# FATE OF DECABROMODIPHENYL ETHER IN ANAEROBIC FRESHWATER SEDIMENT

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## Introduction

The environmental fate of decabromodiphenyl ether (also known as decabromodiphenyl oxide) was studied in an anaerobic sediment/water microcosm[1]. Intact core microcosm systems were used to simulate fate processes in the complex ecosystem of freshwater anaerobic sediment. Sediment cores were dosed with a combination of $^{14}$C-labelled and nonlabelled decabromodiphenyl ether (DecaBDE) at nominal concentrations of 5 and 500 mg/Kg. Positive controls dosed with $^{14}$C-labelled and nonlabelled glucose were used to verify the integrity of the test apparatus and the viability of the test sediment. Test sediments were incubated at 21-25 °C throughout a 32-week test period and the production of $^{14}CO_2$ and $^{14}CH_4$ was monitored over time. Concentrations of DecaBDE in the test sediments were measured at the beginning and end of the test using high performance liquid chromatography (HPLC) with UV and radiometric detection. In addition, a radiochemical mass balance was conducted.

## Methods and Materials

Freshwater sediment and accompanying river water were collected from the Schuykill River, Valley Forge. PA using coring devices constructed of clear, acrylic pipe. The coring devices were inserted into the sediment to a depth greater than the depth of biological activity and then sealed while underwater. Upon collection the redox potential of the sediment was –284 mV. Prior to use, the surface water was decanted from above the sediment and placed in a separate container. The surface water and sediment were characterized. The sediment characterization included pH, % organic matter (Walkley-Black), cation exchange capacity (Ca, Mg, Na, K & H), disturbed bulk density, % sand-silt-clay, USDA textural class, and water holding capacity (1/3 bar). The surface water characterization included pH, nitrate-nitrogen, sulfate-sulfur, and total phosphorus. The collected sediment cores were stored at room temperature in an anaerobic chamber for 4 days. The average percent moisture of the freshwater sediment was 26.0%. The decanted surface water was stored under refrigeration during this time. A 0.2 mg resazurin/L solution was prepared using the surface water.

The nonlabelled decabromodiphenyl ether was a composite of material received from three manufacturers, Great Lakes Chemical Corporation, Albemarle Corporation and Bromine Compounds Ltd. Analysis indicated the composite test substance was homogeneous and contained 0.04% octabromodiphenyl ether, 2.5% nonabromodiphenyl ether and 97.4% decabromodiphenyl ether. The radiolabelled substance, decabromodi[U-$^{14}$C]phenyl ether; was synthesized by Nycomed Amersham (Buckinghamshire, England). The reported radiochemical purity of decabromodi[U-$^{14}$C]phenyl ether was 96.8%. Radiolabelled ($^{14}$C) and non-labelled forms of

glucose were purchased from Sigma Chemical Company (St. Louis, MI) and EM science (Gibbstown, NJ), respectively.

The test chambers (500 mL glass media bottles, Wheaton) were transferred to an anaerobic chamber. Sufficient sediment to reach the 300 mL graduation was added to each chamber. Each sediment was added to the appropriate test chamber in a manner consistent with maintaining the integrity of the sediment column structure (i.e. bottom of column on bottom of vessel, top of column on top). The numbers of bacteria are typically highest in surface sediments and decrease rapidly within sediments at greater depths (3). The test chambers were capped then removed from the anaerobic chamber and weighed. All test chambers were returned to the anaerobic chamber then uncapped and allowed to equilibrate overnight. After the equilibration period, the appropriate amounts of test or reference substance were added to their respective test chamber. Each sediment system was mixed using a wooden applicator so that the test and reference substances were distributed throughout the top 1 inch of sediment The lower part of the wooden applicator was broken off and left in the test chamber. Approximately 10 mL of a resazurin/surface water solution was added to each chamber. The chambers apportioned to the mineralization test apparatus (duplicate reference vessels, triplicate treatment vessels at 5 mg/Kg, and triplicate treatment vessels at 500 mg/Kg) were then sealed and transferred out of the anaerobic chamber and connected to the gas collection system. The mineralization apparatus was set up as described by Nuck and Federle (3). The test chambers were incubated in a water bath at 21 to 25 °C. $CO_2$ trapping solutions were periodically analyzed by liquid scintillation counting (LSC) using a Packard 2500 TR scintillation analyzer (Canberra-Packard, Downers Grove, IL).

