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# Seasonal variations and the influence of geomembrane liners on the levels of PBDEs in landfill leachates, sediment and groundwater in Gauteng Province, South Africa

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ABSTRACT

In the present study, the seasonal concentrations of polybrominated diphenyl ethers (PBDEs) in leachate and sediment samples, and the influence of geomembrane liners on PBDE levels and the extent of their infiltration into groundwater on selected landfill sites in Gauteng Province, South Africa were determined. Leachate and sediment samples were collected from seven operational landfill sites namely: Goudkoppies, Robinson Deep, Marie Louis, Soshanguve, Onderstepoort, Hatherly and Garankuwa from Johannesburg and Pretoria, in winter and summer. Groundwater samples were collected from monitoring boreholes from two landfill sites. Liquid-liquid and Soxhlet extraction techniques were employed for the extraction of leachate and groundwater, and sediment respectively using dichloromethane. The extracted samples were subjected to column clean up and, thereafter, analysed using gas chromatography–mass spectroscopy (GC-MS). PBDEs selected for the study were: BDE-17, -28, -47, -100, -99, -153, -154, -183 and -209. The $\sum_9$PBDE concentrations in leachate samples for winter and summer ranged from 0.316–1.36 ng $L^{-1}$ and 0.560–1.08 ng $L^{-1}$ respectively. The $\sum_9$ PBDE concentrations obtained for sediment in winter and summer were 3.00–4.91 ng $g^{-1}$ and 2.50–3.71 ng $g^{-1}$ respectively. Winter samples exhibited higher ($p < 0.05$) concentrations for both leachate and sediment samples compared to summer samples. This trend was attributed to high precipitation rate in summer which may have infiltrated into the landfills, subsequently diluting the leachate and sediment samples. In contrast, the winter period is generally dry and PBDEs are, therefore, more likely to be concentrated. The concentrations of PBDEs in leachate and sediment samples were higher in landfill sites with geomembrane liners compared to those without liners. Groundwater samples taken from the vicinity of selected landfill sites without geomembrane liners exhibited high concentrations of $\sum_9$PBDEs, indicating possible migration of PBDEs from landfill site into groundwater. Pearson correlation (r) and statistical significant *t*-test (p) for the PBDE congeners versus dissolved organic carbon (DOC) resulted in positive moderate interactions with a statistical significance for most congeners. Suggesting that there is a possible influence of organic carbon on the levels of PBDEs.



## 1. Introduction

Flame retardants are substances which inhibit or delay the spread of fires by suppressing the chemical reactions in the flame or by formation of a protective layer on the surface of a material [1]. Of all the organohalogen flame retardants, brominated flame retardants (BFRs) have been widely used since the 1970's because of their effectiveness in fire retardation [2,3]. PBDEs are a group of BFRs that are commonly used in consumer products [4]. PBDEs exist in three major commercial mixtures namely, Penta-BDE: which consists of 37% (BDE-47 and -99) and small amounts of tetra-, Penta- and hexa-BDE; Octa-BDE: which is a mixture of 10–12% hexa-, 44–46% hepta-, 33–35% Octa- and 10–11% nona-; and Deca-BDE: 98% BDE-209 and 2% nona-BDE [5]. The Penta product was employed principally to flame retard polyurethane foams in carpet underlay, vehicle interiors, furniture and bedding

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[5,6]; the Octa formulation was used to flame retard thermoplastics such as high impact polystyrene [5,7]; and the Deca-product is used principally in plastic housings for electrical goods such as televisions, computers and textiles [5,7]. However, among all brominated flame retardants, PBDEs have attracted most attention because of their persistence, bioaccumulation and toxicity [2]. Consequently, they were listed by the United Nations Environment Programme (UNEP) under the Stockholm Convention for Persistent Organic Pollutants (POPs) for global elimination [4].

In most developing countries, products which may have been treated with PBDEs are disposed of together with municipal wastes into municipal landfill sites without any pre-treatment once they have reached the end of their life-cycle [8]. Since PBDEs are used as additives in products, they have the tendency to leach out of products into the surrounding environment [9,10]. There are concerns that some congeners of PBDEs might affect human development and reproduction in addition to producing neurobehavioral effects [11,12]. Animal studies have demonstrated that exposure to PBDEs can lead to endocrine disruption, liver damage, hyperactivity and changes in motor behaviour [13–15]. Exposure to PBDEs is commonly through inhalation of airborne matter [16], dust ingestion [17], direct dermal contact in the work environment or home [18], ingestion through food [19] and water [16,17].

The presence of PBDEs has been reported in landfill leachates in China [9], South Australia [20], Japan [21], USA [22], UK [23] Netherlands [24], Sweden [25], Canada [26], and South Africa [8,10,27]. The aforementioned studies measured PBDEs only in leachates. However, the influence of physicochemical and chemical parameters on PBDEs in leachates and sediments was conducted by Olukunle et al. (2015) [10]. The study found a positive correlation between the sum of PBDEs with selected trace metals, which suggested a possible influence of trace metals on PBDE concentrations in leachates. However, the test between some anions and the sum of PBDEs yielded a positive relationship with an insignificant statistical difference [10].

Studies on the leaching of PBDEs from landfill sites are still scanty. However, Osako et al. (2004) reported the concentrations of BDE-47, -99 and -100 from seven different leachate samples to range from not detectable to 4.00 ng $L^{-1}$ for raw and treated leachate respectively. In the same study, it was observed that landfill leachate with large amounts of organics have extremely high concentrations of PBDEs. Groundwater contamination as a result of leachate infiltration from landfill sites and the evaluation of the influence of geomembrane liners on leachate infiltration to groundwater were not given adequate attention. However, a study by Jan Schwatsbauer et al. (2010) investigated the occurrence and alteration of organic contaminants in seepage and leakage water from a waste deposit landfill and found a wide variety of organic substances which were attributed to natural or xenobiotic waste components. Sediments are an important reservoir for many inorganic and organic pollutants, particularly PBDEs [28]. Therefore, proper profiling of PBDEs and full understanding on their concentrations in landfill sediment, leachate and groundwater are important since such studies will improve our knowledge of PBDEs in different landfill compartments.

