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Research article

Polychlorinated biphenyls (PCBs), hexabromocyclododecanes (HBCDDs) and degradation products in topsoil from Australia and the United Kingdom

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ABSTRACT

Hexabromocyclododecane (HBCDD) is listed under the Stockholm Convention on persistent organic pollutants, yet very few data are available on HBCDD concentrations in soil. Median concentrations of total hexabromocyclododecanes (ΣHBCDDs) from soils from the UK (n = 24) were 0.73 ng g^{-1} dry weight (range <0.01–430 ng g^{-1}) and exceed significantly (p = 0.002) those in Australian soils (n = 17, median = 0.10 ng g^{-1}, range <0.0002–5.6 ng g^{-1}). Concentrations of polychlorinated biphenyls (PCBs) (average = 4.7 ng ΣPCBs g^{-1}, range = 0.39–21 ng g^{-1}) were determined in 19 UK samples and found to be statistically indistinguishable (p > 0.05) from those of HBCDDs; thereby underlining the extent to which HBCDDs have migrated into the UK environment. Moreover, PCB concentrations in this study are not markedly lower than those recorded in UK soils sampled in the mid-1980s indicating that the initial rapid decline in UK contamination with PCBs following bans on their manufacture and use, has not been maintained. Degradation products of HBCDD: pentabromocyclododecenes (PBCDs) and tetrabromocyclododecadienes (TBCDs) were detected in some UK soil samples with semi-quantitative concentrations ranging between 0.01 and 7.3 ng g^{-1} for ΣPBCDs and 0.01–1.3 ng g^{-1} for ΣTBCDs. In Australian soils only ΣTBCDs were detected at concentrations ranging from 0.0023 to 0.45 ng g^{-1}. Chiral signatures of HBCDDs were racemic or non-racemic in all samples indicating minimal edaphic enantioselective degradation. A horizontal transect at the most contaminated UK location (a suburban garden) revealed a marked decrease in concentrations of HBCDDs with increasing distance from buildings.

1. Introduction

Hexabromocyclododecane (HBCDD) was a widely used brominated flame retardant (BFR) with a reported global market demand in 2001 of 16,700 metric tonnes, of which most (9500 t) was produced in Europe [1]. Major applications of HBCDD were as an additive to expanded and extruded polystyrene foams for thermal insulation of buildings and to a lesser degree to high impact polystyrene (HIPS) used in enclosures for electronic equipment such as TVs, along with back-coating of fabrics like sofa covers and curtains [2]. This has raised concerns because of the potential adverse health impacts of HBCDD in laboratory animals. These include: liver and thyroid hormone disruption [3,4] and reproductive disorders [5]. As a consequence of these health concerns, coupled with evidence of its persistence and capacity for bioaccumulation and long range environmental transport; in 2013, HBCDD was listed as a persistent organic pollutant (POP) by the United Nations Environment Programme (UNEP) under Annex A of the Stockholm Convention on POPs [6].

HBCDD was not bound to products chemically (i.e. it is an "additive" flame retardant) and is persistent; this coupled with its extensive use has led to demonstrable contamination of the environment and humans [7,8]. In the UK, HBCDDs have been

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quantified in a variety of matrices including air, lacustrine sediments and water [9,10], but hitherto have not been measured in soils. Although some data on HBCDD concentrations in background soil samples have emerged recently from China [11,12]; within Europe, knowledge of HBCDD contamination of soil is otherwise restricted to locations in the vicinity of industrial activities associated with HBCDD manufacture and use [13–16]. This is an important omission, given the known importance of soil as a sink for other persistent organohalogen compounds such as polychlorinated biphenyls (PCBs) [17].

We have reported previously on the presence of HBCDD degradation products, namely pentabromocyclododecenes (PBCDs) and tetrabromocyclododecadienes (TBCDs) in lacustrine sediments, indoor dust, and human milk [10,18,19]. However, there are no data on these compounds in soil that could help in further understanding the long-term environmental fate of HBCDD. In a similar vein, while enantioselective metabolism of chiral HBCDD diastereomers has been reported in humans, fish and other biota; a recent study reported no enantioselective degradation of HBCDDs in soils from China [13].

