BROMINATED FLAME RETARDANTS IN THE ENVIRONMENT

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Abstract. Environmental contamination by brominated flame retardants (BFRs) has received a lot of attention in the scientific literature since the late 1990s. A number of BFRs, such as penta- and octabromodiphenyl ethers (penta- and octaBDE's) and hexabromocyclododecane were identified as bioaccumulating and potentially toxic compounds. For others the databases are still incomplete. This chapter gives an overview of recent trends of BFR concentrations in the environment, with some attention to the analytical methods and difficulties, and their toxicology. The European ban on penta- and octaBDE's has already initiated decreasing trends in their environmental levels in Europe. However, the concentrations of these BFRs in the USA are considerably higher than in Europe and decreasing trend have not been observed yet. In sediments, much higher decaBDE concentrations have been found as compared to pentaBDE concentrations, both in Europe and the USA. DecaBDE was recently banned in Europe for use in electric circuit boards, but applications in textile and furniture are still allowed. Endocrine disruption, often through the thyroid gland is the most worrying effect of several BFRs.

Keywords: brominated flame retardants, polybromodiphenyl ethers, hexabromocyclododecane, decabromodiphenylethane, environment, analysis, risk.

1. Introduction

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) have been found in the environment and in food since the 1960s [24, 43]. Although most of these chemicals have been phased out, residues are still being found, emphasizing the persistent character of these POPs [10]. On top of that, chemical contaminants that remained undiscovered in food and the environment for many years have recently been identified. One such category is the group of brominated flame retardants (BFRs). About 75 commercially available BFRs are currently being used worldwide to flameproof electronic

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equipment such as personal computers and televisions, but also in upholstery textile, building materials, planes, cars, etc. [13]. The amounts in which they are added to the plastics or fibers range from 1% to more than 10% by weight. Some BFRs, tetrabromobisphenol-A (TBBP-A) for example, are chemically bound to the materials to be flame proofed, while others, for example pentabrominated diphenylethers (PBDE's) and hexabromocyclododecane (HBCD), are applied as additives. During production, impregnation and after use (end-of-life disposal) both types of chemicals "escape" to the environment and can accumulate in sediments and organisms. Fish and meat, as well as human milk are now known to contain these chemicals at the level of micrograms per kilogram. The important issue is the dose-response relationship: Do the present environmental levels of BFRs cause toxic effects or not and, if not, what are the margins of safety? Since 1998, many studies on BFR exposure have been carried out. PBDE concentrations in North America are ca. 10-fold higher than those in Europe [43], most likely caused by the more stringent fire safety regulations in the USA.

Apart from the well-known polybrominated diphenylethers (PBDE's), other BFRs have been discovered in food and environmental samples. One of them is HBCD, a highly bioaccumulative BFR. TBBP-A is another BFR, which is produced in high volumes. However, this BFR is of a more polar character, and, therefore, does not bioaccumulate as much as most PBDE's and HBCD. Other BFRs, produced in lower volumes, have also been found in the environment today. Examples are pentabromotoluene (PBT) [23] decabromodiphenylethane (DBDPE) [27], 2,4,6-tribromotoluene (TBT) and 2,4,6-tribromoanisole (TBA) [35].

Toxicological information on BFRs came slower than reports on exposure data, partly due to the relatively long time needed for *in vivo* studies. Clearly, the toxic effects of BFRs are different from those caused by chlorinated dibenzo-*p*-dioxins and dibenzofurans and PCBs, as they elicit a much lower response at the Ah receptor or do not activate this receptor at all. Over the last years, increasing evidence has become available that many BFRs are endocrine disruptors [17]. A large European study ("FIRE") on the possible endocrine effects of BFRs has provided evidence for some of these effects [21, 48]. Based on the current knowledge, health risks due to BFR-contaminated food items seem to be limited [31]. However, margins of safety in the USA may be small for some BFRs, and a more precise assessment of those margins is urgently needed.

