
Brominated Flame Retardants:

Assessing DecaBDE Debromination in the Environment

HEATHER M. STAPLETON (PhD, MS, BS)
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28 Boulevard Charlemagne
1000 Brussels (Belgium)
Tel.: +32 2 234 3640
Fax.: +32 2 234 3649
info@env-health.org
www.env-health.org

About the Author

Heather Stapleton's expertise is in the fate and biotransformation of organic contaminants in aquatic systems, focusing on persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). She is presently carrying out research on DecaBDE debromination at Duke University, Nicholas School Faculty, Environmental Sciences and Policy Division in her capacity as an Environmental Chemist.

I. Context from European Public Health Alliance – Environment Network.

The draft addendum environmental risk assessment report for decabromodiphenyl ether (DecaBDE) was distributed to the Technical Committee for New and Existing Substances (TC NES) on August 11, 2005 (The addendum can be found at the European INventory of Existing Commercial chemical Substances (EINECS), [<http://ecb.jrc.it/existing-chemicals/>]). The previous risk assessment, agreed in May 2004, had concluded that further information was required before definitive conclusions could be drawn on the concerns from DecaBDE to the environment.

One of the key areas identified for further clarification was the extent and importance of the debromination of DecaBDE in the environment. The conclusion in the draft addendum prepared by the UK government highlights that it is still not possible to give a reliable assessment of the overall significance of debromination based on expert judgment. Although the conclusions state that the published data on debromination heightened the concern, it did not necessarily mean that debromination was a significant pathway in the environment. This view was also elaborated in a TNO report commissioned by the Brominated Science Environment Forum¹, an industry based association.

¹ A.O. Hanstveit MSc, Dr. C.T. Bowmer, Dr. A.P. Freidig. TNO Netherlands Organisation for Applied Scientific Research. A review of the anaerobic and abiotic degradation of the flame retardant decabromodiphenyl ether (CAS # 1163-19-5) in the context of an EU environmental risk assessment report, customer BSEF – Bromine Science and Environmental Forum & The International Organization of the Bromine Chemical Industry. 17 August 2005 (ECB TRACKING NO. COM013_ENV_IND 09)

The intent of this overview is to provide a summary on the significance and extent of DecaBDE debromination in the environment. If DecaBDE is a 'significant' pathway for the formation of lower brominated congeners, there are both potential adverse environmental and health consequences. The potential persistency and bioaccumulation properties of the lower congeners must be taken into consideration in the risk assessment. Moreover, there may be legal implications for putting on the market indirectly through DecaBDE and into the environment these lower congeners, such as PentaBDE and OctBDE, which are already restricted under existing EU regulation.

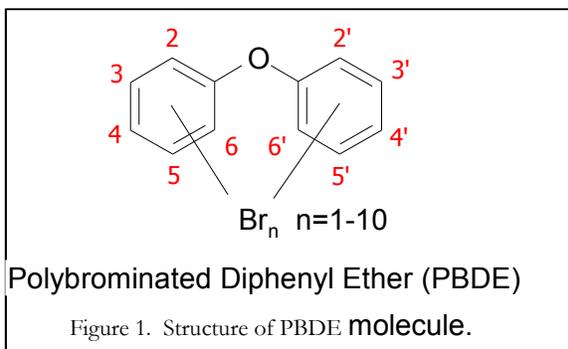
II. Introduction

Decabromodiphenyl ether (BDE 209) is a multi-halogenated organic chemical used primarily as a flame retardant in a commercial mixture known as DecaBDE. It has been used as an additive flame retardant since the late 1970s, and because it is well suited to flame retard in particular plastics, its market demand has increased significantly over the past few decades with the increasing use of plastics in electrical goods¹. Commercially produced DecaBDE consists primarily of BDE 209 (<97%) with minor contributions (0.3 to 3.0%) of octa- and nonaBDE congeners (or iso-forms), which are impurities in the technical mixture. A particular concern regarding BDE 209 is the potential for degradation *via* debromination. Debromination is a process by which bromine atoms are sequentially removed or cleaved from an organic compound, resulting in a smaller lower brominated molecule which is slightly more water soluble. These lower brominated congeners have the potential to be more persistent and more bioaccumulative than their larger parent chemical.

