PHOTODEGRADATION OF DECABROMODIPHENYL ETHER (BDE 209) IN NATURAL AND AMENDED HOUSE DUST

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Introduction

Studies have now reported PBDEs in house dust, which have been measured at concentrations as high as 170,000 µg/kg dry weight [1, 2]. PBDEs are synthetic chemicals added to numerous plastics and resins that are then incorporated into commercial products such as furniture, TVs and other electronic products. Over the last thirty years the concentrations of PBDEs in the North American population has increased with a doubling time of 5 years and are approximately 20 times higher than levels in the European Union population[3]. The primary pathway by which people are exposed to PBDEs is still unclear and is most likely either related to dietary exposure and/or indoor exposure[4]. The elevated concentrations of PBDEs reported in house dust have raised numerous questions about their exposure potential in indoor environments. House dust is a repository for many types of environmental pollutants [5, 6]. These pollutants accumulate in house dust from various pathways, including off-gassing from products within the home, deterioration of products within the home and movement of soil and aerosols from the outdoor to the indoor environment. Because people spend a majority of their time indoors, and specifically in their homes, indoor exposure to pollutants is important to assess.

Toxicity studies have found PBDEs to be potentially neurotoxic and affect thyroid hormone homeostasis[7]. In general, it appears that the bioaccumulation and toxicity potential increases with decreasing bromination among PBDE congeners [8-11]. This is important issue because higher brominated congeners have the potential to photolytically debrominate in the environment [12-14]. Past studies have focused on the photolytic decomposition of decabromodiphenyl ether (BDE 209), the dominant congener found in the commercial mixture known as DecaBDE. These studies were all performed in solvent/water mixtures or on sediment and soil applications. No study to date has examined the potential for photolytic debromination in house dust. Considering that high levels of PBDEs, particularly BDE 209, have been found in house dust [1, 2], it is important to determine the extent of debromination that may occur indoors which could lead to further exposure and accumulation in people.

This study was designed to examine photolytic debromination of BDE 209 in house dust. The objectives were to determine: 1) the half-life of BDE 209 when exposed to sunlight in natural and amended (artificially spiked) house dust and 2) if debromination of BDE 209 to lower brominated congeners occurs. In addition, a mass balance of BDE 209 was conducted in this experiment to determine if debromination could account for all degradation of BDE 209 observed following the sunlight exposure.

Materials and Methods

The house dust used in this study was an indoor dust standard reference material (SRM 2585) supplied by the National Institute of Standards and Technology (NIST) in Gaithersburg, MD. This SRM is a well characterized and homogenous indoor dust material that was prepared from vacuum cleaner bag contents collected from homes in several U.S. states and a few motels and hotels. More details on the preparation of SRM 2585 can be found at NIST's web site for SRMs: http://ts.nist.gov/ts/htdocs/230/232/232.htm.   The indoor dust SRMs supplied by NIST have recently been analyzed for PBDEs and certified concentrations are available for up to 15 BDE congeners [15].

The objective of this study was to examine the photodegradation of BDE 209 in natural and amended house dust. Natural house dust consisted of unamended SRM 2585. The amended dust was prepared by cleaning SRM 2585 of all native PBDEs and then spiking the dust with BDE 209 dissolved in toluene. Amended dust was prepared by Soxhlet extracting approximately 30 g of SRM 2585 with dichloromethane for 48 hours. Following the extraction, the dust was allowed to air dry and later analyzed for PBDEs according to the method presented in Stapleton et al.[1]. The analysis of this material revealed that all the PBDEs in this material were removed and were below the limits of detection (<0.2 ng/g). The pre-cleaned dust was then spiked with 1.298 g of a solution of BDE 209 in toluene (at a concentration of 46.999 µg/g toluene). The target BDE 209 concentration for this dust experiment was 2.0 µg/g, similar to the mean concentration of BDE 209 reported in house dust samples from an earlier study[1]. The dust was allowed to air dry for 8 hours to allow for evaporization of the toluene. Afterwards, the dust was placed into a pre-cleaned amber bottle and shaken on a shaker table for 24 hours to ensure thorough distribution and homogenization of the BDE 209. Before initiation of the sunlight exposure, three replicates of the spiked dust were extracted and measured for BDE 209 levels. The concentration of BDE 209 in the material was determined to be 2180 ± 130 ng/g dry weight.