Following scientific publications on the occurrence of PBDE's in the European environment and a risk assessment was carried out by the European Union, *Pentamix* (technical pentabromodiphenyl ether mixture) and *Octamix* (technical octabrominated diphenylether mixture) production and use was banned in Europe in 2004, recently followed by a ban on *Decamix* (technical decabrominated diphenyl mixture) per 1 July 2008 for use in electric and electronic instruments [49]. DecaBDE may still be used in textiles and furniture, providing that further research on environmental concentrations and fate of this BFR will show that effects are minimal. After the discovery the much higher PBDE concentrations in North America, as compared to Europe, a voluntary production stop of the

Pentamix was seen in Canada and the USA in 2004. However, HBCD, TBBP-A and DecaBDE are still being produced until today. This is understandable as the termination of the *Pentamix* and part of the *DecaBDE* production must have caused a serious demand for alternatives. Non-brominated alternatives, such as phosphorous-based FRs (PFRs) may become available in higher quantities, but the environmental safety of those FRs has not convincingly been demonstrated. Some reports on the presence of PFRs in environmental matrices have seen already in the literature. The outlook for this field is therefore mainly on a search for alternatives for the banned PBDE's and on a demonstration of their environmental acceptability, fire safety and production feasibility. In 2009 a new European research project called "ENFIRO" will start to study the environmental safety of a number of alternative flame-retardants, based on phosphorous, metals, or nanotechnology. This project will include complete life-cycle assessments to ensure the safety of these chemicals throughout their existence, from mining until disposal ("from cradle to grave").

This overview is a summary of the main developments seen recently in the field of environmental issues around BFRs. It certainly does not claim to be complete, as it is almost not possible to keep track of the multitude of studies on BFRs that appear in the literature. A number of good reviews on environmental levels of BFRs have appeared recently. As this paper was presented at a NATO Workshop in Chisinau, Moldova, under the "Science for Peace" Program, this paper also means to be of some help for Eastern-Europe research on BFRs. Trends in environmental levels of BFRs are discussed with reference to recent papers and reviews. Some attention will be paid to the analytical difficulties associated with the determination of BFRs in environmental matrices, and to potential toxic effects of BFRs.

2. Environmental levels of BFRs

BFRs were detected to be present in the environment in 1981 [1]. During the 1980s, not much attention was paid to these compounds, as most of the research in this field was focussed on PCBs and chlorinated dioxins and furans. Only after the reports on PBDE's in stranded sperm whales in the Netherlands [12], and on exponentially increasing trends of PBDE's in Swedish mothers milk [37] many research groups from all over the world started to analyse BFRs in various environmental matrices. Very soon it became clear that in addition to the pentabromodiphenyl ethers (pentaBDE's), represented by the tetraBDE 47 (2,4,2′,4′-tetraBDE) and the pentaBDE 99 (2,4,5,2′,4′-pentaBDE), the decaBDE (BDE209) was by far the highest in concentrations in sediments. The steep increase of decaBDE concentrations in sediments since the late 1970s was convincingly shown by Zegers et al. [50] who determined a suite of BDE's including decaBDE in sediment cores from various places in the world (Fig. 2.1).

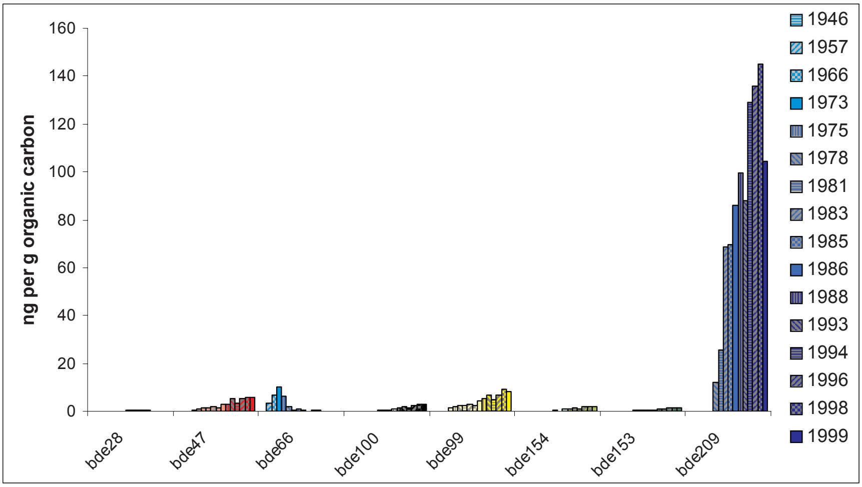

Fig. 2.1. Strong increase of DecaBDE in sediments from the Drammenfjord/Oslofjord, Norway [51].

