

## PHOTODEGRADATION OF DECABROMODIPHENYL ETHER: KINETICS, REACTION QUANTUM YIELD AND PENETRATION OF LIGHT INTO KAOLINITE

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### *Introduction*

Decabromodiphenyl ether (BDE-209) is widely used as a flame retardant in products such as electronic equipment and upholstered furniture. Its estimated annual global market demand was 56,100 tons in 2001<sup>1</sup>. The environmental fate and safety of BDE-209 (e.g. bioavailability, persistence, toxicity) is a subject of on-going discussions. Photodegradation is thought to be a possible degradation pathway for BDE-209.

In order to calculate the photodegradation rate constant ( $k$ ) of a compound quantitatively, three parameters and their dependence on the wavelength have to be known: the light absorption coefficient of the molecule ( $\epsilon$ ), the reaction quantum yield ( $\Phi$ ) and the light intensity ( $I$ ) (see eq. 1).

$$k_{photo} = \frac{d c}{dt} = - \int_{\lambda} I(\lambda) \epsilon(\lambda) \Phi(\lambda) d\lambda c \quad (1)$$

For various liquids, absorption coefficients of BDE-209 ( $\epsilon$ ) and its reaction quantum yield ( $\Phi$ ) have been reported<sup>2,3,4</sup>. Applying a typical outdoor light intensity (summer, noon, mid-latitude), one can calculate that the near surface half-life of BDE-209 is less than an hour, which has been confirmed by experimental measurements.

For photodegradation on surfaces (e.g., soil, sand, minerals), only overall degradation rates have been reported<sup>5,6,7</sup>. They varied substantially and analysis of BDE-209 residues in soil did not indicate rapid degradation in the real environment. In order to address these apparent differences, we determined reaction quantum yields of BDE-209 on a model soil mineral (kaolinite) and measured the penetration of light into this mineral by combining the Kubelka-Munk<sup>8</sup> theory of light transport in porous media, diffuse reflectance spectroscopy, and chemical analysis<sup>9,10,11</sup>. In combination with the known absorption coefficient of BDE-209 on kaolinite<sup>9</sup>, our results enable the calculation of degradation rates for any layer thickness.

### *Methods and Materials*

**Kubelka-Munk theory.** The Kubelka-Munk theory<sup>8</sup> uses two parameters  $k$  (absorption coefficient) and  $s$  (scattering coefficient) to describe the transport of light in a porous media. These two parameters of a material can be determined experimentally by measurement of the diffuse transmittance and the diffuse reflectance of a series of thin layers exhibiting different thicknesses<sup>10</sup>. The knowledge of these two parameters is necessary to determine the absorption spectra ( $\epsilon(\lambda)$ ) of a compound by measuring the diffuse reflectance spectrum of thick layers of this material spiked with different concentrations of the compound. Finally, measurement of decreasing concentrations by chemical analysis in controlled irradiation experiments allows the calculation of reaction quantum yields ( $\Phi(\lambda)$ ).

**Chemicals.** Chemicals were obtained from following sources: technical DecaBDE (98%) from Aldrich (Buchs, Switzerland), kaolinite (purum, natural) from Fluka (Buchs, Switzerland). Standards were purchased from Cambridge Isotope Laboratories (Andover, USA): <sup>13</sup>C<sub>12</sub>-BDE-183 and <sup>13</sup>C<sub>12</sub>-BDE-

209; from Wellington Laboratories (Guelph, Canada): BDE-196, BDE-197, BDE-206, BDE-207, and BDE-208; from AccuStandard (New Haven, USA): BDE-198, BDE-203, BDE-204 and BDE-205.

**Preparation of thin layers.** Thin layers of model kaolinite, were prepared according to Ciani et al.<sup>10</sup> with some modifications: the surface of the quartz glass was wetted before application of the kaolinite/solvent slurry; the solvent of the kaolinite/solvent slurry was optimized for the application of the apolar BDE-209 (i.e. isooctane/toluene 95/5 (v/v)).

