Investigation of photodegradation products generated after UV-irradiation of five polybrominated diphenyl ethers using photo solid-phase microextraction

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Abstract

In this study, the photoinduced degradation of five polybrominated diphenyl ethers (PBDEs), BDE-47, BDE-100, BDE-99, BDE-154 and BDE-153, is studied using solid-phase microextraction polydimethylsiloxane fibers as photolytic support. PBDEs are extracted from aqueous solutions using SPME fibers that are subsequently exposed to UV irradiation for different times (from 2 to 60 min). Photodegradation kinetics of the five PBDEs, tentative identification and photochemical behavior of the generated photoproducts, as well as photodegradation pathways, have been studied employing this on-fiber approach technique (photo-SPME) followed by gas chromatography–mass spectrometry analysis. Aqueous photodegradation studies have also been performed and compared with photo-SPME. All the photoproducts detected in the aqueous experiments were previously found in the photo-SPME experiments. In this study, reductive debromination by successive losses of bromine atoms is confirmed as the main photodegradation pathway of PBDEs. A large number of PBDEs were obtained as photoproducts of the five target analytes. Other mechanism of photodegradation observed was intramolecular cyclization from the homolytic dissociation of the C−Br bond; thus, polybromo-dibenzofurans were generated. This work contributes to the study of the photodegradation of PBDEs and shows the potential of photo-SPME to evaluate the photo-transformation of organic pollutants.
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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of compounds widely used as flame retardant additives. The environmental concerns about these substances have risen in the last years and they are now considered as emerging environmental pollutants [1–3]. Three major commercial formulations of PBDEs are produced: deca-BDE, octa-BDE and penta-BDE. In general the lower brominated mixtures are more toxic than the higher brominated ones. The toxicological concerns about exposure to low environmental concentrations of PBDEs focus on their potential to act as hormone disruptors, neurodevelopmental toxics, and, in some cases, carcinogenic agents. In addition, the combustion of these compounds could generate highly toxic products, such as polybrominated dibenzofurans and polybrominated dibenzo-*p*-dioxins [3–6].

Therefore, it is of great concern to understand the degradation of PBDEs in the environment. Deca-BDE and other highly brominated PBDEs are rapidly debrominated in the environment to less brominated PBDEs as recent studies indicate [7,8]. Biodegradation might not be significant while

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photodegradation appears to be one of the main causes of degradation.

Several authors have investigated the photolytic lability of individual congeners, mainly of decabromo-diphenyl ether, and found that when PBDEs are dissolved in organic solvents, debromination occurs in the presence of UV light [9–12]. Ohta et al. [9] studied the photochemical behavior of deca-BDE in organic and water-like solvent (a mixture of toluene–ethanol–water, 1:3:6) under UV light and sunlight. They observed a rapid photodecomposition of deca-BDE in toluene under UV-light and they confirmed the debromination as the photochemical pattern of the studied compound. Söderström et al. [10] also studied the photodegradation of deca-BDE in different matrices (toluene, silica gel, sand, soil and sediment) under UV-light and outdoor sunlight, showing the same conclusions that Ohta et al. [9], but they identified the presence of polybrominated dibenzofurans (PBDFs) in some of the analyzed samples. Photodegradation studies have rarely been performed on other PBDE congeners than BDE-209. Recently, however, Peterman et al. [13] briefly reported on sunlight photolysis of a mixture of 39 PBDEs in triolein. Also, in a very recent study Eriksson et al. [12] examined the UV-light degradation rate of individual PBDE congeners in methanol, tetrahydrofuran and methanol–water mixtures. They observed that the rate of photodecomposition of PBDEs seems to be dependent on the degree of bromination; the lower brominated congeners degrade slowly, whereas the octa- and deca-BDE congeners decompose rapidly. In addition, they studied the decomposition products of BDE-209. Several nona-, octa-, hepta- and hexa-BDEs were identified, whereas, the generated compounds with less than six bromine atoms were tentatively identified as PBDFs.

