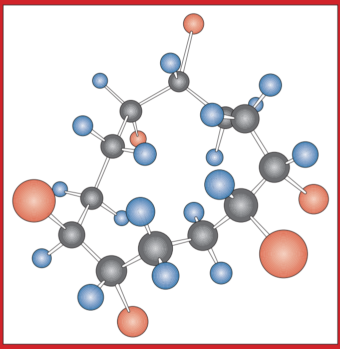

Hexabromocyclododecane (HBCDD) – a brominated flame retardant of "very high concern"[1]

Introduction

Hexabromocyclododecane (HBCDD or HBCD) is used mainly as a flame retardant in polystyrene-based insulation products. What is of particular concern is this lipophilic and persistent organic pollutant's capacity to accumulate in the food chain – leading to progressively increasing levels in human tissues and in wildlife. The extent of accumulation correlates directly with its ever-more prevalent use. Despite this alarming trend, only limited toxicological information is available to assess its long-term implications for health or the environment. Nevertheless, HBCDD continues to be used despite the availability of alternatives.

Perhaps then it is not surprising that in 2008 the European Chemicals Agency (ECHA) identified HBCDD as 1 of 14 substances of "very high concern", and that the ECHA added HBCDD to the REACH Authorisation List in September 2010. Later in 2010 a Stockholm Convention committee concluded that HBCDD meets the criteria of a "persistent organic pollutant" (POP), and recommended a worldwide ban on using HBCDD.

This document provides a brief overview of HBCDD's properties, and outlines the risks associated with its prevalence in our homes, workplaces and immediate environment.

Chemical characteristics of HBCDD

Commercial HBCDD products (CAS: 25637-99-4) are a mixture of mainly three isomers: (i) α-HBCDD; (ii) β-HBCDD and (iii) γ-HBCDD, as shown in Figs 1 and 2.

Each isomer is a pair of enantiomers (mirror images). A typical ratio of the three isomers in technical products is: 10–13%, 1–12% and 75–89%, respectively. The single isomers have slightly different physicochemical characteristics: α-HBCDD is the most thermodynamically stable isomer. The HBCDD mixture is characterized by: very poor water solubility (66 µg/L at 20°C); high lipophilicity (log K_{ow}: 5.6); low volatility ($6x10^{-5}$ Pa at 21°C) and a melting point of 190°C.

Uses of HBCDD

Most HBCDD (approximately 80%) produced is used as a flame retardant in expandable polystyrene (EPS) and extruded polystyrene (XPS) products for the building and construction industry. Other than for "underground use" and encapsulated in concrete, the addition of flame retardants to EPS and XPS is usually necessary for compliance with existing standards and/or building regulations and codes. In addition, HBCDD is applied to high impact polystyrene (HIPS) in electrical or electronic parts. It can also be found in polymer-dispersion coating agents used in textiles for upholstered fabric, furniture, mattress ticking and for seating in vehicles.

Environmental emissions

HBCDD is emitted easily into the environment. Since it isn't bound chemically to polymers, it can be released at any stage during its life-cycle – from production to the end-product to its ultimate disposal as waste.

In 2009, annual HBCDD emissions into air, surface water and waste water in Europe were estimated at 500

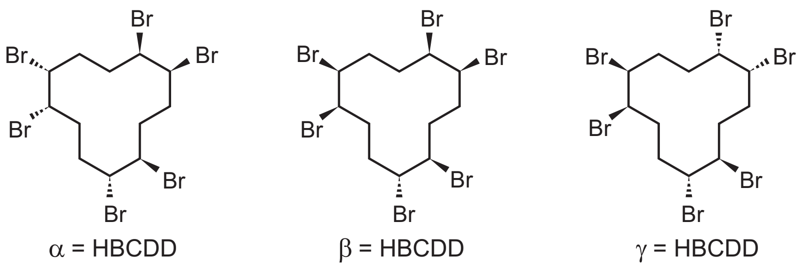

Figure 1 Chemical structures of the three main HBCDD (hexabromocyclododecane) isomers

