

Photolytic debromination of decabromodiphenyl ether (DeBDE)

U. Sellström*, G. Söderström, C. de Wit*, M. Tysklind

*Institute of Applied Environment Research (ITM), Stockholms University,
S-106 91 Stockholm, Sweden

Institute of environmental Chemistry, Umeå University, S-901 87 Umeå, Sweden

Introduction

Polybrominated diphenyl ethers (PBDE) are additive flame retardants used in plastics, textiles and electronic equipment. Some Te- and PeBDEs have been found to bioaccumulate and biomagnify in biota and concentrations have increased during the 1970s and 80s (1,2). Te- and PeBDEs have been shown to be biologically active and potentially toxic (3). The most commonly used PBDE products contain mainly decabromodiphenyl ether (DeBDE), but in environmental samples lower brominated PBDEs dominate (1). However, in sediments taken near user sites DeBDE has been found (4-7). Previous studies show that PBDE and other brominated organic compounds in solvents undergo rapid photolytic debromination in the presence of ultraviolet (UV) light under laboratory conditions (8). Photolytic debromination could be one reason for the relative dominance of lower brominated PBDE in the environment. The aim of this study was to investigate the debromination process of DeBDE on different matrices (both dissolved in toluene and layed on natural matrices such as sand, soil and sediment) and exposed to sunlight or artificial UV light and to characterize and possibly identify the degradation products. The results of these experiments will increase the understanding of the possible transformation and fate of DeBDE in the environment.

Materials and Methods

Samples. Five different matrices were used in the experiments, viz. toluene, silica gel, sand, soil and sediment. The toluene was a glasdistilled quality from Fluka (Burdick and Jackson). The silica gel (Merck) and the lake-sand (Kebo) were thoroughly washed with toluene to remove any organic matter. The soil was an agricultural soil from Jydeved, Denmark, selected as a typical Nordic soil (9) and the sediment was from Dättern, a bay on Lake Vänern, Sweden, with low contaminant levels (10). The matrices were portioned into Pyrex-tubes and DeBDE, dissolved in toluene, was added. The toluene was then allowed to evaporate while the samples were kept in the dark.

Experimental setup. UV-exposure experiments were performed both in the laboratory with artificial UV-light and under natural conditions with outdoor sunlight (sand, soil, sediment). The laboratory exposure light-source consisted of four mercury UV-lamps, Philips TLK 40W/09N, equipped with filters to give a spectra as close as possible to sunlight in the UV-range. The irradiance intensity from the UV-lamps at the exposure spot was 1.6 mW/cm². Sunlight exposures were performed in July 1997 in Umeå, Sweden (63° 51' N, 20° 17' E, 20 m altitude above sea level). The weather conditions were excellent with clear skies. Maximum UV-irradiance from the sun at mid-day was 2.3 mW/cm². Subsamples of each matrix were exposed to artificial UV-light in the laboratory. Subsamples of sand, soil and sediment were exposed to outdoor sunlight. Irradiance from 24 hours of sunlight corresponds to approximately 9 hours of artificial UV-light in this experiment.

Experimental procedure. Each series consisted of blanks, dark controls and the samples to be exposed and the experiments were performed in triplicates. Sediment samples were reconstituted in water before exposure. The Pyrex tubes with DeBDE adsorbed to the matrices were placed on a "rocking/rolling action" apparatus. For the indoor experiments the setup was placed under mercury UV-lamps in a hood and samples were taken from 0 to 32 hours. For the outdoor experiments the set-up was placed on a shadowless roof adjacent to the laboratory and samples were taken from 0 to 96 hours.

Analytical procedure. All samples were extracted in the Pyrex tubes used for UV exposure. The method used was a scaled down version of the method described by Nylund et al. (2). Sulphur was removed from the sediment and soil samples (2). The silica gel, sand, soil and sediment samples were then treated with concentrated sulphuric acid to remove less persistent substances. The analyses were done by GC-MS measuring the negative ions formed at chemical ionisation (m/z -79 and -81 for the brominated compounds) (7). Extraction and work-up were performed avoiding exposure of samples to light.

Results and Discussion

In Figure 1 the time course for the debromination of DeBDE and the formation/debromination of lower brominated PBDE (nona- to hexaBDEs) in toluene and on sand is shown. The congeners shown all correspond to components found in technical PBDE flame retardant

