



**Stockholm Convention
on Persistent Organic
Pollutants**

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Persistent Organic Pollutants Review Committee

Fourth meeting

Geneva, 13–17 October 2008

Item 7 (b) of the provisional agenda*

**Consideration of chemicals newly proposed for inclusion in
Annexes A, B or C of the Convention: hexabromocyclododecane**

**Summary of the proposal for the listing of
hexabromocyclododecane (HBCDD) in Annex A to the
Convention¹**

Note by the Secretariat

1. The annex to the present note contains a summary of the proposal submitted by Norway for listing hexabromocyclododecane in Annex A of the Stockholm Convention on Persistent Organic Pollutants pursuant to paragraph 1 of Article 8 of the Convention. The summary is being circulated as prepared by Norway and has not been formally edited. The complete proposal may be found in document UNEP/POPS/POPRC.4/INF/15.

Possible action by the Committee

2. The Committee may wish:

- (a) To consider the information provided in the present note and in document UNEP/POPS/POPRC.4/INF/15;
- (b) To decide whether it is satisfied that the proposal fulfils the requirements of Article 8 and Annex D of the Convention;
- (c) To develop and agree on, if it decides that the proposal fulfils the requirements referred to in paragraph 2 (b) above, a workplan for preparing a draft risk profile pursuant to paragraph 6 of Article 8.

* UNEP/POPS/POPRC.4/1.

1 Stockholm Convention, Article 8, paragraph 1.

Annex

Proposal for listing hexabromocyclododecane (HBCDD) in Annex A of the Stockholm Convention on Persistent Organic Pollutants

Introduction

1. Commercially available hexabromocyclododecane (HBCDD) is a white solid substance which is used as an additive flame retardant on its own, or in combination with other flame retardants. HBCDD is used mainly in expanded and extruded polystyrene. Most of this HBCDD-treated polystyrene is used for insulation boards in, e.g., buildings and vehicles. Other applications include its use in textile coatings and in high impact polystyrene for electrical and electronic equipment. HBCDD is the third most used brominated flame retardant and the global market demand in 2001 was 16 700 tonnes. Technical HBCDD is a mix of mainly three diastereomers (compounds that are identical except for the spatial disposition of the atoms), alpha-, beta-, and gamma-HBCDD, and the final distribution of these diastereomers in technical HBCDD varies with a range of about 70-95 % γ -HBCDD and 5-30 % α - and β -HBCDD.

2. Alternative chemicals and techniques for avoiding the use of HBCDD are available for most of its uses. European industry has already started voluntary programs to manage the releases from industrial sites.

3. The present dossier and review provided by the proponent² focuses solely on the information required under paragraphs 1 and 2 of Annex D of the Stockholm Convention and it is mainly based on information from the following review reports:

(a) Risk Assessment Hexabromocyclododecane, CAS-No.: 25637-99-4, EINECS-No.: 247-148-4, Final draft October 2007. European Commission 2007 (available at <http://ecb.jrc.it/documentation/>).

(b) Strategy for limiting risks, hexabromocyclododecane (HBCDD), Draft on 4 September 2007, Swedish Chemical Agency 2007.

4. These reviews and the document of additional information provided by the proponent (with over 100 references)² also serve as sources of the additional information referred to in paragraph 3 of Annex D of the Stockholm Convention on this candidate POP chemical.

1. Identification of the chemical

5. Producers and importers have provided information under the European statutory requirements under two names with corresponding CAS- and EINECS-numbers. The numbers correlate to the isomer composition, and one set of numbers refer to an unspecific isomer composition (all isomers), while the other refers to the composition with the three main diastereomers (see below). Both of these substances are covered in this dossier. There are no known differences in molecular structure or properties of these two substances. Separate CAS-numbers have also been reported for the three diastereomers, but they are not accounted for in this dossier.

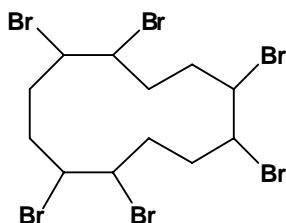
² Hexabromocyclododecane as a possible global POP. TemaNord 2008:520. Nordic Council of Ministers, Copenhagen 2007. 91 pp.

