TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVB SUBSTANCES

RESULTS OF THE EVALUATION OF THE PBT/VPVB PROPERTIES OF:

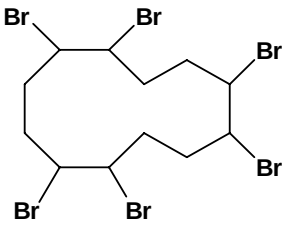
Substance name: Hexabromocyclododecane

EC number: 247-148-4

CAS number: 25637-99-4; 3194-55-6

Molecular formula: C12H18Br

Structural formula:



Summary of the evaluation:

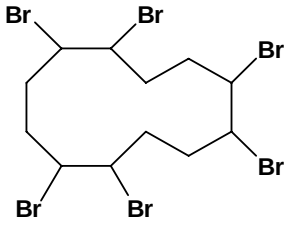
Hexabromocyclododecane (HBCDD) is considered to be a PBT–substance. It fulfils the vB criterion based on experimental data and measured data from biota. T criterion is also met. The available soil degradation simulation test data indicate, that half-life of HBCDD in aerobic soil is > 180 d. According to some of the sediment degradation simulation studies available the P-criterion is met, whereas other studies substance indicates that the substance is degradable in certain experimental conditions. However, data from dated sediment cores gives support to HBCDD being persistent also in sediment. Furthermore, HBCDD has potential for long-range environmental transport based on environmental monitoring data and modelling.

This summary relies on the EU risk assessment of HBCDD (European Commission, 2007) and the references therein.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name: Hexabromocyclododecane
EC Number: 247-148-4
CAS Number: 25637-99-4; 3194-55-6
IUPAC Name:
Molecular Formula: C12H18Br



Structural Formula:
Molecular Weight: 641.7
Synonyms: Cyclododecane, hexabromo; HBCD; Bromkal 73-6CD; Nikkafainon CG 1; Pyroguard F 800; Pyroguard SR 103; Pyroguard SR 103A; Pyrovatex 3887; Great Lakes CD-75P™; Great Lakes CD-75; Great Lakes CD75XF; Great Lakes CD75PC (compacted); Dead Sea Bromine Group Ground FR 1206 I-LM; Dead Sea Bromine Group Standard FR 1206 I-LM; Dead Sea Bromine Group Compacted FR 1206 I-CM;

1.1 Purity/Impurities/Additives

Depending on the producer, technical grade HBCDD consists of approximately 70-95 % γ-HBCDD and 3-30 % of α- and β-HBCDD due to its production method (European Commission, 2007). Two additional stereoisomers, δ-HBCDD and ε–HBCDD have been found by Heeb et al. (2005) in commercial HBCDD in concentration of 0.5 % and 0.3 %, respectively.

1.2 Physico-Chemical properties

Table 1.1 Overview of physico-chemical properties used in the EU risk assessment. For details, references and further data available, see European Commission (2007)

REACH ref Annex, §	Property	Value	Comments
VII, 7.1	Physical state at 20 C and 101.3 Kpa	White colourless solid	
VII, 7.2	Melting / freezing point	Ranges from approximately: 172-184 °C to 201-205 °C 190 °C , as an average value, was used as input data in the EU risk assessment 179-181 °C α-HBCDD	Smith et al. (2005) Smith et al. (2005)

		170-172 °C β-HBCDD 207-209 °C γ-HBCDD	
VII, 7.3	Boiling point	Decomposes at >190 °C	Peled et al. (1995)
VII, 7.5	Vapour pressure	$6.3 \cdot 10^{-5}$ Pa (21 °C)	Stenzel and Nixon (1997)
VII, 7.7	Water solubility	See Table 1.2	
VII, 7.8	Partition coefficient n-octanol/water (log value)	5.625 (technical product) 5.07 ± 0.09 α-HBCDD 5.12 ± 0.09, β-HBCDD 5.47 ± 0.10 γ-HBCDD	MacGregor and Nixon (1997) Hayward et al. (2006)
	Dissociation constant	-	

Table 1.2 Summary of the results of valid water solubility studies using generator column method, as evaluated by European Commission (2007)

Test substance	Water	Water solubility (µg l^{-1})	Reference
α -HBCDD	Water	48.8±1.9	MacGregor and Nixon (2004)
β -HBCDD		14.7±0.5	
γ -HBCDD		2.1±0.2	
HBCDD technical product, sum of above		65.6	
α -HBCDD	Salt-water medium	34.3	Desjardins et al. (2004)
β -HBCDD		10.2	
γ -HBCDD		1.76	
HBCDD technical product, sum of above		46.3	
γ -HBCDD	Water	3.4±2.3	Stenzel and Markley (1997)

2 MANUFACTURE AND USES

According to the producers, HBCDD is manufactured by bromination of the starting material *cis,trans,trans*-1,5,9-cyclododecatriene (European Commission, 2007). The uses identified in the EU risk assessment are presented in Table 2.1.

Table 2.1 Uses of HBCDD identified by European Commission (2007).