The aim of this work is to contribute to the study of the photodegradation of PBDEs, employing a new, simple and fast methodology called photo solid-phase microextraction (photo-SPME). In this study, the compounds included—BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154—are the most abundant congeners in penta-BDE commercial formulations which are considered as the most toxic ones [14]. In addition, three of these compounds—BDE-47, BDE-99 and BDE-100—are the PBDE congeners most commonly found in environmental samples. SPME is a suitable technique for the extraction of persistent organic pollutants that has been recently applied to the determination of PBDEs [15]. The possibility of performing photochemical studies in SPME fibers has been demonstrated [16–21]. In this technique, after the extraction of the target compounds, the fiber is exposed to light for a selected period of time. Finally analyses are performed by gas chromatography–mass spectrometry (GC–MS).

Photo-SPME presents the well-known advantages of SPME and permits to simplify the classical way to carry out photochemical studies. Moreover, as the photoproducts are generated "in situ" in the fiber coating, they are directly analyzed, so sample manipulation and possible losses of photoproducts are minimized. Thus, photodegradation kinetics of

the five studied PBDEs, photodegradation pathways, identity and photochemical behavior of generated photoproducts have been determined by photo-SPME. Among the generated photoproducts, various polybromo-dibenzofurans have been found.

In this work, SPME was also used to extract photoproducts in direct photodegradation of aqueous solutions containing PBDEs, through experiments conducted in the classical way (extraction after irradiation), in order to compare photo-SPME and aqueous photodegradation. Close photodegradation behavior was observed in both cases and the generation of the same photoproducts was confirmed.

2. Experimental

2.1. Reagents and materials

2,2′,4,4′-Tetrabromo-diphenyl ether (BDE-47); 2,2′,4,-4′,5-pentabromo-diphenyl ether (BDE-99), 2,2′,4,4′,6-pentabromo-diphenyl ether (BDE-100), 2,2′,4,4′,5,5′-hexabromo-diphenyl ether (BDE-153) and 2,2′,4,4′,5,6′-hexabromo-diphenyl ether (BDE-154) at 50 μg/mL in nonane were supplied by Wellington Labs. (Techno Spec, Barcelona, Spain). Water solutions of each PBDE (2 ng/mL) were prepared by the addition of an intermediate acetone solution of 2 μg/mL. All solvents used (analytical grade) were purchased from Merck (Mollet del Vallés, Barcelona, Spain).

2.2. GC–MS analysis

Analysis were performed using a Varian 3800 gas chromatograph (Varian Chromatography Systems, Walnut Creek, CA, USA) equipped with a 1079 split/splitless injector and a Saturn 2000 ion trap mass spectrometer (Varian Chromatography Systems). The system was operated by Saturn GC–MS WorkStation v5.4 software. Experimental parameters were as follows: column HP-5MS, 30 m × 0.25 mm i.d., 0.25 μm film; temperature program: 60 °C, hold 2 min, rate 15 °C/min to 250 °C, rate 5 °C/min to a final temperature of 280 °C, hold for 8 min. Helium was employed as carrier gas, with a constant flow of 1.2 mL/min. Injector was programmed to return to the split mode after 2 min from the beginning of a run. Injector, trap, manifold and transfer line temperatures were 280, 250, 120 and 280 °C, respectively. The mass spectrometer was used in the positive electron ionization mode at 70 eV with automatic gain control. A range of m/z 100–650 was scanned at a scan rate of 1 s/scan. Multiplier was set at a nominal value of 1850 V.

2.3. Solid-phase microextraction and photodegradation procedures

A headspace solid-phase microextraction (HS-SPME) sampling procedure for PBDEs was taken from that

previously described by Polo et al. [15]. This procedure is, in general, characterized by a relative standard deviation (R.S.D.) minor than 12%. In brief, 10-mL of a water sample are placed in a 22-mL vial, and heated for 5 min at 100 °C in a thermostatized bath. The fiber, 100 μm polydimethylsiloxane (PDMS) (Supelco), is then exposed to the headspace above the sample for 30 min and finally desorbed in the GC injection port for 3 min.

A laboratory photoreactor model was used for photolysis experiments; this photoreactor is equipped with two low-pressure mercury lamps (8–10 W). In the experiments performed with 18 W power, both lamps are switched on, whereas in 8 W experiments, only the lamp with 8 W power is used. In photo-SPME experiments, after the extraction, the SPME fiber with the analyte already absorbed is irradiated for the selected time.