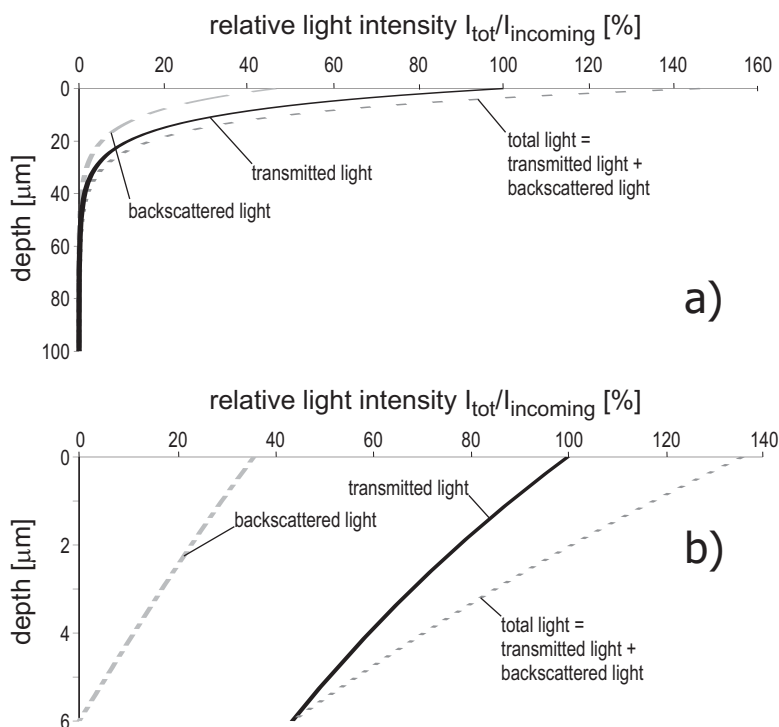
**Diffuse reflectance spectroscopy for the determination of  $k$  and  $s$  of kaolinite and  $\epsilon_i$  of DecaBDE.** These experiments were performed on a Uvikon 860 spectrophotometer equipped with an integrating sphere (Ulbricht-bowl). Approximately 10 layers of different thickness of kaolinite were measured. The parameters  $k$  and  $s$  were obtained by fitting the measured curves of reflectance and transmittance versus layer thickness applying the least square method.

**Degradation of DecaBDE under natural sunlight to determine the reaction quantum yield  $\Phi_i$ .** Sunlight irradiations were performed in Dübendorf (Switzerland) around noon on clear summer days, because estimation of the photon flux is best for such meteorological conditions. A series of thin solid layers spiked with BDE-209 were exposed to sunlight for predetermined time intervals. Usually, samples were conditioned at 50% relative humidity (dry conditions), for a few experiments water was added to the mineral layer (wet conditions). Special care was taken to avoid exposure to light before and after the experiment. Dark controls were performed as well. Temperature was controlled by performing all experiments in a water bath.

**Analysis.** Irradiated samples and dark controls were spiked with isotope labeled standards (<sup>13</sup>C<sub>12</sub>-BDE-183 and <sup>13</sup>C<sub>12</sub>-BDE-209) and extracted twice with hexane. Thereafter the volume was reduced to 100  $\mu$ l. GC analysis was carried out with a DB-1 equivalent stationary phase (PS347.5, 10 m  $\times$  0.28 mm, film 0.1  $\mu$ m). Hydrogen at an estimated flow rate of 4 ml min<sup>-1</sup> served as mobile phase. The GC oven temperature program was as follows: isothermal at 110  $^{\circ}$ C for 1 min, 12  $^{\circ}$ C/min to 320  $^{\circ}$ C, and held at 320  $^{\circ}$ C for 5 min. The GC-to-MS transfer line was held at 350  $^{\circ}$ C. In all GC/MS analyses, samples were injected cold on-column (1  $\mu$ l out of 100  $\mu$ l final volume). Positive ion EI-MS signals were acquired on a MAT 95 high resolution mass spectrometer (Thermo Finnigan MAT) in single ion monitoring mode at an ionization energy of 60 eV and a mass resolution of 8,000. For hepta-, octa-, nona-, and decabromodiphenyl ethers, the two most intense ions of the [M-2Br]<sup>+</sup> cluster were monitored. Response factors for BDE-206, BDE-207 and BDE-208 versus <sup>13</sup>C<sub>12</sub>-BDE-209 were determined and used for quantification. The mean response factor of BDE-198, BDE-203, BDE-204, and BDE-205 versus <sup>13</sup>C<sub>12</sub>-BDE-183 was used to quantify the sum of the (partially coeluting) octabromodiphenyl ethers.

### Results and Discussion

**Penetration of light into kaolinite.** On the basis of diffuse reflectance and diffuse transmittance experiments, absorption and scattering coefficients were calculated for all wavelengths between 250 and 700 nm. The scattering coefficient varied between 2500 cm<sup>-1</sup> (at 250 nm) and 1000 cm<sup>-1</sup> (at 700 nm), where as the absorption coefficient varied between 1200 cm<sup>-1</sup> (at 250 nm) and 0 cm<sup>-1</sup> (at 700 nm). In dry kaolinite, light penetrates only to a very small extent below 50  $\mu$ m, as shown in Figure 1 for 300 nm. Small penetration depths (below 1 mm) were also reported for other minerals and soils<sup>10</sup>. Thus, only BDE-209 that is sorbed to particles at the very top of a (unstirred) soil or mineral layer may undergo photolysis. Also, transport by diffusion from deep dark areas to the light receiving layer is expected to be very slow for BDE-209, as BDE-209 exhibits a very low vapor pressure. These two facts may explain why laboratory experiments with different stirred or unstirred layers of soils or minerals resulted in different half-lives. And these two facts, may also explain why no indications for photodegradation have been found in environmental soil samples. Soil samples usually have a thickness of several centimeters and consequently much of the BDE-209 contained in the sample is protected from light.