However, bioaccumulation of decaBDE is limited, possibly due to the extremely low water solubility that makes it difficult for this compound to be transferred from sediments and suspended particulate matter via the water to organisms. The large size of the molecule is also not facilitating bioaccumulation. DecaBDE was, however, found in peregrine falcon eggs from Sweden [34]. This could be explained by exposure of terrestrial birds to soil directly, or indirectly through their preys. Aquatic birds seem to contain less decaBDE, because the fish they consume has also low decaBDE concentrations. This was confirmed by Chen et al. [7] who reported higher BDE levels in terrestrial birds. Following the first bird studies, it was shown that decaBDE and other BDE's could be present in dust, due to use of it in furniture and possibly electronic instrumentation (TV, computers, etc.). This observation resulted in a different view on human exposure: different from PCBs, BDE's can be taken up from dust and indoor air. This would imply an extra risk for children. This was made even clearer by Dye et al. [18] who showed a correlation between the occurrence and increase of feline hyperthyroidism (FH) and BDE levels in cats. They proposed cats to serve as sentinels for humans with regard to effects of indoor PBDE contamination. Takigami et al. [45] found substantial levels of BFRs in dust inside TV cabinets. In the most recent review of Law et al. [32] the BDE contamination of dust is emphasised. Harrad and Diamond [22] discuss the contamination of indoor environments through dust. This may represent an important exposure route, which distinguishes the PBDE contamination from that by PCBs, which come mainly though our food. The review on BFR concentrations in the European and Asian environment by Law et al. [32] shows the most recent developments in environmental BFR levels. It covers more than 100 studies on PBDE's and HBCD in the environment from the period 2005–2007. Together with an earlier review from the same authors [31] it is a comprehensive dataset, which shows global environmental trends in BFR concentrations during the last decade. Generally, trends for PBDE's in Europe and Asia are levelling off, while HBCD concentrations increase at most locations. DecaBDE concentrations also increase in Asia. The authors call for more research into BFR contamination of local populations that are exposed to e-waste recycling activities [20]. Julander et al. [25] reported BDE concentrations in indoor air from an electronics recycling facility in Sweden. Law et al. [32, 36] report a paucity of data on PBDE's, although production is ongoing in Asia and consumption of fish that contains PBDE's is relatively high in some areas such as Hong Kong. Polder et al. [40] and Borghesi et al. [6] presented further evidence of the global distribution of BFRs by their reports on BFR levels in birds and fish from the southern hemisphere, South Africa and Antarctica, respectively. A multitude of data is meanwhile available on PBDE contamination of North America [e.g., 43, 44, 46].

A specific review on HBCD was made by Covaci et al. [9]. The bioaccumulative properties of HBCD are highlighted in this review. Interesting is the predominance of α-HBCD whereas the technical HBCD mixture mainly consists of γ-HBCD. This change in composition is presumably caused by a selective uptake, (partly) caused by the better water solubility of the α diastereomer. Transfer of γ into α-HBCD inside organisms is unlikely, as atoms should change place. During impregnation processes a conversion of γ into α-HBCD may also take place as process temperatures rise to above 160 ºC. This change of diastereomer composition would enable the identification of sources of HBCD pollution: producers when γ-HBCD would be high in water or sediments and users, when α-HBCD would be high. However, due to the complication of the transfer in biota this research has not been successful until today [38]. The further development of the BDE trend in Swedish human milk was shown by Fängström et al. [19], but now including HBCD data (Fig. 2.2).

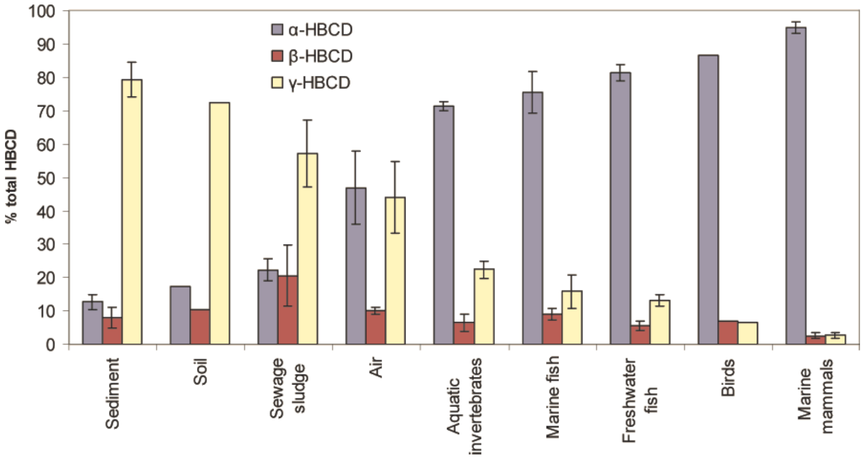

Fig. 2.2. HBCD patterns in biotic and a-biotic matrices [39].

