

DIRECT PHOTOLYTIC DECOMPOSITION OF POLYBROMINATED DIPHENYL ETHERS IN SURFACE WATERS

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Introduction

Polybrominated diphenyl ethers (PBDEs) prevent ignition and slow down the burning of human made consumer products. Their function as fire retardants saves human lives and reduces economical losses. The reverse side of the coin is that PBDEs exist ubiquitously in environment, where they can accumulate in biota with endocrine and neurotoxic effects¹⁻³. According to the laboratory experiments, PBDEs decompose photochemically, but their photolytic half-lives in environment are poorly known⁴⁻⁶. The objective of this study was to assess the direct decomposition of dissolved PBDEs in natural surface waters.

In our approach three PBDE-congeners were first exposed to sunlight. For the determination of apparent quantum yields for the direct photolysis of the parent congeners (ϕ), the experimentally determined photolytic decomposition rates were related to the number of absorbed photons by PBDEs. These ϕ s were used to calculate the rate of direct photochemical decompositions of PBDEs in natural surface waters. For this purpose, we used the information about the solar radiation and the absorption spectra of PBDEs and accounted for the absorption by natural particles and dissolved organic matter. In order to demonstrate the effect of natural absorbing components and mixing regimes on the photolysis rate, we calculated the direct photochemical decomposition in two optically different marine systems, the Baltic Sea and the Atlantic Ocean.

Materials and Methods

PBDE standards, 2,2',4,4'-tetrabromodiphenyl ether (#47), 2,2',4,4',5-pentabromodiphenyl ether (#99), 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether (#209) (50 $\mu\text{g ml}^{-1}$ in isooctane, except #209 9:1 ratio isooctane:toluene), were purchased from Accustandard Inc. The purities were for 100 % for #47 and #99; and >98.3 % for #209 according to the gas chromatography-mass spectrometric (GC-MS) analyzes done by manufacturer. HPLC grade isooctane was from Fisher Inc.

For the photolytical experiments, the PBDEs in isooctane (250 ng ml^{-1}) were introduced into custom made quartz GC-autosampler vials and glass vials wrapped in aluminium foil (dark controls). The vials were placed into a pool on the roof at Helsinki, Finland (60°20'N 24°97'E). The pool was constructed from black tarpaulin and wood board, flushed with tap water (20-23 °C) and had a water depth of 50-60 mm. The exposure times were 60 min for #209 (October 5th), 4 days for #99 (June 13th), 12 days for #47 (July 7th). The concentration of parent PBDEs were analysed four to five times along the exposures. Each time had three replicates, a dark control and an isooctane blank.

The PBDEs were analysed with an Agilent GC-MS (model 6890/5973) using on-column injection. The GC columns for # 209 were a 1-3 m long retention gap column (id. 0.53 mm) and an analytical 5-7 m long DB-5MS column (5 % diphenyl, 95% dimethyl polysiloxane, id. 0.25 mm and 0.1 μm film). The gas flow was 1.6 ml min^{-1} (constant flow) and the temperature for the GC-oven was 90-320 °C (25 °C min^{-1}). For #47 and #99 we used an

analytical 13.9 m long HP-5MS column (5 % diphenyl, 95% dimethyl polysiloxane, id. 0.18 mm and 0.18 μm film), a gas flow of 0.9 ml min^{-1} (constant flow), and the temperature program of 50-300 $^{\circ}\text{C}$ (25 $^{\circ}\text{C min}^{-1}$). Common MS-parameters for all congeners were the temperature of 320 $^{\circ}\text{C}$ at the GC-MS interphase, 250 $^{\circ}\text{C}$ at the ion source and 200 $^{\circ}\text{C}$ at the quadrupole, a 2 min solvent delay, electron ionization (70 eV) and selected ion monitoring.

The numbers of absorbed photons by PBDEs were calculated according to the geometry of the pool and the vials, the absorption coefficients of PBDEs and the solar radiation incident to the pool⁷. The solar radiation incident to the pool was calculated with a DISORT2 radiative transfer code included in the libRadtran program package using measured pyranometer data⁸. The absorption coefficients of PBDEs were calculated according to the concentrations of PBDEs and their measured specific absorptivities. The specific absorptivities were measured with a Gary 100 (Varian Inc.) spectrophotometer from the PBDEs (in isooctane, 50 $\mu\text{g ml}^{-1}$) using a scanning rate of 30 nm min^{-1} , a slit width of 2 nm and a 10 mm quartz cuvette.

