

Leaching of decabromodiphenyl ether and hexabromocyclododecane from fabrics under simulated landfill conditions

Harrad, Stuart; Drage, Daniel; Sharkey, Martin; Berresheim, Harald

DOI:

[10.1016/j.emcon.2019.12.005](https://doi.org/10.1016/j.emcon.2019.12.005)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Harrad, S, Drage, D, Sharkey, M & Berresheim, H 2020, 'Leaching of decabromodiphenyl ether and hexabromocyclododecane from fabrics under simulated landfill conditions', *Emerging Contaminants*, vol. 6, pp. 33-38. <https://doi.org/10.1016/j.emcon.2019.12.005>

[Link to publication on Research at Birmingham portal](#)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.



Research article

Leaching of decabromodiphenyl ether and hexabromocyclododecane from fabrics under simulated landfill conditions

Stuart Harrad^{a,*}, Daniel S. Drage^a, Martin Sharkey^b, Harald Berresheim^b^a School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, UK^b School of Physics, National University of Ireland Galway, Galway, Ireland

ARTICLE INFO

Article history:

Received 25 November 2019

Accepted 19 December 2019

Available online 30 December 2019

Keywords:

Brominated flame retardants

Leachate

pH

Organic matter content

Temperature

waste:leachate ratio

ABSTRACT

A series of laboratory experiments were conducted to examine the leaching of decabromodiphenyl ether (BDE-209) and hexabromocyclododecane (HBCDD) from a mix of three fabrics. Consistent with previous reports that such leaching is governed by second order kinetics, concentrations in leachate were markedly higher in the first 24 h of leaching, and diminished by an order of magnitude after 1 week. The influence of the waste:leachate ratio was examined for the first time, with leaching of both BDE-209 and HBCDD significantly greater ($p < 0.05$) at a waste:leachate ratio of 0.005 g/mL than at 0.05 g/mL. Using dissolved humic matter (DHM) solutions as proxy for simulating organic landfill leachates we found that leaching of both BDE-209 and HBCDD was also significantly greater at a DHM concentration of 1,000 mg/L in leachate compared to that observed at DHM values of 100 and 0 mg/L. Agitation of waste:leachate mixtures significantly enhanced leaching. While leaching of HBCDD decreased significantly as leachate pH increased from 5.8, through 6.5, to 8.5; no significant impact of pH on leaching of BDE-209 was detected. Concentrations in leachate of both BDE-209 and HBCDD decreased significantly on increasing leachate temperature from 20 °C to 60 °C and 80 °C. This is considered most likely due to volatilisation of these contaminants into the headspace of the leaching vessel at higher temperatures.

Copyright © 2020, KeAi Communications Co., Ltd. Production and hosting by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) are two classes of chemicals that have had extensive use worldwide as flame retardants added to polymeric materials to help meet fire safety regulations in various jurisdictions. Such materials include plastic housing of electrical and electronic equipment (EEE) like TVs, computer monitors etc, as well as soft furnishings comprising polyurethane furniture foam and synthetic fabrics such as polyester curtains and covers for furniture foam [1]. While three major types of PBDE formulations (Penta-, Octa- and Deca-BDE) have been used (BSEF, 2003), analysis of Irish waste samples suggests that it is Deca-BDE that was the predominant formulation applied to consumer articles in Ireland [2]. Within the European Union, a key objective of the waste EEE (WEEE) Directive recast is to reduce the quantity of WEEE sent to

landfill by promoting recycling and reuse [3]. In contrast however, no such restrictions exist on landfilling of waste soft furnishings. This is of potential concern given both the volume of this waste stream (an estimated 3,580 t of furniture foam and fabrics are generated annually in Ireland alone [2]) and the presence in furniture foam and fabrics of flame retardants including decabromodiphenyl ether (BDE-209 - the major component of the Deca-BDE product [1]) and HBCDD at concentrations at the low per cent level [2]. Although EU policies [4,5] aim to virtually eliminate landfill as a waste disposal option by 2020, it is likely that a substantial reservoir of waste soft furnishings and associated flame retardant chemicals have already been disposed to landfill. This reservoir represents a long-term potential emission source of brominated flame retardants (BFRs) to the environment given that even under effective management, aftercare timelines for landfills are of the order of 75 years [6]. We recently reported on the presence of PBDEs (including BDE-209) and HBCDD in leachate from landfills in Ireland [7]. While BFRs associated with waste soft furnishings are not the only putative source of such contaminants in landfill leachate, this study's main objective is to enhance

* Corresponding author.