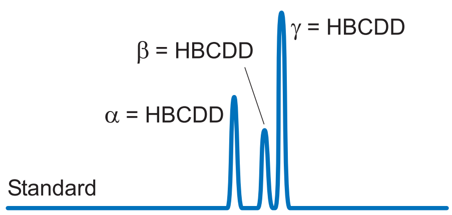

Figure 2 Typical HBCDD (hexabromocyclododecane) product

[1] Updated, December 2010.

kg, 1900 kg and 6300 kg, respectively. Air emissions are caused mainly by its use in EPS and XPS insulation boards; emissions into water generally result from its use in the textile industry. In other parts of the world – for example, Japan – relatively more HBCDD is emitted into the air than into water.

Environmental fate

HBCDD is lipophilic and very persistent in the environment. It usually adsorbs strongly to suspended matter and sediment in aquatic environments and to soils. As a result, it has low potential for leaching through soil. Modelling of the long-range transport of HBCDD in air and water suggests that it has a moderate capability for reaching remote areas. In common with other brominated flame retardants, the estimated maximum distance is approximately 2600 km in air.

Biomagnification

In large freshwater ecosystems, the trophic magnification factor (TMF) of HBCDD is a little higher than for the well-known environmental toxins, DDE and PCB. It was found that α-HBCDD is more persistent and much more bioaccumulative than the other isomers, and that it biomagnifies more in marine and aquatic food webs. High up in food chains, the γ-isomer disappears and α-HBCDD dominates (see Fig. 3).

Environmental levels and trends

HBCDD has been detected in air, water, soil and sediments in many countries. Very high levels have been found especially in aquatic sediments at close-to-point sources, such as industries producing or using the substance. In recent years, background levels have increased significantly; Fig. 4 depicts the rise in sediment levels in a remote Swiss lake with background air fall-out as the only input.

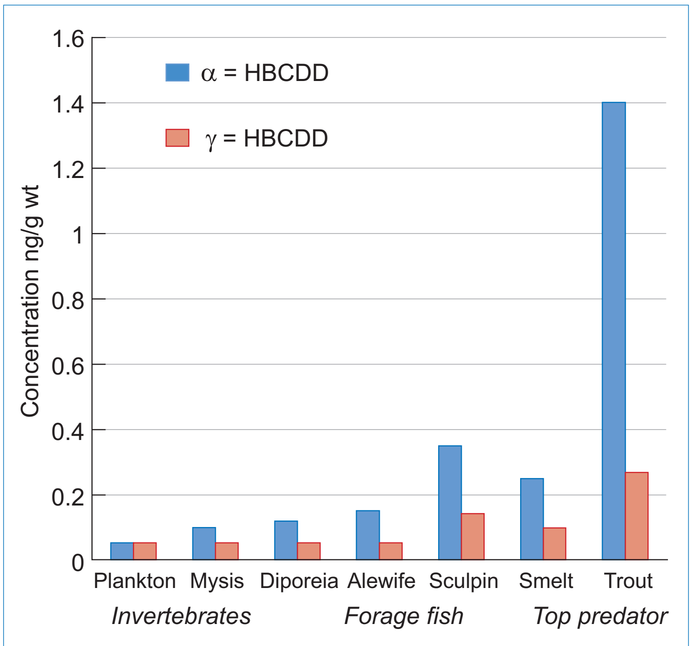

Figure 3 HBCDD (hexabromocyclododecane) biomagnification in a Lake Ontario food chain

