Environmental problems of organic pollutants: Hexabromocyclododecane

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ABSTRACT

This article investigates the environmental impact and toxicity of an organic pollutant called "hexabromocyclododecane" (GBSD). GBSD has been widely used as a flame retardant since the 1960s and is mainly found in building materials and other industrial products. This substance spreads over long distances due to its stability in the atmosphere, water and soil, which increases the environmental risk. The article also assesses the harmful effects of GBSD on human health and aquatic organisms, accumulation and stability over a long period of time. However, the article provides information on alternative products that replace GBSD, but emphasizes that they are not as effective as GBSD. The main conclusion of the article is that GBSD has a hazardous effect on the environment and has the nature of biological accumulation, so control is necessary to ensure environmental safety

Keywords: Hexabromocyclododecane (GBSD), Organic Pollutant, Flame Retardant, EC, Bioaccumulation, Toxicity, Persistent Organic Pollutants, Environment, Construction Industry, Alternative Products,

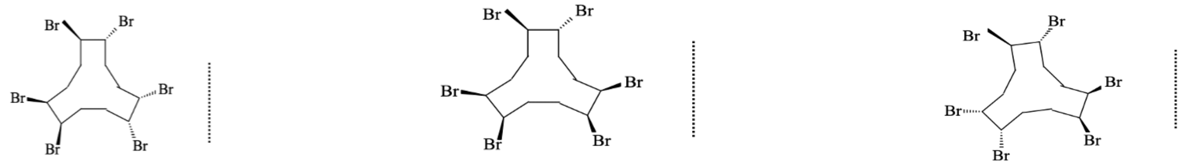
Introduction:

The compound 1,2,5,6,9,10 hexabromocyclododecane (HBCD, $C_{12}H_{18}Br_6$) has been produced since the 1960s and is the most used cycloaliphatic additive of brominated flame retardant (BFR) today. The main industry that uses HBCD is construction, where extruded or expanded polystyrene foam products typically contain 3% or less by weight. Upholstered furniture, car seats, interior fabrics, and electrical and electronic devices are a few examples of secondary uses. Global production of HBCD was 31,000 tonnes in 2011, of which 11,000 tonnes were used in the EU in 2007 (POPRC, 2011).

According to industry information, HBCD is mainly used (90%) for flame retardant polystyrene (EU, 2008), predominantly expandable polystyrene (EPS) and extruded polystyrene (XPS). to take into account, as textile backcoat (industrial) is estimated to be the dominant category of emissions to wastewater and surface water (EU, 2008).

Technical HBCD (t-HBCD), which is produced by adding bromine to 1.5 9-cyclododecatries, is mainly composed of diastereomers: α, β and γ. The proportions of these isomers in t-HBCD ultimately vary by manufacturer, although the γ isomer makes up more than 70% of the total, while the α isomer and β isomers make up approximately 10% and 6% of the mixture, respectively. Traces of other diastereomers (such as δ and ε) are present in t-HBCD, but quantitative data are not yet available. Due to its persistence, bioaccumulation, long-range transport and toxicity profile, HBCD was included in the US Environmental Protection Agency's List of Chemicals of Concern in 2010 and HBCD was nominated and considered for listing as a persistent organic pollutant (POPs) by the Persistent Organic Pollutants

Review Committee (POPRC) under the Stockholm Convention in 2010 (Encyclopedia of Toxicology, 3rd edition, 2014).



α-HBCD (CAS 134237-50-6), the line indicates a mirror plane β-HBCD (134237-51-7), the line indicates a mirror plane γ-HBCD (134237-52-8), the line indicates a mirror plane

Figure 1. The three main diastereomers (pairs of enantiomers) of t-HBCD (reconstructed from EC (2008); data from (Heeb et al. 2005)).

1 PHYSICAL AND CHEMICAL PROPERTIES

The CAS register lists two numbers for undefined combinations of commercial or t-HBCD: 25637-99-4 (without bromine substitution template location numbering) and 3194-55-6 for 1,2,5,6, 9 and 10 HBCD. HBCD has a complex stereochemistry of 16 stereoisomers and can isomerize both in the manufacturing process and outside the environment. Most of the chemical performance and toxicity tests published to date concern t-HBCD, a mixture of isomers.