In the aqueous photodegradation experiments, aliquots of solutions containing each PBDE are placed in synthetic quartz precision cells and submitted to UV radiation. After the irradiation period, the solution is placed in 22-mL vials and subjected to the same SPME procedure indicated above. For each set of experiments an extraction control (same SPME procedure but without irradiation) is carried out.

3. Results and discussion

Based on previous studies regarding on on-fiber photodegradation of different organic compounds, PDMS coating is the suitable fiber to perform photo-SPME [16–19]. With other available coatings, such as polydimethylsiloxane–divinylbenzene (PDMS–DVB), the extent of photodegradation was very limited. In addition, PDMS is the most suitable coating to extract PBDEs [15]. Therefore, all the experiments in this study were performed using PDMS SPME fibers.

The photoreaction kinetics of each individual PBDE was monitored by studying the influence of irradiation time on the analytical response. Five series of experiments were carried out, one for each compound. The analytes were first extracted from aqueous solutions and then, the fiber was exposed to UV light (18 W) for the selected time. Finally, GC–MSD analysis was carried out (see Section 2 for more details). Table 1 summarizes the obtained results, expressed as percentage of compound that remains in the fiber after

Table 1
Percentage of compound that remains in the fiber after UV irradiation (18 W)

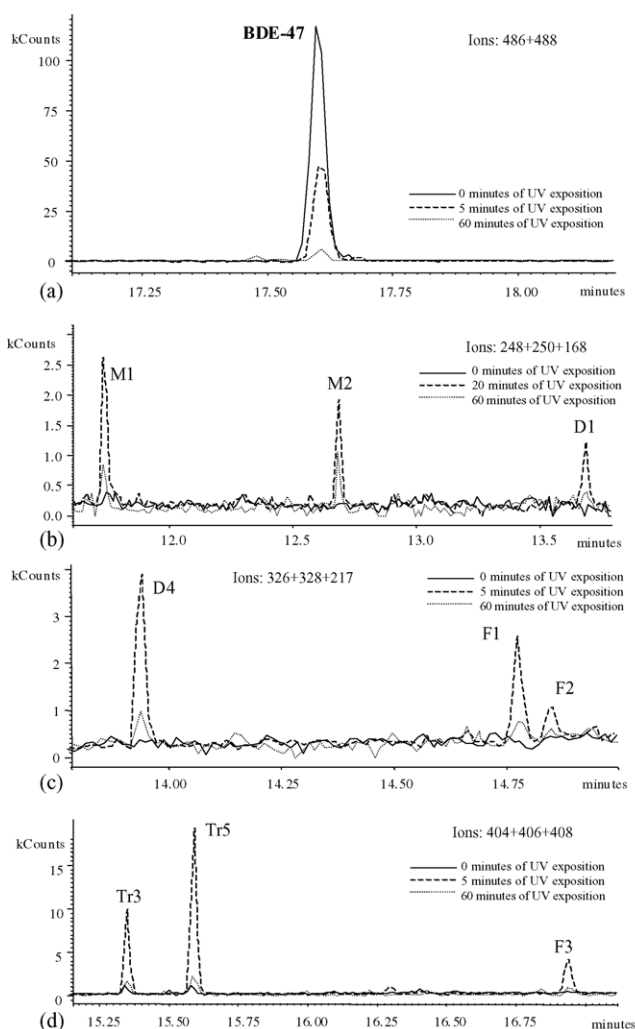| Irradiation time (min)	Percentage of undegraded compound (%)				
	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153
0	100	100	100	100	100
2	32	30	30	23	28
5	5	8	10	9	15
10	1	<1	<1	<1	5

Fig. 1. Ion chromatograms showing the photodegradation of BDE-47 (a) and ion chromatograms showing the photoformation–photodegradation of the generated photoproducts (b–d). See Table 2 for compound identification.

UV exposition, normalized to time zero. As can be seen, after 10 min of irradiation, photodegradation is practically complete. This fast photodegradation makes difficult to follow the photodegradation pathways and to identify the possible generated photoproducts. So, the same experiments were repeated working at lower nominal power (8 W). The irradiation time selected was from 0 to 60 min (seven points). Figs. 1a and 2a show the quantification ion chromatograms obtained for 0, 2 and 60 min of irradiation for BDE-47 and BDE-99. In these graphs, the decrease in analytical response as the UV exposition time increases can be clearly observed. All PBDEs manifest comparable photodegradation behaviors and they are rapidly photodegraded. After 20 min of UV irradiation, the percentage of response is lower than 10% for all PBDEs. The amount of compound that remains in the fiber after 60 min of irradiation ranged from <1% (BDE-99) to 4% (BDE-154).

