



# Concentration of novel brominated flame retardants and HBCD in leachates and sediments from selected municipal solid waste landfill sites in Gauteng Province, South Africa



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## ABSTRACT

In this study leachate and sediment samples were collected from six municipal solid waste landfill sites across Gauteng Province in South Africa to determine the levels of 2-ethylhexyl 2,3,4,5 tetrabromobenzoate (EH-TBB), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and hexabromocyclododecane (HBCD). Soxhlet as well as liquid–liquid extraction were employed for sediment and leachates respectively followed by GC–EIMS analysis. Concentrations of novel brominated flame retardants (NBFRs) ranged from below detection (<dl)–310 ng g<sup>-1</sup> and <dl–142 µg L<sup>-1</sup> for sediment and leachate samples while percentage proportions of detected NBFRs and HBCD analytes in leachate samples was observed to be approximately 64%, 22%, 9% and 5% for TBB, ΣHBCD, BTBPE and TBPH respectively. Frequency of detection was lower in sediment (<20–50%) compared to leachate (75–100%) samples. Decabromodiphenyl ethane levels in sediment and leachate samples were found below the limit of quantitation. A positive correlation with NBFRs was, however, observed with some water quality parameters except for sulphate.

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## 1. Introduction

The history of flame retardants dates back to the early 200BC when the Romans and the Egyptians used alum and vinegar to soak wood. Since then, a wide number of chemicals have been used to retard fires (Blum et al., 2010). The development of synthetic brominated flame retardants started in the early 1970s with polybrominated diphenyl ethers (PBDEs) (La Guardia et al., 2010), subsequently paving way for the synthesis of a number of brominated flame retardants being used at relatively high quantities in some consumer and industrial products for safety purposes. Several regulations and stringent fire safety requirements for televisions, furniture and building materials make the use of these chemicals inevitable (D'Silva et al., 2004). Until recently the most widely used BFRs were PBDEs, PBBs, HBCD, and TBBP-A. However the ban and restrictions on the use of some of these compounds, led to their replacements with newer compounds. These substitute flame retardants have been referred to in different publications as 'alternative', 'novel', 'emerging' or 'non PBDE' flame retardants (Ali et al., 2011; Guerra et al., 2010; Harju et al.,

2009; Moller et al., 2011; Yang et al., 2012). "Novel" brominated flame retardants (NBFRs) have been introduced to replace some widely-used BFRs (PBBs, penta and octaBDE formulations) (Stapleton et al., 2008). Some notable examples of NBFRs include decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), 2-ethylhexyl 2,3,4,5 tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP), tetrabromobisphenol A -bis(2,3-dibromopropylether) (TBBPA–BDBPE) and hexachlorocyclopentadienyldibromo-cyclooctane (DBHCTD) (Bergman et al., 2012; Covaci et al., 2011). Hexabromocyclododecane (HBCD) technical mixtures comprises three diastereoisomers (α, β and γ-HBCD), which are not easily separated by gas chromatography techniques except by some achiral or chiral HPLC columns (Yang et al., 2012). The dominant congener in the technical mixture is γ-HBCD (>70%) while in biota, the α-HBCD has been found to be most prevalent (Janák et al., 2008). In the year 2013, HBCD was designated as Persistent Organic Pollutants (POPs) under the United Nations Environmental Programme (UNEP) Stockholm Convention. Similarly, in Japan some organizations such as the Extruded Polystyrene Foam Industry Association and the Japan Textile Federation have already started to voluntarily decrease its usage (Ichihara et al., 2014).

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Current production levels and usage volume of these chemicals is unknown and difficult to determine (Harju et al., 2009). According to Fink et al. (2008) estimated global consumption of BFRs in 2008 to be about 410,000 tons. The ban on production and usage of HBCD came into effect when its amendment listing in Annex A to the Stockholm Convention entered into force on 26 November 2014 (UNEP, 2014).

