RESEARCH ARTICLE

Influence of physicochemical and chemical parameters on polybrominated diphenyl ethers in selected landfill leachates, sediments and river sediments from Gauteng, South Africa

O. I. Olukunle & I. V. Sibiya & O. J. Okonkwo & A. O. Odusanya

Abstract Polybrominated diphenyl ethers (PBDEs) are known to be persistent, endocrine disruptors and bioaccumulative and can cause adverse health effects in animals and humans. In this study, river and landfill sediment samples were collected from selected rivers and municipal solid waste landfill (MSWL) sites across Gauteng Province in South Africa to determine the levels of common PBDEs (BDE-17, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209). The mean and median concentrations of Σ_8 PBDEs from river sediment samples was 2.4 and 0.4 ng g^{-1}, respectively, and a range of 0.8–114 ng g^{-1}. The highest concentration of Σ_8 PBDEs (43.6 ng g^{-1}) was observed at Jukskei River with more than two orders of magnitude greater than the rest. The observed total PBDE concentrations in landfill sediment and leachate samples ranged from 0.8 to 8.4 ng g^{-1} and 127–3,702 pg L^{-1} for the two matrices. BDE-209 was predominantly detected in most of the sediment samples. Two of the MSWLs which are lined with geomembranes gave the highest concentrations of $\sum_7$ PBDEs (2,678 and 3,702 pg L^{-1}). Correlation values for $\sum_7$ PBDEs versus Co (r=0.65), Cu (r=0.52), Mn (r=0.10), Mg (r=0.76), Ca (r=0.66) and Ni (r=0.77) with a statistical significance (p<0.05) were observed except for Na, Cr, Pb, K, Fe and Zn (p>0.05). The observed positive correlation may suggest a possible influence of trace metals on PBDE concentrations in leachates. Furthermore, a test of relationship between major anions and PBDEs yielded positive relationship with Cl$^-$ (r=0.94, p=0.16), F$^-$ (r=0.97, p=0.21), Br$^-$ (r=0.6, p=0.29) and NO$_3$ (r=0.96, p=0.08) with an insignificant statistical difference. However, evaluation of the relationship between some water quality parameters (pH, dissolved oxygen and electrical conductivity) gave negative correlation with PBDE concentrations.

Keywords Polybrominated diphenyl ethers · Municipal solid waste landfill · Leachate · Landfill sediment · River sediment

Introduction

Polybrominated diphenyl ethers (PBDEs) are synthetic chemicals used as additives in a wide variety of consumer and industrial products such as plastics, television sets and textiles to reduce the occurrence of accidental fires. PBDEs belong to the group of brominated flame retardants (BFRs) that have gained very wide application and, as a result, are found in a variety of consumer products. Reports indicate that nothing less than 75 different types of brominated chemicals have been produced on a commercial scale for use in products to meet a wide range of fire standards (Alaee et al. 2003; Covaci and Dirtu 2008). Three major commercial formulations of PBDEs were produced globally in the last decade: PentaBDE, OctaBDE and DecaBDE. Penta mixture was mainly used for printed circuit boards, cable sheets, furniture and textiles and Octa mixture used for television sets, computer housings, business machines, household appliances and other small electronics such as remote controls while Deca mixture is used mainly for high impact polystyrene, printed circuit boards, furniture and textiles. The latter is also widely used in transportation, construction and building sector (Leiswitz et al. 2001; de Wit et al. 2010). Because of suspected endocrine-disrupting properties of Penta and OctaBDE derivatives, their production and use were banned by the European

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Union (EU) in August 2004 (BSEF 2006). Since then, Penta and OctaBDE derivatives have been recognised as persistent organic pollutants (POPs) and now included in the list of the new POPs under the Stockholm Convention. According to a report, the production of DecaBDE among brominated flame retardants is second after TBBPA (BSEF 2011).

PBDEs have shown to be persistent, bioaccumulative and have endocrine-disrupting properties; 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 (Darnerud et al. 2011; de Wit et al. 2006; Devanathan et al. 2012; Jakobsson et al. 2002; Johnson-Restrepo et al. 2005; Johnson et al. 2010).

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 when they are disposed to landfills. Generally, landfills serve as the final destination of old, obsolete and end of life wastes that may have been treated with BFRs, particularly with PBDEs. These waste materials are, most often, disposed into landfill sites with household waste. For example, in Europe, about 96 % of electrical and electronic waste generated in 2002 was dumped in landfills or incinerated (Vehlow et al. 2002). According to a report by e-waste South Africa, between 1,129,000 and 2,108,000 t of potential e-waste is estimated to be in South African households (Finlay and Liechti 2008). Many of which will find their way into municipal landfills.

