



# Anaerobic Microbial Debromination of Polybrominated Diphenyl Ethers (PBDEs)

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*The purpose of this research is to understand how microorganisms in the environment might transform the toxic polybrominated diphenyl ethers (PBDEs). We found that anaerobic bacteria can remove bromines from the molecule, creating potentially more toxic less brominated PBDEs. We are currently testing the ability of aerobic bacteria to breakdown the byproducts of anaerobic debromination.*

Polybrominated diphenyl ethers (PBDEs) are flame retardants that have been used for three decades in a wide variety of manufactured materials. The PBDE family comprises 209 different compounds, or congeners, that have different chemical and toxicological properties. Recent discoveries of the endocrine-disrupting ability of some of these compounds as well as exponentially increasing human breast-milk concentrations have raised concern about their use and have led to regulatory bans for some of the compounds in California.

Anaerobic dehalogenating microorganisms are capable of removing halogens from a variety of compounds. Given that the toxicity of PBDEs increases with fewer bromines, it is important to understand whether anaerobic microorganisms can debrominate PBDEs. The objectives of our project are to 1) determine whether highly-brominated deca and octa-BDE congeners can be debrominated by anaerobic dehalogenating microorganisms; 2) evaluate the debromination pathway; and 3) quantify the debromination kinetics.

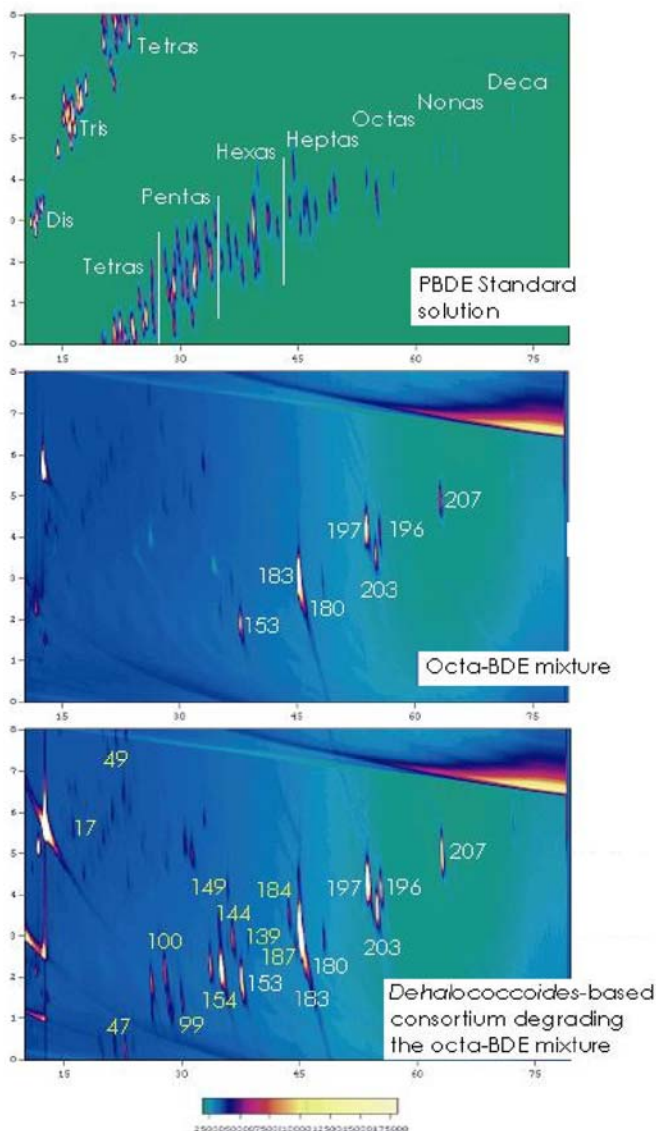
We have mostly completed the first two objectives of this research project. Experiments were conducted with a variety of dehalogenating bacteria on two different highly brominated PBDE mixtures to determine which species are capable of transforming PBDEs. By comparing live samples with autoclaved controls, we found that some of the species were capable of

debrominating the octa-BDE mixture down to di-BDE congeners. Several species were capable of carrying out these reactions, including *Dehalococcoides ethenogenes* 195 and three *Desulfitobacterium* species. Only one species, *Sulfurospirillum multivorans*, was able to debrominate deca-BDE to octa-BDE congeners.

Given the complexity of analyzing PBDE congeners with conventional analytical techniques, collaborated with Dr. Peter Korytár at Wageningen IMARES in the Netherlands to use two-dimensional chromatography (GCxGC) to better separate and identify our by-products. When we analyzed the octa-BDE debromination samples using GCxGC, there were many more product congeners than we had previously thought. Among these, we identified several of the most toxic penta and tetra congeners, indicating that the breakdown of less toxic highly-brominated PBDEs can create more toxic products.

Once we had identified bacteria capable of debrominating PBDEs, we exposed three species to seven important PBDEs—five of which are within the octa-BDE mixture, and two of the toxic by-products—to determine the debromination pathway. Using GCxGC techniques, we found that all the PBDE congeners we studied were debrominated to some degree. The debromination pathways were almost identical for all three microbial species tested. Furthermore, we found that certain bromines are prefer-

entially removed. Debromination occurs very slowly for the higher congeners, with only a few parts per billion transformed over the course of three months, while the less brominated tetra and penta congeners can be completely removed by three months. Our results indicate that anaerobic bacteria in the environment might debrominate PBDEs in the same fashion, thereby producing the same by-products.



Our third objective was to determine the kinetic rates of debromination. However, given the extreme hydrophobicity of PBDEs, we experienced difficulty obtaining adequate mass balances and quantifying concentrations with the accuracy required for

kinetic calculations. We therefore decided to change our focus to study the aerobic degradation of the less brominated PBDE congeners that are most frequently detected in the environment. We are currently testing bacterial species known to transform PCBs for the ability to degrade PBDEs, notably *Rhodococcus* sp RHA1 and *Burkholderia xenovorans* LB400. Our goal is to understand which congeners are degradable under aerobic conditions, how quickly this process occurs and what by-products are produced. Since partially oxidized PBDEs are more endocrine disrupting than PBDEs themselves, it is important to understand the exact degradation mechanism.

### Publications

He, J., K. Robrock, and L. Alvarez-Cohen. 2006. "Microbial reductive debromination of polybrominated diphenyl ethers (PBDEs)". *Environmental Science and Technology*, 40 (14): 4429-4434.

Robrock, K., P. Korytár and L. Alvarez-Cohen. 2007. "Pathways for the Anaerobic Microbial Debromination of Polybrominated Diphenyl Ethers", *Environmental Science and Technology*, in press.

### Professional Presentations

Robrock, K. P. Korytár, and L. Alvarez-Cohen. "Anaerobic microbial degradation pathways for seven environmentally relevant PBDE congeners". American Society for Microbiology General Meeting, Toronto, Canada, May 2007.

### Collaborative Efforts

Dr. Peter Korytár at Wageningen IMARES in the Netherlands, Dr. Bill Mohn and Dr. Lindsay Eltis at the University of British Columbia in Vancouver, Canada.

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