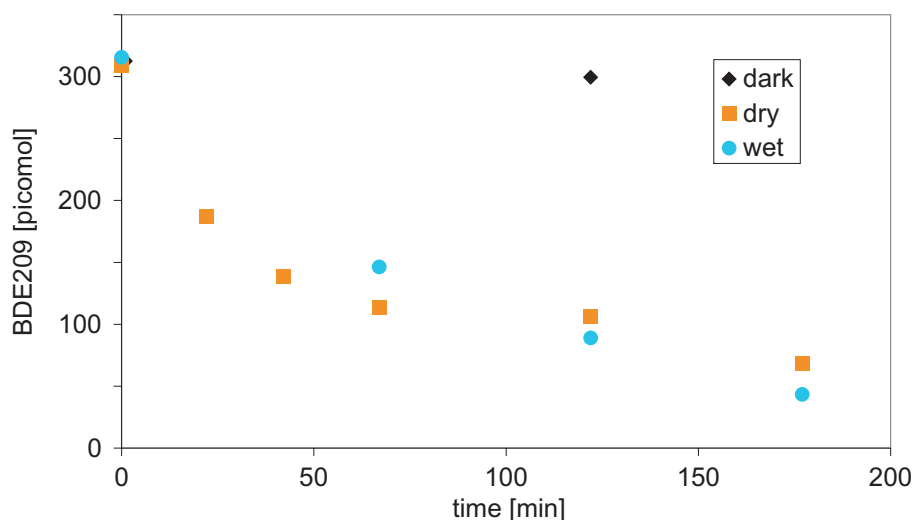


**Figure 1.** Penetration of light (300nm) into dry layers of kaolinite calculated using absorption and scattering coefficients,  $k$  and  $s$ , derived from diffuse reflectance and diffuse transmittance experiments. In the upper part (a), light penetration is shown for a layer thickness of 100  $\mu\text{m}$ . The lower part (b), reflects light penetration in a very thin layer of kaolinite (6  $\mu\text{m}$ ). Degradation experiments were performed on such thin layers.

**Degradation experiment and reaction quantum yield.** Degradation kinetics for DecaBDE on kaolinite were measured under natural sunlight (see Figure 2). Under the chosen conditions, we observed a non-exponential decrease of DecaBDE, reflecting the fact that even in this very small layer light intensity varies by more than a factor of two between the top and the bottom side. Nevertheless, to compare our degradation data with results from other studies and for a first estimation of the reaction quantum yield, we assumed a first order degradation behavior on the whole course of the experiment. The resulting half-lives were 76 and 73 minutes for dry and wet conditions. Thus, BDE-209 sorbed to kaolinite undergoes rapid photodegradation independent of the presence of a bulk water phase, if the light is able to reach the sorbed BDE-209 molecule.

The sunlight photon flux was calculated with the EPA-program GC-Solar for the date and location of the experiment. These photon flux data were combined with the absorption coefficient and the pseudo first order degradation rate constant in order to calculate the reaction quantum yield for BDE-209 on kaolinite. The calculated reaction quantum yield was 0.1 ( $\pm 50\%$ ), which is comparable to the reaction quantum yield of a water/methanol system (i.e. 0.14)<sup>4</sup>, but a factor of five smaller than in hexane (i.e. 0.47)<sup>3</sup>.

**Transformation products.** Under dry conditions, the majority of the degradation products were lower brominated diphenylethers. Under wet conditions, a large part of the transformation products remained unidentified so far.



**Figure 2.** Degradation of BDE-209 sorbed to a thin layer of kaolinite (6  $\mu\text{m}$ ) and exposed to natural sunlight. Under dry conditions, the kaolinite layer was conditioned at 50% relative humidity, where as under wet condition water was added to the kaolinite layer.

**Conclusions and outlook:** BDE-209 sorbed to kaolinite undergoes rapid photodegradation if it is reached by light. However, light is only able to penetrate a very small layer of minerals and soil (< 1mm) and hence photodegradation of BDE-209 in real soil is limited to the very top layers. So far, we have studied the degradation on one model surface, kaolinite, and we have not yet identified many transformation products. Further experiments, will focus other surfaces and on the identification of transformation products.

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