E-mail address: S.J.Harrad@bham.ac.uk (S. Harrad).

Peer review under responsibility of KeAi Communications Co., Ltd.

understanding of the extent to which BDE-209 and HBCDD present in waste fabrics can undergo leaching in landfills, and the factors that influence such leaching. We have previously conducted laboratory studies of the leaching of PBDEs from waste cathode ray tube (CRT) plastic housing [8], as well as HBCDD from polystyrene building insulation foam [9], and polyester curtain fabrics [10]. Moreover, other researchers such as [11,12] have undertaken laboratory studies of PBDE leaching from WEEE. To our knowledge however, no such controlled studies of leaching of PBDEs from fabrics have been undertaken. Moreover, our previous study of the leaching of HBCDD from fabrics was conducted using deionised distilled water as the leaching fluid. We therefore set out to examine HBCDD leaching using leaching fluids containing varying concentrations of organic matter to more accurately reflect real landfill leachate. Furthermore, as our previous work had examined PBDE and HBCDD leaching at a single waste:leachate ratio, we also study here, the influence of waste:leachate ratio on leaching of these contaminants from fabrics.

2. Methods

2.1. Preparing homogeneous mixtures of PBDEs and HBCDD

A “waste” fabric mixture was created by homogenising aliquots of three polyester fabrics determined to contain elevated concentrations of either HBCDD or BDE-209. Although two of the fabrics originated from Japan and the other from the UK; we have shown previously that HBCDD and BDE-209 are the BFRs present at highest concentrations in waste furniture fabrics in Ireland [2]. Three aliquots (60 mg) of the fabric mix were analysed for BDE-209, as well as α -, β -, and γ -HBCDD, to evaluate its homogeneity.

2.2. Leaching experiment protocols

Leaching experiments were carried out in 250 mL high density polyethylene (HDPE) bottles (Thermo Fisher). To an accurately weighed mass of fabric mix (either 5 g or 0.5 g depending on the waste:leachate ratio examined) was added 100 mL of leaching fluid. The resultant mixture was sealed within the leaching vessel and left for 24 h, after which the leaching fluid was removed and filtered for analysis. The fabric mix was returned to the leaching container and replaced with a further 100 mL of fresh fluid of identical composition to the initial leaching fluid. The vessel was again sealed and the fabric and leaching fluid left in contact for a further 24 h before removal of the leachate for analysis. This process of leaching fluid removal for analysis at the end of the contact time, and its replenishment with fresh fluid was conducted on a total of 5 occasions, thereby generating samples where the fabric mix had been leached for 24, 48, 72, 96 and 168 h.

As well as examining the effect of waste:leachate contact time, we also examined the impact on leaching of the following parameters: (1) leaching fluid temperature (20 °C, 60 °C, and 80 °C), (2) dissolved humic matter content (0 mg/L (i.e. distilled deionised water), 100 mg/L, and 1,000 mg/L), (3) pH (5.8, 6.5, and 8.5), (4) agitation of the waste:leaching fluid mix, and (5) waste:leachate ratio (0.005 and 0.05 g/mL). Study of these parameters was achieved by: (1) immersion of the leachate vessel in a constant temperature water bath, (2) mixing known masses of humic matter (dissolving 100 mg or 1,000 mg of humic acid (Sigma Aldrich, technical grade) in 1 L of distilled deionised water), (3) monitoring pH levels using a pH meter (Hanna, USA) and adjusting pH using either glacialacetic acid (Sigma-Aldrich) or ammonium hydroxide (Fisher Scientific) solutions, (4) agitating the leaching vessel continuously on an automatic shaker, and (5) mixing 0.5 g and 5 g of waste fabric respectively with 100 mL of leaching fluid. Overall, a

total of 9 unique leaching experiments (each conducted in duplicate) were conducted. Full details of the parameters examined in each experiment are provided as supplementary information (Tables SI–1).