During the 1980s, the practice of covering municipal solid waste with soil was adopted in major cities with a final top cover of soil (with grass/vegetation) after the landfill achieved its full height. In the 1990s, the focus shifted towards developing engineered landfills having well-designed cover and liner systems for both municipal solid waste as well as hazardous waste. The latest move on landfill design was to protect groundwater pollution *inter alia*. Consequently, several studies have been conducted on the impact of landfill leachate on surface and groundwater [29–32]. To assess the pollution of the groundwater, it has been suggested that either estimation through mathematical modelling or experimental determination can be adopted [33]. Furthermore, the extent of contamination of groundwater due to leachate percolation depends on factors such as leachate composition, rainfall, depth and distance of the well from pollution source [33]. Therefore, landfill liners are expected to exhibit durability and stability over years, because model calculations for a composite and mineral liner show that complete failure and cracks of a geomembrane liner are expected after 80 years. To date, the influence of geomembrane liners on the concentrations of PBDEs and the seasonal trend in a given landfill site has not been reported adequately. However, model calculations by Sarsby et al. (1998) show that composite liners reduce concentrations in leachate much more efficiently for the first 120 years demonstrating that a composite liner is much safer in the most crucial initial period when contaminant concentrations are at their highest [34].

The present study, therefore, focused on seasonal concentrations of PBDEs in leachate and sediment samples obtained from landfill sites with and without geomembrane liners as well as the extent of pollutant infiltration into groundwater. Correlation studies of PBDEs with DOC were carried out to investigate if there is a relationship between PBDEs and DOC. Instead of total organic carbon (TOC), DOC was measured since the samples were first filtered prior to extraction. In addition, it is envisaged that the results of this study will help to enhance our understanding of the efficiency of geomembrane liners to protect groundwater from contamination as well as provide an indication of potential management options that could be put in place and thus alleviate the risk of groundwater contamination via landfill sites. Since a number of articles have been published on PBDEs in landfill sites in some parts of South Africa, particularly Gauteng Province, the present study, therefore, assessed the impact of ongoing waste management initiatives in Johannesburg and Pretoria by measuring the concentrations of PBDEs in some of the landfill sites previously studied.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Ultrapure water was dispensed from Labostar ultrapure water equipment (Siemens, Germany) supplied by Separations, South Africa. Each certified standard solutions (1.20 mL of 50.0 mg $L^{-1}$) of 9 PBDE (BDE-17, BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183 and BDE-209) congeners were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Copper powder (purity 99.9%) from Saarchem (Pty) Ltd., (Muldersdrift, South Africa), while silica gel (100–200 mesh), sodium sulfate (purity 99.9%), glass wool and HPLC grade solvents: acetone, hexane, dichloromethane, methanol, toluene and sulfuric acid (purity 99.9%) were purchased from Sigma Aldrich (Pty) Ltd.

### 2.2. Study area, sample collection

Gauteng Province is the most urbanized and industrialized province in South Africa and Johannesburg and Pretoria are the two largest cities within the province. Fig. 1 shows the map of South Africa (top left) and Gauteng Province (bottom right) with the locations of the landfill sites. Triplicates of seven sediment and leachate samples were collected from seven operational landfill sites, three in Johannesburg (Goudkoppies, Robinson Deep and Marie Louis) and four in Pretoria (Soshanguve, Onderstepoort, Heatherly and Garankuwa), in winter and summer. Parameters such as age, lining of landfill, size and waste type (municipal solid waste) in all landfills, was considered during selection. Landfill sites

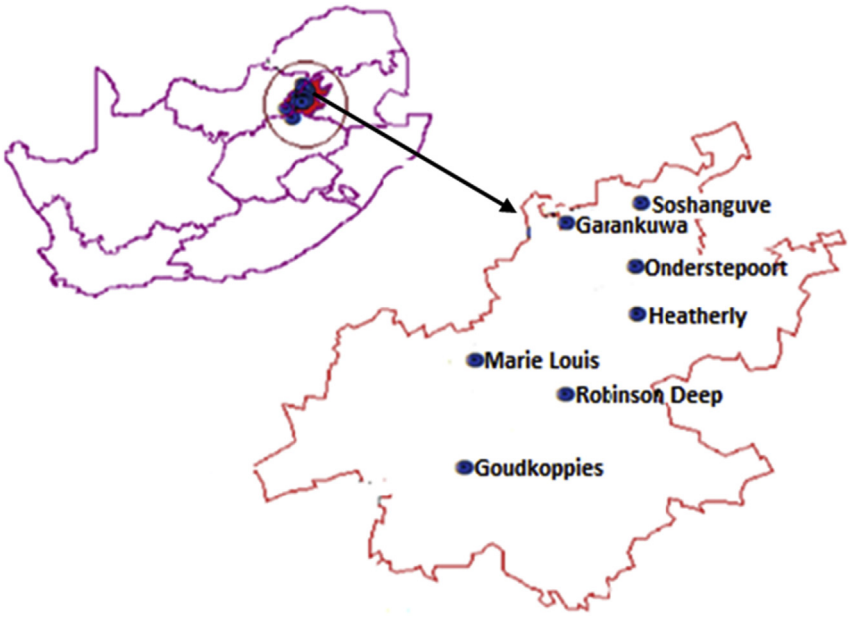


**Fig. 1.** Map of South Africa (top left) and Gauteng area (bottom right) showing landfill sites.

from Pretoria have no geomembrane liners and all sites from Johannesburg are lined with the geomembrane called geosynthetic clay liner. Robinson deep and Hatherly are the largest and busiest landfill sites in Johannesburg and Pretoria respectively. Marie Louis has a geomembrane liner but it only covers 0.61 $km^2$ of the waste footprint.

The average composition of waste types in Pretoria landfill sites comprises mainly 32% greens, 46% household, 14% builder's rubble and 8% industrial; and in Johannesburg 24% household, 40% commercial, 6% greens and 13% builders' rubble wastes [28].

Raw leachate (2.50 L each) and sediment (1000 g) samples were collected in pre-washed and acetone rinsed amber bottles in June–August 2014 and September–December 2014, for winter and summer respectively. Grab method was used to collect leachate samples from leachate ponds and sediment samples were collected 5 cm below the surface of the leachate pool from the same location as the leachate sample. In one site at the leachate pond, leachate and sediment samples were taken from the North, South and Central side of the pond. The samples were covered immediately after sampling and stored in cooler boxes and transported to the laboratory where they were kept at −4 °C in a cold room prior to extraction. Sediment samples collected were then air dried and homogenised prior extraction.

