

Reductive debromination of decabromodiphenyl ether (BDE 209) by anaerobic sediment microorganisms

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Introduction

The environmental fate and effects of brominated flame retardants have been receiving increasing interest. Because of their high hydrophobicity, polybrominated diphenyl ether (PBDE) flame retardants in the aquatic environment are mainly present in sediments and biota. The long-term fate of these compounds will to a large extent depend on the potential for microbial degradation in sediments. Dehalogenation in anaerobic sediments has been found for many chlorinated aromatic compounds such as PCBs and PCDDs [1]. Although there is little information available on the microbial degradation of PBDEs, there are reports showing that polybrominated biphenyls [e.g. 2] are readily debrominated in anaerobic sediments. Complete debromination of PBDEs in marine sediments may be an important route by which these compounds are removed from the marine environment. On the other hand, incomplete debromination may lead to the accumulation of PBDE congeners that are more bioavailable and more readily taken up by marine organisms. Recent reports indicate that BDE 209 is debrominated in the gut of carp [3]. In this study we investigated the potential for reductive debromination of BDE 209 in anaerobic sediment suspensions.

Methods and Materials

Anaerobic sediment samples were taken at Hansweert in the Western Scheldt, and area containing high concentrations of BDE 209 in particular [4]. Twenty grams of sediment were suspended in 60 ml of the anaerobic medium used in previous experiments to study the reductive dechlorination of PCDDs [5]. The suspensions were spiked with BDE 209 (14.0 ug/g sediment) and incubated anaerobically at room temperature in the dark. At appropriate times, duplicate sediment samples and sterilised controls were analysed for PBDEs. Samples were extracted with hexane/acetone, followed by cleanup using acidic and basic silica gel [5] and analysed using GC-LRMS on a ThermoQuest Trace instrument.

Results and Discussion

A significant decrease in the concentration of BDE 209 in the sediment was observed during the first two months of the experiment (Fig. 1). A similar decrease was also seen in the sterile controls, but this was probably caused by incomplete sterilisation of the control sediment. Incomplete sterilisation of the controls was confirmed by the production of methane in these suspensions after

addition of lactic, pyruvic and acetic acids at 10 mM (data not shown) and is probably due to the formation of heat-resistant microbial spores. We therefore conclude that the removal of BDE 209 was caused by the activity of microorganisms in the sediment.

Examination of the GC-MS chromatograms of samples taken during the course of the experiment showed that new peaks appeared which were not present in chromatograms of samples of the original sediment or in chromatograms of the BDE 209 used to spike the sediment (Fig. 2). These peaks had retention times slightly shorter than that of BDE 209 (40.63 and 41.20 minutes compared to 45.22 minutes) and were tentatively identified from their retention times and mass spectra as being due to nona-brominated diphenyl ethers. The congeners responsible for these peaks have not been identified so far due to the absence of authentic standards. Although precise determination of the concentrations of these congeners was not possible due the lack of standards, the yields do not appear to be quantitative. This suggests that further debromination of nonabrominated diphenyl ethers to lower brominated congeners may also be taking place.

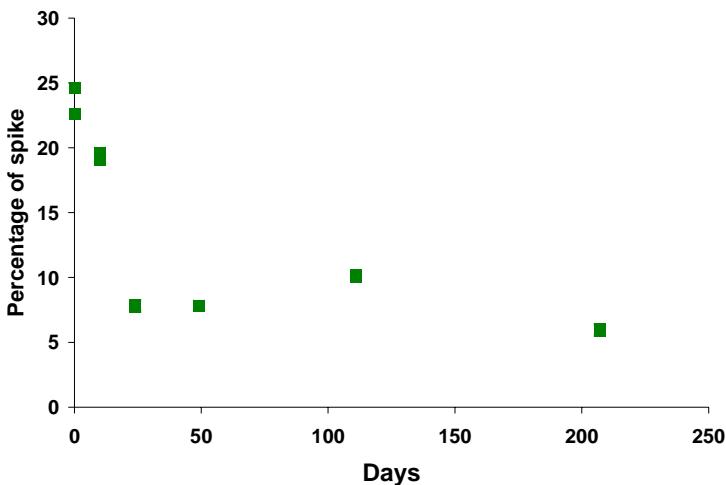


Fig. 1. Removal of BDE 209 from anaerobic Western Scheldt sediment suspensions.

The results of this study demonstrate that BDE 209 is debrominated in anaerobic sediment from the Western Scheldt and that this is probably due to bacteria present in the sediment. Although this process could contribute significantly to the removal of this compound from the environment, it may also be a reason for concern, as it would convert the relatively poorly bioavailable BDE 209 into congeners more readily taken up by biota. We will therefore continue to study the potential for debromination of BDE 209 and other PBDE congeners in anaerobic sediment and to identify the pathways of debromination. Enrichment of debrominating cultures from this sediment for use in further studies is currently in progress. The identification of characteristic debrominated products would enable studies of potential debrominating reactions occurring in sediments in the environment.

Acknowledgements

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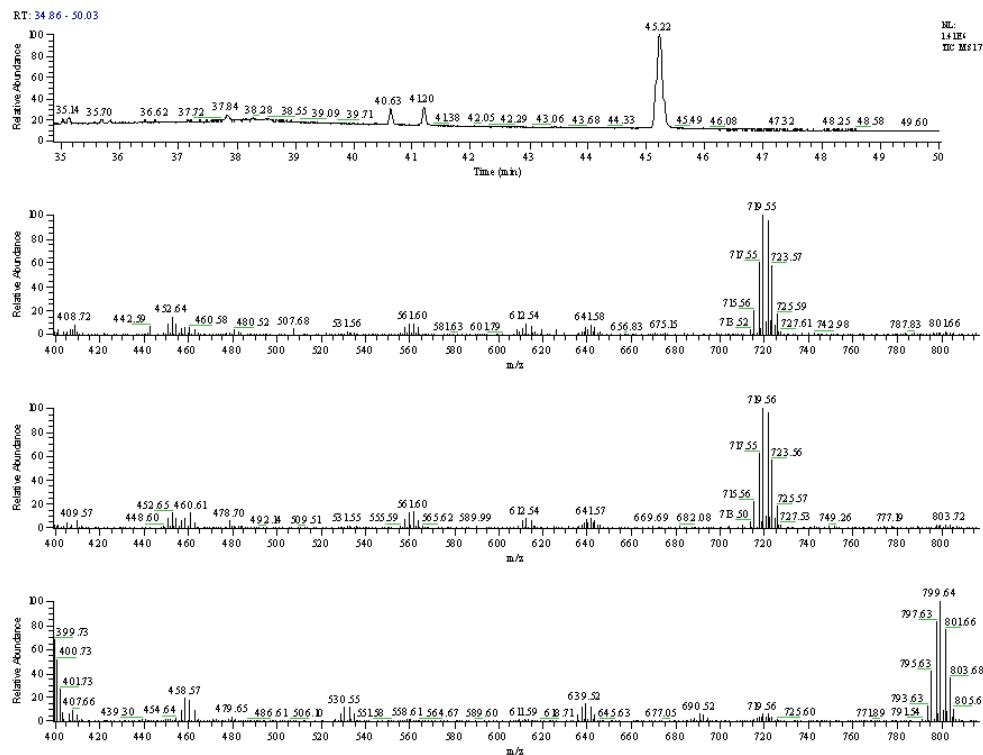


Fig. 2. Formation of new BDE peaks in anaerobic sediment incubations spiked with BDE 209 and mass spectra of the peaks at 40.63, 41.20 and 45.22 (BDE 209) minutes.

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