# BFRs - with focus on Environmental Fate and Risks of Decabromodiphenyl ether and Hexabromocyclododecane

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## Introduction

Brominated flame retardants (BFRs) never became an environmental issue neither in the 1970s' nor the 1980s', even though the accidental spread of polybrominated biphenyls, FireMaster BP-6, occurred in Michigan in 1973 [1], the identification of pentabromotoluene was made in biosolids samples from Sweden in 1975[2] and a range of BFRs were listed by Norström and co-workers in 1976 as potential environmental contaminants of concern[3]. The interest was sparked by the identification of high concentrations of PBDEs in fish from Viskan, a river on the Swedish west coast, floating through a district well known for its textile industry[4]. In the second part of the 80s' there were a few more reports pointing out PBDEs both in biota and in sediments from Japan[5] and TBBPA in sediments and mussles[6].

The BFR use was considered an environmental risk and the "First International Workshop on BFRs" was gathered in Skokloster, Sweden, 1989. However no actions were taken from the legislative side but voluntarily the use PBDEs decreased, both in Sweden and Germany. The research took off at the time when authentic reference standards of the PBDEs became available and after PBDEs were reported in increasing concentrations in mothers' milk at the Dioxin 98 symposium [7,8]. Today it is possible to look back on an exponential increase in the number of scientific publications on BFRs with >200 scientific articles 2003 dealing with BFRs in an environmental perspective.

Since it is not longer possible to make a review covering all aspects of BFRs without writing a book, I have the intention to focus and briefly discuss commercial BFRs produced today and then in some detail review the present status of our knowledge on DecaBDE, dominated by BDE-209, and on hexabromocyclododecane (HBCDD).

## BFRs in general

The listing of BFRs that was made by IPCS 1997 has been adopted by several governments and scientists as being the actual list of BFRs in use [9]. Additional chemicals have been mentioned and isomers and homologues of certain classes of BFRs are sometimes mentioned as single BFR chemicals. Also the BFR producers have indicated a large and disparate production of bromine containing chemicals to be applied as BFRs, as such or after being incorporated in polymers. In a present study Örn and Bergman presents a list of 21 chemicals being produced by three, two or one of the dominating BFR

producers in the world[10]. After the ban of PentaBDE and OctaBDE within EU and the voluntarily production phase out by Great Lakes Chemicals we may still see tetrabromobisphenol A (TBBPA), DecaBDE and HBCDD as the major BFRs. Other BFRs, produced by two or three of the major manufacturers are TBBPA bis(2,3-dibromoproyl) ether, tetrabromophthalic anhydride and decabromodiphenyl ethane. The identification of decabromodiphenyl ethane in the environment is of course an additional indication of this compound being a BFR of concern[9,11]. Further, the presence of bis(2,4,6-tribromophenoxy) ethane (BTBPE) in air at an electronics dismantling facility[12] and potentially its presence in human blood among the dismantlers are indications of an emerging BFR issue, particularly since it is still in production[10]. The potential environmental fate of the major commercial BFRs will be discussed.

**Decabromodiphenyl ether – BDE 209**

BDE-209 has very poor water solubility but also difficult to dissolve in many organic solvents, it is extremely lipophilic and it is difficult to vaporise the compound[13]. On the other hand it is a rather reactive compound as shown by 1) fast degradation when subjected to UV-light above 290 nm [14-16] either it is irradiated in a solvent or on a surface; 2) when subjected to nucleophiles such as methane thiolate[17] and 3) when treated with hydride reagents such as sodium borohydride[18]. The high reactivity of BDE-209 is in agreement with the observed half-life of this compound both in humans and in rats, being 14 and 2.8 days, respectively[19,20]. Several metabolites were detected in the rat[21] and also in pike[22] and in carp[23], in fish it seems likely that the lower brominated diphenyl ethers are formed through reductive debromination. In the rat both hydroxylated and methoxylated metabolites were detected, as well as metabolites substituted with both these two groups[21]. Considering only the reactivity and metabolism of BDE-209 it can be concluded that this is not a persistent chemical, neither in the abiotic environment nor in organisms. Still, with a large production and elimination to the environment it is possible to keep up a steady-state level that must not be overlooked. The elimination rate has been well studied in workers handling DecaBDE[19]. It is also notable that the background level of BDE-209 is a commonly experienced problem when it is analysed for. If the background problem can be handled the concentrations of BDE-209 seem to have increased over the years, something that need further attention, though.

Analysis of BDE-209 was for some time a problem and a common reason for not including it in the analysis. Today the analytical technical problems have been largely overcome and it is possible to choose between methods for its analysis which may be performed by 1) GC/low resolution MS by electron capture negative ion detection of m/z 79 and 81[24]; b) high resolution MS[25]; c) applying an isotope dilution technique followed by low resolution MS/ECNI[26]. The detection problem is related to contamination of the samples during work up but still this can be handled but require a number of preventive measures. BDE-209 concentrations have been reported in a number of studies from where data have been extracted for Table 1 summarising some of the BDE-209 levels reported from wildlife and in humans. The most intriguing results are the BDE-209 levels in bird of prey, e.g. the pelegrin falcon[27]. Also, BDE-209 in mothers milk from the U.S and more

recently also indicated in milk from Sweden and Mexico, the latter holding the highest concentrations[25,28]. The conclusion is that individuals seem to be subjected to DecaBDE exposures more or less continuously and hence levels in the low ppb area can be detected independent of the short half-life of BDE-209 in humans. It is evident that BDE-209 is bioavailable, either this is a result of passive uptake or active transport in the organisms.