### 2.3. Sample extraction and clean - up

Liquid samples were extracted using liquid - liquid extraction (LLE). The samples were first filtered and spiked with one hundred microliters of 3.30 ng $\mu L^{-1}$ PBDE surrogate standards ($^{13}C_{12}$ BDE-139 & -209) which was first dissolved in 5 mL acetone then poured into 250 mL leachate and left for 24 h for equilibration. The liquid samples were extracted three times with 50.0 mL dichloromethane.

Solid samples were extracted using Soxhlet extraction (SE). Ten grams of sediment was sieved with a 150 μm sieve and fortified with 120 μL of 1.00 ng μL ($^{13}C_{12}$ BDE-139 & -209) which was dissolved in acetone before spiking. The impregnated sediment was transferred into a glass fibre thimble, 2.00 g activated copper was added to the mixture and extracted with 180 mL hexane/acetone (2:1, *v/v*) for 16 h.

A pasteur pipette column (5 mm i.d x 230 mm) was used for clean – up and packed from bottom to top with: neutral silica gel (0.20 g), basic silica (0.20 g), neutral silica gel (0.20 g), acidic silica gel (0.40 g) neutral silica gel (0.20 g) and sodium sulfate (0.20 g) at the top. Glass wool was used for partitioning between each level of packed materials from the bottom to the top. Each of the packed pasteur pipette columns was first eluted with 2 × 10 mL of hexane Olukunle et al. (2012). The eluent was further concentrated under $N_2$ to 200 μL. Before injection, BDE-118 (10.0 μL of 2.50 ng $\mu L^{-1}$) was added to monitor deviation in the instrument condition and 1 μL was injected into the GC-MS.

### 2.4. Instrumental analysis

After column clean up, the purified extracts were analysed using Shimadzu model 2010 plus gas chromatograph coupled with a model QP 2010 Ultra mass spectrometer (Shimadzu, Japan) using electron ionisation and injected in triplicates by a Shimadzu A0C-20i autosampler. Optimized GC MS conditions were: 1.5 mL $min^{-1}$carrier gas flow rate high purity helium (99.999%), 290 °C injection temperature, 90 °C (1 min) to 300 °C @ 30 °C $min^{-1}$ (5 min) to 310 °C @ 10 °C $min^{-1}$ (5 min) oven temperature programme and 300 °C detector temperature. InertCap ™ 5 MS/NP capillary column (15 m, 0.25 mm I.D., 0.1 μm $d_f$) and split-less time of 1 min were used.

### 2.5. Quality assurance and quality control

Quality control measures were taken to ensure the correctness and integrity of results. This includes the use of spiked pre-extracted leachate and sediment, which gave mean percentage recoveries ranging from 41.7–101% and 67.6–130%. Sediment pre extraction was performed as follows: three sediment samples were collected from each site then mixed, sieved and extracted three times and one leachate sample from the middle of the leachate pond was filtered and extracted three times. The same procedure was used for blank and real sample analysis.

Prior to sample analysis and after, an initial solvent blank and a

laboratory performance standard check (linearity of the calibration curve) was performed using individual and mixtures of the target analytes. This was to ensure proper performance of the GC-MS. A calibration standard was run after every five samples to monitor retention time deviation. The use of surrogate standards during extraction 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 external methods. A six level external standard calibration standard mixture was used and the concentration ranged from 0.02 to 1.28 ng $L^{-1}$. The instrument limit of detection was taken as 3 times the signal-to-noise ratio. For all the congeners, good linear regression of 0.999 was obtained. LOD and LOQ values range between 0.01 and 0.02 ng $\mu L^{-1}$ and 0.09–0.33 ng $\mu L^{-1}$ respectively.

### 2.6. Dissolved organic carbon (DOC) analysis

DOC standards were prepared using deionized water. About 1.00 mg $L^{-1}$, 5.00 mg $L^{-1}$, 10.0 mg $L^{-1}$, 20 mg $L^{-1}$, and 25 mg $L^{-1}$ concentrations were prepared using a 50 mg $L^{-1}$ potassium hydrogen phthalate (KHP) stock solution. Leachate samples containing particles were allowed to settle then filtered by pouring into glass funnel lined with Whatman filter paper pore size 0.45 μm and collected in a flat bottom flask. Ten millilitre sample aliquot was transferred into sample vials and loaded into the auto sampler. DOC in the filtrates was measured in leachate using TOC analyser (Shimadzu TOC-500).