Table 1. Summary of Physical and Chemical Properties

Link "REACH" Appendix, §	Property	Meaning	Comments
VII, 7.1	Physical condition at 20 and 101.3 kPa	White, odorless solid	
VII, 7.2	Melting temperature	fluctuates around 172–184 °C, as the average was used as input to the EU risk assessment	Smith et al. (2005)
		179-181 °C α-HBCD 170-172 °C β-HBCD 207-209 °C γ-HBCD	Smith et al. (2005)
VII, 7.3	Boiling point	Decomposes at >190°C	Peled et al. (1995)
VII, 7.5	Gas pressure	6.3 x 10^{-5} Па (21 °C)	Stenzel and Nixon (1997)
VII, 7.7	Solubility	48.8±1.9 мкг/л α-ГБЦД 14.7±0.5 мкг/л β- ГБЦД 2.1±0.2 мкг/л γ- ГБЦД 65.6 µg/L (HBCD Technical Product, sum of the above)	MacGregor and Nixon (2004)
VII, 7.8	n-octanol/water partition coefficient (logarithmic value)	5.07±0.09 α- ГБЦД 5.12±0.09 β- ГБЦД 5.47±0.10 γ- ГБЦД 5.625 (technical product)	MacGregor and Nixon (1997) Hayward et al. (2006)

HBCD is mainly formed as a result of the reaction of addition of bromine to trans, trans, cis-1,5,9-cyclododecatriene, the cyclic trimer of butadiene. The hexabromocyclododecane produced by this reaction consists of a mixture of stereoisomers of 1,2,5,6,9,10 hexabromocyclododecane ranging from oils to an isomer with a melting point of 205–208 °C. Commercially available hexabromocyclododecane contains a mixture of solid isomers and has a melting point in the range of 170–180 °C (185–195 °C). (Ullmann Encyclopedia of Industrial Chemistry. 6th ed., Vol. 1: Federal Republic of Germany: Wiley-VCH Verlag GmbH & Co. 2003-present, pp. V5 625 (2003)).

2 Characteristics Of Transformation In The Environment

2.1 Degradation

Based on the estimated half-life of the reaction with OH radicals of 3.2 days using AOP v1.91 (24 hours a day; $5*^{10-3}$ OH cm), indirect photochemical decay in the atmosphere is considered to be slow. Using the same model but with different variables, Wania (2003) calculated a photochemical half-life of 51.2 hours.

It has also been observed that HBCD degrades during the abiotic control of biodegradation experiments.

Due to the extremely low solubility of HBCD in water, hydrolysis is not considered a major source of environmental degradation.

Biodegradation. There are two large standard studies on modelling the degradation of HBCD for sediment and soil (Davis et al., 2003a, b and Davis et al., 2004).

In Davis et al. 2004, no evidence of aerobic soil degradation was found. Davis et al. (2003b) reported a half-life of 119 days; however, this number may be too low, as only the disappearance of HBCD was estimated. In contrast to Davis et al. (2004), markedly faster extinction has been reported in sediment studies conducted by Davis et al. (2003a). Based on the results of Davis et al. (2004), the half-life of aerobic sediment at 12 °C was 214 days (α-HBCD), 129 days (β-HBCD) and 197 days (γ-HBCD), and for anaerobic deposition it was 210 days. 80 d and 125 d, respectively. According to Davis et al. (2004), the stepwise reduction dehalogenation of HBCD via tetrabromocyclododecene and dibromocyclododecadiene to 1,5,9-cyclododecatriene (CDT) occurs both in aerobic, and in anaerobic sediments. Since no CO2 or other volatiles were formed during the study, there was no indication that 1,5,9-cyclododecatriene was undergoing further transformation. Modelling and degradation verification experiments of HBCD did not reveal any mineralization, although primary degradation and even mineralization were observed in two credible biodegradation tests using CDTs. This can be explained by the short period of HBCD testing, which may not have been sufficient to detect any mineralization even under ideal conditions, when CDT was produced in significant quantities from HBCD. Moreover, significant degradation of HBCD to CDT was observed only under anaerobic conditions, although it is likely that aerobic conditions are necessary for further degradation of CDT. As a result, it is not possible to determine the overall environmental degradation potential of MDCs from HBCD degradation data and vice versa. (ESNA, 2008)