Source: Tomy et al. 2004

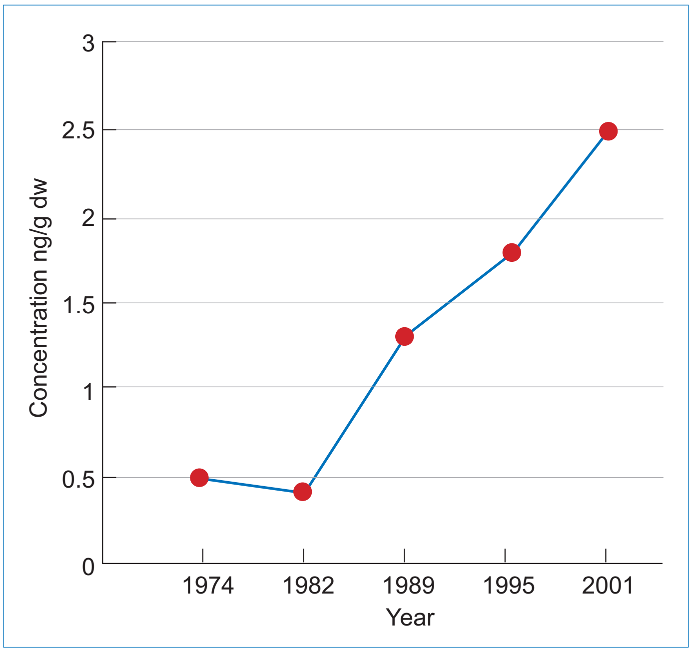

Figure 4 Time trend of HBCDD (hexabromocyclododecane) in sediment from Lake Greifensee, Switzerland

Source: Data from Kohler et al. 2008

Toxicity

HBCDD has a very low acute toxicity in animals by oral and dermal routes of administration, and no LD_{50} value is available in higher animals. It mainly targets biotransformation processes in the liver, affecting key metabolic pathways (including the metabolism of lipids and sex hormones). The most consistent effect found after repeated doses in rats was a dose-dependent increase in liver weight. A no-observable-adverse-effect-level (NOAEL) of 22.9 mg/kg per day was estimated for this effect in female rats. Pituitary and thyroid weight also increased significantly, accompanied by thyroid follicular cell hypertrophy. This effect on the pituitary induces an increased synthesis of thyroid-stimulating hormone (TSH).

It has also been found that exposure to HBCDD can have wide-ranging and potentially severe effects – particularly to the neuroendocrine system and to offspring during the early phases of development. There are several studies on HBCDD's reproductive effects: in a two-generation study, thyroid effects were observed both in dams and offspring (Ema et al. 2008). The NOAEL in that study was 10 mg/kg per day. Another study (Eriksson et al. 2006) indicated that neonatal HBCDD exposure may cause statistically significant changes in spontaneous behaviour and learning and may also induce memory defects. An indicative lowest-observable-adverse-effect-level (LOAEL) of 0.9 mg/kg per day was also deduced from this study.

A one-generation reproduction feeding study showed that HBCDD induces disturbances in hearing function and changes in dopamine-dependent behaviour (van der Ven et al. 2009). It is worth noting however that the majority of studies that administered the substance orally were performed with HBCDD particles suspended in oil, resulting in low absorption and as a result uncertain exposure measures.

HBCDD in wildlife – levels and trends

HBCDD bioaccumulates in wildlife, including fish, birds and mammals. Marine mammals and fish-eating birds (high in the food chain) generally show the highest levels of contamination, and it appears that this increase in HBCDD levels is ongoing (Law et al. 2008b). The temporal trend between 1994 and 2006 of HBCDD levels in the blubber of stranded harbour porpoises from the United Kingdom increased steeply from 2000 to 2003, and then quickly decreased – but to levels that were still many times higher than before 2000. The reversal of the trend is most likely explained by the closure of an HBCDD manufacturing plant in north-east England in 2003 (see Fig. 5).