Material	Use/Function	End-products (examples)
Expandable polystyrene (EPS)	Insulation	Construction, insulation boards, (packaging material) Packaging material (minor use and not in food packaging) Insulation boards (against cold or warm) of transport vehicles e.g. lorries and caravans Insulation boards in building constructions e.g. houses' walls, cellars and indoor ceilings and "inverted roofs" (outdoor) Insulation boards against frost heaves of road and railway embankments
Extruded polystyrene (XPS)	Insulation	Construction, insulation boards, Insulation boards (against cold or warm) of transport vehicles e.g. lorries and caravans Insulation boards in building constructions e.g. houses' walls, cellars

Material	Use/Function	End-products (examples)
		and indoor ceilings and "inverted roofs" (outdoor) Insulation boards against frost heaves of road and railway embankments
High impact polystyrene (HIPS)	Electrical and electronic parts	Electric housings for VCR Electrical and electronic equipment e.g. distribution boxes for electrical lines Video cassette housings
Polymer dispersion on cotton or cotton/synthetic blends	Textile coating agent	Upholstery fabric bed mattress ticking Flat and pile upholstered furniture (residential and commercial furniture), Upholstery seatings in transportation, draperies, and wall coverings, Interior textiles e.g. roller blinds automobile interior textiles

3 CLASSIFICATION AND LABELLING

The substance is not classified under Directive 67/548/EEC.

Classification of HBCDD with N; R50/53 (very toxic to aquatic organisms) was agreed at a Technical Committee for Classification & Labelling (TC C&L)-meeting on 11-12 June, 2003. Classification for health effects has not yet been discussed and HBCDD is therefore not included in Annex I to Directive 67/548/EEC.

4 ENVIRONMENTAL FATE PROPERTIES

4.1 Degradation (P)

4.1.1 Abiotic degradation

Indirect photochemical degradation in the atmosphere is considered to be slow based on the estimated half-life of 3.2 days for the reaction with OH-radicals using AOP v1.91 (24 h day^{-1}; $5*10^5$ OH^- cm^{-3}). Wania (2003) estimated a photochemical degradation half-life of 51.2 hours using the same model but different settings.

Additionally, HBCDD has been observed to degrade in the abiotic controls of biodegradation tests described in the next section.

Hydrolysis is not likely to be a relevant path of degradation for HBCDD already due to its very low water solubility.

4.1.2 Biotic degradation

One reliable ready biodegradability test result is available for HBCDD. Schaefer and Haberlein (1996) observed no degradation in an OECD 301D –test with a test concentration of 7.7 mg l^{-1}. Based on the result, HBCDD is considered to be not readily biodegradable.

Two large degradation simulation studies and supporting screening tests have been conducted by Davis et al. (2003a, b and 2004). Below the results and test conditions are briefly discussed. More details are presented by European Commission (2007).

Simulation tests, soil

In an aerobic soil-dissipation study according to OECD 307 (Davis et al., 2003a), γ-HBCDD disappeared with a half-life of ca. 4 months (119 days) at 12 ^{o}C from sandy loam soil amended with 5 mg kg^{-1} sewage sludge. The nominal test concentration was 25 µg technical HBCDD kg^{-1} dw. In abiotic soil samples almost no dissipation occurred during 119 days indicating that biotic mechanisms may be involved in the dissipation of γ-HBCDD from aerobic soil. However, no transformation products were detected and the fate of the α- and β-diastereomers was not studied. The extraction method was not completely reliable (recovery relatively low) and thus, the half-lives derived from this study may not solely represent biodegradation.

In an aerobic soil simulation study of Davis et al. (2004) conducted according to OECD 307, no indications of any transformation of ^{14}C-HBCDD during 112 days of incubation at 20±2^{o}C were observed. The nominal test concentration was 3.0 mg technical HBCDD kg^{-1} dw. The recovery of radioactivity was very good throughout the test. Even if metabolites would have been formed at levels below the detection limit (0.4 % of added radioactivity), such potential transformation is not considered to contradict the indicated persistence of HBCDD in soil. The result from this study also supports the assumption that the results of Davis et al. (2003a) may overestimate the degradability of HBCDD in soil.

Simulation tests, sediment

In a simulation study of Davis et al. (2003a) only the disappearance of the γ-diastereomer was followed, since the test concentration was too low to allow for quantification of the α- and β-diastereomers. The test was performed at 20±1^{o}C with nominal test concentrations of 34 and 60 µg technical HBCDD kg^{-1} dw in two different sediments. The disappearance of γ-HBCDD from the aquatic water/sediment systems resulted in approximate DT50-values of 21 and 61 days (recalculated to 12 ^{o}C) under **aerobic** conditions in the two systems, respectively. The disappearance half-lives under **anaerobic** conditions were around 2 days in both systems (recalculated to 12 ^{o}C). Lack of disappearance in abiotic samples (steam sterilisation at 120^{o} C; 15 psi; 60 minutes) indicates that biotic mechanisms were probably involved. No degradation products were detected, neither in the headspace of the microcosms nor in the water or sediment phases. Since radiolabelled substance was not used and test concentrations were very low, mineralisation of HBCDD could not be followed and no mass balance could be established. It is noted that the recovery varied significantly (33-125 %) indicating problems with the extraction method. Therefore, it is not certain that the disappearance in this study only reflects biodegradation. The half-life values obtained from this study may overestimate the degradability of γ-HBCDD.

In the second sediment simulation study (Davis et al., 2004), the aim was to identify potential metabolites by means of using ^{14}C-labelled HBCDD and optimised methods for the extraction and analyses. By using approximately 100-fold higher HBCDD concentrations than in the simulation study of Davis et al. (2003a) (4.7 mg kg^{-1} dw in aerobic sediment, 4.3 mg kg^{-1} dw in anaerobic sediment) the disappearance of the α- and β-diastereomers could also be followed. There were no indications of an influence of HBCDD on the biological activity of the samples. Table 4.1 provides an overview of the results.