2.3. Determination of concentrations of BDE-209 and HBCDDs in fabric mix and leaching fluid

Fifty mL of leachate was spiked with 50 ng of each internal standard ($^{13}\text{C}_{12}$ -BDE-209, $^{13}\text{C}_{12}$ - α -HBCDD, $^{13}\text{C}_{12}$ - β -HBCDD, and $^{13}\text{C}_{12}$ - γ -HBCDD (Wellington Laboratories)). A Strata-XAW (3 mL, 200 mg (Phenomenex)) solid phase extraction (SPE) cartridge was pre-conditioned with 6 mL hexane:DCM (1:1 v/v) followed by 12 mL distilled water. The sample was allowed to load on to the cartridge gravimetrically and the cartridge washed with a further 12 mL of distilled water. The cartridge was dried under vacuum for 30 min, and target compounds were eluted with 10 mL of hexane:DCM (1:1, v/v ratio). Extracts were concentrated to near dryness, reconstituted in 1 mL toluene and transferred to autosampler vials ready for analysis.

HBCDDs were measured using a Shimadzu LC-20AB Prominence binary pump liquid chromatograph, equipped with a SIL-20A autosampler, a DGU-20A3 vacuum degasser coupled to an AB Sciex API 2000 triple quadrupole MS. Chromatographic separation was achieved using a Restek Force C₁₈ column (150 mm × 2.1 mm I.D., 3 μm particle size) and a mobile phase of (a) 1:1 methanol/water and (b) methanol at a flow rate of 180 $\mu\text{L}/\text{min}$. Full LC-MS/MS parameters have been reported previously [13].

BDE-209 was determined on a Thermo TRACE 1300 GC equipped with a Restek Rtx-5ms (15 m × 0.25 mm i.d. × 0.25 μm) coupled to a Thermo ISQ MS. Full GC/MS methods have been described previously [14].

2.4. Calculating BDE-209 and HBCDD leached fractions

The percentage of PBDEs present in the test textiles that was leached into each leachate sample (PL) was calculated as in equation (1):

$$PL = \left[\frac{C_{leachate} \times V}{C_{waste} \times W} \right] \times 100\% \quad (1)$$

PL = percentage leached (%)

$C_{leachate}$ = Conc. of PBDEs collected in leachate (mg/L)

V = volume of leachate (L)

C_{waste} = Conc. of PBDEs in waste sample (mg/kg)

W = total weight of waste sample (kg)

The cumulative percentage leached (CPL) represents the sum of PL values recorded for each sample taken within a given time period during each experiment – e.g. CPL at 48 h contact time = the sum of the PL values for the 0–24 h and 24 h–48 h samples.

3. Results and discussion

3.1. Concentrations of BDE-209 and HBCDDs in fabric mix

Table 1 summarises the concentrations detected in the 3 aliquots of the fabric mix used in all leaching experiments, along with their average and relative standard deviation (RSD). This reveals acceptable reproducibility with RSD in the range of 11–14% for individual HBCDDs and 3.6% for BDE-209. Concentrations in the fabric mix (i.e. in the low % range) are consistent with those

Table 1
Concentrations (mg/kg) of BDE-209 and HBCDDs in Fabric Mix used in Leaching Experiments.

	BDE-209	α -HBCDD	β -HBCDD	γ -HBCDD	Σ -HBCDD
Replicate 1	1600	2700	1100	1700	5500
Replicate 2	1500	2700	890	1600	5200
Replicate 3	1600	3400	960	2000	6900
Arithmetic mean	1600	2900	980	1800	5700
Relative standard deviation (%)	3.6	14	11	12	16

reported to be used to impart flame retardancy to fabrics as well as those reported in some samples of waste fabrics in a recent survey of waste furniture fabrics in Ireland [2]. The fabric mix used can thus be considered a realistic representation of BFR-treated fabrics present in landfills.