NBFRs are mostly used as additives, and, therefore, can easily be released into the environment from products. In addition to the benefits of flame inhibition, one thing they possess in common is their persistence in the environment (de Jourdan et al., 2013). Like their predecessors, they have been found in different environmental compartments (Covaci et al., 2011; Devanathan et al., 2012; Schecter et al., 2010), and also currently generating serious concerns about their effects on the environment and humans (Covaci and Dirtu, 2008; Ogunbayo and Michelangeli, 2007; Schauer et al., 2006). A number of studies have reported that PBDEs and some non-PBDE brominated BFRs such as HBCD are persistent, bioaccumulative and globally distributed in the environment (Eguchi et al., 2013; Fromme et al., 2014; Ichihara et al., 2014; Lankova et al., 2015; Sander et al., 2013). They have also been implicated in adverse health effects which makes this group of compounds a source of concern to humans and the environment, hence the need to determine their levels in the environment. Ali et al. (2011) reported on the high detection frequencies of NBFRs in indoor dust from homes and offices in Belgium and the UK, suggesting that these compounds have become ubiquitous in indoor environments as a consequence of their use as alternatives to PBDEs. Fig. 1 shows the chemical structures of some important NBFR compounds determined in the present study.

In South Africa and probably in most developing countries, municipal wastes containing waste products that may have been treated with NBFRs are generally not treated before disposing into landfill sites. Since the NBFRs are additively incorporated into consumer products, it is very likely that they leach out from products, particularly in landfill sites where chemical and biological processes take place. Studies on BFRs carried out so far in the South African environment have shown varying degrees of contamination in a number of matrices (Darnerud et al., 2011; Daso et al., 2012; Kefeni and Okonkwo, 2012; Polder et al., 2008). The work of Odusanya et al. (2009) showed, for the first time in the African continent the presence of BFRs in landfill leachates. However, to date little is known about the concentrations of novel brominated flame retardants in the South African environment. The only

probable study so far conducted on NBFRs in South Africa was by La Guardia et al. (2013) who reported relative higher mean levels of NBFRs of 545, 96, 34 and 171 ng g<sup>-1</sup> for EH-TBB, BEH-TEBP, BTBPE and DBDPE in sediment samples obtained from the Durban bay. Available information indicates that NBFRs are not manufactured in South Africa. However, since South Africa imports large quantities of finished products that may have been treated with NBFRs, it is most likely that this could serve as the only source of NBFRs in the South African environment. Therefore, the main objective of the present study is to determine the occurrence and concentrations of some NBFRs (DBPDE, BTBPE, EH-TBB and BEH-TEBP) and HBCD in landfill leachates and sediments from selected landfill sites in Gauteng Province. The province was chosen because of the large number of industrial activities which makes it industrial hub of South Africa.

## 2. Materials and methods

### 2.1. Chemicals and preparation

Each 1.2 mL of 50 µg mL<sup>-1</sup> pure standards of 1,2 bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), 2-ethylhexyl 2,3,4,5 tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP), hexabromocyclo-decane isomers (α, β, and γ-HBCD), BDE-118, BDE-128, and <sup>13</sup>C-BDE-139 & BDE-209 were purchased from Cambridge Isotope Laboratories Inc, Andover, USA. Ultrapure water was dispensed from Labostar ultrapure water equipment (Siemens, Germany) supplied by Separations Pty, Pretoria, South Africa, Pesticarb and Strata florasil 500 mg mL<sup>-1</sup>, supplied by Separations (Pty), Multi anion standards (Cl<sup>-</sup>, F<sup>-</sup>, Br<sup>-</sup>, NO<sup>2-</sup>, PO<sub>3</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>2-</sup>) were purchased from Merck Chemicals, Pretoria, 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, *n*-hexane, dichloromethane, methanol, isooctane and toluene (products of Sigma-Aldrich (Chemie GmbH, Steinheim, Germany), supplied by Sigma Pretoria, South Africa. All solvents used were of analytical grade and kept away from contamination. Working standards were prepared in isooctane and serially diluted to lower concentrations to form calibration standards. Anhydrous sodium sulphate and silica gel at first use were heated in a muffle furnace at 450 °C for 16 h. Prior to each experiment, silica and sodium sulphate was reactivated by heating for 2 h at 160 °C and all glassware was washed

