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# Direct Photolysis of Polybrominated Diphenyl Ethers in Surface Waters

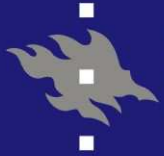
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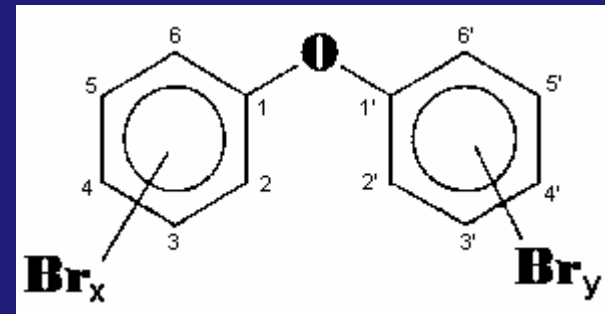
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# Introduction

- Polybrominated diphenyl ethers (PBDE) are additives in plastics (e.g. electric housing, upholstery textiles, mobile phones etc.)
- Annual global PBDE-production is 67 000 t
- PBDEs are used to prevent or minimize fire damage





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## Introduction

- PBDEs are ubiquitous in the environment and they have endocrinic and neurotoxic effects in mammals
- PBDE resist microbial decomposition in the presence of oxygen, but can decompose through microbial reductive dehalogenation in anaerobic environment
- Photolysis can debrominate PBDEs





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## Objectives

- Study the direct photolysis of dissolved PBDEs
- Calculate the direct photolytic half-lives of PBDEs in the Baltic Sea and North Atlantic
- Calculate seasonal latitudinal half-lives of PBDEs in North Atlantic





## Photolytical Experiments

- For the photolytical experiments, the PBDEs, 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),  
in isooctane were introduced into custom made quartz GC-autosampler vials. The vials were placed into a pool on the roof at Helsinki, Finland (60°20'N 24°97' E)
- PBDEs were analysed during the experiments with an GC-EI-MS (Agilent model 6890/5973)



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# Photolytical Experiments

## GC parameters for #209

GC column, 7-5 m long DB-5MS (id. 0.25 mm and 0.1  $\mu\text{m}$  film), 3-1 m long retention gap (id. 0,53 mm) gas flow: 1,8 ml/min, oven: 90-320  $^{\circ}\text{C}$  (25  $^{\circ}\text{C}/\text{min}$ ), injection: On-column, inject ion volume 1  $\mu\text{l}$ , GC-MS interphase: 320  $^{\circ}\text{C}$