In order to calculate the direct photochemical decomposition of PBDEs in the surface waters, we collected optical information from oceanic and coastal waters⁹. On 31 Aug 2005, water (0-5 m) was collected with a Limnos sampler in the northern Baltic Sea (59 $^{\circ}$ 49'N, 23 $^{\circ}$ 18'E). During the collection of sample, the temperature at the surface was 15 $^{\circ}\text{C}$, salinity was 5.5 ‰ and the mixing depth of surface water was 5 m according to a conductivity depth temperature (CTD) profile. On 4 Oct 2004, water was collected (10 m) with a Niskin bottle attached to a Sea Bird rosette at the subtropical gyre of Atlantic Ocean (23 $^{\circ}$ 01'N, 29 $^{\circ}$ 16'W). A CTD-profile revealed that in the 40 m deep mixing layer, temperature was 26 $^{\circ}\text{C}$ and salinity 37.3 ‰. The vertical attenuation coefficient for irradiance at 320 nm was determined with a PUV 500 (Biosherical Instruments Inc.). The absorption coefficients of natural absorbing components, dissolved and particulate matter, were determined with spectrophotometers⁷.

Results and Discussion

When the PBDE-congeners were exposed to solar radiation, their concentration decreased according to the first order kinetics, but not in the dark control vials indicating that solar radiation decomposed parent congeners. Isooctane was transparent to solar radiation, and only PBDEs absorbed solar UV-radiation (Figure 1). Therefore, the direct photolytic decomposition accounted for the decay of PBDEs. The congener #209 decomposed 50-300 times faster than #47 and #99 (Table 1). The degree of overlap between solar radiation and the absorption spectra of PBDEs explained the photolysis rate. The higher brominated diphenyl ethers degrade faster than lower brominated congeners, because the overlap between the solar radiation and the absorption of PBDEs increases along the degree of bromination.

The calculated apparent quantum yields (ϕ) were 0.37 \pm 0.06 for #209, 0.10 \pm 0.01 for #99 and 0.19 \pm 0.04 for #47. Our ϕ for #209 is similar, but ϕ for #47 lower than what has been reported before (i.e., $\phi_{\#47}$ of 0.63 in⁶).

