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BROMINATED FLAME RETARDANTS

In view of the high cost of fire damage (in the US in 2003 alone, there were 3925 deaths, 18,125 injuried, and about $12 billion of property damage (*1*)), flame retardants were developed to decrease the risks of personal and material damage. Flame retardants work by a) raising polymer ignition temperatures; b) reducing burn rate; c) reducing flame spread; or d) reducing smoke generation (*1*).

BFR CHEMISTRY

The four steps involved in the combustion process are preheating, volatilization/ decomposition, combustion and propogation (*2*) (See figure below).

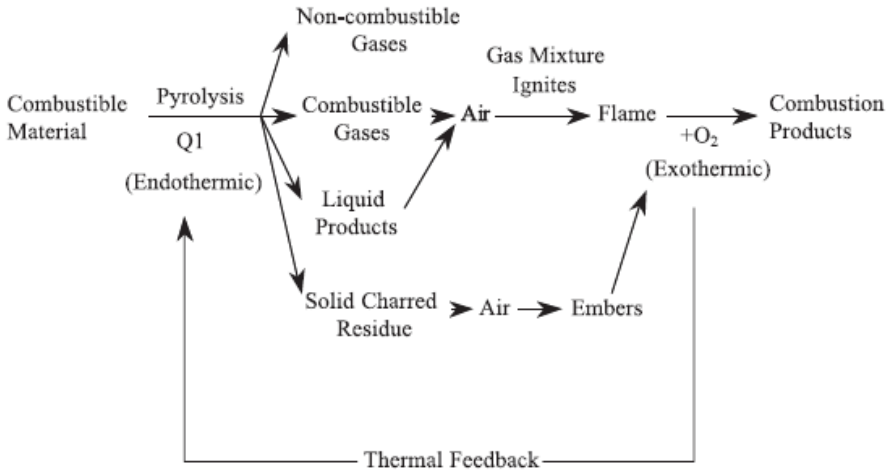


Fig. 1. The four steps of the combustion process (Troitzch, 1990).

Brominated flame retardants (BFRs) act primarily by interfering with the radical chain mechanism that occurs during gas phase combustion, thereby preventing or delaying ignition and slowing burn rate once initiated (*1*). In other words, the large bromine is very effective at trapping the free radicals (highly oxidizing agents) created during combustion and necessary for flame propogation (2).

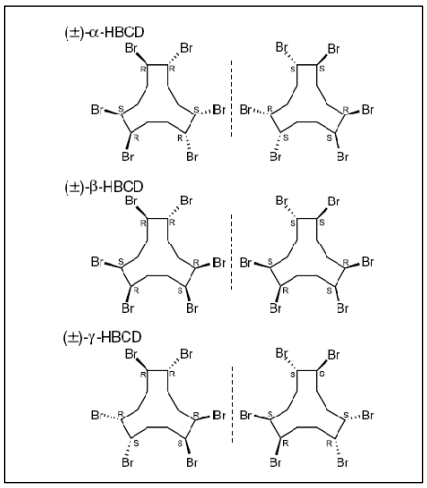
HBCD USE

Of particular interest is hexabromocyclododecane (HBCD), which accounted for 8% (16,700 metric tons) of the BFR global market demand in 2001 (*3*):

Table 1. The usage of selected brominated flame retardants in different areas of the world in 2001 (in tonnes) (3).

	America	**Europe**	**Asia**	**Rest of the world**	**Total**	**% of total world usage**
TBBP-A	18 000	11 600	89 400	600	119 700	59
HBCD	2800	9500	3900	500	16 700	8
Deca-mix PBDE formulation	24 500	7600	23 000	1050	56 100	27
Octa-mix PBDE formulation	1500	610	1500	180	3 790	2
Penta-mix PBDE formulation	7100	150	150	100	7500	4
Total	53 900	29 460	117 950	2430	203 790	

Figure 2. Industrial HBCD consists of a mixture of six isomers—(+/-) alpha, (+/-) beta, and (+/-) gamma (*3*):



HBCD is an additive (i.e. simply blended, as opposed to chemically bonded) flame retardant, which make it more vulnerable to leaching (*2*). According to the Lowell Center for Sustainable Production,

"The primary use of HBCD is as a flame retardant additive in expanded polystyrene (EPS) and extruded polystyrene (XPS) applications. . . typically used for thermal insulation foams. . . in the building and construction industry. HBCD is also used for textile [e.g. upholstery in furniture, vehicles, draperies] and high impact polystyrene (HIPS) applications [e.g. electronics, wire, and cable]). There are four types of commercial HBCD mixtures produced, each with different melting points. All mixtures contain the isomers alpha-HBCD, beta-HBCD, and gamma-HBCD. HBCD is a lipophilic compound with a log K_{ow} of 5.6, and is considered bioavailable and bioaccumulative based on studies of fish and fish eating animals (*1*)."

