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DOI:

[10.1016/j.emcon.2019.02.003](https://doi.org/10.1016/j.emcon.2019.02.003)

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Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Stubbings, WA & Harrad, S 2019, 'Laboratory studies on leaching of HBCDD from building insulation foams', *Emerging Contaminants*, vol. 5, pp. 36-44. <https://doi.org/10.1016/j.emcon.2019.02.003>

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Laboratory studies on leaching of HBCDD from building insulation foams

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ARTICLE INFO

Article history:

Received 10 October 2018

Received in revised form

7 February 2019

Accepted 10 February 2019

Keywords:

Expanded polystyrene

Extruded polystyrene

Hexabromocyclododecane

Landfill

Brominated flame retardants

ABSTRACT

A series of laboratory experiments were conducted to study emissions of hexabromocyclododecane (HBCDD) into aqueous leaching fluid under simulated landfill conditions. Expanded (EPS) and extruded (XPS) polystyrene building insulation foam samples containing HBCDD were contacted with deionised Milli-Q water containing 0, 100 and 1000 mg L⁻¹ dissolved humic matter (DHM) as leaching fluid. Concentrations of HBCDD were determined in the resulting fluid and single and serial batch experiments conducted. The impacts on HBCDD concentrations in the leaching fluid temperature and pH were examined. Data from these experiments show that HBCDD concentrations in leaching fluid following contact with EPS and XPS almost all exceeded the aqueous solubilities for each diastereomer and the technical HBCDD formula. This indicates that agitation and abrasion of EPS and XPS were significant mechanisms of HBCDD emission to leaching fluid. Specifically, under such conditions, HBCDD is likely associated with fine abraded particles of the foam and concentrations in the leaching fluid are therefore not limited by the aqueous solubility of HBCDD. Consistent with this, the length of contact time had a significant positive effect on concentrations of all diastereomers in the leaching fluid for XPS and for the least soluble diastereomer, γ -HBCDD for EPS. Generally, the presence of DHM in the leaching fluid and elevated leaching fluid temperatures had significant positive effects on HBCDD concentrations in leaching fluid for both EPS and XPS. Overall, while leaching fluids of pH 8.5 significantly enhanced concentrations of α -HBCDD released from EPS, pH exerts a minor effect on concentrations of HBCDD in leaching fluid.

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1. Introduction

Hexabromocyclododecane (HBCDD) has been identified as an endocrine disrupting chemical that induces enzymes and alters thyroid homeostasis with potential to cause adverse effects in humans at relatively low exposure levels [1–5]. This is compounded by evidence that its presence in the environment is ubiquitous [6–18]. In a legislative context, HBCDD has been identified by the European Union as a Substance of Very High Concern, meeting the criteria of a PBT (persistent, bioaccumulative and toxic) substance [19]; while in Japan, HBCDD has been designated as a Monitoring Chemical Substance under the Chemical Substances

Control Law because of its persistence and high bio-accumulation. Moreover, in 2013, HBCDD was listed as a persistent organic pollutant (POP) by the United Nations Environment Programme (UNEP) under the Stockholm Convention on POPs. In 2011, annual global production of HBCDD was an estimated maximum of 28,000 tonnes (9000 to 15,000 tonnes in China, 13,426 tonnes in Europe and the US) [20]. Approximately 90% of HBCDD is used in the building industry, typically added at ~3% by weight into extruded (EPS) or expanded polystyrene (XPS) foam in rigid insulation panels/boards [21,22].

Currently, used building insulation foams treated with HBCDD are widely treated as municipal rather than hazardous waste, and are thus landfilled or incinerated. This reservoir of HBCDDs within building insulation foams is substantial and will continue to gradually enter the waste stream [23]. Hence, there is a pressing need to understand the fate of chemicals like HBCDD associated with waste building insulation foams following disposal. Potential emission pathways for chemicals associated with landfill include

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

contamination of leachate and volatilisation [24]. The physico-chemical properties of HBCDD (water solubility = α -HBCDD (41,000 ng L⁻¹), β -HBCDD (15,000 ng L⁻¹) and γ -HBCDD (2400 ng L⁻¹) at 20 °C, vapour pressure = 6.3×10^{-5} Pa at 21 °C and Log K_{ow} = 5.6 [25,26]), suggest that following disposal to landfill, such leaching and volatilisation of HBCDD associated with treated building insulation foams may not be extensive. However, other brominated flame retardants with similar physicochemical properties like polybrominated diphenyl ethers (PBDEs), have been reported in landfill leachate [27–29]. To our knowledge, empirical data related to the fate of HBCDD in landfill is scarce. The present study, therefore, conducts a series of controlled laboratory experiments to test the hypothesis that HBCDDs are capable of leaching from waste building insulation foams.

2. Materials and methods

2.1. Samples

We investigated two types of flame-retardant-treated building insulation foams: EPS and XPS foams. Both were commercial grade and obtained from the Japan Expanded Polystyrene Association and the Extruded Polystyrene Foam Industry Association of Japan, respectively. [30]; confirmed that both building insulation foams had been treated with technical HBCDD. Concentrations of HBCDDs in these insulation foams were previously reported at 970 mg kg⁻¹ and 33,000 mg kg⁻¹ for α -HBCDD, 620 mg kg⁻¹ and 6500 mg kg⁻¹ for β -HBCDD and 3900 mg kg⁻¹ and 3900 mg kg⁻¹ for γ -HBCDD for EPS and XPS respectively [30]. However, the concentrations measured in these foams in the present study were slightly different but at the same general ranges and profiles reported previously (Table 1 & Fig. S3).

2.2. Leaching test methods

Four distinct experimental scenarios were undertaken to examine the effects of: (a) contact time (single batch experiments); (b) duration of serial or periodic wetting and draining of waste (serial batch experiments); (c) temperature; and (d) pH level of the leaching fluid on the release of the target analyte from the sample material (SI; Table S1). In scenario (a) contact time, the treated sample was contacted once with the leaching fluid for a set pre-determined time of either 6 h, 24 h or 48 h. In scenario (b) serial batch, the sample was contacted with the leaching fluid for 168 h in total, with the resulting leaching fluid being extracted from the contact vessel and replenished with fresh leaching fluid 6 times, at intervals of 6 h (batch 1), 24 h (batch 2), 48 h (batch 3), 72 h (batch 4), 96 h (batch 5) and 168 h (batch 6). Each batch of leaching fluid was analysed for HBCDD concentrations at the given time intervals.

The leaching fluid was extracted from the contact vessel via pouring or draining through a 0.45 μ m pore size glass fibre filter (Advantec, Japan), in which the contact vessel was inverted for approximately 5 min to ensure as much leaching fluid was removed as possible. In all experiment scenarios, dissolved humic matter (DHM) solutions of 0 mg L⁻¹ (Type 1 ultrapure Milli-Q[®] water only), 100 mg L⁻¹ and 1000 mg L⁻¹ were employed as leaching fluids. Landfill site leachates can contain a wide spectrum of dissolved

organic matter concentrations, usually in the range between ~100 mg L⁻¹ up to ~50,000 mg L⁻¹ [31]. DHM solutions were prepared by dissolving Aldrich humic acid (sodium salt) in Type 1 ultrapure Milli-Q[®] water. The solution was stirred for 5 min until total dissolution and then the pH was adjusted to the desired level, before finally it was centrifuged at 2000 rpm for 1 min. The pH levels were determined before each experiment using a pH meter (Hanna, USA) and levels were corrected using either glacial acetic acid (Sigma-Aldrich) or sodium hydroxide (Sigma-Aldrich) solutions.