In addition to experimental results, the studied sediment core samples show that HBCD degrades in sediments more slowly than predicted by modeling studies. Moreover, according to many time series, HBCD concentrations in biota are increasing, and this has been detected in biotic and abiotic samples from even the most remote locations. (ESNA, 2008)

HBCD was concluded to meet the criteria for persistence in soil and sediment, although disappearance or degradation was observed under several experimental conditions.

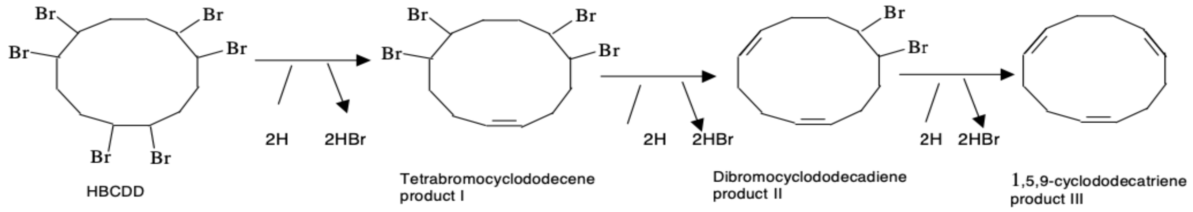


Figure 2. Stepwise dehalogenation of HBCD (Davis et al., 2004)

2.2 Environmental Distribution

According to EU RAR, 2008, the logarithmic partition coefficient of organic carbon ($logK_{OC}$) is 4.66, indicating an extremely high adsorption potential. It is reasonable to assume that HBCD has relatively little mobility in soil and sediments. According to the observed vapour pressure, HBCD is very slightly volatile (6.3x10-5 Pa at 20 °C). Henry's Law Constant at 20–25 °C is 0.75 Pamol, based on the sum of solubilities of individual diastereomers (66 μg/l). Thus, HBCD has a low probability of evaporation from water surfaces. The evaporation of HBCD appears to be a less significant route of propagation due to its low volatility and high particulate adsorption capacity.

2.3 DISTRIBUTION MODELING

According to the EUSES modelling used to assess the risk of HBCD in the EU (ECHA, 2008), the mass fractions of HBCD at steady state at the regional level are as follows:

Fresh water	0.003%
Sea water	0.0003%
Air	0.00003%
Agricultural soil	45%
Industrial soil	0.015%
Freshwater sediment.	0,02%
Seawater sediment	0.0003%

Assuming equal emissions to air, water and soil, the Epiwin 3.20 level III fugiivity model gives the following HBCD distribution:

Air	0.03%
Water	8.1%
Soil	83%
Sediment	9.1%

HBCD degrades very slowly in the atmosphere (half-life> 2 days), suggesting the possibility of long-range atmospheric transport in the vapour phase. Despite this, most of the long-range environmental transport of HBCD is predicted to occur in aerosol form due to its low volatility and strong adsorption potential (Wania, 2003). The scientists claim that among the compounds they studied, HBCD reflects one of the strongest long-range transport abilities. However, it should be emphasized that for HBCD, the significance of the correlation between distance and concentration was quite low (r2 = 0.45; p = 0.33) and the standard errors of estimation were quite high, possibly due to the small number of sites included (four sites used). as the basis of regression). However, when the HBCD results are considered in conjunction with those of other organohalogen chemicals studied, the results of Ueno et al. (2006) can be seen as evidence of the potent long-range transport potential of HBCD.

2.4 BIOACCUMULATION

Aqueous bioaccumulation. The technical product has measured logarithmic octanol-water partition coefficients (logK_{ow}) of 5.625. In another study (Hayward et al. 2006) it was predicted that logK_{ow} would be 5.07 for α-, 5.12 for β-, and 5.47 for γ-HBCD for each unique diastereomer. Given these log K_{ow} values, BCFwin (v 2.17) predicts bioconcentration factor (BCF) values of 4240, 1600, 1750, and 3250 for the technical product and diastereomers α, β, and γ, respectively.

