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EVALUATION OF REMEDIATION ALTERNATIVES FOR REDUCTIVE DEBROMINATION OF POLYBROMINATED DIPHENYL ETHERS IN SEDIMENTS

H. Demirtepe[1], I. Imamoglu[1]

[1]*Department of Environmental Engineering, Middle East Technical University, Ankara*

Introduction

Brominated flame retardants (BFRs) were widely used to protect certain commercial goods against fire throughout the world. An extensively used BFR is polybrominated diphenyl ethers (PBDEs). When products having flame retardants are used and/or discarded, PBDEs can reach water bodies and accumulate in organic media (esp. biota and sediments[1, 2]). Due to their toxicity, potential health effects and persistence [3, 4], behavior of PBDEs in the environmental compartments is a significant issue. The aim of this study is to investigate the fate of PBDEs in aquatic sediments under various conditions, thereby to assess effectiveness of possible remediation strategies.

PBDE degradation was shown to occur via various mechanisms; aerobic/anaerobic microbial debromination [5, 6], photochemical degradation [7] and oxidation processes [8]. For in-situ remediation of contaminated sediments, anaerobic reductive debromination is an important mechanism for hydrophobic organic compounds. Studies conducted on anaerobic debromination of PBDEs so far investigated the process in sludge, sediments, and soils or biomimetic systems. Anaerobic debromination of PBDEs in sludge was demonstrated in the presence of primers (e.g.2,6-dibromobiphenyl)[9,10] and nutrients [11]. Sediment and soil microcosms were established to observe the anaerobic debromination of PBDEs with the addition of buffers [12], nutrients, carbon sources and electron donors [13,14]. Studies were also conducted to identify the debromination pathways of PBDE congeners with different dehalogenating cultures [6]. The scope of this study, therefore, was to compare debromination of BDE-209 in sediments with no amendments, microbial consortia amendment and carbon source/electron donor amendment to simulate in-situ remediation strategies: natural attenuation, bioaugmentation, and biostimulation, respectively.

Materials and methods

Sediment microcosms. Sacrificial microcosms were prepared and operated for 90 days, with details given in Table 1. For each set and each sampling time, duplicate 20 mL reactors were established. Sediments that were used in microcosm studies were collected from a pond in a specially protected forest area (Camkoru National Park) in Ankara, Turkey. A part of collected sediments was air-dried overnight, and were spiked with BDE-209 standard in acetone. After thorough mixing of spiked dry sediments, wet sediments were added and a homogeneous mixture was obtained. Spiked sediments were distributed equally among the microcosm bottles to get approximately 3 g wet sediments in each. Similarly, non-spiked control set was established by spiking dry sediment with high grade acetone and mixed with wet sediments. Except for the organic set, all sets were topped with distilled water. Sterile microcosms were autoclaved at 120 °C at 1.1 atm pressure for one hour on three consecutive days. All sets were purged with high purity nitrogen stream after capping with Teflon lined septa crimp caps. They were incubated in the dark at 25°C. ECl medium added to the organic set was prepared as given in Berkaw et al. [15]. This medium was originally used to subculture Dehalobium chlorocoercia strain DF-1 [16]. A carbon source (sodium formate) and electron donor (ethanol) at 10 mM was also added to the medium. DF-1 culture used in microcosms was obtained from the Institute of Marine & Environmental Technology, University of Maryland, Baltimore, MD, USA, and culturing information is given in Payne et al. [16]. A negative control set was established for microbial set to observe the effects of adding a culture medium without DF-1 cells. For this purpose, a spent growth medium was obtained by passing DF-1 medium through 0.22 μm filter [16] so that no cells remained in the medium.

PBDE- analysis. US EPA method 3550C Ultrasonic Extraction was followed for extraction of samples [17.] Shortly, one gram of sample, mixed with one gram of anhydrous sodium sulfate in 40 mL bottles, were extracted ultrasonically in an ultrasonic bath with 30 mL DCM: HEX: ACE mixture (7:7:1 v/v) for 30 minutes twice, following overnight soaking in the solvent mixture. Sulfur removal was achieved with the addition of copper powder into extraction solvents. The two sonicated extracts were combined and concentrated to 5-10 mL via a rotary evaporator. To remove possible interfering organic compounds, colored extract after concentration step was treated with concentrated sulfuric acid [18]. The top clear extract was purified with 0.5 g of alumina (deactivated to 6%) topped with anhydrous sodium sulfate, and

eluted with 2 mL of n-hexane. The collected extract was concentrated to 2 mL by high purity nitrogen stream. One mL of this extract was spiked with internal standard and analyzed with gas chromatography coupled with micro-cell electron capture detector (Agilent 6890N GC-μECD) with DB-5 MS capillary column (15 m x 0.25 mm ID x 0.10 μm). Instrumental conditions were as follows: Helium was used as the carrier gas with 1.8 mL/min flowrate using a constant flow mode. The make-up gas for the detector was nitrogen with a flowrate of 30 mL/min. The injector and detector temperatures were 250°C and 350°C, respectively. The sample injection was carried out at 1 μL with splitless injection mode. Oven temperature program started at 90 °C, raised at 20°C/min to 310 °C, and hold there for 6 min.