Table 4.1 Estimated primary degradation half-lives of HBCDD derived from the results of the degradation simulation tests of Davis et al. (2004) for the EU risk assessment (European Commission, 2007).

Medium/Standard	Sampling site	Degradation half-life of HBCDD in viable	Dgradation half-life of HBCDD in abiotic

		flasks (value in parenthesis corrected to 12 °C)	flasks (value in parenthesis corrected to 12 °C)
Aerobic sediment/OECD 308	Schyukill River, Valley Forge, Pennsylvania, U.S.	Total HBCDD: 101 d (191 d) α-HBCDD: 113 d (214 d) β-HBCDD: 68 d (129 d) γ-HBCDD: 104 d (197 d)	Not estimated
Anaerobic sediment/ OECD 308	Schyukill River, Valley Forge, Pennsylvania, U.S.	Total HBCDD: 66 d (125 d) α-HBDD: 113 d (ca. 210 d) β-HBCDD: 44 d (ca. 80 d) γ-HBCDD: 65 d (ca. 125 d)	Not estimated

The study of Davis et al. (2004) also showed that HBCDD undergoes a step-wise reductive dehalogenation via tetrabromocyclododecene and dibromocyclododecadiene to 1,5,9-cyclododecatriene in aerobic as well as anaerobic sediment (see Figure 4.1). There were no indications of further transformation of 1,5,9-cyclododecatriene as no CO_2 or other volatiles were formed during the course of the study.

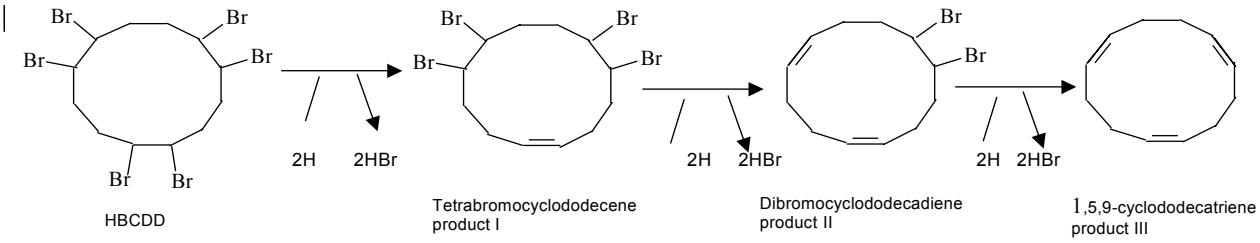


Figure 4.1. Stepwise dehalogenation of HBCDD (Davis et al., 2004).

Degradability of 1,5,9-cyclododecatriene (CDT) has been studied in two reliable modified ready biodegradation tests (Davis et al., 2006a, Davis et al., 2006b). CDT clearly is not ready biodegradable, but does not fulfil the P criterion of the TGD, either. The properties of CDT have been described in the PBT summary no. 39. Despite the fact, that primary degradation and even mineralisation was observed in two reliable biodegradation screening tests with CDT, no mineralisation was observed in the simulation and screening degradation studies with HBCDD. This is likely to have been have been caused by at least two facts. Firstly, the duration of HBCDD-experiments could not be long enough to discover any mineralisation even in those favourable conditions, where HBCDD was degraded in relevant amounts to CDT. Secondly, significant amounts of HBCDD were observed to degrade to CDT only in anaerobic conditions, whereas it is likely, that further degradation of CDT would need aerobic conditions. Hence, the available degradation data on CDT cannot be directly used to judge on the overall degradation potential of HBCDD in the environment and vice versa.

4.1.3 Other information [1]

Kohler et al. (2006) found HBCDD in one Lake Greifensee (CH) sediment core, sampled at a depth of 31 m, at concentrations of 2.5 µg kg^{-1} dw at the surface (year 2001), 1.8 µg kg^{-1} dw in a layer sedimented in 1995, 1.2 µg kg^{-1} dw in a layer sedimented in 1989 and 0.25 µg kg^{-1} dw (LOD) or lower in layers sedimented in 1982 and 1974. The initial exposure of sediment for the same years cannot be estimated retrospectively, and therefore it is not possible to estimate degradation half-life from the sediment core. It is nevertheless likely, that the exposure has not been considerably higher in the earlier years than in the year 2001, but more likely lower due to the increased market volumes of brominated flame retardants in the last decades. Christensen et al. (2004), Fjeld et al (2006b), Remberger et al. (2004) and Sternbeck et al. (2001) have also measured HBCDD in sediment core samples.

Although there are some uncertainties embedded to the dating of the sediment samples, the results show a significantly slower apparent decrease of HBCDD concentrations with time compared to what would be expected based on the half-lives obtained from biodegradation simulation tests.

HBCDD has been found in abiotic and biotic samples of even the most remote areas (see Table 4.2) and concentrations in biota have been increasing based on several temporal series (see section 4.3.3). These findings indicate that HBCDD behaves in the environment like a persistent substance.