1.1 Names and registry numbers

IUPAC ³ name:	Hexabromocyclododecane
EINECS ⁴ name:	Hexabromocyclododecane
CAS ⁵ number:	25637-99-4 ⁶
EINECS number:	247-148-4
EINECS name:	1,2,5,6,9,10-Hexabromocyclododecane
CAS number:	3194-55-6 ⁷
EINECS number:	221-695-9
Synonyms:	cyclododecane, hexabromo-HBCDD
Trade names:	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

1.2 Structure

Chemical structure:



Molecular formula: $C_{12}H_{18}Br_6$

Molecular weight: 641.7

2. Persistence

6. Photochemical degradation half-life of HBCDD in the atmosphere is estimated by AopWin v1.91 to be 76.8 hours (3.2 days). Hydrolysis can be assumed to be an insignificant degradation route for HBCDD due to its very low water solubility (66 µg/l for the sum of three diastereomers). Theoretically abiotic degradation of HBCDD is possible. According to Kirk-Othmer (1993), HBCDD is rather easily dehydrobrominated and has a lower thermo-stability than aromatic brominated flame retardants. In practice abiotic degradation is probably of low significance because of the rather rigid ring-structure of HBCDD and its low water solubility.

7. The degradation of HBCDD was studied in a Closed Bottle Test carried out in accordance with OECD Guideline 301D and GLP (Schaefer and Haberlein, 1996). According to this study, HBCDD is not readily biodegradable and no biodegradation was observed during 28-days at a test concentration of 7.7 mg HBCDD/l. In the degradation simulation tests with sediment (Davis et al., 2004), (α+β+γ)-HBCDD was observed to be subject to primary degradation with half-lives of 66 and 101 days in anaerobic and aerobic sediment at 20 °C, respectively. These half-lives corresponded with 125 and 191 days, after a temperature correction to 12 °C was made. Degradation half-lives in aerobic sediment were calculated at 20 °C to be 113, 68 and 104 days for α-, β- and γ-HBCDD, respectively. The temperature corrected values at 12 °C were 214, 129 and 197 days. Based on the investigations of Davis et al. (2004) and Gerecke et al. (2006), α-HBCDD seems to be subject to a slower degradation than β-

³ International Union of Pure and Applied Chemistry.

⁴ European Inventory of Existing Chemical Substances.

⁵ Chemical Abstract Service.

⁶ This number is more specific in terms of the diastereomeric composition of the substance.

⁷ This number refers to an unspecific isomer composition (all isomers).

and γ -HBCDD. No degradation was observed in the aerobic soil degradation simulation test of Davis et al. (2004).

8. Davis et al. (2004) identified the primary degradation products of HBCDD to be products of a stepwise dehalogenation. They observed formation of tetrabromocyclododecane, dibromocyclododecadiene and 1,5,9-cyclododecatriene. For this reaction, anaerobic conditions with biological activity seemed to be favourable, but dehalogenation was also observed in aerobic and abiotic conditions, although with significantly slower disappearance rates of HBCDD. The main dehalogenation product, 1,5,9-cyclododecatriene (CDT; CAS 4903-66-4), is not readily biodegradable, but based on an enhanced ready biodegradation test modified from OECD 301F the substance was observed to be mineralized completely in 63-77 days.

9. The concentrations measured in the sediment core samples by Christensen et al. (2004), Fjeld et al. (2006b), Kohler et al. (2006), Remberger et al. (2004) and Sternbeck et al. (2001) provide an indication that HBCDD is degraded in sediment more slowly than predicted by the simulation tests. The abundance of HBCDD in biota and abiotic samples of remote regions also provides solid evidence of the persistency of HBCDD.

3 Bioaccumulation

10. The experimental log octanol-water partition coefficient ($\log K_{ow}$) value for technical HBCDD has been determined to 5.62 (MacGregor and Nixon, 1997), indicating a high potential for bioaccumulation.

11. Bioconcentration for HBCDD in fish has been determined in two reliable flow-through tests, and the bioconcentration factors (BCF) were found to be in the range of 8973-21940. Based on both studies an overall BCF of 18100 for HBCDD is used in the European Commission Risk Assessment (2007). This value well exceeds the limit of 5000 in the screening criteria of Annex D, indicating a high potential for bioaccumulation.

12. In a Lake Ontario (Canada) food web, a trophic magnification factor (TMF) based on ^{815}N relationship of all collected data was estimated to be 6.3 (sum-HBCDD). For the comparison, TMF for p,p'DDE and for the sum of PCBs were 6.1 and 5.7 in the same study, respectively. Fjeld (2006a) found higher levels of HBCDD in brown trout (*Salmo trutta trutta*) compared to its prey species European smelt (*Osmerus eperlanus*) and vendace (*Coregonus albula*). The measured field data from various surveys compiled by European Commission (2007) provide additional evidence that HBCDD is bioaccumulated in biota in freshwater and marine environments and that the substance is biomagnified between trophic levels.

4 Potential for long-range environmental transport

13. HBCDD has a vapour pressure of 6.3×10^{-5} Pa at 21 °C (Stenzel and Nixon, 1997), which indicates very low volatility. The substance is slightly volatile from aqueous surfaces based on the calculated Henry's law constant of 0.75 Pa m³/mol. Atmospheric degradation half-life has, in two different models, been estimated to be 76.8 hours and 51.2 hours. Despite its low volatility and very high adsorption potential, HBCDD has been found in air samples at concentrations above detection limits.