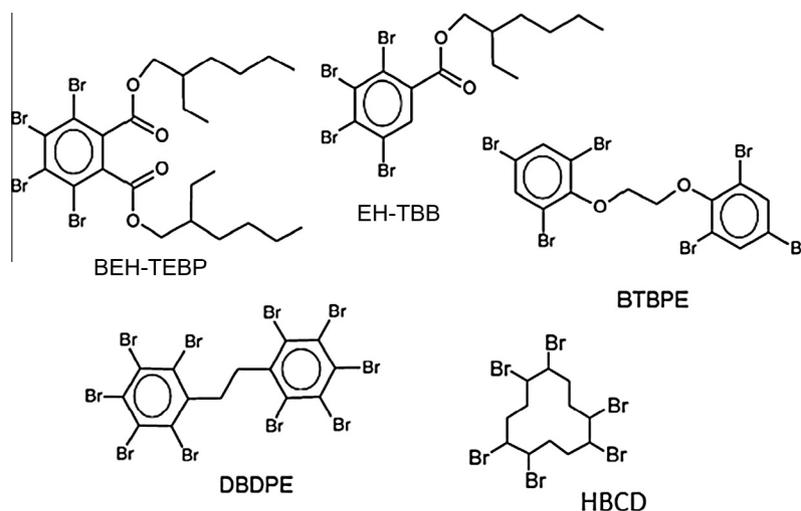


Fig. 1. Chemical structures of investigated NBFRs and HBCD.

with detergent, rinsed with water, dried at 100 °C, and rinsed with hexane.

## 2.2. Sampling sites

Samples were collected from six operational MSWLs, three samples each for sediment and leachates from the same site. These MSWLs were selected across Gauteng (Fig. 2). Two out of the six MSWLs, namely Chloorkop and Robinson Deep are equipped with geomembrane liners to prevent leachates infiltration into groundwater. These two MSWLs also receive industrial wastes including combustible and incombustible materials. The remaining four MSWLs namely Soshanguve, Hatherly, Garstkloof and Onderstepoort are traditional landfills with no geomembrane liners. The waste composition of most of the MSWLs were dominated by household wastes ranging between 75% and 80% (Odusanya et al., 2009).

## 2.3. Collection of leachate and sediment samples

Raw leachate samples (2 L each) were collected between June and August 2013 using grab method into pre-washed amber bottle rinsed with acetone, from leachate ponds in the selected landfill sites. Samples were stored in cooler boxes for transportation to the laboratory where they were kept at  $-4\text{ }^{\circ}\text{C}$  in a cold room prior to extraction. Parameters such as pH, conductivity, cations and anions were measured immediately on arrival at our laboratory. The physical appearance of the leachate samples vary from light to dark brown in colour. Because Persistent Organic Pollutants

(POPs) settle in environmental media via dry and wet deposition, sediment samples were collected with stainless grab at depth of about 5 cm below the surface at the same points as leachates, in wide mouth 500 mL amber bottles. Samples were treated in the same procedure as leachates for transportation and storage pending the time of extraction and subsequent analysis.

## 2.4. Sample extraction and clean up

Recovery experiments and cleanup followed previously reported procedures with a slight modification (Olukunle et al., 2014). Sediment samples were spread on aluminium foil pre rinsed with acetone and air dried in the dark at room temperature. Dried and caked sediment was ground and homogenised in a mortar and sieved with a stainless sieve (150  $\mu\text{m}$ ). Briefly, 10 g of dry sediment (in the dark at room temperature) was spiked with surrogate standards; BDE-128,  $^{13}\text{C}$  BDE-139 and 209. These were used in similar study by Ali et al. (2011). Spiked samples were left in the dark overnight to equilibrate, and then extracted by Soxhlet with 180 mL of a mixture of *n*-hexane and dichloromethane (1:1, v/v) for 16 h. Similarly, 500 mL leachate samples were filtered with a vacuum filtration apparatus and spiked with the surrogate standards before extraction using LLE. The crude extracts were fractionated with column chromatography by passing it through multilayer silica gel in a Pasteur pipette loaded with about 0.16 g silica, 0.06 g pesticides, and 0.16 g silica, topped with 0.5 g sodium sulphate. Before introduction of 1 mL reduced extract the packed column was eluted to saturation with 12 mL hexane. Sample was introduced into the column before the solvent reached the bed of