Kierkegaard et al. [26] identified and quantified decabromodiphenylethane (DBDPE) in sediment from the river Western Scheldt, the Netherlands, and in various sewage sludge samples from Sweden. In the Western Scheldt sediment a concentration of 24 ng/g dry weight (dw) was found. Maximum decaBDE concentrations in Swedish sewage sludge were 100 ng/g dw.

3. Analytical issues of BFRs

Lower brominated BDE's are relatively easy to determine [8, 14, 15]. The required methods are basically the same as those used for the determination of polychlorinated biphenyls (PCBs). A Soxhlet extraction with a mixture of polar and non-polar solvents, e.g., *n*-pentane and dichloromethane or *n*-hexane and acetone, or an accelerated solvent extraction (ASE) is followed by a lipid removal step, e.g., on alumina or florisil columns or by gel permeation chromatography (GPC). A further fractionation is normally necessary to isolate the BDE's and a sulphuric acid treatment may be needed in case of dirty samples, to ensure a clean extract. The sulphuric acid may also be combined with a silica gel column. Lipids can also be removed simultaneously with the extraction when using ASE by adding a fat remover to the extraction cell [3–5]. The BDE's are normally determined by gas chromatography in combination with mass spectrometry (GC/MS) [11]. Electron capture negative ion (ECNI) is a sensitive technique for most of the BDE's. However, a drawback is that ^{13}C labeled internal standards cannot be used as the spectra normally only show the bromine cluster, m/z 79/81. Electron impact would be the alternative and allows the use of ^{13}C labeled standards but often lacks the required sensitivity. High resolution (HR) MS is the ultimate, but obviously expensive solution. Interesting results were obtained by comprehensive multi-dimensional GC in combination with ECD or time-of-flight (ToF) MS [28, 29]. The two-dimensional chromatogram makes the use of an MS often redundant.

The analysis of decaBDE is, however, of a different degree of difficulty [16]. Until now, results of interlaboratory studies on decaBDE have been relatively poor, for a number of reasons. These include:

- Possible degradation under influence of daylight
- Poor solubility, also in organic solvents
- High background concentrations, e.g. in dust
- Very low concentrations in biota (if present at all)
- Thermal degradation during the GC analysis
- Degradation in aqueous samples

The fully brominated molecule is instable and may easily loose bromine atoms. DecaBDE may disappear from organic solutions when placed on laboratory benches and in direct sunlight. The use of UV filters at laboratory windows and at fluorescent lightings is, therefore, highly recommended. The solubility of decaBDE in organic solvents used should be checked before preparing stock solutions or highly concentrated extracts. Dust normally contains high concentrations of decaBDE [23]. The laboratory should therefore be kept as clean as possible. Introduction of packing materials in the laboratory should be avoided. Blank analyses should be carried out more frequently than usually. The treatment of the blanks should be identical to that of the samples. When blanks have a shorter residence time at the bench than the sample extracts, deca BDE may remain on the (contaminated) glass wall, whereas it will migrate into the blank when stored for longer periods. This results in unrealistically low blank values. Thermal degradation in the injector of the GC or at the GC column [30] should be checked and minimized by using short and narrow, thin film GC columns, moderate injector and column temperatures (<270°C), and short injector residence times, or cold injectors. A short residence time can be achieved by using a pressure-pulse splitless injection. Longer residence times will cause degradation problems, not only for decaBDE, but also for other higher brominated BDEs. Fortunately, the use of ^{13}C-labeled internal standards is possible for decaBDE as the m/z 486.4 and 488.4 can be used for quantification with GC/ECNI-MS.

Since 2000, the analysis of HBCD has been carried out in a relatively small number of laboratories. Initially, total HBCD was analyzed by GC, together with the PBDEs. However, the three diastereomers (α-, β- and γ-HBCD) are normally not separated. This problem is compounded at GC temperatures >160 ºC, at which the isomers tautomerize [39]. As the diastereomers have different response factors, a reliable total-HBCD concentration cannot be determined by GC. Also, the broad HBCD peak causes CV values higher than those of the BDEs. The solution to this problem was offered by Morris et al. [38], who developed an isomer-specific HPLC method for HBCD. In addition to the three HBCD diastereomers, TBBP-A can be determined in the same analytical run. The identification and quantification of the three HBCD isomers is important because the isomeric patterns differ under different production conditions, and also differ between biota and sediments. The sensitivity of the HPLC method is nowadays comparable to that of the GC-ECNI-MS method, which makes it less suitable for analyzing samples with extremely low HBCD concentrations. A prerequisite is the use of a triple quadrupole (QQQ) MS detector. Meanwhile, showed that there are also a number of enantiomers of HBCD that can be separated and determined by HPLC using chiral columns.