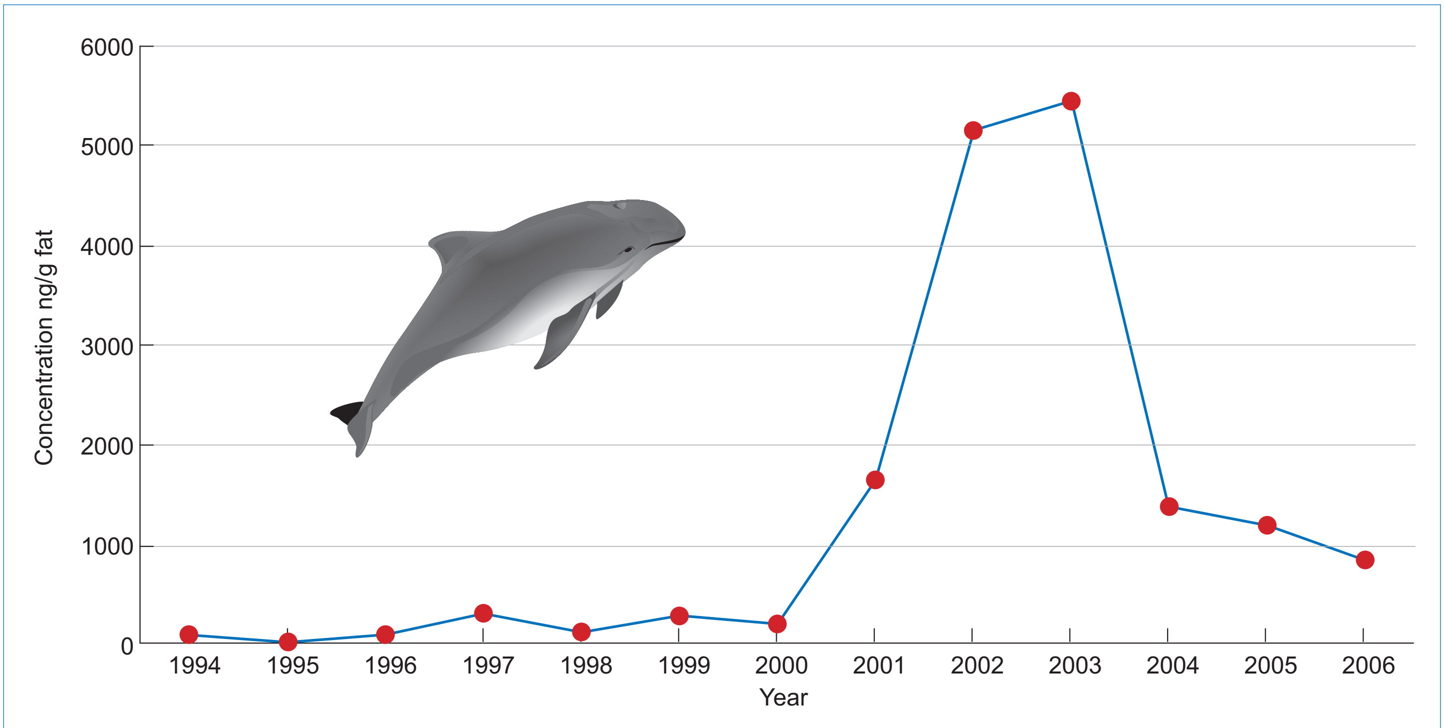

Figure 5 Time trend of HBCDD (hexabromocyclododecane) in blubber of harbour porpoises stranded in the UK