## GC Parameters for #47 and #99

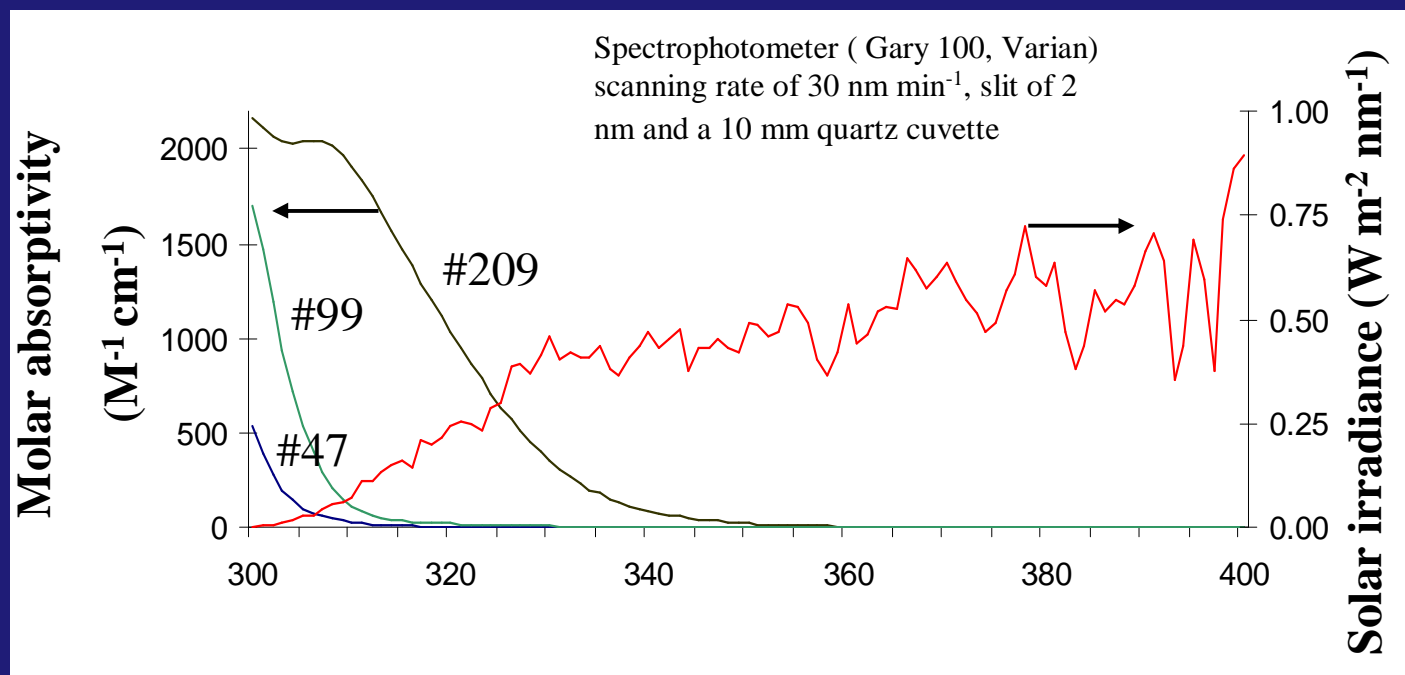
GC column 14 m long HP-5MS (id. 0.18 mm and 0.18  $\mu\text{m}$  film) and 3-5 m long retention gap (id. 0,53 mm), gas flow: 0,9 ml/min (constant flow), oven: 50-300  $^{\circ}\text{C}$  (25  $^{\circ}\text{C}/\text{min}$ )

## MS parameters

solvent delay: 2 min, quadrupole temperature 200  $^{\circ}\text{C}$ , ion source temperature 250  $^{\circ}\text{C}$ , electron energy 70 eV, SIM: 325 .9 m/z for #47, 403.8 m/z for #99 and 399.7 m/z #209



# Photolytical Experiments

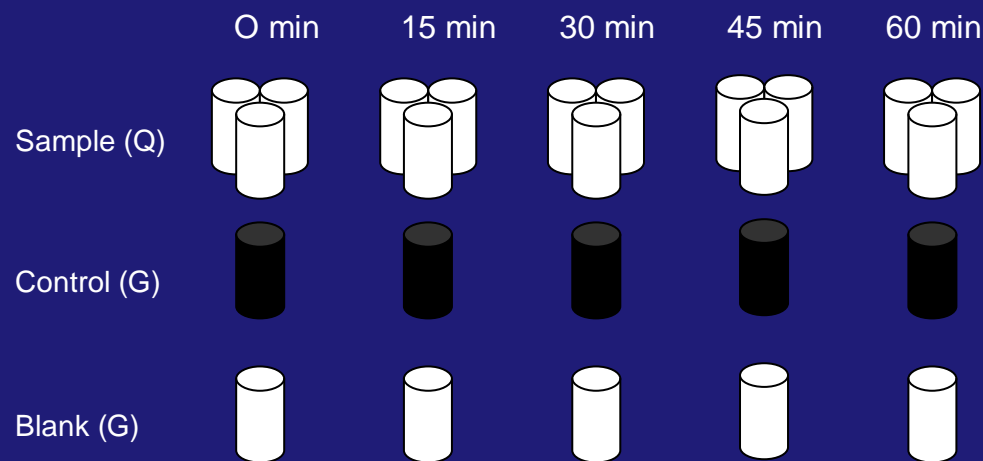


The specific absorptivities of PBDEs in isooctane (50  $\mu\text{g ml}^{-1}$ ) and mean solar irradiances in Helsinki on July 7. 2005.