PERSISTENCE:

Atmospheric Persistence:

Measurements of total HBCD in air samples at various locations in Sweden (0.013-0.75 ng/m^3 near landfills and the textile industry (N=4); 0.076 and 0.61 ng/m^3 at urban sites in Stockholm; <0.001-0.28 ng/m^3 in more remote locations (N=6)) indicated that HBCD may be "sufficiently long-lived to undergo long-range atmospheric transport away from point sources of production and use (*4*)."

Sewage Sludge, Sediments, and Soil:

As BFR's leach from products into wastewater streams, they often find their way into sewage sludge (*3*).

Table 2. The mean, standard deviation and range of concentrations (μg kg^{-1} dry weight) for each BFR compound determined in sludge from 50 Swedish sewage treatment plants in 2000 (3).

Substance	Mean	Standard deviation	Range
BDE47	49	22	7.0–100
BDE99	60	29	8.1–150
BDE100	11	4.8	1.5–22
BDE153	6.1	3.3	0.8–18
BDE154	4.1	2.1	0.6–10
∑BDE	130	60	18–260
BDE209	120	160	5.6–1000
HBCD	45	94	3.8–650
TBBP-A	40	33	<4–180
BB209	5.6	3.1	<0.4–10

HBCD was found in sludge from Swedish sewage treatment plants (See table) and also found in UK sludge (530-2680 ug/kg dry weight, N=5), Ireland (15-9120 ug/ kg dry weight, N=6), and the Netherlands (<0.4-93 ug/kg dry weight, N=10) (*3*).

The half-life for technical HBCD degradation in anaerobic conditions in sewage sludge was measured to be a relatively short 0.66 days, but the alpha isomer had a half-life nearly double that of the isomers (*5*). This may account for the dominance of the alpha isomer in biotic samples, in one study, it accounted for greater than 80% of total HBCD concentration in the seal and porpoise liver and blubber samples (*6*).

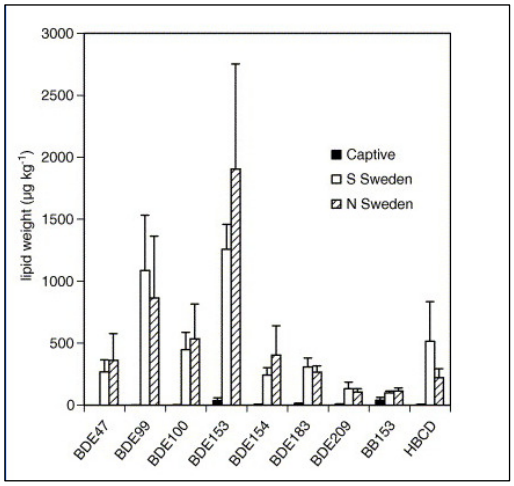
HBCD was also detected in river and estuarine sediments in Belgium, the Netherlands, and the UK (ranging from <0.2 ug/ kg dry weight to 1700 ug/ kg dry weight near a site of BFR manufacture) with isomer profiles similar to industrical formulations, dominated by gamma-HBCD (*6*).

BIOACCUMULATION:

As aforementioned, HBCD has a log K_{ow} of 5.6, which qualifies it as bioaccumulative, since its lipid solubility is $10^{5.6}$ greater than its water solubility. Among the studies that support this is a Swedish study that measured higher

HBCD levels in wild peregrine falcons (which would consume contaminated game and fish, increasing exposure and biomagnifying HBCD concentrations) as compared to those falcons raised in captivity (520 ug/ kg lipid weight (south wild); 220 ug/ kg lipid weight (north wild); below detection limit (captive)) (*7*):

Fig. 3. Concentrations (μg kg^{-1} lipid weight, mean ± SE) of BDE47, BDE99, BDE100, BDE153, BDE154, BDE183, BDE209, BB153 and HBCD in eggs from two wild and one captive population of peregrine falcons in Sweden (7).



HBCD was also measured in fish (cod, hake, whiting), eels, cormorant livers, common tern eggs, harbor seal and harbor porpoise blubber in the UK and the Netherlands, where the major increase in HBCD concentration appeared at the transition from gill-breathing to lung-breathing animals (*6*), which may mean that inhalation/ absorption is as important as or of greater importance than ingestion/ absorption as a means of exposure.

In another Dutch study led be Leonards, et al (2004) the transfer of HBCD was measured by analyzing sediment, suspended particulate matter, invertebrates, tern eggs, and adult male seal blubber samples. HBCD concentrations increased from invertebrates to fish, but decreased from fish to tern eggs, suggesting that terns may be able to metabolise HBCD (3).