Given this background, this study reports concentrations of HBCDDs, PBCDs, and TBCDs, along with chiral signatures of HBCDDs in samples of topsoil from both the UK and Australia. To our knowledge, this study provides the first information on the presence of HBCDDs and its degradation products in Australia and the first data worldwide on HBCDD degradation products in soil. These two countries provide an opportunity to examine the extent of environmental contamination and environmental fate of HBCDD in two geographically and climatically distinct regions. Moreover, we hypothesised that the greater use of HBCDD in Europe than elsewhere, would be reflected in higher concentrations in UK than Australian soils. This study also compares HBCDD contamination of UK soils with concentrations of PCBs to provide a "benchmark" for the extent to which HBCDDs have migrated into the environment. Moreover, while PCBs are often viewed as a "legacy" contaminant following the cessation of their manufacture in the UK in the late 1970s, recent data suggests a slowing rate of decline in environmental contamination as a result of continuing emissions from buildings [20].

2. Methods and materials

2.1. Sampling strategy

Soil samples from the UK were taken to 5 cm depth at 24 different locations from a range of rural, suburban, and urban locations. At each location, three sub-samples were taken within a 1 m^2 area. These were combined and homogenised for analysis. Most samples ($n = 20$) were taken in 2005, with the remainder taken in 2008 ($n = 2$), 2009, and 2010 ($n = 1$ in each year). In all cases samples were transferred immediately in the field to hexane-rinsed amber glass bottles, prior to transport to the University of Birmingham, where they were stored in the dark at 4 °C until analysis. PCBs were analysed in 19 samples in 2005, while HBCDDs were determined in all samples in 2008 and 2009.

Additional samples ($n = 4$) were taken from a suburban garden in West London where analysis of the initial sample revealed elevated levels of HBCDDs. Samples were taken in April 2010 at increasing distances from the house at approximately 3, 5, 7 and 12 m in a 14 m length garden. These samples were analysed for HBCDDs only.

The Australian soils were collected as part of the National Dioxin Program between 2002 and 2003 [21]. The samples were taken from industrial, urban, agricultural and remote locations across Australia. In this study, samples from 17 locations were selected for analysis. They were collected from the top 10 cm using aluminium tubes from 3 subsampling sites which were combined to form a composite sample. This was sealed in aluminium foil and freeze dried prior to storage. Australian samples were analysed for HBCDDs and degradation products only.

2.2. Analytical procedures for PCBs

Analysis of UK soil samples for PCBs was conducted in accordance with previously published methodology [20,22]. In summary, samples (50 g accurately weighed) were mixed with an equal mass of pre-extracted anhydrous Na_2SO_4 and 5 g Cu powder and treated with 10 ng of internal standards (PCBs 34, 62, 119, 131, and 173), prior to Soxhlet extraction for 16 h with dichloromethane. Concentrated crude extracts were eluted through a Florisil column (5 g) with dichloromethane (50 mL). Following concentration with solvent exchange to hexane, concentrates were washed with an equal volume of concentrated H_2SO_4, prior to further Florisil chromatography (1 g, eluted with 20 mL hexane), and lipid removal via solvent exchange between dimethyl sulfoxide and hexane. Final purification to remove residual sulfur was effected via elution through a Florisil column combined with 1 g of $AgNO_3$-impregnated aluminium oxide with hexane. After concentration and solvent exchange to nonane, GC/MS analysis was conducted on a Fisons MD-800 instrument fitted with a Varian Factor 4 VF-5ms column (60 m × 0.25 mm i.d., 0.25 μm film thickness). ΣPCB concentrations reported here are the sum of the 84 individual tri- through heptachlorinated PCBs monitored (the full list is available as Supplementary Data along with information on method accuracy, precision, and detection limits).