4.1.4 Summary and discussion of persistence

Two large standard degradation simulation studies on HBCDD are available for sediment and soil (Davis et al., 2003a,b and Davis et al., 2004). A significantly faster disappearance was observed in the sediment tests of Davis et al. (2003a) than in the study of Davis et al. (2004). Degradation half-lives calculated based on the results of Davis et al. (2004) are for aerobic sediment at 12 ºC 214 d (α-HBCDD), 129 d (β-HBCDD) and 197 d (γ-HBCDD) and for anaerobic sediment ca. 210 d, 80 d and 125 d, respectively. No degradation was observed in the study of Davis et al. (2004) in aerobic soil.

Despite significantly higher test concentrations of the study of Davis et al. (2004) compared to the study of Davis et al. (2003a), there are several reasons for considering the results of Davis et al. (2004) more reliable. Firstly, no mass balance could be made and the recovery was generally bad at the start in the tests of Davis et al. (2003a). Dissipation to non-extractable residues and problems with extraction may have influenced the results. Furthermore, brominated degradation products were not detected at any time in the microcosms according to the authors. In the degradation simulation tests of Davis et al. (2004) a mass balance could be derived. Non-extractable adsorption to soil occurred only in the viable aerobic microcosms, which encountered for the ^{14}C-HBCDD losses observed in the extract. In abiotic control of the aerobic soil test and in the sediment tests the radioactivity was recovered in the extracts at a very good level throughout the study. The authors could also follow the emergence of several degradation products. The amount of HBCDD mineralised (measured as $^{14}CO_2$) and other volatile ^{14}C-degradation products were monitored and remained negligible in all tests. Davis et al. (2004) observed, that α-HBCDD was degraded more slowly in the sediment test than β- and γ-HBCDD.

1,5,9-cyclododecatriene (CDT) was observed by Davis et al (2004) to be the main degradation product of HBCDD. Data on CDT have been presented in the PBT summary no. 39. Despite the fact, that primary degradation and even mineralisation has been observed in two reliable

[1] For example, half life from field studies or monitoring data

biodegradation screening tests with CDT, no mineralisation was observed in the simulation and screening degradation studies with HBCDD. This may be explained by the duration of HBCDD-experiments could not be long enough to discover any mineralisation even in those favourable conditions, where HBCDD was degraded in relevant amounts to CDT. In addition, significant degradation of HBCDD to CDT was observed only in anaerobic conditions, whereas it is likely, that further degradation of CDT would need aerobic conditions. Hence, the available degradation data on HBCDD cannot be directly used to judge on the overall degradation potential of CDT in the environment and vice versa.

In addition to the experimental data, HBCDD has been found in abiotic and biotic samples of even the most remote areas and concentrations in biota have been increasing based on several temporal series. Furthermore, sediment core samples analysed indicate a slower degradation of HBCDD in sediment than what would be expected based on the simulation studies. It is concluded, that HBCDD is persistent in the environment, although it has been observed to degrade in certain experimental conditions in the aquatic environment.

4.2 Environmental distribution

4.2.1 Adsorption

No experimental data on adsorption are available. A logKoc of 4.66 has been derived by European Commission (2007) indicating very high adsorption potential. HBCDD's mobility in soil and sediment can be expected to be very low.

4.2.2 Volatilisation

Based on the measured vapour pressure (6.3×10^{-5} Pa at 20 °C), HBCDD is very slightly volatile. Henry's law constant at 20-25 °C is 0.75 Pa m^3 mol^{-1} using the sum of the water solubilities of the individual diastereomers (66 µg l^{-1}). HBCDD has hence a low potential to evaporate from aqueous surfaces. Due to the low volatility and high adsorption potential to suspended matter, evaporation of HBCDD seems to be a less important route of distribution.

4.2.3 Long-range environmental transport

HBCDD has a very slow atmospheric degradation rate (half-life > 2 days, see section 4.1.1), which indicates potential for long-range atmospheric transport in vapour phase. Despite of this, due to the low volatility and high adsorption potential, the majority of long-range environmental transport of HBCDD is likely to occur in aerosol form (Wania, 2003).

Measured data from remote regions provide evidence that HBCDD is subject to long-range environmental transport (see Table 4.2). In addition to data in Table 4.2, HBCDD has also been found in birds (i.e., in eggs, liver, blood) in remote Arctic areas in several studies. HBCDD has been found in these studies in the majority of samples (see European Commission, 2007, for references).

Table 4.2 Measured environmental concentrations of HBCDD in remote Arctic areas (bird data excluded).