Other series of experiments was performed in order to compare photo-SPME and aqueous photodegradation of
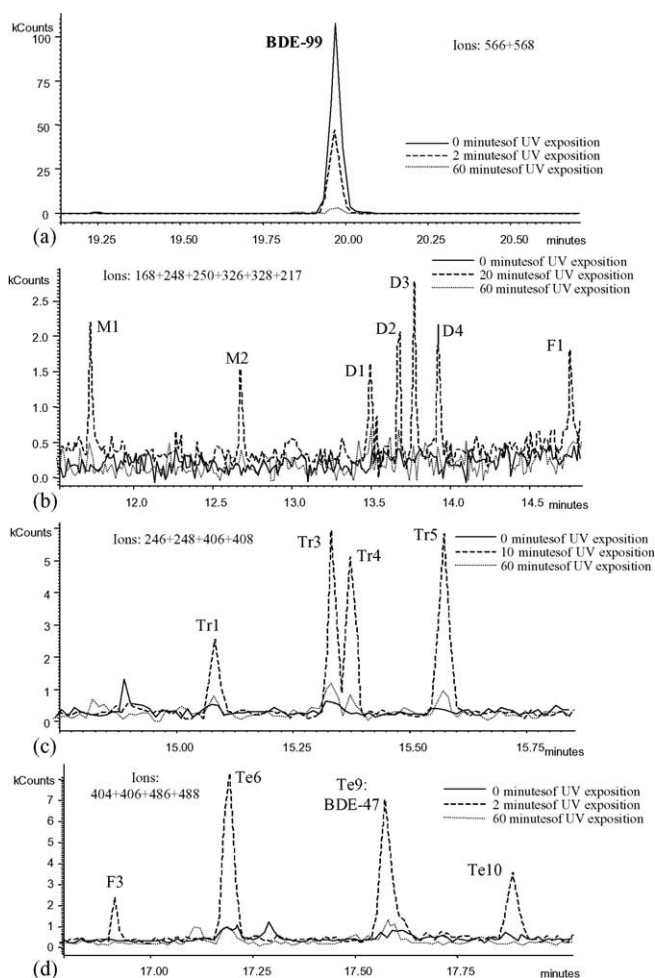
Fig. 2. Ion chromatograms showing the photodegradation of BDE-99 (a) and ion chromatograms showing the photoformation–photodegradation of the generated photoproducts (b–d). See Table 2 for compound identification.

the target PBDEs. In these experiments, aliquots of water containing the target PBDE were exposed to UV irradiation for different periods of time (from 0 to 20 min, five points) and then HS-SPME–GC–MS analyses were performed. Fig. 3 shows the overlaid results of the experiments of photo-SPME and aqueous photodegradation for BDE-47, BDE-100, BDE-99, BDE-154 and BDE-153. These results are presented as percentage of compound that remains in the fiber after the UV exposition. As it can be seen, also in aqueous solution all the studied compounds undergo photodegradation, showing kinetics that were slightly faster.

Table 2 summarizes the more than 30 photoproducts obtained in the photo-SPME experiments. Photoproducts are characterized by their retention times and by their mass spectra. Most of the generated photoproducts were tentatively identified as less brominated PBDEs. Thus, reductive debromination by successive losses of bromine atoms is confirmed as the main photodegradation pathway of PBDEs.

As can be seen in Table 2, two mono-BDE (M1, M2), four di-BDE (D1–D4), five tri-BDE (Tr1–Tr5), 10 tetra-

BDE (Te1–Te10), and seven penta-BDE (P1–P7), have been found. Three of the target analytes—BDE-47, BDE-99, BDE-100—were also obtained as photoproducts of some of the other target compounds. On the basis of the mass spectra of each photoproduct, it is possible to distinguish between homologous (different number of bromine atoms), but it is not possible to know the positions that are occupied by these bromine atoms. The most probable debromination route is to dehalogenate on the most substituted ring. This is a general trend for PCBs [16,17,22,23] and it appears also to be the most probable for PBDEs [13]. Nevertheless, other possible dehalogenation patterns, as well as possible isomerizations cannot be discarded.