Aliquots of the natural and amended dust (0.5 g) were transferred to clean disposable UV cuvettes (Fisher Scientific, 14-385-938). The UV cuvettes are small (4.5 mL volume) methylacrylate chambers used in spectrophotometer cell holders for measuring UV absorbance. They are rated to transmit throughout the UV/VIS range, 285 to 750 nm. The dust aliquot was sealed inside two UV cuvettes by placing the open ends together and sealing the join with a strip of clear laboratory tape. Cuvettes were kept inside the laboratory in the dark until the exposure began.

To begin the sunlight exposure, UV cuvettes were removed from the aluminum foil packet and transferred to a tray lined with aluminum foil. The tray was placed outdoors at the NIST campus in Gaithersburg, MD, in the United States. As long as there was no precipitation in the forecast, cuvettes were placed outside every day, Monday through Friday, from approximately 9:00am to 5:00pm until a cumulative 200 hour exposure was achieved. To monitor solar intensity, the readout from a pyranometer was monitored. Incoming solar irradiance, measured in W/m^2, and temperature were monitored on hourly intervals during the time course of dust exposure study. When not exposed to sunlight, all cuvettes were kept wrapped in aluminum foil within the laboratory at room temperature. Three cuvettes filled with each dust type were kept enclosed in aluminum foil and placed outdoors along with the samples as controls for the duration of the experiment. On pre-determined time intervals (Table 1), three cuvettes were removed from the tray, wrapped in aluminum foil packets and stored at room temperature in the laboratory until analysis. Dust samples were extracted and analyed for PBDEs in the method used by Stapleton et al., 2005[1].

Results and Discussion

Concentrations of BDE 209 were found to decrease in both natural and amended house dust samples but with varying degradation rates (Table 1). Assuming first order kinetics, the degradation rate of BDE 209 in amended and natural dust was 2.3×10^{-3} hr^{-1} and 1.7×10^{-3} hr^{-1}, respectively. This translates to half-lives of 301 and 408 sunlight hours, respectively. Previous studies have examined the degradation of BDE 209 in soils, sediments and minerals using both UV lamps and sunlight exposures. The half-lives reported here in dust are longer than the half-lives measured in sand, sediment and soils, but equivalent to half-lives measured in minerals and humic acid coated sand [12, 14]. The longer half-live of BDE 209 in natural dust may be attributed to matrix factors in the dust absorbing sunlight and decreasing the available irradiance for photodegradation of BDE 209. Alternatively, BDE 209 may be bound or sorbed to materials in the dust which were removed during preparation of the amended dust. These materials may limit the ability of BDE 209 to photodegrade via direct or indirect photolysis. Additionally, BDE 209 may be found in a solid form in the natural dust, as opposed to being spiked into the amended dust in a dissolved form. The solid form of BDE 209 may have a limited surface area available for absorption of sunlight relative to the dissolved form.

Analysis of the amended dust samples provided the opportunity to measure the degradation products formed from BDE 209 photolysis. As seen in Figure 1, hepta-, octa- and nonabrominated diphenyl ether congeners were observed in the amended dust samples. These congeners were found to significantly increase throughout the 200 hour exposure. Over the 200 hour sunlight exposure, approximately 860 pmoles of BDE 209 was degraded, and the accumulation of these lower brominated congeners accounted for 380 pmoles, or 44% of the BDE 209 loss (Figure 2). Therefore, over half of the BDE 209 was lost to unknown pathways/products.

The concentration of BDE 209 was also observed to decrease in the natural house dust during the 200 hour exposure. Approximately 700 pmoles of BDE 209 was degraded during the 200 hour sunlight exposure. In the natural dust, lower brominated
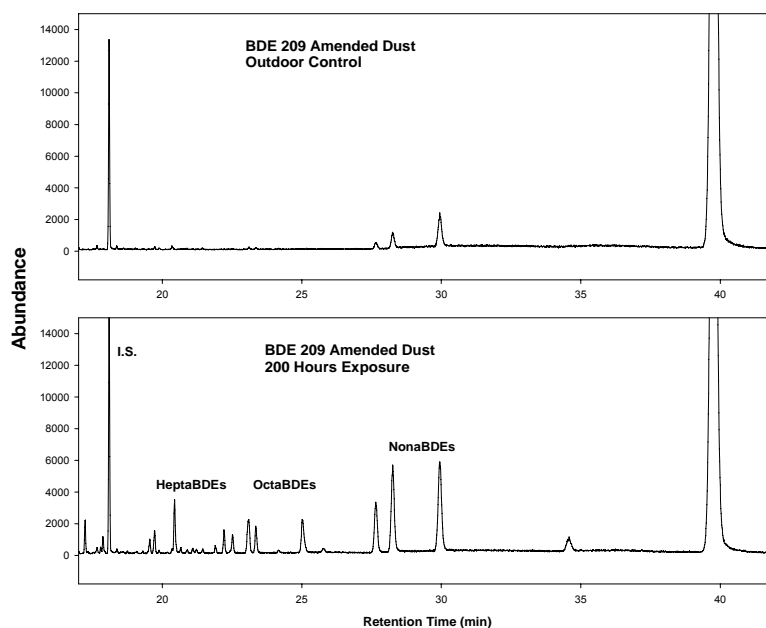