2.3. Analytical procedures for HBCDDs

For UK soils, all analysis was conducted at the University of Birmingham. For Australian soils, sample spiking and extraction was conducted at the University of Queensland using the same HBCDD internal standards as for UK soils. Following extraction, the crude extracts of the Australian soil samples were concentrated to 1 mL and shipped to the University of Birmingham where sample purification and analysis was conducted as for UK soils.

2.4. Sample extraction and extract purification

For UK soils approximately 50 g of soil was weighed accurately into a clean glass beaker and mixed with 50 g of pre-extracted anhydrous sodium sulfate and 5 g copper powder. More sodium sulfate was added if the sample was particularly wet. The soil was then transferred to a pre-cleaned soxhlet thimble (Whatman 41 mm id, 123 mm length), spiked with 10 ng of ^{13}C α-, β-, and γ-HBCDDs as internal (or surrogate) standards, and extracted with acetone:hexane (60:40, v/v) in soxhlet apparatus for 8 h. The acetone was removed by shaking with 2 × 50 mL of distilled water, the lower aqueous phase was discarded to waste and the hexane layer retained.

For the Australian soils approximately 100 g (accurately weighed) of each sample was treated with 10 ng of ^{13}C α-, β- and γ-HBCDDs and extracted using pressurized liquid extraction (ASE 300, Dionex). Extraction conditions were: temperature 50 °C, pressure 1500 psi, heat time 5 min, static time 5 min, flush volume 50%, purge time 60 s, static cycles 3, the solvent used was hexane:dichloromethane (40:60, v/v).

Crude sample extracts were reduced using a Turbovap sample concentrator to approximately 0.5 mL, prior to transfer to a pre-cleaned column containing 50 g of acid silica topped with 1 g sodium sulfate and 3 g of copper powder and eluted with 100 mL hexane:DCM (50:50, v/v). The eluate was concentrated in a Turbovap tube to 0.5 mL in hexane, and transferred to a finger vial with washes of 3 × 0.5 mL of hexane and 2 mL of sulfuric acid added. This

was mixed well and allowed to separate for at least 2 h at 4 °C. The acid layer was carefully removed and the process repeated. The hexane layer was then passed through a florisil column containing 1.5 g of florisil topped with sodium sulfate and eluted with 30 mL hexane:DCM (50:50, v/v). Prior to instrumental analysis, samples were solvent exchanged into 200 μL methanol containing 5 ng d_{18}-γ-HBCDD as a recovery determination (or syringe) standard.

2.5. LC-MS/MS conditions

2.5.1. Determination of HBCDD diastereomers

Individual HBCDD diastereomers were separated and analysed using LC-MS/MS. The equipment used was a Shimadzu LC-20AB Prominence liquid chromatograph interfaced with a Sciex API 2000 triple quadrupole mass spectrometer. The diastereomers were separated using a C18 reversed phase analytical column (150 mm × 2 mm i.d., 3 μm particle size). The mobile phases used were (a) 1:1 methanol/water and (b) methanol at a flow rate of 150 μL min^{-1}. The elution program was started at 50% (b) then increased linearly to 100% (b) over 7 min, held for 4 min followed by a linear decrease to 60% (b) over 4 min, held for 1 min and ending with 100% (a) for 10 min. The HBCDD isomers were monitored using m/z 640.6 → 79, m/z 652.4 → 79 and m/z 657.7 → 79 for the native, ^{13}C and d_{18} analogues respectively.

2.5.2. Determination of pentabromocyclododecenes (PCBDs) and tetrabromocyclododecadienes (TBCDs)

PBCDs and TBCDs were monitored at transitions m/z 560.8 → 79 and m/z 480.4 → 79, respectively using the same LC column and conditions as for the HBCDD diastereomers [10]. These degradation products could not be accurately quantified as at the time of conducting these analyses (2010) no reference standards were available with which response factors may be calculated. Their concentrations were therefore calculated in a semi-quantitative fashion using the average relative response factor for the three HBCDD diastereomers [10].