Source: Data from Law et al. 2008a

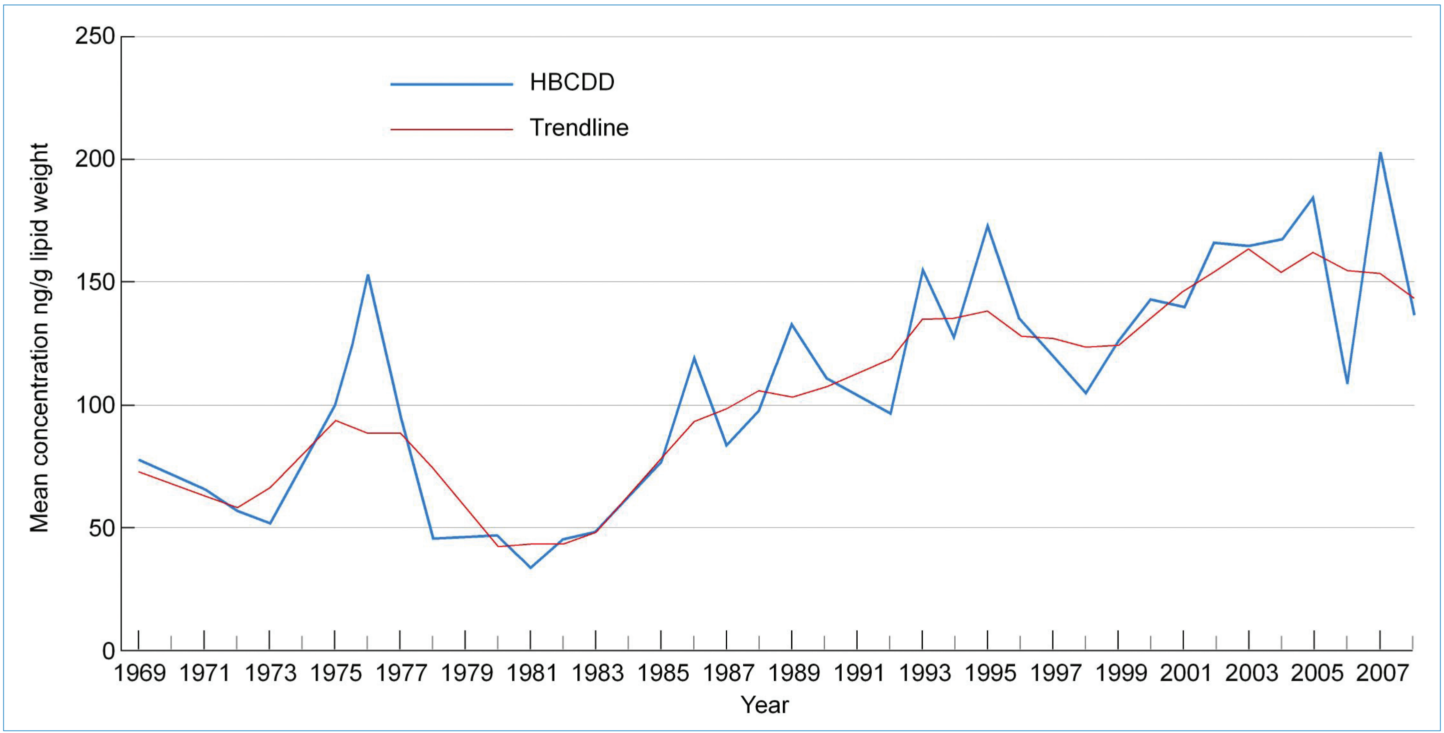

Figure 6 Time trend of HBCDD (hexabromocyclododecane) in guillemot eggs from the Baltic Proper

Source: Data from the Swedish Museum of Natural History 2008, 2010

In another example of increasing pollution by HBCDD, the average concentration of HBCDD in the eggs of the Baltic Proper guillemot (collected between 1969 and 2008) more than tripled – from 50 ng/g lipid weight in the early 1970s to approximately 200 ng/g in 2007 (see Fig. 6).

Ecotoxicity

In early life-stage toxicity tests performed on newly fertilized eggs of the rainbow trout (*Oncorhynchus mykiss*), the no-observable-effect-concentrations (NOEC) of HBCDD for end points such as hatching success, time to swim-up, larvae and fry survival were all ≥3.4 µg/L. In water fleas (*Daphnia magna)* exposed to low concentrations of HBCDD, there was also an effect on reproduction (reduced length, weight and fewer young), with an NOEC of 3.1 µg/L. Both values meet the European Union T-criterion of chronic ecotoxicity of NOEC <10 µg/L.