Fig. 4 shows all the possible photoproducts obtained by successive losses of bromine atoms of BDE-47 assuming debromination on the most substituted ring. Thus, two tri-BDEs, three di-BDEs and two mono-BDEs might be generated. As can be seen in Table 2 same number of photoproducts were confirmed as photoproducts of BDE-47. Fig. 1b and c show the ion chromatograms corresponding to the generated photoproducts of this compound. In Fig. 2, the degradation of BDE-99 and the formation of different debrominated photoproducts is clearly appreciated. The different debrominated congeners are gradually formed. In this way, after the first minutes of photodegradation (2 min) the most abundant congeners are the tetra-BDEs (Fig. 2d); after 10 min, the tri-BDE photoproducts are the predominant ones (Fig. 2c). The less chlorinated congeners mono- and di-BDEs appears later and their maximum response is reached after 20 min (Fig. 1b). BDE-47 is generated as a photoproduct of BDE-99, thus, all the photoproducts found in the photodegradation of BDE-47 were also found in the photodegradation of BDE-99 (see Table 2).

The photodegradation of BDE-100 produced also the formation of mono-, di-, tri- and tetra-BDE congeners (see Table 2). Two tri-BDEs, two di-BDEs and two mono-BDEs were also identified in the photodegradation of BDE-99. BDE-47 is obtained as a photodegradation product of BDE-100. Thus, the two tri-BDEs, two of the di-BDEs and the two mono-BDEs found in the photodegradation of BDE-47 were also identified in the photodegradation of BDE-100.

Fig. 5 shows the possible penta- and tetra-BDE photoproducts of BDE-153 generated following the mechanism of serial losses of bromine atoms, assuming debromination on the most substituted ring. The same number of BDE-photoproducts with equivalent number of bromine atoms have been found (see Table 2). One of the penta-BDEs generated in the photodegradation of BDE-153 is BDE-99. BDE-47 is also generated as photoproduct of BDE-153.

Similarly, the photodegradation of BDE-154 produced the sequentially formation of penta-, tetra-, tri-, di- and mono-BDEs (see Table 2). BDE-99, BDE-100 and BDE-47 were among the photoproducts found.