2.5.3. Determination of enantiomer fractions

Enantiomers of α-, β-, and γ-HBCDDs were separated using a chiral permethylated cyclodextrin LC column (200 mm × 4 mm I.D., 5 ìm particle size) (NUCLEODEX beta-PM, Macherey–Nagel; GmbH & Co, Düren, Germany). The separation used mobile phases of: (a) 1:1 methanol/water with 2 mM ammonium acetate and (b) 3:7 methanol/acetonitrile at a flow rate of 500 μL/min. Starting with 50% (b) it then increased linearly to 100% (b) over 4.5 min and held for 5.5 min, followed by a linear decrease to 65% (b) over 4 min and then held for 2 min. To overcome potential matrix effects, enantiomer fractions (EFs) reported are the ratio of the (+) enantiomer over the sum of both enantiomers corrected using responses of the corresponding ^{13}C-labelled diastereomer standards [23].

2.6. Method accuracy and precision

Currently, no standard reference material exists for which there are certified concentrations for HBCDDs. Hence, we conducted 5 replicate analyses of SRM 2585 (organics in house dust) for which values have been reported previously [24]. Table SD-1 shows good agreement with previously reported values and satisfactory precision as relative standard deviations were 8, 15, and 6% for α-, β-, and γ-HBCDD respectively.

2.7. Blanks and limit of detection (LOD)

One reagent blank was run with each batch of 5 samples. For UK soils, low concentrations (equivalent up to 0.3 ng ΣHBCDDs g^{-1}) were detected, and hence the LOD was defined as 0.3 ng ΣHBCDDs g^{-1}. For Australian soils, no detectable concentrations of HBCDDs were found in reagent blanks, and the LOD for these samples is thus lower at 0.5 pg ΣHBCDDs g^{-1}.

2.8. Internal standard recoveries

These were determined in each sample relative to the d_{18}-γ-HBCDD recovery determination standard added just prior to LC-MS/MS. For UK samples, average$\pm\sigma_{n-1}$ values were 79 ± 35, 59 ± 28, and 46 ± 18% for ^{13}C α-, β-, and γ-HBCDD respectively. For Australian soils, the corresponding values were 90 ± 34, 63 ± 27, and 93 ± 34% respectively for ^{13}C α-, β-, and γ-HBCDD. We are unable to definitively account for the lower recoveries of the ^{13}C-γ-HBCDD internal standard in the UK samples, but it may suggest that pressurized liquid extraction (as provided by the ASE-300 for the Australian samples) is more effective in extracting this diastereomer than the soxhlet extraction technique employed for the UK samples. As the internal standard method corrects inherently for analyte losses, no correction is necessary for recoveries.

3. Results and discussion

3.1. HBCDD concentrations in UK and Australian soils

Table 1 summarises the concentrations of HBCDDs in both UK and Australian soils. Visual inspection, combined with Kolmogorov–Smirnov analysis, confirmed concentrations in both datasets displayed a log-normal distribution. Concentrations in UK and Australian soils were thus log-transformed prior to t-test comparison. This revealed concentrations of ΣHBCDDs in UK soils exceed significantly those in Australian soils ($p = 0.002$). This is consistent with production and use figures [1] that show European consumption of HBCDD to exceed substantially that in other regions.

There is a limited database available from other studies of HBCDDs in soil. This is summarised in Table 1 and shows concentrations in UK soils to be broadly consistent with the range reported from Belgium [25], and a variety of locations in China [11–14]. Moreover, while the concentration detected in the garden of a suburban London home (430 ng ΣHBCDDs g^{-1}) in this study was within the range reported around HBCDD production and use facilities in Europe [15,16]; concentrations in this study were generally much lower than those detected in such industrial locations.