# Photolytical Experiments

- Three samples, dark control (wrapped in aluminium foil) and Isooctane (blank) for each of the time point
- Initial concentration was 250 pg/ $\mu$ l (isooctane)
- Experiment Setup for #209:



(Q) Quartz, (G) Glass



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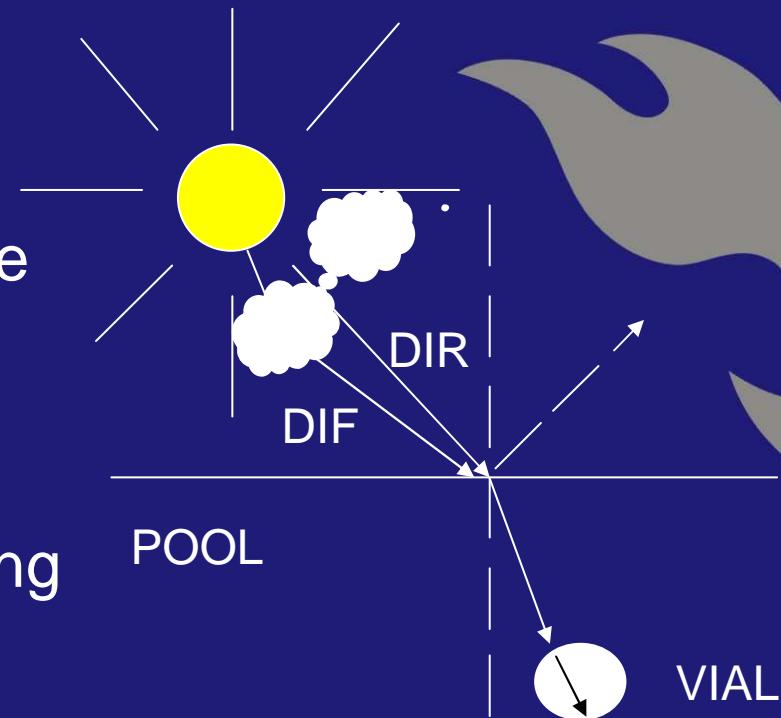
# Photolytic Experiments





# Optical Model

- Solar radiation (direct+diffuse) incident to the pool, was calculated using radiative transfer code (Disort 2, libRadtran), FMI
- Number of photons absorbed by the PBDEs in the pool was calculated using Matlab (v. 6.5)\*



\* Vähätalo, A. V.; Salkinoja-Salonen, M.; Taalas, P.; Salonen, K. Spectrum of the quantum yield for photochemical mineralization of dissolved organic carbon in a humic lake. *Limnol.Oceanogr.* 2000, 45, 664-676.



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# Optical Model, Quantum Yield

Photolytic decomposition rates of the congeners were related to the number of absorbed photons ( $Q_a$ ) to determine apparent quantum yields ( $\phi$ )

$$\phi_{\text{PBDE}} = \Delta \text{PBDE } Q_a^{-1}$$



# Optical Model

Decomposition of PBDEs at the surface ( $\text{mol m}^{-3} \text{d}^{-1}$ )

$$\Delta PBDE_z = \int_{\lambda_{min}}^{\lambda_{max}} Q_{Z,\lambda,S} a_{PBDE,\lambda} \phi_{PBDE} d\lambda$$

$Q_{z,\lambda,s}$  = scalar photon flux density at the depth of  $z$

and wavelength  $\lambda$  ( $\text{mol photons m}^{-2} \text{d}^{-1} \text{nm}^{-1}$ )

$a_{PBDE,\lambda}$  = absorption of the PBDE ( $\text{m}^{-1} \text{nm}^{-1}$ )

$\phi_{PBDE}$  = quantum yield ( $\text{mol PBDE} / \text{mol absorbed photons}^{-1}$ )

$\lambda = 300\text{-}400 \text{ nm}$



# Optical Model

Decomposition of PBDEs in the mixing stratum (mol  
 $\text{m}^{-2} \text{d}^{-1}$ )

$$\Delta PBDE = \int_{\lambda \min}^{\lambda \max} Q_{abs, \lambda} \left( \frac{a_{PBDE, \lambda}}{a_{tot, \lambda}} \right) \phi_{PBDE} d\lambda$$