In this study was also possible to estimate the percentage of photoproduct generation in the photodegradation of each target BDE. As an example, percentages of penta- and tetra-
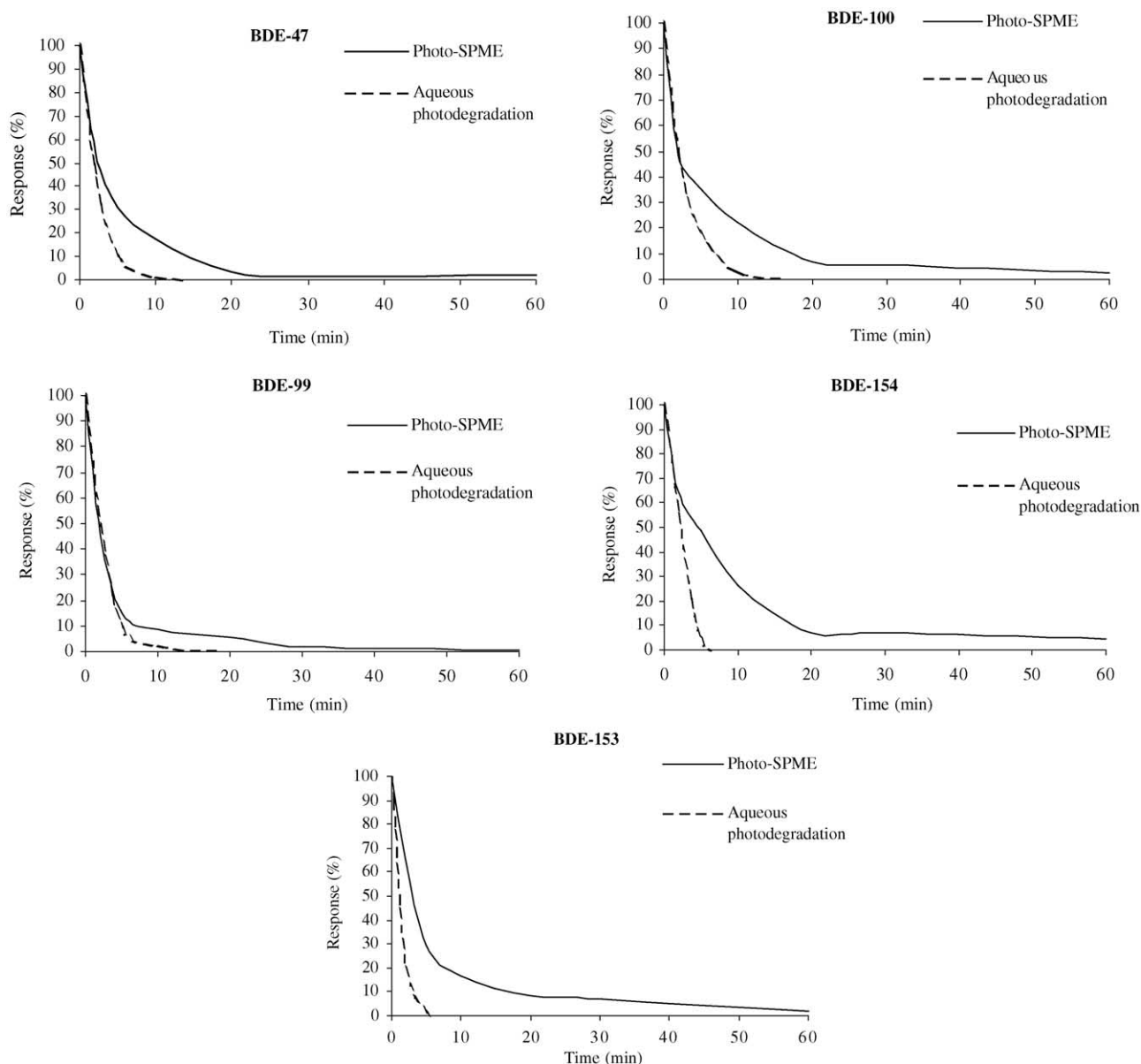
Fig. 3. Percentage of undegraded compound after UV exposition in photo-SPME experiments and in aqueous photodegradation experiments.

BDEs generated from BDE-154 have been calculated and are presented in Table 3. These data must be taken as semi-quantitative due to the no availability of standards for each one of the congeners formed (penta- and tetra-BDEs were quantified assuming to have same detector responses as BDE-100 and BDE-47, respectively).

Other mechanism of photodegradation of PBDEs is the intramolecular cyclization from the homolytic dissociation of the C−Br bond, thus, polybromo-dibenzofurans can be generated. The possible formation of these compounds has already been underlined for some authors [5,6,9,12]. In our study two dibromo-dibenzofurans (F1, F2) and one tribromo-dibenzofuran (F3) have been identified (see Table 2). F1 and F3 were obtained in the photodegradation of BDE-47, BDE-100 and BDE-99, whereas F2 was found in the photodegra-

dation of BDE-47 and BDE-100. Figs. 1c, d and 2b, d show the formation of these compounds in the photodegradation of BDE-47 and BDE-99, respectively.

The obtained photoproducts are also photodegraded in presence of UV radiation. Thus, photo-SPME allows to draw the kinetics of photoformation–photodegradation of the photoproducts generated. Some of these compounds were rapidly degraded whereas others showed slower degradation rate. Fig. 6 shows the photoformation–photodegradation kinetic of one of the dibromo-dibenzofurans detected (F1). The mass spectrum of this compound is also included.