Results and discussion

BDE-209 decrease. Microcosm sets were established by spiking BDE-209 to sediments with no previous PBDE contamination as monitored by Research Centre for Toxic Compounds in the Environment, Czech Republic [19]. Initial BDE-209 concentrations of microcosms were in the range of 625 – 725 ng/g dry sediment. The decrease in BDE-209 concentrations in different microcosm sets and corresponding percent removal rates are given in Figure 1. There was no decrease in BDE-209 level in sediment set up to 60 days. This stability was attributed to an acclimation period for the indigenous species in the sediment. However, at t=90 days, 35% reduction in concentration was observed in this set, revealing perhaps the end of lag period. In organic and microbial sets, there was a steady BDE-209 reduction throughout the course of the incubation period. At the end of 90 days, BDE-209 decrease reached 40% and 27% for organic and microbial microcosms, respectively. Similar degradation rates were observed in the literature. For example, Song and colleagues showed 39.7% reduction of BDE-209 in soil microcosms with lactate as carbon source operated for 90 days [20]. Also, 11% reduction in 90 days was achieved by Qiu and colleagues with and without addition of ethanol as an electron donor, with the highest rate observed in the first 30 days for methanol and ethanol [14]. Negative control set, prepared to control the effect of organic media added with microorganisms in microbial set, demonstrated a sharp decline at the beginning, but stayed stable afterwards. The initial reduction may be due to the triggering effect of organic media added. Lack of substrates after 20 days may explain the following stability of BDE-209 levels. The reduction in BDE-209 reached 22% at t=90 days in this negative control set. The sterile set did not have a net trend in BDE-209 concentration. A variation exists in concentration possibly due to the use of sacrificial reactors. Although a visibly clear appearance was observed in sediment/water interaction at each sampling bottle, some bottles may have insufficient sterilization during autoclave. Lastly, there was a PBDE control set, in which no BDE-209 was observed throughout the incubation period.

Debromination pathways and products. BDE-209 debromination in microcosms resulted in the formation of nona-, octa-, hepta-, hexa-, and penta-BDEs in 90 days (Figure 2). Formation of lower brominated congeners followed different patterns for each set. As can be seen from Figure 2, some of the products were observed in single sets. Also, other than BDE-183, there was another hepta-BDE formation, undefined due to lack of individual standards. Having the highest percent reduction in BDE-209, organic set achieved debromination up to tetra-BDE at day 90. For the first time in this study, new pathways for the formation of octa-BDEs (BDE-202, -201 and -194) were determined. Other debromination pathways observed were also shown to occur in previous sediment microcosms [12,13,21] and anaerobic culture media [6,22]. However, some of the previously identified pathways cannot be confirmed.

Implications on bioremediation strategies. Traditionally applied remediation techniques such as dredging and/or capping can cause further environmental concerns. Hence, more sustainable strategies should be applied while dealing with contaminated sites. In this study, three remediation approaches have been investigated at laboratory scale, namely, natural attenuation, biostimulation and bioaugmentation. Application of these three techniques to the same sediments with same contamination showed how they can differ either in efficiency or in products formation. Although they revealed similar efficiencies at the end of incubation, biostimulation had the highest rate in BDE-209 removal and in the formation of lower brominated congeners. Bioaugmentation with Dehalobium chlorocoercia strain DF-1 also exhibited a consistent debromination pattern. It was the first time that this strain was investigated for PBDE reductive debromination, and it served well for the purposes of bioaugmentation. The findings of this study can help assess remediation strategies for contaminated sites, revealing possible debromination pathways, accumulating product congeners, and extent of debromination under different conditions. Furthermore, identification of debromination mechanisms and end-products of debromination facilitates in-depth examination on bioaccumulative congeners and monitoring of toxicity in contaminated sites.

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Table 1. Details of microcosm sets

Reactor	BDE-209	Distilled water	DF-1	ECl medium
Sediment	+	+ (3.5 mL)	-	-
Organic	+	-	-	+ (3.5 mL)
Microbial	+	+(3 mL)	+ (0.5 mL)	-
Negative control	+	+(3 mL)	+(spent growth medium - 0.5mL)	-
BDE Control	-	+(3.5 mL)	-	-
Sterile	+	+(3.5 mL)	-	-

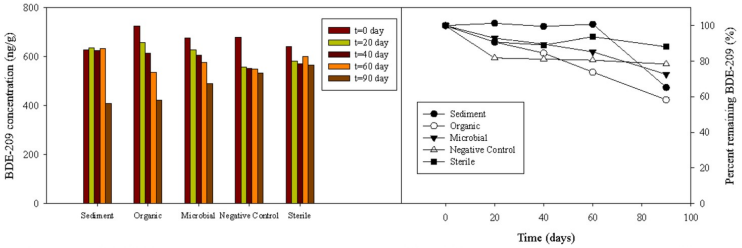

Figure 1. BDE-209 concentrations and percent remaining BDE-209 in different microcosm sets for 90 days incubation period

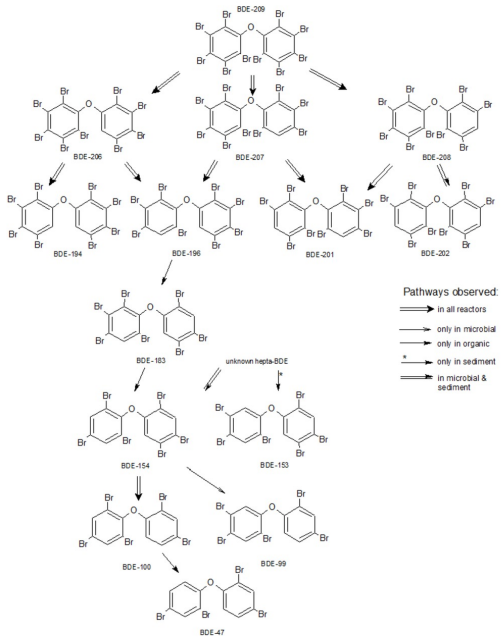

Figure 2. Debromination pathways observed in sediment, organic and microbial sets