## 3. Results and discussion

### 3.1. Seasonal variation of concentrations in leachate and sediment

The concentrations of PBDEs in leachate and sediment samples collected from the seven landfill sites in winter and summer are presented in Tables 2 and 3. The reported mean concentrations and standard deviations of leachate and sediment are results of triplicate extraction and analysis of each sample. All target PBDE congeners were detected in winter. However, in summer, BDE-17 and -28 were not detected in Soshanguve and BDE-153 observed below detection in the Garankuwa and Robinson Deep landfill sites. As can be seen in Table 2, Marie Louis landfill exhibited the highest mean concentrations of BDE-99 (0.108 ± 0.103 ng $L^{-1}$) in winter and this was followed by Robinson Deep and Garankuwa landfill sites for BDE-47 (0.235 ± 0.08 ng $L^{-1}$) and BDE-47 (0.176 ± 0.130 ng $L^{-1}$) respectively. For summer concentrations; BDE-209 was the highest congener with a concentration of 0.480 ± 0.211 ng $L^{-1}$ at the Goudkoppies landfill site. Furthermore, BDE-209 showed high concentrations in all the landfill sites for both seasons. Disposal of products containing BDE-209 in landfill sites could be the reason of its high abundance. It is also possible that BDE-209 containing waste has been accumulating over the years resulting in the high concentrations detected. Also, BDE-47 (0.192 ± 0.160 ng $L^{-1}$) and BDE-100 (0.144 ± 0.005 ng $L^{-1}$) were fairly high after BDE-209 at Goudkoppies for summer samples. The Marie Louis and Robinson Deep landfills also showed high concentrations of BDE-47; 0.141 ± 0.130 ng $L^{-1}$ and 0.141 ± 0.120 ng $L^{-1}$ respectively. The PBDE congener profile in the seven landfill sites was observed to be in the following order: BDE -209 > -99 >-47 > -100 > -154 > -28 > -153 > -17 > -183 in winter and BDE -209 > -47 > -100 > -154 > -99 > -17 > -28 > -183 >-153 in summer. The concentrations of PBDEs in leachate samples obtained in this study were significantly lower than the values reported in Cape Town [27]. The Cape Town study by Daso et al. (2013) [27] reported an overall mean concentration of total PBDEs excluding BDE-209 in winter (July) to range from 0.420–2.73 ng $L^{-1}$ in Belville, 0.250–0.780 ng $L^{-1}$ in Coastal Park and 7.11–49.2 ng $L^{-1}$ in Visserhoek. In summer BDE concentrations in the same study were reported to range from 0.120–33.7 ng $L^{-1}$ in Belville, ND–0.10 ng $L^{-1}$ in Coastal Park and 0.230–123 ng $L^{-1}$ in Visserhoek. The concentrations observed in the Cape Town study can be attributed to the frequency of precipitation, temperature and age of the landfill sites as these can influence the quality and quantity of leachate produced. The available information indicates that those landfill sites were constructed well before the new dispensation in South Africa (1994). It is also possible that the Cape Town landfill site studied may have received other types of waste in addition to the normal municipal wastes. As a result the concentrations of the Cape Town study were high. Also, compared to the study by Odusanya et al. (2009) [8], the concentrations of PBDEs in leachate samples are by far higher than the concentrations of PBDEs obtained in the current study. The study reported concentrations for ∑PBDEs of 9.79 ng $L^{-1}$ for Temba, 7.23 ng $L^{-1}$ and 4.01 ng $L^{-1}$ for Hatherly and Soshanguve MSWLs respectively. This was found to be a slightly higher from the present results. In the present study, $\sum_9$ PBDEs of 0.150 and 0.127 ng $L^{-1}$ were reported for Hatherly and Soshanguve respectively. In addition, Olukunle et al. (2015) [10] reported PBDE concentration in leachate samples to range from 0.127 to 3.70 ng$L^{-1}$. This concentration range is higher than the concentrations found in the present study. It is possible that the various ongoing recycling initiatives in Pretoria and Johannesburg may have contributed to the low concentrations of PBDEs observed in the current study. The various recycling initiatives include, but are not limited to, waste sorting from source and waste re-use [35]. In addition, there is well organised intensive waste sorting at some of the municipal landfill sites studied [35]. Furthermore, kerb recyclers are very much on the increase in both cities, and all these activities may have contributed to the observed low levels of PBDEs [36]. In this study, the sum of leachate concentrations range from 0.560–1.08 ng $L^{-1}$ in summer and 0.316–1.36 ng $L^{-1}$ in winter. Other studies have reported higher PBDE concentrations in leachate samples. For example, values that range from ND-4.00 ng $L^{-1}$ [20], 2.50–12.0 ng $L^{-1}$ [37], 4.00–290 ng $L^{-1}$ [20], 0.03–102 ng $L^{-1}$ [38] and ND-97.93 ng $L^{-1}$ [39] in Japan, China, USA, Canada and South Africa respectively.

As can be seen in Table 3, all the PBDE congeners were detected in all the landfill sites except BDE-28 (winter and summer) and BDE-154 (summer) in Hatherly and BDE-153 (winter) in Goudkoppies. As shown in the leachate results in winter, BDE-209 in sediment exhibited the highest concentrations ranging from Marie Louis 1.270 ± 0.490 ng $g^{-1}$- Soshanguve 3.000 ± 0.100 ng $g^{-1}$, in all the sites. The high concentration of BDE-209 in sediment could be due to the fact that all PBDEs preferably bind to sediment against water [40], it is also likely to be due to its high usage as Deca-BDE [8]. BDE-47 (winter) was found to be the second highest congener with concentration ranging from Garankuwa 0.450 ± 0.400 ng $g^{-1}$- Goudkoppies 0.620 ± 0.440 ng $g^{-1}$ this could be as a result of Penta-BDE containing materials being the second most highly used to

**Table 1**
Detailed description and general information on selected landfill sites.

| Site name | Landfill age (years) | Type of geomembrane liner | Size ($km^2$) |
|---|---|---|---|
| Soshanguve | 18 | No liner | 0.392 |
| Hatherly | 15 | No liner | 0.960 |
| Garankuwa | 18 | No liner | 0.419 |
| Onderstepoort | 16 | No liner | 0.518 |
| Goudkoppies | 30 | Geosynthetic clay liner | 0.672 |
| Robinson Deep | 83 | Geosynthetic clay liner | 1.210 |
| Marie Louis | 28 | Geosynthetic clay liner | 41.90 |

Source: Adapted from general waste minimization plan for Gauteng (GDARD), 2009.

**Table 2**
Mean concentrations of PBDEs in leachate ± SD (standard deviation) from seven selected landfill sites in winter and summer.