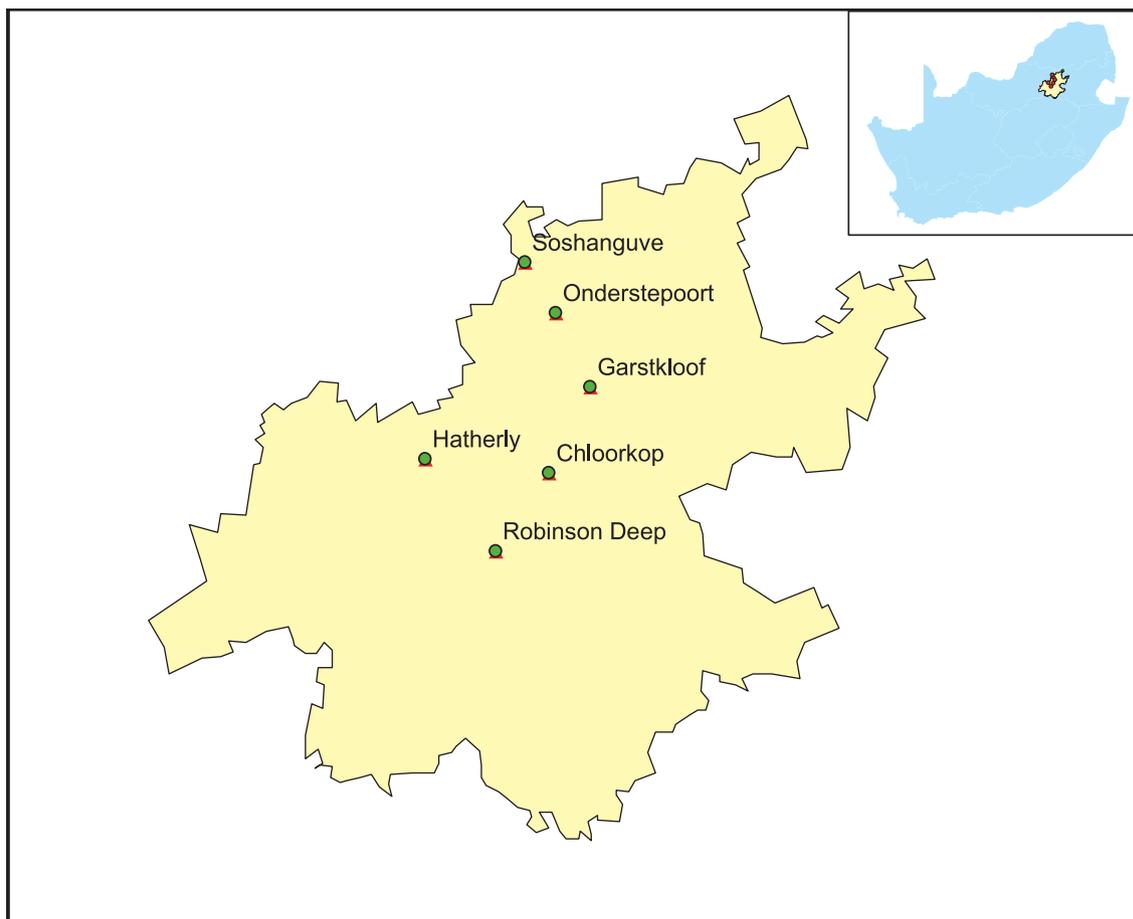


Fig. 2. Map of South Africa (top) showing Gauteng Province and six MSWL landfill sites (bottom).

the sodium sulphate plugged with glass wool and was further eluted with 4 mL hexane. The eluent was concentrated to near dryness under N<sub>2</sub> and reconstituted to 200 µL in isoctane. Before injection, BDE-118 (10 µL of 2.5 ng µL<sup>-1</sup>) was added to monitor changes in instrument analytical conditions and 1 µL injected into the GC–MS. The recovery of surrogates ranged between 65% and 110%.

