STUDY OF THE SUNLIGHT PHOTODECOMPOSITION OF FIVE PBDEs BY PHOTO-SPME

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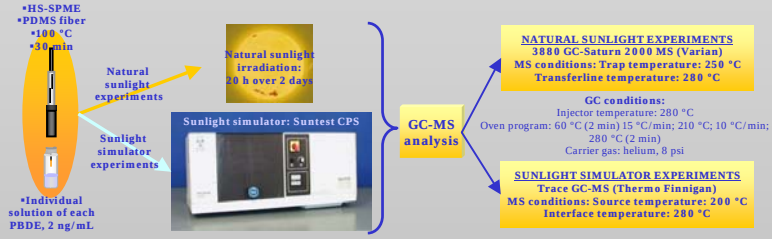
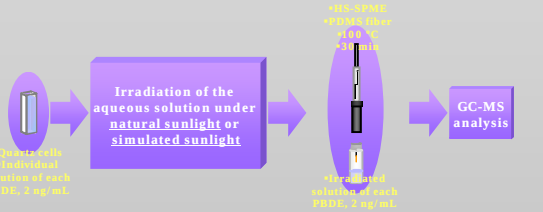
INTRODUCTION

- Sunlight photolysis is one of the most important potential abiotic degradation pathways for polybrominated diphenyl ethers (PBDEs) [1].
- Previous work of our research group using the photo solid phase microextraction approach (photo-SPME) [2, 3] have contributed to extend the knowledge about the kinetics and the identities of the photoproducts produced during UV photochemical decomposition of these compounds.
- In photo-SPME, the SPME fiber is employed as a support for photochemical studies. First the target analytes are extracted by SPME, and then the fiber is exposed to the radiation for the required time. Thus, the sunlight photolytical behaviour of five PBDEs (BDE 47, BDE 100, BDE 99, BDE 154 and BDE 153) has been studied.
- Aqueous photodegradation studies have also been carried out. In this case, SPME is only used as extraction procedure.
- Up to now, photo-SPME studies had been carried out using UV irradiation at 254 nm [4, 5]. In the present study, the photo-SPME approach is combined for first time with both natural sunlight irradiation and from a solar simulator (Suntest CPS, Atlas).