III. Environmental Levels of DecaBDE

Numerous studies have investigated the prevalence of polybrominated diphenyl ether (PBDE) congeners in the environment^{2,3}.

BDE 209 is a fully brominated PBDE congener containing ten bromine atoms (See Figure 1). A majority of environmental samples, specifically



human and biological samples, contain PBDE congeners that are dominated by congeners with four to six bromine atoms^{4, 5}. PentaBDE and OctaBDE are two additional commercial brominated flame retardant mixtures containing PBDE congeners with four to eight bromine atoms (see Table 1), and are believed to be the source of these congeners in biological samples. However, debromination of BDE 209 cannot be ruled out as a source of these lower brominated congeners.

BDE 209 has been measured in house dust⁶⁻⁸ at concentrations up to 10,000 ppb, which could be a potential pathway of human exposure, particularly for young children. Toddlers have a predisposition to put dirty hands and toys in their mouth and inadvertently ingest larger amounts of house dust. This predilection has been responsible for large cases of lead poisoning in U.S. children,⁹⁻¹¹ due to the high lead levels in house dust. No studies have investigated the levels of PBDEs in children under the age of 5; however, modeling studies suggest toddlers are receiving greater exposure to PBDEs than adults because of the high levels in house dust¹². In some homes studied, BDE 209 comprises 90% of the total PBDE burden,⁷ therefore, BDE 209 exposure could be unique to young children.

Conclusion

Debromination of BDE 209 cannot be ruled out as a source of lower brominated congeners.

DecaBDE is mainly found in dust in the indoor environment including our homes and cars which may result in elevated exposures in children.

IV. Photolytic Debromination of BDE 209

BDE 209 absorbs sunlight in the UV region of the electromagnetic spectrum that reaches the surface of the earth. Due to this light absorption, BDE 209 is susceptible to photodegradation, which can occur significantly through debromination. A majority of the UV spectrum is blocked by glass windows and does not reach indoor environments. However, substrates containing BDE 209 in direct sunlight do receive UV radiation. Several studies have investigated the photodegradation of BDE 209 to determine the time it takes for 50% of the BDE 209 mass to degrade (known as the half-life). Half-lives vary from a few minutes up to several years, depending upon the substrate and light source (Table 2). Söderström et al.¹³ examined the photolytic decomposition of BDE 209 in several different types of substrates using both natural sunlight and a UV-lamp. Their study demonstrated that BDE 209 degraded very quickly in organic solvents but was slower when adsorbed to sediment and soils. Ahn et al.¹⁴ also observed longer half-lives of BDE 209 when adsorbed onto sediment and minerals compared to dissolution in water and organic solvents. These studies suggest that adsorption of BDE 209 onto suspended material in the water column decreases the photodegradation of BDE 209 in aquatic environments. Stapleton¹⁵ exposed BDE 209 spiked house dust to sunlight and found that the half-life was approximately 220 hours of continuous sunlight exposure, or assuming 10 hours of sunlight a day, approximately 22 days. However, it is difficult to assess the magnitude and duration of sunlight that house dust would be exposed to in an average home. Most windows will block out UV wavelengths of light which would hinder degradation. In contrast, car dust has recently been found to contain elevated levels of BDE 209 (http://www.ecocenter.org/releases/20060111_autotoxics.shtml), which is susceptible to greater sunlight exposure and in which debromination can be expected to occur significantly.

The degradation products of BDE 209 photolysis are primarily lower brominated PBDE congeners formed via debromination. In soils, sediment and house dust, the primary congeners identified are hepta-, octa- and nonaBDE congeners¹³⁻¹⁵, and very little degrades to congeners with fewer than six bromine atoms. When dissolved in water or

organic solvents, BDE 209 degrades quite rapidly and leads to greater formation of the lower brominated congeners, including tri-, tetra- and pentaBDE congeners, and also polybrominated dibenzofurans (PBDFs)^{13,16,17}. In the environment, it is expected that BDE 209 will be found primarily bound to solids in the water column, and bound to particles in the atmosphere. Therefore, degradation of BDE 209 dissolved in water (or organic solvents) is not expected to be of environmental relevance.