3.2. Diastereomer patterns of HBCDDs

Previous studies have reported an almost exclusively α-HBCDD signal in biota (including humans) [10,19], that contrasts with the predominance of γ-HBCDD in the commercial formulation [26]. The average ± σ_n percentage contributions of γ-HBCDD to ΣHBCDDs in Australian and UK soils are 60 ± 19% and 82 ± 7% respectively. While in most samples, the predominant diastereomer was γ-HBCDD, α-HBCDD predominated in five of the UK samples. The causes of such diastereomer shifts in some samples are not clear, but similar enrichment of α-HBCDD has also been observed in a number of other studies into soils and sediments. In two out of three Chinese soils examined, the relative abundance of α-HBCDD was substantially higher than in the commercial product [12]; while a survey of soils from e-waste and industrial sites in China, reported α-HBCDD as the most predominant isomer in 37 of the 90 samples [13]. Moreover, α-HBCDD was predominant in around 20% of sediments from the Detroit River [27].

Table 1
Summary of Concentrations (ng g^{-1} dry weight) of HBCDDs and PCBs in Soils from Australia, the UK, and elsewhere.

Location, #samples (reference)	Median concentration (range in parentheses) of …				
	α-HBCDD	β-HBCDD	γ-HBCDD	ΣHBCDDs	ΣPCBs
UK, n = 24, (this study)	0.24 (<0.01–59)	0.07 (<0.01–28)	0.49 (<0.01–340)	0.73 (<0.01–430)	1.5 (0.39–19)
Australia, n = 17 (this study)	0.01 (<0.0002–0.47)	0.002 (<0.0001–0.16)	0.08 (<0.0002–4.9)	0.10 (<0.0002–5.6)	–
UK, n = 200 [29]	–	–	–	–	2.5 (0.27–80)
UK, n = 83 [30]	–	–	–	–	6.5 (1.7–1200)
Belgium, n = 20 [25]	–	–	–	0.18	–
Sweden (vicinity of factory using HBCDD), n = 3 [16]	–	–	–	8100 (average) (140–1300)	–
Belgium/Germany, (vicinity of HBCDD processing plants) n = 5 [15]	–	–	–	4900 (average) (110–23,000)	–
China (e-waste and industrial locations), n = 90 [13]	(0.00–62)	(0.00–13)	(0.01–220)	(0.01–280)	–
China (Chongming Island), n = 22 [11]	0.0055 ± 0.00047	0.0012 ± 0.0013	0.017 ± 0.014	0.023 ± 0.019	–
China (Guangzhou), n = 3 [12]	–	–	–	(1.7–5.6)	–
China (vicinity of HBCDD manufacturing plant), n = 7 [14]	–	–	–	(2.8–150)	–

3.3. Attenuation of HBCDD concentrations with distance from housing

Fig. 1 illustrates the concentrations of ΣHBCDDs in soil samples taken on a horizontal transect with increasing distance from housing in the suburban London garden displaying elevated concentrations. There is a clear decline in concentrations as one moves away from housing. The diastereomer pattern in all of these samples displayed a similar predominance of the γ-HBCDD (78–87%). While it is not possible to identify the exact source of the elevated concentrations in this location; the diastereomer pattern is similar to that detected in the commercial formulation [26]. Moreover, the decline in concentrations on moving away from housing and the widespread use of HBCDD in expanded polystyrene building insulation foam [28] suggests the source to be emissions from building insulation.

3.4. Comparison of concentrations of HBCDDs and PCBs in UK soils

Also summarised in Table 1 are concentrations of ΣPCBs in 19 of the UK soils analysed also for HBCDDs. A paired t-test of log-transformed data revealed no significant difference between concentrations of ΣHBCDDs and ΣPCBs in these samples. Although PCB manufacture in the UK ceased three decades ago, the presence of HBCDDs at similar levels to PCBs indicates that there has been substantial migration of HBCDDs into the UK environment.