Few reports have indicated landfills as one of the sources of BFRs to the environment (Devanathan et al. 2012; Eggen et al. 2010; Weinberg et al. 2011). For example, Odusanya et al. (2009) describe leachates as a complex product derived from the biodegradation of solid wastes, consisting of primarily organic and inorganic pollutants, which need to be treated before they constitute a threat to public health and the environment. Osako et al. (2004) suggested that leachability could either be affected by other constituents present in the leachate which may happen in the incident of rainwater penetrating landfill layers or solubility aided by dissolved organic matter. Leachates may infiltrate into the underlying soil if the landfill site is not properly lined or if the lining materials are damaged. However, only a handful of studies have so far focused on PBDEs' fate in landfill leachate (Eggen et al. 2010; Kalantzi et al. 2011; Li et al. 2012; Odusanya et al. 2009; Oliaei et al. 2002; Osako et al. 2004). In other studies, high concentrations of PBDEs were observed in leachate, in the ambient atmosphere and in vegetation near landfills, as well as in the blood serum of computer clerks and children living next to the dumping sites (Perez-Maldonado et al. 2009; St-Amand et al. 2008; Weinberg et al. 2011). Huang et al. (2013) reported on the levels of PBDEs in Shanghai Laogang Municipal landfill leachates and sediment which is said to be

the largest landfill in China. Osako et al. (2004) also reported on levels of PBDEs in Japan. There have been few other reports on leachates in different regions (Kwan et al. 2013; Li et al. 2012, 2014).

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 the surrounding groundwater. However, out of the few reports from South Africa, Odusanya et al. (2009) reported levels of PBDEs in leachates from municipal solid wastes landfill (MSWL) sites from the city of Tshwane. Daso et al. (2012) also reported PBDEs in leachates from a landfill in Cape Town. The aforementioned studies have measured PBDEs only in leachates and none in sediment. Other researchers have also reported the presence of PBDEs in river sediment (Olukunle et al. 2012) in South Africa. These reports suggest a strong need for further investigation of BFRs in the environment, especially in landfill sediments and river sediments in South Africa, particularly rivers that are likely to be polluted due to a range of land use activities surrounding such rivers. Furthermore, they have also presented no data regarding landfill and river sediment compositions such that the possible influence of other contaminants such as trace metals on the levels of PBDEs can be evaluated. It has been reported that trace metal partition between the colloidal and dissolved phase of landfill leachates, which affect their mobility (Jensen and Christensen 1999; Matura et al. 2010). Also, Claret et al. (2011) reported that Pb, Cd, Ni, Cu and Zn are strongly complexed with organic matter. According to Kefeni and Okonkwo (2013), the influencing mechanism of trace metals on PBDEs may be from the point of view that a number of trace metals have empty d-orbitals with low lying energy levels which are suitable for the formation of coordination compounds, suggesting that the co-existence of trace metals and PBDEs in environmental samples may lead to the formation of coordination compounds, thereby limiting the number of free or extractable PBDE congeners resulting in low concentrations consequent upon alteration of the chemical composition of PBDEs. Similarly for anions, it is possible they exhibit an interaction with PBDEs which may influence the presence and detection levels of PBDEs in case of the present study.

Because of the complex nature of landfill leachates and sediment, there is a need to clearly understand factors influencing the determination of PBDEs in waste mixture, particularly trace metals which are capable of forming complexes with PBDEs. The current paper is, therefore, centred on the determination and reliable analysis of PBDE levels in some selected river sediments and landfill (lined or unlined with geomembrane material) leachates and sediments to explore the correlation between PBDEs and some trace metals and the influence of other water quality parameters on levels of PBDEs in Gauteng Province, South Africa. Although results on landfill leachates have been reported on some landfill

sites in South Africa, analyses of leachate samples from selected landfill sites are included in the present study in order to present a clearer distribution of PBDEs in landfill environment.

Materials and methods

Sampling sites

In this study, samples were collected from six operational MSWLs. These MSWLs were selected across Gauteng (Fig. 1); out of which, two, namely Chloorkop and Robinson deep, are equipped with liners (Bentonite modified soil liner constructed on top of Kaymat 34 wrapping) to prevent leachates infiltration into groundwater. These two MSWLs also receive industrial wastes including combustible and incombustible materials which are incinerated before finally dumping the residues into the landfill sites. The remaining four unlined MSWLs including Soshanguve, Hatherly, Garstkloof and Onderstepoort are traditional landfills where no waste sorting, separation and incineration takes place. The composition of most of the MSWLs were dominated by household waste, 80 and 75 % in the case of Soshanguve and Hatherly, respectively, 10 % garden, 5 % industrial and 10 % building wastes.

Jukskei River is the third largest river in Johannesburg, about 50 km long, its source is the Bezuidenhout valley and it flows through the northern part of the densely and industrialised Witwatersrand complex before flowing into the Crocodile River while the latter drains into the Hartbeespoort Dam which is used for recreational purposes and as a source of raw water for Magalies Water Board. It receives effluent from industries, runoff in vast amounts from illegal, unmanaged waste dumps and high human activities from the squatter camp on the west bank in Alexandra Township. Other rivers identified as hotspots of pollution because of industrial, sewage treatment plants and agricultural activities around them include Alberton, Fouriespruit (Meyerton), Clarington, Lowerklip and Vaal River.

Collection of leachate and sediment samples

Raw leachate samples (2 L each) were collected using grab method in pre-washed and acetone rinsed 2 L amber bottles from leachate 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. Water quality parameters such as pH, conductivity, metals and anions were measured immediately on arrival to our laboratory. Appearance of the leachate samples vary from light to dark brown in colour. Sediment samples were collected with stainless grab at about 5 cm below the surface at same points as

leachates in wide mouth 500 mL amber bottles and treated in same procedure for transportation and storage pending the time of extraction and subsequent analysis. Samples were collected between June and August 2013, representing the dry winter period.

