DEBROMINATION OF THE FLAME RETARDANT DECABDE: IS IT ENVIRONMENTALLY RELEVANT?

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Introduction

Commercial production of the flame retardant compounds polybrominated diphenyl ethers (PBDEs) historically included three different formulations commonly referred to as PentaBDE, OctaBDE, and DecaBDE. These three mixtures contain diphenyl ether compounds with varying degrees of bromination. Due to the fact that the PentaBDE and OctaBDE commercial mixtures contain chemicals that were persistent, bioaccumulative, and potentially toxic, the use and production of these mixtures was banned and/or voluntarily withdrawn in most regions. However, the use of the third mixture, DecaBDE, has remained a contentious issue in several countries and numerous risk assessments have attempted to evaluate the hazards and benefits of using this flame retardant chemical in high production volumes.

One of the concerns with using DecaBDE is its potential to experience reductive dehalogenation reactions (i.e. debromination) in the environment. Debromination of DecaBDE (BDE 209) can lead to the formation of congeners with fewer bromine atoms. These less brominated congeners are more bioaccumulative and may be more toxic than the fully brominated BDE 209, thus the reason that the PentaBDE and OctaBDE mixtures were originally restricted from use. Thus any pathways that can lead to significant debromination of DecaBDE in the environment may be cause for concern. This presentation will review the studies that have documented debromination of DecaBDE through biotic and abiotic pathways and discuss their environmental relevance.

Metabolic Debromination

The metabolism of PBDEs has been investigated in a number of animal models including rats (1,2), mice (3), fish (4-7), and birds(8) and reviewed by Haak and Letcher (9). These studies demonstrate that metabolism of PBDE congeners is both species and congener specific. Oxidative metabolism of PBDEs to form hydroxylated PBDEs (OH-BDEs) has been documented in several rodent studies (1,10,11), and is similar to the metabolic pathway described for other halogenated organic compounds (12). However, reductive metabolism, particularly of BDE 209, has been observed in several animal models, including rats, fish and birds. Huwe and Smith (2) exposed rats to BDE 209 via the diet and observed significant accumulation of octa- and nonaBDE congeners which could not be explained by the presence of impurities in the food. They observed as much as 800% recovery (relative to levels in food exposure) of some octaBDE congeners in rat tissues, suggesting that debromination of BDE 209 and nonaBDE congeners had to be occurring. In addition Van den Steen (8) also observed accumulation of octa- and nonaBDE congeners in European starlings following exposure to BDE 209 through silastic implants. Lastly, the greatest evidence to support metabolic debromination has been observed in fish models. Studies by Kierkegaard et al. (4), Stapleton et al. (5,6) and Tomy et al (7) have all observed significant debromination of BDE 209 following dietary exposure, and there appears to be little to no evidence supporting the formation of OH-BDEs via metabolism in fish. Thus fish appear to have a greater potential to debrominate PBDE congeners, particularly BDE 209, which is likely attributed to different enzyme systems in the liver, and/or high activity of fish hepatic enzymes relative to mammals (6).

While metabolic debromination has been observed in the laboratory following dietary exposure, the environmental relevance of this pathway has been called into question. However, recent studies by La Guardia et al (13) have documented what is likely the greatest evidence to support metabolic debromination in the environment. Fish living

downstream of a wastewater treatment plant emitting effluent with BDE 209 were found to accumulate significant levels of octa- and nonaBDE congeners in their tissues. These octa- and nonaBDE congeners were not present in the sediment or tissues of their prey items; they are also not present in any commercial mixture. Accumulation patterns of these higher brominated congeners (e.g. hepat-, octa-, nonaBDEs) in chub and sunfish from this river looked identical to the patterns observed in common carp and rainbow trout (respectively) following controlled dietary exposure in the laboratory(6) (See Figure 1). Chub fish are a member of the *Cyprinidae* family, as are the common carp, which may explain the similarities in their patterns if they share similar metabolizing enzymes. Thus there does appear to be evidence documenting metabolic debromination of BDE 209 in fish in the environment.

Abiotic Debromination

Abiotic debromination has been observed in laboratory studies investigating bacteria-mediated and photolytic pathways of degradation (14-19). Generally debromination via microbial pathways appears to be relatively slow and strain specific relative to photodegradation pathways. However, the photolysis of DecaBDE is also very dependent upon the matrix to which it is adsorbed, and on the environmental conditions. Photodegradation half-lives for BDE 209 range from less than 15 minutes up to 408 days, depending on the matrix to which it is adsorbed and the radiation wavelengths. Due to the high hydrophobic character (K_{ow} ~10), DecaBDE is typically found adsorbed to solids in the environment. This adsorption may lead to shielding effects and reduce its potential for degradation. Yet, the primary degradation products of DecaBDE photolysis have consistently been documented as lower brominated congeners, suggesting debromination is the primary route of photodegradation (See Figure 2). Thus it is likely that DecaBDE will debrominate via photolysis, however, the relative rate of this pathway is difficult to assess.