| Leachate concentrations (ng $L^{-1}$) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Soshanguve | | Hatherly | | Garankuwa | | Onderstepoort | | Goudkoppies | | Marie Louis | | Robinson Deep | |
| | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum |
| BDE-17 | 0.028 ± 0.030 | ND | 0.014 ± 0.012 | 0.026 ± 0.030 | 0.006 ± 0.005 | 0.036 ± 0.030 | 0.028 ± 0.020 | 0.026 ± 0.024 | 0.042 ± 0.030 | 0.056 ± 0.050 | 0.009 ± 0.006 | 0.042 ± 0.030 | 0.070 ± 0.030 | 0.042 ± 0.040 |
| BDE-28 | 0.026 ± 0.010 | ND | 0.012 ± 0.011 | 0.024 ± 0.001 | 0.048 ± 0.040 | 0.036 ± 0.030 | 0.026 ± 0.003 | 0.026 ± 0.016 | 0.039 ± 0.380 | 0.048 ± 0.027 | 0.010 ± 0.001 | 0.039 ± 0.030 | 0.060 ± 0.060 | 0.036 ± 0.0320 |
| BDE-47 | 0.094 ± 0.080 | 0.094 ± 0.060 | 0.047 ± 0.038 | 0.094 ± 0.080 | 0.176 ± 0.130 | 0.141 ± 0.050 | 0.092 ± 0.038 | 0.094 ± 0.083 | 0.138 ± 0.027 | 0.192 ± 0.160 | 0.035 ± 0.005 | 0.141 ± 0.130 | 0.235 ± 0.080 | 0.141 ± 0.120 |
| BDE-100 | 0.056 ± 0.030 | 0.070 ± 0.030 | 0.035 ± 0.032 | 0.058 ± 0.050 | 0.124 ± 0.103 | 0.039 ± 0.160 | 0.066 ± 0.057 | 0.074 ± 0.016 | 0.081 ± 0.080 | 0.144 ± 0.005 | 0.112 ± 0.009 | 0.072 ± 0.068 | 0.070 ± 0.060 | 0.072 ± 0.050 |
| BDE-99 | 0.004 ± 0.030 | 0.072 ± 0.010 | 0.034 ± 0.005 | 0.038 ± 0.030 | 0.084 ± 0.070 | 0.036 ± 0.030 | 0.030 ± 0.010 | 0.064 ± 0.016 | 0.015 ± 0.007 | 0.024 ± 0.003 | 0.108 ± 0.103 | 0.030 ± 0.010 | 0.095 ± 0.083 | 0.018 ± 0.003 |
| BDE-154 | 0.066 ± 0.030 | 0.078 ± 0.030 | 0.031 ± 0.030 | 0.038 ± 0.020 | 0.136 ± 0.070 | 0.009 ± 0.004 | 0.060 ± 0.020 | 0.054 ± 0.050 | 0.096 ± 0.080 | 0.116 ± 0.007 | 0.008 ± 0.005 | 0.096 ± 0.080 | 0.115 ± 0.110 | 0.060 ± 0.008 |
| BDE-153 | 0.004 ± 0.003 | 0.002 ± 0.002 | 0.003 ± 0.100 | 0.006 ± 0.005 | 0.012 ± 0.010 | ND | 0.006 ± 0.003 | 0.002 ± 0.001 | 0.006 ± 0.0030 | 0.012 ± 0.005 | 0.005 ± 0.004 | 0.006 ± 0.003 | 0.065 ± 0.040 | ND |
| BDE-183 | 0.008 ± 0.007 | 0.004 ± 0.003 | 0.004 ± 0.003 | 0.006 ± 0.003 | 0.012 ± 0.010 | 0.009 ± 0.008 | 0.004 ± 0.003 | 0.010 ± 0.08 | 0.004 ± 0.003 | 0.012 ± 0.005 | 0.003 ± 0.001 | 0.009 ± 0.003 | 0.010 ± 0.008 | 0.012 ± 0.003 |
| BDE-209 | 0.264 ± 0.300 | 0.244 ± 0.200 | 0.136 ± 0.080 | 0.270 ± 0.230 | 0.468 ± 0.108 | 0.408 ± 0.380 | 0.238 ± 0.140 | 0.294 ± 0.160 | 0.238 ± 0.161 | 0.480 ± 0.211 | 0.101 ± 0.100 | 0.384 ± 0.200 | 0.645 ± 0.030 | 0.462 ± 0.380 |

*Concentration and standard deviation values are mean of triplicate analysis, ND = not detectable.

**Table 3**
Mean concentration of PBDEs sediment ± SD (standard deviation) from seven selected landfill sites in winter and summer.

| Sediment concentrations (ng $g^{-1}$) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Soshanguve | | Hatherly | | Garankuwa | | Onderstepoort | | Goudkoppies | | Marie Louis | | Robinson Deep | |
| | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum | Win | Sum |
| BDE-17 | 0.120 ± 0.110 | 0.090 ± 0.090 | 0.090 ± 0.006 | 0.090 ± 0.050 | 0.100 ± 0.090 | 0.050 ± 0.040 | 0.120 ± 0.100 | 0.050 ± 0.040 | 0.140 ± 0.100 | 0.080 ± 0.040 | 0.120 ± 0.100 | 0.070 ± 0.040 | 0.130 ± 0.001 | 0.120 ± 0.140 |
| BDE-28 | 0.100 ± 0.019 | 0.040 ± 0.040 | ND | ND | 0.120 ± 0.090 | 0.010 ± 0.005 | 0.130 ± 0.120 | 0.010 ± 0.010 | 0.120 ± 0.110 | 0.040 ± 0.040 | 0.130 ± 0.100 | 0.020 ± 0.030 | 0.110 ± 0.100 | 0.020 ± 0.010 |
| BDE-47 | 0.480 ± 0.460 | 0.470 ± 0.410 | 0.470 ± 0.490 | 0.470 ± 0.400 | 0.450 ± 0.040 | 0.480 ± 0.400 | 0.470 ± 0.420 | 0.480 ± 0.400 | 0.620 ± 0.440 | 0.450 ± 0.400 | 0.490 ± 0.490 | 0.460 ± 0.400 | 0.600 ± 0.400 | 0.440 ± 0.140 |
| BDE-100 | 0.370 ± 0.290 | 0.050 ± 0.003 | 0.700 ± 0.490 | 0.380 ± 0.270 | 0.260 ± 0.190 | 0.340 ± 0.090 | 0.180 ± 0.001 | 0.340 ± 0.330 | 0.220 ± 0.140 | 0.360 ± 0.300 | 0.570 ± 0.490 | 0.370 ± 0.340 | 0.350 ± 0.340 | 0.340 ± 0.340 |
| BDE-99 | 0.310 ± 0.260 | 0.360 ± 0.300 | 0.420 ± 0.390 | 0.320 ± 0.290 | 0.360 ± 0.190 | 0.350 ± 0.300 | 0.330 ± 0.300 | 0.350 ± 0.340 | 0.550 ± 0.440 | 0.320 ± 0.240 | 0.800 ± 0.490 | 0.270 ± 0.140 | 0.920 ± 0.490 | 0.250 ± 0.140 |
| BDE-154 | 0.220 ± 0.210 | 0.170 ± 0.090 | 0.320 ± 0.300 | ND | 0.230 ± 0.190 | 0.220 ± 0.190 | 0.270 ± 0.190 | 0.220 ± 0.200 | 0.400 ± 0.300 | 0.350 ± 0.250 | 0.310 ± 0.300 | 0.350 ± 0.330 | 0.360 ± 0.330 | 0.270 ± 0.180 |
| BDE-153 | 0.110 ± 0.090 | 0.020 ± 0.001 | 0.030 ± 0.005 | 0.040 ± 0.001 | 0.020 ± 0.010 | 0.030 ± 0.002 | 0.230 ± 0.200 | 0.030 ± 0.040 | ND | 0.060 ± 0.040 | 0.210 ± 0.190 | 0.040 ± 0.039 | 0.330 ± 0.290 | 0.020 ± 0.010 |
| BDE-183 | 0.060 ± 0.030 | 0.120 ± 0.009 | 0.010 ± 0.004 | 0.120 ± 0.090 | 0.050 ± 0.040 | 0.130 ± 0.001 | 0.020 ± 0.020 | 0.130 ± 0.100 | 0.070 ± 0.040 | 0.130 ± 0.100 | 0.090 ± 0.090 | 0.120 ± 0.140 | 0.120 ± 0.100 | 0.130 ± 0.100 |
| BDE-209 | 3.000 ± 0.100 | 2.500 ± 0.490 | 1.560 ± 0.490 | 1.83 ± 0.090 | 1.96 ± 0.490 | 1.23 ± 0.490 | 1.58 ± 0.490 | 1.23 ± 0.490 | 2.140 ± 0.490 | 1.30 ± 0.390 | 1.270 ± 0.490 | 2.01 ± 0.490 | 1.99 ± 0.090 | 1.46 ± 0.490 |