Collection of river water and sediment samples

Six rivers were sampled with respect to their accessibilities. Three samples each (water and sediment) were collected from Alberton, Fourie spruit (meyerton), Clarington, Taaiboschspruit in the lowerklip, Vaal and seven points on Jukskei River because of its size; in addition, it receives inflow from other small rivers and effluent from industries, between August and September 2013. These samples represent the winter period. The seven sampling sites identified on Jukskei River include Eastgate (Marlboro), Midrand (Eastgate), N14 (KNP), Bruma Lake, Eastbank, Kyalami and Buccleuch. Collection of sediment samples was described in "Collection of leachate and sediment samples".

Chemicals, reagents and their purification

Materials used for the determination of some selected polybrominated diphenyl ethers frequently detected in most matrices include the following: Strata florisil 500 mg/mL, ultrapure water was dispensed from Labostar ultrapure water equipment (Siemens, Germany) supplied by Separations, South Africa. Each certified standard solutions (1.2 mL of 50 mg L^{-1}) of 10 PBDE (BDE-17, BDE-47, BDE-77, BDE-99, BDE-100, BDE-118, BDE-153, BDE-154, BDE-183 and BDE-209) congeners were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Multi anion standards (Cl^-, F^-, Br^-, NO_2^-, PO_3^{4-}, SO_4^{2-}, NO_3^{2-}) were purchased from Merck Chemicals, South Africa. Trace metal standards used are products of Immelman Chemicals Pty, South Africa. Copper powder (purity 99.98 %) from Saarchem (Pty) Ltd., (Muldersdrift, South Africa), silicagel (100−200 mesh), sodium sulphate (purity 99.9 %), glass wool and HPLC grade solvents: acetone, hexane, dichloromethane, methanol and toluene (products of Sigma-Aldrich (Chemie GmbH, Steinheim, Germany)), 50 mL of nonane (Purity 99.8 %, Sigma-Aldrich, product of Switzerland) were purchased from Industrial Analytical Pty.

All solvents used were of analytical grade and kept away from contamination. Other materials such as silica gel, sodium sulphate and copper powder were activated before use at the recommended conditions. Anhydrous sodium sulphate and silica gel at first use were heated in a muffle furnace at 450 °C for 16 h. Acidic silica and basic silica were prepared according to USEPA 1614 method (2007). For acidic silica, 44 g of concentrated H_2SO_4 was added to 100 g of previously
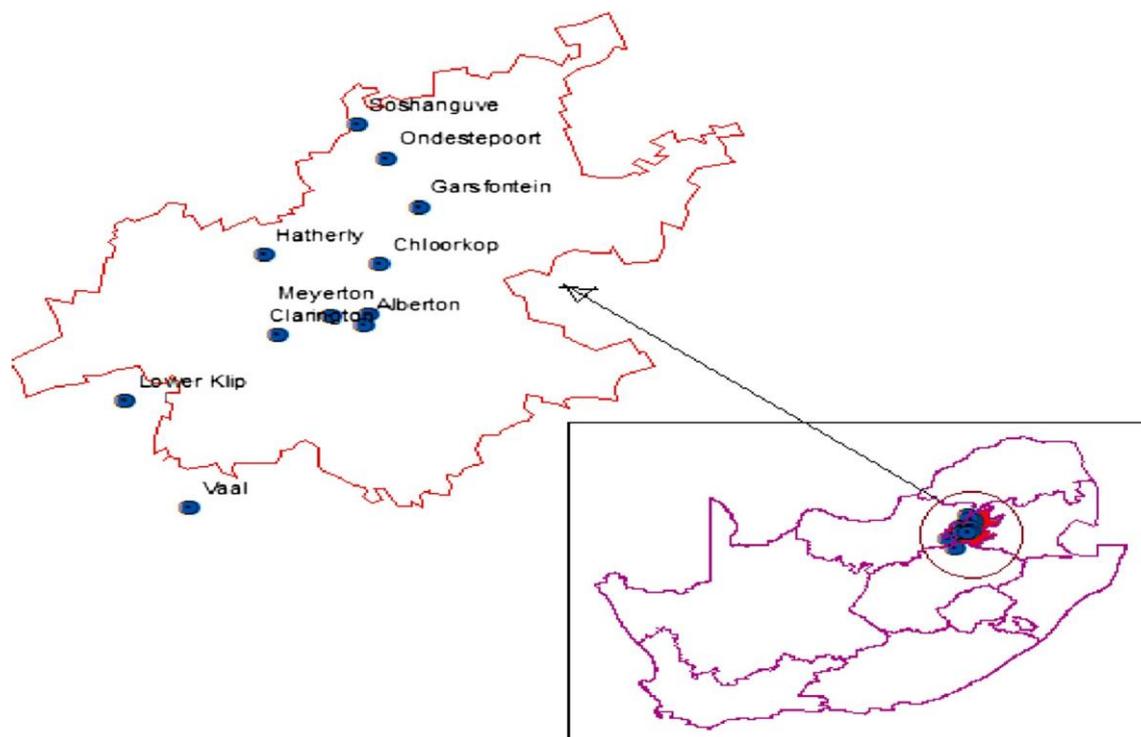
Fig. 1 Map of South Africa and Gauteng (inset) showing locations of six MSWLs and Rivers

activated silica gel and stirred until fine powder was achieved. Basic silica was prepared by mixing 30 g of 1 N NaOH with 100 g of previously activated silica and stirred into fine powder. Copper powder was activated by soaking in 6 N HCl for 3 min then rinsed thoroughly with ultrapure water followed by methanol and kept under toluene until use. Preparation of standards and serial dilution of working standards were done under fume hood.