Terrestrial bioaccumulation. Studies of BCF in earthworms are lacking. However, the HBCD content of earthworms has been measured in a study of earthworm survival and reproduction (Aufderheide et al., 2003). The study found that bioaccumulation factors based on wet mass concentrations of worms and soil ranged from 0.03 to 0.08. In worm tissues, the α-HBCD fraction accounts for about 60% of the total HBCD concentration, whereas α-diastereomer accounts for approximately 6% of the total concentration in the soil. For α-HBCD (0.3–0.8), the diastereomeric specific bioconcentration factor is more than an order of magnitude higher than for γ-HBCD (0.005–0.02). This is consistent with what has been observed in other biotas, such as mammals and fish, where α-HBCD is the dominant diastereomer. It is not known why there is such a difference. This may be caused, for example, by greater absorption of the α-diastereomer or by differences in metabolism between the diastereomers.

Other. According to concentration measurements made in European surface waters and freshwater fish and collected in EU RAR (2008), HBCD accumulates in fish in the wild. The latest HBCD values in filtered water samples from European surface waters (n = 14) range from 0.016 (or below the detection limit) to 1.5 μg/l (point source-receiver, Skern River). Another important study was published by Law in 2006: he measured the HBCD in the fat of 85 porpoises that were stranded or died in the United Kingdom between 1994 and 2003. The mean concentration increased from 100 g kg-1 wet weight in the mid-1990s to 9400 g kg-1 wet weight in 2003. The increase was particularly noticeable between 2000 and 2003. In addition, abiotic samples do not typically include the dominant species, HBCD. The predominance of α-HBCD in biota can be due to many reasons. First, given its higher water solubility and lower logK_{ow} value, the weight transfer limits are the lowest for α-HBCD among the three diastereomers. Due to these characteristics, it is more readily absorbed from the gastrointestinal tract and the environment. Based on in vitro experiments in mammals and fish, α-HBCD has the lowest metabolic capacity (Zegers et al., 2005; Janák et al., 2005b). In microsomal liver preparations of the common smear, Janák et al. (2005b) found that α-HBCD is the least biotransformed of the three main diastereomers studied. The degradation simulations in Davis et al. (2004) also suggest that of the three diastereomers, α-HBCD will decay the slowest. Moreover, it has been noted that fish are able to bioisomerize γ-HBCD and β-HBCD into α-HBCD (Law et al., 2006a).

Human exposure to HBCD through food is an important route of exposure because it is a persistent and bioaccumulative chemical that is released from both point and diffuse sources. The EU RAR determined a maximum intake of 22 ng HBCD/kg/day based on studies of food samples purchased from Swedish grocery stores and including fish, meat, chicken, milk and eggs. The average was 10 times lower (European Commission, 2008).

In the risk assessment, a bioconcentration factor of 18,100 was chosen as representative (European Commission, 2008). In addition, a significant collection of field measurements of biota indicates that HBCD has biomagnification. HBCD concentrations increase over several time periods, including among birds and marine mammals. There are no bioconcentration factors specific to diastereomers. Although α-HBCD is present in commercial HBCD at the lowest concentration, it usually has the highest concentration of the three main diastereomers in biota. However, there may be several reasons for the differences in the distribution of diastereomers between biota and technical products. Conclusion: HBCD has a very high potential for bioaccumulation.

3 ASSESSMENT OF THE DANGER TO HUMAN HEALTH

3.1 TOXICOKINETICS

There are few available data on the toxicokinetics of HBCD. The highest amounts of properly dissolved HBCD are likely to be found in adipose tissue and muscle, followed by the liver and, in much smaller amounts, the lungs, kidneys, blood, and brain of rodents. Although the exact percentage of oral absorption is unknown, it is most likely that it is between 50% and 100%. However, 100% oral absorption is assumed for the calculation of DNEL. Although women reach more than men, the chemical accumulates in both sexes. The accumulation of the α diastereomer is significantly higher than the accumulation of the other two HBCD diastereomers in the technical product, especially at higher exposure levels. It seems that it will take months to reach a steady state. Although the full extent of the technical metabolism of HBCD is unknown, exposure to -HBCD has resulted in the detection of three polar metabolites, as well as non-extractable compounds in the faeces and urine. Stepwise reduction debromination of HBCD via tetrabromocyclododecene and dibromocyclododecadiene to 1,5,9-cyclododecatriene, which appears to be the final degradation product in environmental samples, has been identified as the only biodegradation pathway in environmental biodegradation studies to date. (ESNA, 2008)