*Concentration and standard deviation (SD) values are mean of triplicate analysis, ND = not detectable.

Deca-BDE [33]. In comparison to winter, BDE-209 in summer sediment was the congener with the highest concentrations ranging from 1.23 ± 0.490 (Garankuwa and Onderstepoort) - 2.500 ± 0.490 ng $g^{-1}$(Soshanguve). BDE-47 concentrations followed those of BDE-209 with concentrations ranging from 0.440 ± 0.140 ng $g^{-1}$ (Robinson Deep) - 0.48 ± 0.400 ng $g^{-1}$ (Garankuwa and Onderstepoort). The concentrations of analysed congeners compared to BDE-47 and BDE-209 in sediment did not follow any regular pattern. PBDE concentrations obtained in winter are generally slightly higher than the concentrations obtained in summer. A dilution effect due to precipitation which is more pronounced in summer could have contributed to the observed difference. Again the concentrations of PBDEs in sediment samples are far below the levels reported by Olukunle et al. (2015) [10].

Osako et al. (2004) observed that most landfill leachates with large amount of organics had extremely high concentration of PBDEs, and the leaching tests proved that BFRs to some extent, can be leached out of materials by the presence of organic matter. Therefore, Pearson correlation (r) and statistical significant *t*-test (p) studies of PBDE congeners with DOC were carried out with winter samples to investigate if there is a relationship. Leachate from lined landfill sites yielded high mean concentrations of DOC; Robinson Deep 56.0 mg $L^{-1}$ (0.830 ng $L^{-1}$), Goudkoppies 44.0 mg $L^{-1}$ (0.238 ng $L^{-1}$) and Marie Lous 36.0 mg $L^{-1}$ (0.101 ng $L^{-1}$) while for unlined landfill sites they were not as high; with Soshanguve and Onderstepoort 14.7 mg $L^{-1}$ (0.238 and 0.264 ng $L^{-1}$), Garankuwa 12.0 mg $L^{-1}$ (0.468 ng $L^{-1}$) and Hatherly 8.00 mg $L^{-1}$ (0.136 ng $L^{-1}$). Correlation values for DOC versus BDE congeners: BDE-47 ($r = 0.64$), BDE-100 ($r = 0.65$), BDE-154 ($r = 0.73$) and BDE-183 ($r = 0.63$) were observed except for BDE-99, BDE-153 and BDE-209. A statistical significance ($p < 0.05$) was observed for all the PBDEs except BDE-49 ($p > 0.05$). This suggests that there is an influence of organic carbon on the levels of PBDEs. However, there is also a possibility that leachate samples analysed may have been recently contaminated and, therefore, concentrated with PBDEs. It was observed that in winter (Table 1), the highest PBDE concentration in leachate samples was from Robinson Deep landfill site with a geomembrane liner. It is highly probable that the observed higher concentration in leachate from the lined landfill was a result of the sites leachate management. Whereby, leachate which was stored in tanks due to overflows of ponds in summer is re-introduced to the landfill to prevent damage or cracking of the geomembrane clay liner due to winter being a very dry season [40]. However, the trend was not observed for sediment samples in winter. Instead, the highest concentration of PBDEs was found in sediment samples from Soshanguve, which is not lined with geomembrane liner. This could be as a result of compaction of waste. Lined landfill sites do not practice compaction. Sediment with waste from highly compacted areas may contain high PBDE levels due to high volume of waste compressed to conserve airspace and extend the landfill's life span [41].

As mentioned earlier, the lower concentrations of PBDEs obtained in the present study compared to previous studies may have been influenced by the better waste management initiatives in both Pretoria and Johannesburg. Table 4 compares the current study with those reported by other researchers. As can be seen in Table 4, the concentrations of PBDEs in landfill leachate from other parts of the world were the highest in Canada and the lowest in Japan, in the order: Canada > USA > China > Japan. In the case of South Africa, the order is as follows: Daso et al. (2013) [27] > Odusanya et al. (2009) [8] > Olukunle et al. (2015) [10] > present study. When compared to all the previous studies, this study showed low levels of PBDEs in both landfill leachate and sediment. This could be due to the continual improvements in recycling and waste sorting in Pretoria and Johannesburg.

### 3.2. Influence of geomembrane liners on PBDE levels

Figs. 2 and 3 show the seasonal variation of the $\sum_9$PBDEs in leachate and sediment samples from selected landfill sites with and without geomembrane liners. The winter $\sum_9$PBDE concentrations in Robinson Deep, Marie Louis, and Goudkoppies in leachate were 1.37 ng $L^{-1}$, 1.36 ng $L^{-1}$, and 0.816 ng $L^{-1}$ respectively (Fig. 2). Also, in summer the $\sum_9$PBDE concentrations in leachate followed the same pattern as winter for the same sites 0.843 ng $L^{-1}$, 0.819 ng $L^{-1}$ and 0.108 g $L^{-1}$. Robinson Deep shows high PBDE concentrations in leachate suggesting that the geomembrane liner may have retained a sizeable portion of the leachate whereby, more PBDEs were leached out of their materials. Also, the practise of re-introduction of stored leachate back into the landfill to prevent damage or cracking of the geomembrane clay liner may have also contributed to the observed high PBDE concentrations.