Recovery tests, sample treatment and analysis

One hundred microlitre of 3.3 ng μL^{-1} PBDE surrogate standards was dissolved in 5 mL acetone then spiked into 500 mL ultrapure water and left for 24 h for equilibration. The mixture was thereafter extracted by liquid-liquid extraction. 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. Observed values for a mixture of n-hexane/toluene (1:1, v/v) ranged from 23 to 103 %, n-hexane/toluene (2:1, v/v) (28–130 %), DCM/toluene (25–96 %), DCM/hexane (39–130 %) and DCM (75–101 %). Similarly, test of solvents as used with LLE was also applied to the SPE. Different solvents were used for elution, and their respective recoveries were compared. However, LLE gave satisfactory results for all analytes and was therefore reported in this work. Three time extraction by LLE with 50 mL DCM

was found adequate for recovery of all analytes. Details of analysis have been reported elsewhere (Olukunle 2012).

Similarly for solids, sodium sulphate fortified with 1 ng $\mu L^{-1} \times 120$ μL ($^{13}C_{12}$ BDE-139 and BDE-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). Cleanup followed the procedure earlier reported by Olukunle et al. (2012) using hexane for elution. The eluant was concentrated to near dryness under N_2 to 200 μL. Before injection, BDE-118 (10 μL of 2.5 ng μL^{-1}) was added as quantitation internal standard and 1 μL was injected into the GC-MS. The method was validated with the recovery of surrogate standards $^{13}C_{12}$ BDE-139 (90 %) and BDE-209 (81 %). Leachates and sediment samples were subjected to same extraction and cleanup 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 15 m column of ZB 5 (0.25 mm ID, 0.25 μm d_f) was used for separation. The initial oven temperature was set at 90 °C (1 min), 30 °C/min to 300 °C (5 min) and at 10 °C/min to

310 (10 min). Carrier gas used was helium (purity 99.999 %) and set at a constant flow of 1.5 mL min^{-1}. The injector, transfer line and ion source temperatures were set at 290, 300 and 250 °C, respectively.

Analysis of basic anions was performed on Metrohm 883 basic IC plus from Switzerland. Four external level calibrations were used for quantitation of basic anions comprising F$^-$, Cl$^-$, NO$_2^-$, Br$^-$, NO$_3^-$, PO$_4$ and SO$_4$. Calibration standards were prepared from stock of mixed (Merck Chemicals) anions from concentration of 1,000 mg/L to 50, 20, 10 and 1 mg/L respectively. Twenty microlitre each of filtered sample was injected by Metrohm (863 Compact autosampler) autosampler. Briefly, eluent used for the mobile phase was composed of sodium hydrogen carbonate and sodium carbonate. For each batch of samples processed, 2 L eluent was prepared by first weighing the two salts (NaHCO$_3$ and Na$_2$CO$_3$), 286 and 382 mg, respectively, as specified for the Metrosep A Supp 4-250/4.0 separation column. Trace metals were analysed using a Spectro Arcos inductively coupled plasma-optical emission spectrometry (ICP-OES) (Model: Arcos FHS and serial no: 07001043 made in Boschstrasse, Germany).

Quality assurance

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 cleanup 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 GC-MS was done using seven level calibration standards. The limit of detection was taken as greater than three times the signal-to-noise ratio. For all the congeners, good linear regression of 0.999 was obtained. LOD values ranged from 0.02 to 0.3 ng μL^{-1} and 0.9 ng μL^{-1} for BDE-209 respectively. Quality of ultrapure water dispensed from Siemens Labostar bench top unit was 0.055 μs cm^{-1}.

Statistical analysis was performed using Microsoft windows statistical package. Pearson correlation coefficient was used to test the linear relationship between PBDE concentrations and trace physicochemical properties.

Results and discussion

A total of seven PBDE congeners (BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183 and BDE-209) were determined and quantified in landfill leachates and sediments while eight congeners were determined in river sediments, with the addition of BDE-17. Consequently, $\sum_8$PBDEs and $\sum_7$PBDEs in the discussion that follows refer to the sum of all congers in river sediment and landfill leachates/sediment, respectively.