A more recent study of dolphins found that only the alpha-isomer was isolated in its fat and liver tissue. The beta and gamma (the most prevalent in industrial mixes) were metabolized by the enzyme complex P450 in the liver by adding oxygen to the isomers. The alpha isomer, however, could not be metabolized and therefore accumulated in fatty tissues (8).

Studies of breast milk in Japanese women from 1973 to 2006 (sampling done roughly every 5 to 6 years) showed no detectable HBCD up to 1983, but a steady increase in HBCD concentration (the alpha-isomer) from 1988 on, which is consistent with Japanese industrial usage of the BFR (9).

TOXICITY*:*

There are few toxicity studies available for HBCD, but one animal study found that a critical effect is seen in the liver and on thyroid hormones (LOAEL 100 mg/ kg body weight/day). It was also mentioned, however, that behavioral effects in mice pups were observed at a much lower exposure concentration of 0.9 mg/ kg bodyweight, indicating that timing, in addition to dosage, may affect toxicity/ sensitivity to exposure (*10*).

Furthermore, because of their similarity in structure to PCBs, there is some concern that BFRs may be endocrine disruptors, though there are few studies as of yet to support this concern (11). A very recent rat study (still in press) indicated that several specific pathways seem to be affected by HBCD exposure. Among those pathways affected are PPAR-mediated regulation of lipid and triacylglycerol metabolism (down-regulated, particularly in females), cholesterol biosynthesis, and phase I and II metabolic pathways (up-regulated, particularly in males) (12). If HBCD affects fat metabolism and storage as indicated, it could also indirectly affect bioaccumulation of other POPs.

CONCLUSION: Is it PBT?

HBCD is somewhat persistent. It is most definitely persistent enough that it is nearly ubiquitous in sewage and sediment and animal samples. This, however, may be a factor more closely tied with its continuous use and production, a steady input of HBCD into environments all over the globe. Because HBCD cannot be detectably measured everywhere, there is evidence, with the exception of the alpha-isomer, that HBCD degrades fairly rapidly in the environment and that concentrations would drop should inputs decrease. The alpha-isomer, however, cannot be broken down by enzymatic oxidation and has a much longer half-life than the other two isomers. It is persistent.

alpha-HBCD is definitely bioaccumulative, resisting degradation by liver enzymes. As for HBCD's toxicity, there is still a scarcity of toxicity studies, but there is some evidence that it may affect fat metabolism and liver function.

BIBLIOGRAPHY

1. Morose, G. *An Overview of Alternatives to Tetrabromobisphenal A (TBBPA) and Hexabromocyclododecane (HBCD)* Lowell Center for Sustainable Production: Lowel, MA, 2006. http://sustainableproduction.org/downloads/AternativestoTBBPAandHBCD.pdf Retrieved on 2008-08-06.
2. Alaee, M.; Arias, P.; Sjodin, A.; Bergman, A. *Environ. Inter.*, **2003**, 29, 683-389.
3. de Wit, C.A.; Alaee, M.; Muir, D.C.G. *Chemosphere*, **2006**, 64, 209-233.
4. Remberger, M.; Sternback, J.; Palm, A.; Kaj, L.; Stromberg, K.; Brorstrom-Lunden, E. *Chemosphere*, **2004**, 54, 9-21.
5. Gerecke, A.C.; Giger, W.; Hartmann, P.C.; Heeb, N.V.; Kohler, H.E.; Schmid, P.; Zennegg, M.; Kohler, M. *Chemosphere*, **2006**, 64, 311-317.
6. Morris, S.; Allchin, C.R.; Zegers, B.N.; Haftka, J.J.H.; Boon, J.P., Belpaire, C.; Leonards, P.G.; van Leeuwen, S.P.J.; de Boer, J. *Environ. Sci. Technol.*, **2004**, 38, 5497-5504.
7. Lindberg, P.; Sellstrom, U.; Haggberg, L.; de Wit, C.A.; *Environ. Sci. Technol.*, **2004**, 38, 93-96.
8. *Toxic Flame Retardant Accumulates in Dolphins.* http://www.nwo.nl/nwohome.nsf/pages/NWOP_6AGDLZ_Eng. Retrieved on 2008-08-06.
9. Kakimoto, K.; Akutsu, K.; Konishi, Y.; Tanaka, Y. *Chemosphere*, **2008**, 71, 1110-1114.
10. Darnerud, P.O. *Environ. Inter.* **2003**, 29, 841-853.
11. Legler, J.; Brouwer, A. *Environ. Inter.* **2003**, 29, 879-885s.
12. Canton, R.F.; Peijnenburg, A.C.M.; Hoogenboom, R.L.A.P., Piersma, A.H.; van der Ven, L.T.M.; van den Berg, M., Heneweer, M. *Toxic. App. Pharmac.* **2008.** In press, available online (Title: Subacute effects of HBCD on hepatic gene expression in rats)