Conclusion

It is difficult to assess the degree of BDE 209 photolytic debromination in house dust, soils and sediments when exposed to light. However, in cars debromination can be expected to occur more significantly. Debromination in water is not expected to be of environmental relevance.

V. Microbial and Reductive Debromination of BDE 209

One published study has investigated the microbial mediated debromination of BDE 209 under anaerobic (no oxygen) conditions. Gerecke et al.¹⁸ used microflora from sewage sludge to examine the bacterial mediated degradation of BDE 209. Their results indicated that debromination of BDE 209 did occur, leading to the formation of nona- and octaBDE congeners. The observed first order degradation rate, $1.0 \times 10^{-3} \text{ day}^{-1}$, is equivalent to a half life of approximately 690 days. However, this degradation rate was accelerated by the use of primers to increase degradation potential. Without the use of primers, the observed degradation rate was 50% lower, resulting in a half-life of approximately 3.8 years. Therefore, anaerobic bacteria can initiate debromination of BDE 209, albeit at a slower rate than photolytic debromination. Given the hydrophobic nature of BDE 209, and the large volumes that enter water treatment facilities, anaerobic degradation may be important in sewage sludge digesters. However, the time that BDE 209 spends in the sewage sludge (residence time) will greatly impact its ability to anaerobically degrade.

Reductive debromination of BDE 209 has also been reported to occur with mineral catalysts. Keum and Li¹⁹ documented a stepwise debromination process using zero-valent iron and sulfide minerals. Zero-valent iron was a good oxidant for degradation,

resulting in a BDE 209 half-life of about one day. The use of iron sulfide and sodium sulfide reduced the debromination/degradation rate to 2 and 33% of the rate observed for zero-valent iron. Both the iron and sulfides resulted in debromination down to congeners with two and three bromines. In all experiments, the initial rate of degradation was rapid and then decreased over time as lower brominated congeners were formed that appeared to be more stable. While this study demonstrates the possibility and feasibility of reductive debromination by minerals, this process is unlikely to occur naturally in the environment. PBDEs will have a greater tendency to be bound to natural organic matter and soils in the environment before binding directly to the mineral surface, which is necessary for the mineral to act as an oxidant.

Conclusion

In sewage anaerobic bacteria can initiate debromination of BDE 209, albeit at a slower rate than photolytic debromination, but due to the large volumes of DecaBDE in sewage sludge this may be significant.

VI. Metabolic Debromination

Debromination of BDE 209 has also been observed in laboratory *in vivo* studies with fish and rats, suggesting it is metabolized. In four separate studies, fish fed food spiked with decabromodiphenyl ether were found to accumulate lower brominated congeners²⁰⁻²³. The assimilation and debromination of BDE 209 varied among the three fish species examined, which included rainbow trout, common carp and lake trout. Common carp accumulated no BDE 209 in their tissues, but they did accumulate one penta-, three hexa-, two hepta- and one octaBDE congener that appeared to result from the debromination of BDE 209. In two separate and independent research studies on rainbow trout, accumulation of BDE 209 was observed, although the uptake was less than 1% in both studies. However, both studies observed an increase in hexa-, hepta-, octa- and nonaBDE congeners over time that comprised a higher percentage of the PBDE body burden relative to the BDE 209 body burden. One study found an accumulation of 0.13% of the BDE 209 dose²⁰, while the second study observed an uptake of 3.2% of the BDE 209 dose²³. Lake trout were found to

accumulate approximately 5% of the BDE 209 dose and debromination was hypothesized to occur. However, the diet in this latter study consisted of a cocktail of 13 BDEs and it was impossible to characterize debromination of BDE 209.

Stapleton et al.,²³ recently conducted several *in vitro* experiments using fish liver microsomes to characterize metabolic biotransformation of BDE 209. Microsomes are cell fractions which contain active enzymes from fish that typically metabolize endogenous compounds (i.e. natural hormones). Using carp and rainbow trout liver microsomes, Stapleton found that as much as 65% of BDE 209 was debrominated in a twenty four hour period. Carp microsomes rapidly debrominated as much as 30% of the BDE 209 mass to form BDE 155 and BDE 154 (hexaBDEs). In contrast, rainbow trout debrominated only 22% of the BDE 209 mass primarily to octa- and nonaBDE congeners. This study demonstrates that there are species specific differences in the biotransformation/debromination capacity of fish, and possibly, other organisms. Stapleton hypothesizes that thyroid hormone enzymes are responsible for this observed debromination, which is similar to endogenous metabolism of thyroid hormones.