3.2. Concentrations of BDE-209 and HBCDDs in leaching fluid

Tables SI–2 provides the concentrations as well as values of CPL for BDE-209 and individual HBCDD diastereomers in the leaching fluid in each leaching experiment. Overall, concentrations in leaching fluid in this study ranged between 0.58 and 270 ng/mL and 1.1 and 260 ng/mL for BDE-209 and Σ HBCDD respectively. As expected, these exceed substantially concentrations in leachate from 48 Irish landfills of <0.001–0.22 and < 0.002–0.043 ng/mL of BDE-209 and Σ HBCDD [7]. However, we note that the maximum concentrations of BDE-209 in Irish landfill leachate were close to the minimum value observed in our experiments, and that BDE-209 was reported to be present at an arithmetic mean of 0.95 ng/mL in South African landfill leachate [15].

3.3. Impact of waste:leachate ratio

Table 2 shows the average values of CPL and concentrations in leaching fluid for the two sets of duplicate experiments that compared the impact of varying the waste:leachate ratio from 0.005 to 0.05. In both sets of experiments, other parameters were identical, viz: temperature = 20 °C, pH = 6.5, DHM = 0 mg/L, and no agitation. To our knowledge, this is the first study of how waste:leachate ratio influences the leaching of BFRs from treated materials. T-test comparison of values of CPL obtained for each experiment at different waste:leachate ratios revealed significantly higher ($p < 0.05$) leaching for both BDE-209 and Σ HBCDD leaching at the lower waste:leachate ratio. The average cumulative percentages leached over 1 week at the lower ratio are 1.4% for BDE-209 and 1.7% for Σ HBCDD compared to 0.18% and 0.29% respectively at the higher ratio. This finding may reflect the lower fabric

surface area to leaching fluid volume ratio at the higher waste:leachate ratio. More specifically, at the higher waste:leachate ratio, the pieces of fabric comprising the mix used will be more prone to overlaying each other, thereby restricting contact between the fabric surface and the leaching fluid.

3.4. The influence of waste agitation on leaching

We have previously shown that agitation of waste/leachate mixtures under laboratory conditions significantly enhances leaching of HBCDD from both expanded (EPS) and extruded (XPS) polystyrene building insulation foam [9] and from fabrics [10], and of PBDEs (including BDE-209) from CRT housing plastic [8]. Here we compared the extent of leaching of BDE-209 and HBCDDs during two sets of experiments where all parameters were held constant, with one set agitated but the other not. In line with previous observations, we observed (Table 2) higher average values of Σ CPL in the agitated experiments (0.71% and 0.45% for BDE-209 and Σ HBCDD respectively) than in the experiments without agitation (0.18% and 0.29% for BDE-209 and Σ HBCDD respectively). T-test comparison of CPL values at each contact time obtained in agitated relative to those observed for non-agitated experiments revealed leaching of both BDE-209 and Σ HBCDD during agitated experiments to exceed significantly ($p < 0.05$) those that were not agitated.

3.5. Influence of dissolved humic matter content of leaching fluid

To examine the impact of the DHM concentration of the leaching fluid, we compared the extent of leaching of BDE-209 and HBCDDs during three sets of experiments where the DHM content of the leaching fluid varied between 0, 100, and 1,000 mg/L, while all other parameters were held constant (pH 6.5, temperature 20 °C, no agitation, and waste leachate ratio 0.05). The resulting concentrations and CPL values are shown in Table 3. Values of Σ CPL increase with increasing DHM content. Specifically, from an average of 0.18% at 0 mg/L, to 0.23% at 100 mg/L, and 0.33% at 1,000 mg/L for

Table 2
Results of leaching experiments^a examining impact of waste agitation and Waste:Leachate ratio.