Figure 1. GC/ECNI-MS chromatograms of house dust extracts. The top chromatogram represents the outdoor control and the bottom chromatogram displays the house dust exposed to sunlight for 200 hours.

congeners were present in the dust prior to exposure and changes in concentration were measured. The octa- and nona-BDE congeners that were observed to increase in the amended dust samples also initially increased in the natural house dust, but then appeared to level off after 100 hours of exposure. Concentration of 2,2',4,4'-tetrabromodiphenyl ether (BDE 47) in the natural dust did not change significantly throughout the 200 hour exposure. In contrast, the concentration of 2,2',4,4',5-pentabromodiphenyl ether
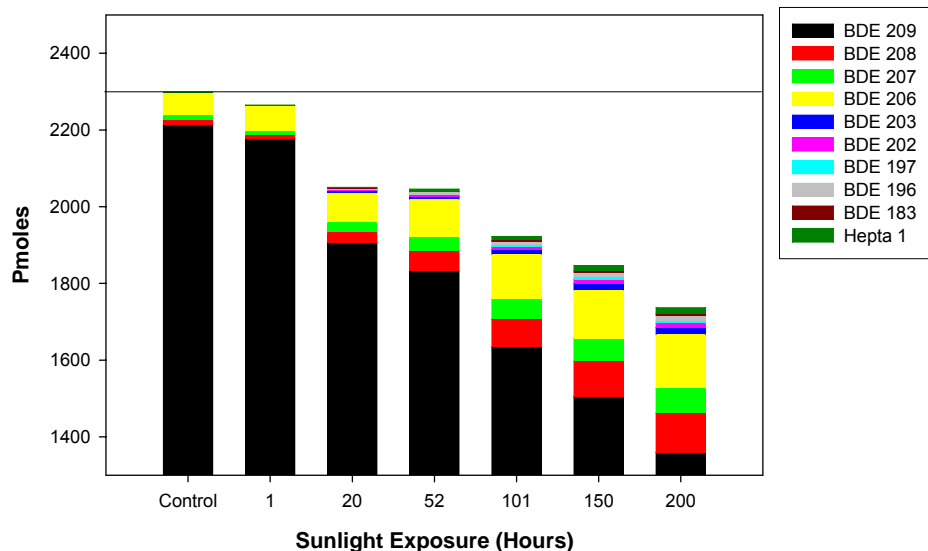

Figure 2. Mass of BDE congeners detected in amended dust samples. An increase in the lower brominated congeners was observed as the concentration of BDE 209 decreased.

(BDE 99) decreased throughout the 200 hour sunlight exposure by 22%.

This study suggests that the concentration of PBDEs will change significantly following exposure to natural sunlight. Recent studies have found elevated levels of PBDEs in both house and car dust[1, 2] (http://www.ecocenter.org/dust/ToxicAtAnySpeed.pdf). Based on the results from the present study, debromination of BDE 209 will occur in dust exposed to natural sunlight, and can lead to the formation of lower brominated congeners, primarily hepta-, octa- and nonaBDE congeners. While sunlight exposure in most homes is limited, sunlight exposure in cars can be expected to be more significant. Future studies are needed to determine what other products are formed from BDE 209 photodegradation and if volatilization of lower brominated congeners to the surrounding atmosphere is possible.

Table 1. Concentrations (ng/g dry weight) of BDE 209 measured in natural and amended dust exposed to sunlight. Values represent the mean ± the standard deviation (n=3).

Sunlight Exposure (Hours)	Natural Dust (SRM 2585)	Amended Dust
Control	2590 ± 75	2120 ± 63
1	2502 ± 115	2090 ± 56
20	2410 ± 169	1830 ± 77
52	2170 ± 10	1760 ± 24
101	1940 ± 51	1570 ± 47
150	1900 ± 74	1440 ± 30
200	1830 ± 83	1300 ± 35

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