3.2 TOXICITY

ECHA reported the following acute toxicity data:
The minimum lethal dose for oral exposure in rats is greater than 20 g/kg.
The minimum lethal dose by inhalation in rats is greater than 200 mg/l.
The minimum lethal dose for dermal exposure in rabbits is greater than 20 g/kg. (ESNA, 2008)

Their conclusion: the current acute toxicity data indicate a very low acute toxicity and do not support the classification of HBCD according to EU standards. (ESNA, 2008)

In addition, the substance does not cause eye irritation and corrosive effects on the skin. (ESNA, 2008)

The available data on the toxicity and carcinogenicity of repeated doses do not suggest the classification of HBCD according to the EU criteria.

HBCD was negative in the in vitro chromosomal aberration and in vivo micronucleus tests and did not cause mutations in the Ames test. Therefore, HBCD can be said to have negligible genotoxic potential both in vitro and in vivo. Currently available mutagenicity data do not support the classification of EU HBCD. (ESNA, 2008)

4 ENVIRONMENTAL HAZARD ASSESSMENT

ECHA proposed the following environmental classification: N; R50-53: Very toxic to aquatic organisms, can cause long-term adverse effects in the aquatic environment.

As indicated in the proposal for limit concentrations of very hazardous compounds (ECBI/65/99 Add.10), the declared L(E)C50 range of 10-100 μg/L would result in the following limit concentrations of formulations:

Concentration limits of the substance Classification of the drug

C ≥ 2,5%	N; P50-53
C ≥ 0,25%	N; P51-53
C ≥0,025%	R52-53

The proposal is based on the extremely high bioconcentration factor (18,100) found in the study bioconcentration factor in fish, the toxic effects observed in a 72-hour study of the seaweed Skeletonema costatum (EC50 52 μg/L), and the lack of biodegradation shown in the standard test. The results of a 21-day life cycle test of Daphnia magna, in which the lowest concentration of the observed effect was estimated at 5.6 μg/L based on lower mean lengths, support the proposed classification. (ESNA, 2008)

Similarly, the U.S. Environmental Protection Agency (EPA) has also concluded that HBCD can adversely affect a variety of organisms, including algae, fish, invertebrates, and soil organisms, at ecologically significant concentrations. "HBCD is toxic to algae and highly toxic to fish embryos (Desjardins, et al., 2004; Deng, et al., 2009)». (Hexabromocyclododecane (HBCD) Action Plan – US Environmental Protection Agency) The US EPA report presented the following results in support of its conclusion:

1) Fish have also been found to experience a number of sublethal effects, such as changes in thyroid status, protein metabolism, oxidative stress, and reproductive activity (Palace, et al., 2008; Kling and Förlin, 2009; Zhang, et al., 2008; Kling and Förlin, 2009; Zhang, et al., 2008; Ronish et al., 2004).

2) According to Drottar and Kruger (1998), the first and second generations of descendants of daphnia turned out to be fewer and smaller in number.

3) Tadpoles (Xenopus laevis) treated with HBCD have shown developmental effects dependent on thyroid hormones (Schriks, et al., 2006).

4) HBCD has been observed to reduce the biomass and egg production of soil organisms (Lumbriculus variegatus) (Oetken, et al., 2001).

5) When HBCD was administered to chicken embryonic hepatocytes (Gallus domesticus) in vitro, the expression of genes (mRNA) associated with thyroid and liver function was significantly altered (Crump, et al., 2008).

6) Thinner eggshells have been measured in American kestrels exposed to the combination of PBDEs and HBCDs (Fernie, et al. 2009).