Human exposure to HBCDD

Because of its use in products throughout society, humans are exposed to HBCDD from a variety of sources. Workers are potentially exposed because of their direct contact with the pure substance – including anyone working near processes emitting HBCDD, packing the substance or transferring the substance to other systems in the chemical industry.

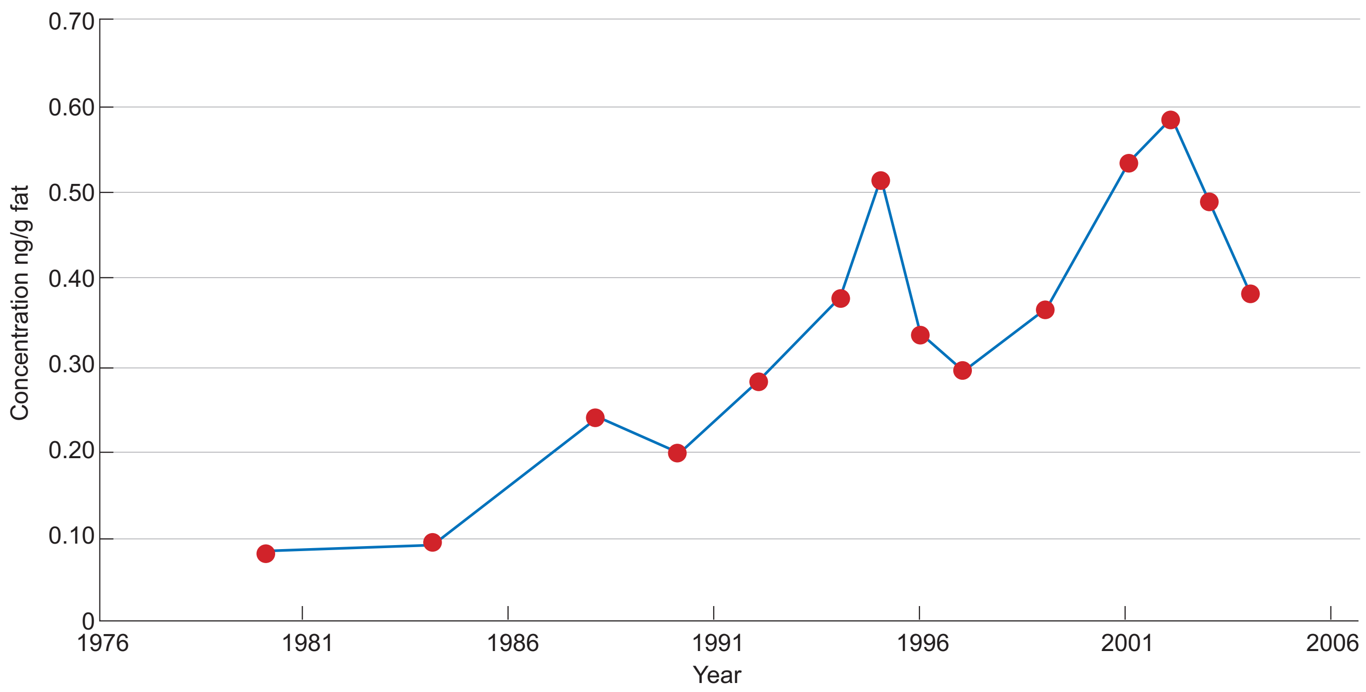

Figure 7 Time trend of HBCDD (hexabromocyclododecane) concentration in Swedish mothers' milk

Source: Data from Fängström et al. 2008

The general population's exposure to HBCDD can come from indoor exposures, from consumer products (textiles, etc.) containing HBCDD and from food and food packaging. Direct exposure from soil, water and air is less important.