High levels of BDE 209 have been documented in house dust (20,21), sewage sludge (22) and in soils near dump sites and electronic waste streams (23). Thus these environments have the greatest potential to form lower brominated congeners via photolysis of BDE 209 if the conditions are optimal. Because house dust can be a significant exposure route for PBDEs, the potential for debromination in dust needs further evaluation. Most windows block a majority of the UV wavelengths required for debromination of BDE 209. However, analysis of house dust has documented the presence of octaBDE congeners that are not found in any commercial PBDE mixture, and which have been shown to be photodegradation products of BDE 209 in laboratory studies, such as BDE 202 (20). In addition, Stapleton and Dodder (19) proposed using the ratio of BDE 197:201 as an indicator of debromination in house dust. The difficulties in evaluating the environmental relevance of BDE 209 photodegradation are likely attributed to a lack of data on the presence and levels of octa- and nonaBDE congeners in environmental samples. Most laboratories do not routinely analyze samples for these congeners. Future studies should consider including the octa- and nonaBDE congeners in their methods to fully evaluate the potential for BDE 209 debromination via photolysis.

Conclusions

In conclusion, there are data suggesting DecaBDE does debrominate in the environment. However, further studies are needed to evaluate the full potential for debromination in environments with high BDE 209 levels, such as sewage sludge, house dust, and soils adjacent to electronic waste sites. Scientists are urged to include measurements of octa- and nonaBDE congeners in their studies to fully evaluate this potential.

References

(1) Morck, A.; Hakk, H.; Orn, U.; Wehler, E. K. *Drug Metabolism and Disposition* **2003**, *31*, 900-907.
(2) Huwe, J. K.; Smith, D. J. *Environmental Science & Technology* **2007**, *41*, 2371-2377.
(3) Staskal, D. F.; Hakk, H.; Bauer, D.; Diliberto, J. J.; Birnbaum, L. S. *Toxicological Sciences* **2006**, *94*, 28-37.
(4) Kierkegaard, A.; Balk, L.; Tjarnlund, U.; De Wit, C. A.; Jansson, B. *Environmental Science & Technology* **1999**, *33*, 1612-1617.

(5) Stapleton, H. M.; Alaee, M.; Letcher, R. J.; Baker, J. E. *Environmental Science & Technology* **2004**, *38*, 112-119.
(6) Stapleton, H. M.; Brazil, B.; Holbrook, R. D.; Mitchelmore, C. L.; Benedict, R.; Konstantinov, A.; Potter, D. *Environmental Science & Technology* **2006**, *40*, 4653-4658.
(7) Tomy, G. T.; Palace, V. P.; Halldorson, T.; Braekevelt, E.; Danell, R.; Wautier, K.; Evans, B.; Brinkworth, L.; Fisk, A. T. *Environmental Science & Technology* **2004**, *38*, 1496-1504.
(8) Van den Steen, E.; Covaci, A.; Jaspers, V. L. B.; Dauwe, T.; Voorspoels, S.; Eens, M.; Pinxten, R. *Environmental Pollution* **2007**, *148*, 648-653.
(9) Hakk, H.; Letcher, R. J. *Environment International* **2003**, *29*, 801-828.
(10) Malmberg, T.; Athanasiadou, M.; Marsh, G.; Brandt, I.; Bergmant, A. *Environmental Science & Technology* **2005**, *39*, 5342-5348.
(11) Qiu, X.; Mercado-Feliciano, M.; Bigsby, R. M.; Hites, R. A. *Environmental Health Perspectives* **2007**, *In Press*.
(12) Letcher, R. J., Klasson-Wehler, E., Bergman, A. Methyl Sulfone and Hydroxylated Metabolites of Polychlorinated Biphenyls. In *The Handbook of Environmental Chemistry* Paasivirta, J., Ed.; Springer-Verlag: Berlin, 2001; Vol. 3, pp 315-359.
(13) La Guardia, M. J.; Hale, R. C.; Harvey, E. *Environmental Science & Technology* **2007**, *41*, 6663-6670.
(14) He, J. Z.; Robrock, K. R.; Alvarez-Cohen, L. *Environmental Science & Technology* **2006**, *40*, 4429-4434.
(15) Gerecke, A. C.; Hartmann, P. C.; Heeb, N. V.; Kohler, H. P. E.; Giger, W.; Schmid, P.; Zennegg, M.; Kohler, M. *Environmental Science & Technology* **2005**, *39*, 1078-1083.
(16) Eriksson, J.; Green, N.; Marsh, G.; Bergman, A. *Environmental Science & Technology* **2004**, *38*, 3119-3125.
(17) Ahn, M. Y.; Filley, T. R.; Jafvert, C. T.; Nies, L.; Hua, I.; Bezares-Cruz, J. *Environmental Science & Technology* **2006**, *40*, 215-220.
(18) Soderstrom, G.; Sellstrom, U.; De Wit, C. A.; Tysklind, M. *Environmental Science & Technology* **2004**, *38*, 127-132.
(19) Stapleton, H. M.; Dodder, N. G. *Environmental Toxicology and Chemistry* **2008**, *27*, 306-312.
(20) Allen, J. G.; McClean, M.; Stapleton, H. M.; Webster, T. F. *Environment International* **2008**, *In Press*.
(21) Wilford, B. S., M.; Harner, T.; Zhu, J.; Jones, K. C. *Environmental Science & Technology* **2005**, *39*, 7027-7035.
(22) Hale, R. C.; La Guardia, M. J.; Harvey, E. P.; Gaylor, M. O.; Mainor, T. M.; Duff, W. H. *Nature* **2001**, *412*, 140-141.
(23) Wang, D. L.; Cai, Z. W.; Jiang, G. B.; Leung, A.; Wong, M. H.; Wong, W. K. *Chemosphere* **2005**, *60*, 810-816.