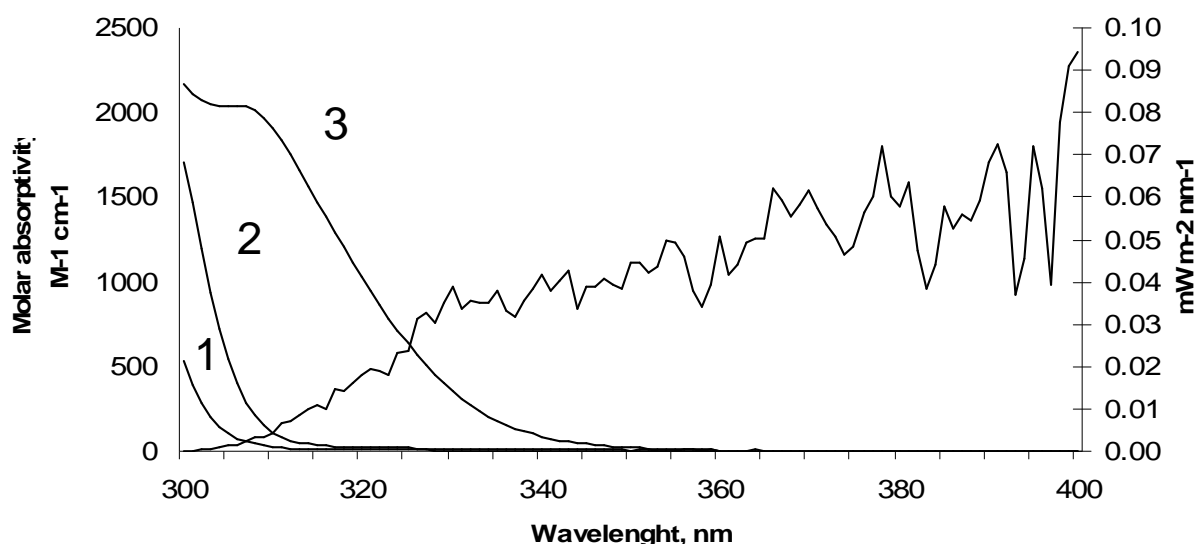


Figure 1. Molar absorptivities of 1) #47 2) #99 in isoctane 3) #209 isoctane toluene 9:1 and solar irradiance at Helsinki, 3:35 pm on October 5, 2005.

We applied the measured ϕ_s to an optical model for the calculations of photolytic half-lives of PBDEs at the surface of Baltic Sea at the environmentally relevant concentrations (30 to 40 pg l^{-1})¹⁰. The model calculations were done with a typical summer solar radiation in the Baltic Sea accounting for the absorption by the natural dissolved and particulate matter. Just below the surface, the calculated photolytic half-lives of PBDEs were similar to those observed in isoctane on the roof (Table 1). Our results show that the model reproduced reliably the observed decomposition rates and that the natural absorbing components affected little the photolytic half-lives in the optically thin layer at the surface.

In order to estimate how the photolysis of PBDEs attenuated with depth, we determined the median wavelength accounting for photolysis ($\lambda_{50\%}$) from the overlap between a solar spectrum and the absorption spectra of PBDEs (Figure 1). The $\lambda_{50\%}$ s were 325 nm, 310 nm and 305 nm for #209, #99 and #47, respectively. The vertical attenuation of solar radiation at $\lambda_{50\%}$ into the water column describes the attenuation of photolysis. The vertical attenuation coefficient for the irradiance at 320 nm was 10 m^{-1} and 0.12 m^{-1} in the Baltic Sea and in the Atlantic Ocean, respectively. The irradiation of 320 nm and thus photolysis takes place >90 % above the depth of 0.46 m in the Baltic Sea and 38 m in the Atlantic Ocean. The depth of photolytic stratum was similar to that of the mixing stratum (40 m) in the Atlantic Ocean, but in the Baltic Sea the depth of photolytic stratum consisted of < 5% that of the mixing stratum, which is typically 10 m in the offshore Baltic Sea.

As long as PBDE stay in the mixing stratum they will expose, at least periodically, to the photolytic solar radiation. We selected to calculate the half-lives of PBDEs in the mixing stratum as the best estimate for their photolytic half life in the offshore environment. In these model calculations, we assumed that the surface solar radiation will absorb completely into the water column and that only the photons absorbed by PBDEs will mediate photolysis. The photolytic half-lives of PBDEs were about 3-6 times longer in the mixing stratum of Atlantic Ocean (40 m) than what was observed at the surface. In the Atlantic Ocean, where the depth of photolytic stratum roughly equalled that of the mixing stratum, the photon competition between PBDEs and the natural absorbing components resulted in longer half-lives in the mixing stratum than at the surface. In the mixing stratum of Baltic Sea (10 m), the photolytic half-lives were about 10 times longer than in the Atlantic Ocean. In coastal waters, such as the Baltic Sea, high concentration of natural absorbing components results in a shallow photolytic stratum and in the severe photon competition between PBDEs and the natural absorbing components.

Table 1. Observed (O) and modelled (M) half-lives (days) at the surface and in the mixing stratum of the Baltic Sea and the Atlantic Ocean.

PBDE	Surface		Mixing stratum	
	I-octane (O)	Baltic Sea (M)	Baltic Sea (M)	Atlantic Ocean (M)
#47	8.5	8.4	587	46
#99	1.4	1.4	71	5,5
#209	0.03	0.02	1.2	0.09

Our photolytic half-lives of PBDEs at the surface agree with those determined earlier in the laboratory studies⁶. The surface half-lives overestimate, up to 70-fold, the photolytic half-lives in the mixing stratum, which are the most relevant for estimating the environmental fate of PBDEs in the offshore waters. Our study shows that the natural absorbing components and the depth of mixing stratum affect greatly the photolytic half live in surface waters, and those need to be accounted for the photolytic fate estimates of PBDEs.

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