Polytetrafluoroethylene (PTFE) bottles (500 mL) were used as contact vessels during controlled leaching experiments. The whole volume of the contact vessel was not completely filled with leaching fluid and as a result a headspace was present inside the contact vessel. In all experiments, 1 g of EPS or XPS foam sample was contacted with 100 mL of leaching fluid giving a liquid-solid ratio of 100:1 (v/w). Following addition of the sample and leaching fluid, contact vessels were horizontally agitated on a mechanical shaker at 200 rpm for the desired contact time. In scenario (c) experiments examining the influence of temperature, the contact vessels were not agitated and instead were submerged in a water bath for 24 h at the desired temperature. In scenario (d) experiments were agitated at 200 rpm for 6 h and the initial pH of the leaching fluid before contact with EPS/XPS was recorded. Each of the aforementioned leaching experiments was conducted in duplicate.

2.3. Sample preparation and chemical analysis

Each leaching fluid sample was filtered through a 0.45 μ m size particle retention glass fibre filter (Advantec, Japan) to remove any large foam particles from the leaching fluid and then spiked with 60 ng each of ¹³C₁₂-labelled α -, β -, and γ -HBCDDs as internal (or surrogate) standards. The filtrate was then extracted in series using 2 \times 50 mL dichloromethane (DCM) by liquid-liquid extraction with mechanical shaking for 30 min each time. The combined DCM extracts were dried via filtration through anhydrous Na₂SO₄. The dried extract was concentrated with solvent exchange to hexane before elution through a pre-cleaned acidified silica (1 g of 22% concentrated sulfuric acid, w/w) and Na₂SO₄ column with 30 mL of *n*-hexane/DCM 9:1 (v/v). The eluate was concentrated with solvent exchange to hexane before evaporation to incipient dryness, addition of d₁₈-labelled α -, β -, and γ -HBCDD as recovery (or syringe) standard and dilution in methanol prior to analysis via LC-ESI-MS/MS.

When analysing EPS and XPS foam samples to determine initial analyte concentrations, small pieces of foam (approx. 5 mm \times 5 mm \times 5 mm) were taken from random points from each sample totalling approximately 50 mg foam and 5 mL of *n*-hexane:acetone (3:2 v/v) were added to a pre-washed test tube, vortexed for 1 min and sonicated for 5 min before being centrifuged for 2 min at 2000 rpm. The supernatant was transferred to a clean tube, the extraction was repeated and both supernatants were combined (10 mL total) and vortexed for 1 min. Approximately, 1 mL of sample was then transferred to a clean tube and diluted using 9 mL *n*-hexane. Finally, 10 μ L of the first dilution was transferred to a GC vial insert and diluted further using 90 μ L methanol containing

Table 1
Mean \pm standard deviation concentrations (mg kg⁻¹) of HBCDD diastereomers in building insulation foams used in this study. ($n = 5$).

Diastereomer/Sample	α -HBCDD	β -HBCDD	γ -HBCDD	Σ HBCDD
EPS	960 \pm 22	720 \pm 93	3900 \pm 190	5600 \pm 260
XPS	40,000 \pm 5500	9500 \pm 530	6400 \pm 870	56,000 \pm 5500

50 ng each of $^{13}\text{C}_{12}$ -labelled α -, β -, and γ -HBCDDs as internal standards. Each building insulation foam tested was analysed in quintuplicate.

2.4. Determination of concentrations of HBCDDs

HBCDDs were quantified using a dual pump Shimadzu LC-20AB Prominence high pressure liquid chromatograph (Shimadzu, Kyoto, Japan) equipped with a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) (see SI for additional details: Fig. S1 and Tables S2, S3, S4).

2.5. Calculation of HBCDD leaching

The percentage of HBCDDs present in the test EPS/XPS foam samples that was released into each leaching fluid sample (PR) was calculated as follows (equation (1)):

$$PR = \frac{C_{\text{leaching fluid}} \times V}{C_{\text{waste}}} \times W \times 100, \quad 1$$

where PR = percentage released (%), $C_{\text{leaching fluid}}$ = Concentration of HBCDD in leaching fluid at end of contact time (mg L^{-1}), V = volume of leaching fluid (L), C_{waste} = Conc. of HBCDD in EPS/XPS (mg kg^{-1}), and W = total weight of EPS/XPS sample subjected to leaching (kg).

The percentage released normalised to contact time (PRT , $\% \text{ h}^{-1}$) is expressed here as the percentage of HBCDD released from the EPS/XPS per hour of contact time. PRT is calculated according to equation (2):

$$PRT = \frac{PR}{t}, \quad 2$$

where t = contact time (h).

2.6. Data analysis

Basic and descriptive statistics were calculated using IBM SPSS Statistics 24, and Microsoft Excel 2013 software. Plots were generated by Microsoft Excel 2013. Additional QA/QC information on analysis of lab blanks, calculated LODs and method LOQs are provided in the SI (Table S5).

3. Results and discussion

The concentrations of HBCDD in leaching fluid samples generated in these experiments very substantially exceed those reported in the limited number of studies measuring HBCDD in landfill leachates [17,32,33]. However, although not directly comparable [32], reported maximum concentrations of HBCDD in leachates from a MSW landfill in the Netherlands as 36 mg kg^{-1} (dry weight) and γ -HBCDD concentrations were at least four times greater than α -HBCDD concentrations. HBCDD concentrations were reported for suspended solids in the leachate. They also substantially exceed HBCDD concentrations reported in other aqueous environments, e.g. in UK lakes Σ HBCDD was 0.08 – 0.27 ng L^{-1} [34], and Japanese rivers Σ HBCDD was 2.5 – 2100 ng L^{-1} [35].

3.1. Initial HBCDD concentrations and diastereomer profiles in the building insulation foam samples

Table 1 displays the initial concentrations of HBCDD and individual diastereomers in the treated foam samples used in this study. The EPS foam is close to the pattern of technical grade

HBCDD, consisting of 75–95% γ -HBCDD, 3–13% α -HBCDD and 0.5–12% β -HBCDD [20,36]. Conversely, the diastereomer pattern in the XPS foam is substantially enriched in α -HBCDD. The difference between the diastereomer patterns observed in these samples is explained by thermal isomerisation of γ -HBCDD to α -HBCDD during the polymer extrusion process during XPS manufacture, which involves high temperatures of over 200°C [30]. Concentrations of Σ HBCDD were a factor of 10 higher in XPS foams than EPS foams. Thermal isomerisation of HBCDD towards a composition relatively enriched in γ -HBCDD compared to the starting material has been demonstrated previously [37] and is the most likely explanation for the pattern observed in our XPS foam samples.