Species, sample type/	Location; sampling yeasr	Concentration	Reference
Air	Ammarnäs, northern Sweden	5.7 pg HBCDD/m^3 in particulate phase 0.2 pg HBCDD/m^3 in vapour phase	Bergander et al. (1995)
	Pallas, Finland	0.003 ng HBCDD/m^3 (autumn 2000), total conc. 0.002 ng HBCDD/m^3 (winter 2001), total conc.	Sternbeck et al. (2001)
Deposition	Pallas, Finland	13 ng/m^2 d, precipitation 21 mm (autumn 2000) 5.1 ng/m^2 d. precipitation 4 mm (winter 2001)	Sternbeck et al. (2001)
Sediment	Ellasjøen, Bjørnøya, Svalbard, Norway	3.8 ng γ-HBCDD /g dw in a sediment layer corresponding years 1973-1987. α- and β-HBCDD were below LOD. All diastereomer concentrations in top layer (1987-2001) and earlier than 1973 were < LOD.	Christensen et al. (2004)
Invertebrates			
Gammarus wilkitzkii	North Atlantic, Svalbard area, Norway; 2003	Not detected	Sørmo et al. (2006)
Fish			
Polar cod (*Boreogadus saida*); whole fish	Svalbard, Norway; 2003	1.73 µg HBCDD/kg lw (median); min-max: 1.38-2.87, n = 7	Sørmo et al. (2006)
Polar cod (*Boreogadus saida*); whole fish	Bjørnøya, Svalbard, Norway; 2003	11.7 ±7.2 µg HBCDD/kg lw (mean±SD), n = 6	Jenssen et al. (2007)
Mammals			
Polar bear (*Ursus maritimus*), adipose tissue (females)	Svalbard, Norway; 2002	26±9.0 µg HBCDD/kg ww (mean±SD), min-max: 9.7-45, n = 15	Gabrielsen et al. (2004)
Polar bear (*Ursus maritimus*), adipose tissue (males)	Svalbard, Norway; 2002-2003	12.6 µg HBCDD/ kg lw (median); min-max: 5.31-16.51, n = 4	Sørmo et al. (2006)
Harbor seal (*Phoca vitulina*), blubber	Svalbard, Norway; 2003	3.66±1.54 µg HBCDD/kg lw (mean±SD), n=5	Jenssen et al. (2007)
Ringed seal (*Pusa hispida*), blubber	Svalbard, Norway; 2003	16.96 µg HBCDD/kg lw (median); min-max: 14.6-34.5, n = 6	Sørmo et al. (2006)

Additionally, Ueno et al. (2006) have determined half-distances for HBCDD, polybrominated diphenyl ethers and "existing" POPs (see Table 4.3).

Table 4.3 Calculated half-distances for HBCDD, PBDEs and POPs in the North Pacific based on skipjack tuna monitoring (compiled in Ueno et al., 2006).

Substance	Number of sites	Correlation coefficient (r^2)	Half-distance±SE (km)
α –HCH	5	0.83	-1700±480
α-HBCDD	4	0.45	8500 ±6700
γ-HBCDD	4	0.73	1600±680
BDE-99	5	0.87	1400±320

BDE-153	5	0.79	1200±380
2378-T4CDF	5	0.93	3200±530
23478-P5CDF	5	0.87	2100±470
∑PCBs	5	0.77	1500±480
p,p'-DDT	5	0.91	950±170

Half-distance was in this study defined as the distance from the source (Japan), where the concentration in tuna muscle drops to 50 % of the concentration at/near the source. Although the authors state, that concentration in tuna muscle lipids reflects well the concentration of pollutants in water at the sampling site, it must be noted, that this method cannot distinguish between long-range transport via air and water, although it can apparently exclude the impact of migration.

According to the authors, the half-distance of HBCDD reflected one of the highest long-range transportabilities among the substances investigated. However, it must be noted, that for HBCDD, significance of the distance-to-concentration correlation was very low (r^2 = 0.45; p=0.33) and standard errors of the estimates were rather high probably due to the low amount of sites included (four sites used as the basis of the regression). Nevertheless, when the results for HBCDD are considered together with the results of other organohalogen compounds studied, the findings of Ueno et al. (2006) can be taken as evidence of a high long-range transport potential for HBCDD.

4.3 Bioaccumulation (B)

4.3.1 Screening data

A measured logKow of 5.625 is available for the technical product. In another study (Hayward, et al. 2006) logKow was estimated for the individual diastereomers to be 5.07 for α- , 5.12 for β- and 5.47 for γ-HBCDD.

4.3.2 Measured bioaccumulation data

Bioconcentration in fish has been determined in two reliable flow-through tests.

Veith et al. (1979) carried out a 32-day flow-through test with *Pimephales promelas*. Mean test concentration was 6.2 µg l^{-1} and test temperature 25 ± 0.5 ºC. The steady-state BCF was calculated to be 18 100.

Drottar and Krueger (2000) conducted a flow-through test according to OECD 305 (and corresponding ASTM and U.S. EPA –standards) with *Oncorhynchus mykiss*. Two exposure groups (0.34 and 3.4 µg l^{-1} nominal) and a solvent control group were run containing 85 fish per group. As test substance, HBCDD with diastereomer composition typical for a commercial product was used. Acetone was used as solvent. Duration of exposure and depuration phases was 35 days each. The aquaria were kept in a temperature of 12 ± 1 ºC. Mean measured exposure concentrations during the uptake phase were 0.18 and 1.8 µg l^{-1}. Apparent steady-state whole fish BCFs of 13 085 and 8 974 were calculated for the low and high exposure group, respectively. Corresponding kinetic BCFs were 21 940 and 16 450. BCFs calculated for muscle were also all above 5 000.

Law et al. (2006a) exposed juvenile rainbow trout (*Oncorhynchus mykiss*) via diet to α-, ß- and γ-HBCDD (separate aquaria for each diastereomer). Additionally, a control aquarium was run. Uptake phase lasted 56 days followed by a 112-day depuration period. Muscle samples were analysed at various points of uptake and depuration phases. No peaks of debrominated or OH-HBCDD metabolites were found in either the muscle or liver tissue extracts. The BMFs for the α-, ß- and γ-diastereomers were calculated to be 9.2, 4.3 and 7.2, respectively.

After the termination of the biomagnification test (day 168) the authors observed, that a major part of HBCDD in muscle samples of fish exposed solely to ß-HBCDD was in the form of α- and γ-HBCDD. In the fish exposed to γ-HBCDD a major part of HBCDD found was α-HBCDD. In the fish exposed to α-HBCDD, no shift to other diastereomers was found. The study shows, that the diastereomeric distribution of HBCDD can be changed by way of bioisomerisation in biological material.