Waste:Leachate Ratio (g/mL)	Agitated (Y/N)	BFR	Contact time	24 h	48 h	72 h	96 h	168 h			
0.05	Y	BDE-209	Leachate concentration ^b (ng/mL)	260	160	92	25	23			
			CPL ^{b,c} (%)	0.33	0.53	0.65	0.68	0.71			
			Σ HBCDD	Leachate concentration (ng/mL)	130	130	44	36	13		
		0.05	N	BDE-209	CPL (%)	0.16	0.33	0.39	0.43	0.45	
					Leachate concentration (ng/mL)	76	37	23	4.7	4.9	
					CPL (%)	0.093	0.14	0.17	0.17	0.18	
0.005	N	Σ HBCDD	Leachate concentration (ng/mL)	140	57	24	1.2	5.3			
			CPL (%)	0.18	0.25	0.28	0.28	0.29			
			BDE-209	Leachate concentration (ng/mL)	37	30	18	20	4.1		
		0.005	N	BDE-209	CPL (%)	0.47	0.84	1.1	1.3	1.4	
					Σ HBCDD	Leachate concentration (ng/mL)	53	36	14	15	18
					CPL (%)	0.66	1.1	1.3	1.5	1.7	

^a Other parameters identical in these experiments, viz leaching fluid pH, temperature and DHM content 6.5, 20 °C, and 0 mg/L respectively.

^b All concentrations and CPL values are the average of duplicate measurements.

^c Cumulative percentage leached.

Table 3
Results of Leaching Experiments^a Examining Impact of pH and Dissolved Humic Matter Content of Leaching Fluid.

Dissolved Humic Matter Content (mg/L)	pH	BFR	Contact time	24 h	48 h	72 h	96 h	168 h
0	5.8	BDE-209	Leachate concentration ^b (ng/mL)	54	63	22	20	3.4
			CPL ^{b,c} (%)	0.067	0.15	0.17	0.20	0.20
0	8.5	ΣHBCDD	Leachate concentration (ng/mL)	200	40	27	50	23
			CPL (%)	0.24	0.29	0.33	0.39	0.42
0	6.5	BDE-209	Leachate concentration (ng/mL)	35	19	55	11	15
			CPL (%)	0.045	0.068	0.14	0.15	0.17
0	6.5	ΣHBCDD	Leachate concentration (ng/mL)	34	57	3.6	18	13
			CPL (%)	0.043	0.11	0.12	0.14	0.17
0	6.5	BDE-209	Leachate concentration (ng/mL)	76	37	23	4.7	4.9
			CPL (%)	0.093	0.14	0.17	0.17	0.18
100	6.5	ΣHBCDD	Leachate concentration (ng/mL)	140	57	24	1.2	5.3
			CPL (%)	0.18	0.25	0.28	0.28	0.29
100	6.5	BDE-209	Leachate concentration (ng/mL)	110	35	19	8.2	9.8
			CPL (%)	0.14	0.18	0.20	0.21	0.23
1,000	6.5	ΣHBCDD	Leachate concentration (ng/mL)	210	62	43	26	26
			CPL (%)	0.26	0.34	0.39	0.42	0.45
1,000	6.5	BDE-209	Leachate concentration (ng/mL)	140	52	52	15	8.7
			CPL (%)	0.18	0.24	0.31	0.32	0.33
1,000	6.5	ΣHBCDD	Leachate concentration (ng/mL)	220	140	84	71	33
			CPL (%)	0.27	0.45	0.55	0.64	0.69

^a Other parameters identical in these experiments, viz leaching fluid temperature 20 °C, no agitation, and waste:leachate ratio = 0.05 g/mL.

^b All concentrations and CPL values are the average of duplicate measurements.

^c Cumulative percentage leached.

BDE-209, with the corresponding values for ΣHBCDD being 0.29%, 0.45%, and 0.69%. The significance of these increases in leaching was evaluated using ANOVA to compare CPL values for each duplicate experiment at each contact time obtained using leaching fluids of different DHM content. This revealed significantly greater ($p < 0.05$) leaching of both BDE-209 and ΣHBCDD at 1,000 mg/L DHM than at either 100 or 0 mg/L. There was no significant difference however between CPL values at 100 and 0 mg/L. As highlighted above, the influence of the DHM content of leachate on leaching has not to our knowledge previously been studied for HBCDD. We have previously examined the influence of DHM on leaching of PBDEs including BDE-209 from waste CRT plastics but detected no significant impact [8]. Our observation here of increased leaching of BDE-209 and HBCDD is however consistent with previous reports of a positive correlation between concentrations of perfluoroalkyl substances in landfill leachate from Australia and the total organic carbon content of the leachate [16]. It is also in line with our report that concentrations of some PFASs and PBDEs (but not BDE-209) in Irish landfill leachate are significantly higher at higher levels of chemical oxygen demand [7].