3.2. Effects of contact time and humic matter content of leaching fluid on HBCDD release (single batch experiments)

The influence of contact time on HBCDD concentrations and mean PRT values ($\% \text{ h}^{-1}$) in leaching fluid in single batch experiments conducted for EPS and XPS foams at 20°C are illustrated in Fig. 1 and Fig. 2, respectively. Individual HBCDD diastereomer concentrations, mean PR (%) and mean PRT values ($\% \text{ h}^{-1}$) for the same experiments are provided in SI (Table S5).

When distilled deionised water is used as the leaching fluid, concentrations of α -HBCDD increase with increasing contact duration, for both EPS and XPS foams. α -HBCDD concentrations in the leaching fluid increase with increasing contact time to a greater extent than those of the other diastereomers and the profile in the leaching fluid is substantially different from what is seen in the foams. This suggests release mechanisms other than abrasion of foams and that α -HBCDD is preferentially dissolved into solution in a secondary solubility-driven phase of leaching. This is consistent with second-order kinetics, as previously observed for HBCDD and PBDEs from fabrics and CRT plastic housing chips [38,39].

With the addition of DHM to the leaching fluid there appears to be a distinct difference between the two insulation foams, with limited differences being observed for EPS foam contacted with a DHM concentration of 100 mg L^{-1} . The results of an ANOVA test show that the only significant differences ($p < 0.05$) in concentrations were for β -HBCDD between 6 h and 24 h, and 6 h and 48 h. Where 1000 mg L^{-1} DHM was contacted with EPS foam, significant differences ($p < 0.05$) in α -HBCDD concentrations were observed between 6 h and 24 h, and 6 h and 48 h.

In contrast, XPS foam experiments exhibited significant differences ($p < 0.05$) between all contact times for all three diastereomers at 100 mg L^{-1} DHM. In experiments where XPS foam was contacted with a DHM concentration of 1000 mg L^{-1} , significant differences ($p < 0.05$) between contact times were only observed for α -HBCDD concentrations in the leaching fluid between 6 h and 24 h, and 24 h and 48 h, where concentrations are highest in the 24 h experiments.

It was observed that during 48 h single batch experiments involving XPS foam and the greatest DHM concentration, the XPS foam noticeably appeared to absorb the humic matter, trapping it within its pore spaces and the resulting leaching fluid contained visibly less DHM (lighter colour) when subsequently drained and filtered. Increasing the DHM concentration of the leaching fluid has a significantly positive effect on HBCDD concentrations for all three diastereomers (SI; Table S6), it is therefore reasonable to hypothesise that the pattern of HBCDD concentrations in leaching fluid would follow on from those observed for 100 mg L^{-1} DHM and increase linearly with increasing contact time. However, because the DHM was absorbed into the XPS foam, the resulting HBCDD concentrations in the leaching fluid were reduced. There is little difference in HBCDD concentrations between 6 h and 48 h contact duration at 1000 mg L^{-1} DHM and concentrations are only slightly

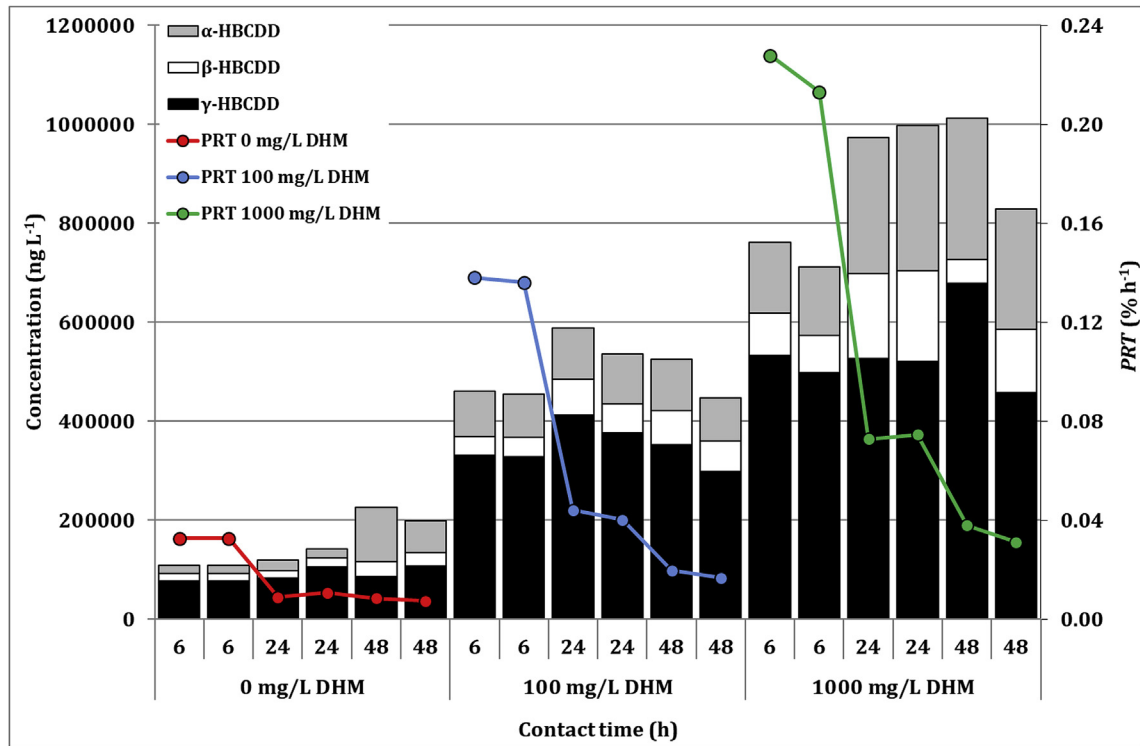


Fig. 1. HBCDD concentrations (ng L^{-1}) and PRT values ($\% \Sigma\text{HBCDD h}^{-1}$) in leaching fluids produced during 24 h single batch experiments (run in duplicate) on EPS foam at different contact times with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids.