Additionally, Janák et al. (2005b) observed diastereomer and enantiomer selective metabolisation rates in microsomal liver preparations of common dab (*Limanda limanda*). According to the authors, α-HBCDD was least biotransformed of the main three diastereomers tested.

4.3.3 Other supporting information[2]

A large set of data on measured concentrations in biota and few trophic transfer studies are available and have been presented comprehensively by European Commission (2007). In the following, only a small part of that information is presented.

Measured concentrations in European surface waters and in freshwater fish as compiled by European Commission (2007) indicate, that HBCDD accumulates in fish in the field. The recent very few measurements of HBCDD in filtered water samples in European surface waters (n=14) show a range from 0.016 (or below detection limit) to 1.5 µg l^{-1} (point source recipient site, River Skerne). Table 4.4 provides an overview of the measured concentrations in freshwater fish muscle in Europe.

Table 4.4 Statistical overview of measured HBCDD concentrations in muscle of freshwater fish in the EU and Norway. The percentiles were calculated using Weighted Average at X(n+1)p (European Commission, 2007).

	Conc.	n	Median	Geometric mean	Arithmetic mean ± SD	90P	Min	Max
All values	µg HBCDD kg^{-1} ww	151	5.5	4.64	321 ± 1130	834	0.005	9432
	µg HBCDD kg^{-1} lw	151	120	171	5223 ± 18745	7927	0.52	160905

It is noted, that concentration in whole fish can be expected to be even higher.

Table 4.5 provides an overview of measured concentrations of HBCDD in fish and marine mammals in Europe.

Table 4.5 Median concentrations of HBCDD in marine mammals and fish muscle collected from specific European regions. As for marine mammals the concentration in blubber is reported conventionally, the data have been converted to whole body concentrations assuming a 1/3 lipid/whole body ratio (European Commission, 2007).

[2]For example, measured concentrations in biota

Region	Species	n	Median concentration	Concentration ratios (marine mammals/fish muscle)	
				ww bw/ ww	lw/lw
Western Europe	Fish	102	0.40 µg HBCDD kg^{-1} ww	272	28
		100	13 µg HBCDD kg^{-1} lw		
	Marine mammals	225	109 µg HBCDD kg^{-1} ww		
		225	368 µg HBCDD kg^{-1} lw		
Baltic Sea	Fish	42	0.31 µg HBCDD kg^{-1} ww	61	5.8
		38	11.5 µg HBCDD kg^{-1} lw		
	Marine mammals	2 (representing 20 + 30 individuals)	19 µg HBCDD kg^{-1} ww		
		2	67 µg HBCDD kg^{-1} lw		
WesternScheldt (approx. region)	Fish	18	1.8 µg HBCDD kg^{-1} ww	187	11
		16	107 µg HBCDD kg^{-1} lw		
	Marine mammals	19	336 µg HBCDD kg^{-1} ww		
		19	1144 µg HBCDD kg^{-1} lw		
U.K.	Fish	300 (5 dietary relevant species; each species pooled data of 60 individuals)	0.44 µg HBCDD kg^{-1} ww	1859	44
		300	63 µg HBCDD kg^{-1} lw		
	Harbour porpoise	34	818 µg HBCDD kg^{-1} ww		
		34	2780 µg HBCDD kg^{-1} lw		

The concentration ratios presented above may overestimate the actual field biomagnification as concentrations in fish muscle have been used for the calculations instead of whole fish. Therefore, European Commission (2007) estimated additionally for the U.K. dataset a ratio based on HBCDD concentration in whole fish. The ratio between harbour porpoise and its diet was calculated at 254.

Temporally increasing concentrations have been observed for several species. Law et al. (2006) measured HBCDD in blubber of 85 harbour porpoises stranded or dying in the U.K. during 1994-2003. The mean concentration in the mid-1990 was 100 µg kg^{-1} lw and increased to 9 400 µg kg^{-1} lw in 2003. Knudsen et al. (2005) found a statistically significant, increasing trend of HBCDD concentrations between 1983 and 2003 in eggs of six marine bird populations (Atlantic puffin, herring gull, kittiwake; n = 89 in total) from two remote locations in the Norwegian Arctic. Concentrations have risen from 1.1-2.9 µg kg^{-1} ww in 1983 to 6.1-17.3 µg kg^{-1} ww in 2003. Sellström et al. (2003) found a temporally increasing trend in Baltic Sea guillemot eggs, although the concentrations seem according to the author to have levelled off in the last decade (see Figure 4.2).