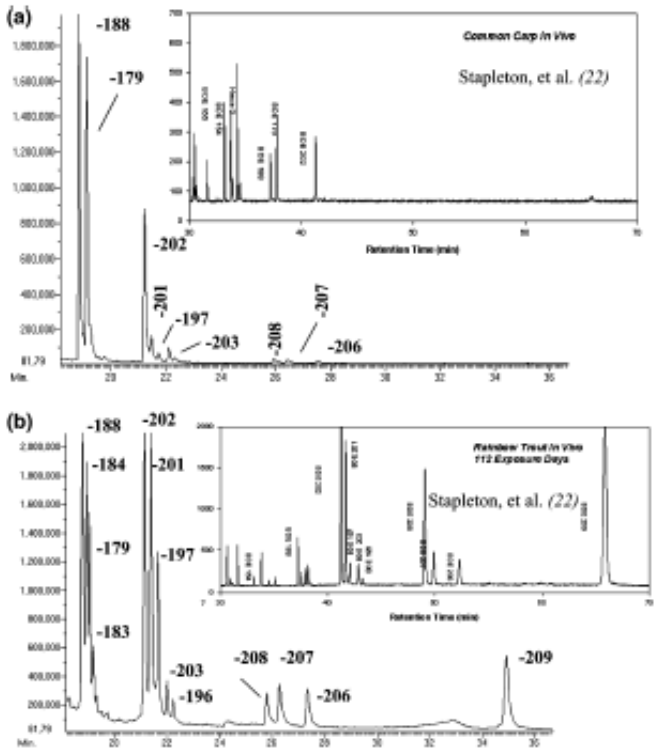

Figure 1. GC/ECNI-MS chromatogram demonstrating similarities in accumulation patterns between chub and carp, and sunfish and rainbow trout, following exposure to DecaBDE. (From La Guardia et al., 2007).

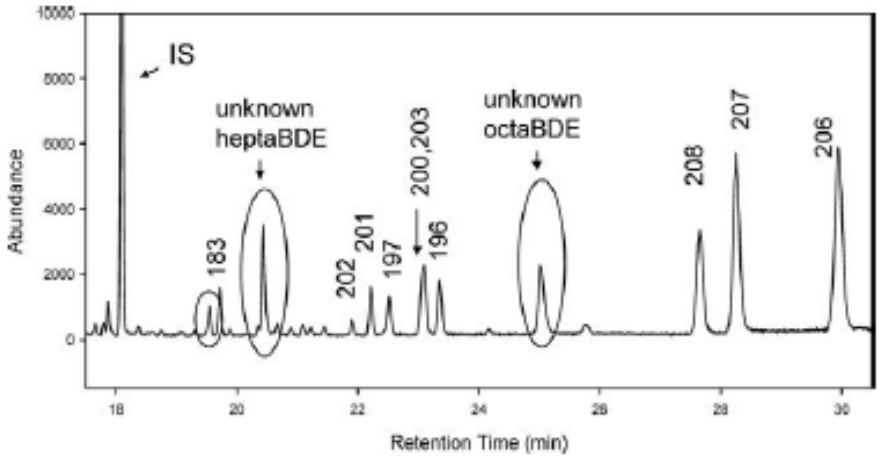

Figure 2. GC/ECNI-MS chromatogram demonstrating products of BDE 209 photodegradation in house dust. (From Stapleton and Dodder, 2008).