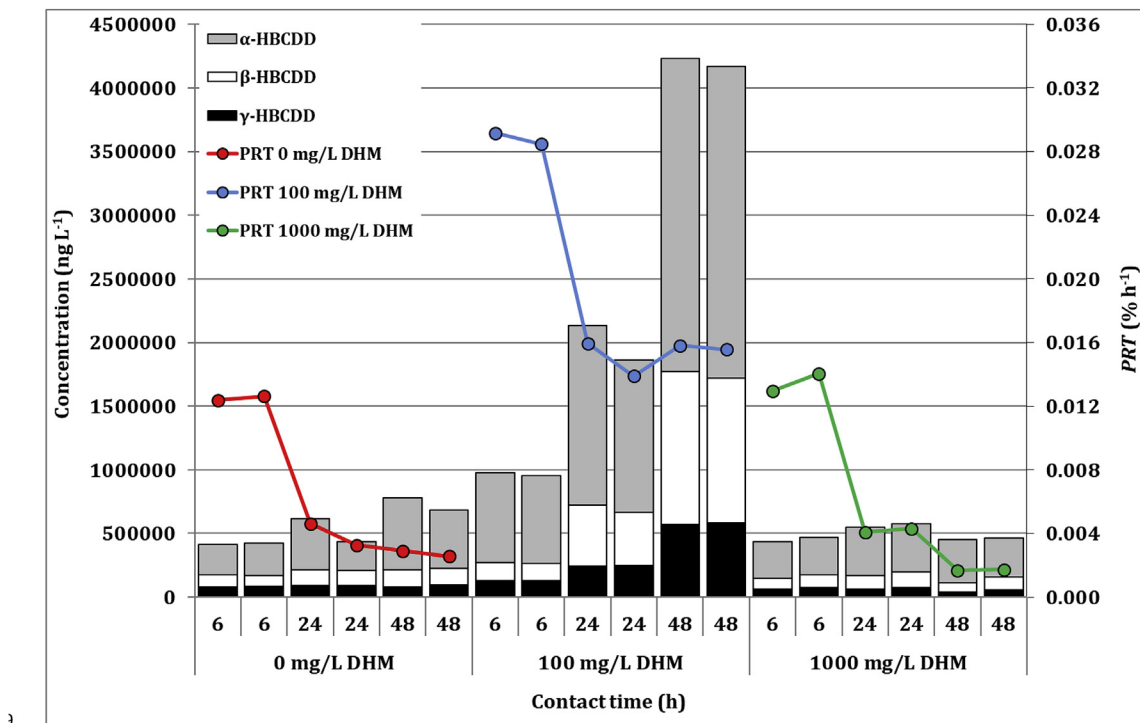


Fig. 2. HBCDD concentrations (ng L^{-1}) and PRT values ($\% \Sigma\text{HBCDD h}^{-1}$) in leaching fluids produced during 24 h single batch experiments (run in duplicate) on XPS foam at different contact times with Milli-Q, 100 mg L^{-1} DHM and 1000 mg L^{-1} DHM leaching fluids.

greater than those observed for the leaching fluid with no DHM at 48 h contact duration.

Due to the weak physical properties of the insulation foam materials, it is likely that mechanical abrasion plays an important

role in HBCDD leaching from both EPS and XPS foams. Longer periods of agitation result in greater abrasion of the foam material. Photographs illustrating the abrasion of XPS foam that occurred within the leaching chamber during agitated experiments are

presented in the SI (Fig. S2). When the resulting leaching fluid was filtered there was a quantity of fine foam particles retained on the filter and the foam sample had broken up and its edges smoothed like a pebble. Abrasion increases the overall surface area of the foam material, facilitating more facile leaching of HBCDD compared to HBCDD treated textiles [38]. Another effect of abrasion on HBCDD leaching behaviour is to enable higher concentrations of the less soluble diastereomers to be present in the leaching fluid associated with foam particles small enough to pass through the glass fibre filter ($<0.45\ \mu\text{m}$).

A strong indicator of this behaviour would be if the HBCDD concentrations present in the leaching fluid exceeded the measured aqueous solubility values reported for each diastereomer and for the technical HBCDD mixture (α -HBCDD = $41,000\ \text{ng L}^{-1}$; β -HBCDD = $15,000\ \text{ng L}^{-1}$; γ -HBCDD = $2400\ \text{ng L}^{-1}$; technical HBCDD = $66,000\ \text{ng L}^{-1}$) at $20\ ^\circ\text{C}$ [25,26]. DHM is hypothesised to increase dissolution above the reported aqueous solubilities, this is because the published solubility value is based on pure water, not solubility in an organically-modified aqueous matrix. However, in all EPS foam contact time experiments (including those with no DHM), γ -HBCDD concentrations in the leaching fluid ($77,000$ – $680,000\ \text{ng L}^{-1}$) substantially exceed the aqueous solubility limit. In 6 h contact experiments, γ -HBCDD was detected at concentrations between 37 and 252 times greater than its aqueous solubility. Moreover, while α -HBCDD was well below the aqueous solubility limit in 6 h experiments when no DHM or $100\ \text{mg L}^{-1}$ DHM leaching fluid was contacted and also in 24 h experiments with no DHM; in all other contact time experiments α -HBCDD concentrations are well above its aqueous solubility. β -HBCDD concentrations are just below the aqueous solubility limit ($14,000\ \text{ng L}^{-1}$). However, in all other contact time experiments on EPS foam it was well above this limit ($15,000$ – $180,000\ \text{ng L}^{-1}$). In all XPS foam contact time experiments, all three diastereomers were well above the aqueous solubility limits, reflecting the weaker, more friable physical properties of the material.

3.3. Effect of cyclical wetting and draining on HBCDD concentrations and leaching behaviour (serial batch experiments)

Mean concentrations of HBCDDs (ng L^{-1}) detected in leaching fluid and mean *PRT* values ($\% \text{ h}^{-1}$) obtained from serial batch experiments on EPS foam are illustrated in Fig. 3. Concentrations of HBCDDs (ng L^{-1}) detected in leaching fluid, mean *PR* (%) and mean *PRT* values ($\% \text{ h}^{-1}$) are provided in the SI (Table S7).

After 24-hour cumulative contact time, concentrations of HBCDD released from both insulation foams in these serial batch experiments plateau with increasing experimental duration, until the final 72-hour duration. The final contact duration 96–168 h elicited greater concentrations of α -HBCDD, possibly due to greater abrasion. Alternatively, the relatively longer contact duration enables a slower secondary phase of solubility-driven leaching to exert a greater effect on preferentially dissolving the more soluble α -HBCDD. The decline in *PRT* values with each subsequent batch may be related to HBCDD aqueous solubility limits – i.e. HBCDD concentrations in leaching fluid approach reported aqueous solubility values for these chemicals.

In serial batch experiments on EPS foams, the concentrations of α -HBCDD in the leaching fluid were between 51% and 65% below the aqueous solubility limit, with the only exception being for the final batch in which α -HBCDD concentrations are between 74% and 76% above the solubility limit. Concentrations of β -HBCDD and γ -HBCDD exceeded substantially the aqueous solubility limit in each of the batches with exception of the initial batch in which β -HBCDD concentrations were $\sim 700\ \text{ng L}^{-1}$ below the solubility limit.

Concentrations of all three HBCDD diastereomers are well above the solubility limits in each batch in which XPS is the material tested. This suggests that abrasion plays an important role in leaching HBCDD from XPS foam in these leaching chamber experiments.