HBCDD in indoor air and dust

HBCDD has a low vapour pressure (gaseous phase air levels of HBCDD are minimal), but it is adsorbed to particulates. Indoor exposure is considered a significant route to human exposure: HBCDD concentrations in interior air are generally ten times higher than outdoors. In addition, HBCDD concentrations in home and office dust can be very high, mostly originating from building materials and textiles. Small children may be very exposed (through house dust) when playing on the floor in homes and institutions.

HBCDD in human milk

HBCDD is absorbed into the body through the respiratory and gastro-intestinal tracts, and it accumulates in body fats. Levels in humans can be monitored by analysis of blood or human milk. Through the latter, HBCDD can be transferred to the nursing infant.

Figure 7 shows that HBCDD concentrations have increased in Swedish mothers' breastmilk over a 20-year period. While levels are low compared to DDT or PCB, they are only slightly lower than the most bioaccumulative polybromodiphenyl ether (PBDE) congeners. In the same study, the most abundant PBDE congener (#153) in the mothers' milk is present at concentrations of 0.06–1.3 ng/g fat.

Risk assessment

A margin of safety (MOS) for HBCDD is calculated from the NOAEL of 22.9 mg/kg per day estimated for liver-weight increase in a 28-day study in female rats. This study is of short duration and has not been confirmed by other studies, so the NOAEL may be too high. An estimated minimal safety factor of 20 for workers and 40 for consumers was used to conclude that only workers filling bags with the chemical are at risk. However, in a scientific opinion on the risk assessment report on HBCDD on 15 January 2008, the EC Scientific Committee on Health and Environmental Risks (SCHER) called the use of the MOS of 20 and 40 “unjustified”.

Regulations

The risks of exposure to HBCDD were recognized by the ECHA (http://ECHA.europe.eu) on 30 June 2008 when HBCDD was announced as a substance of “very high concern”, because of its properties as a persistent, bioaccumulative and toxic substance (PBT). In June 2009 the ECHA decided to recommend HBCDD for inclusion in the REACH Authorisation List, and in September 2010 HBCDD was added to that list.

In October 2010 the Persistent Organic Pollutant Review Committee under the Stockholm Convention assessed the risks from HBCDD and concluded that HBCDD fulfils the criteria of a POP, and the committee recommended a global ban on the use of HBCDD (http://chm.pops.int/).

HBCDD was included in the "San Antonio Statement on Brominated and Chlorinated Flame Retardants" signed in September 2010 by 245 scientist from 22 countries (diGangi et al. 2010).

Conclusions

HBCDD is known to accumulate extensively in the food chain and in humans. However, only limited information is available on its toxicology and nothing is known about the differences in susceptibility between animals and humans. As a result, it is currently not possible to provide a definitive assessment of the long-term risks of this substance to health and the environment.

Despite this, HBCDD continues to be used extensively, even though viable insulation alternatives are available – such as mineral wool (stone wool and glass wool) and foam glass, which do not require the use of flame retardants.

References

Information for this brochure was compiled by Allan Astrup Jensen, FORCE Technology (aaj@force.dk) and Åke Bergman, University of Stockholm (ake.bergman@mk.su.se) with financial support from Rockwool International A/S.

An important source of information was: "Risk Assessment Report on Hexabromocyclododecane, CAS-No. 25637-99-4", Final draft May 2008, produced by the Swedish Chemicals Agency for the EU Risk Assessment, http://ecb.jrc.ec.europa.eu/documents/Existing-Chemicals/RISK_ASSESSMENT/REPORT/hbcddreport044.pdf

Other references used include:

Abdallah MA-E, Harrad S, Covaci A. **Hexabromocyclododecanes and tetrabromobisphenol-A in indoor air and dust in Birmingham, UK: Implication for human exposure.** Environ Sci Technol 2008; 42: 6855–6861.