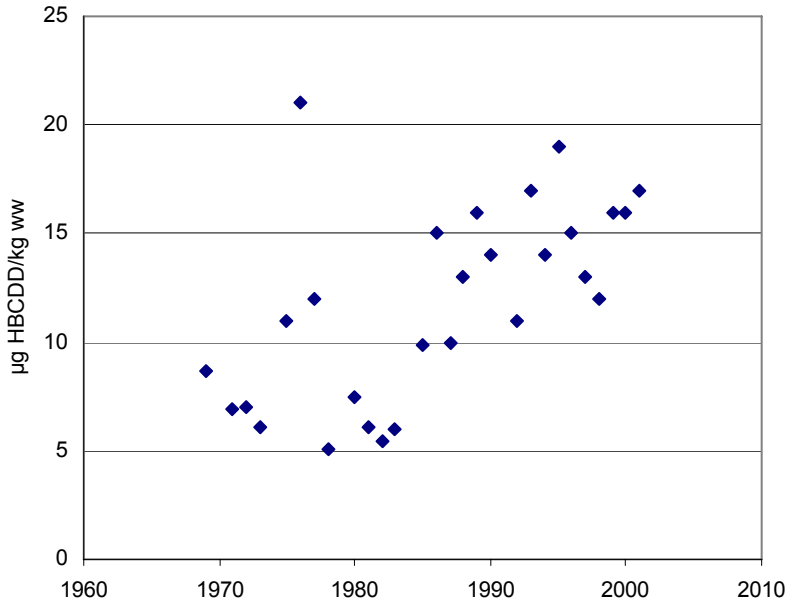


Figure 4.2 Concentration of HBCDD over time in guillemot (*Uria aalge*) eggs in the Baltic Sea (data from Sellström et al., 2003).

Increasing temporal trends have been reported also from other parts of the world (e.g., Kajiwara et al., 2006b; Stapleton et al., 2006).

Although α-HBCDD is present in a minor concentration in the commercial product, it is in general found at the highest concentrations of the three diastereomers in biota (e.g., de Boer et al., 2002; Schlabach et al., 2002; Gerecke et al., 2003; Tomy et al., 2004a; Janák et al., 2005a; Zegers et al., 2005; Law et al., 2006b; Ueno et al., 2006). Furthermore, α-HBCDD is not a generally dominant species in abiotic samples. Several factors may lead to the dominance of α-HBCDD in biota. Firstly, the mass-transfer limitations are lowest for α-HBCDD of the three diastereomers based on its higher water solubility and lower logKow -value. These properties make it more readily available for uptake from environmental compartments and from gastrointestinal tract. Secondly, α-HBCDD seems to have the lowest potential to be metabolised based on *in vitro* tests with mammals and fish (Zegers et al., 2005; Janák et al., 2005b). The simulation degradation tests of Davis et al. (2004) also indicate, that α-HBCDD would be degraded slowest of the three diastereomers. Additionally, bioisomerisation of γ-HBCDD and β-HBCDD to α-HBCDD has been observed to occur in fish (Law et al., 2006a).

4.3.4 Summary and discussion of bioaccumulation

Reliable experimental BCFs from two flow-through bioconcentration tests with fish are available. As a representative BCF -value 18 100 was chosen in the EU risk assessment (European Commission, 2007). Furthermore, a large set of measured data in biota in the field show, that HBCDD is biomagnified in the environment. Increasing concentrations of HBCDD have been found in several time series of, i.a., birds and marine mammals. No diastereomer specific BCFs are available. Despite being present in commercial HBCDD at the lowest concentration, α-HBCDD generally has the highest concentration of the three main diastereomers in biota. However, several

reasons may have lead to this difference in diastereomeric distribution in biota compared to technical product. It is concluded, that HBCDD has a very high bioaccumulation potential.

5 HUMAN HEALTH HAZARD ASSESSMENT

Data not reviewed for this report.

6 ENVIRONMENTAL HAZARD ASSESSMENT

The results of ecotoxicity tests, which have been considered reliable by European Commission (2007), are presented in Table 6.1.

Table 6.1 Acute and chronic ecotoxicity data, which are considered reliable according to European Commission (2007)

Compartment/Species	Method	Results#	Remark and reference
AQUATIC COMPARTMENT			
FISH			
Onchorhyncus mykiss	OECD 203 and TSCA 40/797/1400, and ASTM Standard E729-88a	No mortalities or other effects around 2.5 µg/l.	Graves and Swigert (1997a)
Onchorhyncus mykiss	Flow-through OECD 210 and OPPTS 850.1400	NOEC: Hatching success ≥3.7 µg/l Swim-up ≥3.7 µg/l Larvae and fry survival ≥3.7 µg/l Growth ≥3.7 µg/l	Drottar et al. (2001)
INVERTEBRATES			
Daphnia magna	OECD 202. Static immobilisation test, and TSCA 40/797/1300, and ASTM Standard E729-88a	48 h EC_{50} >3.2 µg/l	Graves and Swigert (1997b)
Daphnia magna	TSCA , OECD Flow through 21 day test.	NOEC 3.1 µg/l LOEC length 5.6 µg/l	Drottar and Krueger (1998)
ALGAE			
Selenastrum capricornutum	OECD 201 and TSCA40/797/1050	96 h EC_{50} >2.5 µg/l	Roberts and Swigert (1997)
Skeletonema costatum *Thallassiosira pseudonana* Chlorella sp.	Marine algal bioassay method, different marine growth media	72 h EC_{50} = 9 µg/l (lowest value) 72 h EC_{50} = 40 µg/l (lowest value) 96h EC_{50} >water solubility	Walsh et al. (1987) Not according to guidelines, results only used as supportive
Skeletonema costatum	OECD 201, ISO 10253:1995 and EU Directive 92/69/EEC – Method C.3. One test concentration at the limit of respective water solubilites of each diastereomer.	NOEC <40.6 µg/l EC_{50} >40.6	Desjardins et al. (2004)
Skeletonema costatum	OECD 201. EC50 obtained from a limit test with one test concentration (54.5 µg/l) at the limit of respective water solubilites of each diastereomer.	NOEC >10 µg/l EC_{50} = 52 µg/l	Desjardins et al. (2005)
SEWAGE TREATMENT PLANT, MICRO-ORGANISMS			
Acivated sludge	Respiration inhibition OECD 209	EC_{50} = 15 mg/l	Limit test with one test concentration, EC_{50} is an estimated value. Schaefer and Siddiqui (2003)
SEDIMENT COMPARTMENT			
INVERTEBRATES			
Hyalella azteca (Amphipod)	Sediment toxicity test 28-day exposure period under flow-through conditions.	LOEC >1000 mg/kg dw of sediment NOEC 1000 mg/kg dw of sediment.	Thomas et al. (2003b)