3.6. Influence of pH of leaching fluid

Average ΣCPL values for 3 sets of experiments where only the pH of the leaching fluid was varied between 5.8, 6.5, and 8.5 were 0.20%, 0.18%, and 0.17% for BDE-209 and 0.42%, 0.29%, and 0.17% for ΣHBCDD. ANOVA of CPL values in these experiments – which along with concentrations in leachate are provided in Table 3 – revealed that leaching of BDE-209 was not significantly influenced by pH ($p > 0.05$). In contrast, CPL values of ΣHBCDD were significantly greater ($p < 0.05$) at pH 5.8 than at either pH 6.5 or 8.5. Moreover, leaching of ΣHBCDD at pH 6.5 exceeded significantly ($p < 0.05$) that measured at pH 8.5. The absence of any discernible influence of pH on the leaching of BDE-209 is consistent with the lack of correlation between leachate pH and concentrations of PBDEs and HBCDD in Irish landfill leachate [7]. Likewise, no influence of leaching fluid pH was detected in a laboratory study of PBDE leaching from CRT plastics [8]. In contrast [12] reported more facile leaching of PBDEs (especially lower brominated congeners) from WEEE at pH values of 4–5 than at pH 7 and 9. With respect to HBCDD, the enhanced

leaching at pH 5.8 (which is observed for each individual diastereomer) contrasts with a report that leaching of α -HBCDD from EPS building insulation foam was greatest at pH 8.5 [9]. The same previous study did not detect any influence of pH on leaching of either β - or γ -HBCDD from EPS, or of any of the 3 diastereomers from XPS building insulation [9]. Our findings for HBCDD leaching from fabrics are more in line with those of [12] for PBDEs. It is possible that the contrasting findings of [9] for building insulation may be matrix-related. Specifically, Stubbings and Harrad agitated their experiments with EPS and XPS insulation foam leading to abrasion of small particles of friable foam. Such abrasion elevated HBCDD concentrations in leachate above the aqueous solubility of HBCDD and thus may have masked any impact of pH.

3.7. Influence of leaching fluid temperature

Three sets of experiments were conducted to examine the impact of leaching fluid temperature on leaching. Heat released during aerobic degradation of waste can raise internal landfill temperatures to as high as 80–90 °C [17]. Average ΣCPL values for BDE-209 were 0.18%, 0.17%, and 0.039% at 20 °C, 60 °C, and 80 °C respectively, while those for ΣHBCDD were 0.29%, 0.21%, and 0.082% at 20 °C, 60 °C, and 80 °C respectively. These data – see Table 4 – imply reduced leaching at higher temperatures and are confirmed by ANOVA analysis of CPL values for these experiments, which show significantly ($p < 0.05$) reduced CPL values for both BDE-209 and ΣHBCDD as leaching fluid temperature increases. This differs from a previous study where leaching of PBDEs (including BDE-209) increased as the leaching fluid temperature was raised from 20 °C, to 50 °C and 80 °C [8]. Moreover, leaching of HBCDDs from curtain fabrics was enhanced at 80 °C compared to 20 °C [10]. This temperature-related enhancement of leaching was noticeably greater for γ -compared to α -HBCDD and was attributed to either isomerisation or isomer-specific changes in aqueous solubility at higher temperatures [10]. By comparison, while leaching of HBCDDs from EPS building insulation foam increased with temperature, this effect was greatest for α -HBCDD [9]. In contrast, some support for our finding in the current study that leaching was reduced at higher temperatures is provided by a study examining the leaching of TCIPP from polyurethane foam, where although

Table 4
Results of leaching experiments^a examining impact of leaching fluid temperature.