Overall – although longer term experiments are required to confirm this - this serial batch experiment indicates that replenishment of leaching fluid as would be expected in a landfill may

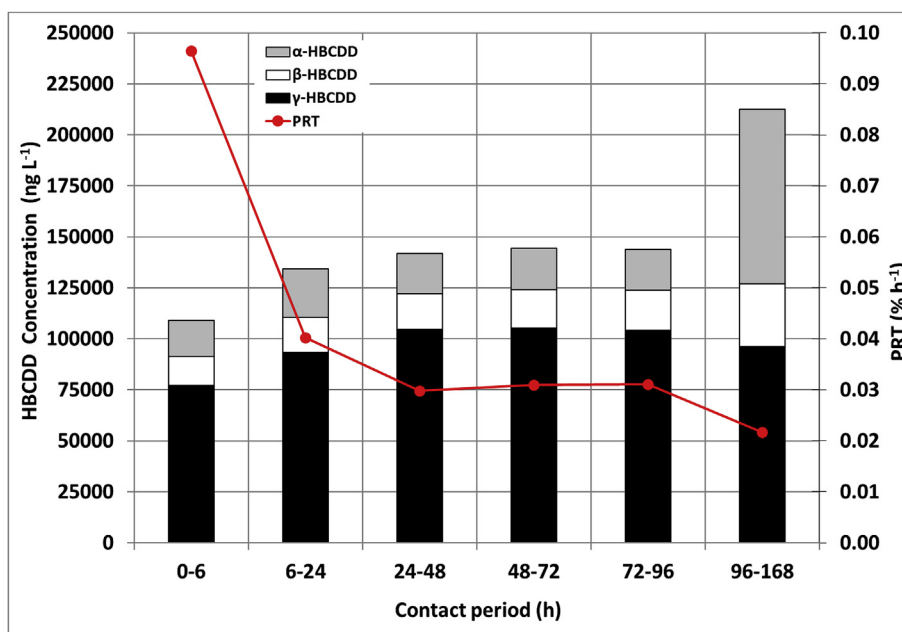


Fig. 3. Average ($n = 2$) HBCDD concentrations (ng L^{-1}) (bars) and *PRT* values ($\% \Sigma\text{HBCDD h}^{-1}$) (red circles) in leaching fluids produced during experiments on EPS foam examining the effect of cyclical wetting and draining.

facilitate HBCDD leaching from building insulation foams over long periods.

3.4. Effects of temperature and humic matter content of leaching fluid on HBCDD leaching from EPS and XPS foams

Within a landfill, temperatures can sometimes reach as high as 80–90 °C due to heat released during aerobic degradation [31]. Therefore, the influence on PRT of leachate temperatures of 20 °C, 50 °C and 80 °C were investigated.

The influence of temperature on HBCDD concentrations and mean PRT values (% h⁻¹) in leaching fluid in single batch experiments conducted at three different DHM concentrations for EPS foams and XPS foams are illustrated in Fig. 4. HBCDD concentrations, mean PL (%) and mean PRT values (% h⁻¹) are provided in SI (Table S8).

In experiments on both insulation foams, HBCDD leaching is enhanced by increasing leaching fluid temperature, regardless of DHM concentration. However, this effect is less marked in XPS foam experiments with 100 mg L⁻¹ DHM. The relative diastereomer pattern of HBCDD in leaching fluid shifts pattern towards a greater relative abundance of γ -HBCDD with increasing temperature. At 80 °C there is more α -HBCDD and less β -HBCDD and γ -HBCDD than at both 20 °C and 50 °C. XPS follows the same pattern of HBCDD diastereomer shift with increasing temperature as EPS but changes are less pronounced.

In all temperature experiments on EPS foam, concentrations of γ -HBCDD in the leaching fluids were well above the aqueous solubility limit at 20 °C. EPS foams contacted with leaching fluids at 20 °C show concentrations of α -HBCDD and β -HBCDD were below the aqueous solubility limits for all three DHM concentrations explored.

In all temperature experiments on XPS foams, concentrations of

all three diastereomers were well above the aqueous solubility limits at 20 °C; with the only exception being for β -HBCDD concentrations in 20 °C leaching fluids with no DHM, in which they were below the solubility limit (8500–14,000 ng L⁻¹).

3.5. Effects of pH and humic matter content of leaching fluid on HBCDD leaching

The pH levels used were based on realistic measured leachate pH levels that with only very few exceptions, lie in the range 5.8–8.5 [40].

The influence of pH on HBCDD concentrations and mean PRT values (% h⁻¹) in leaching fluids in single batch experiments conducted at 20 °C for EPS foams are illustrated by Table S9. HBCDD concentrations, mean PR (%) and mean PRT values (% h⁻¹) are provided in SI (Table S9).

In experiments on EPS foams contacted with leaching fluids of pH 5.8 and pH 8.5, concentrations of each HBCDD diastereomer was well above the aqueous solubility limits for each DHM concentration explored (i.e. 0, 100, 1000 ng L⁻¹); with the only exception being for β -HBCDD concentrations in leaching fluids with no DHM and pH 8.5, in which they are at the solubility limit (13,000–15,000 ng L⁻¹).

In experiments on XPS foams contacted with leaching fluids of pH 5.8 and pH 8.5, concentrations of each HBCDD diastereomer was well above the aqueous solubility limit for all three DHM concentrations explored.

In general, more HBCDD was released under acidic (5.8) and alkaline (8.5) conditions when the leaching fluid contained no DHM. When DHM solutions are present, more HBCDD is released under alkaline (8.5) conditions and less under acidic (5.8) conditions. α -HBCDD appears to be more readily released when contacted with alkaline (8.5) leaching fluids. There is relatively more α -

