

OCCURRENCE AND PHASE DISTRIBUTION OF HEXABROMOCYCLODODECANE (HBCD) AND TETRABROMOBISPHENOL A (TBBPA) IN LANDFILL LEACHATE

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Introduction

Both hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) are important class of brominated flame retardants (BFRs) commonly used in different applications. The technical HBCD, which mainly comprises three diastereoisomers (α , β and γ), finds extensive application in extruded and expanded polystyrene commonly used for thermal insulation in buildings in colder regions. Sometimes, it is also used in upholstery textiles¹. On the other hand, TBBPA is bound covalently to the polymeric materials and its main area of application is in the electronic circuit boards of electrical and electronic appliances. Presently, there are growing concerns over the environmental persistence, toxicity and bioaccumulation potentials of these pollutants. Recently, HBCD was enlisted in Annex A of the Stockholm Convention on persistent organic pollutants. Despite these concerns, there is still an unprecedented increase in the production and consumption of TBBPA with an annual global consumption exceeding 170,000 tons in 2004².

Obsolete treated products containing these chemicals often end-up in dumpsites and landfills without prior sorting in most developing countries. The presence of dissolved organic matter in landfill may facilitate the rapid leaching of these chemicals, thus posing an imminent threat to the environment. Interestingly, several landfills operating in this region were not designed to receive e-wastes and hence do not have appropriate liners or barriers to prevent any leachate leakage. This situation remains a cause for concern, particularly due to the possible contamination of both surface and groundwater sources, which are inevitable under these circumstances. Unlike polybrominated diphenyl ethers (PBDEs) which have been widely characterized in landfill leachate in this region³⁻⁵, the assessment of both HBCD and TBBPA in this matrix has not been adequately undertaken. Furthermore, the need to investigate their phase distributions in landfill leachate has not been given the required attention globally. Considering the fact that pollutants' phase distribution is one of the primary factors influencing their ultimate environmental fate and transport in aqueous matrices, there is a need to investigate the partitioning behaviours of these pollutants in landfill leachate. Consequently, this study was aimed to investigate the occurrence and phase distribution of HBCD and TBBPA in landfill leachate from selected South African landfill sites.

Materials and methods

A total of 2.5 L of landfill leachate was collected from each of the three landfill sites located in different parts of Pretoria, South Africa. Two hundred millilitres of each leachate sample in triplicate were filtered with pre-weighed Whatman 95 filter papers (Sigma-Aldrich: Aston Manor, South Africa) to separate the samples into dissolved and adsorbed phases. The adsorbed solids were dried in an oven at 25°C and re-weighed to determine the actual mass of the retained solids. The adsorbed solids were subjected to ultrasonic extraction with 40 mL of n-hexane:dichloromethane (1:1, v/v) for 45 min. at 65°C. Upon cooling to room temperature, the extract was decanted into a 250 mL round-bottom flask. The sample was further extracted with 40 mL of the extraction solvent for 25 min. under similar conditions. The combined extract was concentrated with a rotary evaporator to approximately 1 mL. The concentrated extract was then purified with 1 g of acidic silica gel packed in a Pasteur pipette previously conditioned with 5 mL of n-hexane. The target compounds were then eluted with 10 mL of dichloromethane:methanol (4:1, v/v). The cleaned extract was blown to incipient dryness under a gentle stream of nitrogen gas. The dried extract was reconstituted with methanol prior to the instrumental analysis.

Similarly, the dissolved phase was extracted with ENVI™-18 solid-phase cartridges (Sigma-Aldrich: Aston Manor, South Africa). Prior to the extraction, the SPE cartridges were pre-conditioned with 5 mL of methanol followed by 5 mL of MilliQ water. During the extraction, the flow rate of one drop per second was maintained. After the extraction, the SPE cartridges were vacuum dried for 45 min. prior to the elution of the target compounds with 12 mL of dichloromethane:methanol (4:1, v/v). The extracts were thereafter subjected to similar

treatments as previously described for the adsorbed phase. Five microlitres of the standards as well as the samples were analysed with liquid chromatography tandem mass spectrometry (Shimadzu LC-MS 8030 triple quadrupole system, Tokyo, Japan). The instrument was equipped with an electrospray ionization (ESI) source and the target compounds were separated on InertSustain C18 (3 μ m, 2.1 i.d. x 150 mm) HPLC column (Tokyo, Japan). The mobile phases employed consisted of A: 100% methanol and 20 mM ammonium acetate with a constant flow rate of 0.15 mL/min. The quantification of the target compounds was based on external calibration. The details of the multiple reaction monitoring (MRM) and the method calibration parameters are presented in Table 1.

Table 1: MRM transitions and method calibration parameters for the target compounds

Target compounds	MRM transitions	Collision energy (V)	Calibration equation	Retention time (min.)	R ²	Calibration range (ng/mL)	% RSD
TBBPA	543.00>447.85	33.0	f(x)=2.86x-32.66	18.707	0.9996	20-200	25.30
	543.00>79.10	49.0					
	543.00>420.00	40.0					
α -HBCD	640.00>80.70	12.0	f(x)=1.01x-29.77	22.342	0.9989	50-1000	17.48
	640.00>79.30	26.0					
	640.00>81.40	25.0					
β -HBCD	640.00>78.80	25.0	f(x)=3.09x+114.08	22.845	0.9987	50-1000	17.35
	640.00>81.25	30.0					
γ -HBCD	640.00>78.90	22.0	f(x)=3.21x-5.80	23.245	0.9997	25-1000	5.29
	640.00>81.00	22.0					