The $\sum_9$PBDE concentrations in Robinson Deep, Marie Louis, and Goudkoppies in winter sediment were 4.91 ng $g^{-1}$, 3.99 ng $g^{-1}$ and 4.26 ng $g^{-1}$ respectively as can be seen in Fig. 2. In summer the concentrations were 3.05 ng $g^{-1}$, 3.71 ng $g^{-1}$ and 3.09 ng $g^{-1}$ but they did not follow the same pattern of decreasing in concentration from Robinson Deep to Goudkoppies as leachate did, instead, Marie Louis had the highest concentration. This could mean that sediments from Marie Louis landfill site may have been contaminated with PBDEs longer and, therefore, more concentrated when compared to values exhibited by Robinson Deep and Goudkoppies.

**Table 4**
Comparison of PBDEs in landfill leachate (ng $L^{-1}$) and sediment (ng $g^{-1}$) with other studies in South Africa and other parts of the world.

| Location | Season | N | Landfill sediment | Landfill leachate | Reference |
|---|---|---|---|---|---|
| USA, Minnesota | NA | 5 | NA | 4.00–29.0 | Oliaei et al. (2002) [22] |
| Japan, Ibaraki | NA | 7 | NA | ND - 4.00 | Osako et al. (2004) [21] |
| SA, Pretoria | NA | 5 | NA | ND – 97.9 | Odusanya et al.(2009) [8] |
| Canada | NA | 28 | NA | 0.030–102 | Li et al. (2012) [26] |
| China, Shangai | Winter & Summer | 11 | NA | 2.500–12.0 | Huang et al. (2013) [37] |
| SA, Cape Town | Summer | 3 | NA | ND - 123 | Daso et al. (2013) [27] |
| | Winter | 3 | NA | 0.250–6380 | |
| SA, Gauteng | Winter | 6 | 0.80–8.40 | 0.127–370 | Olukunle et al. (2015) [10] |
| SA, Gauteng | Summer | 7 | 2.50–3.87 | 0.560 1.08 | Present study |
| | Winter | 7 | 3.00–4.91 | 0.318–1.36 | |

*ND = not detected, NA = not available, N = number of samples.

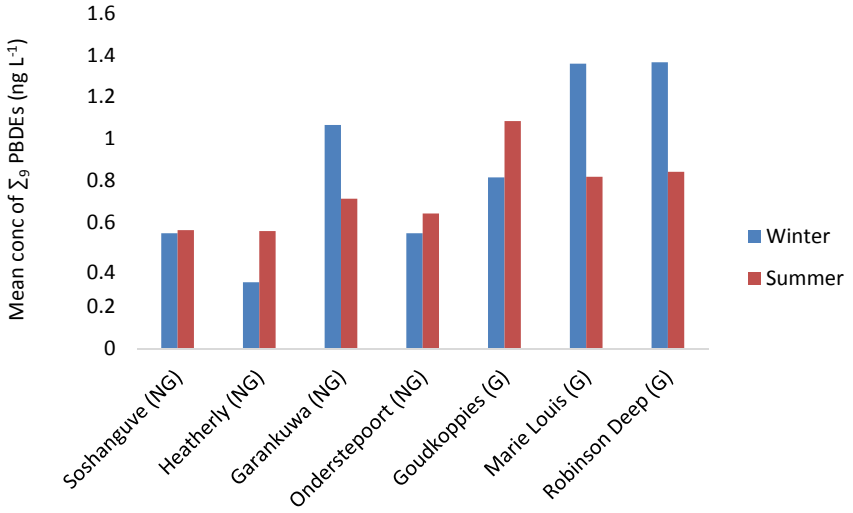


**Fig. 2.** Variation of $\sum_9$PBDEs in winter and summer leachate from selected landfill sites with and without geomembrane liners (NG = no geomembrane, G = geomembrane).

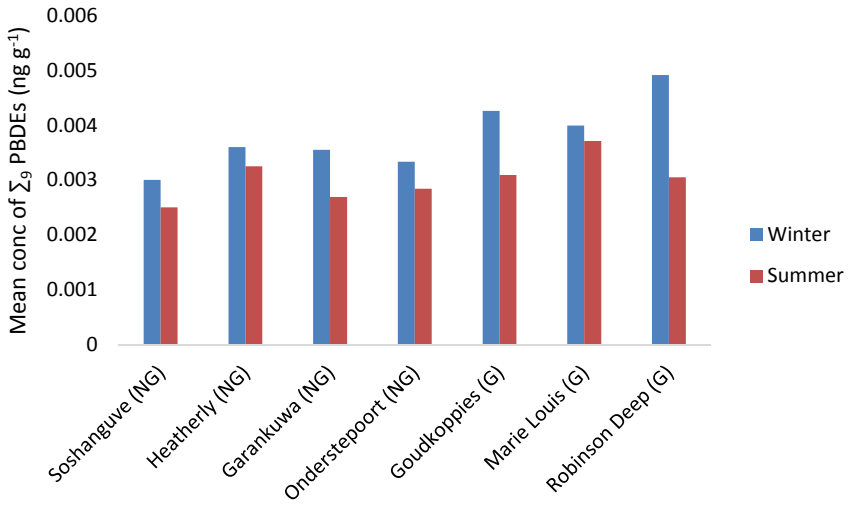


**Fig. 3.** Variation of $\sum_9$PBDEs in winter and summer sediment from selected landfill sites with and without geomembrane liners (NG = no geomembrane, G = geomembrane).

The high PBDE concentrations from the three Johannesburg landfill sites could be due to the effectiveness of geomembrane liners in retaining leachate from infiltrating into groundwater. Regardless of the landfill age, another possibility could be the leachate treatment process whereby leachates are pumped out from the landfill when the levels are too high. Due to rainfall, the excess leachate is stored in tanks on site, so that when leachate levels are too low, it gets re-introduced to the landfill to keep a head level and prevent cracking or damage to the geomembrane clay liner [40]. Also, the landfills could be containing more sources of PBDEs in them. The $\sum_9$PBDE concentrations in leachate and sediment observed in summer were significantly lower than in winter and this could be due to removal of leachate to tanks as a result of the overflow of ponds [40]. It could also be that clay composite liners are reduce leachate contaminant concentrations as they are designed to do that for the first 120 years [34].