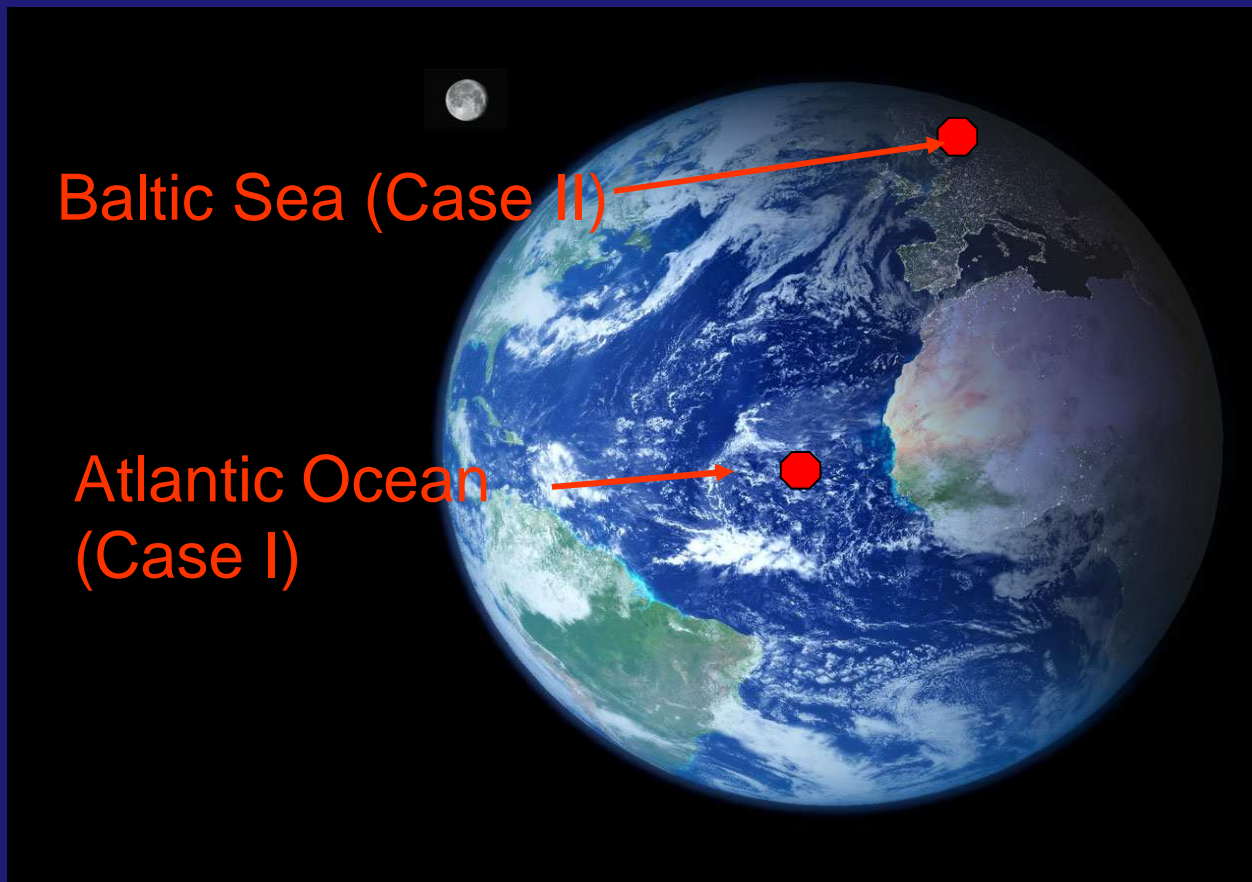
$Q_{abs, \lambda}$  = Photon flux density of photons absorbed  
by the photolytic column of water ( $\text{mol photons m}^{-2} \text{d}^{-1}$ )

$a_{tot, \lambda}$  = total absorption of the water column ( $\text{m}^{-1} \text{nm}^{-1}$ )



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# Optical Model, Case I vs Case II