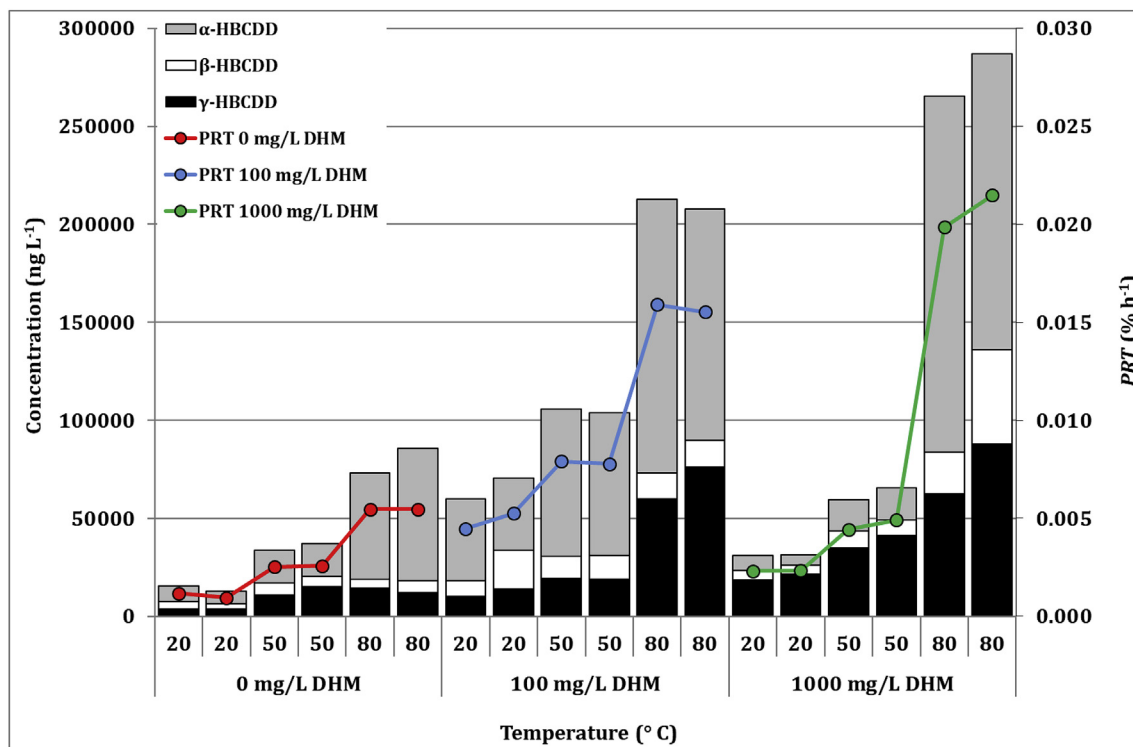


Fig. 4. HBCDD concentrations (ng L⁻¹) and PRT values (% Σ HBCDD h⁻¹) in leaching fluids produced during 24 h single batch experiments (run in duplicate) on EPS foam at different temperatures with Milli-Q, 100 mg L⁻¹ DHM and 1000 mg L⁻¹ DHM leaching fluids.

HBCDD and γ -HBCDD in acidic and alkaline leaching fluids than at the slightly acidic pH 6.5. The effect of pH appears to be smallest for the β -HBCDD diastereomer.

3.6. Effect of agitation on release of HBCDD

By comparing the results of experiments conducted at 20 °C with contact times of 24 h in the agitated contact time experiments and the non-agitated temperature experiments; the effect of agitation on release of HBCDD from the both EPS and XPS foams can be examined (Fig. 5).

The results of paired sample t-tests are presented in the SI (Table S10) and indicate that agitation strongly influences HBCDD release from building insulation foams. In experiments on EPS foam, highly significant differences ($p < 0.05$) were observed in β -HBCDD and γ -HBCDD leaching fluid concentrations between agitated and non-agitated samples. There was also a weaker significant difference ($p = 0.07$) between α -HBCDD concentrations in leaching fluids in agitated and non-agitated samples.

In XPS foam experiments, highly significant differences ($p < 0.05$) were observed for all HBCDD diastereomer concentrations between agitated and non-agitated experiments. Agitation of leaching fluids from XPS experiments containing no DHM and DHM concentrations of 100 mg L⁻¹ generated increases of total HBCDD concentrations in the leaching fluid by 590% and 195% respectively. As previously detailed, XPS foam experiments contacted with leaching fluids containing DHM concentrations of 1000 mg L⁻¹ DHM yielded lower than expected concentrations of HBCDD due to anomalous behaviour in which the humic matter was absorbed into the XPS material. Despite this behaviour, HBCDD concentrations in the leaching fluid when XPS foams were contacted with DHM concentrations of 1000 mg L⁻¹, agitation yielded increases of total HBCDD concentrations of 303%.

However, α -HBCDD concentrations in the 0 mg L⁻¹ and 1000 mg L⁻¹ DHM leaching fluids increased proportionally with

contact time more than the other diastereomers (SI; Figs. S4 and S5). This suggests that abrasion of polystyrene particles isn't the only release mechanism. Should this have been the case, the increase with contact time would have been the same for all diastereomers. More generally, if abrasion formed micro-particles are the dominant transfer mechanism, we would expect the profile in the leaching fluid to very closely match the profile in the EPS or XPS foams. For reference, the relative abundances of HBCDD diastereomers in EPS and XPS foams from single batch 24 h non-agitation experiments at 20 °C are presented in the SI (Figs. S6 and S7).

3.7. Effects of DHM on HBCDD release

In general, HBCDD concentrations and PRT values increase with increasing DHM concentrations. DHM enhances HBCDD solubility in the leaching fluid by enabling more HBCDD to be suspended in water associated with DHM. However, the DHM in leaching fluids containing 1000 mg L⁻¹ was absorbed by the XPS foam and resulting HBCDD concentrations in the analysed leaching fluid were diminished.

3.8. Statistical analysis of the whole data set

The results of a multiple linear regression analysis (MLRA) for both EPS and XPS foams are provided in SI (Table S11). Agitation of the sample had a highly significant ($p < 0.05$) positive effect on β -HBCDD and γ -HBCDD diastereomers for both EPS and XPS foams. Agitation has the largest effect (importance) on γ -HBCDD (0.490) in both EPS foams and XPS foams (0.455) suggesting that agitation enhances the release of relatively less soluble diastereomers. However, this observed effect is most likely to be due to increased abrasion and formation of micro-particles of foam that were small enough to pass through the 0.45 μ m glass fibre filter and therefore not directly related to leaching, but it does demonstrate that

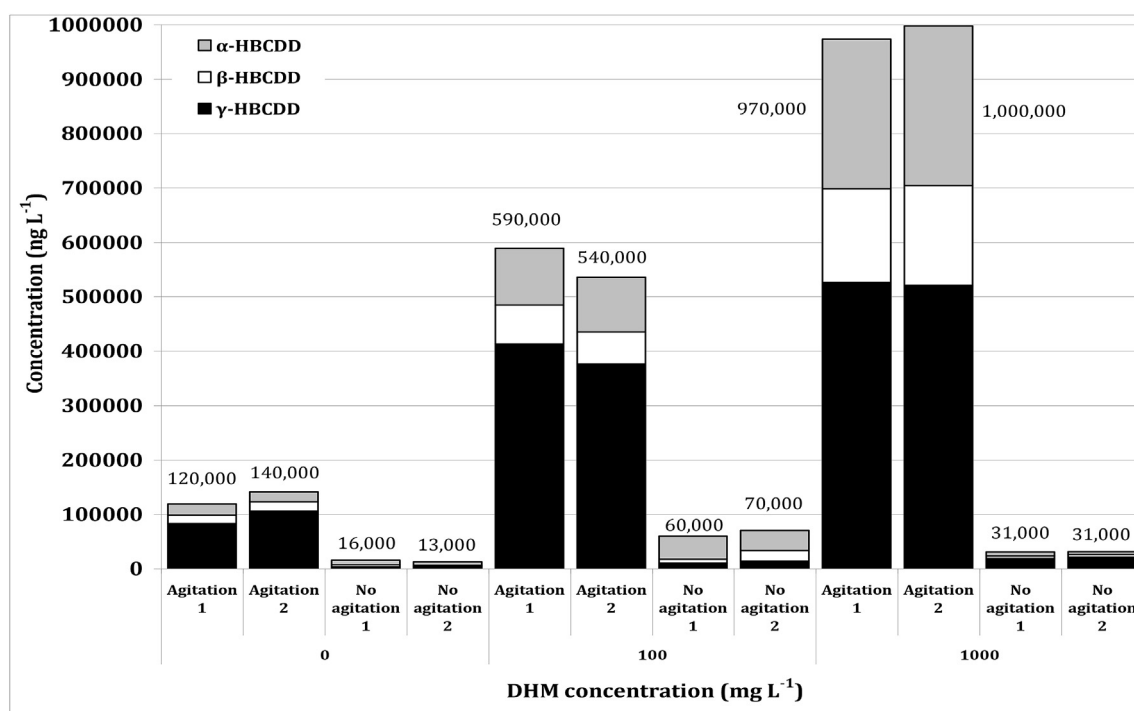


Fig. 5. HBCDD concentrations (ng L⁻¹) in leaching fluids produced during duplicate experiments examining the effects of agitation on EPS foam from 24 h single batch experiments using 0, 100 and 1000 mg L⁻¹ DHM as leaching fluid. Data labels on bars are for Σ HBCDD and rounded to two significant figures.