In the aqueous photodegradation studies, the same photoproducts than in photo-SPME experiments have been found. Photoproducts showed similar photodegradation behavior that in photo-SPME experiments. Therefore, it is confirmed

Table 2
Photoproducts generated in on-fiber photodegradation of BDE-47, BDE-100, BDE-99, BDE-154 and BDE-153

| Key	Retention time (min)	Compound	Identification ions	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153
M1	11.73	Mono-BDE	248,250,141	+	+	+		
M2	12.69			+	+	+	+	+
D1	13.50		168,328,326	+		+		
D2	13.68	Di-BDE		+	+	+	+	
D3	13.77					+		+
D4	13.94		328,326,168	+	+	+		
Tr1	15.08		248,246,408			+	+	+
Tr2	15.16				+			+
Tr3	15.34	Tri-BDE	406,408,248	+	+	+	+	+
Tr4	15.36					+	+	+
Tr5	15.56			+	+	+	+	+
Te1	16.64						+	
Te2	16.68						+	
Te3	16.79		326,486,488		+		+	
Te4	16.86							+
Te5	17.05	Tetra-BDE	488,486,328		+		+	
Te6	17.20					+	+	+
Te7	17.29		326,486,488			+		+
Te8	17.37							+
Te9	17.58	BDE-47	488,486,328		+	+	+	+
Te10	17.89	Tetra-BDE				+	+	+
P1	18.69	Penta-BDE					+	
P2	19.24						+	
P3	19.42	BDE-100					+	
P4	19.47		566,568,406					+
P5	19.60	Penta-BDE					+	
P6	19.97	BDE-99					+	+
P7	20.45	Penta-BDE						+
F1	14.78	Dibromo-dibenzofuran	326,217,219	+	+	+		
F2	14.85			+	+			
F3	16.93	Tribromo-dibenzofuran	406,404,298	+	+	+		
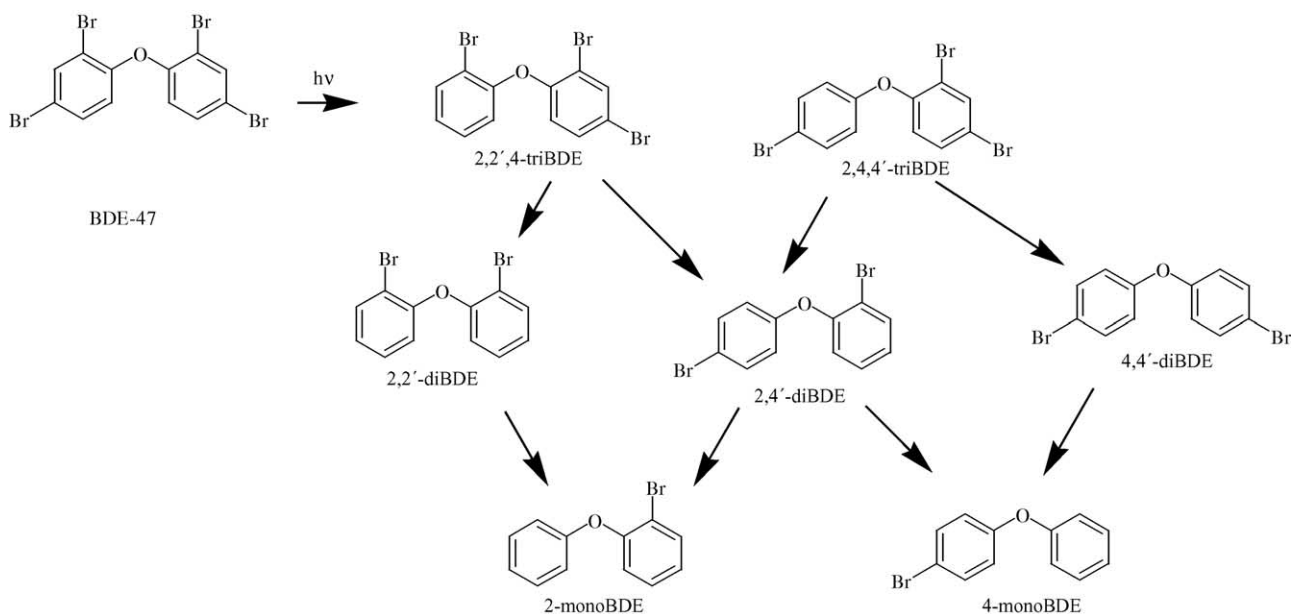
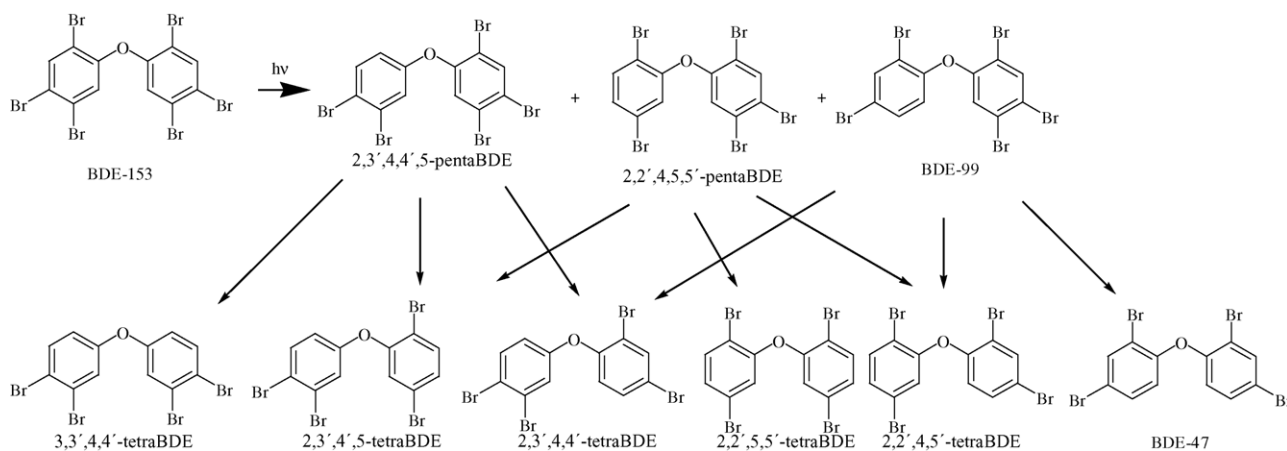Fig. 4. Possible photoproducts obtained by successive losses of bromine atoms of BDE-47.