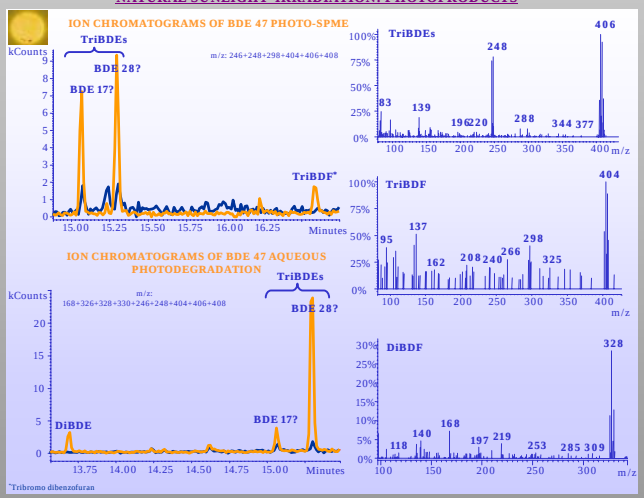
EXPERIMENTAL PHOTO-SPME PROCEDURE



EXPERIMENTAL AQUEOUS PHOTODEGRADATION PROCEDURE



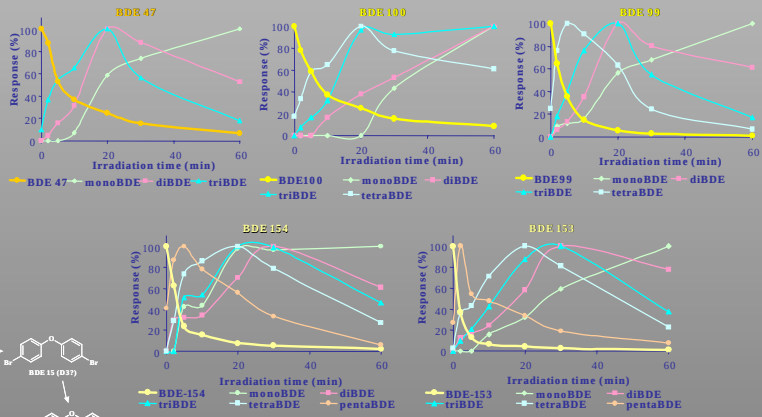
NATURAL SUNLIGHT IRRADIATION: PHOTOPRODUCTS



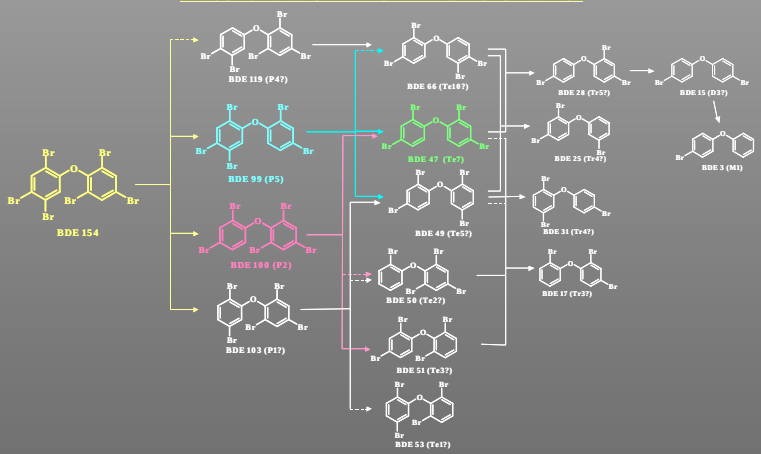
KINETIC PARAMETERS IN THE SOLAR SIMULATED EXPERIMENTS: PHOTO-SPME vs AQUEOUS PHOTODEGRADATION

	Photo-SPME		Aqueous photodegradation	
	k (min^{-1})	$t_{1/2}$	k (min^{-1})	$t_{1/2}$
BDE 47	0.103	6.72	0.167	4.16
BDE 100	0.096	7.19	0.150	4.62
BDE 99	0.187	3.71	0.317	2.18
BDE 154	0.189	3.67	0.288	2.41
BDE 153	0.401	1.73	0.334	2.07

PHOTOFORMATION AND DEGRADATION OF PBDEs OF DIFFERENT BROMINATION DEGREES BY PHOTO-SPME



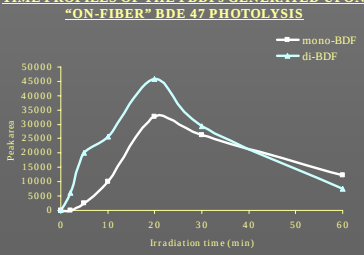
REDUCTIVE DEBROMINATION PATHWAYS FOR BDE 154



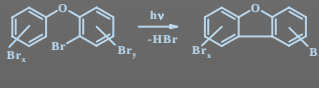
BDEs SIMULATED SUNLIGHT IRRADIATION PRODUCTS OBTAINED IN THE PHOTO-SPME EXPERIMENTS

Congeners	Key	Proposed identification	RT (min)	RT range (min)	Identification ions	Source
monoBDE	M1	BDE 3	12.07	12.07	248+250	All studied BDEs
diBDE	D1	BDE 8	14.02	14.02-14.32	168 326+328+330	BDE47,BDE100,BDE99,BDE153
	D2	BDE 13	14.15			BDE99,BDE153
	D3	BDE15	14.32			All studied BDEs
triBDE	Tr1	BDE 18	15.45	15.45-16.42	246+248 404+406+408	BDE99
	Tr2	BDE 32	15.57			BDE100,BDE153
	Tr3	BDE 17	15.75			All studied BDEs
	Tr4	BDE 25 or BDE 31	15.82			BDE99,BDE154,BDE153
	Tr5	BDE 28	16.02			All studied BDEs
	Tr6	BDE 37	16.42			BDE99,BDE153
tetraBDEs	Te1	BDE 53	17.13	17.13-18.48	324+326+328 484+486+488	BDE154
	Te2	BDE 50	17.20			BDE100,BDE154
	Te3	BDE 51	17.55			BDE100,BDE154
	Te4	BDE 75	17.60			BDE100
	Te5	BDE 49	17.72			BDE99,BDE154,BDE153
	Te6	BDE 48	17.77			BDE99,BDE153
	Te7	BDE 47	18.10			BDE100,BDE99,BDE154,BDE153
	Te8	BDE 52 or BDE 70	18.20			BDE153
	Te9	BDE 74	18.28			BDE99,BDE153
	Te10	BDE 66	18.48			BDE99,BDE154,BDE153
pentaBDEs	P1	BDE 103	19.22	19.22-21.23	404+406+408 562+564+566	BDE154
	P2	BDE 100	19.97			BDE154
	P3	BDE 101	20.13			BDE153
	P4	BDE 119	20.23			BDE154
	P5	BDE 99	20.62			BDE154,BDE153
	P6	BDE 118	21.23			BDE153

TIME PROFILES OF THE PBDFs GENERATED UPON "ON-FIBER" BDE 47 PHOTOLYSIS



FORMATION PATHWAYS OF PBDFs FROM PBDE DURING SUNLIGHT DEGRADATION



CONCLUSIONS

The photo-SPME technique can be successfully combined with sunlight irradiation, either natural or artificial. The photochemical behaviour in the fiber mimics the processes that happen in water also under sun irradiation (verified here for PBDEs as a case study). The results obtained under simulated sunlight match with the results obtained in the previous work under UV radiation. Photodegradation pathways for the five BDEs under consideration are for first time proposed for simulated sunlight irradiation. Reductive debromination is the main pathway. PBDFs have been formed under both natural and sola simulated irradiation.

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