### 2.5. GC–MS analysis

The optimised conditions for the GC–EIMS are as summarised; an injection temp of 225 °C, ion source and interface temperature at 250 °C and 300 °C respectively, oven temperature programme; initial temp @ 100 °C held for 2 min, ramped @ 10 °C min<sup>-1</sup> to 160 °C held for 2 min, again ramped @ 40 °C min<sup>-1</sup> to 300 °C held for 10 min. Helium was used as carrier gas at a constant flow rate of 2 mL min<sup>-1</sup>. The mass spectrometer was operated in selected ion monitoring (SIM) mode. Chromatographic separation of target NBFs was carried out on a DB-5 MS column (15 m 0.25 mm ID, 0.1 µm d<sub>p</sub>). One micro litre extract was injected. Other parameters were splitless sampling time @ 2 min, total and purge flow @ 50 mL min<sup>-1</sup>, and 3 mL min<sup>-1</sup> respectively at a pressure of 68.7 kPa. The identification of BTBPE, DBDPE, TBB, TBPH, HBCD, BDE-118, BDE-128, <sup>13</sup>C BDE-139 and -209 was based on their retention times and the relative intensity of the fragment ions monitored. Since most of the NBFs did not give any molecular ions, quantification was based on the monitoring of fragment ions *m/z* 357 & 687 for BTBPE, 465 for TBB, 487 for DBDPE, 421 for TBPH and 563 for HBCD.

### 2.6. Analysis of physicochemical parameters

Analysis of basic anions was performed on Metrohm 883 basic IC plus from Switzerland. Six external level calibrations were used for quantitation of anions comprising F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>. Calibration standards were prepared from stock of mixed (Merck Chemicals) anions from concentration of 1000 mg/L. Twenty microlitre each of filtered sample was injected by Metrohm (863 Compact auto sampler) auto sampler. Briefly, eluent used for the mobile phase was prepared with sodium hydrogen carbonate and sodium carbonate. For each batch of samples processed, 2 L eluent was prepared by first weighing the two salts (NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>), 286 and 382 mg, respectively, as specified for the Metrosep A Supp 4-250/4.0 separation column. The eluent was degassed to remove excess carbon dioxide. 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).

### 2.7. Quality assurance

Exposure of samples to UV-light was minimised by the use of amber bottles, wrapping all glassware containing samples in aluminium foil when they were transported and during Soxhlet extraction. Laboratory glassware was cleaned thoroughly and rinsed with hexane prior to use. All calibration standards and spiking solutions were prepared by serial dilution in isoctane. Eight-point calibration plots were created for quantification purposes and high correlation coefficients ( $R^2 > 0.996$ ) and linearity were obtained. One procedural blank was included with each batch of five samples. Four matrix spikes containing 10 g of Na<sub>2</sub>SO<sub>4</sub> spiked with target NBFs were processed and run with the samples. The target NBFs were not detected in the procedural blanks. Descriptive statistical analysis was performed with Statistica software package (version 2010). Relationship testing of contaminants to anions, cations, pH and electrical conductivity were carried out

by Pearson correlations followed by student's *t*-test for level of significance.

## 3. Results and discussion

A total of 4 novel brominated flame retardants (EH-TBB, BEH-TEBP, BTBPE and DBDPE) and HBCD were analysed and quantified in landfill leachates and sediments. The final concentration of each measured contaminant was calculated by multiplying their amounts in the final extract divided by actual weight of sediment used and in the case of leachates, the volume extracted. With respect to HBCD, it was extremely difficult to separate the three isomers of HBCD as a result of their thermal transformation in the GC column at temperatures above 160 °C (Becher, 2005; Morris et al., 2004). Thus, HBCD values in this study have been reported as total or sum ( $\sum$ HBCD). Because concentrations of NBFs in samples were not evenly distributed, data were log transformed to test the correlation between, anions, cations, electrical conductivity and pH in leachates. LOD was determined by using a signal to noise ratio (S/N) > 3 and LOQ (S/N) > 10 of the lowest concentration detected by the instrument. Concentration values were taken at fragment ion intensity >20%

### 3.1. Physicochemical and chemical characteristics of the raw leachates

The mean pH values of 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<sup>-1</sup>. The highest values of 13 and 23 mS cm<sup>-1</sup> were exhibited by the two lined MSWLs, Chloorkop and Robinson deep respectively. These values suggested high amount of dissolved salts which are more than one order of magnitude higher than the other landfill sites. This difference may be attributed to the effective containment of leachates by the geomembranes. These two MSWLs also receive hazardous materials from industries. Most of the anions (analysed by Metrohm Ion Chromatograph (IC) 883) were found within acceptable limits for waste water quality standards, except for Soshanguve leachates with high levels of chloride. Phosphate levels were found below detection limit in all the samples except for Robinson deep.