Physicochemical and chemical characteristics of the raw leachates

As shown in Table 1, the mean pH values of the selected six MSWLs range from 7.34 to 8.46, generally indicating a neutral to alkaline characteristic with values for Hatherly, Robinson deep and Chloorkop observed to be in the alkaline region. Electrical conductivity ranged from 0.3 to 23 mS cm^{-1}. The highest values of 13 and 23 mS cm^{-1} correspond to the two lined MSWLs of Chloorkop and Robinson deep, respectively, suggesting high amount of dissolved salts about more than one order of magnitude higher than the rest and the possibility of effective containment of the geomembranes to prevent leachates infiltrating into groundwater. These two MSWLs also receive hazardous materials from industries. Results of the major cations, anions and other

Table 1 Physicochemical parameters of leachate samples in milligrams per liter and millisiemens per centimeter for electrical conductivity (EC)

Site	Anions (mg L^{-1})						Cations (mg L^{-1})				Physicochemical parameters	
	Cl$^-$	F$^-$	Br$^-$	NO$_3^{2-}$	PO$_4^{3-}$	SO$_4^{2-}$	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	pH	EC (mS cm^{-1})
L1	124	1.1	0.4	2.1	<dl	15	71	7.6	152	116	7.48	0.5
L2	28	<dl	0.1	5	<dl	31	73	15	82	211	7.34	0.3
L3	49	0.4	<dl	2.1	<dl	3.3	193	10	137	75	8.46	0.6
L4	756	1.4	1.7	1.4	<dl	35	890	140	180	123	7.58	1.4
L5	5,306	16	30	15	26	114	5,731	2,400	362	212	8.2	23
L6	2,144	16	166	11	<dl	29	3,721	1,400	228	213	7.97	13

L1 Onderstepoort, L2 Garstkloof, L3 Hatherly, L4 Soshanguve, L5 Chloorkop, L6 Robinson deep, dl less than detection

Fig. 2 PBDE profile in landfill leachates

PBDE levels in landfill leachates

The following PBDEs (BDE-47, BDE-100, BDE-99, 154, BDE-153, BDE-189 and BDE-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 to 3,703 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 inciner-ation respectively. Elevated levels of BDE-209 (1,930 pg L^{-1}) was found in a sample from Chloorkop MSWL. Robinson deep MSWLs was second with ∑PBDEs of 2,678 pg L^{-1}.

physicochemical parameters are as shown in Table 1. Most of the anions (analysed by Metrohm basic IC 883) were found within acceptable limits, except for Soshanguve leachates with high levels of chloride. Phosphate levels were found below detection in all the samples except for Robinson deep. Figure 3 shows the levels of trace metals detected in leachate samples analysed by ICP-OES.

Both Chloorkop and Robinson deep MSWLs are lined, con-tributing 86.2 % of the total PBDEs (7,264 pg L^{-1}) from the six MSWLs in the present study. Congener profiles of PBDEs per site are shown in Fig. 2.

Findings from the present study were compared to previous work by Odusanya et al. (2009) in the city of Tshwane. They reported concentrations for ∑PBDEs of 9,793 pg L^{-1} for Temba and 7,230 and 4,009 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, ∑$_7$ PBDEs, of 150 and 127 pg L^{-1} for Hatherly and Soshanguve, respectively, are reported. The observed differ-ences between the values of ∑PBDEs reported by Odusanya et al. (2009) 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 5 years ago. The various recycling activities may have reduced the quantities of products that may have PBDEs from entering the landfill sites. Daso et al. (2012) reported the highest concentrations (2,240 ng L^{-1}) of ∑PBDEs in leachates from a landfill in the city of Cape Town, South Africa. Li et al. (2014) reported a concentration range of 4,000–352,000 pg L^{-1} from selected

Fig. 3 Trace metals profile of landfill leachates
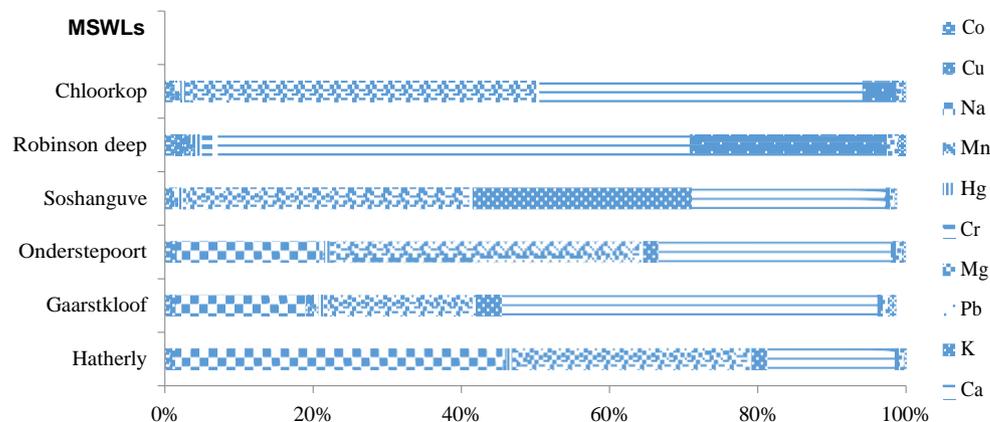
Table 2 Congener patterns in selected landfill sediment from Gauteng (ng g^{-1} dry weight)