In rats, metabolism of BDE 209 appears to occur through different mechanisms. Two studies have examined the uptake of BDE 209 in rats and both identified hydroxyl- and methoxyBDE congeners in tissues and plasma and only trace levels of nonaBDE congeners. This suggests that rats may initially debrominate BDE 209, but then other metabolic pathways become more dominant, resulting in the formation of more polar metabolites that are likely to be excreted.

Conclusion

Some fish appear capable of debrominating BDE 209 through metabolism. The extent of the metabolism varies among fish and it is difficult to determine the extent of debromination that would occur in the wild.

VII. Human Debromination Potential

In a recent study, Thuresson et al.²⁴ measured PBDE levels in workers occupationally exposed to

BDE 209. Analysis of their serum identified several hepta- and octa-BDE congeners that were not present in the decaBDE commercial mixture nor in the reference groups. The congener pattern observed in these workers was very similar to the congener pattern observed in the rainbow trout by Stapleton et al.²³. A follow up study examined the BDE concentrations in these workers when they had taken a vacation and reduced their exposure to BDE 209²⁴. This study found that while BDE 209 concentrations decreased in these workers with a half life of approximately 15 days, concentrations of the hepta- and octaBDE congeners increased, suggesting that debromination of BDE 209 was occurring in humans.

More studies are needed to determine if BDE 209 debromination does occur in human tissues. Exposure to BDE 209 is suggested to be greater for young children relative to adults, due to the higher levels present in house dust and thus, may need to be investigated further.

Conclusion

Studies suggest that DecaBDE debrominates in humans however, more studies are needed to confirm this analysis.

VIII. Summary

Table 1 compares the PBDE congeners that are present in the commercial mixtures to the congeners that have been identified as products of BDE 209 debromination. As evident in the table, all the congeners present in the commercial products also can be formed via debromination of DecaBDE. Of particular concern in human and environmental samples is the accumulation of lower brominated congeners (i.e. tetra-, penta- and hexaBDEs). Based on the current data available, the potential for significant formation of these congeners in the environment due to debromination is low. The only studies demonstrating formation/production of these congeners from debromination occurred when BDE 209 was dissolved in organic solvents and exposed to sunlight and/or UV sources, which is not environmentally relevant. Additionally, reductive debromination catalyzed by iron and iron sulfides also can lead to these congeners. However, the likelihood of BDE 209 being directly bound to

these types of mineral surfaces in the environment is also low.

In contrast, the formation of hexaBDE congeners (e.g. BDE 153, BDE 154 and BDE 155) from debromination of DecaBDE has more realistic probabilities. Metabolic debromination resulted in the formation of several hexaBDE congeners, including BDE 154, in several fish species^{20, 21, 23}. In these studies, less than 1% of the BDE 209 exposure debrominated to the hexaBDE congeners, but as much as 2% debrominated into hepta-, octa- and nonaBDE congeners. In the past year, a few studies have documented a shift in the PBDE congener patterns in human tissues. In most studies, BDE 47 (tetraBDE) was the largest contributor to the PBDE body burden; however recent studies suggests some populations have a PBDE body burden dominated by BDE 153, a hexaBDE^{25, 26}. The reason for this is unknown but could be related to debromination of BDE 209, exposure to different PBDE commercial sources, or to longer half-lives for BDE 153 relative to BDE 47.

Photolytic debromination of DecaBDE in dust, soils and sediments also leads to the formation of several hepta-, octa- and nonaBDE congeners, which is environmentally relevant. Because house, office and car dust are enriched in BDE 209, the potential for debromination is high when exposed to sunlight. Current studies suggest that photolytic debromination of BDE 209 leads to significant accumulation of hepta-, octa- and nonaBDE congeners which are persistent and potentially bioaccumulative. There are very few studies which have investigated the bioaccumulation potential and environmental levels of hepta- through nonaBDE congeners, which makes an assessment of their fate difficult. More studies are needed to determine the levels of these congeners in the environment (particularly in sediment and dust) in order to determine if debromination of BDE 209 is occurring.