HBCDD from the foams may be released into landfill leachate associated with microplastics. A highly significant ($p < 0.05$) positive effect was also observed for α -HBCDD in agitated experiments on EPS foam. Elevating leaching fluid temperatures had a highly significant ($p < 0.05$) positive effect on α -HBCDD concentrations in experiments on EPS foam. DHM also has a highly significant positive effect on all diastereomers for EPS foam. This effect is not observed in the MRLA for XPS foam because of the aforementioned anomalous behaviour of DHM in XPS foam experiments.

In experiments on XPS foams, the length of contact time has a significant positive effect on all diastereomers, but only for γ -HBCDD in EPS foam experiments. The pH of the leaching fluid has a highly significant effect on α -HBCDD in XPS foam experiments, with the alkaline pH 8.5 leaching fluids eliciting the greatest concentrations.

4. Summary

This study demonstrates that leaching of HBCDD from EPS and XPS building insulation foams using distilled deionised water and DHM solutions as leaching fluid is potentially a second order process. Following an initial period of source:leaching fluid contact during which leaching is relatively facile, subsequent leaching is slower.

HBCDD concentrations in leaching fluid samples in our laboratory studies almost all exceeded the aqueous solubilities for each diastereomer and the technical HBCDD formulation. This is important because it means that agitation and abrasion play a large role in facilitating the release of HBCDD from building insulation foam materials via the formation of microplastic particles. Agitation exerted a significant positive effect on the removal of HBCDD from both EPS and XPS foams. It is likely that both dissolution and abraded micro-particles are driving mechanisms in the release of HBCDD. It also means that the aqueous solubility limit does not necessarily limit the viable amount of HBCDD present in leachates as the HBCDD is associated with fine abraded particles of the foam. In a landfill environment, deposited wastes are subjected to size reduction, compaction and percolation of waters, resulting in abrasion and degradation of the foam materials. Our data suggest building insulation foams could be a substantial source of HBCDD to landfill leachate.

The length of contact time had a significant positive effect on the release of all HBCDD diastereomers from XPS foams and γ -HBCDD from EPS foams. Enhanced abrasion from longer contact times facilitates HBCDD release from EPS/XPS foam and this is particularly highlighted for the least soluble diastereomer γ -HBCDD.

The presence of DHM had significant positive effects on HBCDD release from EPS foams. In leaching fluids containing 1000 mg L^{-1} DHM the XPS absorbed the humic matter and resulting HBCDD concentrations in leaching fluids were reduced. This difference in behaviour between the two foams is likely to be because the XPS foam is more porous and permeable than the relatively more rigid and tough EPS foam.

Temperature was identified by MLRA as having a significant positive effect on the release of α -HBCDD from EPS foams. In general, elevated temperatures elicited greater concentrations of HBCDD in leaching fluids from both foams.

Overall, pH has only a small effect on the release of HBCDD from building insulation foams. Leaching fluids with an alkaline pH 8.5 had a significant positive effect on α -HBCDD release from EPS foams only.

The data presented here are preliminary and to the author's knowledge, there are no comparable studies examining HBCDD leaching from waste materials in the literature. Further work is required to bridge knowledge gaps and develop a greater

understanding of HBCDD leaching behaviour from HBCDD treated materials in order to accurately gauge the magnitude of the problem.

Acknowledgements

The authors acknowledge gratefully the provision of an Open Competition CASE studentship award to WAS by the UK Natural Environment Research Council (NERC ref NE/I018352/1). Additional financial support to WAS from Ricardo-AEA is also acknowledged gratefully. The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007–2013) under grant agreement 295138 (INTERFLAME).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.emcon.2019.02.003>.

References

- [1] P.O. Darnerud, Brominated flame retardants as possible endocrine disrupters, *Int. J. Androl.* 31 (2008) 152–160.
- [2] P.O. Darnerud, Toxic effects of brominated flame retardants in man and in wildlife, *Environ. Int.* 29 (2003) 841–853.
- [3] L.T. van der Ven, T. van de Kuil, P.E. Leonards, W. Slob, H. Lilienthal, S. Litens, M. Herlin, H. Hakansson, R.F. Canton, M. van den Berg, T.J. Visser, H. van Loveren, J.G. Vos, A.H. Piersma, Endocrine effects of hexabromocyclododecane (HBCDD) in a one-generation reproduction study in Wistar rats, *Toxicol. Lett.* 185 (2009) 51–62.
- [4] L.T. van der Ven, A. Verhoef, T. van de Kuil, W. Slob, P.E. Leonards, T.J. Visser, T. Hamers, M. Herlin, H. Hakansson, H. Olausson, A.H. Piersma, J.G. Vos, A 28-day oral dose toxicity study enhanced to detect endocrine effects of hexabromocyclododecane in Wistar rats, *Toxicol. Sci.* 94 (2006) 281–292.
- [5] T. Yamada-Okabe, H. Sakai, Y. Kashima, H. Yamada-Okabe, Modulation at a cellular level of the thyroid hormone receptor-mediated gene expression by 1,2,5,6,9,10-hexabromocyclododecane (HBCDD), 4,4'-diiodobiphenyl (DIB), and nitrofen (NIP), *Toxicol. Lett.* 155 (2005) 127–133.
- [6] A. Covaci, A.C. Gerecke, R.J. Law, S. Voorspoels, M. Kohler, N.V. Heeb, H. Leslie, C.R. Allchin, J. De Boer, Hexabromocyclododecanes (HBCDDs) in the environment and humans: a review, *Environ. Sci. Technol.* 40 (2006) 3679–3688.
- [7] C.A. de Wit, An overview of brominated flame retardants in the environment, *Chemosphere* 46 (2002) 583–624.
- [8] C.A. de Wit, M. Alae, D.C.C. Muir, Levels and trends of brominated flame retardants in the Arctic, *Chemosphere* 64 (2006) 209–233.
- [9] A.C. Gerecke, M. Kohler, M. Zennegg, P. Schmid, N.V. Heeb, Detection of α -isomer dominated HBCD (hexabromocyclododecane) in Swiss fish at levels comparable to PBDEs (polybrominated diphenyl ethers), *Organohalogen Compd.* 61 (2003) 155–158.
- [10] S. Harrad, J. Desborough, M.A.-E. Abdallah, An overview of contamination of the UK environment with HBCDD and its degradation products, *Organohalogen Compd.* 72 (2010) 193–196.
- [11] S. Harrad, M.A.-E. Abdallah, N.L. Rose, S.D. Turner, T.A. Davidson, Current-use brominated flame retardants in water, sediment, and fish from English Lakes, *Environ. Sci. Technol.* 43 (2009a) 9077–9083.
- [12] K. Janak, A. Covaci, S. Voorspoels, G. Becher, Hexabromocyclododecane (HBCD) in marine species from the Western Scheldt Estuary: diastereomer and enantiomer-specific accumulation, *Environ. Sci. Technol.* 39 (2005) 1987–1994.
- [13] M. Kohler, M. Zennegg, C. Bogdal, A.C. Gerecke, P. Schmid, N.V. Heeb, M. Sturm, H. Vonmont, H.-P. Kohler, W. Giger, Temporal trends, congener patterns, and sources of octa-, nona-, and decabromodiphenyl ethers (PBDE) and hexabromocyclododecanes (HBCD) in Swiss lake sediments, *Environ. Sci. Technol.* 42 (2008) 6378–6384.
- [14] R.J. Law, C.R. Allchin, J. de Boer, A. Covaci, D. Herzke, P. Lepom, S. Morris, R.J. Tronczynski, C.A. de Wit, Levels and trends of brominated flame retardants in the European environment, *Chemosphere* 64 (2006) 187–208.
- [15] R.J. Law, M. Kohler, N.V. Heeb, A.C. Gerecke, P. Schmid, S. Voorspoels, A. Covaci, G. Becher, K. Janak, C. Thomsen, Hexabromocyclododecanes challenge scientists and regulators, *Environ. Sci. Technol.* 39 (2005) 281A–287A.
- [16] C.H. Marvin, G.T. Tomy, M. Alae, G. MacInnis, Distribution of hexabromocyclododecanes in Detroit River suspended sediments, *Chemosphere* 64 (2006) 268–275.
- [17] M. Remberger, J. Sternbeck, A. Palm, L. Kaj, K. Strömberg, E. Brorström-Lundén, The environmental occurrence of hexabromocyclododecane in Sweden, *Chemosphere* 54 (2004) 9–21.
- [18] G.T. Tomy, W. Budakowski, T. Halldorson, D.M. Whittle, M.J. Keir, C. Marvin, G. MacInnis, M. Alae, Biomagnification of alpha- and gamma-