Congener	Minimum	Maximum	Median	Mean	Std. deviation	Percent contribution
BDE-47	N.D	1.36	0.22	0.40	0.51	8.02
BDE-99 and 100	N.D	1.70	0.38	0.46	0.48	18.20
BDE-154 and 153	0.06	3.85	0.47	0.74	1.03	29.38
BDE-183	0.14	1.51	0.53	0.65	0.47	13.00
BDE-209	N.D	4.17	1.29	1.58	1.61	31.40

MSWLs in North China. A value of 4,000 pg L^{-1} was found in some seven MSWL in Japan (Osako et al. 2004). Huang et al. (2013) reported a range of 4,000–12,000 pg L^{-1} in treated leachate effluent and a maximum of 234 ng g^{-1} for $\sum_8$ PBDEs in the top soil of one MSWL in Shanghai, China. BDE-209 was predominant in leachates and soil samples from China; this is not surprising because China produces Deca BDE and consumption is high (Chen et al. 2012). Concentration of PBDEs was reported in leachate samples from 28 landfills across Canada with a range of 1,020–21,300 ng L^{-1} (Li et al. 2012). The highest concentration of 3.7–133,000 ng L^{-1} was reported in MSWL leachates from major cities in selected Asian countries (Kwan et al. 2013).

Correlation of PBDEs in leachates with trace metals and anions

The Pearson correlation analysis between PBDE concentration and physicochemical properties of leachate samples was performed. Correlation values for $\sum_7$ PBDEs versus Co (r= 0.65), Cu (r=0.52), Mn (r=0.10), Mg (r=0.76), Ca (r=0.66) and Ni (r=0.77) with a statistical significance (p<0.05) were observed except for Na, Cr, Pb, K, Fe and Zn (p>0.05). The observed positive correlation above may suggest a possible influence of trace metals on PBDE concentrations in leachates, although no metal-ligand interaction experiment was conducted to confirm this in the present study. Similar to our study, a positive correlation was observed between some

water quality parameters and PBDE concentration in river surface sediment (Chen et al. 2013). Trace metals profile of leachate samples are as shown in Fig. 3. Furthermore, a test of relationship between major anions and PBDEs yielded positive relationship with Cl$^-$ (r=0.94, p=0.16), F$^-$ (r=0.97, p=0.21), Br$^-$ (r=0.6, p=0.29) and NO$_3^{2-}$ (r=0.96, p=0.08) with an insignificant statistical difference. Sulphate (SO$_4^{2-}$) (r=−0.15, p=0.01) was the only exception with a negative correlation and significant statistical difference. Phosphate was not tested because it was found below detection in most of the leachate samples.

PBDEs in landfill sediment

All target congeners were quantified except BDE-209 in Soshanguve and BDE-47 and BDE-100 in Garstkloof samples which were observed below limits of detection. Concentration ranged from 0.8 to 8.4 ng g^{-1} dry weights. Total PBDE was 30 ng g^{-1} and BDE-209 was observed to be the predominant congener with a concentration of 9.5 ng g^{-1} followed by BDE-153, BDE-99 and BDE-47 with concentrations of 3.9, 3.8 and 2.4 ng g^{-1}, respectively. The mean and median percentage contribution of congers and other parameters are shown in Table 2. PBDE profiles of the six MSWLs are shown in Fig. 4. Pearson correlation of ∑PBDEs with major anions (Table 1) determined from leachate samples was observed to be positive with an insignificant difference except in the case of sulphate.

Fig. 4 PBDEs profile in landfill sediment
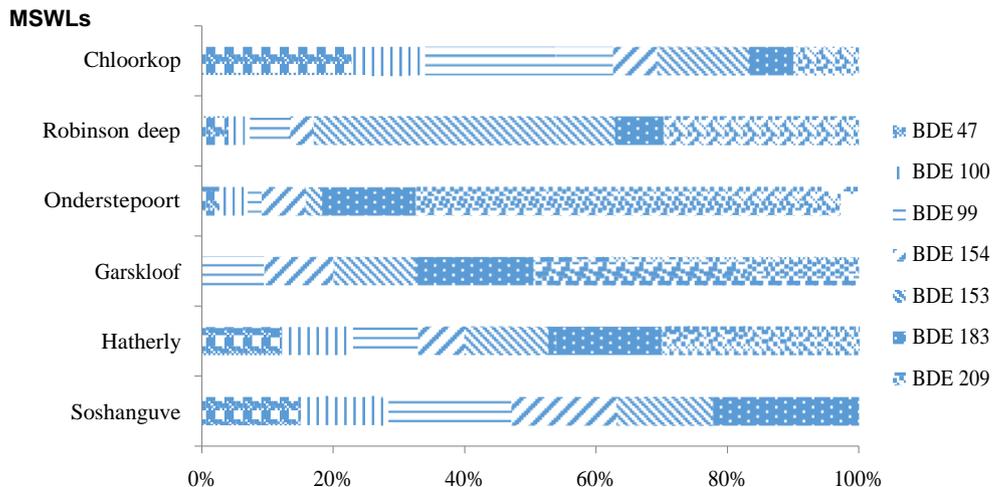
Fig. 5 PBDE concentrations in
river sediment (ng g^{-1})
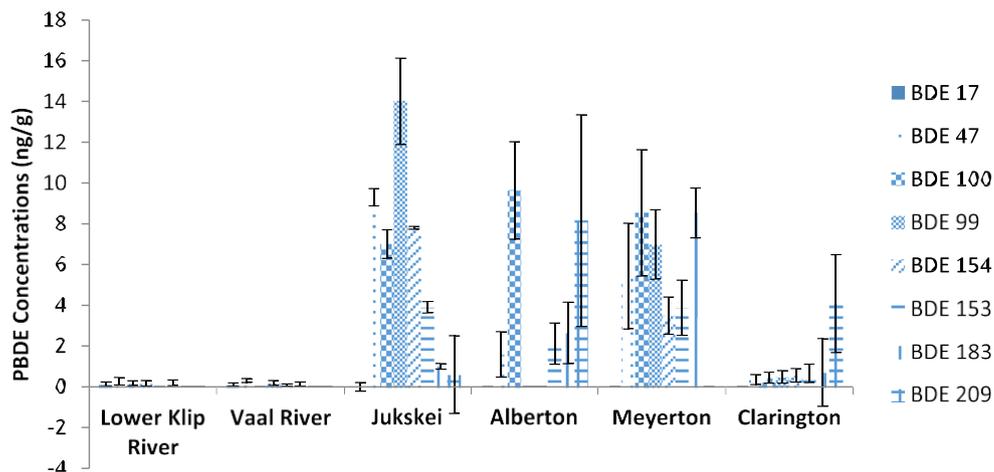
PBDEs in river sediment