In spite of its high production figures (highest of all BFRs), TBBP-A is not frequently analyzed in environmental laboratories. One reason may be its lower bioaccumulation potential, since environmental concentrations are generally lower than those of the PBDEs and HBCD. However, TBBP-A, being a phenolic compound, may have a greater adverse effect on humans and wildlife. Also, more complicated clean up methods are needed for a proper determination of TBBP-A and that may further deter analysts from measuring it. Direct injection into the

GC without derivatization is not a viable option. Acidification is required after extraction prior to HPLC determination. These steps normally introduce additional errors and/or losses. The use of ^{13}C-labeled TBBP-A may help to reduce the effects of such errors. At present, the determination of TBBP-A by HPLC, together with the HBCD diastereomers, seems to be the simplest, most attractive option [39]. Until more data are produced in interlaboratory studies, TBBP-A results appearing in the literature should be carefully scrutinized for appropriate internal quality assurance (QA).

The analysis of DBDPE was reviewed by Kierkegaard [28]. This compound has a great similarity with decaBDE, being fully brominated as well. The difference is the ethane in the center of the molecule instead of the oxygen atom. It is presumable used as an alternative for decaBDE.

4. Toxicology and risk assessment

Different from PCBs BFRs constitute a diverse group of compounds that all have their specific characteristics. Consequently, it is not possible to generalize the toxic effects of BFRs. Until now most effects found in toxicological studies on BFRs point to potential endocrine disrupting effects. A review on endocrine disrupting effects was recently made by Legler [33]. *In vivo* studies have found effects of various BFRs on thyroid hormone, estrogen and androgen pathways. Neurodevelopmental effects have also been found. However, in many studies a wide margin of safety between effect concentrations in rodent studies and environmental and human concentrations has been found. Nevertheless, and in particular for the higher levels in the USA for most BFRs, health risks due to chronic exposure cannot be excluded. Further chronic studies are necessary, which should definitely include metabolites as they may be more potent than the mother compounds of several BFRs. Kuiper et al. [30] emphasize the high sensitivity of the zebra fish reproduction assay and found a statistically significantly reduced larval survival and *non-significant* indications for decreased egg production at internal levels that were more than 55 times the highest environmental recordings. Those results indicate limited risk for endocrine or reproductive effects of current environmental PBDE contamination in fish [31]. Rattfelt Nyholm et al. [41] have studied the maternal transfer of BFRs with zebra fish, finding higher BFR concentrations in the fish eggs.

Bakker et al. [2] recommend further monitoring of BDE’s in Dutch food although the concentrations of, e.g., BDE99 are well below the human exposure threshold level. The HBCD intake in the Netherlands from fish is estimated at 0.12 ng/kg bodyweight/day [48].

5. Conclusions

A number of BFRs are widespread in the global environment. Also, they occur in food and feed from all continents. There is generally agreement among scientists, and between scientists, authorities and the industry about the undesirable properties of the Penta- and Octamix, and HBCD. These compounds will no doubt be phased out in the near future. Debate is ongoing on decaBDE. For other BFRs, there is little information available. Concentrations of DBDPE have been reported in biota and sediments. TBBP-A is only found at relatively low concentrations in biota but due to the limited amount of information on the possible effects of this compound it remains unclear if effects occur at these relatively low environmental levels. Even less is known about pentabromotoluene and other BFRs. This clearly calls for more studies on exposure and toxicity of BFRs. Future up-to-date information on BFRs and environmental contamination will no doubt be available through the BFR symposia that are organized every 3 years, with the next one in 2010 in Kyoto, Japan, through the annual International Symposium Dioxin, with the next one in 2009 in Beijing, China, and though the annual Canadian/American BFR workshops, the next one being organized in 2009 in Ottawa, Canada.

BFRs will not be the last group of chemicals that we will see occurring in our food and the environment. The vast number of chemicals that we produce and need in our modern society for all sorts of purposes from fire safety to pharmaceutical applications will continue to contribute to the spectrum of chemical residues present in our food and in the environment. Knowledge on existing classes of chemicals and modern analytical and toxicological techniques will help us make an inventory of the associated risks in an early stage, long before those residues reach levels of concern.

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