14. Atmospheric degradation half-life of vapour phase HBCDD varies on both sides of 2 days depending on the model settings. Characteristic travel distance (CTD)⁸ in air was estimated to be approximately 1500 km using ELPOS model. This is approximately in the range of CTDs estimated for pentabromodiphenyl ether and other POPs. The half-distances calculated by Ueno et al. (2006) based on skipjack tuna monitoring in the North Atlantic seem also to suggest a high potential for long-range environmental transport.

15. HBCDD has been detected in very remote areas, such as in air in northern Sweden and Finland, far from potential sources (Bergander et al., 1995; Sternbeck et al., 2001). HBCDD has also been found in birds and fish from remote areas, e.g. in liver from Atlantic cod from northern Norway (Fjeld et al., 2004), in Polar cod and ringed seal from Svalbard in the arctic region (Jensen et al., 2007; Sørmo et al., 2006), in marine bird and bird eggs from northern Norway (Knudsen et al., 2005; Verreault et al., 2004;

⁸ Characteristic travel distance (CTD) = distance at which 37 % of initial mass in air is present.

Gabrielsen et al., 2005), and in polar bears from Svalbard in the Arctic Ocean (Gabrielsen et al., 2004; Sørmo et al., 2006). These findings suggest that HBCDD undergoes long-range atmospheric transport.

16. HBCDD is ubiquitous in the environment, being also found in remote areas far away from point sources (e.g. in polar bears in the arctic). The highest concentrations of HBCDD are detected in marine top-predators such as porpoise and seals showing that HBCDD biomagnifies up the food chain. The trend also shows an increase in tissue concentrations of HBCDD in biota over time (Stapleton et al., 2006; Kajiwarra et al., 2006b; Isobe et al., 2007a).

5 Adverse effects

17. Results from acute and long-term aquatic ecotoxicity studies are available for fish, daphnids and algae (freshwater and saltwater). In addition, long-term tests with three sediment organisms, terrestrial plants and earthworm are available. Based on the long-term ecotoxicity test with *Daphnia magna* (28d-NOEC 3.1 µg/l; Drottar and Krueger, 1998) and on the growth inhibition test with *Skeletonema costatum* (72h-EC50 52 µg/l; Desjardins et al., 2005), HBCDD is considered very toxic to aquatic organisms. In addition, effects were observed in earthworm reproduction rate (NOEC 59 mg/kg dw; Aufderheide et al., 2003), but no effects were observed in plants at the highest levels tested (5000 mg/kg dw; Porch et al., 2002).

18. According to the available laboratory studies with mammals, HBCDD is not carcinogenic, mutagenic or toxic to reproduction (European Commission 2007). HBCDD was observed to cause effects in repeated dose studies in liver, thyroid gland and thyroid hormone homeostasis. A NOAEL of 22.9 mg/kg bw/day for liver weight increase (van der Ven et al., 2006) was the lowest observed NOAEL in the available repeated dose studies with oral administration in rats. Furthermore, developmental neurotoxicity and changes in sexual organs were observed, but these findings need to be confirmed by additional studies including properly designed multi-generation studies.

6 Statement of the reasons for concern

19. The proposal of the Government of Norway contains the following statement of concern:

“HBCDD is highly toxic to aquatic organisms, and according to laboratory tests with mammals, it affects the functioning of the thyroid system and liver. There are also indications of effects on fertility and developmental neurotoxicity of mammals. HBCDD is according to the available data also transferred from mother to child during pregnancy via blood and after delivery via breast feeding.

The monitoring data available from remote areas provide inevitable evidence that HBCDD is transported over long distances in the environment. HBCDD has been detected in a number of samples in the abiotic environment, biota and/or humans of the Arctic, Europe, Asia and North and South America regions. Furthermore, HBCDD is degraded slowly in the aquatic environment and soil. It has a great potential for bioaccumulation and in addition there is evidence of its biomagnification. The highest concentrations of HBCDD are detected in marine top-predators such as porpoise and seals showing that HBCDD biomagnifies up the food chain.

HBCDD is used as a flame retardant in a wide variety of articles in all parts of the world. The releases, as quantified in Europe, are at present entering the environment mainly from a large number of industrial point sources. However, HBCDD is also released from articles during and at the end of their service-life. In addition, the volume of HBCDD constantly increases in the built technosphere (articles in use), and future releases are therefore unpredictable. As HBCDD can move far from its sources, single countries or groups of countries alone cannot abate the pollution caused by it. Due to the harmful POP properties and risks related to its widespread production and use, international action is warranted to control this pollution.”