### 3.2. NBF levels in sediment and leachate samples

The concentrations of NBFs in sediment ranged from <dl (less than detection)–310 ng g<sup>-1</sup> with a maximum of 56 ng g<sup>-1</sup>, 186 ng g<sup>-1</sup>, 310 ng g<sup>-1</sup> and 60 ng g<sup>-1</sup> recorded for EH-TBB,  $\sum$ HBCD, BTBPE and BEH-TEBP respectively in all the samples as shown in Table 1. A low frequency of detection ranging from less than 20% to 50% was observed in the sediment samples. TBB was detected in samples from two landfills namely, Soshanguve and Garstkloof

**Table 1**

Descriptive data of NBFs and HBCD level in leachate (in bracket) in pg L<sup>-1</sup> and sediment in ng g<sup>-1</sup> dry weight samples.

	EH-TBB	$\sum$ HBCD	BTBPE	BEH-TEBP
Min	<dl (8.7)	<dl (4.8)	<dl (4.4)	<dl (20)
Max	56 (142)	186 (40)	310 (15)	60 (7)
Median	<dl (42)	<dl (25)	<dl (<dl)	<dl (<dl)
Mean	10 (60)	33 (24)	51 (11)	11 (1.1)
SD	20.5 (44)	69 (10)	117 (3.3)	19.6 (2.5)
5th%	<dl (9)	<dl (5)	<dl (4)	<dl (<dl)
95th%	6.1 (142)	17.3 (40)	<dl (15)	<dl (7)
LOD (ng µL <sup>-1</sup> )	0.025	0.025	0.025	0.005

*n* = 18.

while HBCD was detected at Soshanguve, Robinson deep and Garstkloof. BTBPE was detected only in Soshanguve samples while BEH-TEBP was detected in Soshanguve and Garstkloof only. Decabromodiphenyl ethane was found below detection limit in all sediment and leachate samples. According to Kierkegaard et al. (2004), DBDPE, like BDE-209 degrades during cleanup and instrumental analysis. Most of the NBFrs detected were reported in open traditional landfills that are not lined with geomembranes. HBCD was observed in Robinson deep and none in Chloorkop. These two are the only landfills lined with geomembranes. In addition, they are modern landfills equipped with incinerators. Leachates emanating from incinerated wastes are also treated which may be the reason for observed differences. On the other hand however, there is no sorting of any kind at the remaining four sites.

All target analytes were found in leachate samples except DBDPE and BEH-TEBP with the latter being detected only in samples from Chloorkop landfill. Concentrations ranged from 8.7–14  $\mu\text{g L}^{-1}$  for EH-TBB, 5–40  $\mu\text{g L}^{-1}$  for  $\Sigma\text{HBCD}$ , 4–15  $\mu\text{g L}^{-1}$  for BTBPE and  $<\text{dl}-7 \mu\text{g L}^{-1}$  for BEH-TEBP. The descriptive statistics comprising minimum, maximum, median, mean, 5th percentile, 95th percentile, percentage contribution and limit of detection of measured values of analytes in sediment and leachate samples are as shown in Table 1.

As can be seen in the Table 1, EH-TBB contributes approximately 64%,  $\Sigma\text{HBCD}$  22%, BTBPE 9% & BEH-TEBP 5%. EH-TBB has been produced since 2003 and used as replacement for penta-BDE in polyurethane foam (PUF) applications. That EH-TBB is 64% and BEH-TEBP 5% which is a ratio of 13:1 is not surprising since the approximate ratio of EH-TBB to BEH-TEBP in Firemaster 550 is 4:1 by mass. However, different detection ratios of EH-TBB/BEH-TEBP have been reported. For example, Stapleton et al. (2008) found a EH-TBB/BEH-TEBP ratio ranging from 1:20 to 50:1 in indoor dust samples. Similarly, La Guardia et al. (2013) reported a EH-TBB/BEH-TEBP ratio of 16:1 in a sample at 899  $\text{ng g}^{-1}$  from the Durban bay. These findings according to La Guardia et al. (2013) may suggest a different chemical composition or manufacturer or different relative fate or transport for ubiquitous contaminants. However, the source of higher EH-TBB cannot be linked in this study to polyurethane foams since there was no sorting done at the MSWLs. Fig. 3 shows the relative proportion of the occurrence of four contaminants in landfill sediment samples from six MSWL. HBCD was the predominant and only contaminant found at Robinson deep. Observations of HBCD levels in three of the MSWLs were found below limit of detection, namely Chloorkop, Onderstepoort and Hatherly. All target contaminants were detected at Soshanguve and Garstkloof with the exception of BTBPE in the latter while BEH-TEBP contributed 68% of