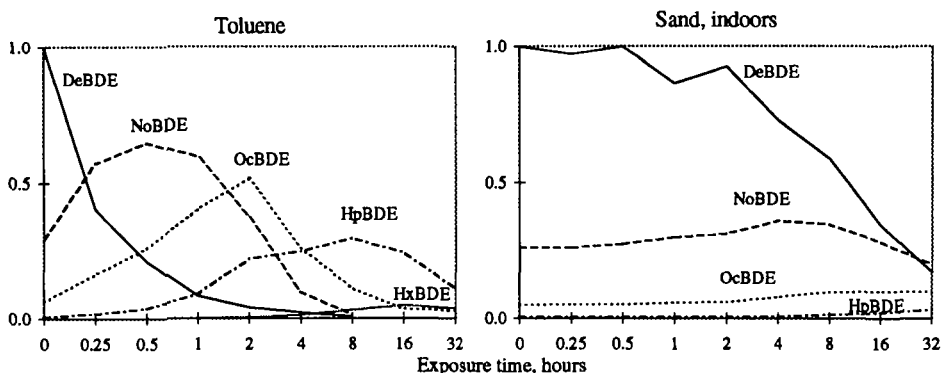


Figure 1. Debromination of DeBDE in toluene solution and on sand exposed to artificial UV-light.

products. The time course in toluene is rapid, with a half-life for DeBDE of less than 15 minutes. The increase and decrease of nona- to hexaBDEs shows that the process is mainly a step-wise debromination process. On sand, the time course for this debromination process is considerably slower. The half-life for DeBDE on sand is about 12 hours in the indoor experiment and about 37 for outdoor experiments. Exposure of sand indoors and outdoors results in similar half-lives for DeBDE when compared to total irradiance since 37 hours sunlight outdoors corresponds to approximately 13 hours of artificial UV-light indoors.

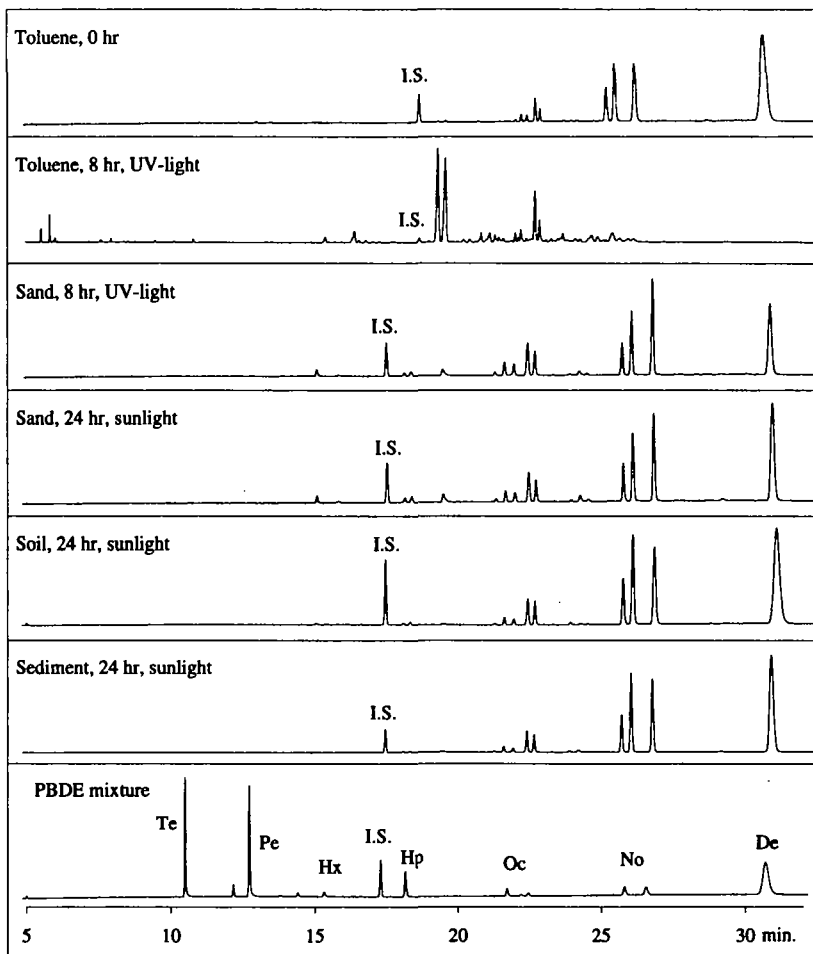


Figure 2. Photolytic debromination of DeBDE added to different matrices and exposed to artificial UV-light or sunlight for approximately the same irradiance time.

In Figure 2, the chromatograms of different matrices at approximately the same irradiance time are shown. The DeBDE product added to the samples is shown as time zero for toluene. The PBDE mixture (chromatogram at the bottom) is a mixture of penta-, octa- and decabromodiphenyl ether products. As can be seen in the figure, the chromatograms for sand at 8 hr UV-light and 24 hr sunlight are nearly identical and those for sand, soil and sediment at 24 hr sunlight are similar. The debromination of DeBDE leads to formation of lower brominated PBDEs but other products are also possible. Watanabe et al. (11) showed the formation of PBDFs as photolytic products from DeBDE dissolved in hexane. The search for these and other transformation products will be included in future work.

Acknowledgements

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