Levels of PBDEs in river water were found below limits of
detection and, therefore, are not reported and as the focus of the
study was on sediment which are natural sinks for many
environmental pollutants. The mean concentrations of common
PBDE congeners in river sediments are shown in Fig. 5. As can
be seen in Fig. 5, low levels of PBDEs were detected in all the
samples with a mean concentration of 2.36 ng g^{-1} and a median
of 0.4 ng g^{-1}. For each of the congener, mean contribution
range from 0.03±0.01 ng g^{-1} (BDE-17) to 4.3±1.01 ng g^{-1}
(BDE-100). In this order, the highest concentration of $\sum_8$PBDE
(44 ng g^{-1}) was observed at Jukskei River, second was
Fouriespruit River (Meyerton) (37 ng g^{-1}), followed by
Alberton (24.1 ng g^{-1}), Clarington (7.3 ng g^{-1}), with corre-
sponding lowest levels determined at Vaal (0.8 ng g^{-1}) and the
lowerklip Rivers at Taaiboschspruit (0.9 ng g^{-1}) respectively

and total PBDE of 114 ng g^{-1}. BDE-17 was not determined in
Alberton, Meyerton and Clarington samples. However, most of
the congeners were detected in all the samples except BDE-99
and BDE-154 in Alberton; BDE-154, 183 and 209 in the
Lowerklip; BDE-100, 183 and 209 at Vaal; and BDE-209 at
Meyerton. All the BDEs were detected in the sediment samples
from all the sites in Jukskei River. The observed BDE concen-
trations ranged from 0.11 to 14 ng g^{-1}, with BDE-17 and BDE-
100 exhibiting the lowest and highest total concentrations,
respectively. The second highest concentration was shown by
BDE-99 (21.83 ng g^{-1}) and BDE-47 (17.25 ng g^{-1}).

Low levels of BDE were detected at six sites while Bruma
Lake had the highest concentration with more than two orders
of magnitude greater than the rest. The sum BDE ranged from
0.4 to 44 ng g^{-1} dw with the latter corresponding to levels in
Bruma Lake. The concentrations of BDE detected in the sed-
iment samples ranged from 0.06 to 14 ng g^{-1}. Lowest
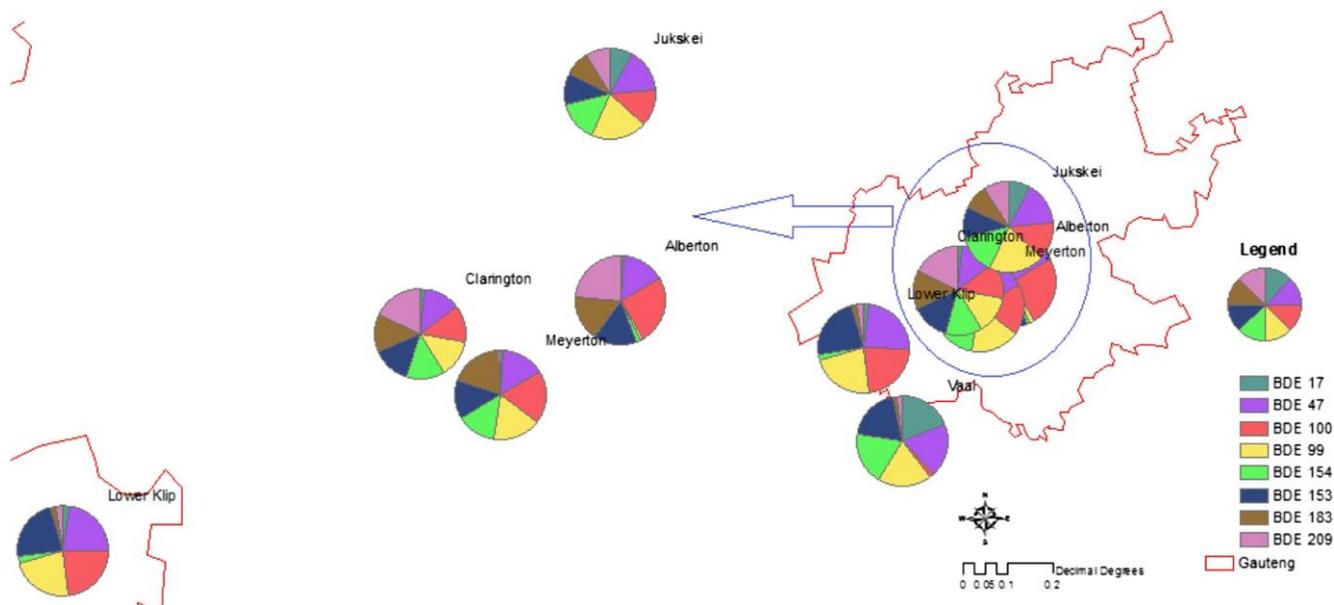
Fig. 6 Spatial distribution of PBDE levels in the six identified rivers in Gauteng