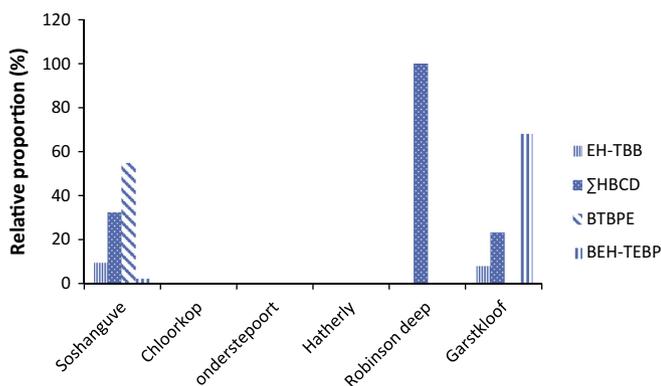


Fig. 3. Relative proportions of NBFrs in sediment samples.

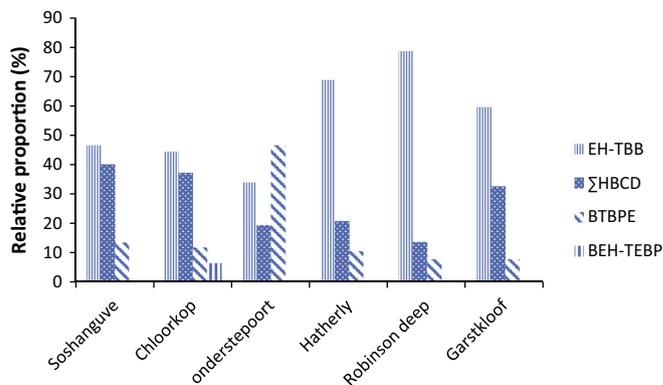


Fig. 4. Relative proportions of NBFrs in leachate samples.

$\Sigma\text{NBFrs}$ . Similarly, Fig. 4 shows relative proportions of measured NBFrs in leachate samples. BEH-TEBP was found below limit of detection in most samples except Chloorkop (6%). Concentrations of NBFrs in leachate samples were correlated with some physico-chemical parameters mentioned in Section 3.1. To test the relationship between the NBFrs and parameters such as pH, electrical conductivity (EC), fluoride, chloride, bromide, nitrate, sulphate, calcium, potassium, sodium and magnesium the concentrations of EH-TBB,  $\Sigma\text{HBCD}$  and BTBPE were correlated using Pearson correlation coefficient followed by students *t*-test for significant levels as shown in Table 2. A positive correlation with NBFrs was, however, observed with all the parameters except for sulphate. Furthermore, a statistical significant ( $p < 0.05$ ) relationship was observed for EH-TBB and pH, EC,  $\text{F}^-$ ,  $\text{NO}_3^-$  and  $\text{Mg}^{2+}$ , for  $\Sigma\text{HBCD}$  with pH, EC,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^{2+}$  &  $\text{Mg}^{2+}$  and BTBPE with EC,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^{2+}$  &  $\text{Mg}^{2+}$  respectively. This result is suggestive of a possible influence of some these parameters on NBFr levels in leachate samples. Similar trend has been reported for PBDE concentrations in river surface sediment by Chen et al. (2013).

### 3.3. Comparison to other studies

Information is still very scarce on levels of NBFrs in landfill leachates and sediment. Most studies in the past decade have mainly focused on polybrominated diphenyl ethers which have been very well researched in biotic and abiotic samples. Brominated flame retardants are known to be persistent in the environment and have been shown to be capable of undergoing long range atmospheric transport (LRT) (de Wit et al., 2010). In addition, burning of waste may contribute to levels of these contaminants in dumping sites thereby posing great risk to groundwater. Therefore, information on BFR burdens in different environmental media is deemed necessary to serve as an aid to identifying their sources. Table 3 shows a handful of studies in abiotic media from different regions. Findings were compared to the present study. In a study from the Durban bay in South Africa, La Guardia et al. (2013) reported relative higher mean levels of NBFrs of 545, 96, 34 and 171  $\text{ng g}^{-1}$  for EH-TBB, BEH-TEBP, BTBPE and DBDPE in sediment samples compared to 60, 11 and 1.1  $\text{ng g}^{-1}$  for EH-TBB, BTBPE and BEH-TEBP for landfill sediment samples obtained in study.  $\Sigma\text{HBCD}$  obtained in the present study are significantly higher than studies conducted on river sediment in Netherlands and Ireland.