3.5. PCBs in this study compared with previous surveys

While the locations studied in this survey were selected for convenience and do not necessarily reflect contamination across the UK, we note that the concentrations of ΣPCBs reported here (median 1.5 ng g^{-1}, range 0.39–21) are similar to those reported in a recent systematic study of 200 UK rural soils (median 2.5 ng g^{-1}, range 0.27–81) [28]. Moreover, the concentrations reported here are not markedly lower than those reported for English and Welsh soils taken in the 1980s (average = 6.5 ng g^{-1}, range 1.7–1200) [30]. This suggests that concentrations of PCBs in UK soils are declining only slowly, and supports the view that action to reduce emissions from the remaining stocks in use in the built environment are needed before further substantial reductions in concentrations can occur.

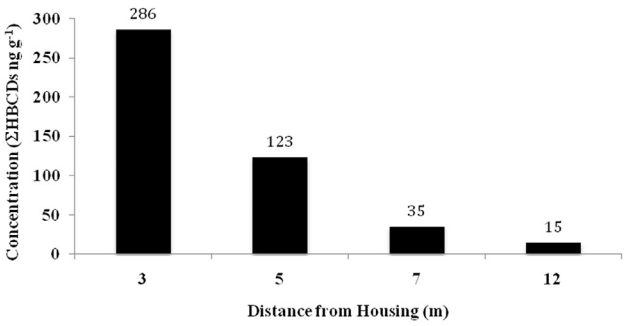

Fig. 1. Attenuation of concentrations (ng g^{-1}) of ΣHBCDDs in soil with increasing distance from housing.

3.6. Concentrations of PBCDs and TBCDs

We have previously reported the presence of the HBCDD degradation products PBCDs and TBCDs in human milk, indoor dust, and lacustrine sediments [10,18,19]. It has been suggested that these compounds are formed via sequential elimination of HBr from HBCDDs [10], but no firm evidence exists as to the relative role played by biodegradation, thermal degradation or photolysis in their formation. Table 2 reports semi-quantitative estimates of their concentrations in both Australian and UK soils. To our knowledge, this is the first report of the presence of these degradation products in soils. Given the significantly higher concentrations of HBCDDs in the UK soils; it is unsurprising that concentrations of both PBCDs and TBCDs are also greater in the UK than in Australia. Another feature of these data is that while both PBCDs and TBCDs are present in UK soils (in 7 and 6 soils respectively), only the TBCDs are detected in Australian soils (in 14 soils). In the UK soils where degradation products were detected; PBCDs > TBCDs in five samples, concentrations were equal in 1, and TBCDs > PBCDs in the remaining two samples. This predominance of PBCDs over TBCDs in most UK soils is the opposite to that observed in UK lacustrine sediments where TBCDs dominate [10]. However, as with UK sediments, we detected four PBCD and two TBCD peaks in soils. To

Table 2
Enantiomer fractions (EFs) of HBCDDs and concentrations (ng g^{-1}) of PBCDs and TBCDs in UK and Australian soils.

Parameter	Average ± σ_n in UK soils	Average ± σ_n in Australian soils
PCBDs	0.34 ± 1.48	<0.0002
TBCDs	0.13 ± 0.34	0.06 ± 0.12
EF α-HBCDD	0.506 ± 0.019	0.501 ± 0.011
EF β-HBCDD	0.502 ± 0.028	0.488 ± 0.010
EF γ-HBCDD	0.502 ± 0.017	0.500 ± 0.013

provide some insight into the origins of these degradation products, we analysed an aliquot of a HBCDD mixture (95% purity, Sigma–Aldrich, UK). Fig. SD-1 shows the PBCD patterns in a soil sample and the HBCDD mixture. While it is likely that environmental weathering and biological processes will influence HBCDD degradation and evidence of this is provided by the presence of a later eluting PBCD peak in the soil that is not present in the commercial mixture (Fig. SD-1); the presence of PBCDs and TBCDs in the commercial product suggests emissions of these degradation products from HBCDD-containing goods may be an important source of these contaminants to the environment.

3.7. Chiral signatures of HBCDDs

Table 2 also summarises the enantiomer fraction values of each HBCDD diastereomer in soil from both Australia and the UK. Similar to our previous report for UK lacustrine sediments [10], but unlike the observations in humans and fish [10,19], EFs in all samples were racemic or near-racemic, suggesting that edaphic enantioselective degradation of HBCDDs is minimal.