Results and discussions

The concentrations of the target compounds in the adsorbed and dissolved phases of the landfill leachate investigated in this study are presented in Table 2. Apparently, most of the BFRs were preferentially accumulated in the adsorbed phase. Given the hydrophobic nature of these compounds, the observed trend in their partitioning behaviours is expected. Of all the BFRs investigated in this study, only TBBPA was detected in both phases, although at different landfill sites on both occasions where it was detected. In contrast, the HBCD isomers were only detected in the adsorbed phase. Unlike TBBPA which may exist in both ionic and non-ionic forms, HBCD isomers (α , β and γ) are neutral compounds with limited aqueous solubility. Hence, their non-detection in the aqueous phase as observed in this study may be a reflection of their unique physicochemical properties. Suzuki and Hasegawa⁶ observed similar partitioning behaviours for both TBBPA and HBCD isomers investigated in landfill leachate. In their work, TBBPA was mainly found in the dissolved phase, while the HBCD isomers were predominantly bound to the suspended solids.

Table 2: Concentrations of the target compounds in the adsorbed and dissolved phases

Sampling sites	Adsorbed phase (ng/g)				Dissolved phase (ng/L)			
	TBBPA	α -HBCD	β -HBCD	γ -HBCD	TBBPA	α -HBCD	β -HBCD	γ -HBCD
HAT	ND	ND	667.18 \pm 603.72 [†]	ND	64.50 \pm 31.16	ND	ND	ND
	-	-	ND – 1175.80 *	-	46.51 – 100.49	-	-	-
OND	ND	779.15 \pm 160.32	1512.60 \pm 237.62	2587.46 \pm 251.68	ND	ND	ND	ND
	-	686.59 – 964.28	1322.36 – 1778.95	2339.23 – 2842.46	-	-	-	-
SOS	8.60 \pm 14.90	ND	13.35 \pm 23.13	9.68 \pm 8.40	ND	ND	ND	ND
	ND – 25.80	-	ND – 40.05	ND – 15.10	-	-	-	-

[†] - mean and standard deviation of three replicates; * - range of concentrations; ND – not detectable; HAT – Hatherly; OND – Onderstepoort; SOS – Soshanguve.

In the present study, all the HBCD diastereoisomers were detected in the adsorbed phase at relatively high concentrations in 1 out of the 3 landfill sites investigated. In this case, the γ -HBCD had the highest mean concentration (2587.46 \pm 251.68), possibly reflecting its relative percent composition in the technical mixture. According to Covaci and co-workers⁷, the γ -HBCD comprises up to 75-89% of the entire technical mixture. The other two major isomers are often present at relatively low concentrations constituting about 10-13% and 1-12% for the α -HBCD and β -HBCD, respectively. Considering their relative abundance in the technical mixture, the relatively high concentration of the β -HBCD as observed in 2 out of the three landfill sites is unexplainable and would therefore require further investigation.

Conclusions

The partitioning behaviours of TBBPA and HBCD isomers were investigated in landfill leachate. Most of the target compounds were preferentially accumulated in the adsorbed. However, only TBBPA was detected in the dissolved phase with 100% detection frequency in one of the three landfill sites investigated. The γ -HBCD had the highest mean concentration and had similar pattern of occurrence as the β -HBCD diastereoisomer. Nonetheless, the relatively high degree of occurrence of the β -HBCD still warrant further investigations. Additionally, the study suggests that the leakage of landfill leachate could significantly contribute to the contamination of both surface and groundwater sources, especially for communities that depend on these sources of drinking water.

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References

1. Abdallah, M.A.-E., S. Harrad, C. Ibarra, M. Diamond, L. Melymuk, M. Robson, and A. Covaci. (2007) *Hexabromocyclododecanes in indoor dust from Canada, the United Kingdom, and the United States*. Environmental science & technology. **42**(2): 459-464.
2. Covaci, A., S. Voorspoels, M.A.-E. Abdallah, T. Geens, S. Harrad, and R.J. Law. (2009) *Analytical and environmental aspects of the flame retardant tetrabromobisphenol-A and its derivatives*. Journal of Chromatography A. **1216**(3): 346-363.
3. Odusanya, D.O., J.O. Okonkwo, and B. Botha. (2009) *Polybrominated diphenyl ethers (PBDEs) in leachates from selected landfill sites in South Africa*. Waste Management. **29**(1): 96-102.
4. Daso, A., O. Fatoki, J. Odendaal, and O. Olujimi. (2013) *Polybrominated diphenyl ethers (PBDEs) and 2,2',4,4',5,5'-hexabromobiphenyl (BB-153) in landfill leachate in Cape Town, South Africa*. Environmental Monitoring and Assessment. **185**(1): 431-439.
5. Olukunle, O.I., I.V. Sibiyi, O.J. Okonkwo, and A.O. Odusanya. (2015) *Influence of physicochemical and chemical parameters on polybrominated diphenyl ethers in selected landfill leachates, sediments and river sediments from Gauteng, South Africa*. Environ Sci Pollut Res Int. **22**(3): 2145-54.
6. Suzuki, S. and A. Hasegawa. (2006) *Determination of hexabromocyclododecane diastereoisomers and tetrabromobisphenol A in water and sediment by liquid chromatography/mass spectrometry*. Analytical sciences : the international journal of the Japan Society for Analytical Chemistry. **22**(3): 469-474.
7. Covaci, A., A.C. Gerecke, R.J. Law, S. Voorspoels, M. Kohler, N.V. Heeb, H. Leslie, C.R. Allchin, and J. de Boer. (2006) *Hexabromocyclododecanes (HBCDs) in the environment and humans: a review*. Environmental science & technology. **40**(12): 3679-3688.