- hexabromocyclododecane isomers in a Lake Ontario food web, *Environ. Sci. Technol.* 38 (2004) 2298–2303.
- [19] European Chemicals Agency (ECHA), Candidate list of substances of very high concern for authorisation, Available at: <http://echa.europa.eu/candidate-list-table>, 2014. (Accessed 9 December 2014).
- [20] United Nations Environment Programme (UNEP), Risk management evaluation on hexabromocyclododecanes, in: Stockholm Convention Document for 7th POP Reviewing Committee Meeting (UNEP/POPS/POPRC.7/5), 2011. Available at: <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC7/POPRC7Documents/tabid/2267/ctl/Download/mid/7441/Default.aspx?id=149&ObjID=13241>. (Accessed 24 September 2013).
- [21] European Commission, Final Report: Study on Waste Related Issues of Newly Listed POPs and Candidate POPs, 2011.
- [22] C.H. Marvin, G.T. Tomy, J.M. Armitage, J.A. Arnot, L. McCarty, A. Covaci, V.H. Palace, Hexabromocyclododecane: current understanding of chemistry, environmental fate and toxicology and implications for global management, *Environ. Sci. Technol.* 45 (2011) 8613–8623.
- [23] 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.
- [24] W.A. Stubbings, S. Harrad, Extent and mechanisms of brominated flame retardant emissions from waste soft furnishings and fabrics: a critical review, *Environ. Int.* 71 (2014) 164–175.
- [25] J. Arnot, L. McCarty, J. Armitage, L. Toose-Reid, F. Wania, I. Cousins, An evaluation of hexabromocyclododecane (HBCD) for persistent organic pollutant (POP) properties and the potential for adverse effects in the environment. European brominated flame retardant industry panel (EBFRIP), Available at: <http://www.unece.org/unece/search?q=hbcd>, 2009. (Accessed 2 December 2014).
- [26] European Commission, Risk Assessment Report on Hexabromocyclododecane: Environmental Part, 2008.
- [27] F. Oliaei, R. Weber, A. Watson, PBDE contamination in Minnesota landfills, waste water treatment plants and sediments as PBDE sources and reservoirs, *Organohalogen Compd.* 72 (2010) 1346–1349.
- [28] F. Oliaei, P. King, L. Phillips, Occurrence and concentrations of polybrominated diphenyl ethers (PBDEs) in Minnesota environment, *Organohalogen Compd.* 58 (2002) 185–188.
- [29] M. Osako, Y.-J. Kim, S. Sakai, Leaching of brominated flame retardants in leachate from landfills in Japan, *Chemosphere* 57 (2004) 1571–1579.
- [30] H. Takigami, M. Watanabe, N. Kajiwara, Destruction behavior of hexabromocyclododecanes during incineration of solid waste containing expanded and extruded polystyrene insulation foams, *Chemosphere* 116 (2014) 24–33.
- [31] 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.
- [32] S. Morris, C.R. Allchin, B.N. Zegers, J.J.H. Haftka, J.P. Boon, C. Belpaire, P.E. Leonards, P.J. Van Leuwen, J. de Boer, Distribution and fate of HBCD and TBBPA brominated flame retardants in North Sea estuaries and aquatic food webs, *Environ. Sci. Technol.* 38 (2004) 5497–5504.
- [33] S. Suzuki, A. Hasegawa, Determination of hexabromocyclododecane diastereoisomers and tetrabromobisphenol A in water and sediment by liquid chromatography/mass spectrometry, *Anal. Sci.* 22 (2006) 469–474.
- [34] S. Harrad, M.A.-E. Abdallah, N.L. Rose, S.D. Turner, T.A. Davidson, Current-use brominated flame retardants in water, sediment, and fish from English Lakes, *Environ. Sci. Technol.* 43 (2009b) 9077–9083.
- [35] J.K. Oh, K. Kotani, S. Managaki, S. Masunaga, Levels and distribution of hexabromocyclododecane and its lower brominated derivative in Japanese riverine environment, *Chemosphere* 109 (2014) 157–163.
- [36] G. Becher, The stereochemistry of 1,2,5,6,9,10-hexabromocyclododecane and its graphic representation, *Chemosphere* 58 (2005) 989–991.
- [37] R. Köppen, R. Becker, C. Jung, I. Nehls, On the thermally induced isomerisation of hexabromocyclododecane stereoisomers, *Chemosphere* 71 (2008) 656–662.
- [38] W.A. Stubbings, N. Kajiwara, H. Takigami, S. Harrad, Leaching behaviour of Hexabromocyclododecane from treated curtains, *Chemosphere* 144 (2016) 2091–2096.
- [39] 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.
- [40] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, *J. Hazard Mater.* 150 (2008) 468–493.