I would like to stress two toxicological outcomes of DecaBDE. First the NTP study from 1986 concluding that there are "some evidence of carcinogenicity" of decaBDE[29]. The conclusion is interesting since the animals were actually only absorbing a very minor fraction of the high dose the researchers tried to give the animals. The results indicate that this minor dose gave rise to the cancer observed. The result is logical from the knowledge that BDE-209 is a rapidly reacting comound that may undergo reactions *in vivo* also with DNA. Studies addressing in vivo arylation with BDE-209 are strongly recommended. Secondly, the neurobehavioural effects observed in the offspring from rats that were dosed with BDE-209 is an important finding[30]. Finally, with BDE-209 being a reactive compound there must be a range of degradation products with hitherto unknown health effects. BFRs including DecaBDE are sources for mixed polybromo-polychlor dibenso-p-dioxins (PBCDD) and dibenzfurans (PBCDFs) under waste combustion conditions and hence a potential source of toxic "dioxins"[31,32].

**Table 1.** Levels of BDE-209 and HBCDD in wildlife and humans

| Species/matrix/location | Sampling Year | HBCDD | BDE-209 | Ref |
|---|---|---|---|---|
| Herring muscle, Baltic Sea | 2000 | 58 ng/g l.w. | | 33 |
| Herring muscle, The Nordic Sea | 1999 | 21 ng/g l.w. | | 33 |
| Farmed salmon | 1996 | 6.7 ng/g l.w. | | 33 |
| Wild salmon | 1999 | 51 ng/g l.w. | | 33 |
| Peregrine Falcon, southwestern Sweden, egg | 1992-1999 | 80-2400 ng/g l.w | <20-430 ng/g l.w. | 27 |
| Dutch mothers, serum | | <0.16-6.9 ng/g l.w. | | 34 |
| Mexican women, milk | 2004 | 0,8-5,4 ng/g l.w. | 0,1-0,6 ng/g l.w. | 28 |
| Mexican women, serum | 2004 | 0,7-2,5 ng/g l.w. | 4,8-15 ng/g l.w. | 28 |
| Sweden male, rubber mixers, serum | 2000 | | 1.4-160 ng/g l.w. | 35 |
| Sweden male, wire manufacturers, serum | 2000 | | 7.9-300 ng/g l.w. | 35 |

**Hexabromocyclododecane**

HBCDD seem to be the third most important BFR with a production volume of almost 16.000 tons annually[36]. Depending on the stereochemistry of the compound it may appear as at least three isomers, known as α-, β- and γ-HBCDD, corresponding to (1R,2S,5S,6R,9S,10S)-, (1R,2R,5R,6S,9R,10S)- and (1S,2S,5S,6S,9S,10S)-HBCDD [37]. It

is a lipophilic compound with log $K_{ow}$ of 5.6 that is bioavailable and bioacc-umulating according to available data of fish (herring and salmon) and the fish eating guillemot[33,38]. Looking at the chemical reactivity of this compound it is evident that it will eliminate hydrogen bromide if heated or treated with an alkali (e.g. sodium or potassium hydroxide for partitioning purposes of other analytes).
The analysis of HBCDD may be performed by GC/MS or by LC/MS, the latter has shown to be favourable for isomer specific analysis. On the other hand GC/MS is suitable if the sum of HBCDD isomers are to be quantified. A method was developed by Weiss et al for work up and analysis by GC/MS with determination of m/z 79 and 81[34]. The recovery of HBCDD was in the range of 70% and found suitable for assessing mother and infant serum in a Dutch population. This method was also used for analysis of HBCDD in blood and milk among Mexican and Swedish women[28].

HBCDD seems to be a ubiquitous environmental contaminant[28,33,34,38-40] but so far data set is more limited than for PBDEs. A selection of concentration data of HBCDD in biota is given in Table 1. Guillemot eggs from Stora Karlsö in the Baltic Proper has been monitored for HBCDD since the early 1970s' showing a steady increase of the levels, approximate 3% per year[39]. This is an alarming situation. The HBCDD levels both in humans and in grey seals seem to be rather low[41]. If this is due to metabolic elimination of HBr, similar to the DDT that eliminate HCl metabolically, is not yet confirmed. However, if this is the case we need to look for bioaccumulative HBCDD metabolites.

In conclusion, both DecaBDE and HBCDD are of environmental concern but from different perspectives; BDE-209 due to its reductive, nucleophilic substitution and photochemical reactivities and indications of toxicity; HBCDD as a persistent and bioaccumulative BFR.

**Acknowledgement**
Financial support for my BFR research comes from the NewS program at MISTRA, Sweden. I am grateful to all my colleagues and students for their hard work within the BFR field.

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