Prior to analysis, test sediments were air dried and then homogenized on a roller mill (U.S. Stoneware, Mahwah, NJ). Ten gram portions of the day-0 and week-32 dried sediments were extracted two times with tetrahydrofuran (THF). Final extracts were concentrated and subsequently diluted using 50% tetrahydrofuran: 50% water, (v:v), filtered through a 0.45 µm Acrodisc and transferred to an amber autosampler vial. The concentrations of DecaBDE in the samples was determined using reversed phase high performance liquid chromatography (HPLC) with UV detection utilizing a system consisting of a Hewlett-Packard Model 1090 High Performance Liquid Chromatograph (HPLC) equipped with a Waters 486 variable wavelength detector operated at 220 nm. The extracts were also profiled using a flow-through radioactivity detector (IN/US β-RAM Model 2B). Chromatographic separations were effected using a Zorbax phenyl analytical column (250 mm x 4.6 mm, 5 µm particle size). Residual activity associated with extracted solids was measured using a Packard Model 307 oxidizer to evaluate the efficiency of the extraction process.

**Results and Discussion**

An average of 95% of the total activity added as radiolabelled glucose was recovered from the sediment in the reference test chambers. Of the recovered activity, 85% was recovered as $^{14}CO_2$ and $^{14}CH$ from the mineralization of the radiolabelled glucose and 10% was associated with the sediment. Mineralization of DecaBDE was not observed. Less than 1% of the total activity added as decabromodi[U-$^{14}$C]phenyl ether was recovered as $^{14}CO_2$ and $^{14}CH$ indicating that no mineralization of the DecaBDE had occurred. Averages of approximately 96% and 98% of total activity added were recovered from the 5 and 500 mg/Kg day-0 sediments. The recoveries from the day-0 sediments were consistent with that of the radiolabelled glucose dosed reference

sediments. Averages of approximately 131% and 123% of total activity added were recovered from the 5 and 500 mg/Kg week-32 sediments.

Seven replicate samples of each test sediment were analyzed by the HPLC-UV procedure. Average measured DecaBDE concentrations in the 5 mg/Kg sediments on day-0 and week-32 were 6.64 ± 0.71 mg/Kg and 6.42 ± 2.07 mg/Kg, respectively. Average measured DecaBDE concentrations in the 500 mg/Kg sediments on day-0 and week-32 were 543 ± 77 mg/Kg and 612 ± 158 mg/Kg, respectively. A statistical test (ANOVA) was carried out in order to assess whether the measured concentrations were significantly different. The differences between the days were analyzed using a nested ANOVA, with vessels nested within days. The denominator of the F test for effect of day was the ANOVA mean square for vessels within days. The F test concluded that the difference between the mean measurements on day-0 and week-32 were due to chance alone, and therefore were not statistically significant.

Measured concentrations of DecaBDE and radioactivity in the test sediments varied due to the composition of the individual sediment core. Sediments containing greater numbers of stones would have proportionately less sediment and would be a source of variability between replicates within and among the test sediments. Measured DecaBDE concentrations were converted to a DecaBDE mass based on the actual dry weight of the sediment and compared to the mass of DecaBDE added at test initiation. For the 5 mg/Kg sediments, the mean differences between the measured mass and the added mass in day-0 and week-32 samples were 0.143 and 0.067 mg, respectively. For the 500 mg/Kg sediments, the mean differences between the measured mass and the added mass in day-0 and week-32 samples were 67.5 and 0.04 mg, respectively. The difference between the measured mass and mass added was analyzed using a paired t-test. The differences between the DecaBDE mass weighed into the test chamber on day-0 and the DecaBDE mass calculated using the measured DecaBDE concentration at week-32 were found not to be statistically significantly.

Additional analytical evaluation of the sediments is ongoing: however, the data evaluated to date indicates that there are no biotransformative reactions of the DecaBDE taking place in the anaerobic test system.

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