### 3.3. Groundwater concentrations

To further investigate the effectiveness of geomembrane liners, two borehole samples in the vicinity of landfills were tested for PBDE concentrations from the largest and busiest landfill sites, one in Pretoria (Hatherly) and the other in Johannesburg (Marie Louis) (Figs. 4 and 5). BDEs -47, -100, -154 and -209 were detected in both landfill sites in winter and summer. However, some congeners were not detected in both seasons. In a geomembrane lined landfill site there is a less number of congeners not detected compared to a geomembrane lined landfill site. Non detection of these PBDE congeners could be due to a possible influence of trace metals and anions reported to be found in ground water, resulting in formation of metal complexes or metal ligand complexes, affecting the levels of PBDEs detected [10]. The $\sum_9$PBDE concentrations for Hatherly and Marie Louis were 0.045 ng $L^{-1}$ and 0.449 ng $L^{-1}$ respectively in winter, and 0.153 ng $L^{-1}$ and 0.293 ng $L^{-1}$ in summer. The detection of PBDEs in groundwater on both landfill sites is an indication of contamination, most probably from the landfill sites. The groundwater samples were taken from the monitoring boreholes and in both seasons, the concentrations of the $\sum_9$PBDEs in groundwater from the landfill sites were lower, except for Marie Louis which was high in winter compared to the $\sum_9$PBDE concentrations found in leachate of these sites. In the geomembrane-lined landfill site, Marie Louis,

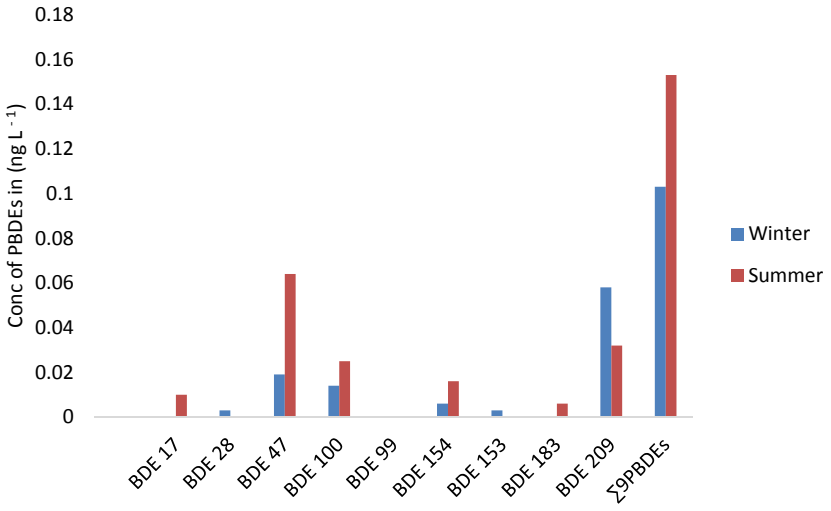


**Fig. 4.** Mean winter and summer concentrations of PBDEs in groundwater from Hatherly landfill.

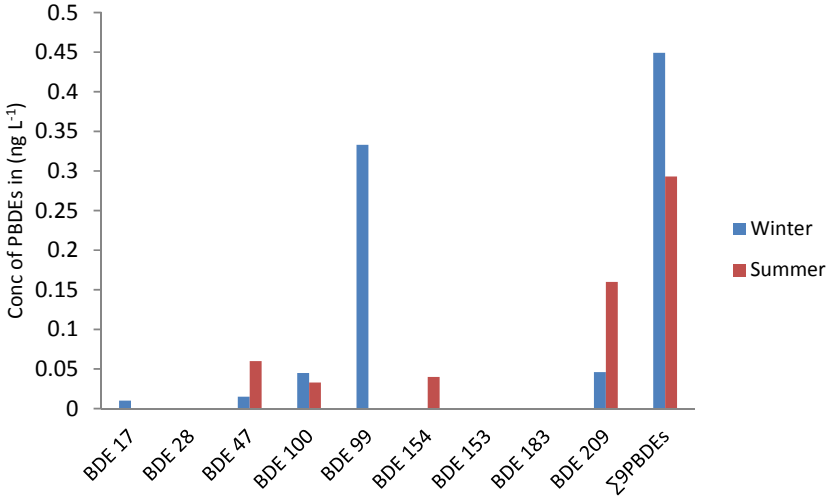


**Fig. 5.** Mean winter and summer concentrations of PBDEs in groundwater from Marie Louis landfill.

the $\sum_9$PBDE concentrations were higher than in the unlined landfill site, Hatherly. Marie Louis landfill site is a big and old landfill site which could not be completely lined with a geomembrane liner due to its capacity, therefore, leachates may have infiltrated into groundwater through the unlined parts of the site. These findings also suggest that there may be some deterioration of the geomembrane liner at the Marie Louis landfill site since it is one of the oldest landfill sites in the province. Furthermore, there could be other sources like improper disposal of by products from the industrial industries near the landfill.

Studies on groundwater contamination have been conducted previously. For example, Kjeldsen (1993) [42] investigated the quantity and the quality of leachate that contaminated groundwater. Baun et al. (1999) [43] conducted some toxicity tests on non-volatile organic chemicals in groundwater polluted with landfill leachate and pharmaceutical compounds in leachate plume and groundwater [44]. These studies reveal that landfill leachate does contaminate groundwater if adequate preventative measures are not taken.

## 4. Conclusions

In this study, the selected PBDEs were detected in all winter and summer leachate samples except BDE-17, BDE-28 and BDE-153, which were not detected in Soshanguve, Garankuwa and Robinson Deep. In sediment samples, the PBDE congeners that were not detected in winter were BDE-28 in Hatherly and BDE-153 in Goudkoppies. In summer, BDE-28 was not detected in Hatherly and Garankuwa and BDE-154 was also not detected in Hatherly. The concentrations of PBDEs were notably higher in winter than in summer in both media. In sediment it could be because of compacting and in leachate because of leachate management in summer and winter [30]. Overall, this study showed a decline in concentrations of PBDEs compared to previous studies in Gauteng Province. This may be due to the ongoing various waste management initiatives in Johannesburg and Pretoria. High concentrations of PBDEs in the groundwater samples from the Marie Louis landfill site suggest deterioration of the liner, seepage through the unlined part of the landfill site or contamination by improper disposal of

end products in nearby industrial industries. The effectiveness of the geomembrane liners could not be adequately proven due to detection of PBDEs in the groundwater of geomembrane lined landfill site. More studied should look into this because there are many factors that can play a role in the elevated leachate concentrations observed in lined landfill sites.

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