# DOES DECABROMODIPHENYLETHER (DECA-BDE) CONTRIBUTE TO THE LOWER BROMINATED DIPHENYLETHERS FOUND IN THE ENVIRONMENT?

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## Abstract

It would seem logical to anticipate that degradation products of Deca-BDE would be found in the environment and that the key question would be “do they present a significant risk above that present from the residual traces of the lower PBDEs already in the environment from the past commercial use of Penta-BDE and Octa-BDE. The most relevant studies on the degradation of DecaBDE are reviewed and their environmental relevance is assessed, with special emphasis on the question of whether or not the described processes could contribute to the levels of lower BDEs typically found in the environment.

Under laboratory conditions various studies have found that Deca-BDE can undergo degradation. However, many of these studies were carried out under conditions that do not seem to be representative of those likely to be found in the environment, e.g., by using organic solvents, specific bacterial strains, or strong UV light sources, etc.

The pattern of the Polybrominated diphenyl ether (PBDE) congeners formed in these experiments is different from the pattern that is typically found in the environment. Were these described processes relevant, a different pattern would also be seen in the environment. The lower PBDE congeners actually found in the environment resemble the commercial PBDE products and are most likely due to past emissions of commercial PentaBDE and commercial OctaBDE, which are no longer manufactured or used.

In an ongoing 10-year environmental monitoring study funded by Industry in collaboration with the European Union (EU) a specific PBDE congener, BDE 126, was analysed as a “marker congener” for degradation of DecaBDE. Now into its 2nd year, the EU study has not detected the marker congener in any of the samples analysed. These results are confirmed by a field study on soil that had been amended with Deca-BDE-containing sewage sludge for many years; it did not find any indications for photolysis of Deca-BDE.

More recent studies indicate that degradation of DecaBDE, e.g., in sewage sludge or via hydrolysis, starts preferentially at the more labile para- and meta-positions of the Deca-BDE molecule. The PBDE congeners typically found in the environment are brominated at both para positions, again indicating that they are unlikely to have been formed from degradation of Deca-BDE.

## Introduction

DecaBDE is subject to intense scrutiny by both regulators and researchers. DecaBDE underwent a 10-year risk assessment in the European Union (EEC/793/93) and hundreds of scientific studies are published on DecaBDE every year. While the use of commercial PentaBDE and OctaBDE has been discontinued due to concerns about bioaccumulation and presence in the environment, the EU concluded that, although there were some “uncertainties”, there are no risks to human health or the environment from the use of DecaBDE.

A question that is contentiously discussed is whether or not DecaBDE “degrades” to more toxic and bioaccumulating PBDE congeners. Relevant studies on photolytic, microbial and abiotic degradation of DecaBDE are discussed and the environmental relevance are examined with special emphasis on the question whether or not the described processes contribute to the levels of lower BDEs found in the environment.

## Results and Discussion

The main compartments where Deca-BDE is found in the environment are the sediment compartment and sewage sludge. The following discussion will therefore mainly focus on the fate of Deca in these compartments.

Anaerobic biodegradation

- The fate of Deca-BDE was studied by Schaeffer et al. in an anaerobic sediment/water microcosm.[1] Intact core microcosm systems were used to simulate fate processes in the anaerobic freshwater ecosystem. $^{14}$C-labelled material was used to ensure high sensitivity. Monitoring for $^{14}$CO2 and $^{14}CH_4$ indicated no statistically significant mineralization. A chemical analysis did not find any indications for formation of lower BDEs.
- The above results are confirmed by Cynthia de Wit et al.[2] who studied the degradation of DecaBDE in an anaerobic water/sediment system. Sub-samples were analysed after selected time intervals but no degradation was found during the incubation of 2 years.
- Gerecke et al[3] studied the degradation of Deca-BDE in anaerobic digester sludge. After incubation of approximately 240 days, degradation to Nona-BDE and possibly Octa-BDE was observed. However, a typical residence time for digester sludge would be approximately 20-30 days, indicating that this process is of limited significance. Furthermore, the study found that the first step in the degradation reaction was a preferential debromination in the para-position of BDE 209; this mechanism is discussed in more detail below.
- A study by He et al.[4] reports that, in a laboratory setting, specific halorespiring anaerobic bacteria can transform Deca-BDE into lower BDEs. Specifically, in-line with the findings of Gerecke, the study found Deca-BDE to degrade to Nona- and Octa-BDE congeners. No further degradation to the environmentally relevant tetra- hexabrominated BDE congeners was found. The study used cultures of special strains of bacteria that are not typically found in the environment. No degradation was found without the presence of the chlorinated solvent trichloroethylene (TCE) being added as an electron acceptor. Since TCE is not normally present in the environment, the conditions used in the recent study are not environmentally relevant. Therefore, no further conclusions regarding Deca degradation in the environment can be drawn from this study.