This study provides valuable new information about the presence of HBCDDs and its degradation products in soils. Our findings suggest that the use of HBCDD in the UK has led to environmental contamination that matches that of the legacy PCBs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.emcon.2016.03.003.

References

[1] Bromine Science Environmental Forum, Major Brominated Flame Retardants Volume Estimates. Total Market Demand by Region in 2001, 21st January 2003 (accessed June 2007), http://www.bsef.com.
[2] KEMI (National Chemicals Inspectorate) Final draft of the EU Risk Assessment Report on Hexabromocyclododecane R044_0805_env_hh.doc May 2008.
[3] L.T.M. Van der Ven, A. Verhoef, T. Van de Kuil, W. Slob, P.E.G. Leonards, T.J. Visser, T. Hamers, M. Herlin, H. Håkansson, 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.
[4] V.P. Palace, K. Pleskach, T. Halldorson, R. Danell, K. Wautier, B. Evans, M. Alaee, C. Marvin, G.T. Tomy, Biotransformation enzymes and thyroid axis disruption in juvenile rainbow trout (*Oncorhynchus mykiss*) exposed to hexabromocyclododecane diastereoisomers, Environ. Sci. Technol. 42 (2008) 1967–1972.
[5] M. Ema, S. Fujii, M. Hirata-Koizumi, et al., Reprod. Toxicol. 25 (2008) 335–351.
[6] Reports and Decisions, United Nations Environment Programme (UNEP), Persistent Organic Pollutants Review Committee (POPRC), 2014, http://chmpopsint/TheConvention/POPsReviewCommittee/OverviewandMandate/tabid/2806/Defaultaspx.
[7] E. Eljarrat, P. Guerra, E. Martinez, M. Farré, J.G. Alvarez, M. López-Teijón, D. Barceló, Hexabromocyclododecane in human breast milk: levels and enantiomeric patterns, Environ. Sci. Technol. 43 (2009) 1940–1946.
[8] L. Roosens, M. Abdallah, S. Harrad, H. Neels, A. Covaci, Exposure to hexabromocyclododecanes via dust ingestion, but not diet, correlates with concentrations in human serum, Environ. Health. Perspect. 117 (2009) 1707–1712.
[9] M.A. Abdallah, S. Harrad, A. Covaci, Hexabromocyclododecanes and tetrabromobisphenol-a in indoor air and dust in Birmingham, UK: implications for human exposure, Environ. Sci. Technol. 42 (2008) 6855–6861.
[10] S. Harrad, M.A. 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 (2009) 9077–9083.
[11] X.Z. Meng, Y.P. Duan, C. Yang, Z.Y. Pan, Z.H. Wen, L. Chen, Occurrence, sources, and inventory of hexabromocyclododecanes (HBCDDs) in soils from Chongming Island, the Yangtze River Delta (YRD), Chemosphere 82 (2011) 725–731.
[12] Z. Yu, P.A. Peng, G. Sheng, J. Fu, Determination of hexabromocyclododecane diastereoisomers in air and soil by liquid chromatography-electrospray tandem mass spectrometry, J. Chromat. A 1190 (2008) 74–79.
[13] S. Gao, J. Wang, Z. Yu, Q. Guo, G. Sheng, J. Fu, Hexabromocyclododecanes in surface soils from E-waste recycling areas and industrial areas in South China: concentrations, diastereoisomer- and enantiomer-specific profiles, and inventory, Environ. Sci. Technol. 45 (2011) 2093–2099.
[14] J. Jin, C.Q. Yang, Y. Wang, A.M. Liu, Determination of hexabromocyclododecane diastereomers in soil by ultra performance liquid chromatography-electrospray ion source/tandem mass spectrometry, Chin. J. Anal. Chem. 37 (2009) 585–588.