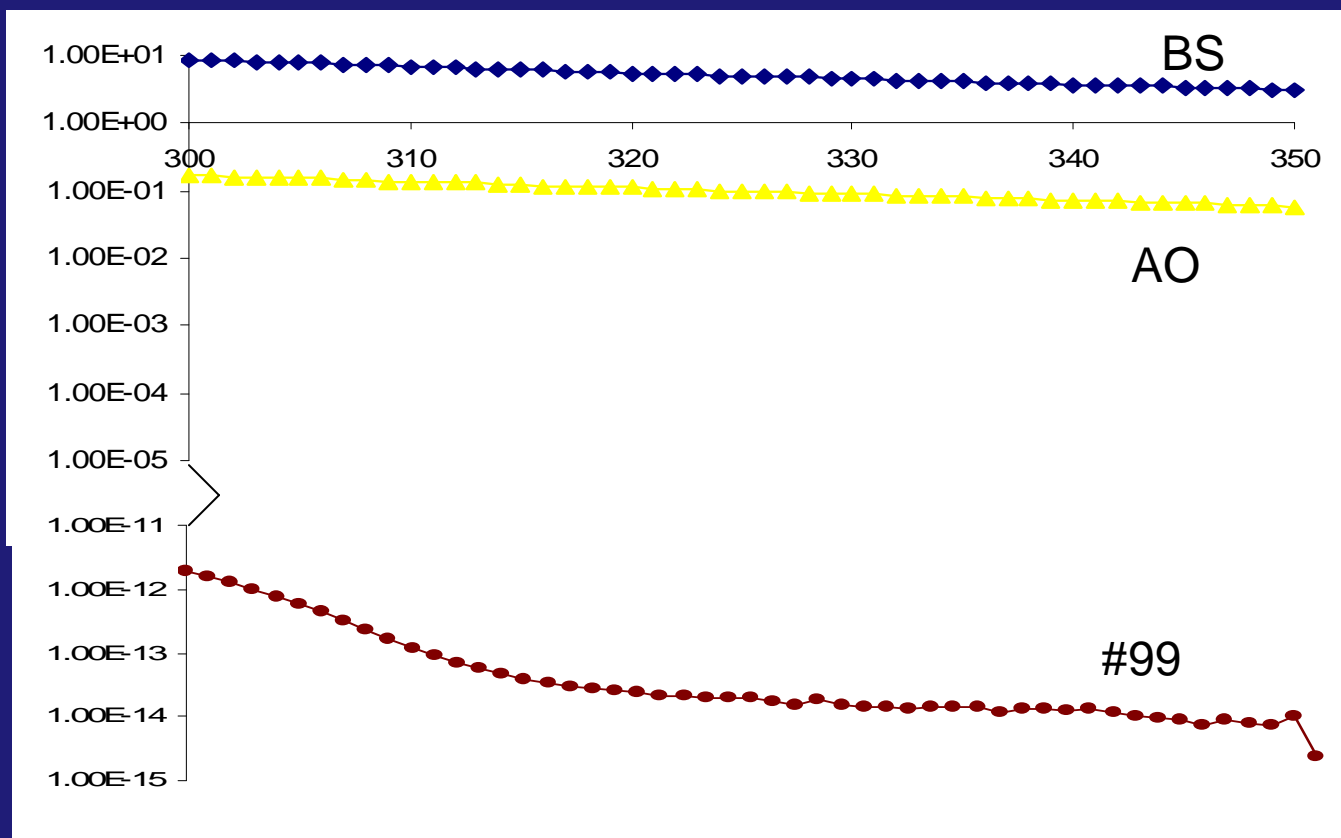


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# Optical Model, Case I vs Case II

Wavelength (nm)