Leaching Fluid Temperature (°C)	BFR	Contact time	24 h	48 h	72 h	96 h	168 h
			20	BDE-209	Leachate concentration (ng/mL)	76	37
		CPL ^b (%)	0.093	0.14	0.17	0.17	0.18
	ΣHBCDD	Leachate concentration (ng/mL)	140	57	24	1.2	5.3
		CPL (%)	0.18	0.25	0.28	0.28	0.29
60	BDE-209	Leachate concentration (ng/mL)	57	34	21	14	9.2
		CPL (%)	0.071	0.11	0.14	0.16	0.17
	ΣHBCDD	Leachate concentration (ng/mL)	100	29	17	15	4.7
		CPL (%)	0.12	0.16	0.18	0.20	0.21
80	BDE-209	Leachate concentration (ng/mL)	19	5.5	2.5	2.6	1.0
		CPL (%)	0.024	0.031	0.034	0.037	0.039
	ΣHBCDD	Leachate concentration (ng/mL)	45	11	3.8	3.6	1.7
		CPL (%)	0.056	0.070	0.075	0.079	0.082

^aOther parameters identical in these experiments, viz leaching fluid pH and DHM content 6.5 and 0 mg/L respectively, no agitation, and waste:leachate ratio = 0.05 g/mL.

^bCumulative percentage leached.

increasing temperature from 20 °C to 50 °C enhanced leaching, leaching was markedly reduced at 80 °C to levels either equivalent to or below that observed at 20 °C [18]. This was attributed to enhanced volatilisation of TCIPP at 80 °C, with concomitant losses on opening the leaching vessel to remove leaching fluid for analysis. We also considered the possibility of temperature-related degradation of BDE-209 and HBCDD, as well as HBCDD isomerisation. However, examination of mass chromatograms for other PBDEs did not reveal convincing evidence of degradation such as enhanced abundance of lower brominated PBDEs in the leaching fluids at 80 °C. Moreover, we detected no evidence of any meaningful temperature-related differences in HBCDD diastereomer pattern. We therefore believe that the difference between our findings and those of the studies of [8,9] may be explained as follows. While in the current study, heated experiments were cooled for only as long as it took for the vessels to be no longer too hot to touch before opening the leaching vessel to remove the fluid for analysis; the heated experiments of Stubbings and Harrad were cooled to room temperature before opening. Combined, the evidence suggests that enhanced leaching of PBDEs and HBCDD occurs at higher leaching fluid temperatures with the leached BFRs either returning to solution when the leachate cools (as observed by Stubbings and Harrad), or volatilising at the higher temperatures, as observed here.

3.8. Influence of waste:leachate contact time

Consistent with previous studies [8–10], CPL values increase with increasing duration of contact between waste and leaching fluid. However, it is also apparent that BFR concentrations in leachate diminish substantially as contact time increases. Although we have insufficient measurements (5 contact time points) for each experiment to permit reliable calculation of leaching rate kinetics, they are consistent with previous data that suggest leaching of both PBDEs and HBCDD from treated materials is a second order process [8–10]. Specifically, concentrations in leachate are markedly higher during the 1st 24 h of fabric:leachate contact time (likely due to more facile leaching of BFRs present on the surface of materials and thus more loosely-bound), than in leachate samples taken at subsequent contact times.

4. Conclusions

Our data suggest that leaching of BDE-209 and HBCDD from landfill is likely greatest in periods just after waste enters landfill. This is in line with reports elsewhere that such leaching is governed by second order kinetics, and our observation that leaching is more

facile while waste is agitated (e.g. during waste disposal) before compressing over time with subsequent reduction in the waste:-leachate ratio. Our findings also imply potential for emissions of BFRs via volatilisation, during periods of active waste decomposition when internal landfill temperatures are elevated. Moreover, maintaining leachate at more alkaline pH and lower organic matter content may reduce leaching rates. Overall, our data add to the weight of evidence that highlights the potential for BFR emissions from landfilled waste. Understanding the long-term fate of BFRs and related chemicals associated with landfilled waste is an urgent research priority.

Declaration of competing interest

I hereby declare that none of the authors of this manuscript have any known conflicts of interest.

Acknowledgements

This project (FUEL, reference 2016-HW-MS-8) is funded under the EPA Research Programme 2014–2020. The EPA Research Programme is a Government of Ireland initiative funded by the Department of Communications, Climate Action and Environment.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.emcon.2019.12.005>.