## 4. Conclusion

This study confirms the presence and levels of 'novel' brominated flame retardants and HBCD in six municipal solid waste landfills for the first time in South Africa. This is very important for data generation as landfills have been identified as a source

**Table 2**Correlation analysis of the relationship between some physical parameters, cations, anions and NBFRs with corresponding *p* values.

	pH	EC ( $\mu\text{S}/\text{cm}$ )	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	NO <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Na <sup>2+</sup>	Mg <sup>2+</sup>
EH-TBB	0.76	0.52	0.31	0.36	0.44	0.49	0.17	0.07	0.54	0.74	0.44
<i>p</i>	0.01	0.00	0.00	0.07	0.05	0.00	0.33	0.05	0.84	0.05	0.02
$\Sigma$ HBCD	0.47	0.45	0.32	0.36	0.52	0.32	0.13	0.35	0.43	0.34	0.17
<i>p</i>	0.02	0.00	0.02	0.02	0.13	0.01	0.84	0.01	0.42	0.01	0.00
BTBPE	0.72	0.51	0.23	0.50	0.54	0.03	-0.18	0.00	0.30	0.46	0.72
<i>p</i>	0.11	0.00	0.06	0.01	0.28	0.07	0.17	0.00	0.19	0.00	0.00

**Table 3**Mean concentrations (ng g<sup>-1</sup>) of NBFRs and HBCD in environmental samples (abiotic) from other regions.

Matrices (n)	Country	$\Sigma$ HBCD	BTBPE	BEH-TEBP	DBDPE	EH-TBB	References
Leachates (7)	Netherlands	5906	– <sup>a</sup>	–	–	–	Morris et al. (2004)
Sediment (9)	Netherlands	3.8	–	–	–	–	
Sediment 22	England	199	–	–	–	–	
Sediment 8	Ireland	3.3	–	–	–	–	
Sediment (10)	USA median	0.3	0.023	–	–	–	Klosterhaus et al. (2012)
Sediment (45)	South Africa	1800	34	96	171	545	La Guardia et al. (2013)
Dust		–	107	–	139	–	Shi et al. (2009)
Sewage sludge		–	–	–	1183	–	
Soil		–	0.05	–	28.1	–	
Soil	Cambodia	0.2	–	–	–	–	Eguchi et al. (2013)
	India	0.09	–	–	–	–	
	Indonesia	0.23	–	–	–	–	
	Malaysia	0.1	–	–	–	–	
	Vietnam	0.14	–	–	–	–	
Soil	China	37.5	–	–	111	–	Zhu et al. (2014)
Dust		516	10	436	323	4.2	Fromme et al. (2014)
Dust (5)		295	–	378	–	–	Kopp et al. (2012)
Dust		–	41.2	–	–	–	Lankova et al. (2015)
Dust(39)	Belgium homes	–	33	212	303	20	Ali et al. (2011)
Dust 6	Offices	–	80	95	789	12	
Dust (36)	UK Schools	–	78	381	293	45	
River water	Japan	–	–	–	–	–	Ichihara et al. (2014)
Sewage influent		–	–	–	–	–	
Sewage effluent		–	–	–	–	–	
Sludge		–	–	–	81	–	Ricklund et al. (2009)
Influent		–	–	–	17–26 <sup>b</sup>	–	
Sediment (18) & Leachates (18)	South Africa	33 (24) <sup>c</sup>	51 (11) <sup>c</sup>	11 (1.1) <sup>c</sup>	<dl (<dl)	10 (60) <sup>c</sup>	This study

<sup>a</sup> Not available.<sup>b</sup> ng L<sup>-1</sup>.<sup>c</sup> pg L<sup>-1</sup>.

of persistent organic pollutants which can leach into the wider environment if not properly constructed and lined with geomembranes.

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