# Decomposition of PBDEs by Direct Photolysis in Marine Surface Waters

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## Indroduction.

Large quantities of brominated flame retardants (BFR) are produced and used in every day consumer products (D'silva et al. 2004 and Hites 2004). Polybrominated biphenyl ethers (PBDE) are most commonly used BFRs. The function of the PBDEs is to prevent ignition or slow burning and this way save human lives and reduce economical loss. Unfortunately PBDEs have spread ubiquitously in environment, where they can accumulate in biota, with endocrinic and neurotoxic effects (Stoker et al. 2003 and Eriksson et al. 2002).

According to the laboratory experiments, PBDEs decompose photochemically, but their photolytic half-lives in environment are poorly known (da Rosa et al. 2003, Söderström et al. 2004 and Eriksson et al. 2004). The objective of this study was to assess the direct decomposition rates of PBDEs in coastal (Baltic Sea) and oceanic surface waters (North Atlantic).

## Materials and Methods.

Apparent quantum yield for photolysis:

The congeners (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), 250 µg $l^{-1}$ in isooctane) were separately enclosed without headspace into custom-made quartz (length of 32 mm and outer diameter 12 mm, Laborexin glass blowery, Finland) or regular glass GC-autosampler vials cleaned by solvent and combustion (600°C 2 h). The quartz vials were exposed to solar radiation together with glass vials wrapped into aluminium foil (dark controls) in an unshaded outdoor pool on a roof (Helsinki, Finland, 51 m above sea level, 60.20° N 24.96° E). The 5-6 cm deep pool was made from matte black tarpaulin and flushed with tap water (20-23 °C). The exposures lasted 60 min (#209, October 5 2:35 pm to 3:35 pm), 4 days (#99; June 13 1:00 pm to June 17 1:00 pm) and 12 days (#47; July 7 2:19 pm to July 19 2:19 pm). During the experiments global radiation (W $m^{-2}$) was measured at one-minute intervals with a pyranometer located next (20 m) to the exposure pool. The concentration of the congeners in the test vials was determined 4-5 times with a GC-EI-MS during the experiments. As no decomposition was found in the dark controls, the photolytically decomposed PBDE ($\Delta C_{PBDE}$; mol $l^{-1}$) was calculated as the difference in the concentration of solar radiation exposed congener between time $T$ and $T$+1 (= $C_{PBDE,T} - C_{PBDE,T+1}$).

The solar irradiances incident to the surface of exposure pool were determined according to the measured global radiation and radiative transfer calculations. Apparent quantum yields for the direct photolytic decomposition of congeners ($\phi_{PBDE}$) were calculated according to:

$$\phi_{PBDE} = \Delta_{PBDE}\, Q_a^{-1} \qquad (1)$$

where $\Delta_{PBDE}$ is the photolytically decomposed parent congener in the quartz vials ($\Delta_{PBDE} = \Delta C_{PBDE}$; mol decomposed PBDE exposure period$^{-1}$) and $Q_a$ is the dose of photons absorbed by the congener during the exposure to solar radiation ($Q_a$; mol photons exposure period$^{-1}$).

Optical model:

Photolytic seasonal half lives of PBDEs (30-40 pg l-1, Oros et al. 2005) in the Baltic Sea and north Atlantic Ocean were calculated according to 1) modeled solar irradiances 2) depth of mixing layer 3) optical conditions and 4) measured $\phi_{PBDE}$ (Vähätalo et al. 2004).