References

- [1] M.J. La Guardia, R.C. Hale, E. Harvey, Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures, *Environ. Sci. Technol.* 40 (2006) 6247–6254.
- [2] D.S. Drage, M. Sharkey, M.A.-E. Abdallah, H. Berresheim, S. Harrad, Brominated flame retardants in Irish waste polymers: concentrations, legislative compliance, and treatment options, *Sci. Total Environ.* 625 (2018) 1535–1543.
- [3] EC, Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE) (recast) (Text with EEA relevance). <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32012L0019>, 2019 accessed 19th November 2019.
- [4] EC, Roadmap to a Resource Efficient Europe. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, 2011. <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52011DC0571>. accessed 19th November 2019.
- [5] EEA, European Environment Agency. Towards a green economy in Europe. EU environmental policy targets and objectives 2010–2050. <https://www.eea.europa.eu/publications/towards-a-green-economy-in-europe>, 2013 accessed 19th November 2019.
- [6] Y. Wang, Leachate Management in the Aftercare Period of Municipal Waste Landfills, PhD, Aalto University, 2013, <http://lib.tkk.fi/Diss/2013/>

- isbn9789526051413/isbn9789526051413.pdf. accessed 19 November 2019.
- [7] S. Harrad, D.S. Drage, M. Sharkey, H. Berrsheim, Brominated flame retardants and perfluoroalkyl substances in landfill leachate from Ireland, *Sci. Total Environ.* 695 (2019) 133810.
- [8] W.A. Stubbings, S. Harrad, Factors influencing leaching of PBDEs from waste cathode ray tube plastic housings, *Sci. Total Environ.* 569–570 (2016) 1004–1012.
- [9] W.A. Stubbings, S. Harrad, Laboratory studies on leaching of HBCDD from building insulation foams, *Emerg. Contam.* 5 (2019) 36–44.
- [10] W.A. Stubbings, N. Kajiwara, H. Takigami, S. Harrad, Leaching behaviour of hexabromocyclododecane from treated curtains, *Chemosphere* 144 (2016) 2091–2096.
- [11] K.I. Choi, S.-H. Lee, M. Osako, Leaching of brominated flame retardants from TV housing plastics in the presence of dissolved humic matter, *Chemosphere* 74 (2009) 460–466.
- [12] M.N. Danon-Schaffer, A. Mahecha-Botero, J.R. Grace, M.G. Ikononou, Transfer of PBDEs from e-waste to aqueous media, *Sci. Total Environ.* 447 (2013) 458–471.
- [13] M.A. Abdallah, C. Ibarra, H. Neels, S. Harrad, A. Covaci, Comparative evaluation of liquid chromatography–mass spectrometry versus gas chromatography–mass spectrometry for the determination of hexabromocyclododecanes and their degradation products in indoor dust, *J. Chromatogr., A* 1190 (2008) 333–341.
- [14] M.A. Abdallah, D.S. Drage, M. Sharkey, H. Berrsheim, S. Harrad, A rapid method for the determination of brominated flame retardant concentrations in plastics and textiles entering the waste stream, *J. Sep. Sci.* 40 (2017) 3873–3881.
- [15] A.P. Daso, O.S. Fatoki, J.P. Odendaal, O.O. Olujimi, Polybrominated diphenyl ethers (PBDEs) and 2,2',4,4',5,5'-hexabromobiphenyl (BB-153) in landfill leachate in Cape Town, South Africa, *Environ. Monit. Assess.* 185 (2013) 431–439.
- [16] C. Gallen, D. Drage, G. Eaglesham, S. Grant, M. Bowman, J.F. Mueller, Australia-wide assessment of perfluoroalkyl substances (PFASs) in landfill leachates, *J. Hazard Mater.* 331 (2017) 132–141.
- [17] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, Present and long-term composition of MSW landfill leachate: a review, *Crit. Rev. Environ. Sci. Technol.* 32 (2002) 297–336.
- [18] W.A. Stubbings, S. Harrad, Leaching of TCIPP from furniture foam is rapid and substantial, *Chemosphere* 193 (2018) 720–725.