Abiotic degradation

- Keum and Li[5] investigated the abiotic reductive dehalogenation of Deca-BDE and other lower BDEs using zerovalent iron (Fe (0)), sodium sulphide ($Na_2S$) and iron sulphide (FeS) as reducing agents. The study found stepwise debromination of Deca down to di- and monoBDEs. Again, as was also seen in other reductive debromination studies, unspecific debromination was observed leading to a wide range of different BDE congeners. Since a big range of BDE congeners was formed (there are 209 possible BDE congeners, so theoretically 208 different BDE congeners can be formed), also the environmentally relevant congeners BDE 47 and BDE100 were found in the reaction mixture. The environmental relevance of these findings is limited by a range of factors, e.g., Fe (0) is not typically present in the environment; the concentrations of the sulphides used in the study were at least 10 times higher than the highest concentrations found in the environment; Sulphate ($SO_4^{2-}$) ions which are present in marine sediment can act as a competing (and preferred) electron acceptor that inhibits the described reductive dehalogenation; in the study Deca-BDE was coated to the respective reducing agents maximising the surface available for a chemical reaction. In the environment the situation would be the reverse: minerals are not easily available for reaction and are typically covered with organic carbon, further minimizing the surface available for reaction.
- Ahn et al [6] also investigated the abiotic reductive dehalogenation of Deca-BDE. DecaBDE was dissolved in tetrahydrofurane (THF) and Birnessite ($\delta$-$MnO_2$) was added as a reducing agent. The study discovered that rather than Birnessite, the THF solvent provided the reducing power. Like the previous studies, a wide range of PBDE congener was found to be formed. Since only GC was used for identification the study could not unequivocally identify individual BDE congeners.
- Although not directly related to sediments/sludge, a recent field study by Sellstroem et al.[7] found no indications for degradation of Deca-BDE in agricultural soil that had been amended with Deca-BDE-containing sewage sludge after 20 years. This finding is also relevant for the discussion on photolysis and this aspect will be discussed later in this paper.

Photolysis

The photolysis of Deca-BDE has been extensively studied, among others by the Fraunhofer Institute, Hannover, Germany[8] and Bayreuth University, Germany,[9 10] and several Swedish research groups, e.g., by Eriksson et al[11] and Soederstroem et al. [12] The studies found that:

- Photolysis of Deca-BDE (in organic solutions) is a stepwise process resulting in sequential debromination from Deca to Nona-BDE to Octa-BDE, etc.,
- Photolysis will produce a congener pattern that is different from the congener pattern of PBDEs found in the environment [11, 12]. Similar to the reductive debromination reactions described above, photolysis was found to produce a mixture of many different PBDE congeners [5]. This process will also produce Tetra- and Penta-BDE congeners as intermediates. However, these congeners are largely different from commercial Penta congeners and will further degrade themselves. For instance, Ahn et al or Stapleton did not find the main environmental PBDEs BDE 47 or BDE 99 in their experiments discussed below (see points e and f below)
- The rates of photolysis decrease with decreasing degree of bromination.[10, 11] The spectral overlap of sunlight and the absorption spectrum of the respective PBDE congeners decreases with decreasing degree of bromination. A decreasing overlap leads to decreasing photolysis rates. This process will not stop at some intermediate degree of bromination but will continue until the fully debrominated diphenyl ether.
- Since the rate of photolysis is expected to decrease with decreasing degree of bromination, this process would be expected to result in the formation of Tri- and Di- and Mono-BDE at similar or higher amounts as Tetra- and Penta-BDE, if this process were significant. This is not seen by environmental monitoring studies and indicates that this process is not significant, probably due to the fact that most DecaBDE in the environment is not exposed to sunlight.
- Ahn et al[13] coated DecaBDE to clay minerals, metal oxides and sediments and photolysed them with UV light. The study found no degradation with soil, natural sediment, ferrihydrite, aluminium hydroxide or birnessite, but found limited degradation for kaolinite and montmorillonite. In the cases where degradation was observed, a similar congener pattern as with other studies was observed. The study reports that it did not find the environmentally dominant PBDE congeners BDE 47 and BDE 99. The described process therefore seems to be of little environmental relevance.
- Heather Stapleton spiked pre-cleaned house dust with Deca-BDE and exposed it to sunlight.[14], [15] In line with what has been found for other matrices (e.g. Soederstroem at al for sand particles[16]), she found degradation of Deca to lower BDE congeners. Again, a wide range of PBDE congeners was formed, which is significantly different from the pattern of PBDEs typically found in the environment. Moreover, no further degradation than to Heptabrominated BDEs was found. Most environmentally relevant BDEs are tetra-hexabrominated BDEs. As the study author pointed out in a later review paper,[17] the above experiments are only relevant for dust exposed to sunlight outdoors but not indoors. Most windows will block UV light and therefore block photolysis of Deca-BDE.

Reaction Mechanism/ Congener Pattern

The reactions described above seem to follow a common reaction mechanism, reductive debromination. Since there are 209 possible BDE congeners, the debromination of BDE 209 can theoretically lead to the formation of 208 different BDE congeners and the above-describe studies report the formation of a broad range of different PBDE congeners. Were the above-described degradation processes to happen to any significant extent in the environment, then these congeners would be found in environmental samples in significant amounts.

So far, environmental monitoring studies report the finding of a few, distinct PBDE congeners, dominated by BDE 47, 99, 100, 153, 154, 209, etc., rather than the broad range of congeners described in the above degradation reactions[18], [19], [20]. The identified PBDE congeners are related to commercial products or previous commercial products, such as Penta-, Octa-, and Deca-BDE, and are more likely present in the environment due to past emissions.

Despite the complex mix of reaction products observed, the reactivities of the different bromine substituents are different and a range of studies have identified a preferential starting point for debromination at the para-, and possibly meta-, positions such as Gerecke et al[21] in anaerobic digester sludge and, although not directly related to environmental degradation discussed here, Heather Stapleton on degradation of Deca-BDE in fish[22]. Nose[23]. et al find that the first step in debromination following hydrothermal treatment of DecaBDE is a debromination at the meta- and para position to BDE 208 and BDE 207.

As mentioned above, the environmental PBDE congeners are dominated by BDE 47, 99, 100, 153, 154, 209. These congeners are all brominated at the para-positions and it is therefore unlikely that they were formed by the above-described degradation reactions.

Field studies/ Monitoring studies

In the EU, the producers of Deca-BDE have voluntarily committed to carry out a large-scale 10-year environmental monitoring study for Deca-BDE. In order to determine the extent the degradation of Deca-BDE could contribute to the presence of lower congeners in the environment a specific marker congener has been identified in collaboration with the EU authorities. BDE 126 is a pentabrominated BDE that has been reported by Keum et al to be formed by reductive degradation of Deca-BDE; it has not been present, or only in trace amounts, in previously commercial lower PBDE mixtures. Initial results indicate that the marker was not detected, indicating no significant degradation of Deca-BDE in any of the samples analysed.

This is confirmed by a recent field study by Sellstroem et al [7], which looked at potential degradation and photolysis of Deca-BDE in soil that had been amended with Deca-BDE-containing sewage sludge for many years. It did not find any indications for photolysis of Deca-BDE even under extreme conditions.

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