**Results and Discussion.**

The concentration of the PBDE-congeners decreased according to first order kinetics when exposed to solar radiation. #209 decomposed 50-300 times faster than #99 and #47, as it absorbs more solar ultraviolet radiation than lower brominated congeners. The calculated $\Phi_{PBDE}$ were 0.28±0.04 for #209, 0.16±0.02 for #99 and 0.22±0.05 for #47 (mean ± SD, n = 3-4). ) Our $\phi_{\#209}$ is similar to that found earlier in tetrahydrofuran (THF; 0.29 in Eriksson et al. 2004) but larger than found in hexane (0.47 in Bezarres-Cruz et al. 2004). The earlier $\phi_{\#47}$s determined in THF and under artificial irradiance (0.63 in Eriksson et al 2004) is larger than our $\phi_{\#47}$ determined under natural solar radiation and in isooctane. The differences in $\phi_{PBDE}$s among the studies may be related to the used irradiance sources and solvents.

The determined $\phi_{PBDE}$s were applied to together with typical summer solar radiation at 60°N and the absorption coefficient of PBDEs ($a_{PBDE,\lambda}$) at the concentrations found in anthropogenically affected coastal ocean (30-40 pg l$^{-1}$; Oros et al. 2005) to calculate the photolytic summertime half lives for the studied congeners at the surface of ocean (depth of 0 m). The calculated half-lives ranged from 0.02 d (#209) to 8.4 d (#47) and agreed with those observed during exposures (Table 1).The calculated photolytic half lives were 4-100 times longer in the mixing layer of Baltic Sea and North Atlantic Ocean than at the depth of 0 m of Baltic Sea (Table 1). In the mixing layer, the photolytic rate was reduced, because of natural absorbing components (chromophoric dissolved organic carbon and particles) competed with PBDEs for the absorption of photolytic photons and the photolytic layer covered only a portion (down to 5 %) of the mixing layer.

Table 1. Observed (O) and modelled (M) half-lives (days) at the surface and in the mixing layer of the Baltic Sea and the Atlantic Ocean in the concentration 3-4 pg/l and 30-40 pg/l of PBDEs in the mixing layer .

| | **Surface** | | **Mixing stratum (3-4 pg/l)** | | **Mixing stratum (30-40 pg/l)** | |
|---|---|---|---|---|---|---|
| PBDE | I-octane (O) | Baltic Sea (M) | Baltic Sea (M) | Atlantic Ocean (M) | Baltic Sea (M) | Atlantic Ocean (M) |
| #47 | 8.5 | 8.4 | 526 | 115 | 526 | 115 |
| #99 | 1.4 | 1.4 | 121 | 27 | 121 | 27 |
| #209 | 0.03 | 0.02 | 1.8 | 0.4 | 1.8 | 0.4 |

We calculated photolytic half-lives also in the North Atlantic Ocean along 30°W meridian through latitudes 0-60°N accounting for the variability in the environmental conditions during four seasons. These results indicate high potential for the photolysis of PBDEs in the mixing layer of tropical oceans and for #209 in all latitudes and seasons. In mid and high latitudes (40-60°N), the photolytic half lives varied among seasons up to 200-fold and had the longest half lives during winter. In 60°N outside summer, the photolytic half lives of #47 and #99 were longer than the length of seasons. These results indicate that solar radiation-induced direct photochemical reactions decompose deposited #47 and #99 very ineffectively from the mixed layer of ocean at high latitudes. The surface half-lives overestimate the photolytic half-lives in the mixing layer, which are the most relevant for estimating the environmental fate of PBDEs in the offshore waters. Our study shows that the natural absorbing components, solar radiation and the depth of mixing layer affect greatly the photolytic half live in surface waters, and those need to be accounted for the photolytic fate estimates of PBDEs. Although solar radiation can effectively decompose #209, our results indicate that direct photolysis decomposes ineffectively lower brominated PBDEs (such as the #47 and #99) with the largest bioaccumalative properties and potential for long-range atmospheric transport into high latitude ocean (Gouin et al 2003). If solar photolysis cannot decompose the lower brominated PBDEs in the 30-180 m deep mixing layer of North Atlantic Ocean, those PBDEs have high potential for bioaccumulation in the mixing layer. Our results about the ineffective photolytic decomposition of low brominated PBDEs are in good agreement with the dominance of these congeners in high latitude marine environments (Soermo et al. 2006)

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