Fig. 5. Possible penta- and tetra-BDE photoproducts obtained by successive losses of bromine atoms of BDE-153.

that the photo-SPME degradation is very close to the aqueous photodegradation of PBDEs.

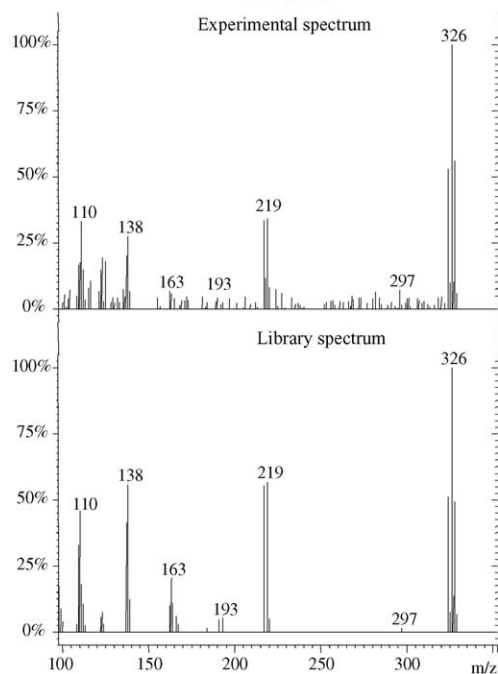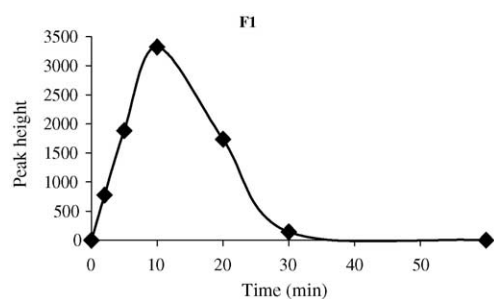Further investigations are being planed to study the photodegradation of PBDEs by photo-SPME using sunlight.

Fig. 6. Kinetics of photoformation-photodegradation of a compound tentatively identified as dibromo-dibenzofuran (F1). The mass spectrum obtained is also included.

Table 3
Percentage of BDE-154 that remains in the fiber and percentage of photoproducts formed after 5 min of UV irradiation

BDE-154	59
Te1	0.77
Te2	0.50
Te3	0.37
Te5	0.61
Te6	3.1
Te9:BDE-47	3.0
Te10	1.5
P1	7.3
P2	2.4
P3:BDE-100	4.7
P5	2.2
P6:BDE-99	9.0

See Table 2 for compound identification.

Acknowledgements

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