Conclusion

The potential for significant formation of BDE 47, BDE 99 and BDE 100 in the environment due to debromination is low as the only study showing this is not environmentally relevant. The formation of hexaBDE has more realistic probability and could be related to debromination of DecaBDE in humans. Photolytic debromination of DecaBDE in dust, soils and sediments, leading to the formation of hepta-, octa- and nonaBDE congeners is environmentally relevant; not withstanding more research on the significance of these lower congeners fate in the environment.

Table 1. PBDE congeners identified in commercial mixtures and in debromination studies. Congener identifications in the PentaBDE and OctaBDE commercial mixtures are from reference 27.

Substitution	Congener	PentaBDE	OctaBDE	DecaBDE	Formed Debromination	From	Reference
2,4,4'-tribromo	BDE 28	X			X		17, 19
2,2',4,4'-tetrabromo	BDE 47	X			X		17, 13, 19
2,2',4,5'-tetrabromo	BDE 49	X			X		17
2,3',4,4'-tetrabromo	BDE 66	X			X		19
2,2',3,4,4'-pentabromo	BDE 85	X			X		14, 17
2,2',4,4',5-pentabromo	BDE 99	X			X		17, 13, 19
2,2',4,4',6-pentabromo	BDE 100	X			X		17, 19
2,2',3,4,4',5'-hexabromo	BDE 138	X			X		17, 19
2,2',4,4',5,5'-hexabromo	BDE 153	X			X		17, 13, 19
2,2',4,4',5,6'-hexabromo	BDE 154	X			X		17, 13, 19, 21, 23
2,2',4,4',6,6'-hexabromo	BDE 155	X			X		21, 23
2,2',3,4,4',5',6'-heptabromo	BDE 183	X	X		X		14, 17, 13, 19
2,2',3,4,4',6,6'-heptabromo	BDE 184				X		23
2,2',3,3',4,4',5,6'-octabromo	BDE 196		X		X		14, 17, 18
2,2',3,3',4,4',6,6'-octabromo	BDE 197		X		X		14, 17, 18
2,2',3,3',4,5',6,6'-octabromo	BDE 201				X		23
2,2',3,3',5,5',6,6'-octabromo	BDE 202				X		23
2,2',3,3',4,5,5',6-octabromo	BDE 203		X	X	X		18
2,2',3,3',4,4',5,5',6-nonabromo	BDE 206		X	X	X		14, 17, 13
2,2',3,3',4,4',5,6,6'-nonabromo	BDE 207		X	X	X		14, 17, 13, 18
2,2',3,3',4,5,5',6,6'-nonabromo	BDE 208		X	X	X		14, 17, 13, 18
2,2',3,3',4,4',5,5',6,6'-decabromo	BDE 209		X	X			

Table 2. Photolytic half-lives of BDE 209 under various conditions.

Light Source	Substrate	Half Life (Reference)
UV lamp	Organic Solvent	<0.25 H ¹³ ;
UV lamp	Silica Gel	<0.25 H ¹³ ;
UV lamp	Sand	12 H ¹³ ;
UV lamp	Sediment	40-60 H ¹³ ; 150 D ¹⁴ ;
UV lamp	Soil	150-200 H ¹³
UV lamp	Methanol/water	0.5 H ¹⁶
UV lamp	Minerals	36 D – 3.9 Y ¹⁴
Sunlight	Hydrated on Quartz	35 H ²⁸ ;
Sunlight	Hydrated with Humics on Quartz	70 H ²⁸
Sunlight	Humic Acid Coated Sand	435 H ²⁸
Sunlight	Hexane	<0.25 H ¹⁷
Sunlight	Minerals	261-990 D ¹⁴
Sunlight	Sand	13-37 H ¹³
Sunlight	Sediment	30-80 H ¹³
Sunlight	House Dust	220 H ¹⁵

H- Hours; D- Days; Y- Years

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