DiGangi J, Blum A, Bergman Å, de Wit CA, Lucas D, Mortimer D, Schecter A, Scheringer M, Shaw SD, Webster TF. **Editorial: San Antonio Statement on Brominated and Chlorinated Flame Retardants.** Environ Health Perspec. 2010; 118: A516–A518.

Ema M, Fujii S, Hirata-Koizumi M, Matsumoto M. **Two-generation reproductive toxicity study of the flame retardant hexabromocyclododecane in rats.** Reprod Toxicol 2008; 25: 335–351.

Eriksson P, Fisher C, Wallin M, Jakobsson E and Fredriksson A. **Impaired behaviour, learning and memory, in adult mice neonatally exposed to hexabromocyclododecane (HBCDD).** Environ Toxicol Pharmacol 2006; 21: 317–322.

Fängström B, Athanassiadis I, Odsjö T, Norén K, Bergman Å. **Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in milk from Stockholm mothers, 1980–2004.** Mol Nutr Food Res 2008; 52: 187–193.

Kohler M, Zennegg M, Bogdal C, Gerecke AC, Schmid P, Heeb NV, Sturm M, Vonmont H, Kohler H-PE, Giger W. **Temporal Trends, congener patterns, and sources of octa-, nona-, and decabromodiphenyl ethers (PBDE) and hexabromocyclododecanes (HBCD) in Swiss Lake Sediments.** Environ Sci Technol 2008; 42: 6378–6384.

Law RJ, Bersuder P, Brady J, Wilford BH, Allchin CR, Jepson PD. **A significant downturn in levels of hexabromocyclododecane in the blubber of harbour porpoise (*Phocoena Phocoena*) stranded or caught in the UK: an update to 2006.** Environ Sci Technol 2008a; 42: 9104–9109.

Law RJ, Herzke D, Harrad S, Morris S, Bersuder P, Allchin CR. **Levels and trends of HBCD and BDEs in the European and Asian environments, with some information for other BFRs.** Chemosphere 2008b; 73: 223–241.

Lilienthal H, van der Ven LT, Piersma AH, Vos JG. **Effects of the brominated flame retardant hexabromocyclododecane (HBCD) on dopamine-dependent behavior and brainstem auditory evoked potentials in a one-generation reproduction study in Wistar rats.** Toxicol Lett 2009; 185: 63–72.

Managaki S, Miyake Y, Yokoyama Y, Hondo H, Masunaga S, Nakai S, Kobayashi T, Kameya T, Kimura A, Nakarai T, Oka Y, Otani H, Miyake A. **Emission load of hexabromocyclododecane in Japan based on the substance flow analysis.** Organohalogen Compounds 2009; 71: 2471–2476.

Swedish Museum of Natural History. **Comments concerning the national Swedish contaminant monitoring programme in marine biota** 2008-03-31. Stockholm, 2008. http://www.nrm.se/

Swedish Museum of Natural History. **Övervakning av metaller och organiska miljögifter i marin biota, 2010.** Report nr. 1. Stockholm, 2010. http://www.nrm.se/

TemaNord. **Hexabromocyclododecane as a possible global POP.** Nordic Council of Ministers, Copenhagen, Denmark, 2008.

Tomy G, Budakowski W, Halldorson T, Whittle M, Keir M, Alaee M. **Biomagnification of α- and γ-hexabromocyclododecane (HBCDD) congeners in a Lake Ontario food web.** Environ Sci Technol 2004; 38: 2298–2303.

van der Ven LT, van de Kuil T, Leonards PE, Slob W, Lilienthal H, Litens S, Herlin M, Håkansson H, Cantón RF, van den Berg M, Visser TJ, van Loveren H, Vos JG, Piersma AH. **Endocrine effects of hexabromocyclododecane (HBCD) in a one-generation reproduction study in Wistar rats.** Toxicol Lett 2009; 185: 51–62.