.49)
$\sum$ PBDE	469.6(2.97)	136.9(8.42)	149.4(0.80)	127.2(3.59)	3702.6(5.96)	2677.8(8.39)

( ) = sediment

Findings from the present study were compared to previous work by Odusanya et al.<sup>10</sup> (2009) in the city of Tshwane. They reported concentrations for  $\Sigma$ PBDEs of 9793  $\text{pg L}^{-1}$  for Temba, 7230  $\text{pg L}^{-1}$  and 4009  $\text{pg L}^{-1}$  for Hatherly and Soshanguve MSWLs respectively. This was found to be a slight deviation from the present results. In the present study  $\Sigma_7$  PBDEs, of 150 and 127  $\text{pg L}^{-1}$  for Hatherly and Soshanguve respectively are reported. The observed differences between the values of  $\Sigma$ PBDEs reported by Odusanya et al.<sup>10</sup> and the values in the current report could be attributed to the difference in the quantity of wastes dumped into the landfill sites in 2009 and 2014. Currently, there is a lot of recycling of waste compared to five years ago. The various recycling activities may have reduced the quantities of products that may have PBDEs from entering into the landfill sites. Daso et al.<sup>17</sup> reported the highest concentrations (2240  $\text{ng L}^{-1}$ ) of  $\Sigma$ PBDEs in leachates from a landfill in the city of Cape Town, South Africa. Comparison of this present work to other studies is as shown in Table 2.

Table 2: PBDE concentrations compared to other studies from different regions

Location	MSWLs	$\Sigma$ PBDEs ( $\text{pg L}^{-1}$ )	Congeners
North China	11	4000-352000	$\Sigma_8$ PBDEs <sup>21</sup>
Japan	7	4000	$\Sigma$ PBDEs <sup>4</sup>
Shanghai, China	1	4000-12000	$\Sigma_8$ PBDEs <sup>20</sup>
	1	234 $\text{ng g}^{-1a}$	$\Sigma_8$ PBDEs
Canada	28	1020-21,300 $\text{ng L}^{-1b}$	$\Sigma_9$ PBDEs <sup>16</sup>
Lao PDR, Cambodia, Vietnam, India, Indonesia, Thailand, the Philippines, and Malaysia	10	3.7-133,000 $\text{ng L}^{-1}$	$\Sigma_{36}$ PBDEs <sup>19</sup>
Capetown, South Africa	3	2,244 <sup>b</sup>	$\Sigma_8$ PBDEs <sup>17</sup>
Gauteng, South Africa	5	112,716	$\Sigma_{13}$ PBDEs <sup>10</sup>
Gauteng, South Africa	6	7264	$\Sigma_7$ PBDEs <sup>d</sup>
	6	30 $\text{ng g}^{-1c}$	$\Sigma_7$ PBDEs

<sup>a</sup> Mean of  $\Sigma$ PBDEs, <sup>b</sup> surface soil of the landfill site, <sup>c</sup> landfill sediment, <sup>d</sup> this study

## Conclusion

All seven PBDE congeners were detected in most of the leachate and sediments collected from six MSWLs. Highest concentrations of  $\Sigma_7$  PBDEs was observed in Chloorkop and Robinson deep samples respectively. This may be attributed to the lining system of the landfills which prevents percolation and on the other hand, wastes are treated before dumping. This may also explain the high electrical conductivity observed from the two sites. Findings from this study was observed relatively low when compared to previous study from landfills in Tshwane city.

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