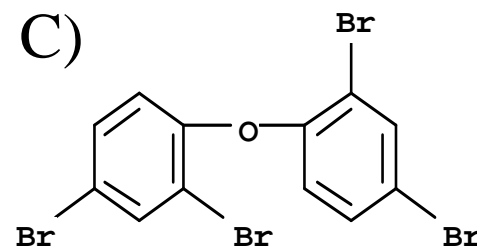
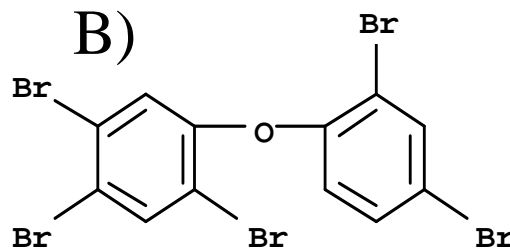
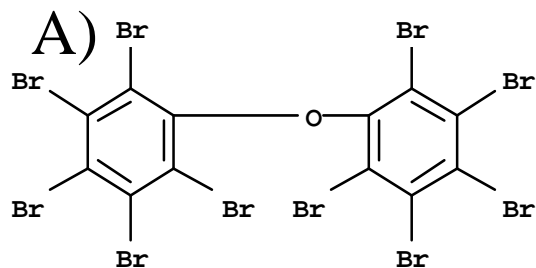
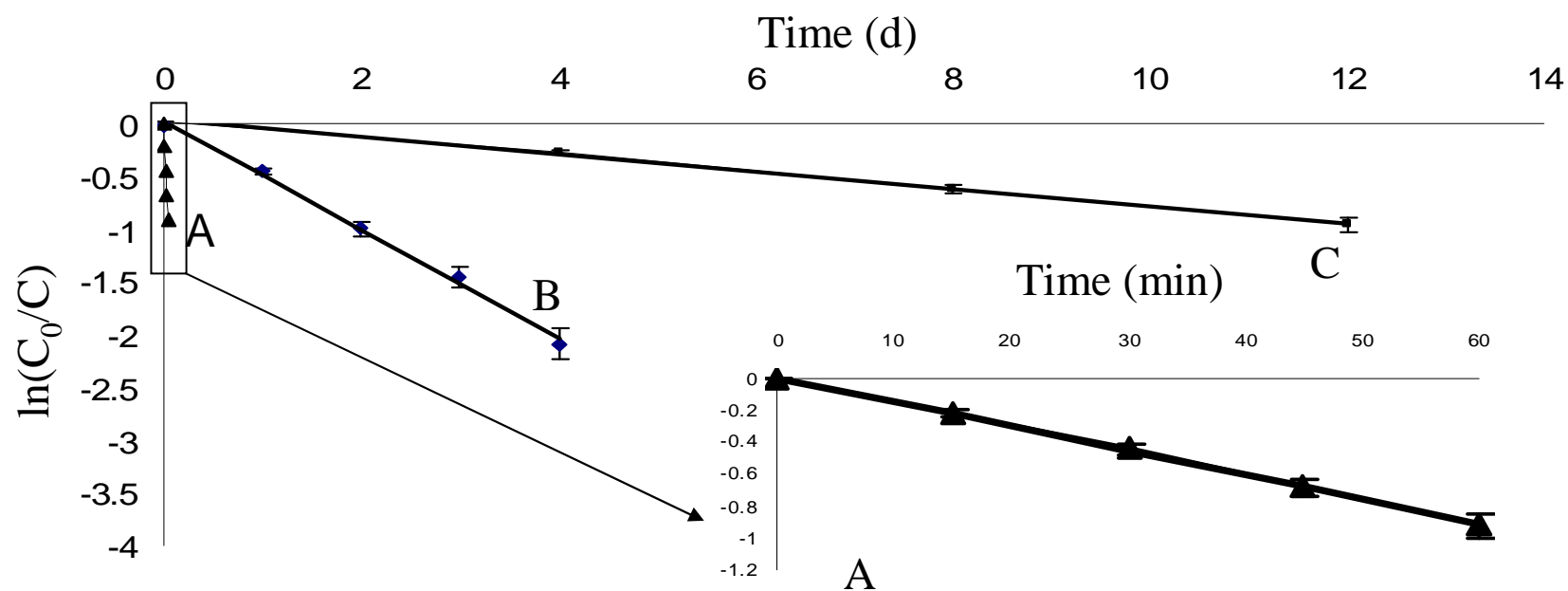
Total Absorption coefficient  
( $m^{-1}$ )



Total Absorption of the Baltic Sea (AO), Atlantic Ocean (AO, 23°N 30°W), and #99 (concentration of 30  $\mu g/l$ ).