5 ASSESSMENT ACCORDING TO THE CRITERIA "PERSISTENT, BIOACCUMULATIVE, TOXIC"

The European Chemicals Agency (ECHA), after comparison with the criteria in Annex XIII, concluded that hexabromocyclododecane (HBCD) meets both the criteria "Bioaccumulative" and "Very Bioaccumulative", based on experimental data (bioconcentration factor = 18100) and biota measurements. At a concentration with no observed effect of 3.1 μg/L for daphnia, the "Toxic" criterion also meets. The "persistent" criterion in soil is met because the half-life of HBCD in aerobic soil is> 120 days according to soil degradation modelling. In addition, the phosphorus requirement for sediment is supported by dated sediment cores and sediment degradation modelling experiments, both of which show a slow rate of degradation of HBCD.

The fact that HBCD is consistently detected in abiotic samples and biota from remote locations reinforces the idea that the substance is persistent in the environment and transports over long distances. According to the European Chemicals Agency (ECHA), HBCD is a substance that is "persistent, bioaccumulative, toxic"; this conclusion is also supported by data from the US Environmental Protection Agency (EPA, 2010) and Swedish monitoring studies (Sellström et al. 1998).

6 ALTERNATIVE PRODUCTS

There does not seem to be a flame retardant that is equally well suited for the main applications of HBCD, especially in expanded polystyrene (EPS) and extruded polystyrene (XPS). The main advantage of HBCD is that it provides exceptional Styrofoam performance as it is effective at low concentrations (EU RAR, 2008).

Commercially available EPS/XPS equivalents are available for use as building insulation, which are technically feasible in many, but not necessarily all, situations. The fact that mineral wool is now widely used and accounts for at least 30% of the building insulation industry in Europe suggests that it is both a technically and financially feasible alternative to EPS/XPS in many applications. However, in some cases, a lower mass density of EPS/XPS or superior moisture resistance can be crucial. Another product available on the market that meets fire safety standards is phenolic foam. It has a low density, is moisture-resistant, and is very thermally efficient. It occupies only a small part of the European insulation market, which is mainly used in situations where moisture resistance or thickness is crucial. This may indicate that it is relatively expensive. Although the chemicals used to make phenolic foam are hazardous to human health, these alternative insulation materials are not particularly harmful to the environment and human health (ECHA/2008/02/SR4/ECA.226).

In impact-resistant polystyrene and textile coatings, commercially available substitutes for HBCD are available that provide the same level of fire protection and functionality. Such substitutes include non-halogenated flame retardants. (ECHA/2008/02/SR4/ECA.226)

7 CONCLUSION

The compound 1,2,5,6,9,10-hexabromocyclododecane (HBCD, $C12H18Br6$) is primarily used as a flame retardant and is a white, odorless solid. In addition, it is used in expanding, extruded, impact-resistant polystyrenes, and in polymer dispersions for textiles. The synthesis of technical HBCD (t-HBCD) is carried out by adding bromine to 1,5,9-cyclododecatriene. T-HBCD is primarily composed of three diastereomers: α, β, and γ, with the latter accounting for more than 70%. It has been established that in reaction with OH radicals, HBCD decomposes in a few days, but indirect photochemical decomposition in the atmosphere is thought to occur slowly. Moreover, hydrolysis is not considered a major source of environmental degradation because HBCD has an extremely low water solubility. Following an environmental risk assessment, the European Chemicals Agency concluded in its 2008 report that the substance met all the criteria for being considered "Persistent, Bioaccumulative, Toxic", which is also supported by American and Swedish counterparts. In addition to its persistence, bioaccumulation and toxicity, HBCD has a strong ability to be transported over long distances because it degrades very slowly in the atmosphere. In terms of danger to human health, the substance has very low acute toxicity and is not carcinogenic. However, HBCD is highly toxic to aquatic organisms and can have long-term negative effects on the aquatic ecosystem. There are several alternative products available to replace HBCD, namely rock wool and phenolic foam, but these products do not work equally well as a flame retardant in mainstream applications such as EPS and XPS. However, non-halogenated flame retardants are commercially available substitutes and provide equivalent functionality and fire safety in impact-resistant polystyrene and textile coatings.

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