Compartment/Species	Method	Results#	Remark and reference
Lumbriculus variegatus (Worm)	28-day sediment bioassay	LOEC = 28.7 mg/kg dw NOEC = 3.1 mg/kg dw Normalized: NOEC = 8.61 mg/kg dw	Oetken et al. (2001)
Chironomus riparius (Mosquito)	28-day sediment bioassay Egg production of F generation	LOEC = 159 mg/kg dw NOEC = 13.6 mg/kg dw Normalized: NOEC = 37.8 mg/kg dw	Oetken et al. (2001)
TERRESTRIAL COMPARTMENT			
PLANTS			
Plants: corn (*Zea mays*), cucumber (*Cucumis sativa*), onion (*Allium cepa*), ryegrass, (*Lolium perenne*), soybean (*Glycine max*), and tomato (*Lycopersicon esculentum*)	Seedling emergence, suvival, height 21 days OECD 308 (proposal for revision), 850.4100 and 850.4225 (public drafts)	NOEC >5000 mg/kg dry soil	Porch et al. (2002)
INVERTEBRATES			
Eisenia fetida (Earthworm)	Survival and reproduction, 56 days OECD prosal and 207 and OPPTS 850.6200	NOEC 128 mg/kg dry soil Normalized: NOEC 59 mg/kg dry soil (EC_{50} 771 mg/kg dry soil)	Aufderheide et al. (2003)

7 PBT AND vPvB

7.1 PBT, vPvB assessment

Persistence: Hexabromocyclododecane (HBCDD) fulfils the P-criterion. Based on a standard degradation simulation study, HBCDD seems to be persistent in aerobic soil. No firm conclusion can be drawn solely from the performed simulation degradation studies regarding whether or not HBCDD fulfils the P-criterion for sediment. The assessment is complicated by the fact that available data indicate that the different diastereomers have different degradability. For α-HBCDD, which seems to be the least degradable, an aerobic DT_{50} of approximately 210 days in sediment at 12°C was determined, which is above the P-criterion of 120 days. For γ-HBCDD the available data indicate very different half-lives depending on test concentration. When tested at a concentration similar to what is measured close to polluted areas, the DT_{50} was 190 days (12°C).

The measured data available from dated sediment cores indicate that HBCDD has degraded in these sediments more slowly than what would be expected based on the available experimental degradation half-lives. Furthermore, HBCDD is found to be ubiquitously present in remote areas in abiotic samples and biota providing evidence, that the substance is persistent in the environment. Also the temporally increasing concentrations found in biota support the picture of HBCDD as a persistent substance.

Bioaccumulation: HBCDD meets the vB criterion based on reliable experimental BCFs from two flow-through bioconcentration tests with fish. A BCF of 18 100 was chosen as a representative value in the EU risk assessment (European Commission, 2007). Furthermore, a large set of measured data in biota in the field indicate, that HBCDD is biomagnified in the environment. No diastereomer specific BCFs are available. However, the concentration of α-HBCDD in biota is generally much higher than the concentration of the other two main diastereomers despite it being present in commercial HBCDD in relatively low concentration. Several reasons may have lead to this difference in diastereomeric distribution.

Toxicity: HBCDD fulfils the T criterion. A 21d-NOEC of 3.1 μg l^{-1} has been derived for *Daphnia magna* in a flow-through test. It is noted, that ecotoxicity testing of HBCDD is highly complicated due to its very low water solubility.

Other: HBCDD has a high potential for long-range environmental transport. Its half-life in the atmosphere is > 2 days and it has been found in remote areas in abiotic samples (air, deposition, sediment) and biota (polar bears, bird eggs, seals) in the majority of samples of the last years. Additionally, a study comparing long-range transport potential of "existing" POPs and HBCDD with the help of tuna fish samples, found HBCDD to have a very high potential for long-range environmental transport.

Summary: Hexabromocyclododecane (HBCDD) fulfils the vB criterion based on experimental data and measured data from biota. The T criterion is also met. The available soil degradation simulation test data indicate, that the half-life of HBCDD in aerobic soil is > 180 d. The experimental data regarding persistence in sediment are varying. According to some of the sediment degradation simulation studies available the P-criterion is met, whereas other studies substance indicates that the substance is degradable in certain experimental conditions. However, data from dated sediment cores gives support to HBCDD being persistent also in sediment.

Furthermore, HBCDD has potential for long-range environmental transport based on environmental monitoring data and modelling.

Overall it is concluded, that HBCDD is a PBT substance.

INFORMATION ON USE AND EXPOSURE

Information on use and exposure has been included in the EU risk assessment of HBCDD (European Commission, 2007). Identification of potential risk reduction measures has been carried out by Swedish Chemicals Agency (2007).

OTHER INFORMATION

The information and references used in this report were mainly taken from the following source:

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