# Results, Decomposition of PBDEs





## Results, Quantum Yield

PBDE	Q <sub>s</sub> (isooctane)	Q <sub>s</sub> (THF)*	Q <sub>s</sub> (THF)**
#209	0.28 ± 0.04	0.38 ± 0.10	0.29
#99	0.16 ± 0.02	-	-
#47	0.22 ± 0.05	0.56 ± 0.16	0.63

\* = Palm, W.-U.; Sossinka, W.; Ruck, W.; Zetzsch, C. *Environ. Toxicol. Chem.* 2004.

\*\* = Eriksson, J., Green, N., Marsh, G., Bergman, Å., *Environ. Sci Technol.*, 2004

THF = Tetrahydrofuran



## Results, half-lives (d) Case I vs Case II

PBDE	Surface		Mixing layer (3-4 pg l <sup>-1</sup> )	
	Isooctane (O)	Baltic Sea (M)	Baltic Sea (M)	Atlantic Ocean (M)
#47	8.5	8.4	526	115
#99	1.4	1.4	121	27
#209	0.03	0.02	1.8	0.4

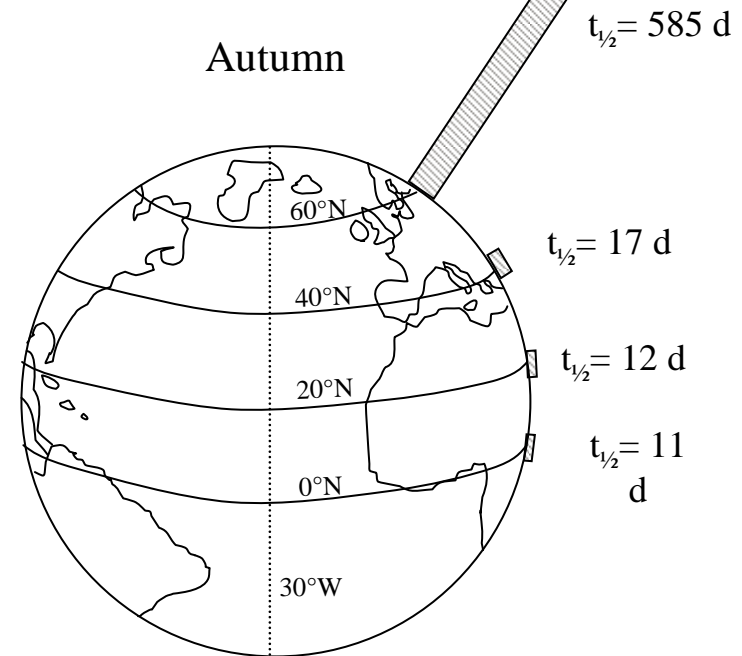
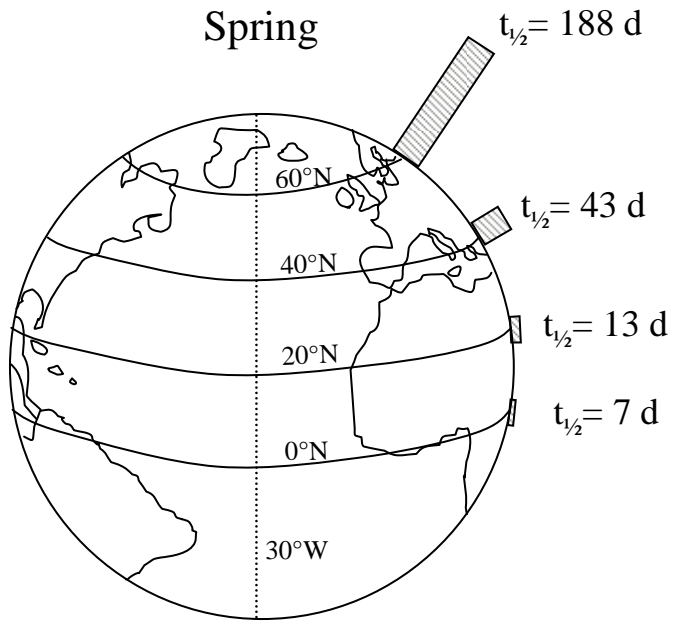
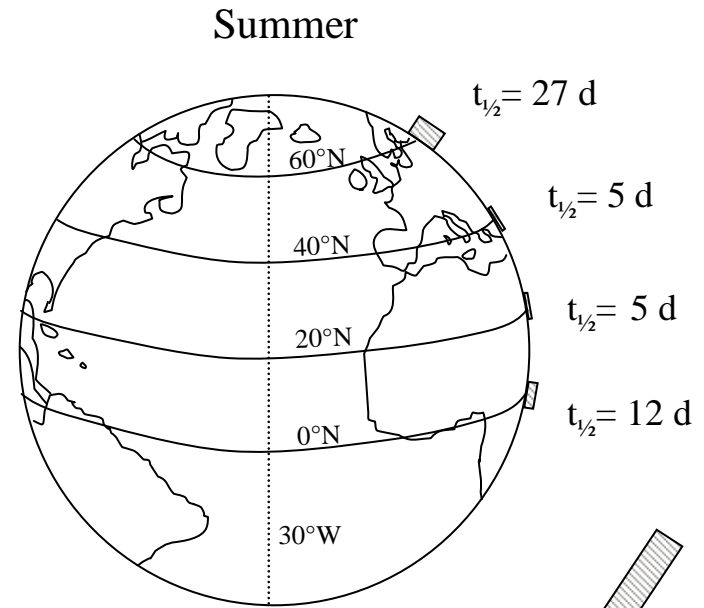
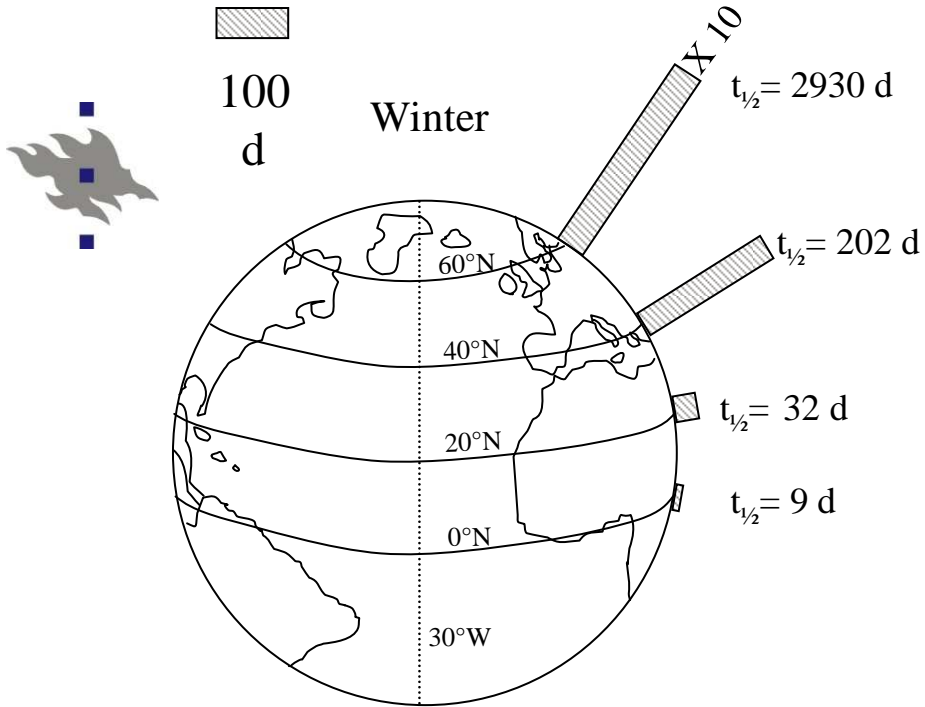
O = Observed ja M = Modeled



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# Results, Seasonal half-lives in North Atlantic

- Seasonal half-lives (latitudes 0,20,40,60 °N) of PBDEs were calculated using:
  - Seasonal changes in solar radiation
  - Seasonal changes in mixing layer depth
  - Seasonal changes in natural absorbing component (CDOM and particles) concentrations





## Conclusions

- The surface half-lives overestimate the photolytic half-lives in the mixing stratum, which is the most relevant for estimating the environmental fate of the PBDEs.
- Study shows that the natural absorbing components and the depth of mixing stratum affect greatly the photolytic half-life of PBDEs in the surface waters





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## Acknowledgements

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