[15] M. Petersen, S. Hamm, U. Esser, Comparative GC/MS and LC/MS detection of hexabromocyclododecane (HBCDD) in soil and water samples, Organohalogen Compd 66 (2004) 226–231.
[16] 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.
[17] S.J. Harrad, A.P. Sewart, R. Alcock, R. Boumphrey, V. Burnett, R. Duarte-Davidson, C. Halsall, G. Sanders, K. Waterhouse, S.R. Wild, K.C. Jones, Polychlorinated biphenyls (PCBs) in the British environment: sinks, sources and temporal trends, Environ. Pollut. 85 (1994) 131–147.
[18] M.A. Abdallah, S. Harrad, Personal exposure to HBCDDs and its degradation products via ingestion of indoor dust, Environ. Int. 35 (2009) 870–876.
[19] M. Abdallah, S. Harrad, Tetrabromobisphenol-A, hexabromocyclododecane and its degradation products in UK human milk: relationship to external exposure, Environ. Int. 37 (2011) 443–448.
[20] A. Jamshidi, S. Hunter, S. Hazrati, S. Harrad, Concentrations and chiral signatures of polychlorinated biphenyls in indoor and outdoor air and soil in a major UK conurbation, Environ. Sci. Technol. 41 (2007) 2153–2158.
[21] J. Mueller, R. Muller, K. Goudkamp, M. Shaw, M. Mortimer, D. Haynes, D. Burniston, R. Symons, M. Moore, Dioxins in Soils in Australia, National Dioxins Program, Technical Report No. 5, Australian Government of Environment and Heritage, Canberra, 2004.
[22] S. Ayris, G.M. Currado, D. Smith, S. Harrad, GC/MS procedures for the determination of PCBs in environmental matrices, Chemosphere 35 (1997) 905–917.
[23] C.H. Marvin, G. MacInnis, M. Alaee, G. Arsenault, G.T. Tomy, Factors influencing enantiomeric fractions of hexabromocyclododecane measured using liquid chromatography/tandem mass spectrometry, Rapid Commun. Mass Spectrom. 21 (2007) 1925–1930.
[24] J.M. Keller, H.M. Stapleton, R. Heltsley, A. Peck, J.R. Kucklick, M. Schantz, S.A. Wise, SRMs Available from NIST for the Analysis of Brominated Flame Retardants, Poster presented at BFR07, Amsterdam, April 2007, pp. 24–27.
[25] A. Covaci, L. Roosens, A.C. Dirtu, N. Waegeneers, I. Van Overmeire, H. Neels, L. Goeyens, Brominated flame retardants in Belgian home-produced eggs: levels and contamination sources, Sci. Total Environ. 407 (2009) 4387–4396.
[26] A. Covaci, A.C. Gerecke, R.J. Law, S. Voorspoels, M. Kohler, N.V. Heeb, H. Leslie, C. Allchin, J. De Boer, Hexabromocyclododecanes (HBCDDs) in the environment and humans: a review, Environ. Sci. Technol. 40 (2006) 3679–3688.
[27] C.H. Marvin, G.T. Tomy, M. Alaee, G. MacInnis, Distribution of hexabromocyclododecane in Detroit River suspended sediments, Chemosphere 64 (2006) 268–275.
[28] AEA Technology, Costs and Benefits of the Addition of Hexabromocyclododecane (HBCDD) to the Stockholm Convention and the 1998 POPs Protocol (Report for Department for Environment, Food and Rural Affairs, Restricted Commercial, ED56226, Issue Number 5, Date 12 October 2010).
[29] E. Heywood, J. Wright, C.L. Wienburg, H.I.J. Black, S.M. Long, D. Osborn, D.J. Spurgeon, Factors influencing the national distribution of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in British soils, Environ. Sci. Technol. 40 (2006) 7629–7635.
[30] C.S. Creaser, A.R. Fernandes, S.J. Harrad, T. Hurst, Background levels of polychlorinated biphenyls in British soils – II, Chemosphere 19 (1989) 1457–1466.