concentration of 0.34 ng g^{-1} dw was detected at Marlboro (Eastgate). The highest sum BDE per site was observed at Bruma Lake. The observed high levels at this site could be attributed to various land use activities around this area including effluent discharge from industries, sewage and water treatment plants.

With respect to the concentrations of BDEs in Lowerklip and Vaal Rivers, the highest concentration of 0.32 ng g^{-1} was observed at Lowerklip River compared to concentration of 0.3 ng g^{-1} observed in Vaal River. The following PBDEs were present in both rivers: BDE-17, BDE-47, BDE-99 and BDE-153. However, BDE-100 was found below detection in the Vaal River together with BDE-154 in Lowerklip River and BDE-183 in both rivers. Figure 6 shows the spatial distribution of PBDEs in the six sampled rivers. As can be seen from Fig. 6, the dominant congeners were BDE-47, BDE-100, BDE-99 and BDE-153.

PBDE concentrations in river sediment have been reported for different countries. Findings from this study were, therefore, compared to few of those previously reported, although total PBDEs are not entirely comparable because of variation in the number of measured congeners and techniques employed. A range of 0.82–44 ng g^{-1} dw was obtained in the present study for $\sum_8$ PBDE and total PBDE of 114 ng g^{-1}. In a study conducted in Spain, the reported $\sum_{12}$PBDE ranged from 2.7 to 136 ng g^{-1} dw (Eljarrat et al. 2005). For Hong Kong, $\sum_{15}$PBDEs of 1.7–53.6 ng g^{-1} dw was reported (Liu et al. 2005), and in Fuhe River and Baiyangdian Lake in China, $\sum$PBDEs of 300.7 and 23.7 ng g^{-1} dw were reported (Hu et al. 2010). Others include USA, 0.72–148 ng g^{-1} d w in Niagara River (Samara et al. 2006); Korea, 2.03–2 253 ng g^{-1} dw in the industrialised bay of Korea (Moon et al. 2007); Spain, 0.29–0.56 ng g^{-1} dw from Asturias (Salgado-Petinal et al. 2006); and a concentration of 0.17 and 261 ng g^{-1} for Da-an and Beinan Rivers in Taiwan, respectively (Chen et al. 2013). As evidenced from the above, the reported sums of PBDE are significantly higher than the sum obtained in the present study with the exception of the values from Hong Kong, Baiyangdian Lake, Da-an River and in sediments from Asturias, northern Spain.

PBDEs in river sediment and water quality parameters

Test results of some water quality parameters performed on water samples collected at same points as sediment samples were used for correlation with PBDE concentrations. An evaluation of the relationship between PBDE concentrations from Jukskei River sediment and some water quality parameters gave an inverse correlation with pH, dissolved oxygen and temperature. For dissolved oxygen ($r=-0.79$, $p<0.05$), a significant difference was observed, i.e. the higher the dissolved oxygen content, the lower the PBDE concentrations. It is expected that lower temperatures will be favourable to

PBDE congeners when there is less likelihood of leaching and debromination; however, a negative correlation ($r=-0.15$, $p<0.05$) was observed. For pH, negative correlation was equally observed ($r=-0.95$, $p<0.05$). A negative correlation of PBDE concentration with pH, DO and temperature has been reported in literature. In the study of Chen et al. (2013), they reported no significant correlation between PBDEs in leachates and temperature, but significant correlation for pH and DO.

Conclusion

All seven PBDE congeners were detected in most of the leachate and sediments collected from six MSWLs. Highest concentrations of $\sum_7$ 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 and other regions like Canada, Japan and China. Highest $\sum_8$ PBDE was observed in the Jukskei River compared to Vaal River with the lowest concentration. A statistical significant difference was observed in the concentrations of PBDE in the six samples. Evaluation of the relationship between pH, dissolved oxygen and electrical conductivity showed negative correlation to PBDE concentrations.

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